

Design and Engineering of Tissue Papers using Cellulose-based Fibrous Materials 3D Simulations: an approach for Furnish Optimization

Flávia Pinto Morais

Tese para obtenção do Grau de Doutor em
Ciência e Engenharia dos Materiais Fibrosos
(3^o ciclo de estudos)

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Covilhã, 22 de novembro de 2022

Declaração de Integridade

Eu, Flávia Pinto Moraes, que abaixo assino, estudante com o número de inscrição D2419 de Ciência e Engenharia dos Materiais Fibrosos da Faculdade de Engenharia/ Ciências, declaro ter desenvolvido o presente trabalho e elaborado o presente texto em total consonância com o **Código de Integridades da Universidade da Beira Interior**.

Mais concretamente afirmo não ter incorrido em qualquer das variedades de Fraude Académica, e que aqui declaro conhecer, que em particular atendi à exigida referenciação de frases, extratos, imagens e outras formas de trabalho intelectual, e assumindo assim na íntegra as responsabilidades da autoria.

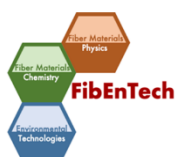
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A handwritten signature in dark ink, reading 'Flávia Pinto Moraes', enclosed within a thin rectangular border.

(Flávia Pinto Moraes)

The experimental work presented in this thesis was carried out at the Fiber Materials and Environmental Technologies Research Unit, Faculty of Engineering/ Science, University of Beira Interior (FibEnTech-UBI), under the scientific supervision of Professors Joana Maria Rodrigues Curto and Maria Emília da Costa Cabral Amaral, and at the Forest and Paper Research Institute (RAIZ), under the scientific supervision of Doctor Ana Margarida Martins Salgueiro Carta.

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Cofinanciado por:



***In memory of my grandmother, Rita Lopes
To my parents, Regina and Zeferino Morais
To you, André Franco***

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Resumo Alargado

Nos últimos anos, a indústria do papel *Tissue* tem sido confrontada com diversos desafios relacionados com a crescente relevância e procura de matérias-primas (*furnish*) e produtos sustentáveis. As fibras de celulose são excelentes matérias-primas devido às suas características intrínsecas, sendo utilizadas em diversos produtos como os papéis *Tissue*. Estes materiais cumprem múltiplos propósitos, combinando a relação custo-benefício, com critérios de higiene cada vez mais exigentes. O conhecimento dos diferentes tipos de fibras celulósicas e dos resultados das suas modificações por processos de engenharia contribui para o projeto de materiais de papel *Tissue* com a melhor combinação de *furnish*, para os diversos tipos de produto final. Este trabalho investiga a otimização do *furnish* para os produtos *Tissue* através do desenvolvimento e aplicação de ferramentas computacionais avançadas. Uma metodologia que combina um planeamento experimental e computacional foi implementada para estabelecer relações entre as propriedades chave das fibras e das estruturas, as etapas do processo que as modificam e as propriedades estruturais e funcionais do papel *Tissue*, que conduziu ao desenvolvimento de um simulador para otimização e gestão do *furnish*, o *SimTissue*. Este trabalho apresenta uma contribuição significativa e inovadora na caracterização e modelação 3D das fibras, na aplicação de abordagens experimentais e computacionais para avaliar a engenharia dos processos de modificação das fibras e das estruturas e na otimização utilizando ferramentas computacionais avançadas a fim de projetar materiais *Tissue* suaves, resistentes e absorventes.

A caracterização das dimensões das fibras na estrutura do papel, nas três dimensões (3D), foi fundamental para modelá-las, utilizando metodologias de imagens SEM e ferramentas computacionais avançadas de modelação das fibras e das estruturas. Como resultado desta estratégia, modelos 3D de fibras foram desenvolvidos, implementados e usados como variáveis de entrada nas simulações computacionais para prever as propriedades estruturais. Um conjunto representativo de pastas de interesse industrial foi selecionado e caracterizado, sendo estas obtidas de espécies de fibra curta (*hardwood*) e de fibra longa (*softwood*), com diferentes processos de cozimento e de branqueamento. A contribuição destas pastas com diferentes propriedades morfológicas, químicas e de interação com a água para as propriedades *Tissue* foi avaliada por meio de diversas correlações. Assim, um planeamento foi implementado do ponto de vista da engenharia das variáveis de processo de modificação das fibras e das estruturas, influenciando o projeto de materiais de papel *Tissue*. Estas pastas foram submetidas a tratamento enzimático e mecânico, e incorporação de aditivos na suspensão, incluindo celulose micro/nanofibrilada (MFC/NFC) e biopolímero. Todos estes conjuntos de ensaios foram investigados de forma a quantificar a sua influência, singular ou em combinação, nas propriedades chave dos papéis *Tissue*: suavidade, resistência e absorção. Uma metodologia de produção de estruturas isotrópicas laboratoriais de 20 g/m² em vez de 60 g/m², com supressão da etapa de prensagem, foi proposta seguindo uma adaptação da ISO 5269-1, a fim de mimetizar os papéis *Tissue* e avaliar

as suas propriedades. O estabelecimento das relações entre estas pastas, as múltiplas alterações resultantes dos diferentes processos e as propriedades funcionais *Tissue* foi obtido por meio de diversas ferramentas computacionais, como árvores de decisão/ regressão, regressões lineares múltiplas, redes neurais artificiais, entre outras, utilizadas como modelos para apoiar à gestão e tomada de decisão na produção industrial. Assim, a validação de modelos computacionais com estas estruturas foi um marco inovador e insubstituível para a obtenção de um simulador computacional 3D com capacidade preditiva de estruturas *Tissue*. Todo esse processo permitiu a implementação computacional do *SimTissue*, programando os algoritmos do motor de cálculo, com integração de uma base de dados, para serem utilizados em casos específicos de apoio à gestão industrial do *furnish*. O design de materiais fibrosos *Tissue* recorrendo a estas ferramentas computacionais possibilitou o desenvolvimento de combinações de *furnish* e de parâmetros de processo que conduzem à otimização de cada papel *Tissue*, permitindo decidir quais as pastas mais aptas para um determinado produto e quais os tratamentos enzimáticos e mecânicos, ou incorporação de aditivos que permitem obter um papel *Tissue* otimizado. Aplicando esta metodologia, produziram-se estruturas *Tissue* com maximização de fibras de eucalipto, minimizando a incorporação de fibra longa e quantificando as implicações das escolhas nas propriedades finais *Tissue*. O *SimTissue* prevê a influência de vários tipos de matérias-primas, utilizadas em formulações para produzir os materiais *Tissue*, a influência dos processos de modificação e da incorporação de aditivos. As estruturas experimentais e simuladas contribuíram para a validação do modelo de previsão das propriedades chave *Tissue*. Cada simulação realizada pode ainda ser comparada com formulações com 100% de pastas de fibras de eucalipto, ou com diferentes percentagens de outras pastas de fibra curta e longa, que reflete a relação usada pela indústria de papel *Tissue*.

O presente trabalho apresenta uma abordagem experimental e computacional, com projeto e desenvolvimento de uma ferramenta de capacidade preditiva, com integração das variáveis fundamentais, para otimizar formulações inovadoras do *furnish*, economizando recursos laboratoriais e industriais. Este sistema multiescala, com múltiplas entradas e múltiplas saídas, foi integrado recorrendo a ferramentas computacionais, métodos de modelação e otimização. O desenvolvimento do *SimTissue* foi um marco inovador para obter capacidade preditiva das estruturas *Tissue*, de forma a apoiar a produção industrial na gestão e otimização do *furnish*. A estratégia de design de materiais utilizando esta ferramenta computacional pode também ser aplicada ao desenvolvimento de materiais fibrosos de valor acrescentado, utilizando como base a fibra de eucalipto e incluindo aditivos e fibras em micro e nano-escala.

Palavras-chave

Celulose Micro/ Nanofibrilada (MFC/NFC); Engenharia de Fibras de Celulose; Modelação 3D das Fibras; Otimização do *Furnish*; Projeto de Materiais de Papel *Tissue*; Simulação Computacional 3D

Abstract

In recent years, the tissue paper industry has been exposed to several challenges related to the growing relevance and demand for raw materials (furnish) and sustainable products. Cellulose fibers are excellent raw materials, due to their intrinsic characteristics, leading to their use in various products, such as tissue papers. These materials serve multiple purposes, combining cost-effectiveness with increasingly demanding hygiene criteria. The knowledge of the different types of pulp fibers and the results of their modifications by engineering processes contributes to the design of tissue paper materials with the best combination of furnish, for the several types of final products. This work explores the furnish optimization of tissue products, through the development and application of advanced computational tools. A methodology that combines experimental and computational planning was implemented to establish relationships between the key fiber and structure properties, the process steps that modify them, and the structural and functional tissue paper properties. This led to the development of a simulator for furnish optimization and management, the *SimTissue*. This work presents a significant and innovative contribution in the 3D fiber characterization and modeling, in the application of experimental and computational approaches to evaluate the engineering of fiber and structure modification processes, and in the optimization using advanced computational tools to design soft, resistant, and absorbent tissue materials.

The characterization of the fiber dimensions in the paper structure, in the three dimensions (3D), was fundamental to model them, using SEM images methodologies and advanced computational tools for fiber and structure modeling. As a result of this strategy, 3D fiber models were developed, implemented, and used as input variables in computational simulations to predict the structural properties. A representative set of cellulose pulps of industrial interest were selected and characterized, obtained from hardwood and softwood species with different cooking and bleaching processes. The contribution of these pulp fibers with different morphological, chemical and water interaction properties to the tissue properties was accessed through several correlations. Therefore, a planning was implemented from the point of view of engineering fiber and structure modification process variables, influencing the design of tissue paper materials. The pulps were subjected to enzymatic and mechanical treatment, and incorporation of additives in suspension, including micro/nanofibrillated cellulose (MFC/NFC) and biopolymers. All these sets of trials were investigated to quantify their influence, singular or in combination, on the key tissue properties: softness, strength, and absorption. A production methodology of laboratory-made isotropic structures of 20 g/m² instead of 60 g/m², with pressing step suppression, was proposed following an adaptation of ISO 5269-1, in order to mimic tissue papers and evaluate these tissue properties.

The establishment of relationships between these pulp fibers, the multiple changes resulting from the different processes, and the functional tissue properties was obtained using several computational tools, such as decision/regression trees, multiple linear regressions, artificial neural networks, among others, used as models to support planning and decision-making in industrial production. Therefore, the validation of computational models with these structures was an innovative and irreplaceable milestone to obtain a 3D computational simulator with predictive capacity for tissue structures. This entire process allowed the computational implementation of the *SimTissue* through the programming of algorithms for the calculation engine and database integration, to be used in specific cases to support industrial furnish management. The design of tissue fibrous materials using these computational tools allowed the development of furnish combinations and process parameters that led to the optimization of each tissue paper. This assisted in the decision of which pulps were most suitable for a given product and which enzymatic and mechanical treatments or additives incorporation enabled an optimized tissue material. By applying this methodology, it was possible to produce tissue structures with maximization of eucalyptus fibers, minimizing the incorporation of softwood pulp fibers, and quantifying the implications of the choices on the final end-use tissue properties. Hence, *SimTissue* predicts the influence of various types of raw materials used in formulations to produce tissue materials, the influence of modification processes, and the incorporation of additives. The validation of the properties' prediction was performed with experimental and simulated structures. Each simulation performed can also be compared with formulations with 100% eucalyptus fiber pulps, or with different percentages of other hardwood and softwood fiber pulps, which reflects the ratio used by the tissue paper industry.

The present work describes an experimental and computational approach, with the design and development of a predictive capacity tool, with the integration of fundamental variables, to optimize innovative furnish formulations, saving laboratory and industrial resources. This multiscale system, with multiple inputs and multiple outputs, was integrated using computational tools, modeling, and optimization methods. The development of the *SimTissue* was an innovative milestone to obtain the predictive capability of tissue structures, to support industrial production in furnish management and optimization. The materials design strategy using this computational tool can also be applied to the development of value-added fibrous materials based on eucalyptus fiber and including additives and fibers with micro and nanoscale.

Keywords

3D Computational Simulation; 3D Fiber Modeling; Cellulose Fiber Engineering; Design of Tissue Paper Materials; Furnish Optimization; Micro/Nanofibrillated Cellulose (MFC/NFC)

Thesis Overview

This doctoral thesis is structured in four chapters, herein summarized:

Chapter I provides a brief **introduction**, presenting the general topic and a short literature review related to this issue. The introduction chapter also defines the scope of the subject, outlining the current situation and including the definition of doctoral thesis motivation and its objectives.

Chapter II is dedicated to the **literature review** that addresses the main theoretical concepts that underlie the experimental work. State of the art description emphasizes three main sections, which determine the development of the thesis.

The first focused on the basics underlining the cellulosic fiber properties, which depend on the raw materials and the pulping and bleaching processes; in the paper structure, with emphasis on its two-dimensional and three-dimensional random fiber networks; and in the description of 3D materials modeling, highlighting different 3D fiber-based models with the ability to predict the properties of different materials. Importance was given to the 3D fibrous material model developed and validated by Curto and co-authors in 2011, the *voxelfiber*, which was adapted for the development of this thesis.

The second section focused on cellulosic fiber modification processes, namely mechanical and enzymatic treatments, and additives incorporation, as well as on the fundamentals of tissue materials, along with their requirements and what are the effects of fiber characteristics on them.

Finally, the third approach focused on advanced computational tools used to develop the *SimTissue*, such as decision/regression trees, multiple linear regressions, and artificial neural networks, in order to optimize the furnish and design new tissue application strategies.

Chapter III presents the published and submitted **publications** that constitute this doctoral thesis. This chapter is **divided into three major topics: 3D fiber characterization and modeling; fiber and structure modification processes using experimental and computational approaches; and optimization using advanced computational tools**. The sections of materials and methods and results and discussion are presented in each publication.

The first topic of this chapter discusses and integrates all the results obtained for the 3D fiber characterization and modeling. A methodology was developed to obtain information of fiber properties' influence on tissue paper network structures. SEM was used to obtain information about fiber collapse in the paper transversal plane (Z direction).

This innovative strategy, together with the traditional characterization of fiber dimensions, allowed the development of 3D fiber models, used as inputs in tissue paper computational simulations to predict their structural properties. Raw materials were defined by a fiber population that is the combination of the proposed 3D fiber models. Additionally, relationships between the different fibers and the structures made by them were established, to be implemented in computational studies and selected for the next steps. The relationship between the pulp fiber properties and the tissue properties of softness, strength, and absorption was established through computational tools, allowing the identification of the most suitable raw materials for each tissue paper material.

The results obtained for the development of strategies to optimize furnish in the tissue products were also presented in the second topic of chapter III, with a focus on maximizing the use of eucalyptus fibers and reducing the softwood fiber content in its production. Pulp fibers were modified using enzymatic and mechanical refining treatments. Additionally, papermaking pulp fibers were further combined with micro/nanofibrillated cellulose and a commercial cationic biopolymer as additives. The formulations were compared with mixtures of eucalyptus and softwood pulps fibers, at different proportions. These experimental data were used in computational studies for furnish optimization. This entire methodology was highlighted to optimize industrial furnish processes, using industrial single-use tissue papers, and laboratory structures produced with different industrial strategies. *SimTissue* predicted the tissue properties of different formulations as well as changing trends in softness, strength, and absorption properties, presenting innovative application strategies for tissue materials with added value.

Finally, in the third topic of chapter III, the results of experimental and computational design approaches were reviewed to optimize tissue products, using innovative computational tools. A computational simulator, the *SimTissue*, was designed and developed to compare and optimize various scenarios of furnish formulations. This simulator establishes relationships between key fiber properties, the fiber modification process steps, and the tissue structural and functional properties. A fibrous materials simulator, the *voxelfiber*, was used to model tissue papers through the inputs of fiber properties and structures made by them. The computationally simulated structures were validated through experimentally produced structures. Subsequently, different computational tools and mathematical models were used to establish relationships between the tissue properties, allowing the computational implementation of *SimTissue* through the calculation engine algorithm programming and database integration. *SimTissue* was used in specific cases to support the industrial furnish management and optimization, including formulations with different fibrous compositions, use of enzymes, a combination of mechanical and enzymatic treatments, and additives incorporation.

Chapter IV presents the main **conclusions** obtained from this work and the general perspectives for **future work**.

Appendix lists and presents the **complementary publications** to this Ph.D. thesis.

List of Publications

3D Fiber Characterization and Modeling

- I. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2020). 3D Fiber Models to Simulate and Optimize Tissue Materials. *BioResources*. **15**: 8833-8848. DOI: 10.15376/biores.15.4.8833-8848
- I.a. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2020). Experimental 3D fibre data for tissue papers applications. *Data in Brief*. **30**: 105479. DOI: 10.1016/j.dib.2020.105479
- II. **Morais, F.P.**, Bértolo, R.A.C., Curto, J.M.R., Amaral, M.E.C.C., Carta, A.M.M.S., and Evtyugin, D.V. (2019). Comparative characterization of eucalyptus fibers and softwood fibers for tissue papers applications. *Materials Letters: X*. **4**: 1000028. DOI: 10.1016/j.mlblux.2019.100028
- II.a. **Morais, F.P.**, Bértolo, R.A.C., Curto, J.M.R., Amaral, M.E.C.C., Carta, A.M.M.S., and Evtyugin, D.V. (2020). Characterization data of pulp fibres performance in tissue papers applications. *Data in Brief*. **29**: 105253. DOI: 10.1016/j.dib.2020.105253

Fiber and Structure Modification Processes using Experimental and Computational Approaches

- III. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Cellulose Fiber Enzymatic Modification to Improve the Softness, Strength, and Absorption Properties of Tissue Papers. *BioResources*. **16**: 846-861. DOI: 10.15376/biores.16.1.846-861
- IV. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Micro/nano-fibrillated cellulose (MFC/NFC) fibers as an additive to maximize eucalyptus fibers on tissue paper production. *Cellulose*. **28**: 6587-6605. DOI: 10.1007/s10570-021-03912-9
- V. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). An innovative computational strategy to optimize different furnish compositions of tissue materials using micro/ nanofibrillated cellulose and biopolymer as additives. *Polymers*. **13**: 2397. DOI: 10.3390/polym13152397

- VI. Morais, F.P.**, Mendes, A.O., Carta, A.M.M.S., Fiadeiro, P.T., Amaral, A.E., and Curto, J.M.R. A 3D fiber-based strategy for optimization of tissue materials using a combination of liquid absorbency/retention methods. In Andreas Öchsner (Editor), *Advanced Structured Materials*. Springer. *In Press*. (Book Chapter)

- VII.** Curto, J.R., Vieira, J.C., **Morais, F.P.**, Mendes, A.O., Carta, A.M., Simões, R.S., Fiadeiro, P.T., Amaral, M.E., and Costa, A.P. (2021). Embossing Influence on the 3D Structure and Key Properties of Tissue Paper. In *Proceedings of the XXV TECNCELPA – International Forest, Pulp and Paper Conference and XI CIADICYP – Iberoamerican Congress on Pulp and Paper Research*, Online Conference, 10-12 March 2021.

- VIII. Morais, F.P.**, Vieira, J.C., Mendes, A.O., Carta, A.M., Costa, A.P., Fiadeiro, P.T., Curto, J.M.R., and Amaral, M.E. (2021). Characterization of absorbency properties on tissue paper materials with and without “Deco” and “Micro” embossing patterns. *Cellulose*. **29**: 541-555. DOI: 10.1007/s10570-021-04328-1.

Optimization using Advanced Computational Tools

- IX. Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Computational Simulation Tools to Support the Tissue Paper Furnish Management: Case Studies for the Optimization of Micro/nano Cellulose Fibers and Polymer-based Additives. *Polymers*. **13**: 3982. DOI: 10.3390/polym13223982

- X. Morais, F.P.** and Curto, J.M.R. (2022). 3D Computational Simulation and Experimental Validation of Structured Materials: Case Studies of Tissue Papers. *BioResources*. **17**: 4206-4225. DOI: 10.15376/biores.17.3.4206-4225

- XI. Morais, F.P.** and Curto, J.M.R. (2022). Challenges in Computational Materials Modelling and Simulation: A case-study to predict tissue paper properties. *Heliyon*. **8**: e09356. DOI: 10.1016/j.heliyon.2022.e09356

- XII. Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E.C.C., Curto, J.M.R. (2022). Development of sustainable cellulose-based tissue materials using an innovative experimental and computational methodology. *KnE Materials Science*. **7**: 34-45. DOI: 10.18502/kms.v7i1.11606

List of Communications in Scientific Meetings

Oral Communications:

- I. **Morais, F.P.**, Bértolo, R.A.C., Curto, J.M.R., Amaral, M.E.C.C., Carta, A.M.M.S., and Evtugin, D.V. (2019). Comparative characterization of eucalyptus fibers and softwood fibers for tissue papers applications. In *Proceedings of the MATERIAIS 2019 - XIX Congresso da Sociedade Portuguesa de Materiais and X International Symposium on Materials*, Universidade NOVA de Lisboa, Lisboa, Portugal, 14-17 April 2019.
- II. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E.C.C., and Curto, J.M.R. (2021). Optimization, Engineering, and Design of Cellulose-based Tissue Papers using 3D Fibrous Materials Simulation. In *Proceedings of the TissueConference2021 - Sustainability, Performance, Risks & Opportunities in Times of Pandemic*, Online Conference, 12-14 January 2021.
- III. Curto, J.R., Vieira, J.C., **Morais, F.P.**, Mendes, A.O., Carta, A.M., Simões, R.S., Fiadeiro, P.T., Amaral, M.E., and Costa, A.P. (2021). Embossing Influence on the 3D Structure and Key Properties of Tissue Paper. In *Proceedings of the XXV TECNCELPA – International Forest, Pulp and Paper Conference and XI CIADICYP – Iberoamerican Congress on Pulp and Paper Research*, Online Conference, 10-12 March 2021.
- IV. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E.C.C., Curto, J.M.R. (2021). Development of sustainable cellulose-based tissue materials using an innovative experimental and computational methodology. In *Proceedings of the 1st International FibEnTech Congress - New opportunities for fibrous materials in the ecological transition*, Online Conference, 9-10 December 2021.

Poster Communications:

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List of Abbreviations

2D	Two-dimensional
3D	Three-dimensional
ANN	Artificial Neural Networks
CBA	Commercial Biopolymer Additive
CMC	Carboxymethylcellulose
CWP	Conventional Wet Press Process
DNS	Dinitrosalicylic Acid
ECF	Elemental Chlorine-free Bleaching Sequences
FPU	Filter-Paper Units
FTIR-ATR	Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance
HF	Handfeel
HW	Hardwood
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
MD	Machine Direction
MFC/NFC	Micro/ Nanofibrillated Cellulose
MIMO	Multiple-Input Multiple-Output
ML	Middle Lamella
MLR	Multiple Linear Regressions
PW	Primary Wall
RBA	Relative Bonding Area
REA	Representative Elementary Area
REV	Representative Elementary Volume
S ₁	External Secondary Wall
S ₂	Medium Secondary Wall
S ₃	Internal Secondary Wall
SEM	Scanning Electron Microscopy
SR	Schopper-Riegler
SW	Softwood
TAD	Through-Air Drying Technology
TCF	Total Chlorine-free Bleaching Sequences
TSA	Tissue Softness Analyzer
UV	Ultraviolet
WRV	Water Retention Value

Chapter I

Introduction

I.1. Introduction

Tissue materials, such as toilet papers, towel papers, napkins, facial papers, and tissue masks, are cellulose fibrous materials designed for personal hygiene and utility purposes. Significant growth in the global tissue sector is projected for the next decade, concentrated in the industrialized parts of the world and with a demand for premium products (de Assis et al., 2018a). Moreover, growing awareness among consumers towards health and hygiene is also contributing to the demand for tissue papers. The current outbreak of COVID-19 has also led to increasing demand for tissue papers around the world (Tissue World Magazine, 2021). The properties required in tissue products, such as softness, strength, and absorption, distinguish them from other cellulose-based materials. The properties of each tissue material depend on the pulps used for its production, its type of pulping and bleaching processes, and the used raw materials, such as hardwoods, like eucalyptus fibers, or softwoods, like pine fibers. To produce these products, a high percentage of bleached hardwood pulps is used, which provides structural and softness properties to the materials, with the incorporation of bleached softwood pulps, which provides strength and ensures the paper machine runnability. Therefore, furnish management optimization by maximizing the eucalyptus fibers incorporation, and the total or partial replacement of softwood pulps consists of a challenge since the required adjustments represent consequences on the runnability of the tissue paper machine and converting lines. Tissue paper machines would have to run at lower speeds, which would lead to lower productivity (cost *vs* benefit). To overcome this limitation and enable the great potential of hardwood pulps in these materials, it is necessary to identify the fiber properties, their relationship with the process, and the final end-use properties. The tissue materials production requires several steps and several factors that can affect the tissue key properties, such as the selection of the raw material, the method and conditions of pulps used, the refining degrees, the enzyme performance in pulps, and the percentage of additives added.

In this industry, The Navigator Company must be highlighted, with its recent entry on the tissue paper market in 2015. In the pulp and paper industry, The Navigator Company is a pioneer, assuming great importance for the national economy (3% of the total goods exported by Portugal, reaching around 1% of the national GDP). It is also the European leader in the production of printing and writing papers. For The Navigator Company, the challenge consists of the need to diversify its activity in the market, and to respond to the continuous consumer demands, while expanding to other businesses to achieve the same differentiation and leadership already achieved for printing and writing paper. The group assumes an important position in the pulp production from *Eucalyptus globulus*, being considered by world experts as the ideal raw material for printing and writing papers. The question is to understand its suitability for tissue paper and the necessary modifications to use eucalyptus pulps to produce these types of papers.

I.1.1. Motivation

This Ph.D. thesis stands up in the scope of R&D Project InPaCTus with The Navigator Company, focusing on the furnish definition and evaluation of engineering strategies for the improvement of pulp fiber properties, as well as the development and design of new differentiated products. Predicting the tissue paper properties from experimental and computational data of pulps used in their production could be an important and interesting milestone not only to the paper tissue industry but also from the point of view of a researcher. Pulp fiber modifications can result in changes in the material properties, which can cause improvements or also several inconveniences. Forecasting is not an easy process because, in addition to the type of pulp used, there are different factors such as mechanical refining, enzymatic treatments, and additives incorporation that influence the final product, to improve the desired properties. The integration of all important variables for the premium tissue materials development with the furnish management optimization can be accomplished using computational tools, modeling, validation, and optimization methods. This methodology can also be used to design new tissue products with innovative features and added value. Over the years, material modeling has become an important tool in the development and design of materials with better performance. The computational tools allow to significantly reduce the experimental work in the new materials development, in order to have a better synergy between the experimental tests design and the simulation of materials specific properties. Despite its importance and the advances achieved in the field of fibrous materials science, engineering, and modeling, an approach to simulate and optimize the relationships between the key parameters and the functional properties of tissue materials is not included in the studies presented in the literature. The advanced computational tools development with predictive capacity allows determining which are the most promising pulps for a specified tissue material and which process operations obtain a tissue material with optimized properties.

Figure I.1 presents an outline of the different steps for the development of this thesis. The experimental plan included the different fibers properties characterization, fibers modification either by mechanical (refining) process, either by enzymatic treatment, or a combination of both, and additives incorporation, such as micro/nanofibrillated cellulose and biopolymers. The key tissue properties were evaluated on laboratory structures of 20 g/m² to mimic the tissue-based sheets, and different relationships were established between these properties, using different innovative computational tools. Therefore, 3D computational simulations of tissue paper structures were performed to calibrate the tissue computational model and then validate its predictive character, with experimental and computational structures. This process allowed the computational implementation and development of a tissue simulator, the *SimTissue*, through the calculation engine algorithm programming, and database integration, to be used in specific cases to optimize furnish industrial management and design premium tissue products.

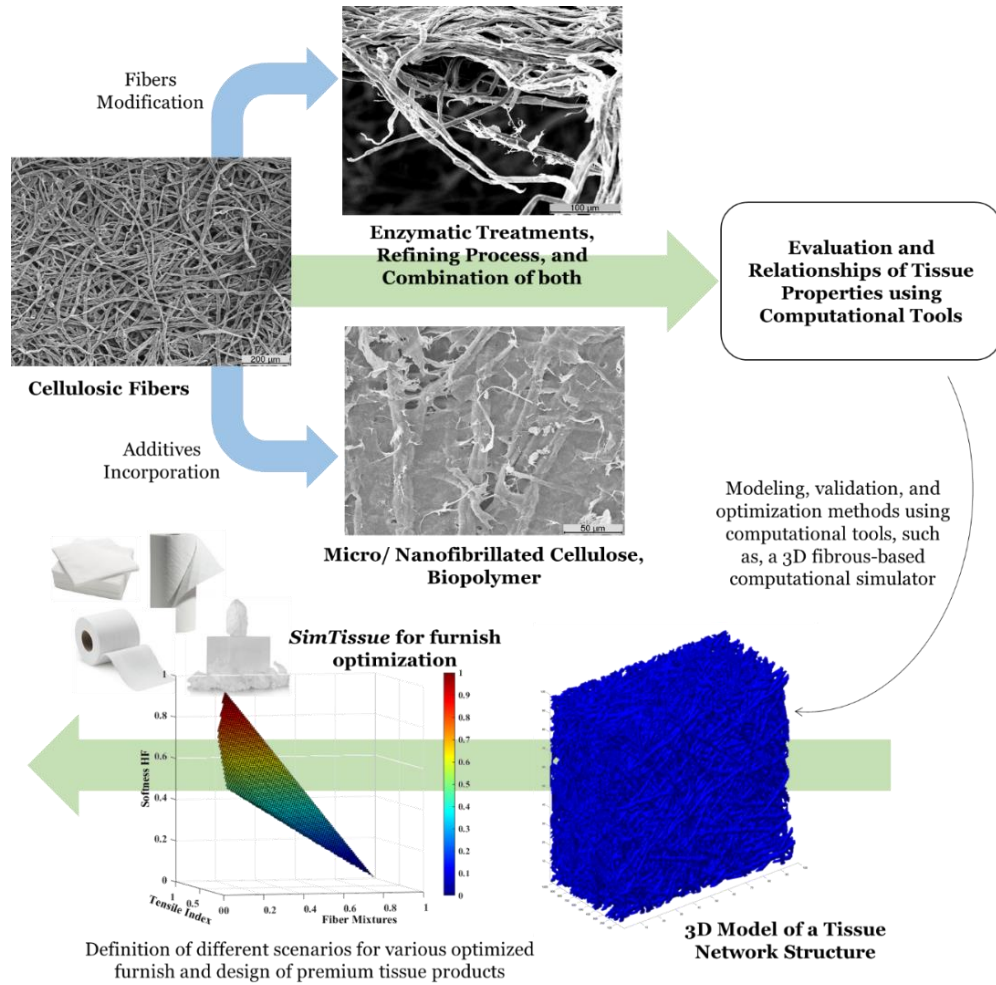


Figure I.1. Outline of the different stages for the development of a computational simulator for furnish process optimization and management, the *SimTissue*.

I.1.2. Objectives

The main goal of this thesis is to optimize the cellulose fibers furnish for the tissue products production, using an innovative methodology approach with predictive capacity, that combines experimental and computational design. To develop and optimize tissue materials with innovative functionalities at the micro and nanoscale, a simulator will be designed to compare various scenarios of furnish formulations, the *SimTissue*. This simulator will integrate the relationships between key fiber properties, the fiber modification process steps, and the tissue structural and functional properties. Hence, cellulosic fibers from different types of pulps will be characterized, modeled, and engineered to design soft, resistant, and absorbent tissue paper materials.

The specific aims outlined for the implementation of this work will be as follows:

- Three-dimensional (3D) characterization and modeling of fibers and structures made by them (Publications I, Ia, II, IIa);
- Experimental and computational approaches to evaluate fiber modification processes by applying enzymatic and mechanical treatments, and additives incorporation, such as micro/ nanofibrillated cellulose and biopolymers, and also evaluate the structure modification processes, such as creping and embossing (Publications III to VIII);
- Computational optimization of various tissue materials, using advanced computational tools (Publications IX to XII).

A combined approach of experimental plan and computational simulation will be investigated. The experimental work will be carried out using different hardwood and softwood pulps of industrial interest, with different cooking and bleaching processes. It is important to access the contribution of different pulp fiber species and classify them according to their influence on the final end-use tissue properties. The correlations between fiber properties and tissue end-use properties are valuable to improve the use of different pulp fibers, for each type of tissue material. The fiber classification according to their morphological and chemical properties and correlating them to the final tissue properties allows suggesting the most suitable pulp fibers to obtain a combination of softness, strength, and absorption properties, for each tissue material. The pulp fibers most suitable to produce tissue products will be selected to evaluate the fiber modification processes. Experimental and computational strategies are applied to optimize the tissue functional properties through the fiber and structure modification process steps, namely, enzymatic and mechanical treatments, additives incorporation, such as micro/nanofibrillated cellulose and biopolymers, and creping and embossing evaluation. The information about fiber biometry and flexibility, and their modification by mechanical and enzymatic treatment processes, is determinant to predict tissue properties. These values correspond to different classification categories for the analyzed samples, regarding to fiber wall thickness, degree of collapse, refining ability, and flexibility values. Therefore, the experimental results for the evolution of bulk, porosity, softness, strength, and absorption properties, constitute valuable information that, using computational modeling strategies, can be applied to other pulps of interest, within this fiber properties and dimensions categories range. The obtention of predictive capacity is one of the innovative goals of this thesis. The experimental results of the fibers and structures will be used to provide realistic parameters in the 3D fiber-based computational model validation. The fibrous material simulator, designated by *voxelfiber* (Conceição et al., 2009; Curto et al., 2011) will be calibrated and validated for tissue paper structures using experimental tissue paper data. This simulator was previously validated for printing and writing paper (Curto et al, 2011), however, it was not validated or applied to low basis weight and high porosity materials such as tissue products.

The final goal is to simulate and optimize different tissue materials using the most appropriate computational tools for this end. For this purpose, a tissue simulator to support the tissue paper furnish management, the *SimTissue*, will be designed and validated, to compare and optimize different formulations, and manufacturing processes, to produce various types of tissue products. Innovative tissue materials using micro/nano fibrillated cellulose, with added value, will be investigated, and proposed based on the use of the optimization methodology developed in this thesis.

Chapter II

Literature Review

II.1. 3D Fiber Characterization and Modeling

The complete 3D characterization of fibers enables the real 3D fiber modeling, and afterward, the simulation of the 3D tissue structure, to optimize the furnish and final end-use properties. Correlations between cellulosic pulp fiber properties and tissue properties are achieved through 3D fiber characterization and modeling. The fiber classification according to their morphological and chemical properties allows the identification of potential pulp fibers for each type of tissue product.

II.1.1. Cellulosic Fibers

Cellulosic fibers are the main structural elements of paper materials that affect the materials' structure formation and consolidation, preserving almost all fiber structures in the pulping and papermaking process (Niskanen, Kajanto, and Pakarinen, 1998). Therefore, cellulosic fibers influence not only the product properties but also the process. In tissue materials production, virgin and/ or recycled fibers can be used, and the paper materials' characteristics are directly related to the type of fibers used, whose morphology and chemical composition influence the paper characteristics. Hence, the features of the materials can be obtained or improved, through the fiber's selection (de Assis et al., 2018a; de Assis et al., 2019). The pulp fiber chemical properties are influenced by the production process conditions, while physical properties are essentially determined by the fiber morphology (Pulkkinen, Ala-Kaila and Aittamaa, 2006). Therefore, for a good fiber furnish management, it is important to know the fiber chemical and morphological properties and to understand how these properties influence the final properties of the products (Trepanier, 2017), since the type of pulp, the conditions of fiber modification and the furnish composition influence the tissue properties and allow to fulfill several requirements for premium tissue products (Fišerová et al., 2019).

II.1.1.1. Wood Fibers Anatomy

Paper materials usually consist of wood fibers. Fiber properties vary considerably with the wood species and growth site and with the pulping and papermaking treatments that the fibers undergo. Wood is composed of a variety of tissue cells. In the cross-section of wood macroscopic structure, it is possible to distinguish different layers: the outer bark, inner bark, vascular cambium, sapwood, and heartwood (Figure II.1). The outbark provides mechanical protection and prevents evaporative water losses, while the inner bark is responsible for transporting nutrients from leaves to the roots or growing portions of the tree. The vascular cambium is responsible for the production of bark (or secondary phloem) and wood (or secondary xylem) each year, and xylem and phloem. The sapwood is responsible for the nutrients transport from the roots to the leaves and the heartwood is the tissue responsible for strength and support. At the center of the heartwood is the pith, which is where the tree started to grow (Wiedenhoef, 2010).

The xylem is the layer formed from the vascular cambium to the center and the most important part of the wood for the pulp and paper industry, which consists mainly of longitudinal cells, whose primary functions are the conservation, support, and storage of nutrients (Plomion, Leprovost and Stokes, 2001). In the xylem, the layers of springwood and summerwood form visible growth rings, which allow knowing the age of the tree (Tyree and Zimmermann, 2002).

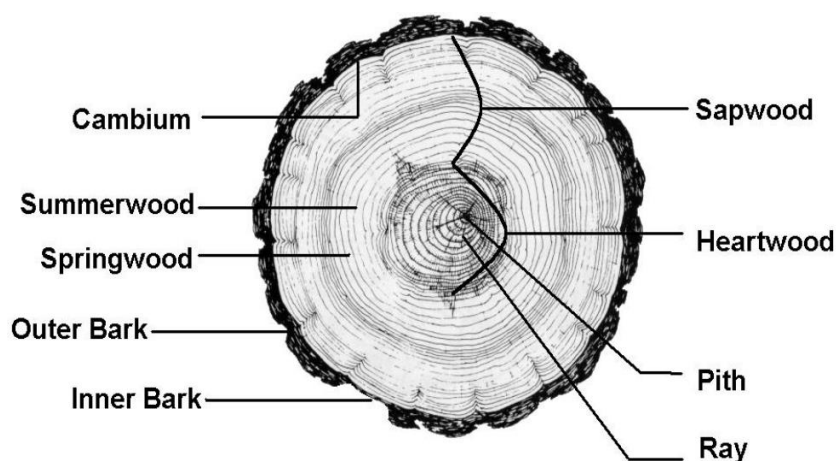


Figure II.1. Cross-section of the wood stem (adapted from Wiedenhoef, 2010).

The concentric arrangement of the cell wall layers of the wood fibers is due to the differences in chemical composition and the different orientations of the structural elements. These layers (Figure II.2) are composed of cellulosic microfibrils oriented in space in a defined way, depending on the layer (Carvalho et al., 2009).

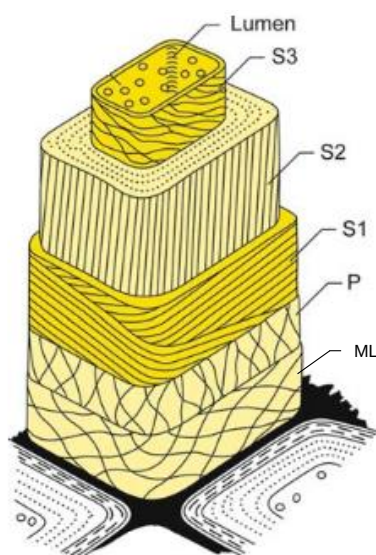


Figure II.2. The cell wall structure of a wood fiber. The cell wall is divided into different layers, the middle lamella (ML), primary wall (PW), secondary wall, which is formed by the outer (S1), middle (S2) and inner (S3) layers, and lumen (adapted from Agarwal, 2006).

The middle lamella (ML) is found between the individual cells, which ensures the adhesion of the cells to each other, forming the plant tissue. The middle lamella is highly lignified and rich in peptides, mainly in the initial formation stage, and presents a thickness of 0.5 to 1.5 μm (Plomion, Leprovost and Stokes, 2001).

The primary wall (PW) is the first layer deposited during cell development, allowing young cell growth. Consequently, the orientation of the fibrils in the external layers is more oblique. The primary wall consists of cellulose, in limited quantities, hemicelluloses, pectin, and proteins immersed in a lignin matrix, presenting a thickness between 0.1 to 0.2 μm (Plomion, Leprovost and Stokes, 2001; Carvalho et al., 2009; Wiedenhoef, 2010).

The secondary wall, with a thickness between 1 and 10 μm , is the layer deposited on the primary wall after its complete superficial growth and can be divided into three layers: external secondary wall (S1), medium secondary wall (S2), and the internal secondary wall (S3) (Plomion, Leprovost and Stokes, 2001; Carvalho et al., 2009). In the S1 layer, with a thickness of 0.2 to 0.3 μm , the cellulose fibrils have a smooth helical orientation. The angle formed between the fibrils and the cell axis can vary between 50 and 70°. This layer is more lignified, resembling in this sense more like the primary wall (Brändström et al., 2003). The S2 layer is the thickest layer of the cell wall (1 to 9 μm). In this layer, the fibrils are arranged at an angle that can vary between 10 and 30°, which decreases with increasing cell length. The angle variation formed by the cellulose fibrils relative to the cell axial axis results from internal and external influences (Rafsanjani et al., 2014). The S2 layer dominates the fiber mechanical properties. In the S2 layer, the microfibrils are spiraling around the fiber axis, at a constant angle to the fibril. Although the S1 and S3 layers also present a spiral fibril structure, they have a smaller contribution to the mechanical properties compared to the S2 layer (Niskanen, Kajanto, and Pakarinen, 1998). The S3 layer is located adjacent to the lumen. In this layer, the cellulose fibrils are arranged at a moderate angle, but not in a strictly parallel shape. It also has a higher concentration of non-structural substances, which gives an almost smooth appearance to the lumen surface (Fahlén, 2005).

Lignocellulosic materials also can be divided into two types: hardwood, which comes from angiosperms (flowering plants), and softwood, which comes from gymnosperms (mainly conifers). Hardwoods and softwoods differ from the types of trees from which they are resulting and from the component cells. Softwoods have a short number of types of cells and little variation in the structure of these cells while hardwoods have a higher number of cell types and a much higher degree of variability within these cell types. Hardwoods have a characteristic type of cell named a vessel element, unlike softwoods (Wiedenhoef, 2010). Both hardwood and softwood are used in the production of different tissue products. The amount of lignocellulosic materials used depends on the type of product produced (Stankovská et al., 2020).

II.1.1.1.1. Hardwood Fibers

Hardwood fibers are short fibers with widths between 15-20 μm and lengths between 0.6-1.3 mm (Baucher et al., 2003). Hardwood fibers, such as *Eucalyptus globulus* (Figure II.3), have caught the attention of the pulp and paper industry, in Portugal. This species is one of the most common species used, presenting very advantageous characteristics, such as uniform raw material having narrow fiber size distribution and low fines content, which lead to obtaining good quality pulps (Pinto, Evtuguin and Neto, 2005; Pirralho et al., 2014). These aspects allow better control of the paper characteristics and papermaking process, including easier drainage and separation, which are mostly limiting factors for high-speed tissue paper machines (de Assis et al., 2018a). Other hardwoods widely used in the industry are those of the genus *Betula spp* and, more recently of the genus *Acacia spp*. Some species of these trees show very interesting properties due to differences in their chemical composition and morphology (Pinto, Evtuguin and Neto, 2005; Santos, Anjos and Simões, 2005; Marinho et al., 2017). Hardwood pulps are mainly used for providing good formation, smooth surface, thinner pore structure, and high opacity. In addition, in tissue products, hardwood fibers also provide bulk, porosity, softness, and absorption (Kibblewhite, 2005; Foelkel, 2016). Hardwood pulps are used in different types of tissue materials at levels ranging from up to 100%, but more typically from 50% to 80% of the fiber furnish (de Assis et al., 2018a). The eucalyptus fibers content in tissue products can vary from 50 to 60% in napkins, bath tissue, and towels to 100% in facial tissues (Hall, 1983; de Assis et al., 2018a).



Figure II.3. *Eucalyptus globulus* species (adapted from Miranda and Pereira, 2015).

Eucalyptus globulus species was the precursor and the most successful wood for the pulp production in temperate regions due to the tree's growth, stems characteristics, wood anatomy, and fiber biometry, as well as a favorable pulp chemical quality (Pirralho et al., 2014; Rana et al., 2014; Neiva et al., 2015).

This species appears as ideal for the tissue materials production due to the relatively short fiber length (0.65-0.80 mm) while other European species are 15 to 40% longer, the low fiber coarseness (7-9 mg/100m) as regards to other cellulosic fibers, and consequently, the high number of fibers per gram (in the order of 22-26 million) (Noe and Demuner, 1997; Magaton et al., 2009). Besides, the collapse resistance of eucalyptus fibers comes from the high cell wall thickness (Dutt and Tyagi, 2011). The fiber wall microfibrils have a small winding angle with the fiber axis compared to other hardwood fibers (Demuner and Claudio-da-Silva, 2005). As reported by Foelkel (2007), to achieve a high bulk, tissue manufacturers should pursue eucalyptus pulp having high coarseness that minimizes fiber collapsibility and structures densification, low fine content to avoid densification and reduction in drainability, low hemicellulose content to reduce binding ability, and high fiber deformations to improve structure bulk, porosity, softness, and absorption properties. For these purposes, as eucalyptus pulps are suitable to produce high-quality tissue papers, low fiber modifications, such as refining processes, are recommended, with Schopper-Riegler values between 22 and 35 degrees (Ramires et al., 2012; de Assis et al., 2018a).

II.1.1.1.2. Softwood Fibers

Softwood fibers are long fibers with widths between 20-40 μm and lengths between 1.7-3.7 mm (Baucher et al., 2003). These fibers, being more common the genus *Pinus spp*, even when present in small proportions in the mixture, not only provide properties such as absorption, porosity, and strength to fibrous structures, but also provide a strong fiber network to increase wet web strength, paper machine runnability and, consequently, converting operations (Guimarães, Figueiredo and Ferreira, 2003; Kibblewhite, 2005; Foelkel, 2015). Within this genus, *Pinus sylvestris* is one of the most important species in Europe (Ek, Gellerstedt and Henriksson, 2009). In addition, the genus *Picea spp* also stands out, since it is the most common in Nordic countries, such as Sweden, and the species most widely used is *Picea abies* (Ek, Gellerstedt and Henriksson, 2009).

The strength properties of the fiber network are achieved with long and thin softwood fibers, with a low coarseness-to-length ratio (Nordström and Hermansson, 2018). In contrast, softwood fibers with thick cell walls are less likely to collapse during the papermaking process, forming bulky tissue materials, with improved structure porosity and water absorption (Stankovská et al., 2019). However, softwood fibers with thin cell walls are more flexible, providing structures with soft properties (Zou, 2017; de Assis et al., 2019). The low fine amount of softwood pulps also contributes to maximizing the long fiber performance, minimizing the use of the chemicals, reducing drainage resistance and paper dusting, and increasing retention (de Assis et al., 2018a). The high unrefined strength of softwood pulps is favored to maximize bulkiness and achieve the desired strength at the same time, without or with minimum application of fiber modification processes, such as refining (Nanko et al., 2005).

II.1.1.2. Wood Fibers Morphology

The wood fiber morphological properties include fiber length, width, coarseness, cell wall thickness, deformations, and fines content (Biermann, 1996; Sixta, 2006).

Fiber length influences the structure strength properties (Trepanier, 2017). Longer fibers can individually establish more bonding between fibers, which promotes strength development (Kullander, 2012; Trepanier, 2017). However, these fibers can lead to a flocculation increase in the paper machine fibrous suspension, contributing negatively to the sheet formation (Jagannadh, Jordan and Brodkey, 1991; Joutsimo, Wathén and Tamminen, 2005; Nordström and Hermansson, 2018).

Fiber width is also one of the fiber pulp fundamental characteristics since this property characterizes and distinguishes different wood fibers, in addition to the fiber length.

Coarseness is defined by the mass per unit fiber length expressed in milligrams per 100 meters and is related to the fiber cell wall thickness, width, and density (Nordström and Hermansson, 2018). Coarseness also presents a high influence on fiber flexibility and, therefore, on fiber compatibility. In addition to coarseness affecting the number of fibers in suspension, it also affects fiber deformations, which influences its flexibility (Kerekes and Schell, 1995; Iribarne and Schroeder, 2000). In softwoods, the early woods present thinner and less dense fibers, while the late woods present thicker and denser fibers, with higher coarseness (Milanez and Rost, 2005).

The fiber wall thickness directly affects the fiber flexibility, namely the fiber's ability to bend, affecting the inter-fiber bonding degree and the material cohesiveness (Curto, 2012). Fiber flexibility plays an important role in the properties of fiber-based materials since it influences the structure's apparent density, porosity, softness, strength, and optical properties (Paavilainen, 1992; Paavilainen, 1993a). The fiber's flexibility occurs simultaneously with the fiber's collapse and is directly related to the fiber's RBA (Tao and Liu, 2011). Different fibers with different cell wall thickness dimensions can present similar coarseness. For this reason, fiber properties are influenced by the relations between fiber coarseness, width, cell wall thickness, and lumen (Paavilainen, 1993b; Curto et al., 2009).

Throughout the production process, several fiber deformations can occur, such as curl and kink (Page et al., 1995). Fiber curl includes the continuous and gradual fiber curvature, being related to the type of wood and operational conditions, such as the temperature and pulp consistency. Fiber curl increases when the fibers are subjected to mechanical stresses at high consistencies, such as during disintegration and refining processes. Fiber kink is the abrupt change in the fiber curvature and is measured by the number of bends in the fibrous network or by the fiber kink angle average. The fiber deformations are important as they can predict the paper formation and fiber bonding (Page et al. 1995; Iribarne and Schroeder, 2000).

Fines content is relevant to the pulps and paper properties. Fines are fiber fragments with lengths less than 0.2 mm, playing an important role in fiber interactions (Sirviö and Nurminen, 2004). In the fibrous network, the thin fibrillar fines fill the empty spaces between fibers, creating a more organized and closed structure, which contributes to the inter-fiber bonding increase and bulk decrease (Joseleau, Chevalier-Billosta and Ruel, 2012). Therefore, a pulp with a low fines content presents weak fiber interactions and, consequently, lower strength values. However, an excess of fines content can cause problems in the water removal in the paper machine and, therefore, higher drying energy consumption (Odabas et al. 2016).

Fiber wood morphological properties can be determined in image analysis-based tools, such as fiber analyzers. Of the various existing fiber suspension analyzers (Guay et al. 2005; Hirn and Bauner 2006), MorFi LBo1 Fiber Size Analyzer (TECHPAP, Grenoble, France) and Lorentzen & Wettre Fiber Tester (Kista, Sweden) can be highlighted. The MorFi presents a high-resolution camera (4 $\mu\text{m}/\text{pixel}$) with non-polarized light and the fiber suspensions are analyzed through a channel while the Fiber Tester uses a 10 $\mu\text{m}/\text{pixel}$ resolution camera with non-polarized light and the fiber suspension is measured by a capillary between glass plates which ensures good fiber alignment (Tourtollet et al., 2003; Li et al., 2011). Although these methods are useful for evaluating the two-dimensional fiber properties, they are unable to analyze the third fiber dimension, namely the fiber effective thickness that included the cell wall and the lumen. These properties can be acquired through other image-based tools, namely SEM (Reme et al., 2002). SEM allows quantifying the 3D fiber dimensions in their structure cross-section. The fiber-based materials production process causes fiber tensions, leading to their collapse in the 3D network. For this reason, the fiber lumen is not occasionally visible in the fiber effective thickness in the structure Z direction (Kallmes and Bernier, 1963). Nevertheless, the quantification of the fiber effective thickness measured in the material structure is crucial since it is the main fiber parameter that influences the 3D material structure, apparent density, thickness, porosity, and end-use properties.

II.1.1.3. Wood Fibers Chemistry

The wood fibers' chemical composition differs significantly depending on the species. The main cell wall constituents are cellulose (structural component), hemicelluloses, and lignin (sub-structural components), which are present in all woods (Rodrigues et al., 2018). There are also other minority components of low molecular weight, such as extractives and mineral substances. The proportions and chemical composition of hemicelluloses and lignin vary in hardwood and softwood fibers; however, cellulose is the majority component of both types of woods (Baucher et al., 2003; Rowell et al., 2005) (Figure II.4). The amount of each compound can also differ between species, with the tree age, different parts of the tree (leaf, stem, root), geographic location, climate, soil, among other factors (Sixta, 2006).

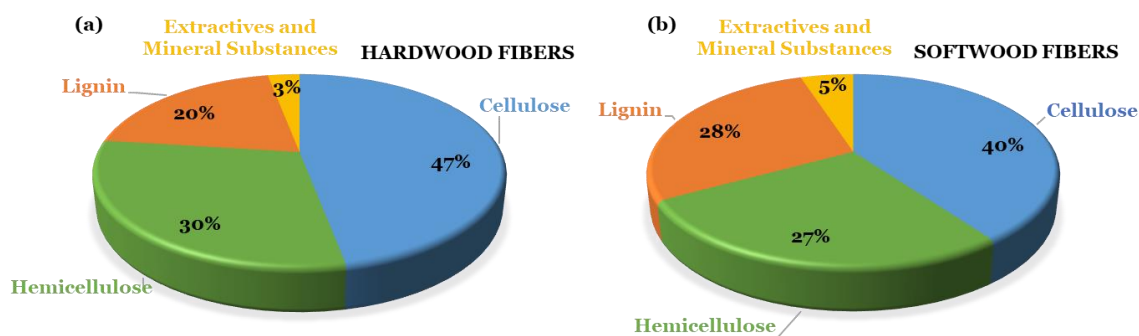


Figure II.4. Average chemical composition of hardwood (a) and softwood (b) fibers (adapted from Baucher et al., 2003; Rowell et al., 2005).

In contrast, different chemical properties are evaluated to characterize the wood fibers, such as hemicellulose content, carboxylic groups content, and intrinsic viscosity, since they can influence the tissue paper properties of the final product (Sixta, 2006).

Hemicelluloses are polysaccharides presenting an amorphous structure with short and branched chains, that are essentially composed of units of hexoses (D-glucose, D-mannose, or D-galactose) and pentoses (D-xylose or L-arabinose) with small amounts of hexuronic acids and deoxyhexoses (Mokfienski et al., 2008; Ek, Gellerstedt and Henriksson, 2009). Hardwood fibers present a higher percentage of pentosans, while softwood fibers have a higher amount of hexosans (Rowell et al., 2005). Hemicelluloses contribute to the establishment of inter-fiber bonds, which positively influence the paper's tensile strength (Anjos, Santos and Simões, 2004; Xu et al., 2006; Neiva et al., 2015). Hemicellulose hydrophilic properties also contribute positively to the fiber absorption capacity, promoting its hydration and swelling (Chai, Hou and Zhu, 2003; Mokfienski et al., 2008). On the other hand, the excess hemicellulose content can compromise the tissue paper softness. Hemicelluloses increase inter-fiber interactions, which can contribute to decreasing structure bulk, and, consequently, paper softness (Biermann 1996; Chai, Hou and Zhu 2003). However, removal of xylans, a group of hemicelluloses, in eucalyptus pulp slurry was found to increase bulk and absorption properties and to decrease the tear and tensile strength properties (Gomes, Ribeiro and Colodette, 2011).

Carboxyl groups can arise both during alkaline fiber pulps degradation, creating terminal carboxylic acid groups at the reducing end of cellulose and hemicellulose chains, as well as during pulp bleaching, or occur naturally in hemicelluloses (Biermann, 1996). Its hydroxyl groups contribute to the establishment of bonds between fibers and water, providing more interaction points (Hon and Shiraishi, 2001; Mokfienski et al., 2008), and between fibers and cationic additives, providing its retention (Chai, Hou and Zhu, 2003).

Intrinsic viscosity is directly related to the polymerization degree of its cellulose chains (Biermann, 1996). Generally, low viscosity values correspond to more degraded fibers, losing some of their intrinsic strength and negatively influencing the structure's tensile strength (Foelkel, 2007). High fines content is also correlated with the high intrinsic viscosity.

Different authors have reported that below a certain viscosity degree, losses of mechanical strength are more significant, and overall, more resistant and better-performing fibers have higher intrinsic viscosity values (Biermann, 1996; Foelkel, 2007).

II.1.1.3.1. Cellulose

Cellulose is the main component of the plants' cell wall due to its chemical and physical properties and its supramolecular structure. The empirical formula of the cellulose polymer is $(C_6H_{10}O_5)_n$, where “n” is the polymerization degree. This polymer is linear and consists of β -glucose units (Figure II.5), interconnected by β -glycosidic bonds ($1 \rightarrow 4$), presenting reactive points represented by the functions of hydroxyl groups (Mousa, Dong, and Davies, 2016). This bond results in the 180° plane rotation of the alternating glucose units, in which two of inverted glycosidic rings form cellulose disaccharide named cellobiose (Klemm et al., 2005). Considering the raw material and the isolation mode, the cellulose polymerization degree varies, mainly, between 5000 and 10,000 (Jorfi and Foster, 2015).

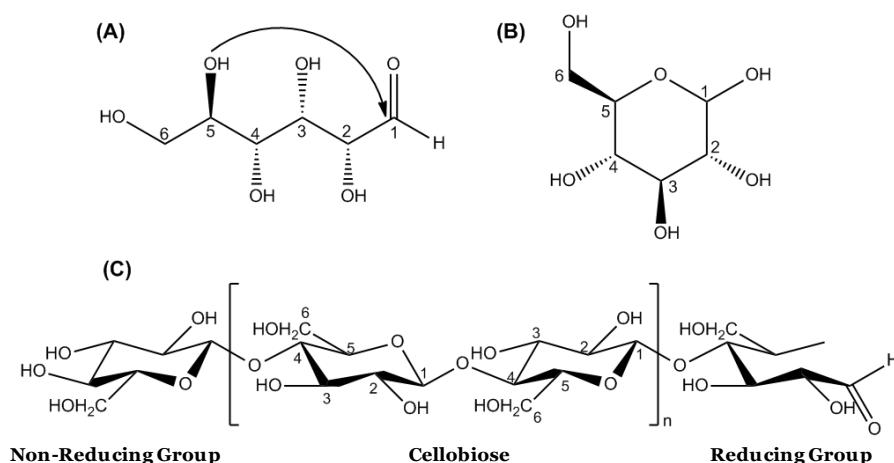


Figure II.5. Molecular structure of the glucose monomer in a linear chain (A) and cyclic chain (B), as well as the natural polymer cellulose and its monomeric cellobiose unit (C) (adapted from Klemm et al., 2005).

According to the organization of the cellulose molecular structure (Figure II.6), the hydrogen bonds between hydroxyl and oxygen groups ($O - H \cdots O$) of the adjacent rings of the cellulose molecules stabilize their bond, resulting in a molecule linear configuration. This structure is referred to as cellulose I or native cellulose. The average $O \cdots H$ distance is 0.17 nm, and the $O - H$ distance is 0.1 nm. Each glucose unit can form three hydrogen bonds. In an ordered region of cellulose, two bonds ($O6 - H \cdots O_3$ and $O_3 \cdots H - O6$) form between chains (cellulose molecules), and the third bond forms within the chain ($O2 - H \cdots O6$) (Retulainen, Niskanen and Nilsen, 1998).

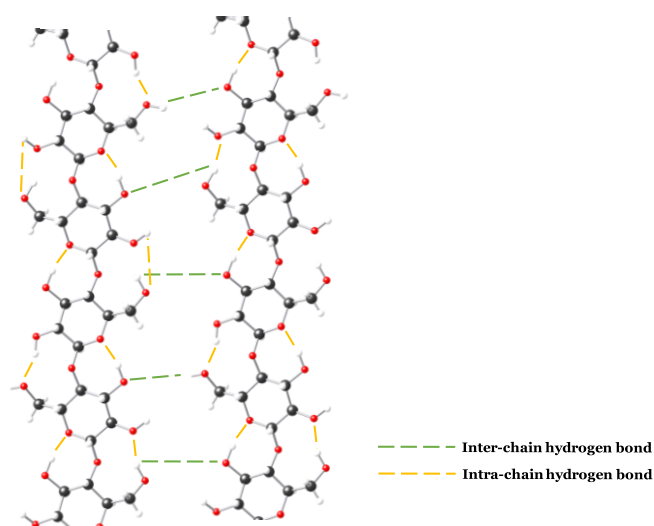


Figure II.6. Planar projection of two cellulose chains showing some inter and intra-chain hydrogen bonds between these cellulose molecules (adapted from Retulainen, Niskanen and Nilsen, 1998).

During biosynthesis, these bonds promote the parallel accumulation of multiple cellulose chains, forming elementary fibrils that aggregate and originate microfibrils, and these macrofibrils, as shown in Figure II.7 (Zimmermann, Pöhler, and Geiger, 2004). In this way, the networks of intra and intermolecular bonds make cellulose a relatively stable polymer and provide fibrils rigidity in the axial direction (Moon et al., 2011). The molecular organization of cellulose is not uniform throughout its structure, presenting crystalline regions and amorphous regions. In crystalline regions, cellulose molecules are arranged with a higher organization degree, which confers higher tensile strength, stretching, and solvation to the fiber. On the amorphous regions, cellulose molecules exhibit a higher disorder arrangement, which confers higher flexibility, being susceptible to attack by reagents and water absorption to the fiber (Kadla and Gilbert, 2000; Klemm et al., 2005). Cellulose can also have accessible and non-accessible regions, which refer to the availability of cellulose for water, microorganisms, among others. The crystalline cellulose surfaces are accessible, unlike the rest of crystalline cellulose. Most of the amorphous cellulose is accessible, but part of it is covered with hemicelluloses and lignin that limits its accessibility. The cellulose accessibility concepts are very important in moisture sorption, pulping, chemical modification, extractions, and interactions with microorganisms (Rowell et al., 2005; Fernandes et al., 2011).

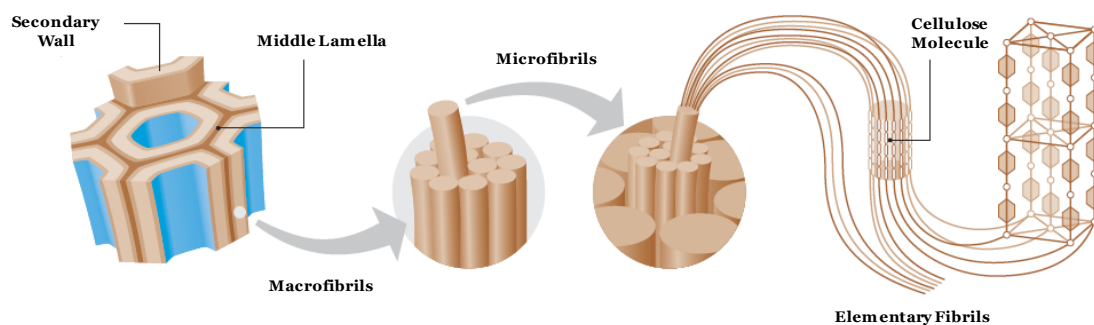


Figure II.7. Schematic representation of the arrangement of cellulose units on the cell wall. Parts of the fibrils are arranged in an orderly fashion and provide crystalline properties (adapted from Zimmermann, Pöhler, and Geiger, 2004).

In the crystalline regions, the geometric arrangement repeats itself in the main axes of the crystal structure to form the total crystal volume. In the case of cellulose, there is more than one polymorphic form, which means that cellulose presents extremely distinct three-dimensional crystal structures. This phenomenon is known as polymorphism. Therefore, in addition to cellulose I or native, cellulose also exhibits other types of polymorphs, such as cellulose II, III, and IV. Cellulose II is an important type of cellulose used to produce cellulose derivatives, which is not found in nature. Cellulose II is obtained from native cellulose by mercerization (treatment with a strong alkali, NaOH) and regeneration (treatment with carbon disulfide to form a soluble xanthate derivative). As this transition is irreversible, cellulose II presents a more stable structure concerning cellulose I. The main differences between both structures are the intermolecular bonds between adjacent cellulose molecules, as well as the positions of the intermolecular hydrogen bonds. On the other hand, cellulose III_I or III_{II} polymorphs are obtained by treating cellulose I or II, respectively, with liquid ammonia at about -80°C followed by evaporation of ammonia. Alkaline treatment of cellulose III also provides cellulose II. Finally, cellulose IV_I or IV_{II} polymorphs are obtained by heating cellulose III_I or III_{II}, respectively, in glycerol at 260°C (Rowell et al., 2005; Moon et al., 2011; Panić et al., 2013).

II.1.1.3.2. Hemicellulose

As previously mentioned, hemicelluloses are polymers formed by different types of sugars, linked by condensation, generally of lower molecular weight compared to cellulose, which can be branched and, essentially amorphous (Figure II.8). Hemicelluloses are associated with cellulose and contribute to the plant structural components since they form the plant cell wall (Rowell et al., 2005; Donate, 2014). The high hemicellulose content of woods is associated with the situations of the tree under stress and compression (Rowell et al., 2005).

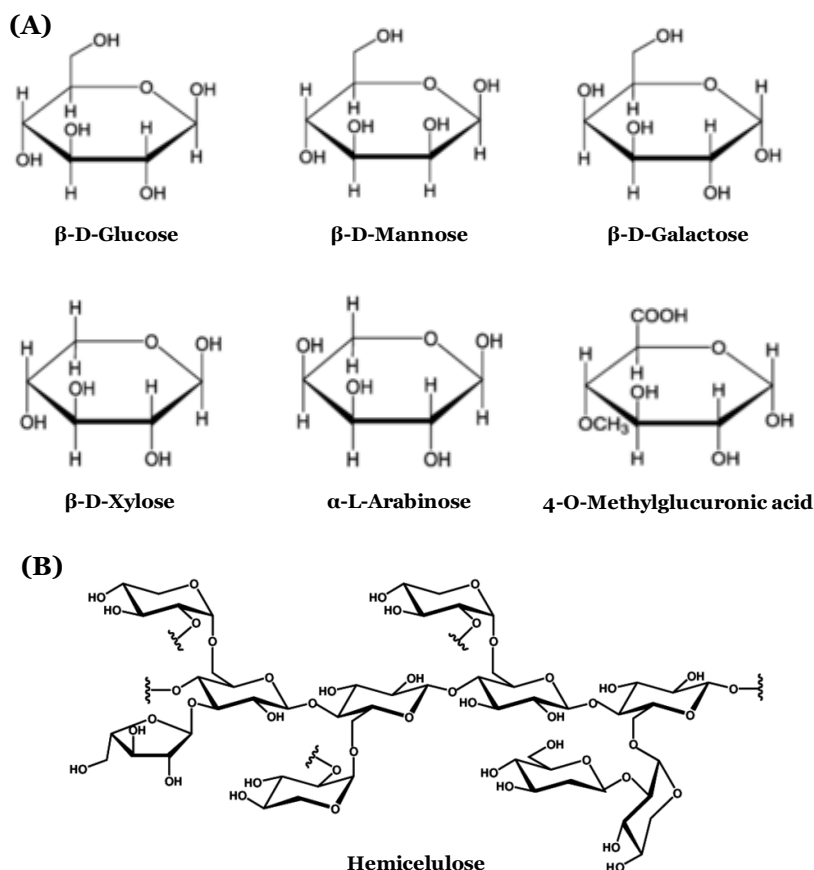


Figure II.8. Sugar monomer components of wood hemicellulose (A) and examples of hemicellulose structure (B). The *D* and *L* configurations are associated with the two optical isomers of glyceraldehyde and designate the hydroxyl group conformation on C-4 for pentoses and C-5 for hexoses. The α and β anomers refer to the configuration of the hydroxyl group on C-1 (adapted from Rowell et al., 2005; Donate, 2014).

Some hemicelluloses in combination with cellulose and lignin molecules, present a storage function and increase strength to enzymatic degradation and insolubility of cell wall components. Additionally, hemicellulose constitutes the cell wall structure and also presents a function of the regulation of the cell growth process (Chen, 2014).

There are four well-defined groups of hemicelluloses in all plants, namely, xylans, galactoglucomannans, glucomannans, and arabinoglucouranoxylans. In hardwood hemicelluloses, xylans predominate (20-35%) and traces of glucomannans are visible (2-5%) (Laine, 2005; Chen, 2014). The xylan is substituted with sidechains of 4-O-methylglucuronic acid units linked to the xylan backbone α -(1 $\rightarrow$ 2) with an average frequency of approximately one uronic acid group per ten xylose units. The glucomannan is composed of β -D-glucose and β -D-mannose units linked (1 $\rightarrow$ 4). The glucose:mannose ratio varies between 1:2 and 1:1 depending on the wood species (Rowell et al., 2005). In softwood hemicelluloses, glucomannans predominate (18-25%), followed by galactoglucomannans (8-20%) and arabinoglucuronoxylans (5-12%) (Laine, 2005; Chen, 2014). The galactoglucomannan presents a linear or possibly slightly branched chain with β -(1 $\rightarrow$ 4) linkages. Glucose and mannose make up the backbone polymer with branches containing galactose.

There are two fractions of these polymers: the low-galactose fraction has a ratio of galactose:glucose:mannose of about 0.1:1:4 and the high-galactose fraction has a ratio of 1:1:3. The arabinoglucuronoxylan consists of a backbone of β -(1 $\rightarrow$ 4) xylose units with α -(1 $\rightarrow$ 2) branches of D-glucuronic acid on an average of every two to ten xylose units and α -(1 $\rightarrow$ 3) branches of L-arabinofuranose, on average, every 1.3 xylose units (Rowell et al., 2005).

II.1.1.3.3. Lignin

Lignin forms about 15 to 30% of wood fibers, has the function of acting as a “cement” between fibers and protecting them against enzymatic degradation of the cell wall, resisting the attack of microorganisms. Lignin allows the tree to grow and assists in the transport of nutrients and water (Chen, 2014). Being deposited on the secondary wall, lignin provides structural rigidity, maintains vertical orientation, and reinforces the cell wall so that during the water conduction, it can withstand the negative pressure generated in the plant transpiration (Weng and Chapple, 2010).

Lignin consists of phenylpropane units and provides interconnected three-dimensional structures. The precursors of lignin biosynthesis are coniferyl alcohol, which is the predominant precursor of softwood lignin, and sinapyl alcohol, which is the precursor of hardwood lignin. Hardwoods present a copolymerization of coniferyl alcohol with sinapyl alcohol, being higher the proportion of the last one. Additionally, *p*-coumaryl alcohol appears only in monocotyledon and grasses (*Gramineae* family), together with the softwoods and hardwoods. It is the minor precursor of both hardwood and softwood lignins (Figure II.9). Hardwood and softwood lignin differ in the content of methoxy groups. Hardwood lignin has a methoxy content of 21%, while softwood lignin has a methoxy content of 15–16% (Baucher et al., 2003; Rowell et al., 2005).

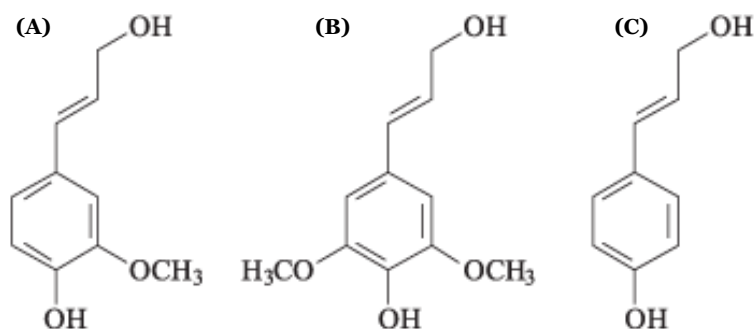


Figure II.9. Chemical structures of lignin precursors, namely coniferyl alcohol (A), sinapyl alcohol (B), and *p*-coumaryl alcohol (C) (adapted from Rowell et al., 2005).

All wood lignins consist mainly of three basic building blocks of guaiacyl, syringyl, and *p*-hydroxyphenyl portions, although other aromatic units also exist in many different types of wood. There is a wide range of structures in different wood species (Baucher et al., 2003; Rowell et al., 2005). Lignin is largely removed in chemical processes, making fibers porous and flexible. When delignification occurs, the fiber tensile strength is affected (Paavilainen, 1990; Paavilainen, 1994).

II.1.1.3.4. Extractives and Mineral Substances

Extractives and mineral substances are natural components in wood that are not necessarily chemically bonded and can be removed by extraction with inert solvents (Rowell et al., 2005). Most extractives are located at the heartwood, and some are responsible for the wood's color, smell, and durability. They comprise a wide variety of organic compounds, including fats, waxes, alkaloids, proteins, phenols, simple sugars, pectins, gums, resins, starches, glycosides, and terpenes. Unlike macromolecular components, extractives do not form the cell wall (Rowell et al., 2005).

Softwoods have a higher extractive content than hardwoods (Rowell et al., 2005). The qualitative difference in the extractive content from species to species is the basis of chemotaxonomy. For example, in softwoods, the terpene group consists mostly of monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), and diterpenes ($C_{20}H_{32}$), whereas triterpenes and sterols dominate in hardwoods. The most common terpenes in eucalyptus trees are eucalyptol, while in softwoods are α -pinene (Granström, 2007). Because they have different properties such as anti-cancer, anti-inflammatory, bactericide, fungicide, among others, the extractives have found application in medicine, cosmetics, and as preservatives (Rowell et al., 2005; Granström, 2007).

II.1.1.4. Pulping and Bleaching Wood Fibers

The pulps obtained from hardwood and softwood fibers are the raw material most used for paper materials production. The pulp can be produced from several different processes, which have undergone some changes over the years, in order to become increasingly economical, effective, and ecological (Sixta, 2006).

Virgin fibers produce paper with higher absorption rates, better color, smoother, and more durable (Sheikhi et al., 2013). Different processes can be used to isolate virgin fibers from wood, namely, mechanical, thermomechanical, chemo-mechanical, semi-chemical, and chemical processes (Biermann, 1996). On a global scale, pulps are mostly produced through chemical processes called soda, acid sulfite, and the most used today, kraft (or sulfate) cooking.

Soda cooking is an alkaline process, using sodium hydroxide (NaOH) or anthraquinone (AQ), as the cooking agent (Biermann, 1996; Sixta, 2006). However, not all raw materials can be used in this type of cooking because it exhibits a high expenditure of NaOH. This fact led manufacturers to improve the process through several changes. Years later, these changes originated the kraft pulp process (Sixta, 2006).

Kraft cooking applies to a wide variety of wood species with a very efficient regeneration of chemicals and energy, and with the capacity to produce pulps with good strength (Sixta, 2006). Overall, in the continuous process, wood chips are inserted into the digester with a solution (white liquor) consisting essentially of NaOH and sodium sulfide (Na_2S), which are the active reagents in removing lignin from wood. Sulfide accelerates this removal and, consequently, the time required for the exposure of wood chips to the alkaline environment is less.

Therefore, the degradation of polysaccharides is also less, producing better quality pulps (Biermann, 1996; Sixta, 2006; Mokfienski et al., 2008). The black liquor containing the dissolved material is extracted during the pulp washing process and is sent to the recovery circuit (Sixta, 2006).

Currently, only about 5.3% of the world's pulp production is obtained through the cooking process with acid sulfite, due to the weakening of the pulp properties (Sixta, 2006). However, initially, it started to be the dominant process, since it originated pulps with a good whiteness, smoothness, and a low cost relative to the use of applied chemicals. In this process, a bisulfite or sulfite solution is used, adding bases of calcium, magnesium, ammonia, or sodium, for example (Hon and Shiraishi, 2001). Wood polysaccharides, especially hemicelluloses, are easily degraded in this type of cooking. There may be some cellulose degradation, depending on the time and cooking conditions, however, the cellulose is not very affected in terms of physical state, since it presents a crystalline structure (Ek, Gellerstedt and Henriksson, 2009).

After the cooking process, the raw pulps obtained are subjected to a bleaching process, to eliminate residual lignin and chromophore compounds in successive steps, obtain, after each phase, increasingly bleached pulps. This process normally presents five bleaching stages, in which an extraction stage with NaOH occurs between two stages, where the pulp is neutralized (Sixta, 2006). Some of the reagents used in this process include oxygen (O_2), chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), and ozone (O_3). However, due to environmental problems, the use of chlorine-based compounds can be a problem, as they can produce organochlorine compounds (Biermann, 1996; Bajpai, 2005; Sixta 2006). These problems have deserved particular attention in recent decades, leading to the elimination of elemental chlorine from the bleaching process. Therefore, elemental chlorine-free bleaching sequences (ECF) and, more recently, total chlorine-free sequences (TCF) have emerged (Bajpai, 2005; Sixta, 2006). The ECF sequence is based essentially on ClO_2 , with or without reinforcement of oxygen-based reagents, while the TCF sequence is based exclusively on oxygen-based reagents. However, disadvantages such as the more intense polysaccharides degradation, consequent yield, and pulp properties loss are observed (Bajpai, 2005).

In general, the chemical composition of all paper materials, except the most specialized ones, is essentially the same. However, the main differences between these products are the fiber choice and their modification process steps (Sampson, 2009).

II.1.2. Structural Hierarchy

The concept of structural hierarchy can be applied to paper structures to establish the role of the fibers in the paper structure. The paper structure is dependent on the size or scale of the features of interest, while the paper physics is independent of the scale being considered (Kortschot, 1997).

Tissue paper materials, for their multiplicity, cost-effectiveness, cleanliness, and convenience, play an important role in society (de Assis et al., 2018a). The use of sustainable raw materials and the absence of competition between the various materials demonstrate that tissue papers present promising future markets.

Therefore, it is expected that the production of these materials will continue to increase, which demonstrates the financial importance of understanding the phenomena in the manufacturing processes and the materials to be used (Raunio and Ritala, 2012).

Paper materials are composed at various scales in a stochastic network of fibers. These materials are produced in the wet state from discrete tubular fibers that are bonded mainly through hydrogen bonds (Bronkhorst, 2003). The fiber orientation distribution is generally weighted in the manufacturing direction, resulting in an anisotropic material. This manufacturing process differentiates them from other fibrous materials (Sampson, 2009). Figure II.10 shows a scanning electron microscopy (SEM) image of the surface of isotropic laboratory-produced paper material, in which fiber orientation is not considered. These laboratory structures are produced with a random fiber deposition.

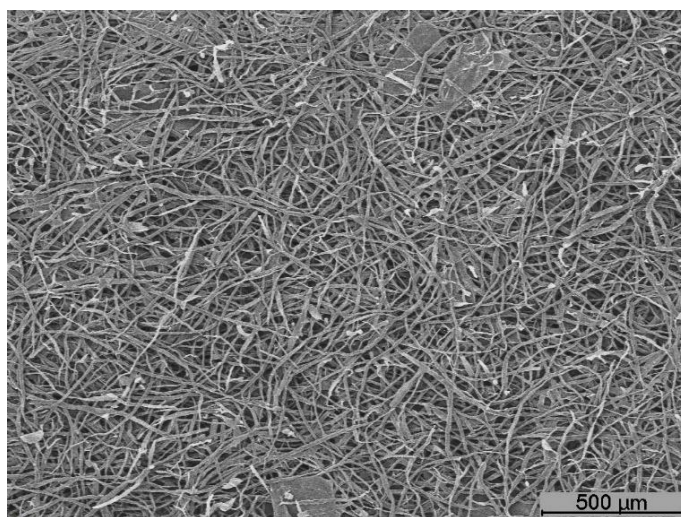


Figure II.10. SEM image of a laboratory paper material sample with a random fiber network, with an average fiber width of 19 μm and an average fiber length weighted by length of 0.7 mm.

Cellulosic fibers, from wood or other similar natural origins, and the porous space formed by and between them are essential for the final paper product. These fibers are separated by industrial pulping and bleaching processes, to produce paper pulps (Alava and Niskanen, 2006).

The formation stochastic process of these materials leads to a planar network structure whose fiber positions, orientations and deformations are random (Figure II.10), showing correlations that influence the final properties (Alava and Niskanen, 2006). The amount of fiber mass per area, in units of grams per square meter, is essential to characterize each type of paper material produced (Sampson, 2009). The small thickness of tissue materials presents great challenges for the network structure study, as the corresponding porosity is a lower limit that does not agree with the porosity measured inside the paper sheet (Alava and Niskanen, 2006).

The two-dimensional (2D) structure determines many paper materials properties, but the three-dimensional (3D) porous structure is also fundamental as the pores provide bulk, opacity, flexibility, and fluid transport properties (Niskanen, Kajanto and Pakarinen, 1998). Although the network structure generally has a lower density than the surface layers, the number of sheet fiber layers and the fiber properties can be increased and changed in the laboratory, in order to obtain a model analog that shows the transition from 2D to 3D structures (Niskanen and Alava, 1994).

II.1.2.1. Two-dimensional (2D) Random Fiber Networks

The 2D random fiber network is characterized by the fiber length and the number or mass of fibers per unit area, defined by basis weight. All correlations between fibers are absent in the random network since the position of each fiber is independent of all other fibers (Niskanen, Kajanto and Pakarinen, 1998). Coverage is a useful concept to characterize a completely 2D random network. For a specified number of fibers in a large area, the average coverage is the median number of fibers at any point of the plane (Sampson, 2009). The coverage value completely specifies the 2D random network when the fiber properties are constant (Bronkhorst, 2003; Sampson, 2001). The coverage provides a precise value for the effective number of fiber layers in the sheet, so this parameter is not changed by altering the thickness subject to the papermaking process (Niskanen, Kajanto and Pakarinen, 1998). The fiber network bonding degree controls the paper materials' properties. The relative bonding area (RBA) generally characterizes the materials' bonding degree. RBA describes the paper material structure and is defined by the fibers bonded surface area divided by its total surface area (Sampson, 2009). RBA also can be calculated from the fiber flexibility coefficient, estimating the fiber bonding, and predicting the paper materials' strength properties (Tao and Liu, 2011). At very low coverage, a connected fiber network is formed only if there is enough fiber connection. The limit is at the percolation point. Below this limit, the network consists of several disconnected parts. The percolation concepts were discovered when the addition of reinforcement fibers to a "weaker" material improved the paper material properties, forming a connected sub-network between the other material components (Niskanen, Kajanto and Pakarinen, 1998). Although the 2D approach overestimates the real fiber network connectivity in the paper, since all fibers whose 2D projections cross cannot connect to each other, the 2D percolation threshold has great relevance to the tissue paper properties. Tissue materials sheets correspond to 2D networks of springs close to a percolation threshold, or with central forces (Alava and Niskanen, 2006).

II.1.2.2. Three-dimensional (3D) Random Fiber Networks

The 3D paper material pore structure influences the paper material properties, indirectly through the RBA. The 3D layered fiber network and the mutual entanglement of fibers are important for the z-direction properties of paper materials. The 3D network pores are characterized by the distribution of free spans between fibers in the in-plane and out-of-plane directions (Niskanen and Rajatorra, 2002). As the basis weight increases, the top surface roughness of the network increases, and the pores begin to form between the fibers in the z-direction of the thickness and a homogeneous 3D bulk phase grows (Hellén, Alava and Niskanen, 1997). In the 3D network formation, the fibers bend more and more in order to contact other fibers. When this flexibility is no longer possible, the pores form between fibers in the z-direction, as shown in Figure II.11.

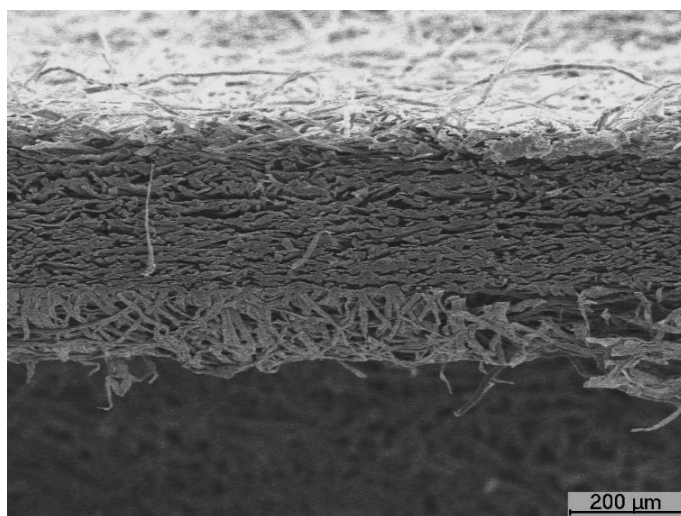


Figure II.11. SEM image of a laboratory paper material cross-section sample, with an average basis weight of 60 g/m² and paper thickness of 240 μm.

The fiber properties and structure basis weight and thickness influence the paper materials' porosity. Throughout the basis weight, the sheet structure can be represented with an increase in the sheet layers. If a structure is represented with three layers, the two surface layers have a higher density than the interior bulk layer (Alava and Niskanen, 2006). The characterization of porosity and pore dimension and distribution properties in different materials is crucial since the ability of liquids to migrate through the paper material depends on the pore sizes (Hassan, Cushman and Delleur, 1998; Lang et al., 2013; Gigac, Stankovská and Fišerová, 2017). The complexity of these porous materials is the fact that they do not have a regular pore distribution, but rather a pore dimension that varies in a wide range and the tortuous paths that the pores provide for the liquid's flow (Ghanbarian et al., 2013; Neumann et al., 2020). 3D porous materials structure knowledge is important for the prediction and development of absorption properties of tissue materials (Axelsson and Svensson, 2010).

Over the years, several techniques have been developed for the 3D porous materials structure characterization. The combination and comparison of different analysis methods can obtain a complete and effective overview of these porous paper materials (Chinga-Carrasco, 2009). Due to the complexity and non-uniformity of the material's porous structure, its quantification may be difficult. To investigate the properties and structures of different paper materials, numerical simulations of material features are needed (Wiltsche et al., 2011). There is not only one method that characterizes pores on only one scale, i.e., nano, micro, and macroscale (Lawrence and Jiang, 2017). Image analysis methods using computational tools are effective in pore properties characterization in processed images from SEM, for example (Chinga-Carrasco and Helle, 2002). The ImageJ software is a computational image processing tool that allows the pore properties characterization (Hotaling et al., 2015). This tool processes and analyzes SEM images using a systematic methodology with well-defined criteria. To use an image fraction for analysis, this fraction must be representative of the original image. This fraction must represent the material for a respective property and be wide enough to contain satisfactory information about the porous material structure to be statistically representative (Bloch and Roscoat, 2009; Xie et al. 2019). It is necessary to prove that the representative elementary area (REA) or volume (REV) is satisfactory to allow the quantification of porosity and pore size and distribution (Kanit et al., 2003; Dirrenberger, Forest and Jeulin, 2014). Other techniques also have been applied for the analysis of 3D porous paper structures, such as X-ray microcomputed tomography (Antoine et al., 2002; Holmstad et al., 2005; Chinga-Carrasco et al., 2008; Wiltsche et al., 2011; Carry et al., 2018). In addition to image analysis, the pore size and porosity can also be obtained by other methods such as the pycnometer which uses the gas displacement method to measure the volume accurately. This technique determines the density and volume by measuring the pressure variation of a gas, such as helium, within calibrated volumes (Lawrence and Jiang, 2017).

II.1.3. 3D Materials Modeling

Due to strong competition, the tissue industry is very research-intensive. The need within this industry for methods for the rational analysis of the fiber materials behavior has been emphasized, and meaningful work has been done in the modeling of fiber materials. To optimize the design of both materials and products made by them, computational methods have been used more and more in the last decades (Simon, 2020). The properties of these fibrous materials are influenced by the microstructure geometry, particularly the fiber orientation. Physical properties can be optimized by adapting the structural geometry parameters (Altendorf and Jeulin, 2011). Fiber geometries, variability in length-weighted fiber shape factor, and fiber lengths have a significant effect (Borodulina, Motamedian, and Kulachenko, 2018). The fiber length, for example, presents a higher impact on the mean values of elasticity modulus, strength, and strain-to-failure, on the other hand, the fiber curl has a more significant effect on the strain-to-failure variation (Kulachenko and Uesaka, 2012). The morphology of fiber-based materials has a deep impact on their functional properties, therefore detailed structural and morphological investigations are needed (Sampson, 2001; Gaiselmann et al., 2012; Simon, 2020).

The material design and optimization establish the need for predictive modeling tools that accurately describe the physical phenomena and 3D microstructure of the materials (Gaiselmann et al., 2012, 2013, 2014; Matouš et al., 2016; Neumann et al., 2016).

Statistical geometric modeling started with the studies by Corte and Kallmes (1960), which presented a geometric model of several 2D rigid fiber networks. These 2D networks were obtained by placing the fibers uniformly and randomly or with different flocculation rules in a rectangular or square area, with a fiber orientation adjusted by samples of known distributions (Corte and Kallmes, 1960; Bronkhorst, 2003; Lavrykov et al., 2012). These authors considered relationships between various network geometric properties, such as the number of fiber crosslinks, the average segment length between fiber and structure crosslinks and properties, the average fiber length, and the fiber population (Heyden 2000). With this work, the fibrous materials modeling appears for the first time, in 1962 (Kallmes and Corte 1962). However, these models only considered the position of the fiber in the plane (XY direction), overlooking its arrangement in the Z direction. Hence, studies with three-dimensional network models constitute the most promising innovation. In this approach, the third fiber dimension is introduced in the model, considering the variations along with the material thickness, where fibers are allowed to bend out-of-plane to account for the interwoven geometry of the fibrous material (Curto, 2012). This 3D approach was first suggested by Niskanen and Alava (1994), proposing the KCL-PAKKA model that simulates the 3D structure geometry with a fiber random arrangement in the XY plane. Additionally, the fiber flexibility allows the fibers to occupy the Z dimension equally, that is, the fibers conform to each other according to the input value for their flexibility, obtaining the 3D structures (Niskanen and Alava, 1994; Niskanen et al., 1997; Alava and Niskanen, 2006). Another 3D model for fibrous fluff materials was proposed by Heyden and Gustafsson (1998). In this model, each fiber is represented by a single circle arc and placed in a box forming a periodic network; however, the fiber bending that occurs when they are fit to the structure already formed is not described (Heyden and Gustafsson, 1998). Over the years, the KCL-PAKKA model showed improvements. Originally fibers only had two possible directions and were only crossing perpendicularly, but in the most recent presented structures, fibers were already randomly deposited (Hellén et al., 2002), and Provatas and Uesaka (2003) have introduced rules for fiber deposition.

The *voxelfiber*, a 3D fibrous materials model developed and implemented in Matlab®, based on the KCL-PAKKA model, was also presented and validated by Conceição et al. (2010) and Curto et al. (2011a), based on cellular automata, in which there is a cell Cartesian division, making each fiber represented as a sequence of voxels, where each one occupies a pre-established volume that can be defined by the user (Curto et al., 2011a). This fiber model includes the fiber internal structure and the possibility to change it and have collapsibility in the material Z direction. The fibers are also deposited one by one, each occupying its space. If any of these is rejected, the deposition process is repeated. Depending on its position, dimension, and flexibility, the fiber follows the underlying structure (Figure II.12).

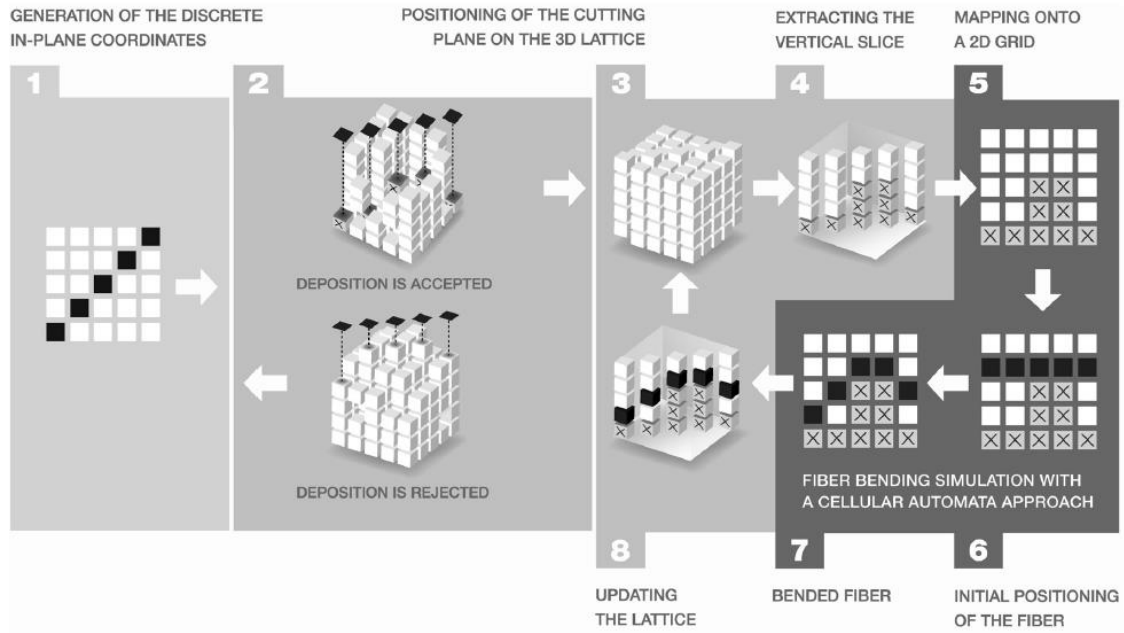


Figure II.12. Schematic diagram of the fiber deposition in the 3D matrix followed by the plane extraction and fiber bending to conform to the underlying structure (adapted from Curto et al., 2011a).

The sequential scheme of fiber deposition in the computational simulator can be described as follows (Curto et al., 2011a; Curto, 2012):

- 1) Generation of a fiber in the in-plane direction.
- 2) Testing particle deposition rule. If the fiber is not accepted, the generation trial is repeated.
- 3) Extraction of the out-of-plane slice from the 3D network where the bending procedure occurs.
- 4) Fiber deposition according to fiber flexibility and conformation to the underlying surface.
- 5) Updating of the 3D network.

The simulation method used for the *voxelfiber* model is based on designs generated from Latin Hypercube Sampling. This method consists of dividing the space formed by two variables in a subdivided square $n \times n$, and selecting, in the sample, the n points in each subframe, so that no two points are occupying the same line or column. This method can also be applied to tree-dimensions (Santner, Williams, and Notz, 2003), as shown in Figure II.13.

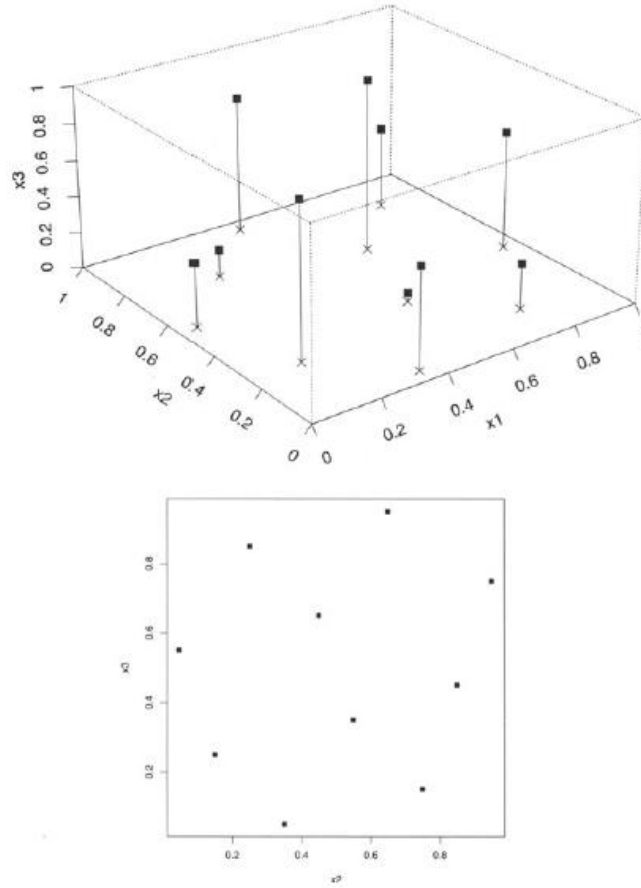


Figure II.13. Example of Latin hypercube design in three dimensions (top figure), and projection of top panel onto x_2 - x_3 plane (bottom figure) (adapted from Santner, Williams, and Notz, 2003).

In this model, fibers are modeled according to their dimensions, flexibility, and collapsibility. The input parameters are fiber length/width ratio, wall thickness, lumen thickness, flexibility, and resolution (number of layers in the Z direction). For the first time, the fiber lumen is introduced in a fiber model, allowing the study of fiber collapse and intra-fiber porosity (Curto et al., 2009), as well as predicting material structural properties (Curto, 2012). The *voxelfiber* can also be extended to incorporate other fiber sedimentation possibilities and for other fibrous materials, such as nanofibrous materials (Curto et al., 2011b; Curto et al., 2011c; Curto, Rodrigues and Santos Silva, 2015), active bi-layer cellulose-based films (Martins et al., 2018), and nanofibrous drug delivery systems (Curto et al., 2016; Morais, 2017; Curto and Morais, 2018; Morais and Curto, 2018; Morais, Simões, and Curto, 2020). The *voxelfiber* can also be applied to low-basis weight and high-porosity materials as is the case of tissue products. For this purpose, it is necessary to introduce 3D fiber data, to obtain a computational implementation adapted for tissue products, as well as to validate structures developed in this 3D computational simulator by comparison with laboratory-made structures. A calibration of the 3D computational model for tissue papers is essential, by adjusting the uniform model parameters, so that it reproduces realistic results, according to experimental data sets independent of the laboratory-made structures. Under conditions other than calibrated, the computational model must be verified, examining its ability to realistically represent the tissue properties.

To increase the reliability of the computational model, an independent set of the initial structures produced should be used to validate the 3D computational model. The fibers are randomly positioned and oriented in the XY plane to simulate the formation of isotropic laboratory handsheets (the ones used to validate the model). The model output is a 3D fiber network structure (Figure II.14) formed with occupied and empty voxels, where the information concerning each fiber is kept. At this stage, this formed structure can predict several structural properties such as thickness (local and average), porosity (interfiber and global), RBA, coverage, and the number of crossings per fiber.

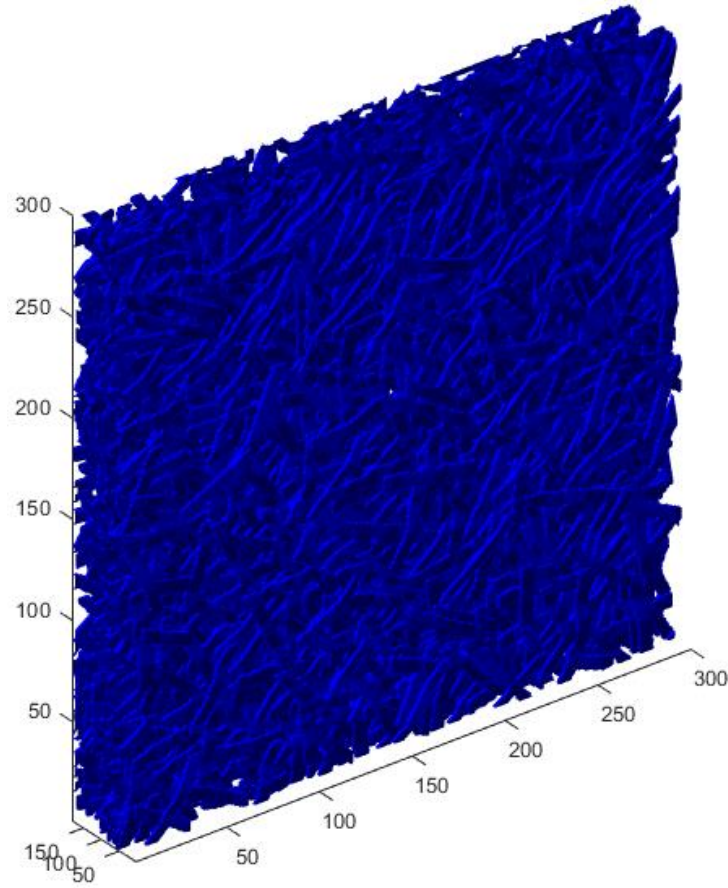


Figure II.14. Example of 3D fiber network structure simulation with a basis weight of 20 g/m², using Matlab and the *voxelfiber* simulator, done by Morais, 2021.

II.2. Fiber and Structure Modification Processes

To take advantage of the cellulosic fibers' potential, these fibers can be modified to optimize the tissue end-use functional properties. The methods currently used for fiber modification are mechanical methods, including refining treatments, biological methods, including enzyme-acting biorefining treatments, and additives incorporation. It is important to investigate several solutions of the modification process steps that allow obtaining the same or improved final properties with the maximization of the fibers suitable to produce tissue papers, such as eucalyptus fibers. The industrial-scale is used to collect information and the laboratory scale to individualize each effect and accurately characterize different formulations. The comparison of the structures without modifications with structures in which physical changes and additives are introduced will allow the introduction of innovative formulations on the market.

II.2.1. Tissue Paper Production

Tissue products must have a good quality/ price ratio and are used for cleaning, hygiene, and cosmetic purposes, including facial papers, toilet papers, towel papers, napkins, diapers, facial masks, among others. Features that add value to different tissue products include grammage or basis weight, bulk, softness, strength, and absorption, considering that each property varies depending on the product produced (Carta, 2016; Tutuş, Çiçekler and Çali, 2016; de Assis et al., 2018a, 2018d). For example, towel papers require more strength, whereas toilet papers require more softness than strength. To produce tissue paper materials, it is important to consider the properties desired by the consumer and understand how they can be achieved in terms of production.

II.2.1.1. Stocks Preparation

The first step of the process consists of the selection of the raw material/ furnish that is disintegrated in a pulper in an aqueous medium to obtain a homogeneous fibrous suspension. This stage enables fibers transportation and its mixture with chemical additives. Then, the refining process is carried out to develop the pulp mechanical properties, supporting the sheet uniformity and formation with the desired quality (Kullander, Nilsson and Barbier, 2012). During the stock preparation, contaminants in suspension are also removed by the action of centrifugal scrubbers and sieving, based on their density/ weight, size, shape, and deformability (Masternak-Janus and Rybaczewska-Błażejowska, 2015). Finally, the diluted fibrous suspension is sent into the paper machine where it is projected onto the wire to produce the tissue paper sheets.

II.2.1.2. Refining Treatments

Refining is a fiber fibrillation process used in tissue materials production to develop fiber mechanical properties, improve sheet formation, and modify the fiber drainability. The structure strength is increased due to hydrogen bonds and Van der Waal forces between the fiber surface (Mou et al., 2013). Consequently, this process decreases the softness properties by increasing the sheet density and elasticity modulus (Laine et al., 2004).

The primary fiber wall is affected/ removed, resulting in internal and external fiber fibrillation, which makes them shorter and more flexible, producing more fines and fiber curling and bending. Fibrillation improves the interfiber bonds and, consequently, the mechanical properties. With the removal of the primary wall, the fibers also improve their water swelling capacity (Joutsimo et al., 2013; Gharehkhani et al., 2015; Bajpai et al., 2018).

The refining process shapes and breaks the innermost fiber structure, resulting in the internal fibrillation phenomenon. The fibrils in the primary wall do not allow fiber radial expansion due to its orientation (Gharehkhani et al., 2015; Bajpai et al., 2018). The water penetrates the cell wall more easily, causing a fiber swelling effect (Joutsimo et al., 2013). Internal fibrillation enhances fiber flexibility with higher conformation capacity. Flexibility is a key factor in internal fibrillation, as it governs the paper formation and strength properties (Gharehkhani et al., 2015). The flexible and collapsible fibers provide a closer contact, which leads to a strong bonding, producing less bulky and porous structures (Guo et al., 2009; Chauhan et al., 2011).

External fibrillation corresponds to the fibril's removal from the fiber surface, exposing the S2 layer. The highest effect of external fibrillation is the fibrils' specific surface area increase. This phenomenon can be observed in Figure II.15a, as the fibrils are attached to the fiber wall. On the other hand, during this process, some hydrophilic compounds from the cell wall are released, producing a gel-like layer (Fig. II.15b), which improves the inter-fiber bonding (Gharehkhani et al., 2015). This type of fibrillation promotes better sheet formation, contributing to a decrease in flocculation and improved mechanical properties (Gurnagul et al., 2009; Mou et al., 2013).

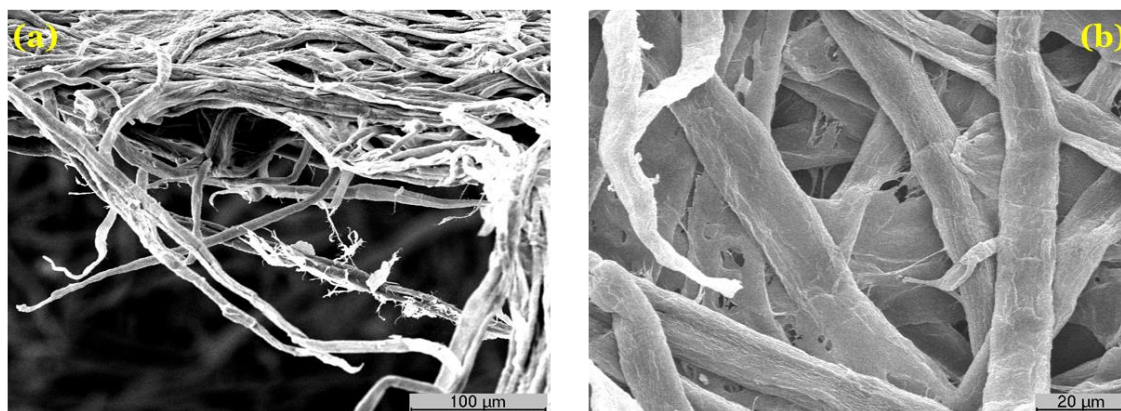


Figure II.15. Examples of SEM image of a laboratory paper material sample with external fibrillation (a), and with gel-like material links (b) of dried bleached kraft eucalyptus pulp.

At the industrial level, refining also increases the adhesion strength of the structures on the Yankee cylinder surface, which can affect the creping process, the fiber flexibility, the contact area between fibers, and the fines content. This process increases the wet tensile strength at the expense of softness and absorption decreased (Gigac and Fišerová, 2008; Chang et al., 2018). Normally, the refining of hardwood and softwood fibers is carried out separately, but this treatment can also be applied to the mixture of both fibers. Mixed refining affects fiber morphology and presents better, or comparable strength, bulk, stiffness, and air permeance properties compared to separate pulp refining (Chauhan et al., 2011). However, in tissue paper production, a good approach would include a first stage of low-intensity refining, to develop its mechanical properties, and a second refining stage, with the fiber mixture to develop drainage properties and sheet formation (Leach, 2017). Industrial refiners commonly used are disc refiners (Figure II.16a), while in the laboratory, a PFI mill refiner (Figure II.16b) is used to evaluate and separate the effects of this process step. In both, the fiber suspension is between a rotor and a stator, in which it is exposed to the mechanical treatment.

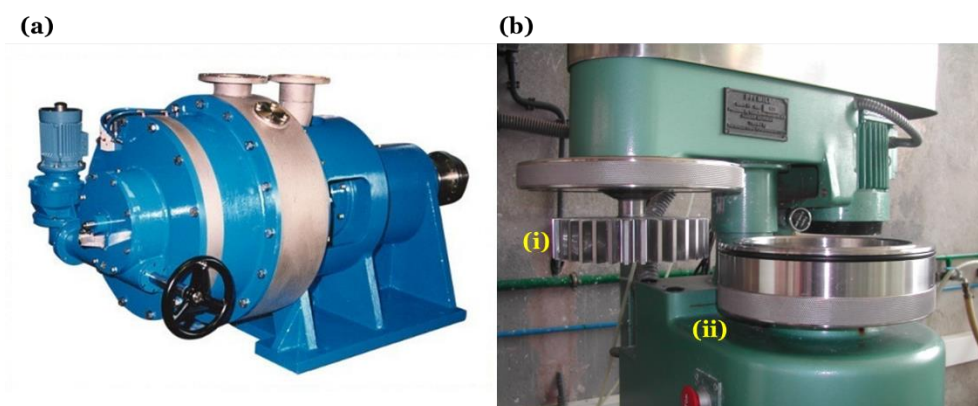


Figure II.16. Examples of an industrial disc refiner (a), and a PFI mill refiner, with an emphasis on the rotor (i) and stator (ii) equipment (adapted from ANDRITZ, 2021; UPC, 2021).

It is important to find strategies to balance these final tissue properties. Chang et al., 2008 reported that the selection of pulps with higher length/ thickness and slenderness ratios, the adjustment of the furnish mixture, and the refining intensity, are important factors to produce products with higher softness with qualities in accordance with the product specifications. Another strategy for applying fiber modifications was also reported by Gigac and Fišerová, 2008, who indicate that sulfite pulps, which present less dry tensile strength, are suitable to produce tissue papers in a mixture with eucalyptus kraft pulps, which present a low wet tensile index.

II.2.1.3. Enzymatic Treatments

Biotechnology has the potential to increase the quality and production of raw materials for pulp and paper, reduce production costs, and create new products with high-added value. New enzymatic technologies can reduce environmental problems and modify fiber properties (Kenealy and Jeffries, 2003).

As previously reported, refining is an essential step in the development of fiber properties to produce paper products. However, this process requires a substantial amount of energy. The enzymatic treatment allows to reduce the refining time and applied energy to reach the desired fiber properties (Jeffries, 1992; Bajpai, 1999). In addition, the application of enzymes in the industry enhances kraft pulping, decreases vessel picking, facilitates retting, selectively removes fiber components, modifying their properties and increasing their flexibility, and also covalently links the side chains or functional groups (Kenealy and Jeffries, 2003). The commercial development of these applications will require a better understanding of the mechanisms and actions of enzymes in fibers, the development of improved processes for their use, and the enzymes' adjustment to function better under existing operating conditions (Kenealy and Jeffries, 2003; Demuner et al., 2011).

Enzymes are biocatalysts, i.e., proteins with catalytic activity constitute amino acids linked together. The type of bonding between amino acids varies and influences the functional activity of enzymes. Enzymatic activity is measured by converting substrates into products over time, under defined conditions of substrate concentration, pH, temperature, among others (Yang et al., 2019). There are several enzymes applied in the production of high-quality dissolving pulps, such as cellulase, xylanase, laccase, mannanase, etc. Moreover, enzyme technology can be combined with other techniques, such as refining, alkaline treatment, additives incorporation, and fractionation treatment (Yang et al., 2019).

The enzymes act on the pulp fiber surface, being responsible for the fibrillation effect, as in the refining process. As a result of this fibrillation, all properties that depend on this effect are also improved, such as strength properties. Therefore, the potential energy reduction from mechanical refining is justified by the biorefining effect (Singh et al., 2016; de Assis et al., 2018b). Different studies have proven that the cellulase action in different pulps increases the fines content, inter-fiber bonds, pulp drainage rate, fiber hydration degree, affecting the fiber morphology that influences the paper properties (Spiridon and Duarte, 2004; Gil et al., 2009; Buzala et al., 2016). Besides, this enzyme decreases the fiber crystallinity index, indicating that the amorphous portion of cellulose is more easily hydrolyzed than the crystalline region (Park et al., 2007; Efrati et al., 2013). The action of xylanase modifies the fiber bonding potential and their morphology, maintaining the pulp viscosity, especially in *Pinus pinaster* kraft pulps, decreasing the relative bonding area and increasing the strength and brightness properties (Spiridon, Belgacem and Duarte, 2001; Spiridon, Duarte and Curto, 2003; Spiridon and Duarte, 2004; Buzala et al., 2016; Salgueiro et al., 2016; Dutta, Neog and Goswami, 2019). Additionally, the action of mannanase promotes fiber breakdown and reduces sugar production better than xylanase and worse than cellulases (Wu et al., 2020). A specific enzyme cocktail can also demonstrate synergistic effects, providing better pulp properties, even without mechanical refining (Gil et al., 2009).

Enzymes have great potential to solve many problems in the tissue industry if they are applied under optimal conditions, being considered environmentally and sustainability friendly. The biggest challenge focuses on the development of enzymes for the production process, namely enzymes suitable for certain raw materials, present the ability to stand process conditions, and reduce the cost of its application. Enzymatic treatments result in less sheet densification, compared to refining treatments, resulting in better bulk to basis weight, less stiffness, and a better bulk softness perception (Buckman, 2021). An et al., 2020 also reported that a green integrated process, which included treatments with ultrasound and cellulases, can effectively improve the softness of tissue structures and other physical properties, to improve fiber flexibility. Fiber modification enzyme technologies also allow the reduction of refining in the tissue industry, to develop strength properties without a negative impact on the absorption properties (Buckman, 2021).

Therefore, enzymatic technologies allow refining to be more efficient, which means that less energy in refining is needed to achieve the same level of fibrillation, which translates into the same final sheet strength. This reduction in the refiner's energy with enzymatic treatments improves the bulk of tissue structures. In recent years, strategies have been found to optimize the performance of enzymes in the tissue field, such as the incorporation of the additive. These additive strategies improve the enzyme activity rate, allowing for a lower end-use application rate of the enzyme (Tissue World Magazine, 2021).

II.2.1.4. Additives Incorporation

The tissue industry has used additives to modify end-use properties or to improve the production process. The use of these additives can also contribute to reducing the water and energy consumption, allowing to increase the use of wastepaper, as well as saving raw material and reducing the basis weight of the products obtained (Ginebreda et al., 2011). Different chemical additives used in the tissue industry are designed and applied according to different needs, including dry strength agents, wet strength agents, softeners, lotions, among others (Park et al., 2019). Usually, these additives are cationic, as the fibers carry negative charges, and also, they are more effective in much lower concentrations than anionic polymers. However, these cationic additives normally adhere excessively to the paper, negatively affecting the creping process and the product quality (Adhikari et al., 2016).

The addition of various chemical additives can lead to interaction between them, and the desired final properties may not be exhibited. Two key parameters for tissue materials are softness and strength. Strength properties can be achieved in several ways that the tissue industry must balance in terms of cost and effect, as noted earlier. However, the processing conditions necessary to maximize softness are often in conflict with those necessary to improve the strength properties. Softener additives improve softness when added to the wet-end or post-process (Park et al., 2019). Dry strength additives are used to improve the paper strength under different conditions, assisting the interfiber bonds.

Examples of these additives include natural or semi-synthetic polymers, such as starch or carboxymethylcellulose (CMC), or synthetic products, such as polyamines, polyamides, and polyacrylamide (Liimatainen et al., 2009; Uematsu et al., 2011; Harrington et al., 2015; Siqueira et al., 2015; Valencia et al., 2020). Gonzalez et al. (2020) showed that the use of a cationic polymer in tissue formulations counteracts the adverse effects on drainability of high fibrillated fiber furnishes, ensuring that tissue paper machine runnability is not affected and that production rates remain at normal levels.

In addition to these additives usually used in the tissue industry, promising new and environmentally friendly alternatives to synthetic dry and wet strength resins are beginning to arise, such as cottonseed proteins and micro/ nanofibrillated cellulose (Cheng et al., 2017; Zambrano et al., 2020a).

II.2.1.4.1. Micro/ Nanofibrillated Cellulose

Micro/ nanofibrillated cellulose (MFC/NFC) is a cellulosic material, composed of expanded high-volume cellulose, moderately degraded and very expanded in the surface area, and obtained by homogenization processes. MFC/NFC consists of aggregates of cellulose microfibrils (Figure II.7), with widths between 20 and 60 nm and lengths of several micrometers (Klemm et al., 2018). The MFC/NFC displays amorphous and crystalline parts and presents a web-like structure. Moreover, the length/ width ratio is very high, which endows it with a very low percolation threshold (Mishra et al., 2018). Therefore, MFC/NFC has a very good ability to form a rigid network (Figure II.17). Increasingly, various mechanical and enzymatic treatments have been used to produce MFC/NFC, depending on the type of MFC/NFC that is desired (Lavoine et al., 2012).

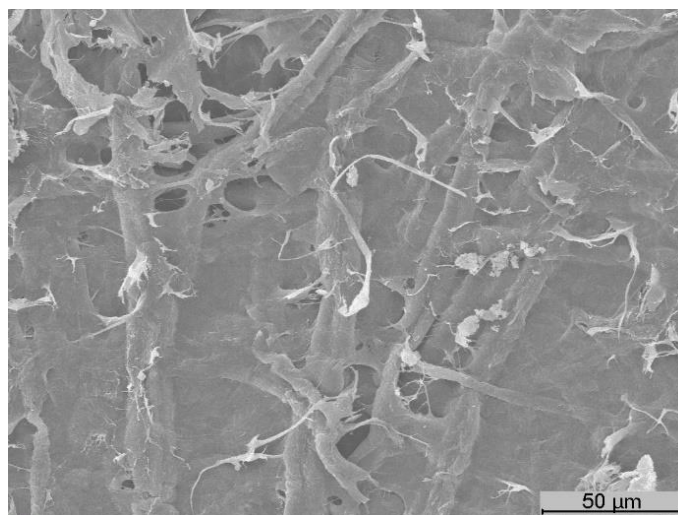


Figure II.17. SEM image of a laboratory paper material sample produced with MFC/NFC. This MFC/NFC was produced by mechanical and enzymatic treatments, from a bleached *Eucalyptus globulus* kraft pulp.

MFC/NFC, due to its high specific surface area, rheological properties, specific orientation, chemical surface reactivity, biocompatibility, biodegradability, lack of toxicity, among other properties, has been applied as an additive in paper-based products, in order to improve different papermaking properties (Ferrer, Pal and Hubbe, 2016). The main cost factors to produce MFC/NFC at the industrial scale are the raw material (such as cellulose pulps), and energy consumption, being this last the most significant one. The addition of MFC/NFC, as an additive, allows reducing the refining intensity as it prevents loss in the sheet porosity and optical and mechanical properties, at the expense of drainage difficulties (Gonzalez et al. 2012). The drainage of a fibrous suspension with MFC/NFC is influenced by pH, microfibrils content, and the level of treatment applied (Taipale et al., 2010). Depending on the treatment applied, different MFC/NFC behave differently during the paper formation, maintaining or improving the strength properties (Hii et al., 2012; Lourenço et al. 2019a, 2020; Sanchez-Salvador 2020). MFC/NFC has also proved to be a potential additive to be used in the food packaging industry, containing active compounds to allow adequate antibacterial properties (Lavoine et al., 2015; Martins et al., 2018).

Recently, MFC/NFC has also attracted great interest in the tissue paper industry. MFC/NFC fills empty spaces and increases inter-fiber bonds. Selective densification of the tissue sheets can be achieved using MFC/NFC and producing multilayer structures (Miller et al., 2014). Selective densification and surface tissue structure play a crucial role in determining their characteristics. MFC/NFC was studied as a coating to convert tissue papers into efficient separation membranes, presenting versatile and advanced applications (Roy et al., 2018). MFC/NFC also presented potential applications with market opportunities in the production of superabsorbent diapers (Patiño-Masó et al., 2019), as well as improving absorption and strength properties of tissue products made with bamboo fibers (Guan et al., 2019). Furthermore, the addition of MFC/NFC can improve the strength properties with adverse effects on the properties of bulk, softness, and absorption, which depend on the MFC/NFC fibrillation, and the type of fiber source used for its production (Zambrano et al., 2021). This suggests that selecting the lowest cost fiber source can help reduce MFC/NFC manufacturing cost; however, the ease of fibrillation needs to be simultaneously considered, as it is fiber dependent and therefore will have an impact on the required fibrillation energy (Zambrano et al., 2021). Additionally, Gonzalez et al. (2020) also proved that highly fibrillated cellulose fibers enhanced significant strength increases in tissue structures that are strategically used to reduce the fiber content in formulations, maintaining the minimum functional strength and softness required for adequate performance and consumer satisfaction. Micro/ nanofibers are identified as a highly suitable material for tissue products, as they increase hydrogen bonds which, in turn, increase inter-fiber bonds and structural strength (Beuther, Veith and Corp, 2009). The potential to combine the different properties of tissue paper materials with micro/ nanofiber properties could enhance the production of tissue products with added value and innovative functionalities.

II.2.2. Tissue Paper Machine

Currently, each stage of tissue paper production has been the subject of optimization to meet the growing consumers' requirements. In general, these steps include stocks preparation, sheet formation, pressing, drying, reel formation, converting, and storage.

The tissue paper machine consists of different sections and equipment, with the function of removing water from the fibrous suspension and forming the tissue paper sheet. Tissue machines present different types of forming web configuration, from the Fourdrinier process to the process by Duoformer and Crescent Former (TissueStory, 2017 a,b). In this last technology, the most common in modern tissue paper machines, the pulp suspension diluted in the Headbox is distributed into forming section, where it is trapped between the wire and the felt. Here, the water removal occurs by gravity and due to centrifugal forces. The wet sheet, transferred into the felt, is then subjected to a pressing step to remove additional water. In modern machines, this step is often carried out by a shoe press. The NIP consists of the contact zone between the press and, usually, a Yankee dryer, where the pressed wet sheet is transferred into the Yankee and, therefore into the drying section. This technology and equivalents describe the conventional wet press (CWP) process, which includes a Yankee cylinder on the drying stage with the creping process at the end (TissueStory, 2017b).

Nevertheless, other technologies include through-air drying (TAD) technology. In this type of technology, the wet web is dewatered and dried by non-compressive means, avoiding sheet compaction. This process enables the production of high bulk, soft and absorbent papers. The improvement in these properties becomes TAD tissue production particularly suitable for toilet papers and paper towels. Additionally, fiber savings are possible for TAD tissue, as the sheet basis weight can be reduced due to the higher bulk. Since fiber is usually the highest cost element in a tissue product, reduced fiber cost is the main advantage associated with the use of TAD technology. However, TAD technology has a high energy cost compared to the conventional process (TissueStory, 2017a; Raunio, Löyttyniemi and Ritala, 2018).

Figure II.18 presents a scheme of the conventional tissue paper machine, highlighting the most important sections such as the forming section, Headbox, pressing section, drying section, creping, and paper reel section.

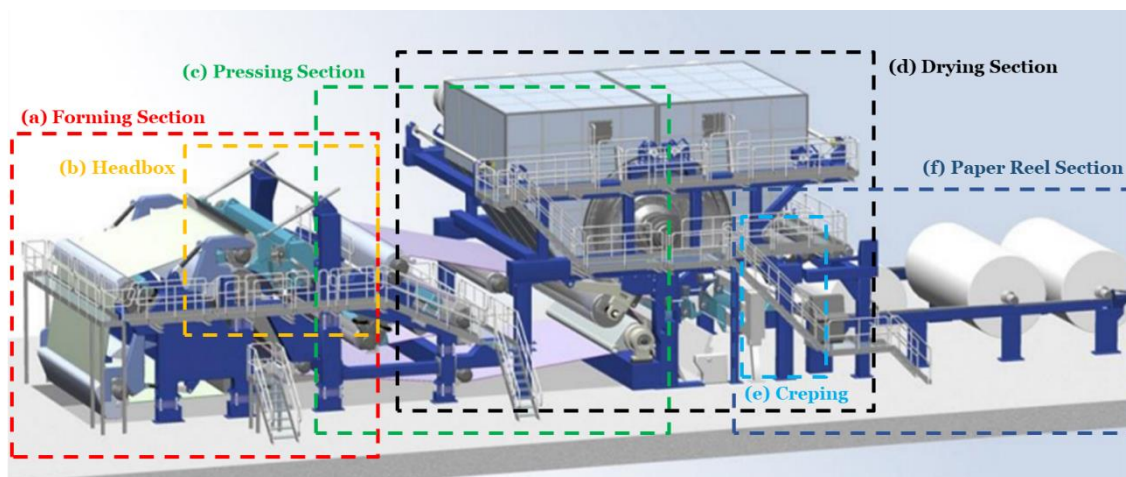


Figure II.18. Scheme of the conventional tissue paper machine, highlighting different sections: (a) forming section, (b) Headbox, (c) pressing section, (d) drying section, (e) creping, and (f) paper reel section (adapted from Gallo, 2014).

In the forming section (Figure II.18a), a continuous wet paper web of certain basis weight and the required uniform quality parameters in both cross (CD) and machine (MD) directions is produced. This is accomplished by feeding a constant volume rate of constant consistency suspension and furnish ratio to the Headbox (Figure II.18b), with a stable current and a uniform pulp distribution for a good formation (Holik, 2006). A water jet containing the stock mixture of water and fibers is ejected at high speed from the Headbox. Then, a web is formed by trapping it between the forming fabric and the felt as they wrap around a large, solid forming roll (TissueStory, 2017b). The sheet-forming process involves first draining off as much of the water as possible in the forming section. In the forming section, this water removal influences the paper structure and its homogeneity, which then influences the fiber orientation, bonding, and hence, the final papermaking properties (Holik, 2006; Kullander, 2012). Factors such as drainage, the type of flow, and the existence of turbulence directly influence the paper sheet formation. To provide the best possible drainage conditions, the following aspects are important: temperature, retention, water drainage, consistency, uniform fiber distribution, and the ratio between the speed of fibrous suspension distribution and the web traveling speed (jet/wire ratio) (Tysén, 2014; TissueStory, 2017b).

In the pressing section (Figure II.18 c), which often consists of a shoe press in modern tissue paper machines, the water is removed by pressing to reduce the water content as much as possible, to reduce the energy spent on the drying section (next step), and to improve the paper mechanical properties. The pressing occurs while the sheet is transferred to the Yankee cylinder (TissueStory, 2017b). In the NIP, the contact area between the felt and the shoe press with the Yankee cylinder, the tissue paper sheet is pressed against the Yankee, where water is removed by the pressing action, while the sheet is transferred from the felt to the cylinder. In tissue paper production, the pressing must be smooth and uniform, to achieve a paper with high bulk, absorbency, and softness (de Assis et al., 2018a).

In the drying section (Figure II.18 d), usually a Yankee cylinder, the drying occurs by heat conduction and convection. The heat conduction process is carried out through contact of the sheet with the heated surface of the Yankee cylinder, while the heat convection occurs employing hot air injections on sheet surface at the Hoods (Escaler, de la Torre and Egusquiza, 2012). The drying capacity of a tissue machine is mainly affected by the size of the Yankee dryer. The Yankee usually consists of a cylinder with a diameter between 5-7 m, with internal steam heating, while the Hoods that cover the Yankee cylinder are heated by injection of hot air and can be separated in a wet and dry area (Boudreau, Hollmark and Beghelli, 2009; Boudreau and Germgård, 2014). The Yankee dryer not only supplies the required energy for the web drying but also transports the sheet during the drying process, functions as a counter roll in the hot-pressing operation, and provides the base for the creping process (TissueStory, 2017b).

The dried sheet is subsequently removed using a creping or doctor blade, that scrapes it from the Yankee producing a paper sheet with an elastic and creped structure. The creping process (Figure II.18 e), which consists of the formation of macro and micro wrinkled on the paper upon its scraping from the Yankee surface, is influenced by the sheet adhesion to the Yankee, the blade geometry, and the difference between the Yankee and the paper reel speed (Ramasubramanian, Sun and Chen, 2011; Raunio and Ritala, 2012; Pan et al., 2019). To ensure and improve adhesion along with the paper detachment, the Yankee cylinder is coated with additives (Rezaei-Arjomand et al. 2013; Valencia, Valencia and Tovar, 2020). Upon exiting the Yankee, the doctor blade scrapes/ removes the paper sheet from the Yankee cylinder surface, promoting the creping process (Figure II.19). The creping process also includes a change in the fiber direction from the MD to the Z-direction, which results in the breaking of inter-fiber bonding, promoting higher softness and elongation capacity (Ramasubramanian, Sun and Chen, 2011; Pan et al., 2019; de Assis et al., 2020).

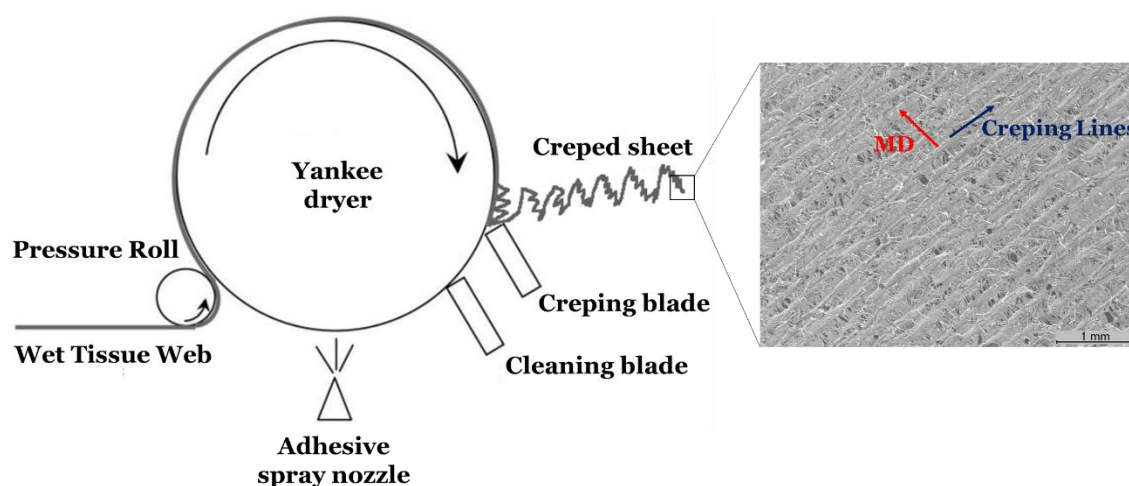


Figure II.19. Scheme of the creping process (adapted from Ramasubramanian, Sun and Chen, 2011), highlighting an SEM image of an example of a creped industrial base tissue paper. The creping lines are perpendicular to the machine direction (MD).

Afterward, the creped industrial base tissue paper goes to the paper reel section (Figure II.18 f). Then, the resultant paper reels are either stored or subject to the converting process, where they are transformed into different types of tissue products. The converting section included several operations such as unwinding, embossing, printing, perforating, rewinding, cutting, and packaging, performed on base tissue paper sheets to form a single layer or multilayer finished product, ready to be placed into the market (Figure II.20) (Mendes et al., 2020). These modifications can improve tissue properties. Additionally, additives may also be added to paper products during the converting process. Examples include the application of lotions to develop paper softness (Park et al., 2019), or fragrances to enhance the product attractiveness. In the case of fragrances, their application is becoming more and more frequent on the paper core of the tissue product, to minimize the risks of allergies or irritation. Fragrances may also be applied on the surface of tissue paper products. In the case of handkerchiefs, sometimes encapsulated fragrances are used to provide a longer and controlled release upon friction and manipulation (Tyagi et al., 2019). The embossing occurs when the paper embossing rolls with patterns engrave them into the paper. After this step, the lamination process often occurs, in which the glue is transferred to the paper in order to confer integrity to multilayered products, such as toilet paper (Figure II.20 a). Embossing patterns are applied to tissue materials to improve bulk, absorption, thickness, and flexibility. Embossing can result in deeper or lowered patterns on the paper, using heat, pressure, and stamping matrices (Spina et al. 2018; Mendes et al. 2020; Vieira et al. 2020a, b). Moreover, the type of embossing pattern applied to tissue papers has an important impact on product perception. For example, in kitchen rolls, the use of a square embossing pattern may transmit the idea of strength, while the use of circles patterns (Figure II.20 c) gives the consumer the perception of a more absorbent paper (Spina et al. 2018). Therefore, consumer requirements have allowed the tissue industry to increasingly demand properties of softness, strength, and absorption, in several types of tissue paper materials.

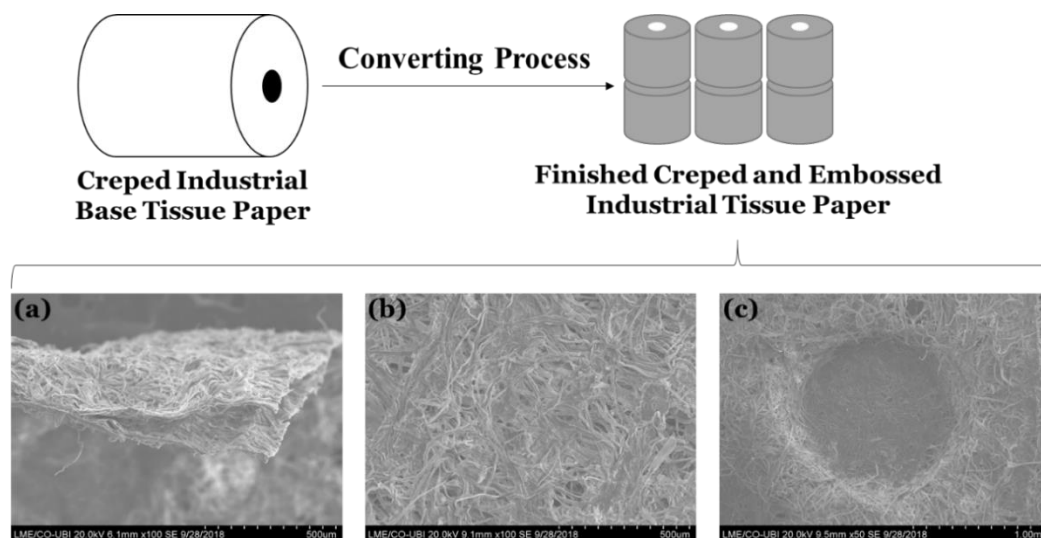


Figure II.20. Converting process is performed on creped industrial base tissue paper to obtain the finished creped and embossed industrial tissue paper. Example of SEM images of a multi-layer tissue product (a), 3D fibrous network with emphasis on creping lines and embossing (b), and a detail of a “micro” circular embossing pattern (c).

II.2.3. Tissue Materials Requirements

As previously mentioned, the main properties of tissue products include basis weight, bulk, softness, strength, and water absorption.

Tissue products have the particularity of being low-weight papers (from 10 to 60 g/m²), depending on the type of tissue paper. The basis weight corresponds to the mass of the paper per square meter and presents a higher influence on the final end-use tissue properties. Low basis weights can be used in multilayer products where softness is important, while high basis weights can be used in single layer products, where strength is essential (Biermann, 1996; I'Anson et al., 2008).

The bulk (cm³/g), the inverse of the apparent density, is inversely influenced by the basis weight and directly by the paper thickness. The bulk influences the softness and absorption properties. A paper with more bulk presents higher porosity, and consequently, higher capillarity and softness. This parameter is also inversely related to the strength properties. Bulk can be improved by various mechanisms such as the raw materials used, sheet formation, refining, additives incorporation, pressing, creping process, and humidity content during creping (Gigac et al., 2019).

Softness is one of the most important tissue paper properties. However, this characteristic is quite subjective and complex, combining the contributions of parameters such as superficial softness, bulk softness, and flexibility. Superficial softness is related to the felt softness when the product surface comes in contact with the skin, while bulk softness is related to the perception of cushion effect given by the product. In the case of flexibility, this parameter is associated with the paper drapability, malleability, and thus ability for deformation (Furman et al., 2010; Ruiz et al., 2010; Ismail et al., 2020; Wang et al., 2020). The superficial softness is affected by the sheet topography and uniformity, the type of fibers, and the use of chemicals (softeners, for example). In contrast, bulk softness and flexibility are influenced by the fibrous structure arrangement. However, in most cases, softness decreases with increasing strength properties (Hollmark and Ampulski, 2004; Raunio and Ritala, 2013). The less compact the sheet is, the better is its bulk, and consequently its softness. This can be achieved by factors such as refining control, sheet pressing, contact with smooth roll surfaces, type of felt, and the web used in the process, among others (Gigac et al., 2018; Gigac, Fišerová and Stankovská, 2019).

Tensile strength is an important feature for tissue papers, as it maintains the tissue sheet integrity, and ensures the paper machine runnability. Strength represents the force, in a certain direction, that a paper sheet can support without breaking (I'Anson, Sampson and Savani, 2008; Park et al., 2020). This property is influenced by the fiber intrinsic strength and the strength of the inter-fiber bonds because when more bonds are present, more energy is needed to separate these bonds.

The creping process also contributes to the tissue paper mechanical properties, since it promotes elongation. Besides contribution from creping, elongation can also be influenced by raw materials, stock preparation, sheet formation, pressing, humidity content, and paper adhesion on the Yankee cylinder (Ketoja et al., 2019; Valencia, Valencia and Tovar, 2020). The mechanical properties of tissue paper sheets can be developed by optimizing refining and changing stocks. As previously mentioned, pulp refining improves the inter-fiber bonds and, consequently, strength properties; however, this treatment can result in fiber damage. To improve the inter-fiber bonding, chemical additives can also be used, as already mentioned (Ketoja et al., 2019; Park et al., 2020; Pöhler et al., 2020). In contrast, the wet tensile strength is related to the fiber's ability to remain linked together in the wet state, being more important in tissue products such as towel papers and napkins (Bajpai, 2015). Usually, wet strength resins are added to confer wet strength. These resins often consist of Polyamideamine-epichlorohydrin (PAE) resins. Additionally, CMC may be added to the process to improve both wet and dry strength, since it promotes more bonding and water-resistant bonds between fibers (Liimatainen et al., 2009; Thorn and Au, 2009; Bajpai, 2015; Lourenço et al., 2019; Park et al., 2019).

Water absorption is related to the water absorption capacity and absorption rate, which are influenced by raw materials, type of fiber network structure, stock preparation, fine content, bulk, sheet formation, pressing, additives, creping and converting operations (Kullander, 2012; Foelkel, 2016). The absorption capacity includes the total amount of water that the paper is able to absorb into its structure, while the absorption rate consists of the time that a paper takes to absorb a certain amount of water (Beuther, Veith and Zwick, 2010; Deng et al., 2018; Gigac et al., 2019; Stankovská et al., 2019). This property also depends on the amount and volume of pores. The water capillary rise is a physical phenomenon that depends on the adhesion and cohesion forces of the water molecules. These molecules can ascend through the fiber walls or between the pores (Ashari et al., 2010; Mullins and Braddock, 2012). Hence, if the pores are too large, the intermolecular bonding between the fibers and the water molecules will not be sufficient to counteract the force of gravity, which impairs the capillary rise. In the case of smaller pores, water progression will be more restricted by the limited space for flow (Mullins and Braddock, 2012). Since bulkier paper often implies higher porosity, the bulk will also influence the water absorption properties. Papers with higher bulk, and thus higher porosity, will present more empty spaces for water accommodation (Beuther, Veith and Zwick, 2010; Gigac et al., 2019; Stankovská et al., 2019). Consequently, porosity is one of the most important factors in liquid absorption, along with the material affinity with water. The structure porosity is influenced by the size of the empty spaces, which depend on the fiber dimensions, the collapse degree, and the inter-fiber bonds (Rosenholm, 2015; Zambrano et al., 2020b). Therefore, it is important to optimize the porosity of the fibrous structures to improve water cohesive/ adhesive forces so that those can exceed the gravity force. This highly influences not only the water absorption capacity but also the rate of absorption and the capillary phenomena (Senden, Knackstedt and Lyne, 2000; Clarke et al., 2002; Starov et al., 2003; Hilpert and Ben-David, 2009; Chen, Nie and Fang, 2020; Zhang et al., 2020).

In addition to softness, water absorption is also a property that progresses inversely to the paper strength. Pulps with better water absorption properties will present a good combination between the formation of a porous structure and fiber affinity for water (Hubbe et al., 2013; Curto et al. 2015). Therefore, there must be a balance in the development of the softness and absorption properties, to avoid significant losses in the minimum strength required in tissue paper.

II.2.4. Effect of Fiber Characteristics on Tissue Materials

The fiber properties influence the tissue's final end-use properties. The fibers source and the type of pulp production can originate fibers with different properties that impact the fibrous structure and, consequently, bulk, softness, strength, and absorption properties.

Bulk is improved by thicker fibers (Figure II.21 a), with more resistance to collapse. Rigid fibers promote more porous and open structures, with less contact area and bonding between fibers. In contrast, fibers with a higher diameter and less thickness (Figure II.21 b) are more susceptible to collapse, resulting in denser structures, with less bulk, softness, and absorption. Flexible fibers promote a higher number of bonds, with a higher bonding area, softness, and, consequently, higher adhesion to the Yankee cylinder (Boudreau and Germgård, 2014; Wang et al., 2019).

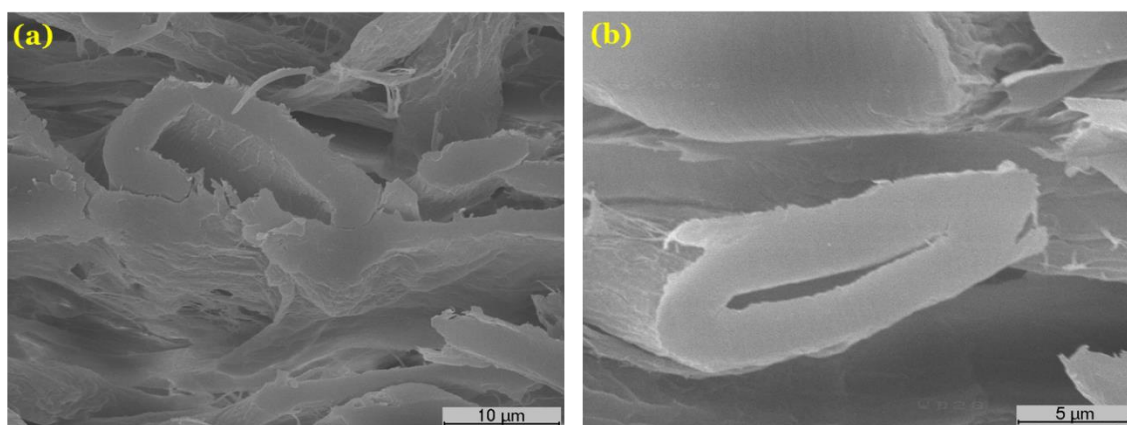


Figure II.21. SEM images of two examples of fibers with different thicknesses, namely a more rigid fiber, with a thicker wall (a), and a more flexible fiber, with higher conformation (b).

Coarseness is also related to the fiber wall thickness, diameter, and tissue sheet density. Softwood fibers with lower coarseness present better formation, higher softness, tensile strength, absorption, less tearing, energy spent to obtain good inter-fiber bonds, among other properties (Curto et al., 2009; Nordström and Hermansson, 2018). Kerekes and Schell, 1995, reported that softwood fibers with high coarseness increase the flake-like structure formation, compared to fibers with low coarseness, for the same consistency, as they exhibit higher mobility. These fibers can also decrease water drainage, causing sheet malformation and hampering the tensile strength index (Kerekes and Schell, 1995). On the other hand, eucalyptus fibers with high coarseness generate tissue papers with high bulk and softness. Since these fibers resist to collapse and have low flexibility, they provide the formation of bulky and soft products (Magaton et al., 2009).

The presence of deformations in eucalyptus fibers also increases the bulk, softness, and absorption of tissue materials. Fiber curl and kink occur due to its processing mostly as a result of mechanical processes (Ferreira, Matos and Figueiredo, 1999). Page et al., 1985, and Kerekes and Schell, 1995 reported that higher curl indexes promote higher porosity, bulk, softness, absorption capacity, wet elongation, drainage, and tear rate. Moreover, fibers with a higher kink index negatively influence tensile strength and tearing and promote bulk development (Page et al., 1985; Kerekes and Schell, 1995).

The fiber length also influences the tissue's mechanical properties, enhancing the several inter-fiber bonds. Hardwood fibers present lower tensile strength and bursting, in contrast to softwood fibers, due to the smaller bonding area and lower number of inter-fiber bonds (Park et al., 2020).

The inter-fiber bonds, and consequently the tissue paper strength, are also influenced by the hemicellulose content. The presence of hemicelluloses promotes the formation of a more cohesive fibrous network, since it contributes positively to the establishment of inter-fiber bonding and, therefore, to the strength development (Anjos, Santos and Simões 2004; Gomers, Ribeiro and Colodette, 2011). The hemicelluloses and carboxylic group content also impact absorption and mechanical properties since they provide further sites for interaction with water or with fibers (Kullander, 2012). The fine content, together with the fiber flexibility and collapsibility, are also other parameters that promote the establishment of inter-fiber bonding, and consequently contribute to the structure strength (Guimarães, Figueiredo and Ferreira 2003). The pulp fine content is a limiting factor in the paper quality, contributing negatively to the paper's softness. To produce tissue papers, the use of pulps with the lowest possible fine content should be preferred, to avoid increasing the pulp consistency and drainage difficulties.

In this context, it is essential to know the fiber properties to select the most appropriate pulps, to produce a target tissue paper grade. For tissue papers, essentially for those in which softness is the key characteristic, such as toilet paper or facial tissues, eucalyptus hardwood pulps are currently considered as a reference for softness development (Foelkel, 2015; Foelkel, 2016; Dutt and Tyagi, 2011). Softwood pulps are used to ensure strength and runnability on the paper machine. Examples of products with higher strength requirements include kitchen rolls and handtowels (Foelkel, 2015; de Assis et al., 2018a). Table II.1 presents different formulations used to produce tissue products.

Table II.1. Different formulations used to produce tissue products (de Assis et al., 2018a).

Type of Paper	Hardwood Fibers (%)	Softwood Fibers (%)
Toilet Paper	60 – 100	0 – 40
Towel Paper	0 – 30	70 – 100
Napinks	0 – 60	40 – 100
Facial Tissue	50 – 70	30 – 50

In addition to hardwood and softwood fibers, recycled fibers can also be used to produce these types of papers. The proportions of virgin and recycled fibers depend on the product quality requirements. High-quality products can be produced with better quality recycled fibers, such as fibers obtained from the waste of printing and writing paper, poorly degraded, and with better paper properties. On the other hand, recycled tissue products with low quality are produced using fibers whose raw materials include magazines, newspapers, among other residues that originate recycled fibers of lower quality, with lower paper properties (de Assis et al., 2018a, 2018d; Fišerová et al., 2019; Wang et al., 2019).

The analysis of the fiber properties with an impact on the tissue properties to be achieved is complex since it presents a series of dependencies between them. Not only the raw material but also the conditions of the overall process determine the suitability of the fibers to produce tissue products. The tissue's final end-use properties are dependent on the final application. All these tissue properties are fundamental to obtaining a high-quality product. The possibility of having computational tools with predictive capacity for these properties would be essential to define which are the key pulp fiber parameters that influence the type of tissue paper desired.

II.3. Optimization using Advanced Computational Tools

Over time, interest in the development and optimization of new cellulosic materials has increased since cellulosic sources present advantages as a renewable, sustainable, and economical resource (Mousa, Dong and Davies, 2016; Bu et al., 2020). Advanced multi-scale modeling and simulation present the potential to reduce development time and optimize tissue paper materials, resulting in considerable cost savings. Computational simulations are used in detailed models to optimize the process and develop adequate theoretical and numerical formulations to describe the behavior of advanced engineering materials (Muñoz-Rojas, 2016; Hossain et al., 2018). Furnish optimization is a multiple-input multiple-output (MIMO) challenge, mainly due to the different fiber and structure properties and the influence of several process operations. The development of tissue paper products will benefit from the modeling of raw material characteristics and their functional properties. The use of computational tools constitutes an innovative strategy to enhance this type of multi-structured materials, through 3D modeling of fibers and structures and data-driven modeling.

Nowadays, the impact of fiber characteristics on paper properties continues to be a subject of research interest since several computer-based simulations of paper formation have been developed (Simon, 2020). The paper structure models assume that fibers are deposited independently and randomly, and therefore, the paper structural and mechanical properties are determined by their constituent fibers and the structure of the fibrous architecture (Dodson et al., 2002; Dodson and Sampson, 2005; Marulier et al., 2015; Kettil et al., 2018; Motamedian, Halilovic and Kulachenko, 2019). Different computational models of tissue materials predicted a non-linear relationship between sheet basis-weight and thickness, with higher density variation (Hellén, Alava and Niskanen, 1997; Dodson, Oba and Sampson, 2001; Bloch, Engin and Sampson, 2019; Alzweighi et al., 2021). Furthermore, many investigations have emerged to predict the structural (basis-weight, thickness, out-of-plane deformation, formation, density, porosity), final end-use properties of tissue products (softness, strength, and absorption), and different systems for the production of tissue papers in the Yankee-hoods, for example (Keller, Branca and Kwon, 2009; Marco et al., 2016; Gigac et al., 2019; Park et al., 2020; Prinz et al., 2021); however, the different authors have not proposed any mathematical model that relates the fiber morphological properties with these functional properties. A general mathematical equation was proposed by Page, in 1969, that characterizes the tensile index (T) for the paper sheet with uniform random fiber orientation as follows:

$$\frac{1}{T} = \frac{9}{8 \cdot Z} + \frac{12 \cdot g \cdot C}{P \cdot l \cdot b \cdot RBA} \quad (II.1)$$

This model is an assessment of relative bonding strength compared to fiber strength, where the contribution of fibers is described by the zero-span tensile index (Z), and the contribution of bonding is merged into a gravitational constant (g), fiber coarseness (C), fiber perimeter (P), fiber length (l), fiber-fiber bond strength (b), and RBA. At a low level of bonding (low Page RBA), bonding is the controlling factor for strength, as is the case of tissue paper materials. Therefore, when fiber strength is higher than bond strength, the assumption approaches the value where fibers do not fracture ($g/8Z = 0$) (Pawlak, 2021). However, some of these parameters are difficult to determine. For this reason, alternative solutions based on data-derived modeling for forecasting and optimizing advanced processes have been evaluated over the years, particularly for the analysis of large, complex, highly nonlinear problems (Kerekes, McDonald and Zhao, 2020). Examples of these modeling methods are decision/ regression trees, multiple linear regressions (MLR), and artificial neural networks (ANN) (Myers, Montgomery and Anderson-Cook, 2016).

II.3.1. Decision/ Regression Trees

Decision/ regression trees are a reliable and effective decision-making technique that provides high classification accuracy with a simple representation of acquired knowledge. This computational tool predicts the data responses. To predict a response, the decisions are taken from the root node to the leaf node, since the leaves (terminal node) contain the responses. Each internal node, a node with outgoing edges, splits the instance space into two or more sub-spaces according to a certain discrete function of the input attributes values (Rokach and Maimon, 2005). Decision trees are one of the most popular approaches for representing classifiers. Researchers from various disciplines have dealt with the issue of growing a decision tree from available data. This exploratory tool allows the analysis of large quantities of data because of their unique properties, namely its straightforward interpretation enhanced by a self-explanatory graphical representation (Curto, et al. 2011c). For example, Curto et al. (2011c) studied the influence of fiber flexibility and fiber dimensions on web structure, using decision/ regression trees. The authors found that fiber flexibility presented a determinant influence on the final web structural properties of nanofibers network (Curto, et al. 2011c; Curto, 2012). Figure II.22 presents an example of this decision/ regression tree. Different models generated by decision/ regression trees can be compared and analyzed to identify which model makes the best prediction of the variables studied (Barrios and Romero, 2019).

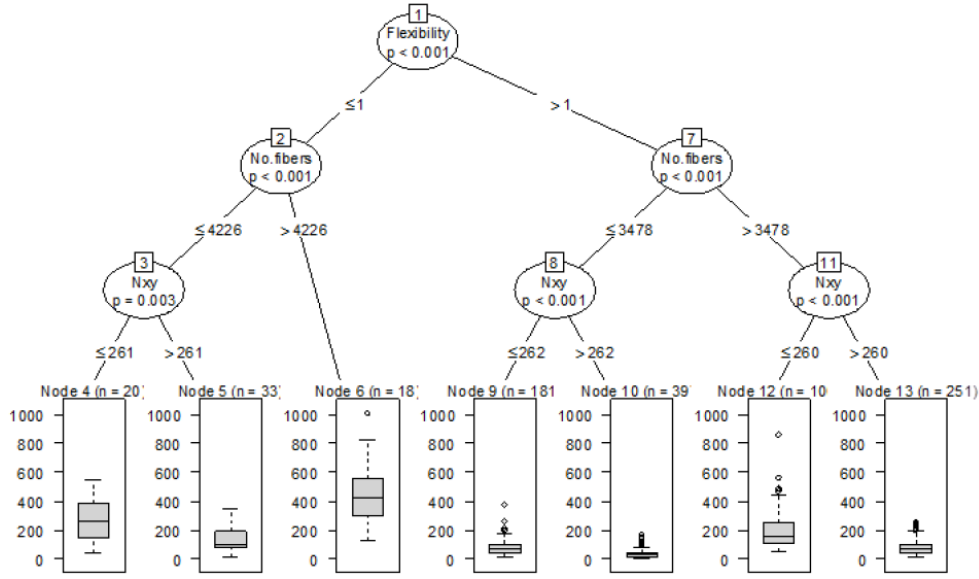


Figure II.22. Example of a decision/ regression tree to study the influence of fiber flexibility and fiber dimensions on web structure (adapted from Curto, et al. 2011c; Curto, 2012).

II.3.2. Multiple Linear Regressions (MLR)

MLR is a collection of statistical techniques useful for building the types of empirical models required in response surface methodology. In general, MLR models the relationship between two or more explanatory variables and a response variable by fitting a linear equation to the observed data. Considering $x_1, x_2, \dots, x_n$ as a set of n independent variables associated with a value of the dependent variable y , the linear regression model that describes this relationship is:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_n x_n + \varepsilon \quad (\text{II.2})$$

Where the parameters $\beta_j, j = 0, 1, \dots, n$, are the regression coefficients, and ε is a random error. This model describes a hyperplane in the n -dimensional space of the regressor variables (x_j). The parameter β_j represents the expected change in response y per unit change in x_j when all the remaining independent variables $x_i (i \neq j)$ are held constant (Myers, Montgomery and Anderson-Cook, 2016). MLR model's application has shown great interest in the pulp and paper industry. Risén, Hultén, and Paulsson (2004) reported that fiber length, lignin content, specific surface area, and total charge were the parameters that influence the network strength, for a given pulp. Another method proposed by Chagaev and Zou (2007) showed that pulp quality and fiber development indexes based on the ratio between fine content and coarse fibers could be used to monitor strength development during mechanical pulp refining. Many efforts have been made to investigate the relationship between morphological and chemical characteristics of fiber pulps and structural and mechanical properties of papers, indicating that the theoretical-experimental methods are valuable for quantitative assessment of different types of fibers for paper applications (Carvalho, Ferreira and Figueiredo, 2001; Joutsimo, Wathén and Tamminen, 2005; Neagu, Gamstedt and Berethold, 2006; Pereira, Santos and Anjos, 2016).

II.3.3. Artificial Neural Networks (ANN)

ANN models perform a non-linear transformation of input data to approximate output data, learning from experimental data examples and exhibiting some ability for generalization beyond training data. The most common ANN is the multilayer feedforward artificial neural network where the nodes (each variable in a layer) involve three layers: the input layer, which is the original predictors; the hidden layer, consisting of a set of constructed variables; and the output layer, made up of the responses. The output value of each node is obtained through an activation function or transfer function, which can be a sigmoid, a hyperbolic tangent, or an exponential (Myers, Montgomery and Anderson-Cook, 2016). Each of the n hidden layer nodes, a_u can be a linear combination of the input variables:

$$a_u = \sum_{j=1}^p w_{1ju} x_j + \theta_u \quad (\text{II.3})$$

Where the w_{1ju} are unknown parameters that must be estimated (weights), and θ_u is a parameter that plays the role of an intercept in linear regression (bias node) (Myers, Montgomery and Anderson-Cook, 2016). Similarly, the application of ANN models in the paper industry has been investigated (Scharcanki and Dodson, 1997; Edwards et al., 1999; Nieminen et al., 2011). Ciesielski and Olejnik (2014) predicted different paper properties such as apparent density, breaking length, and tear strength, based on refined pulp characteristics including pulp WRV, fine content, and fiber length, using ANN models. The prediction revealed that this approach could be applied as an additional paper quality control system in a paper mill. Additionally, Almonti et al. (2019) also developed an ANN model to optimize a fiber refining system. It was found that fiber length prediction allowed the optimization of additives amount and the process parameters to obtain detailed properties of the final product. A neural network provides, at best, a prediction model, but not a fundamental insight into the underlying process mechanism that produced the data. Moreover, the prediction properties of these models are not superior to those obtained from a well-designed MLR study (Myers, Montgomery and Anderson-Cook, 2016). Neural networks can be a complement to the statistical tools of regression analysis to model the effects of fibers on paper parameters (Monga et al., 2017a,b).

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Chapter III

Publications

III.1. 3D Fiber Characterization and Modeling

The contents of this subchapter are published in the following publications, listed on pages xvii and xviii of the thesis:

- I. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2020). 3D Fiber Models to Simulate and Optimize Tissue Materials. *BioResources*. **15**: 8833-8848. DOI: 10.15376/biores.15.4.8833-8848
- II.a. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2020). Experimental 3D fibre data for tissue papers applications. *Data in Brief*. **30**: 105479. DOI: 10.1016/j.dib.2020.105479
- II. **Morais, F.P.**, Bértolo, R.A.C., Curto, J.M.R., Amaral, M.E.C.C., Carta, A.M.M.S., and Evtyugin, D.V. (2019). Comparative characterization of eucalyptus fibers and softwood fibers for tissue papers applications. *Materials Letters: X*. **4**: 1000028. DOI: 10.1016/j.mlblux.2019.100028
- II.a. **Morais, F.P.**, Bértolo, R.A.C., Curto, J.M.R., Amaral, M.E.C.C., Carta, A.M.M.S., and Evtyugin, D.V. (2020). Characterization data of pulp fibres performance in tissue papers applications. *Data in Brief*. **29**: 105253. DOI: 10.1016/j.dib.2020.105253

III.1.1. 3D Fiber Models to Simulate and Optimize Tissue Materials

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III.1.1.1. Abstract

Tissue materials development using 3D computational tools to predict the influence of combining different fibers can be employed in the design of innovative tissue products and furnish optimization. Fibrous materials can be designed using different 3D fiber models for each type of fiber, detailed to the point where the wall fiber thickness, fiber lumen, and collapse degree are considered and presented in this work. *Eucalyptus*, *Pinus*, and *Picea* kraft cellulose pulp fibers were selected because they are representative of differentiated fiber types. The fiber morphological measurements were obtained using two methods: one uses the fibers in suspension, without restraints, and the other uses a capillary fiber alignment. The results indicate good repeatability for both methods but differences of 14% for fiber length weighted in length, 2% for fiber width, 11% for coarseness, 35% for curl, and 88% for fines content. Scanning electron microscopy images were used to identify the fiber dimensions inside the tissue structure. Four different types of fiber models for eucalyptus fibers, with different fiber wall thickness and lumen dimensions, were presented and used to predict 3D computational fibrous structures.

Keywords

3D Fiber model; Cellulose; Fibrous materials simulation; Tissue materials

Inspired from Paper I:

Morais, F.P., Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2020). 3D Fiber Models to Simulate and Optimize Tissue Materials. *BioResources*. **15**: 8833-8848. DOI: 10.15376/biores.15.4.8833-8848

III.1.1.2. Introduction

Natural cellulosic fibers are structural elements with high relevance to produce paper materials, such as tissue products. The three-dimensional (3D) tissue paper structure is directly influenced by the fiber type in its composition, and consequently, this structure affects the performance of tissue products. Pulp fibers can have different origins, namely hardwood and softwood species, and different dimensions and characteristics, depending on the pulping process to which they are subjected (Paavilainen, 2002). In this way, the tissue paper properties required by the consumer can be obtained or improved by fibers selection (de Assis et al., 2018). Therefore, it is necessary to know the fibers' morphological properties suitable for tissue paper production to optimize the furnish management. Consequently, 3D fiber modeling is essential to simulate tissue papers, predicting their 3D structural properties that influence the final end-use properties.

According to Heikkurinen et al. (1991), the fiber properties can be classified according to their size distribution, including fibers length, width, wall thickness and coarseness, their shape, including curl and kink deformations, and their cell wall structure, including the flexibility and collapsibility properties. These concepts suggest that fiber characterization with precision can be difficult (Heikkurinen et al., 1991). There are several automatic optical analyzers for fiber properties analysis available on the market, including FS-200, FQA (Fiber Quality Analyzer), FiberLab, MorFi, FiberMaster, Galai CIS-100, and FiberTester (Carvalho et al., 1997; Tourtollet et al., 2003; Guay et al., 2005; Meyers and Nanko, 2005; Turunen et al., 2005; Hirn and Bauer, 2006; Li et al., 2011). The measurement differences between these instruments are due to the different hardware and software designs (Li et al., 2011). Comparative results with the L&W FiberTester analyzer are scarce in the literature, as well as there are no studies available comparing the results between L&W FiberTester and MorFi analyzers.

All analyzers can measure fiber length, but the same is not true for fiber width measurements. However, the analyzers that can determine this property are correlated reasonably well, although differences in the absolute width levels are observed (Guay et al., 2005; Turunen et al., 2005). The fiber length influences the tissue paper strength properties since enables more contacts between fibers in the 3D paper structure (Trepanier, 2017). Almost all fiber analyzers are unable to measure the fiber wall thickness. Therefore, this property is often determined using other image analysis techniques (Kibblewhite and Bailey, 1988; Chinga et al., 2007) such as confocal laser scanning microscopy (CLSM) (Jang et al., 1996) or scanning electron microscopy (SEM) (Reme et al., 2002). SEM also allows measuring the fiber effective thickness (fiber wall plus lumen) in the Z direction of the 3D paper structure (Morais et al., 2020a). The effective fiber thickness morphology measured in the paper structure is the main fiber parameter that influences the 3D paper structure, thickness, bulk, porosity, and end-use properties. The fiber coarseness is related to the width and fiber wall thickness (Nordström and Hermansson, 2018). The fiber coarseness and fiber length are inversely proportional to the fiber population. These three fiber properties have an important impact on paper apparent density.

Measuring this property accurately in fiber analyzers is difficult because only a small amount of dry fiber mass is analyzed, and there is a lot of debris, such as fibrils and fines, in industrial pulps (Paavilainen, 1993a). Fibers with equivalent coarseness can have very different fiber effective thickness dimensions. Therefore, the fiber properties are affected not only by the coarseness, but also by the relationship between fiber width, wall thickness, and lumen (Paavilainen, 1993a; Curto et al., 2009). In addition, fiber collapse in the 3D paper structure has a major impact on tissue paper structure-related properties. In order to describe the relationship between the fiber cross-sectional dimensions and the paper's structural properties, different parameters, such as the Runkel coefficient and the flexibility coefficient, were established (Dutt and Tyagi, 2011). These factors are associated with stiffness or flexibility properties and fiber collapsibility (Paavilainen, 1993b). Fiber flexibility is also directly related to the fiber relative bonding area (RBA) in the 3D paper structure. RBA is the parameter that best defines the paper structure and the fiber bonding degree. Consequently, this parameter can be calculated from the fiber flexibility coefficient, estimating the fiber bonding, and predicting the tissue paper strength properties (Tao and Liu, 2011). Therefore, a combined analysis of coarseness and these parameters may result in a much more accurate interpretation of the results.

Fibers present deformations throughout the pulp production process (Page et al., 1985). The fiber wall morphological properties affect the development of these fiber deformations. In tissue paper production, the use of curly fibers decreases the tensile index properties and, consequently, increases the softness properties (Morais et al., 2020b). Therefore, deformations increase contributes to a more open 3D paper structure, with less inter-fiber bonding, and consequently, an increase in bulk, porosity, and absorption properties (Trepanier, 2017). In addition to the fiber deformations, the fine elements present in cellulose pulps also have an impact on the tissue paper properties. In the 3D paper structure, the fines fill the voids between fibers, creating a more organized and closed structure, which contributes to the inter-fiber bonding increase and bulk decrease (Odabas et al., 2016).

Due to strong competition, the tissue industry is looking for innovative methods to analyze the behavior of tissue paper properties. The influence of fibers' morphological properties reveals the need for 3D fiber modeling. Several 3D computational simulation studies of the fibers impacts on the paper properties have been developed over the years (Kallmes and Corte, 1960; Niskanen and Alava, 1994; Bloch and Roscoat, 2009; Curto et al., 2011; Lavrykov et al., 2012; Marulier et al., 2015). However, this study is the first to use different 3D fiber models to simulate tissue materials.

The main goal of the present work is to identify the 3D fiber model for each type of fiber and to use it in 3D fiber-based computational simulations for the tissue materials. For this purpose, the measurements from two different fiber analyzers were compared on different pulp mills suitable for tissue paper materials.

III.1.1.3. Experimental

III.1.1.3.1. Materials

Industrial hardwood and softwood virgin fiber pulp mills were selected for this study (Table III.1). The selected pulps presented the morphological and final end-use properties suitable for their use in tissue paper production, as shown previously (Morais et al., 2019).

Table III.1. Description of the pulp samples, fiber reference, the type of cooking, and the bleaching sequences applied.

Pulp Samples	Pulp Denomination	Fiber reference	Cooking	Bleaching Sequences*
1	H_A	<i>Eucalyptus</i> (Brazil)	Kraft	ECF (OECF)
2	H_B	<i>Eucalyptus</i> (Portugal)	Kraft	TCF (OOZPP)
3	H_C	<i>Eucalyptus</i> (Portugal)	Kraft	ECF (DEpDD)
4	S_A	<i>Pinus</i> (Finland)	Kraft	ECF
5	S_B	<i>Pinus</i> (Finland)	Kraft	TCF (OOQPo)
6	S_C	<i>Pinus</i> and <i>Abies</i> (Sweden)	Kraft	ECF

* ECF: Elemental Chlorine Free; TCF: Total Chlorine Free. The description of the different bleaching sequences can be found in Morais et al. (2019).

III.1.1.3.2. Methods

Before testing, pulp samples were disintegrated according to ISO 5263 (1995). The morphological properties of the six pulp samples were automatically analyzed by two fiber analyzers for comparison: MorFi LBo1 Fiber Size Analyzer (TECHPAP, Grenoble, France) and Lorentzen & Wettre Fiber Tester (Kista, Sweden). Both instruments were calibrated and used according to the manufacturers' specifications. More detailed information about MorFi and FiberTester can be found in Tourtollet et al. (2003) and Li et al. (2011), respectively. Table III.2 summarizes the major features of these analyzers. The MorFi equipment presents a high-resolution camera (4 $\mu\text{m}/\text{pixel}$) with non-polarized light, and the fiber suspensions are analyzed through a channel (Hirn and Bauer, 2006). The Fiber Tester equipment uses a 10 $\mu\text{m}/\text{pixel}$ resolution camera with non-polarized light, and the fiber suspension is measured by a space between glass plates, which ensures good alignment of the fibers (Li et al., 2011). Because some air bubbles can be detected as fine elements when non-polarized light is applied, the two analyzers use vacuum to remove the air before measurements.

Table III.2. Features characteristics of MorFi and Fiber Tester analyzers.

Analyzer	Camera resolution ($\mu\text{m}/\text{pixel}$)	Light	Measurement Cell Shape	Sample (mg)	Fiber population (million/g)	Fine elements
MorFi	4	Non-polarized	Channel	600	5-30000	Length < 200 μm and/or width < 5 μm
Fiber Tester	10	Non-polarized	Capillary	100	5-30000	Length < 200 μm

Diluted suspensions of 20 mg/L (for hardwoods samples) and 30 mg/L (for softwoods samples) were analyzed in the MorFi, while 10 mg/L (for both hardwoods and softwoods samples) were analyzed in the Fiber Tester. The pulp fiber properties, such as fiber length weighted in length, width, coarseness, curl, and fine elements, were determined by the two analyzers. The ratio between fiber length and fiber width was also determined (Dutt et al., 2011). The repeatability of the analyzers was determined with a total of five replicates of Eucalyptus kraft bleached pulp (sample H_C). For the other samples, triplicate assays were performed, and the properties average was reported.

In addition, the fiber wall and lumen dimensions were analyzed in 100 fibers of the pulps in suspension, using an optical microscope (Leitz Wetzlar, Wetzlar, Germany) with the use of an integrated image analysis system (Leica Microsystems, IM500, Heerbrugg, Switzerland). From these measurements, the Runkel and flexibility coefficient were calculated (Dutt et al., 2011).

Using these pulp samples, a complementary study by SEM analysis was carried out in handsheets with a basis weight of 20 g/m² produced according to an adaptation of the ISO 5269-1. This modification consisted of the suppression of the handsheet pressing process and the basis weight modification, to mimic tissue papers (Morais et al., 2020b). Then, the handsheets were cut and the cross-sections were covered with gold using a Sputter Quorum Q 15 OR ES (Laughton, East Sussex, UK) and analyzed by Hitachi S2700 SEM (Tokyo, Japan), with a Bruker detector (Karlsruhe, Germany) operating at +20 kV and at different magnifications.

A 3D simulator of fibrous materials (Conceição et al., 2010; Curto et al., 2011) was used to simulate the 3D structures with the fiber dimensions obtained experimentally. This simulator, named *voxelfiber*, is open-source software, and the code is available on GitHub (<https://github.com/eduardotrincaconceicao/voxelfiber>). *Voxelfiber* is a morphological simulator for porous materials that can be modeled as planar random networks, as is the case of tissue papers. The fibers are represented by a chain of voxels in a 3D discrete spatial grid, allowing the direct use of methods developed for the 3D image field. The 3D simulator uses the fiber dimensions and properties, such as length/width ratio, fiber wall thickness, lumen thickness, fiber flexibility, and resolution (number of layers in the thickness direction), in order to produce the resulting 3D structure made from these modeled fibers. The key property of fiber flexibility is implemented through the mechanism originally proposed for the KCL-PAKKA simulator, by Niskanen and Alava (1994). A more detailed description of the 3D simulator can be found in Conceição et al. (2010) and Curto et al. (2011). An approach of different 3D fiber models, with different dimensions of fiber wall thickness and lumen, was also performed. The 3D computational structures will be processed to obtain important properties, such as apparent thickness, inter and intrafiber porosities. Computational studies were carried out using Matlab® (R 2020a, 9.8.0.1323502, MathWorks, Natick, MA, USA).

III.1.1.3.3. Statistical Analysis

All data analysis was performed using Microsoft Excel Office 365, and statistical analysis was performed using independent samples t-test with a 95% confidence level with IBM SPSS Statistics 25 (Armonk, NY, USA).

III.1.1.4. Results and Discussion

III.1.1.4.1. Fiber Pulps Morphology

The knowledge of the fibers' 2D morphological properties of two different analyzers is an important milestone of pulp characterization. These properties influence the tissue product properties and are important for 3D fiber modeling in a realistic way. The fiber length is an important property because it influences the strength and the formation of the paper sheets, especially softwood fibers (de Assis et al., 2019). The fiber length weighted by length is the quotient of the sum of individual fiber lengths squared and the sum of the individual fiber lengths (Guay et al., 2005). From Figure III.1a, the MorFi results showed fiber length weighted by length between 0.71 and 1.96 mm, while the Fiber Tester results showed between 0.66 and 2.41 mm. Fiber Tester measurements averaged 14% higher than those of MorFi. The fiber lengths weighted by length showed a relative agreement between both analysis instruments for the hardwood samples, but the same did not happen for the softwood samples. These small differences may be due to the different image analysis systems of both methods, such as camera resolution, for example (Li et al., 2011). For both analysis instruments, fibers pulp H_C and S_C were the longest of the hardwood and softwood samples, respectively.

The differences of fiber width were smaller compared with those of fiber lengths (Figure III.1b), and the MorFi results were on average 2% higher than the Fiber Tester. Fiber widths between 18 and 30.9 μm were obtained for the MorFi, while fiber widths between 17.6 and 40.0 μm were obtained for the Fiber Tester. Overall, these measurements of both equipment were in good agreement for all samples studied. Pulp H_C was the widest of the hardwood samples for both analysis instruments; however, pulp S_B and pulp S_C were the widest of the softwood samples for MorFi and Fiber Tester, respectively. In the Fiber Tester, the largest fibers were also the longest, for both hardwood and softwood samples. The same did not occur for MorFi, as only the hardwood samples showed this trend. In addition, the slenderness ratio also showed some differences because the length and width measurements were also different in both analyzers. These differences were, again, more pronounced in softwood pulps. On average, the Fiber Tester results were 24% higher than the MorFi. This ratio is related to the handsheet density and strength properties, as the fibers with a good slenderness ratio are readily collapsed, producing good surface contact and inter-fiber bonds (Dutt et al., 2011; Joutsimo and Asikainen, 2013). However, despite these small differences, measurements of the length and width properties on both analyzers did not show significant differences (Table III.3). The critical value of student's t distribution with 10 degrees of freedom is 1.812, with 95% confidence level.

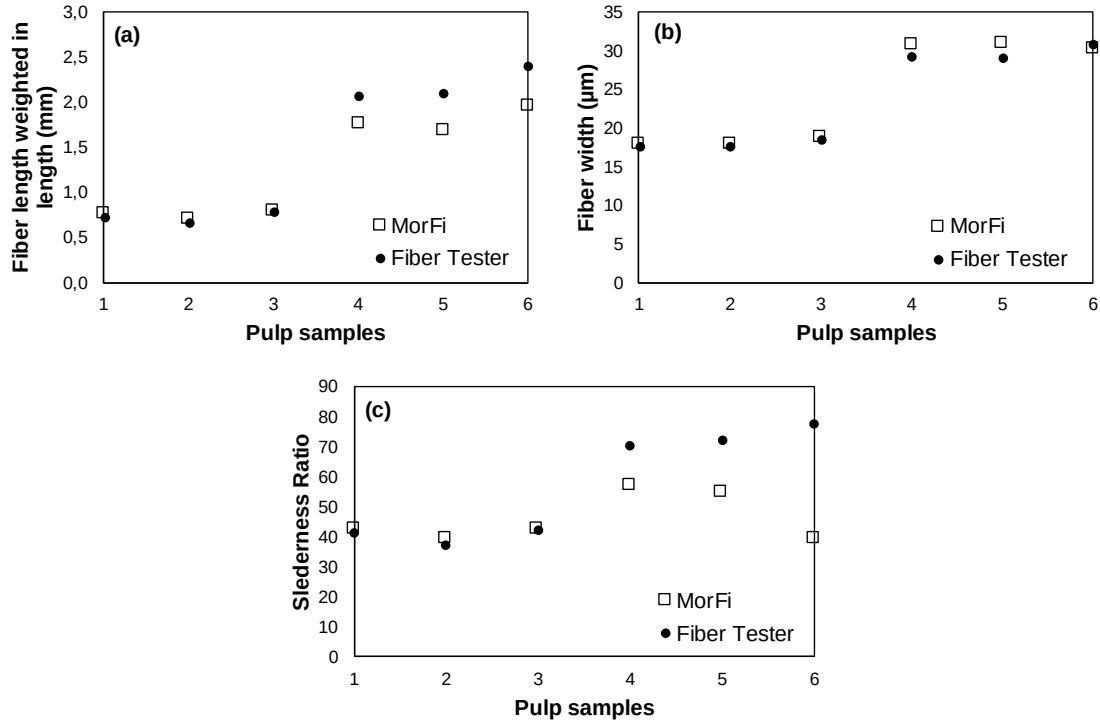


Figure III.1. Comparison of (a) fiber length weighted in length, (b) fiber width, and (c) Slenderness ratio between MorFi and Fiber Tester.

Table III.3. Statistical analysis using independent samples *t*-test with 95% confidence level of the parameters analyzed in MorFi and FiberTester.

	<i>t</i> *	df*	<i>p</i> *
Length weighted in length	-0.793	10	0.446
Width	0.150	10	0.884
Coarseness	0.418	10	0.685
Curl	-2.192	10	0.053
Fine elements content	13.107	5.114	0.000

* *t*: *t*-values; df: degrees of freedom; *p*: significance level

For the 3D tissue paper simulation process to be as realistic as possible, it is important to generate a 3D structure with the structural elements, the fibers, according to their distribution in the pulp furnish (Lavrykov et al., 2012). Therefore, the distribution of length and width properties studied for the six pulps by MorFi was considered (Figure III.2). In hardwood pulps, fiber lengths between 0.71 and 0.97 mm were further observed for pulp H_A (38%) and pulp H_C (37%), while pulp H_B presented 38% of the fibers with lengths between 0.46 and 0.71 mm. Fibers with lengths larger than 1.74 mm were barely visible in these three samples. In softwood pulps, 49%, 51%, and 48% of the pulp S_A, S_B, and S_C, respectively, presented lengths between 1.50 and 3.00 mm. Widths between 15 and 20 μm were mostly observed in the hardwood samples (35%, 34% and 30% of the pulp fibers H_A, H_B, and H_C, respectively) and between 30 and 50 μm in the softwood samples (46 %, 44% and 45% of the pulp fibers S_A, S_B, and S_C, respectively).

Overall, the pulps studied showed good distribution of fiber dimensions, concluding that both hardwood and softwood samples did not have only small and large dimensions, respectively, for the fiber lengths and widths.

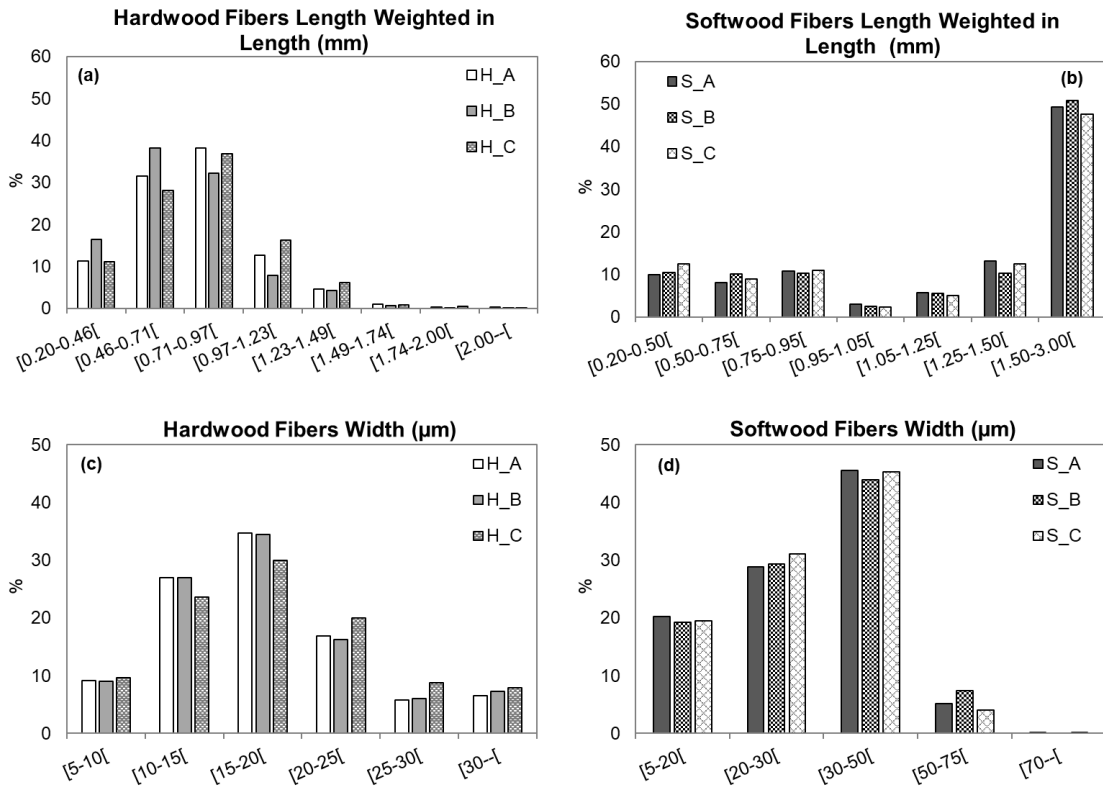


Figure III.2. Distribution of (a) hardwood and (b) softwood fibers length weighted in length, and (c) hardwood and (d) softwood fibers width, measured in MorFi.

The fiber coarseness is defined as the oven-dried pulp mass per unit total fiber length, depending on the total number of fibers analyzed (Li et al., 2011). Coarseness is influenced by fiber thickness, width, and pulp fiber population (Curto et al., 2009). Therefore, it is also important to analyze factors that are related to fiber thickness, such as the Runkel and flexibility coefficients. However, these parameters are obtained with fibers in suspension, so the fiber morphology in water suspension or the paper structure can be different. Consequently, an analysis of the fiber effective thickness in the paper structure is essential to understand its influence on the tissue structural properties, model the third dimension of the fiber, and optimize the tissue structure-related properties (Morais et al., 2020a). From Figure III.3a, the results obtained for the coarseness by MorFi (values between 6.71 and 19.66 mg/100m) were on average 11% higher than those of Fiber Tester (values between 6.30 and 19.38 mg/100m). These results were obtained since the fiber length measured by MorFi was systematically smaller than that measured by Fiber Tester. The total number of fibers analyzed by MorFi (21.1 million/g for hardwood and 5.2 million/g for softwood) was even higher than those analyzed by Fiber Tester (19.3 million/g for hardwood and 3.2 million/g for softwood). The higher Runkel index is related to the lower fiber collapse potential and the higher flexibility coefficient with the lumen diameter and, consequently, with the more flexible fibers.

Eucalyptus fibers with high coarseness, Runkel coefficient, and low flexibility coefficient are ideal for tissue papers (de Assis et al., 2018). However, softwood fibers with low coarseness, Runkel coefficient, and good flexibility coefficient are desired to ensure the tissue strength properties and the paper machine runnability (de Assis et al., 2019). The Runkel and flexibility coefficients obtained for the six pulps did not present a linear correlation with the coarseness properties of MorFi or Fiber Tester (Figure III.3b). It is also for this reason that a complementary SEM analysis of the fiber thickness in the paper structure is important to follow the differences found for coarseness in both analyzers in order to identify the most realistic measurement with different hypotheses of 3D fiber modeling. Although the coarseness measurements of both analyzers were not comparable, they did not show significant differences (Table III.3).

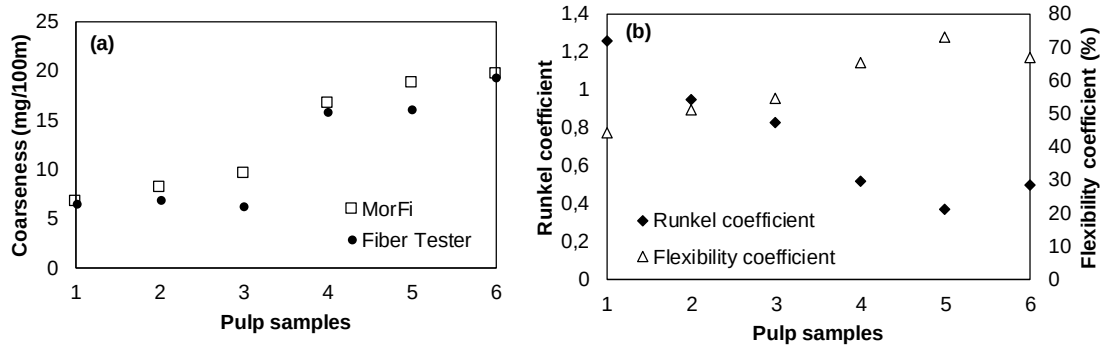


Figure III.3. Comparison of (a) fiber coarseness between MorFi and Fiber Tester, and (b) Runkel and flexibility coefficients of the six pulp samples.

The fiber curl is described as the deviation from the fiber axis straightness (Li et al., 2011) and is important to achieve higher softness properties in tissue products (de Assis et al., 2018). From Figure III.4a, the results obtained for the curl by Fiber Tester (values between 9.2 and 22.6 %) were on average about 35% higher than those of MorFi (values between 8.6 and 14.4 %). These differences may be related to the higher fiber length obtained for the Fiber Tester, because the longer fibers are more likely to have a higher fiber curvature (Li et al., 2011). Despite these differences, the trend in the curl measurements was similar, and the two analyzers did not show statistically significant differences (Table III.3). In addition, the fine elements (% in length) are defined as the quotient between the sum of the fines length and the total fibers and fines length in the samples (Guay et al., 2005). Higher fines content will promote better adhesion between the Yankee surface and the paper web (de Assis et al., 2018). From Figure III.4b, the MorFi showed fines content between 30.4 and 44.1%, while the Fiber Tester showed fines content between 4.2 and 5.9%. MorFi measurements averaged 88% higher than Fiber Tester. The fines content did not show a good relative agreement between both analyzers for the six samples. The independent t-test showed that, on average, both analyzers presented statistically significant differences for the fines content ($t(5.114) = 13.107$; $p < 0.05$), as presented in Table III.3. The critical value of student's t distribution with 5 degrees of freedom is 2.015, with 95% confidence level. This may be due to the fact that MorFi considers fine elements with lengths inferior to 0.2 mm and/or widths smaller than 5 μm , while the Fiber Tester considers only lengths smaller than 0.2 mm.

In general, the fines in pulps may not significantly affect fiber length measurements, but they affect the fiber coarseness measurements.

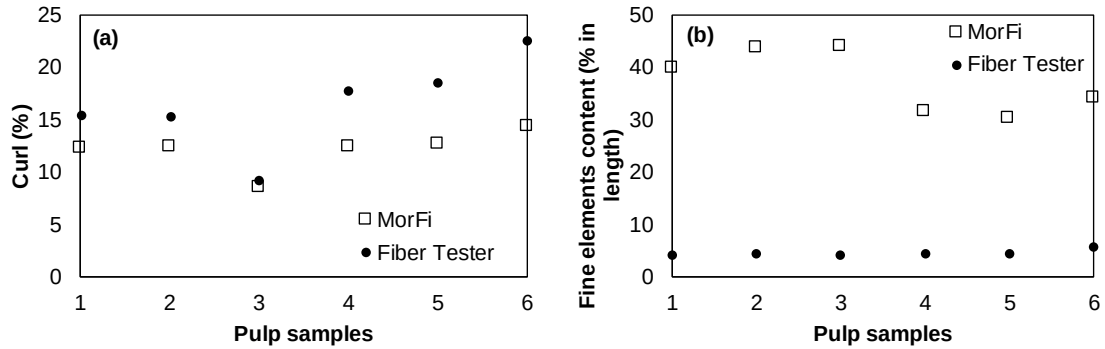


Figure III.4. Comparison of (a) fiber curl, and (b) fine elements content between MorFi and Fiber Tester.

The repeatability of the assays was analyzed in five replicates of the pulp H_C. Both analyzers showed good repeatability, since low variation coefficient values were obtained for each parameter, as shown in Table III.4. The fines content was the property with the highest variability for both analyzers; however, the Fiber Tester also showed some variability of the fiber curl measurements. Despite this good precision, the measurements of the properties analyzed for the six pulps cannot be compared. Both analyzers have different functionalities that must be considered when analyzing the measurements on each equipment.

Table III.4. Repeatability of MorFi and Fiber Tester performed in five replicates of the pulp H_C.

	Length Weighted in length (mm)	Width (μm)	Coarseness (mg/100m)	Curl (%)	Fine elements content (%)
*SV _{MorFi}	0.00	0.00	0.00	0.00	0.90
Mean _{MorFi}	0.80	18.80	9.56	8.60	44.10
*VC _{MorFi}	0.25	0.00	0.01	0.00	2.04
SV _{Fiber Tester}	0.00	0.10	0.00	0.10	0.10
Mean _{Fiber Tester}	0.79	18.60	6.30	9.20	4.20
VC _{Fiber Tester}	0.00	0.54	0.00	1.09	2.38

* SV: standard deviation; VC: variation coefficient

III.1.1.4.2. Hypothesis for Different 3D Fiber Models

Cellulose fibers are complex structural elements with different properties that influence the structural properties of tissue materials. Designing a realistic 3D fiber model to make use of the fiber properties obtained experimentally is essential. The experimental planning reported in this work can serve as a source for the introduction of fiber dimensions in simulators based on 3D fiber modeling. Table III.5 summarizes the fiber dimensions important to be implemented in these models, for example for the pulp H_C. The fiber effective thickness reported in this table was obtained through a previous study to analyze a significant number of fibers (322 fiber measurements) in the cross-section paper structure (Morais et al., 2020a). This study was carried out by the vector placement method in the SEM images of the handsheet cross-section structure made with pulp H_C.

Obtaining this third fiber dimension allows investigating different approaches to modeling the fiber thickness realistically. This property, as previously mentioned, is related to the fiber coarseness and the data from the two fiber analyzers showed differences for it. In order to understand the most correct coarseness value to simulate the 3D tissue paper structures, it is essential to model different hypotheses of the fiber wall and lumen dimensions and to understand which one relates effectively to the fiber coarseness of each analyzer. Our 3D computational simulator uses fiber properties such as fiber length/width ratio, fiber flexibility, fiber wall thickness, and fiber lumen, as input parameters, which is directly related to fiber coarseness. Therefore, through the modeling of 3D structures and different hypotheses, we can understand which fiber properties best reflects the fiber coarseness for the different pulps (in this case, H_C). As the coarseness showed differences in the two fiber analyzers, the computational simulator is also capable of predicting which coarseness best reflects the structural properties of the low basis weight structures produced and, consequently, optimizing the 3D modeling of these materials.

Table III.5. Fiber properties of pulp H_C important for 3D fiber modeling, as obtained by MorFi and Fiber Tester analyzers.

Analyzers	Length weighted in length (mm)	Width (μm)	Coarseness (mg/100m)	Fiber effective thickness (μm)*
MorFi	0.80	18.80	9.56	4.00
Fiber Tester	0.79	18.60	6.30	

* Third fiber dimension obtained by SEM according to the vector placement method in (Morais et al., 2020a).

The fiber effective thickness of the pulp H_C pulp (4 μm) includes the fiber wall and lumen, obtained from the paper structure, being different from that obtained from the fibers in water suspension. These differences are verified due to the tensions and pressures that the fibers are subjected in the paper formation, causing their collapse and variations in the cross-sectional fiber thickness (Kallmes and Bernier, 1963). In SEM images, differentiating the fiber wall thickness and lumen is not always possible. Due to these pressures, the fibers can have different shapes, from tubular to ribbon, as shown in Figure III.5a. The fiber lumen may not be visible due to the fiber collapse (Figure III.5b). In other cases, the fibers can collapse differently and present different fiber wall thickness and lumen dimensions (Figure III.5c, d).

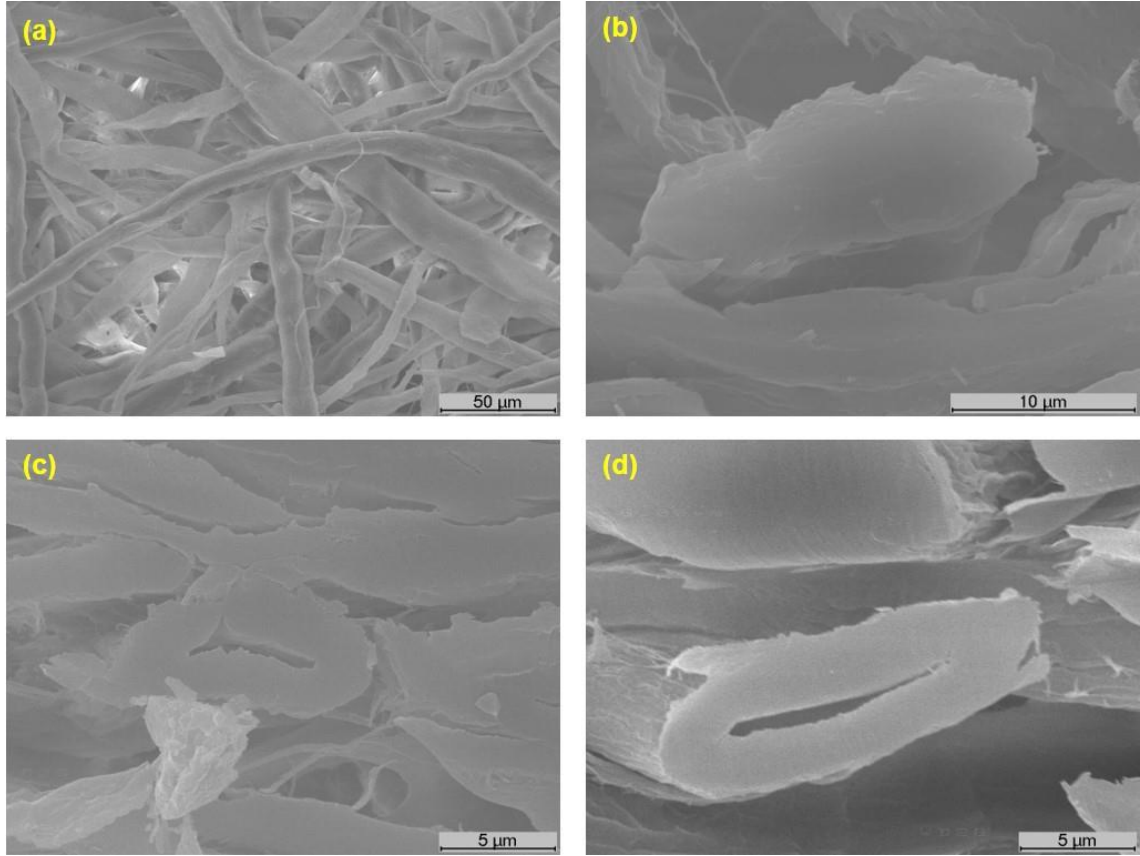


Figure III.5. SEM images of the (a) 3D network structure of handsheets with 20 g/m² made with pulp H_C (magnification of 500x). SEM images of the fiber thickness in the cross-section of these handsheets, where a (b) fiber without lumen (magnification of 4000x) and (c, d) fibers with different lumen dimensions and shapes (magnification of 5000x) were visible.

Due to the differences found in the 3D tissue paper structure, different hypotheses for fiber modeling were suggested for the H_C pulp fibers (Figure III.6). According to the proposed collapse models, the fibers can have a fiber thickness without lumen (Figure III.6a) or with a lumen with different dimensions (Figure III.6b-d) according to the fiber collapsibility and conformability. The proposed fiber model in Figure III.6a presents only one thickness dimension. With different dimensions of fiber length, width and thickness, namely length less than 0.2 mm and widths smaller than 5 μm, this model can also describe the fines and fillers present in pulp H_C. Fiber deformations, namely fiber curl, were not considered for these fiber models. In these conditions, a 3D tissue paper structure can be simulated with the different proposed fiber models, according to the fiber size distribution in pulps (Figure III.2).

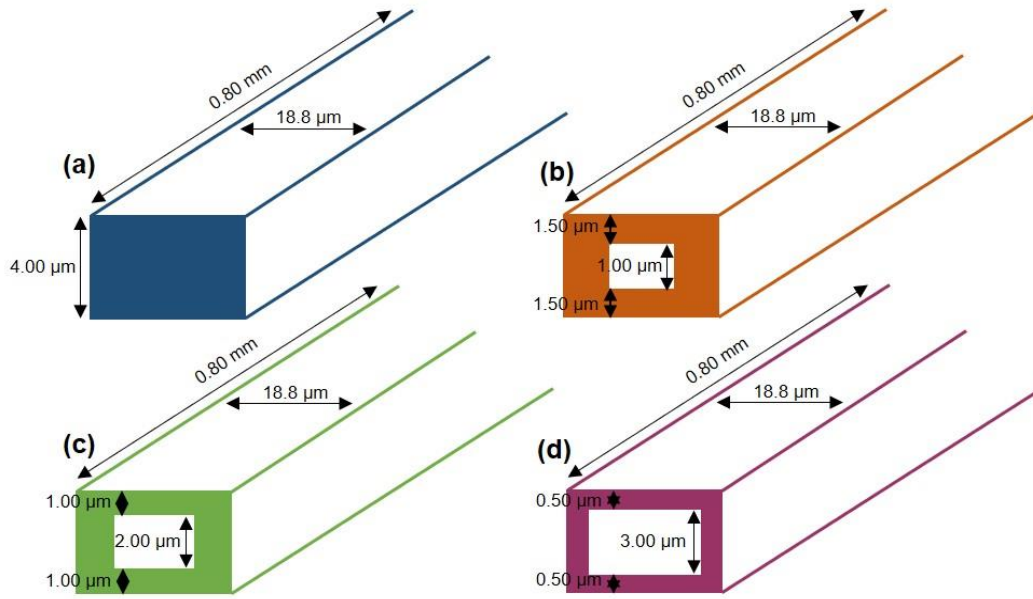


Figure III.6. The four 3D fiber models proposed for the eucalyptus fibers. The proposed models consist of (a) fiber without lumen, with a fiber thickness of 4 μm , or fibers with lumen with different dimensions, namely (b) 1 μm , (c) 2 μm and (d) 3 μm .

Using the 3D fiber-based computational simulator, it was possible to model the fibers individually. The 3D structure was formed by the sequential fiber deposition and conformation to the existing structure. The simulation results (Figure III.7) were presented to study the different hypotheses of the fiber models and the variations in structural properties (Table III.6). The model included the fiber properties shown in Table III.5 and Figure III.6. To simulate the tissue materials, the 3D structures presented a basis weight of 20 g/m^2 . The results showed that the different simulated fiber models formed structures with different thickness and inter- and intra-fiber porosities. These differences are due to the presence or absence of the lumen and its dimensions. It was evident that the different fiber collapse degrees had a great influence on the tissue structures' thickness. The thickness of the simulated structures (cross-section images of Figure III.7) increases with the increase of the lumen dimensions in the simulated fibers. As a lumen equal to zero corresponds to a fully collapsed fiber, the structures made with these fibers showed a low thickness. In contrast, the lumen equal to three, corresponding to approximately 75% of the fiber wall thickness, presents a structure with a thickness twice as large as the structure made with fibers without a lumen. On the other hand, the differences in the inter-fiber porosity were not significant according to the different fiber collapse models. The properties of intra-fiber porosity are in accordance with the increase of the fiber lumen. The different 3D fiber models can also be simulated simultaneously in order to form a more realistic 3D structure for tissue materials.

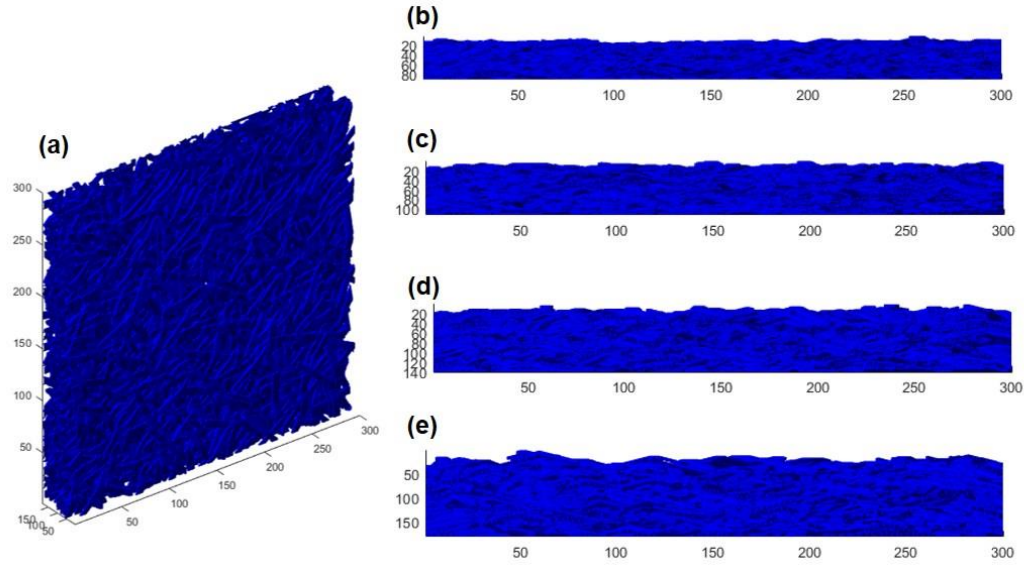


Figure III.7. Modeling results of different 3D structures simulated with fiber dimensions presented in Table III.5 and Figure III.6. The computational simulator makes it possible to model a 3D structure that mimics tissue materials of low basis weight (20 g/m²) (a), with different structural properties. The 3D structure thickness (cross-section image) is changed using different 3D fiber models: modeling of fibers without lumen (b) and with different lumen dimensions (c-e).

Table III.6. Inputs and outputs parameters of 3D computational simulations used to produce the 3D structures with different fiber wall thickness and lumen.

Input Parameters				Output Parameters		
Basis weight (g/m ²)	Number of fibers	Fiber wall thickness*	Lumen dimension*	Apparent thickness*	Interfiber porosity*	Intrafiber porosity*
20	2720	2	0	70	0.5777	0.0000
20	2718	2	1	90	0.5909	0.2000
20	2684	2	2	114	0.6085	0.3333
20	2696	2	3	139	0.6268	0.4286

* Units in computational voxel

From this stage, a comparison of the computational and experimental structures can be performed in order to validate the predictive character of the structural properties of tissue papers, with the aim of optimizing the production of each type of tissue paper. An approach of combining experimental characterization and computational modeling contributes not only to valuable information for the study of the relationships between fibers and the network structures formed by them, but also to predict the influence of the combination of different fibers on the design of innovative tissue materials and furnish optimization.

III.1.1.5. Conclusions

1. In this study, a comparison of the morphological properties of six pulps, suitable for tissue paper production was performed in two fiber analyzers, in order to propose different 3D fiber models to realistically simulate the 3D structure of these materials, and consequently, optimize the furnish management and the final tissue paper properties. The two analysis methods contributed to a better perception of the differences found in the morphological properties (e.g., coarseness), which are essential for a realistic 3D modeling of the fiber properties, and to simulate tissue paper materials.
2. The results showed that both analyzers presented good repeatability but different fiber properties measurements. Compared to MorFi, FiberTester measurements were, on average, 14% and 35% higher for fiber length and curl, respectively, and 2%, 11%, and 88% lower for fiber width, coarseness, and fines content, respectively. Statistically, the two methods are not comparable with regards to the fines' properties.
3. The 3D fiber modeling together with the study to obtain 3D data of the fibers and the structures formed by them were essential to propose different fiber models and simulate them in the computational simulator. Four different types of fiber models for eucalyptus fibers, with different fiber wall thicknesses and lumen dimensions, were used to simulate the 3D fibrous structure more accurately and, consequently, to predict tissue paper properties, in order to optimize the various types of tissue materials.

III.1.1.6. References

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III.1.2. Experimental 3D Fiber Data for Tissue Papers Applications

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III.1.2.1. Abstract

Tissue paper consumption has been growing for the past years, with a forecasted increase in demand for premium products. In premium tissue paper products, a balance between softness, strength, and absorption properties is essential, being optimized for each kind of tissue paper. These properties are influenced by the three-dimensional structure, made from the spatial distribution of cellulose fibers. To our knowledge, the efforts made to date to improve the softness, strength and absorption properties have overlooked the 3D structure. There is an absence of 3D experimental data in the literature for the simultaneous characterization of individual eucalyptus fibers and the paper structure made from these fibers. The 2D fiber morphology determination, including fiber length and fiber width, was obtained by an image analysis method for pulp fiber suspensions, using the MorFi® equipment. The third fiber dimension, the fiber thickness morphology in the out-of-plane direction, was obtained using SEM images of non-pressed isotropic laboratory-made paper sheets. The effective fiber thickness morphology, consisting of the fiber wall and lumen, was measured in the paper structure, as this is precisely the key fiber parameter, influencing not only the structure-related properties, such as paper thickness, bulk, and porosity, but also the final end-use properties. The paper structures were produced using an ISO standard adapted method, for tissue paper structures, without pressing, with a basis weight range from 20 to 150 g/m². These data are important, among other possible uses, for paper property optimization and simulation studies with 3D fiber-based simulators.

Keywords

3D Paper Structure; Cellulose Fiber; Eucalyptus Fiber Morphology; Effective Fiber Thickness; Tissue Paper

Inspired from Paper Ia:

Morais, F.P., Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2020). Experimental 3D fibre data for tissue papers applications. *Data in Brief*. **30**: 105479. DOI: 10.1016/j.dib.2020.105479

III.1.2.1.1. Specifications

- Parameters for data collection:

Hardwood isotropic handsheets for different basis weights were obtained using an adaptation of the paper ISO standard (ISO 5269) without the pressing operation, adapted for tissue papers.

- Description of data collection:

MorFi® analysis was performed to determine the 2D fiber morphology of eucalyptus pulp fiber suspensions (H_C, presented in subchapter III.1.1). Modified ISO 5269 was used to produce isotropic paper handsheets, dried under tension at 23°C and 50% humidity (ISO 187). SEM image analysis was performed on paper laboratory-made handsheets to measure the fiber thickness morphology. Paper thickness was measured using paper tissue standard (ISO 12625-3) in a conditioned room (ISO 187). Mass determination was done at 23°C and 50% humidity (ISO 187).

III.1.2.1.2. Value of the Data

- The eucalyptus fibers and the paper structure 3D data are important for paper property optimization and simulation studies with 3D morphology fiber-based simulators.
- The data can be used in computational simulation studies to optimize the 3D paper structure-related properties.
- The data is suitable for the calibration process of a computational model for 3D tissue paper (Conceição et al., 2010; Curto et al., 2011).
- The data is relevant in tissue paper materials research to obtain premium tissue paper materials.

III.1.2.2. Data

A compilation of 3D eucalyptus fibers experimental data, including the 2D fibers morphology characterization (around 15 million fibers per gram), is presented in this work. The 2D eucalyptus fiber morphology is available in Table III.7. The key fiber dimension, the effective fiber thickness, was measured using SEM images of eucalyptus paper laboratory-made handsheets, obtained with an adaptation of the ISO standard 5269, without the pressing stage, to better represent tissue paper structure. The fiber thickness measurements, 322 measurements, were performed in nine images (Table III.8; Figure III.8). Figure III.8 presents SEM images at different locations in the handsheet cross-section, where the fiber thickness is visible. These measurements were made along the entire handsheet cross-section using the vector placement method. All fibers were identified, numbered, and measured, to ensure that each fiber was measured only once, without repetition. A systematic image analysis methodology approach was developed in order to identify the key features and image analysis criteria to obtain fiber thickness dimensions (wall thickness plus lumen) in the handsheet. An image fraction can only be used if it is representative of the original image.

The criterium used to ensure the statistical representativeness is the threshold value for the number of fibers above which the mean value of a property becomes stable. Mass and thickness of eucalyptus handsheets for different basis weights are presented in Table III.9.

Table III.7. 2D fibers morphology analysis of eucalyptus pulp suspension using the fiber analyzer MorFi®.

	R1	R2	R3	Mean	Standard deviation
Fibers (million/g)	15.657	15.127	15.191	15.325	0.289
Length arithmetic (mm)	0.684	0.689	0.687	0.687	0.003
Length weighted in length (mm)	0.797	0.801	0.799	0.799	0.002
Width (μm)	18.8	18.8	18.8	18.8	0.0
Coarseness (mg/m)	0.0938	0.0965	0.0964	0.0956	0.0015
Kink angle (°)	128	128	128	128	0
Kinked fibers (%)	37.1	37.2	37.2	37.2	0.1
Curl (%)	8.6	8.6	8.6	8.6	0.0
Rate in length of MacroFibrills (%)	0.429	0.426	0.405	0.420	0.013
Broken Ends (%)	22.33	22.49	22.53	22.45	0.11
Fine elements (% in length)	43.2	44.9	44.2	44.1	0.9
Percentage of fine elements (% in area)	16.17	16.52	16.74	16.48	0.29

R = number of replicates (1, 2 and 3) used to perform the morphological assays

Table III.8. Measurements of the third fiber dimension, the effective fiber thickness in the isotropic handsheet cross-section of the SEM images.

N	Fiber Thickness (μm)	N	Fiber Thickness (μm)	N	Fiber Thickness (μm)
1	1.061	108	3.085	215	4.278
2	1.186	109	3.085	216	4.363
3	1.186	110	3.085	217	4.376
4	1.210	111	3.094	218	4.414
5	1.210	112	3.094	219	4.414
6	1.278	113	3.094	220	4.414
7	1.384	114	3.121	221	4.458
8	1.424	115	3.121	222	4.458
9	1.443	116	3.121	223	4.477
10	1.501	117	3.166	224	4.477
11	1.661	118	3.166	225	4.477
12	1.678	119	3.192	226	4.502
13	1.711	120	3.192	227	4.509
14	1.853	121	3.192	228	4.509
15	1.853	122	3.228	229	4.515
16	1.853	123	3.297	230	4.515
17	1.898	124	3.297	231	4.515
18	1.898	125	3.305	232	4.515
19	1.913	126	3.305	233	4.534
20	1.913	127	3.305	234	4.564
21	1.913	128	3.356	235	4.583

22	1.913	129	3.373	236	4.583
23	1.913	130	3.373	237	4.607
24	1.913	131	3.398	238	4.607
25	2.014	132	3.422	239	4.662
26	2.014	133	3.455	240	4.680
27	2.027	134	3.455	241	4.746
28	2.027	135	3.504	242	4.746
29	2.027	136	3.504	243	4.746
30	2.027	137	3.504	244	4.775
31	2.027	138	3.528	245	4.775
32	2.041	139	3.528	246	4.805
33	2.041	140	3.528	247	4.805
34	2.149	141	3.528	248	4.869
35	2.239	142	3.528	249	4.886
36	2.251	143	3.559	250	4.886
37	2.251	144	3.559	251	4.892
38	2.337	145	3.559	252	4.892
39	2.349	146	3.559	253	4.938
40	2.349	147	3.559	254	4.955
41	2.373	148	3.559	255	4.989
42	2.373	149	3.559	256	4.989
43	2.443	150	3.567	257	4.989
44	2.443	151	3.614	258	5.006
45	2.443	152	3.614	259	5.028
46	2.443	153	3.622	260	5.034
47	2.443	154	3.622	261	5.204
48	2.477	155	3.622	262	5.210
49	2.477	156	3.622	263	5.221
50	2.477	157	3.630	264	5.242
51	2.522	158	3.630	265	5.253
52	2.522	159	3.630	266	5.269
53	2.522	160	3.630	267	5.269
54	2.522	161	3.684	268	5.306
55	2.522	162	3.691	269	5.354
56	2.556	163	3.707	270	5.380
57	2.556	164	3.707	271	5.411
58	2.556	165	3.707	272	5.416
59	2.556	166	3.707	273	5.422
60	2.567	167	3.752	274	5.463
61	2.567	168	3.752	275	5.463
62	2.621	169	3.797	276	5.519
63	2.621	170	3.804	277	5.540
64	2.621	171	3.826	278	5.640
65	2.621	172	3.826	279	5.695
66	2.653	173	3.834	280	5.700
67	2.653	174	3.834	281	5.715
68	2.653	175	3.863	282	5.715
69	2.706	176	3.892	283	5.715
70	2.706	177	3.892	284	5.715
71	2.706	178	3.892	285	5.735
72	2.706	179	3.892	286	5.774
73	2.706	180	3.914	287	5.779
74	2.706	181	3.949	288	5.793
75	2.767	182	3.949	289	5.837
76	2.767	183	3.949	290	5.870
77	2.767	184	3.949	291	5.932
78	2.767	185	3.978	292	5.932
79	2.767	186	3.978	293	5.937

80	2.777	187	3.978	294	5.989
81	2.777	188	4.034	295	6.050
82	2.848	189	4.034	296	6.050
83	2.848	190	4.034	297	6.050
84	2.857	191	4.041	298	6.064
85	2.857	192	4.041	299	6.124
86	2.857	193	4.041	300	6.188
87	2.857	194	4.041	301	6.211
88	2.857	195	4.041	302	6.211
89	2.867	196	4.041	303	6.318
90	2.897	197	4.041	304	6.367
91	2.897	198	4.083	305	6.425
92	2.897	199	4.083	306	6.563
93	2.935	200	4.096	307	6.649
94	2.935	201	4.144	308	6.882
95	2.935	202	4.151	309	6.979
96	2.973	203	4.151	310	7.356
97	2.973	204	4.198	311	7.356
98	2.973	205	4.198	312	7.360
99	3.002	206	4.198	313	7.582
100	3.002	207	4.205	314	8.072
101	3.002	208	4.245	315	8.546
102	3.002	209	4.245	316	8.546
103	3.020	210	4.245	317	8.546
104	3.020	211	4.271	318	8.595
105	3.039	212	4.278	319	9.255
106	3.039	213	4.278	320	9.255
107	3.039	214	4.278	321	9.267
				322	10.939

N = number of fiber measurements using the different SEM images

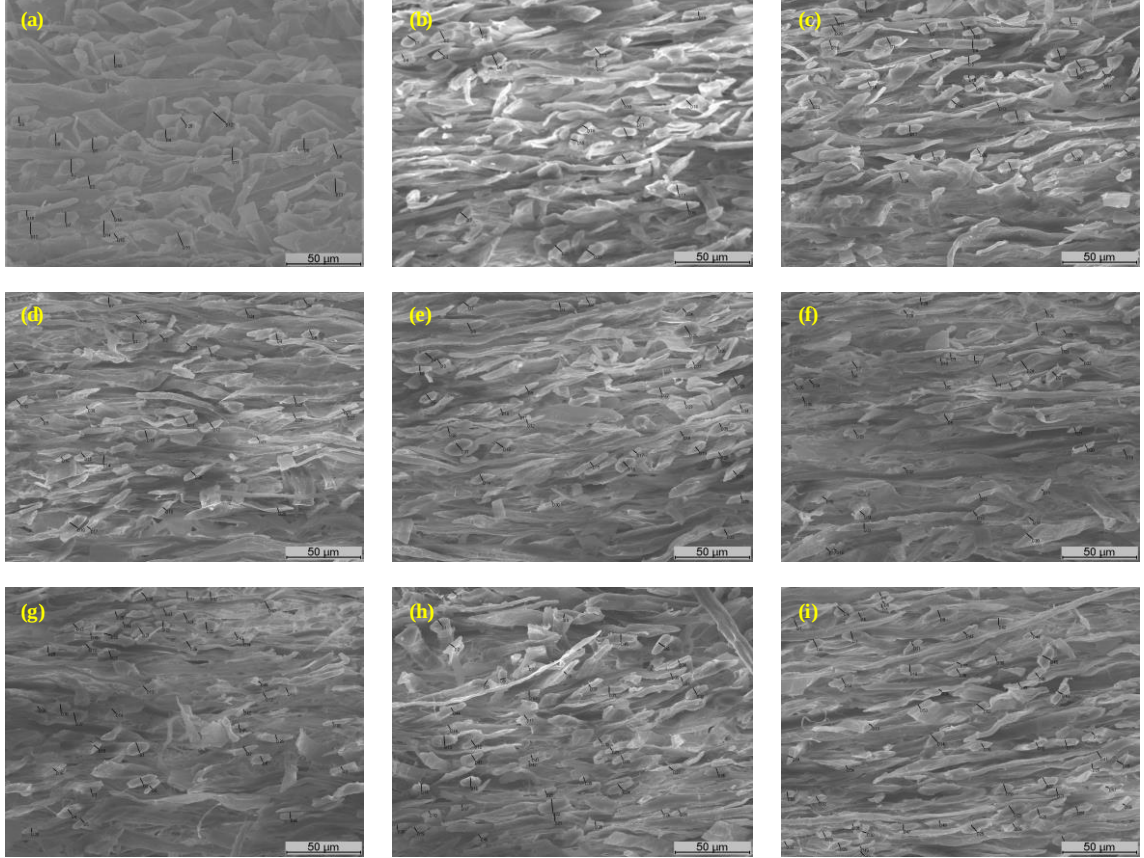


Figure III.8. Out-of-plane handsheets SEM images cross-section (Z-direction) were taken scanning the paper structure from left to right (X-direction) with the same depth (Y-direction). Measurements of 322 fiber thicknesses (Table III.8) were performed in nine SEM images. The vectors used to measure each fiber thickness are visible in each SEM image. The cross-section (a) represents the measurements of 1-20 fiber' thickness described in Table III.8; (b) of 21-41; (c) of 42-73; (d) of 74-103; (e) of 104-138; (f) of 139-174; (g) of 175-219; (h) of 220-264; and (i) of 265-322.

Table III.9. Mass and thickness (tissue ISO 12625-3) of laboratory isotropic handsheets (adaptation of ISO 5629, without pressing) made from Kraft pulp eucalyptus fibers (H_C pulp) in a conditioned room at 23°C and 50% humidity (ISO 187) with basis weights in the range of 20-150 g/m².

Eucalyptus handsheets basis weights (g/m²)							
10 handsheets average	21.1	42.4	63.9	87.0	109.1	129.0	150.9
Mass (g)	0.437	0.911	1.354	1.862	2.323	2.747	3.254
Mass (g)	0.444	0.911	1.369	1.864	2.343	2.764	3.238
Mass (g)	0.456	0.911	1.337	1.870	2.350	2.745	3.242
Mass (g)	0.458	0.912	1.364	1.878	2.344	2.725	3.252
Mass (g)	0.468	0.902	1.370	1.925	2.289	2.730	3.187
Mass (g)	0.452	0.907	1.378	1.880	2.350	2.774	3.172
Mass (g)	0.441	0.883	1.368	1.858	2.339	2.748	3.227
Mass (g)	0.461	1.022	1.376	1.802	2.308	2.756	3.242
Mass (g)	0.465	0.740	1.381	1.841	2.339	2.817	3.227
Mass (g)	0.437	0.968	1.374	1.830	2.347	2.773	3.218
Thickness 1 (μm)	109	175	269	323	422	492	613
Thickness 2 (μm)	104	174	265	309	425	459	544
Thickness 3 (μm)	113	185	257	326	408	474	573
Thickness 4 (μm)	104	185	258	341	409	512	540
Thickness 5 (μm)	113	176	247	315	419	496	593
Thickness 6 (μm)	112	181	238	328	405	475	517
Thickness 7 (μm)	107	168	233	312	416	484	566
Thickness 8 (μm)	110	191	239	313	427	474	549
Thickness 9 (μm)	115	157	228	323	427	497	566
Thickness 10 (μm)	111	195	235	322	416	494	568

Commercial tissue products, such as napkins, toilet papers, towels papers, facial papers, have total paper thicknesses between 50 and 90 μm, produced by the conventional method, for basis weight between 16 and 22 g/m² (Tutuş, Çiçekler and Çali, 2016). These materials are usually produced with an arrangement of one to five plies of paper sheets (or more), increasing their basis weight and thickness. Therefore, a variety of thickness and basis weight data of isotropic handsheets that mimic tissue papers (without the pressing operation) are considered a highly relevant subject of research.

The analysis of these different 3D fibers data of tissue paper has great relevance, for example, for a computational calibration process of heterogeneous material models, required for the identification of problems and evaluation of possible optimization solutions for these premium papers. The analysis of this data is performed as follows:

1. The morphological properties of the eucalyptus pulp fibers were analyzed, using a fiber analyzer (MorFi®);
2. The unpressed isotropic handsheets were produced with a basis weights range of 20 to 151 g/m², using an adaptation of an ISO standard;
3. The fiber thickness morphology (wall thickness plus lumen) in handsheet cross-section was analyzed, using the vector placement method in the SEM images (fibers morphological analysis is essential to promote more real computational representations);

4. The thickness (out-of-plane paper dimension) and basis weights of isotropic handsheets were measured, according to a tissue ISO standard (these measurements are essential to understand and quantify the structural changes in the paper).
5. From these data, an analysis of the structures' apparent density can be made, being related to the structures' effective porosity (Sampson, 2001).

III.1.2.3. Experimental Design, Materials, and Methods

III.1.2.3.1. Pulp Samples

A kraft bleached eucalyptus pulp was selected (H_C pulp, presented in subchapter III.1.1). Laboratory isotropic handsheets were produced from an adaptation of ISO 5269-1 (without the pressing process) to mimic tissue paper materials. A sheet former with a circular shape surface of 0.02138 m² was used to make handsheets with different basis weights (between 20 and 151 g/m²) with replicates of 10 times. The samples were conditioned at 23 ± 1 °C and 50 ± 2% relative humidity, according to ISO 187.

III.1.2.3.2. Fibers Properties Analysis

III.1.2.3.2.1. MorFi® Analysis

The pulp sample was disintegrated according to ISO 5263. Diluted suspensions of 20 mg/L were tested using a MorFi® equipment, to obtain the biometric and morphological properties of eucalyptus kraft bleached pulp. This equipment includes a digital camera and 2D image analysis software for the automatic measurement of suspended fibers. The assays were performed in triplicate.

III.1.2.3.2.2. Fiber Thickness Morphology Analysis

The morphology of each effective fiber thickness (wall thickness plus lumen) was evaluated by SEM (Hitachi S2700, with a Bruker detector operating at +20 kV and different magnifications). Previously, the handsheet samples were cut transversely and placed on an aluminum support with double-side adhesive tape, so that the plane in the handsheet z-direction was analyzed. Then, the samples were gold plated using a Sputter Quorum Q 15 OR ES equipment. Throughout this cross-section it was possible to measure 322 fiber thicknesses, using the vector placement method.

III.1.2.3.3. Paper Properties

Basis weight or grammage is the mass per unit area (g/m²) is the structure property of the paper. The paper handsheet thickness was determined using a micrometer (FRANK-PTI GMBH, Birkenau, Germany), according to ISO 1262-3, for tissue paper.

III.1.2.4. References

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III.1.3. Comparative Characterization of Eucalyptus Fibers and Softwood Fibers for Tissue Papers Applications

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III.1.3.1. Abstract

Significative growth and demand for premium tissue products, in which softness and absorbency are key consumer requests, pointed out the need for the establishment of relations between fiber properties and tissue paper properties. For this purpose, an experimental plan was designed using a representative group of pulp fibers, six hardwood, and six softwoods, for the production and characterization of low basis weight paper structures (20 g/m²). The pulp fibers morphology and chemical content were evaluated, and hardwoods showed lower fiber length (0.70-0.84 vs 1.57-1.96 mm), coarseness (6.71-9.56 vs 16.77-19.66 mg/100m) and higher pentosan content (6.3-21.1 vs 7.6-10.3 %). Even though the paper structures were produced with the same basis weight, they presented a broad range for bulk (3.46-8.04 cm³/g), tensile index (2.00-11.45 Nm/g), softness (65.7-86.9) and absorption capacity (8.08-9.48 g/g). The results indicated that softness was directly influenced by structural properties, increasing with bulk, while tensile strength correlated inversely. Therefore, the correlations obtained were used to identify the most suitable pulp fibers properties for each type of tissue paper.

Keywords

Absorption; Cellulose Fiber Materials; Pulp Fiber Morphology; Softness; Tissue Papers

Inspired from Paper II:
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III.1.3.2. Introduction

Today's cellulose industry offers a growing range of pulps produced by different delignification processes. Each pulp has unique characteristics, depending on the fiber's wood original properties and fiber modifications that are introduced by the pulping and bleaching processes. A combination of lignin removal, oxidation, and extraction unit operations will originate different pulps (Sun et al., 2014). The correlations between key pulp fibers properties and end-use specifications constitute a novelty, that will be applied to select the most suitable pulps to obtain high quality tissue papers. Tissue products are produced predominantly with hardwoods eucalyptus fibers (Pirralho et al., 2014) with a percentage of softwoods to confer strength and runnability in the paper machine process (de Assis et al., 2018). Depending on the type of tissue paper, there will be a specific formulation with specific percentages of hardwood and softwood. Higher percentages of hardwood fibers will improve softness and the addition of softwoods will increase wet and dry strength, lowering softness (Neelagar et al., 2018). The main goal of the present study was to analyze and compare different pulp properties, relating them with tissue paper performance. For this purpose, hardwoods and softwoods pulps were characterized in terms of morphological and chemical properties. The pulps drainability and water retention value were also evaluated. Tissue isotropic 20g/m² handsheets were produced and their structural, mechanical, absorption and softness properties were measured.

III.1.3.3. Experimental

Six hardwood eucalyptus kraft pulps (H_A to H_F) and six softwood kraft pulps (S_A to S_F) with different bleaching sequences (Table III.10) were selected for being representative market pulps. The morphological properties of pulp fibers were evaluated in MorFi® (TECHPAP, Grenoble, France) equipment, in triplicate. The pulps were characterized through viscosity (SCAN-CM 15:88), pentosan content (TAPPI T 223 cm-10), and carboxyl group content (TAPPI T 237 om-97). The drainability of the pulps suspension (°SR) was determined by Schöpper-Riegler methodology according to ISO 5267-1. The water retention value (WRV) index of pulp fibers was determined according to the method described by Jayme, 1958, in triplicate. To evaluated tissue paper properties, handsheets were produced with a basis weight of 20 g/m², according to an adaptation of ISO 5269-1, i.e. unpressed handsheets, to be representative of the low basis weight industrial tissue paper. The handsheets produced were characterized by measuring the thickness and bulk (ISO 12625-3), basis weight (ISO 12625-6), tensile index (ISO 12625-4), water absorption capacity (ISO 12625-8), capillary rise (ISO 8787) and softness using a TSA - Tissue Softness Analyzer (Emtec) equipment.

Table III.10. Bleaching sequences process identification of each hardwood and softwood pulp used in the study.

	Pulps	Bleaching Sequences
Hardwood	H_A	Elemental Chlorine Free (ECF), with OECF sequence
	H_B	Total Chlorine Free (TCF), with OOZPP sequence
	H_C	ECF, with DEpDD sequence
	H_D	ECF, with ODED sequence
	H_E	ECF
	H_F	TCF, with EOP sequence
Softwood	S_A	ECF
	S_B	TCF, with OOQPo sequence
	S_C	ECF
	S_D	ECF
	S_E	ECF
	S_F	TCF

III.1.3.4. Results and Discussion

Regarding the hardwood eucalyptus pulp fibers biometry, it showed a range in length (0.70-0.84 mm) and in width (18.0-19.1 μm) lower than softwoods. These properties may be related to each other by the felting power, since is expected that the papers produced from these fibers will have relatively good mechanical properties. For instance, H_F and S_F pulps had the lowest slenderness ratio values (fiber length/fiber width), namely 38.0 and 52.7. Eucalyptus fibers coarseness presents the highest percentage of variation (6.71-9.56 mg/100m), where H_C pulp had the highest coarseness and S_A pulp registered the lower coarseness. This parameter is related to the fiber wall thickness and influences the fiber collapse degree and development of bulk (Levlin and Söderhjelm, 1999). A more open fibrous network structure, with lesser interfiber bonds, will influence positively the softness and negatively the tensile strength (Pirralho et al., 2014). Generally, eucalyptus pulps showed a low coarseness, but a high number of fibers per gram and may point to a larger bonded area. H_F pulp had the highest values of curl and kinks. Curl and kinks are fiber deformations that contribute to a more developed network, generating less inter-fiber bonds and leading to a potential development of bulk, porosity, and smoothness in the final product. The high fines content may correspond to the fibers that are more flexible (H_D and S_C pulps).

Viscosity is related to the cellulose polymerization degree. H_B pulp presented the lower viscosity value (453 mL/g), possibly related with the use of oxygen and ozone in the bleaching stage. This bleaching process is not selective because the high oxidation potential of these reagents induces the depolymerization and pulp polysaccharides degradation (Levlin and Söderhjelm, 1999). Pentosans are hydrophilic and contribute positively to fiber water absorption capacity. H_B pulp presented the higher pentosan content (21.1%), while H_F pulp presented the lower pentosan content (6.3%). The value for the H_F pulp is justified since it is a pulp from an acid sulfite cooking process.

The hardwood pulps presented a drainability resistance ($^{\circ}\text{SR}$) higher than softwoods, which could be related to the fines content. Regarding WRV, the H_E and S_C pulps presented higher values for this property (76.9 and 75.0 %) and higher carboxyl groups content values (9.61 and 10.60 mmol/g). The pulps chemical composition is one of the factors that influence WRV since it influences the fibers binding to water (Levlin and Söderhjelm, 1999). This ratio was also observable, for example, for H_F pulp because it had low carboxyl groups content (4.36 mmol/g) and, in addition, little presence of pentosans, and consequently a low WRV value (63.1 %). It was possible to verify that the main parameter responsible for the differences in $^{\circ}\text{SR}$ may be the fibers length, while in WRV, higher fibers coarseness may explain the results obtained for the H_E, H_C and S_C pulps.

Hardwood and softwood fibers showed different bulk values (3.55-5.83 vs 3.46-8.04 cm³/g). H_C and H_F pulps presented the same bulk, but high differences in tensile index properties (Figure III.1). This may be because of differences in flexibility and morphological properties. While H_C pulp had the highest coarseness, H_F pulp showed low coarseness. H_C and S_A pulps had higher values of the tensile index (9.96 and 11.45 Nm/g). H_F pulp presented the lowest value for the tensile index (2.00 Nm/g). This result may be related to the low pentosan content and, consequently, to a lower establishment of interfiber bonds. Deformations (curl and kinks) contribute to the reduction of fiber strength. The pulps with the highest tensile index also showed the lowest values of curls and kinks and vice-versa. According to the estimated values for softness (handfeel-HF) (Figure III.9), H_B, H_F, and S_B pulps presented high values for this property (81.7, 86.9 and 75.8). The low hemicelluloses content in H_F pulp may have contributed significantly to the production of a structure with fibers less linked to each other and more open structure (Levlin and Söderhjelm, 1999). In addition, this pulp also showed the highest deformation values, which also contributed to the softness potential (Levlin and Söderhjelm, 1999). The tensile index and handfeel property are inversely proportional, and the factors that contribute to the increase of the resistance are the same that contribute negatively to the softness potential. Therefore, from result analysis for both properties, this relationship was easily verified (Figure III.9). H_C and S_A pulps had the highest values of tensile strength and the lowest softness values. For the hardwood and softwood pulps the relations were Tensile = -2.4133 Handfeel + 88.885 ($R^2 = 0.9004$) and Tensile = -1.3475 Handfeel + 80.442 ($R^2 = 0.7182$).

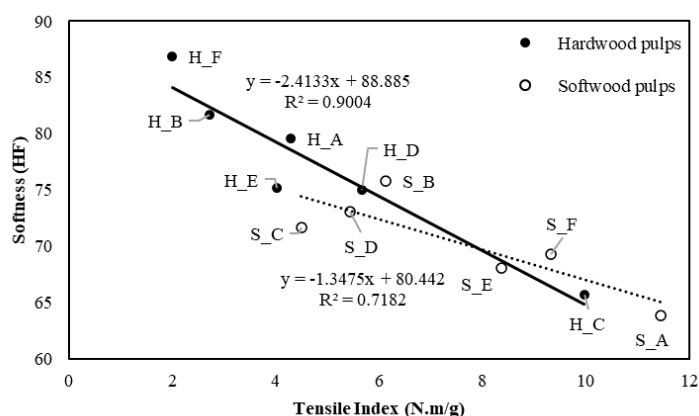


Figure III.9. Correlation of tensile index and softness for hardwood and softwood pulps.

Water absorption is a key property of tissue products (Beuther, Veith and Zwick, 2010). This property was analyzed by the total water absorption capacity and the capillary rise (Figure III.10). H_D and S_C pulps presented higher values for the total water absorption capacity (8.83 and 9.48 g/g). The high pentosans content and the high carboxyl groups content in these pulps, respectively, will promote more interaction points. H_C pulp showed the lowest values for this property (8.08 g/g) which may be related to a more closed fibrous network, having less space available to retain water. H_D and S_A pulps revealed better performance in the capillary rise. It is also important to note that the H_F pulp had an intermediate absorption capacity value (8.45 g/g). This pulp had a low pentosan content, which explains the capillary rise value. In contrast, H_F pulp had also a high bulk and an increase in pore volume. This means that there will be more space for water retention, hence increasing water absorption capacity.

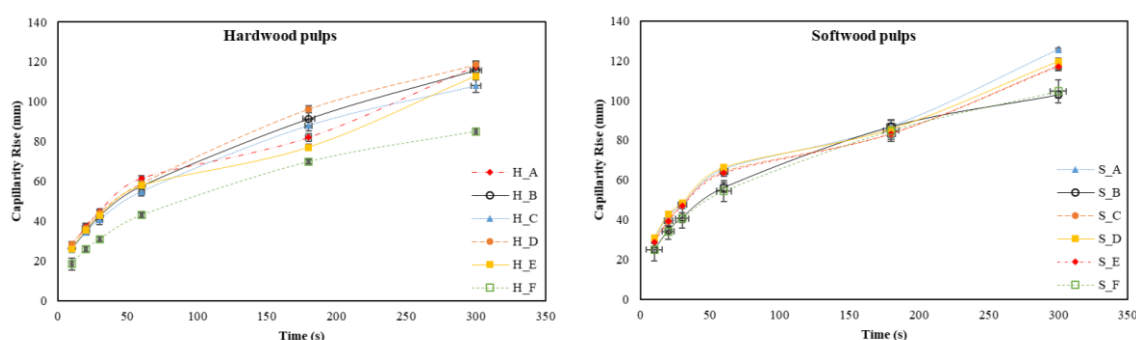


Figure III.10. Capillary rise as a function of time for hardwood and softwood pulps.

III.1.3.5. Conclusions

The morphological properties and chemical composition of different hardwood and softwood pulps showed a distinctive influence on tissue paper properties. The eucalyptus pulps more suitable for tissue paper should have high coarseness (H_C or H_D), deformations (H_F), low fines content (H_A or H_B) and low pentosan content (H_F). Each tissue paper type has different specificities and the management of furnish supply will be optimized according to the information obtained in this study. Eucalyptus pulps with higher water absorption capacity and softness (H_B and H_F) will be selected to be used in premium toilet and facial papers. Eucalyptus pulps with the highest tensile index (H_C) will be used in towel papers, where wet strength is essential. The addition of softwood S_A pulp proved to be the most suitable to promote paper machine runnability.

III.1.3.6. References

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III.1.4. Characterization Data of Pulp Fibers Performance in Tissue Papers Applications

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III.1.4.1. Abstract

The data presented in this subchapter derived from the research discussed in the previous subchapter III.1.3. – “Comparative characterization of eucalyptus fibers and softwood fibers for tissue papers applications” (Morais et al., 2019). In this work, six eucalyptus hardwood pulps and six softwood pulps were characterized in terms of morphological, chemical, and water-related (by drainability and water retention index) properties. In addition, using these pulps, unpressed laboratory isotropic handsheets were produced with a basis weight of approximately 20 g/m², similarly to tissue papers. The key properties of tissue papers, namely structural properties, tensile index, absorption, and handfeel softness were analyzed in these handsheets.

Keywords

Cellulose Materials; Fibers Morphology; Pulps Chemical Properties; Tissue Papers Properties

Inspired from Paper IIa:

Morais, F.P., Bértolo, R.A.C., Curto, J.M.R., Amaral, M.E.C.C., Carta, A.M.M.S., and Evtugin, D.V. (2020). Characterization data of pulp fibres performance in tissue papers applications. *Data in Brief*. **29**: 105253. DOI: 10.1016/j.dib.2020.105253

III.1.4.1.1. Specifications

- Parameters for data collection:

Hardwood and softwood pulps suspension were obtained in standards conditions. Low basis weight and unpressed isotropic laboratory handsheet were obtained with an adaptation to an ISO standard.

- Description of data collection:

MorFi® were performed to analyze morphology fibers of hardwood and softwood pulps. SCAN and TAPPI standards were performed to analyze chemical hardwood and softwood pulps (viscosity, pentosan content and carboxyl group content). Water retention method was performed to analyze water retention value of the pulp's suspension. ISO standard and TSA analysis were performed to analyze pulps suspension and isotropic handsheets (Schöpper-Riegler degree, thickness, bulk, tensile index, water absorption capacity, handfeel softness).

III.1.4.1.2. Value of the Data

- This data is useful to demonstrate and understand the effect of fibers morphological and chemical analysis on tissue paper properties.
- This data can be useful to the paper tissue industry and from the point of view of the researcher.
- This data can be used in future studies as comparison of different eucalyptus hardwood and softwood pulps in the market and looking for the most suitability pulp for each tissue paper (toilet paper, towel paper, napkins, facial paper, etc).
- To the best of our knowledge, this is the first published vast amount of characterization techniques used that justify the suitability of different fibers pulps for tissue papers application.
- Our data will be the starting point for optimized formulations of eucalyptus pulps modified to produce premium tissue papers.

III.1.4.2. Data

Here we report experimental characterization data on six eucalyptus hardwood and six softwood pulps and un-pressed laboratory isotropic handsheets with a basis weight of approximately 20 g/m². Analysis of fibers morphology, chemical properties, drainability (Schöpper-Riegler degree - °SR), water retention value (WRV), structural, tensile, absorption and handfeel (HF) softness tissue properties are shown (Table III.11). Some correlations found about these properties also are shown, namely tensile index versus curl and kinked fibers (Figure III.11) and tensile index versus softness (Figure III.12).

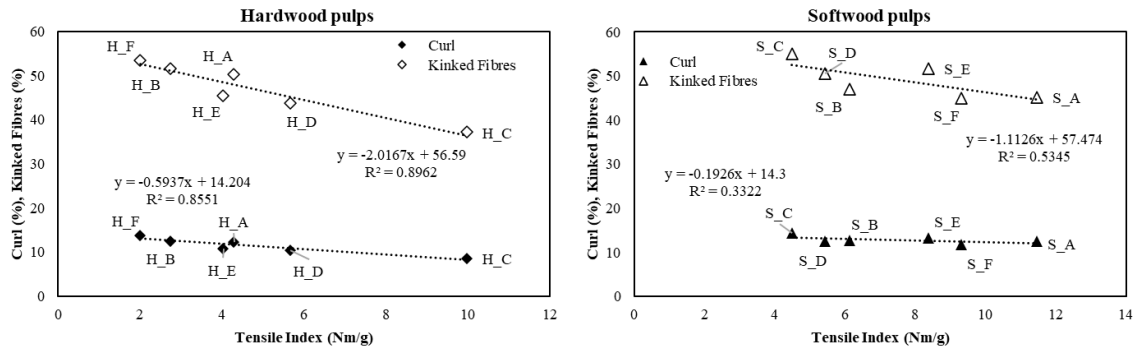


Figure III.11. Correlation of tensile index and curl and kinked fibers for hardwood and softwood pulps.

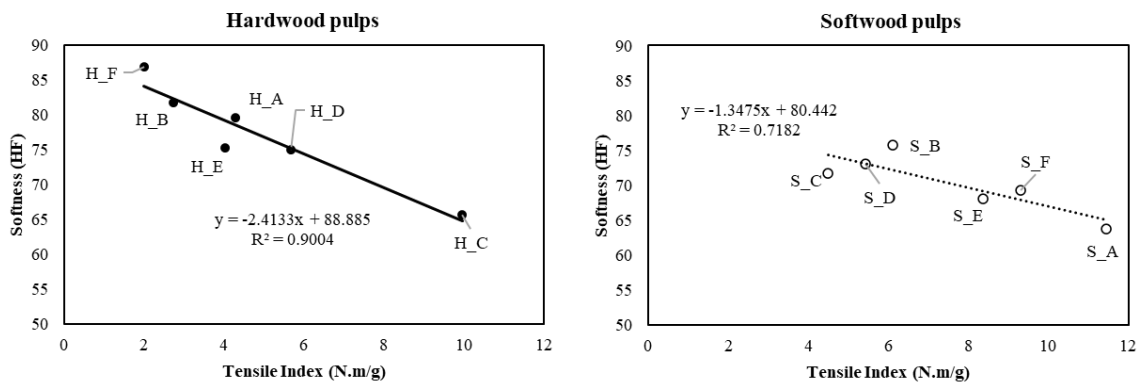


Figure III.12. Correlation of tensile index and softness for hardwood and softwood pulps.

Table III.11. Fiber's morphology, chemical composition, and tissue paper properties characterization for hardwood and softwood pulps.

Pulp samples	H_A	H_B	H_C	H_D	H_E	H_F	S_A	S_B	S_C	S_D	S_E	S_F
Fiber length*, mm	0.77±0.00	0.71±0.00	0.80±0.00	0.84±0.00	0.76±0.00	0.70±0.00	1.76±0.02	1.69±0.08	1.96±0.03	1.75±0.03	1.73±0.03	1.57±0.02
Fiber width, µm	18.0±0.2	18.0±0.1	18.8±0.0	19.1±0.2	18.2±0.0	18.3±0.1	30.8±0.2	30.9±0.3	30.3±0.5	29.4±0.1	30.4±0.2	29.9±0.4
Coarseness, mg/100m	6.71±0.06	8.22±1.07	9.56±0.15	8.44±0.14	9.36±0.18	7.02±0.63	16.77±1.72	18.83±4.78	19.66±2.01	19.13±2.88	16.81±2.07	17.37±1.71
Kinked fibers, %	50.4±0.3	51.6±0.4	37.2±0.1	43.7±0.5	45.4±0.5	53.4±0.5	45.2±0.7	47.1±0.2	55.1±1.0	50.5±0.8	51.7±1.3	45.0±1.0
Curl, %	12.3±0.1	12.5±0.2	8.6±0.0	10.4±0.1	10.7±0.2	13.7±0.2	12.5±0.2	12.7±0.1	14.4±0.1	12.5±0.2	13.2±0.1	11.8±0.2
Fines elements**, %	40.0±0.3	43.7±2.5	44.1±0.9	45.6±0.6	44.9±0.2	42.0±1.6	31.6±2.8	30.4±3.8	34.1±1.7	33.6±3.2	29.9±2.9	31.6±1.4
Viscosity, mL/g	630±0	453±0	915±4	814±0	790±0	973±0	844±2	808±0	683±9	699±14	865±4	656±0
Pentosan content, %	16.4±0.0	21.1±0.2	19.6±0.3	19.5±0.2	17.4±0.0	6.3±0.0	7.6±0.1	10.3±0.2	8.6±0.1	8.1±0.0	8.3±0.1	9.7±0.5
Carboxylic groups content, mmol/100g	9.26±0.12	5.02±0.01	7.03±0.05	5.05±0.03	9.61±0.18	4.36±0.05	7.27±0.04	1.89±0.16	10.60±0.42	8.92±0.32	8.73±0.10	2.98±0.04
°SR	21±1	20±0	20±0	18±0	18±0	18±0	14±1	14±0	12±1	12±1	13±1	15±0
WRV index, %	72.2±2.1	60.6±2.6	76.3±2.8	73.7±1.9	76.9±2.8	63.1±1.9	70.1±1.2	69.0±2.4	75.0±1.5	63.7±1.1	64.2±3.9	72.5±3.6
Bulk, cm ³ /g	5.83±0.02	3.71±0.02	3.55±0.03	3.61±0.03	5.68±0.02	3.55±0.00	6.53±0.01	3.46±0.03	8.04±0.03	7.49±0.02	6.43±0.02	3.54±0.03
Tensile Index, Nm/g	4.29±0.21	2.73±0.41	9.96±0.21	5.67±0.38	4.03±0.19	2.00±0.35	11.45±0.99	6.12±0.70	4.49±0.80	5.43±0.58	8.36±0.17	9.31±0.34
Softness (HF)	79.6±1.7	81.7±2.5	65.7±2.1	76.0±1.5	75.2±2.5	86.9±3.7	63.8±3.0	75.8±2.6	71.7±1.8	73.1±2.0	68.1±2.1	69.3±2.7
Water Absorption Capacity, g/g	8.17±0.02	8.59±0.37	8.08±0.28	8.83±0.05	8.19±0.02	8.45±0.02	8.34±0.20	8.64±0.22	9.48±0.19	9.03±0.29	8.82±0.36	8.42±0.09

* Length weighted in length; ** % in length; Values reported are the mean ± standard variation.

III.1.4.3. Experimental Design, Materials, and Methods

III.1.4.3.1. Pulp Samples

Twelve industrial kraft pulps (six eucalyptus hardwood and six softwood pulps), with different bleaching sequences, were analyzed. For all samples, the dry matter content was determined by placing the samples on an infrared scale at 105°C for 30 minutes, following an adaptation of ISO 638 standard.

III.1.4.3.2. Fibers Morphological Properties and Pulps Composition

The pulps morphological analysis was performed using a system based on image analysis, namely MorFi® (TECHPAP, Grenoble, France) equipment. The equipment integrates a digital camera and image analysis software for the automatic measurement of suspended fibers. Parameters such as length, width, coarseness, curl, kinks and fines were analyzed. All assays were done in triplicate.

III.1.4.3.3. Chemical characterization

The pulp's viscosity, the pentosan content and the carboxyl group content was determined according to SCAN-CM 15:88, TAPPI T 223 cm-10, TAPPI T 237 om-97 standard, respectively.

III.1.4.3.4. Pulps suspension characterization

The pulps drainability was evaluated considering the measurement of the Schopper-Riegler degree according to ISO 5267-1 standard. For each sample, triplicate assays were performed.

The Water Retention Value (WRV) was determined according to the method described by Jayme, 1958. This method is based on centrifugation at 7000 revolutions per minute, about 2 grams of wet pulp for 10 minutes. Thereafter, the already centrifuged pulp was removed and weighed exactly to the tenth of a milligram. Finally, centrifuged pulp samples were dried in the oven (105 ± 2 °C) for further determination of the sample dry weight. For each sample, triplicate assays were performed.

III.1.4.3.5. Laboratory isotropic handsheets preparation and testing

The handsheets of each pulp were produced according to an adaptation of ISO 5269-1 standard. Handsheets with a basis weight of approximately 20 g/m² and unpressed were produced to approximate more tissue paper, using a laboratory handsheet former according to the respective standard. Finally, the handsheets were removed from the former web with a blotting paper and placed in a conditioned room (temperature of 23.0 ± 1.0 °C and relative humidity of 50.0 ± 2.0 %). For each assay, 10 replicates were carried out for each sample.

The handsheets produced were tested for various tissue paper properties like, thickness and bulk (ISO 12625-3), basis weight (ISO 12625-6), tensile index (ISO 12625-4), water absorption capacity (ISO 12625-8), and softness using a TSA - Tissue Softness Analyzer (Emtec) equipment, and the algorithm QAI.

The handsheets porosity was also determined by the Henriksson et al., 2008, equation:

$$\text{Porosity (\%)} = 1 - \frac{\rho_{\text{handsheets}}}{\rho_{\text{cellulose}}} \times 100 \quad (\text{III.1})$$

where $\rho_{\text{handsheets}}$ corresponds to the handsheet's apparent density and $\rho_{\text{cellulose}}$ corresponds to the cellulose density (1.5 g/cm³).

III.1.4.4. References

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Morais, F.P., Bértolo, R.A.C., Curto, J.M.R., Amaral, M.E.C.C., Carta, A.M.M.S., Evtyugin, D.V. (2019). Comparative characterization of eucalyptus fibers and softwood fibers for tissue papers applications. *Materials Letters: X*. **4**: 1000028. DOI: 10.1016/j.mlblux.2019.100028

III.2. Fiber and Structure Modification Processes using Experimental and Computational Approaches

The contents of this subchapter are published in the following publications, listed on pages xvii and xviii of the thesis:

- III. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Cellulose Fiber Enzymatic Modification to Improve the Softness, Strength, and Absorption Properties of Tissue Papers. *BioResources*. **16**: 846-861. DOI: 10.15376/biores.16.1.846-861
- IV. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Micro/nano-fibrillated cellulose (MFC/NFC) fibers as an additive to maximize eucalyptus fibers on tissue paper production. *Cellulose*. **28**: 6587-6605. DOI: 10.1007/s10570-021-03912-9
- V. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). An innovative computational strategy to optimize different furnish compositions of tissue materials using micro/ nanofibrillated cellulose and biopolymer as additives. *Polymers*. **13**: 2397. DOI: 10.3390/polym13152397
- VI. **Morais, F.P.**, Mendes, A.O., Carta, A.M.M.S., Fiadeiro, P.T., Amaral, A.E., and Curto, J.M.R. A 3D fiber-based strategy for optimization of tissue materials using a combination of liquid absorbency/retention methods. In Andreas Öchsner (Editor), *Advanced Structured Materials*. Springer. *In Press*. (Book Chapter)
- VII. Curto, J.R., Vieira, J.C., **Morais, F.P.**, Mendes, A.O., Carta, A.M., Simões, R.S., Fiadeiro, P.T., Amaral, M.E., and Costa, A.P. (2021). Embossing Influence on the 3D Structure and Key Properties of Tissue Paper. In *Proceedings of the XXV TECNCELPA – International Forest, Pulp and Paper Conference and XI CIADICYP – Iberoamerican Congress on Pulp and Paper Research*, Online Conference, 10-12 March 2021.
- VIII. **Morais, F.P.**, Vieira, J.C., Mendes, A.O., Carta, A.M., Costa, A.P., Fiadeiro, P.T., Curto, J.M.R., and Amaral, M.E. (2021). Characterization of absorbency properties on tissue paper materials with and without “Deco” and “Micro” embossing patterns. *Cellulose*. **29**: 541-555. DOI: 10.1007/s10570-021-04328-1.

III.2.1. Cellulose Fiber Enzymatic Modification to Improve the Softness, Strength, and Absorption Properties of Tissue Papers

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III.2.1.1. Abstract

Effects of enzymatic modification were evaluated in bleached Eucalyptus kraft and sulfite cellulosic pulps, separately, to improve key tissue paper properties and design new Eucalyptus fiber applications. Different cellulase dosages (0.01 mg and 0.1 mg of enzyme/g of pulp) and reaction times (30 min and 60 min) were used to modify the fibers and replace the traditional mechanical based refining or beating process. The results showed that for enzymatic modified kraft and sulfite pulps, the softness properties were improved by 1 and 2 units, respectively, for each unit of decreased strength properties. To achieve a balance between the tissue properties, the different fiber pulp furnishes that contained 80% of the enzymatically treated kraft pulp and 20% of the sulfite pulp with and without enzymatic treatment, were studied. Overall, the structures made with these mixtures presented softness properties in the commercial range (57.8 to 74.4), improved absorption properties (107 mm to 120 mm of capillary rise), and good strength properties (13.0 to 17.7 Nm/g). This study was conducted in order to adjust the fiber furnishes according to industrial tissue standards, using one Eucalyptus fiber type providing strength and another providing softness.

Keywords

Biorefining; Enzymatic treatment; Eucalyptus pulps; Softness; Tensile Strength; Tissue Materials; Water Absorption

Inspired from Paper III:

Morais, F.P., Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Cellulose Fiber Enzymatic Modification to Improve the Softness, Strength, and Absorption Properties of Tissue Papers. *BioResources*. **16**: 846-861. DOI: 10.15376/biores.16.1.846-861

III.2.1.2. Introduction

In recent years, the tissue paper industry has shown great growth potential. The abundance of raw materials, increased hygiene awareness, rising health spending, and better living standards have driven the global growth of this market. Tissue papers, such as toilet paper, towel paper, napkins, and facial tissues, are lightweight creped papers (Raunio et al., 2018). The fibers used in tissue paper manufacturing are predominantly hardwoods (60% to 100%), with a small percentage of softwoods (0 to 40%). Eucalyptus fibers have adequate dimensions and properties to develop tissue paper softness, absorption, and bulk (Pinto et al., 2005; Pirralho et al., 2014). Studies have shown that different Eucalyptus species presented different fiber dimensions that can be targeted to enhance specific paper properties (Dutt and Tyagi, 2011; Pirralho et al., 2014; Morais et al., 2019). However, softwood fibers are necessary to confer strength properties to tissue products, which are important for the runnability of the paper machine (de Assis et al., 2018). Depending on the type of tissue paper, there will be a specific formulation with specific percentages of hardwood and softwood fibers. However, in order to enhance fiber suitability and establish a more resistant three-dimensional matrix, the fibers are also subjected to fiber modification processes. These processes have potential to achieve diverse applications of Eucalyptus hardwoods in the tissue papers manufactured with optimized properties. Replacing softwood fibers with enzyme-modified Eucalyptus fibers can also be advantageous, allowing manufacturers to achieve the desired quality of these tissue materials and optimize the furnish management.

Refining is a mechanical treatment that improves the fiber quality by modifying its structure and morphology (Chauhan et al., 2011; Mou et al., 2013; Gharekhani et al., 2015; Bajpai, 2018). In general, the papermaking pulp refining process consists of applying compression and shear forces to the fibers in order to develop flexibility and ability to form inter-fiber bonds. This mechanical process also promotes fiber internal fibrillation, external fibrillation, and cutting (Bajpai, 2018). The refining process increases the wet tensile strength properties of tissue papers and decreases their absorption properties (Gigac and Fišerová, 2008). However, many efforts are currently underway to conserve energy during the refining process by treating pulps more efficiently with enzymes (Gharekhani et al., 2015). Several industrial studies have shown that the use of different enzymes significantly reduced the refining energy necessary to achieve the required specifications for tissue papers, such as increased fiber bulk, tensile strength, and softness. Any treatment that promotes lower energy consumption will have a positive impact on global energy consumption in the pulp and tissue paper industries (Pathak et al., 2016).

In recent decades, the development of enzymatic technologies in the pulp and paper industry has increased. As a green and sustainable technology, enzymatic treatments have been studied extensively in different applications, such as improving the dissolving properties of pulps and reducing the chemicals used (Yang et al., 2019).

The enzymes increase the fiber flexibility and pulp carboxylic group content, improve the handsheet density and smoothness, promote water absorption, swelling, fibrillation, and improve the tensile strength and burst strength properties (Jeffries, 1992; Kenealy and Jeffries, 2003; Lin et al., 2018). Nevertheless, an enzyme excess may reduce the pulp strength and erode the fiber surface (Kenealy and Jeffries, 2003).

The influence of enzymes such as cellulase and xylanase or a mixture of these has been widely studied by several authors. The action of cellulases before refining has been shown to increase the pulp drainage, the fiber hydration degree, the handsheet mechanical properties and cell wall fiber surface degradation, and the bonding area of the water molecules (Wong et al., 2000; Gil et al., 2009; Efrati et al., 2013). The use of xylanases can produce refining energy savings and increase wet-fiber flexibility. Consequently, this can improve the inter-fiber bonding capacity by slowly decreasing the relative bonding area, improving optical brightness, and improving the physical strength properties (Spiridon et al., 2003; Spiridon and Duarte, 2004; Buzala et al., 2016; Dutta et al., 2020). Even without mechanical refining, enzymatic treatment with the mixing of both enzymes results in modified pulp properties, such as increased tear strength, clear defibrillation, reduced fiber length, and increased fines (Žnidaršič-Plazl et al., 2009; Kumar et al., 2018). To the best of our knowledge, the application of enzymes in unrefined Eucalyptus pulp, with the goal to optimize tissue properties in order to produce a paper material with only Eucalyptus fibers has not been thoroughly investigated in the literature.

This study evaluated the effect of a treatment with a commercial enzyme in two Eucalyptus pulps. Different pulp mixtures with different treatments were still performed in order to optimize tissue properties, which increased the potential applications for the Eucalyptus fiber. The effects of this enzyme and the mixtures were evaluated at different dosages and reaction times in terms of morphological, chemical and water interaction (swelling and pulp drainability) properties, as well as the softness, tensile strength, and absorption structure properties.

III.2.1.3. Experimental

III.2.1.3.1. Pulp Sample

An elemental chlorine-free (ECF) bleached Eucalyptus globulus kraft pulp (H_C) and a total chlorine-free (TCF) bleached Eucalyptus globulus sulfite pulp (H_F) were used in this study. These pulps were selected from the previous studies on subchapters III.1.3 and III.1.4 (Morais et al., 2019, 2020) because the kraft pulp presented the best strength properties and the sulfite pulp presented the best softness properties, without any fiber modification treatment.

III.2.1.3.2. Enzyme Sample

The enzymatic treatments were carried out with an enzymatic preparation provided by a Portuguese company, consisting of the cellulase enzyme, with a density of 1.02 g/mL and an enzymatic activity of 2.2 filter-paper units (FPU)/mL.

III.2.1.3.3. Enzymatic Activity

The enzymatic activity of the commercial enzymatic preparation was determined according to the filter paper method, an International Union of Pure and Applied Chemistry (IUPAC) method (Ghose, 1987; Yu et al., 2016). Whatman No. 1 filter paper (1.0 cm × 6.0 cm strips, with 50.0 mg ± 0.5 mg) was the substrate used in this procedure. Initially, 1 mL of 0.05 M Na-citrate buffer with a pH of 4.8 and filter paper strips were added to the test tubes. In order to saturate the filter paper strips, the test tubes were placed in a 50 °C bath for approximately 10 min. Then, 0.5 mL of diluted enzyme preparation was added to the tubes. Nine dilutions of the enzyme preparation were prepared. The tubes were incubated at 50 °C for exactly 60 min. After being removed from the bath, 3.0 mL of dinitrosalicylic acid (DNS) was added to each tube to stop the reaction. All the test tubes were placed in a boiling water bath for 5 min, followed by an ice water bath for 5 min. Finally, 20.0 mL of distilled water was added to each test tube. The prepared blanks (B1: 1.5 mL of citrate buffer; B2: 1.0 mL of citrate buffer + 0.5 mL of diluted enzyme preparation; B3: 1.5 of citrate buffer + filter paper strip) were treated the same as the above samples. The absorbance at 540 nm was measured using an ultraviolet (UV) spectrophotometer. Through the glucose calibration curve, it was possible to quantify the sugars released during the assay. The enzymatic activity was calculated to be $FPU = 0.37 / \text{cellulase concentration to release 2.0 mg glucose}$.

III.2.1.3.4. Methods

III.2.1.3.4.1. Enzymatic Treatments

The pulps were treated with 0.01 mg and 0.1 mg of enzyme/g of pulp. These enzyme concentrations were selected because they correspond to extreme values, within the range of the standardized tissue industrial process. These treatments were carried out with pulp suspensions that had a pH of 7 and a consistency of 4% at 40 °C, with continuous mechanical agitation. An impeller was used to ensure the mass transfer effectiveness. Reaction times of 30 min and 1 h were tested. After the enzyme treatment, a minimum amount of sodium hypochlorite was added to the pulp samples to stop the pulp enzyme reaction. Table III.12 summarizes the assays performed.

Table III.12. Enzymatic treatment assays performed for the Kraft and Sulfite pulps.

Assay	Kraft Pulp (H_C)	Assay	Sulfite Pulp (H_F)
1	Without Treatment	6	Without Treatment
2	0.01 mg/g, 30 min	7	0.01 mg/g, 30 min
3	0.01 mg/g, 1 h	8	0.01 mg/g, 1 h
4	0.1 mg/g, 30 min	9	0.1 mg/g, 30 min
5	0.1 mg/g, 1 h	10	0.1 mg/g, 1 h

III.2.1.3.4.2. Pulp Mixtures

After studying the enzyme-treated kraft and sulfite pulps, an experimental design was performed with different fiber pulp furnishes, containing 80% of the kraft Eucalyptus pulp enzymatically treated and 20% of the Eucalyptus sulfite pulp with and without enzymatic treatment (Table III.13). The first four assays were carried out with the combination of kraft pulp with the different enzymatic treatments and sulfite pulp without any treatment. The last four assays were performed with the combination of kraft and sulfite pulps subjected to different enzymatic treatments.

Table III.13. Mixtures of 80:20% performed for the enzymatically treated Kraft and Sulfite pulps.

Assay	Treatments	Assay	Treatments
1	80% Assay 2 : 20% Assay 6	5	80% Assay 2 : 20% Assay 7
2	80% Assay 3 : 20% Assay 6	6	80% Assay 3 : 20% Assay 8
3	80% Assay 4 : 20% Assay 6	7	80% Assay 4 : 20% Assay 9
4	80% Assay 5 : 20% Assay 6	8	80% Assay 5 : 20% Assay 10

III.2.1.3.4.3. Pulp Characterization

The fiber morphological properties were determined automatically by image analysis of a diluted suspension (20 mg/L) in a flow chamber, using the MorFi LBO1 Fiber Size Analyzer (Techpap, Grenoble, France). The assay was performed in triplicate.

To understand the changes in the pulp functional groups, Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) was performed (Thermo Scientific, Nicolet IS 10 model, Waltham, Massachusetts, EUA).

The FTIR-ATR technique made it possible to characterize, identify and quantify the efficiency of the enzymatic treatment in the kraft and sulfite pulps, through the presence or not of physical inter-fiber bonds. The handsheets surfaces produced with pulps without enzymatic modification (assays 1 and 6) and with application of maximum enzyme dosage and reaction time (assays 5 and 10) were analyzed. The samples were analyzed at a wavelength of 600 cm⁻¹ to 4000 cm⁻¹, with a resolution of 4 cm⁻¹.

The Schopper-Riegler degree (°SR) method was determined, in triplicate, according to the ISO standard 5267-1 to measure the pulp drainability.

The water retention value (WRV) was determined according to the method described by Silvy et al. (1968), which is used to evaluate the fiber hydration. The wet pulp samples were centrifuged at a speed of 5,000 revolutions per min (4,640 g Force) for 10 min, using a centrifuge Kn-70 model, Kubota (Osaka, Japan). Then, the samples were removed, weighed, and oven-dried at (105±2) °C for 24 h. The samples were again weighed.

The assay was performed in triplicate, and the WRV index (%) was calculated according to equation:

$$WRV = \frac{M_1 - M_2}{M_2} \times 100 \quad (III.2)$$

where M_1 is the mass of the wet sample after centrifugation, and M_2 is the mass of wet sample after drying at 105 °C.

III.2.1.3.4.4. Isotropic Laboratory Handsheet Production and Characterization

The laboratory handsheets with a basis weight approximately of 20 g/m² (tissue paper simulation in the laboratory) were prepared according to an adaptation of the ISO standard 5269-1. The pressing process was suppressed for the 20 g/m² handsheets. The structures were conditioned in a room at 23 ± 1 °C with a relative humidity of 50 ± 2%.

The scanning electron microscopic (SEM) images were obtained using a Hitachi S-2700 (Tokyo, Japan). Initially, the samples were coated with gold using a Sputter Quorum Q 15 OR ES (Laughton, East Sussex, UK) and analyzed with an accelerating voltage of 20 kV at different magnifications.

The basis weight was measured according to the ISO standard 12625-6. The thickness and bulk were determined according to the ISO standard 12625-3. A FRANK-PTI micrometer was used for thickness analysis. The solids volume of handsheets was determined using a helium-gas displacement pycnometer (AccuPyc II), in a 10 cm³ sample chamber. Through these volumes, the porosity (%) was calculated according to equation:

$$Porosity (\%) = \frac{Volume_{Total} - Volume_{Solids}}{Volume_{Total}} \times 100 \quad (III.3)$$

The tensile index was determined according to the ISO standard 12625-4. The softness was analyzed using a Tissue Softness Analyzer (TSA) (Emtec, Leipzig, Germany). This analyzer uses different algorithms in order to calculate parameters related to the tissue paper softness, such as handfeel index (HF) and TS7 (parameter related to the surface softness from the fibers and the paper material) (Mendes et al., 2020). The algorithms selection depends on the sample analyzed, therefore the QAI algorithm was selected for the handsheets. For this analysis, five readings were made. The capillary rise was also determined by the ISO standard 8787.

III.2.1.3.5. Statistical Analysis

All data analysis was performed using Microsoft Excel Office 365, and statistical analysis was performed using independent samples t-test with a 95% confidence level with IBM SPSS Statistics 25 (Armonk, NY, USA).

III.2.1.4. Results and Discussion

III.2.1.4.1. Kraft and Sulfite Pulps Enzymatic Treatments

The fiber morphological properties of the enzymatically treated pulps are shown in Table III.14. The weighted fiber length and the weighted fiber width decreased for both the pulps. The fiber lengths of the kraft and sulfite pulps decreased by 1.6% and 1.3%, respectively, for the maximum enzyme dosage and reaction time conditions compared to the pulps without enzymatic treatment. After the enzymatic treatment, the fiber widths ranged from 18.8 μm to 19.1 μm for the kraft pulp, and 18.3 μm to 18.9 μm for the sulfite pulp, which corresponded to a decreased fiber width of 1.6% and 0%, respectively. This slight decrease in the fiber length and width indicated that these two dimensions were not notably affected by the enzyme treatment. These results are in line with the higher fines content of 7.8% and 5.5% for the kraft and sulfite pulps, respectively, and the higher macrofibrils contents of 4.3% and 4.9% for the kraft and sulfite pulps, respectively. The coarseness of the sulfite pulp was approximately 2.75 times higher than the sulfite pulp (9.1% vs 3.3%).

Table III.14. Effect of enzymatic treatments on the pulp morphological, drainability, and swelling properties.

Assays*	Weighted Length (mm)	Width (μm)	Coarseness (mg/100m)	Length of Macrofibrils (%)	Fines Elements (% in Length)	°SR	WRV (%)
1	0.798±0.004	19.1±0.1	6.83±0.10	0.509±0.005	37.1±0.3	20±0	76.3±2.6
2	0.797±0.002	18.8±0.1	6.76±0.09	0.526±0.027	37.4±0.1	21±0	89.7±2.8
3	0.795±0.001	18.9±0.1	6.64±0.18	0.526±0.010	38.4±0.6	22±1	90.3±3.1
4	0.792±0.002	18.8±0.1	6.48±0.17	0.529±0.009	39.2±1.0	26±0	92.3±2.4
5	0.785±0.003	18.8±0.1	6.21±0.10	0.531±0.017	40.0±0.3	28±1	92.5±1.7
6	0.696±0.002	18.3±0.1	7.26±0.28	0.588±0.018	42.0±1.6	18±0	63.1±1.8
7	0.696±0.004	18.9±0.1	7.17±0.25	0.600±0.030	42.2±0.5	19±1	73.9±4.3
8	0.690±0.002	18.6±0.0	7.16±0.24	0.603±0.044	42.2±0.4	20±0	77.8±2.7
9	0.690±0.001	18.5±0.1	7.06±0.14	0.616±0.015	42.8±1.9	22±1	79.9±3.1
10	0.687±0.003	18.4±0.1	7.02±0.63	0.617±0.011	44.3±0.3	23±0	80.1±3.1

Values reported are the mean $\pm$ standard deviations.

*Conditions specified in Table III.12. Assays 1-5 correspond to kraft pulp and assays 6-10 correspond to sulfite pulp. Without treatment: assays 1 and 6. With 0.01 mg/g for 30 minutes (assays 2 and 7) and 60 minutes (assays 3 and 8). With 0.1 mg/g for 30 minutes (assays 4 and 9) and 60 minutes (assays 5 and 10).

Table III.14 also shows the °SR and WRV properties of the enzyme-treated pulps. The biorefining process increased the drainage degree by 40% and 28% for the kraft pulp and the sulfite pulp, respectively, which is in line with the proportional increase in the pulp fines content. The enzymatic refining contributed to the increased fiber flexibility, which promoted the accessibility of the water molecules to the fiber structure (Spiridon et al., 2003). The °SR values were in the range of values used in the industrial tissue process (22 °SR to 28 °SR).

The same drainage properties (22 °SR) were obtained for the kraft and sulfite pulps using different process conditions. The enzyme was dosed at 0.01 mg/g with 1 h of reaction time for the kraft pulp and 0.1 mg/g with 30 min of reaction time for the sulfite pulp. The WRV of the sulfite pulp was slightly higher than that of the kraft pulp. The WRV for the sulfite pulp increased by 27%, while the WRV for the kraft pulp increased by 21%. In this case, internal fibrillation and limitation of the enzyme penetration in the fiber wall were related to the WRV index increase (Gil et al., 2009; Gu et al., 2018), which facilitated higher fiber interaction and water retention.

To complement this study, the FTIR-ATR technique was used to identify some differences in the functional groups, with and without the enzymatic treatment applied to the pulps. Figure III.13 shows the FTIR spectrum of assays 1 and 5 for the kraft pulp and assays 6 and 10 for the sulfite pulp. The differences found in the spectrum were also supported by studies by other authors (Sridevi et al., 2016; Kumar et al., 2018; Dutta et al., 2020). The bands observed at the different wavelengths corresponded to the structural changes, as well as the cooking process used in the production of both pulps. The broad band at 3,000 cm^{-1} to 3,400 cm^{-1} indicated that the -OH stretching of the hydrogen-bonding and the band at 2,870 cm^{-1} to 3,000 cm^{-1} indicated that the =C-H stretching of the methyl group of cellulose and hemicelluloses. The band at 2,358 cm^{-1} to 2,360 cm^{-1} was due to the OH asymmetrical stretching vibration of the carboxylic acid in enzymatically treated pulps. The bands at 1,650 cm^{-1} to 1,652 cm^{-1} and at 1,202 cm^{-1} were due to the C=O stretch and the C-O stretch of hemicelluloses, respectively. It was still possible to verify that the bands at 1,428 cm^{-1} , 1,315 cm^{-1} , and 1,160 cm^{-1} indicated the C=H stretching, C=O stretch vibration in syringyl ring, and -COO- (carboxylate ion) group vibration, respectively.

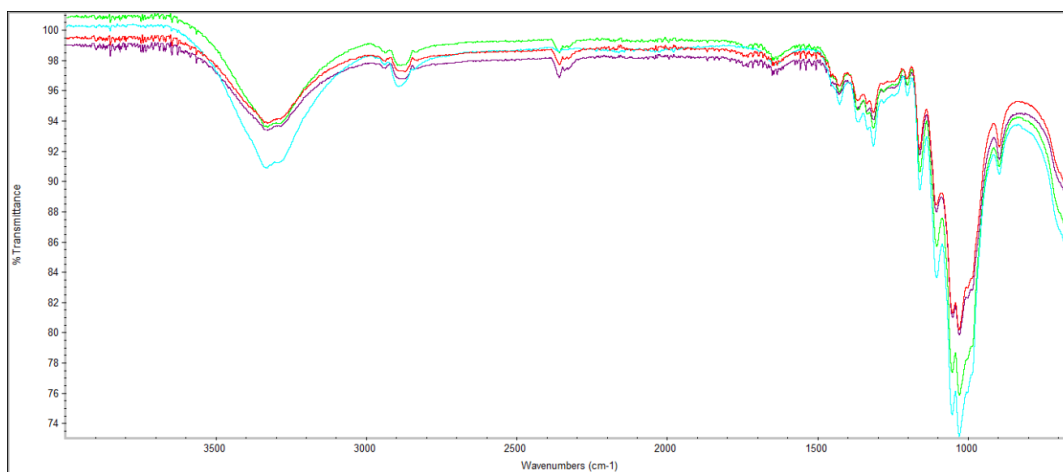


Figure III.13. The FTIR-ATR spectrum of the kraft pulp (assay 1, red) and sulfite pulp (assay 6, green) and the changes in these suspensions during the enzymatic treatment of assay 5 (purple) and assay 10 (blue) (0.1 mg/g, 1 h).

The SEM images (Figure III.14) also showed changes in the pulp fiber morphology after the enzymatic treatment. The enzymatic activity at the fiber surface level, which exposed external fibrillation, was observed for both pulps (Figure III.14b, d). The untreated pulps (Figure III.14a, c) also showed the presence of some fibrils, which was a result of the different cooking processes. Enzymes can hydrolyze the fines and cellulosic components accessible in the exposed fiber regions, smoothing their surface. In this enzyme dosage range, the bonds between fines and fibrils or between other fibers arise, modifying the morphological properties and drainage conditions (Table III.14). This slight external fibrillation is also responsible for increasing the bonding points between fibers and, consequently, increasing the strength properties and decreasing the softness properties (Figure III.15).

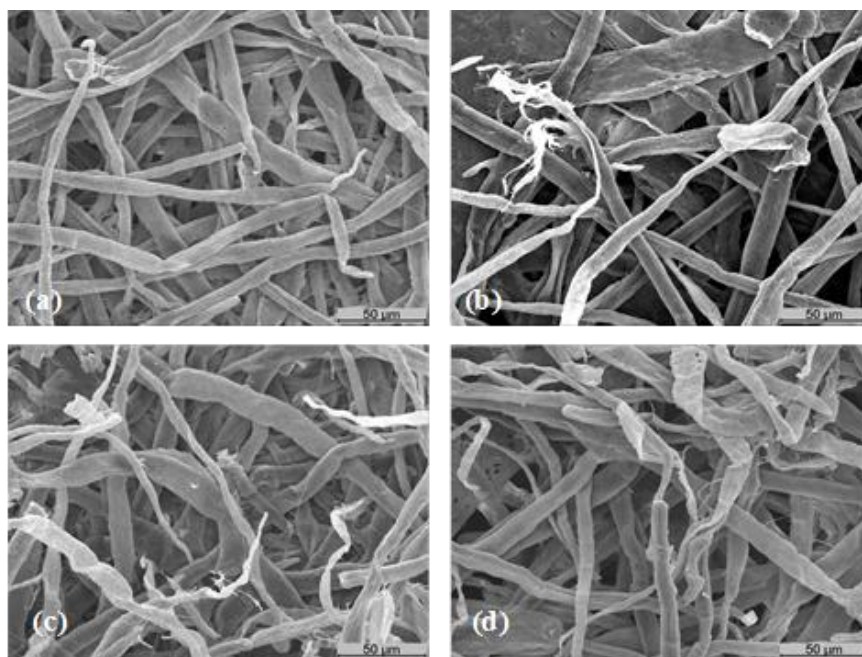


Figure III.14. The SEM images of (a) untreated kraft pulp, (b) treated kraft pulp from assay 5, (c) untreated sulfite pulp, and (d) treated sulfite pulp from assay 10. The treatment was an enzyme dosage of 0.1 mg/g and a reaction time of 1 h.

This enzymatic degradation corresponded to changes in the tissue properties of the pulp structures, as shown in Figure III.15. The enzymatic action degrades the fiber wall, which forms macrofibrils and fines. Therefore, a more closed and compact structure formation with increases in the enzyme dosage and reaction time is expected. An increase in the enzymatic refining process caused a decrease in the handsheets porosity by 2.1% and 3.6% for the kraft and sulfite pulps, respectively (Figure III.15a). This was a result of the increased relative bonding area between the fibers, which produced denser handsheets. Consequently, the bulk properties also decreased by 7% and 41% for the kraft and sulfite pulps, respectively (Figure III.15a).

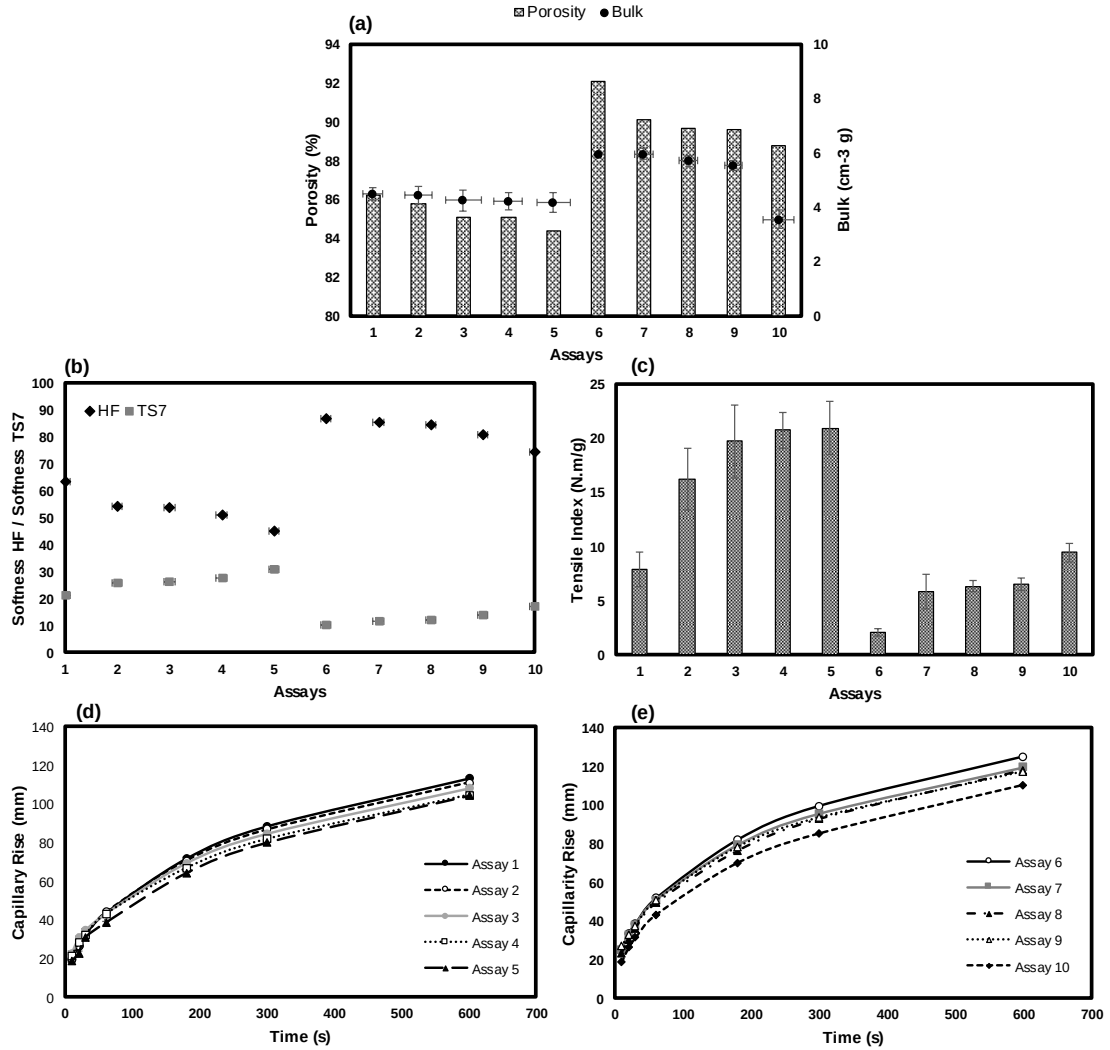


Figure III.15. The evolution of the tissue properties of the kraft and sulfite pulp handsheets during the enzymatic assays performed, namely, a) porosity and bulk, b) softness HF and TS7, c) tensile index, and the d,e) water capillary rise during enzymatic assays performed.

The softness HF, one of the essential properties for tissue papers, was negatively affected for both pulps over the enzyme dosage and reaction times (Figure III.15b). The decreased softness properties were promoted by the increase in the fiber flexibility, the fines content, and the inter-fiber bonding. The HF properties decreased by 29% and 14% for the kraft and sulfite pulps, respectively. The sulfite pulp samples had higher HF values (74.6 to 86.9) than the kraft pulp samples (45.1 to 63.2). This difference is due to the different production conditions for the pulps. The TS7 property is related to the material softness, in this case, the softness from the fibers present on the handsheet surface (Wang et al., 2019). The TSA equipment registered the noise that the ceramic blades produced when they passed across the sample surface. The more rigid fibers produced and registered more noise because the resistance of the fibers against the blades was higher. As the enzyme dosage and reaction time increased, the higher TS7 values were verified (Figure III.15b).

This suggested that the enzymatically treated pulp fibers were more attached to the handsheet structure. The softness TS7 increased by 45% and 63% for the kraft pulp and sulfite pulp, respectively.

Unlike the softness HF, the tensile index was positively affected for both pulps throughout the enzyme dosage and reaction times (Figure III.15c). This parameter is important in tissue paper to ensure paper quality and paper machine runnability. The increased tensile index was a consequence of the enzymatic action, which promoted fibrillation by attacking the cellulosic fiber chains. This parameter increased by 166% for the kraft pulp and 371% for the sulfite pulp. The kraft pulp presented higher tensile indexes which agreed with the slightly lower porosities that were obtained.

The tissue paper absorption properties depend on the porosity and fibers' hydrophilicity. Fiber fibrillation promoted a decrease in the water capillary rise in the structures. The kraft pulp presented values of capillary rise between 104 mm to 113 mm (Figure III.15d), while the sulfite pulp presented values between 110 mm to 125 mm (Figure III.15e). This trend was consistent with the softness HF values and the morphological properties. Decreases in the capillary rise at 10 min of 8% for kraft pulp and 12% for sulfite pulp were observed. However, despite these small differences found, the different levels of enzymatic treatment did not show significant differences in the capillary rise properties in both kraft and sulfite pulps ($t(5) = 0.55$, $p > 0.05$; $t(5) = 0.97$, $p > 0.05$). The critical value of student's t distribution with 5 degrees of freedom is 2.015, with a 95% confidence level.

With the different enzymatic treatments applied, the strength properties of the kraft pulp and the softness properties of the sulfite pulp were maintained. Therefore, it is important to select the process conditions that allow a good compromise between the key tissue properties, in order to study the viability of producing tissue papers with different eucalyptus fiber pulps furnishes.

III.2.1.4.2. Pulp Mixtures Treatments

During the production of premium tissue papers, the optimization and management of furnish plays a key role in the resulting tissue paper materials characteristics. In order to adjust the key tissue properties, the next step of this work was to mix both pulps with the different enzyme treatments (Table III.13) in order to evaluate the improvements in the tissue final end-use properties.

Table III.15 presents the morphological and water interaction properties according to the studied mixtures. Comparing mixtures 1 and 2 (mixtures with 80% of kraft pulp treated with 0.01 mg/g and reaction times of 30 min and 60 min, respectively, and with 20% of sulfite pulp without enzymatic treatment), it was found that the weighted fiber length decreased by 0.27%, the coarseness decreased by 1.47%, the macrofibrils content increased by 1.29%, and the fines content increased by 4.40%. The drainage degree increased by 4.76% and the WRV increased by 13.18%.

Regarding the analysis of mixtures 3 and 4 (mixtures with 80% of kraft pulp treated with 0.1 mg/g and reaction times of 30 and 60 min, respectively, and with 20% of sulfite pulp without enzymatic treatment), the weighted fiber length and the coarseness decreased in percentages similar to mixtures 1 and 2 (0.26% vs 1.15%), the macrofibrils content increased by 2.90%, and the fines content only increased by 0.25%. Additionally, increases of 7.69% and 28.84% were observed in the °SR and WRV properties for these mixtures, respectively.

Regarding mixtures 5 and 7 (mixtures of the kraft and sulfite pulps treated with an enzyme dosage of 0.01 mg/g and 0.1 mg/g, respectively, for 30 min), the fiber length decreased by 0.13%, the coarseness decreased by 0.59%, the macrofibrils content increased by 3.3%, and the fines content increased by 4.8%. The drainage properties by 35% and the WRV increased by 42%. For mixtures 6 and 8 (mixtures of kraft and sulfite pulps treated with an enzyme dosage of 0.01 mg/g and 0.1 mg/g, respectively, for 1 h), the fiber length decreased by 0.90%, the coarseness decreased by 4%, the macrofibrils content increased by 3.9%, and the fines content increased by 1.8%. The drainage properties were found in the same range of mixtures 5 and 7 (33%), and the WRV increased by 61%.

Table III.15. Effect of pulp mixtures in the pulp morphological, drainability, and swelling properties.

Assays*	Weighted Length (mm)	Width (µm)	Coarseness (mg/100m)	Length of Macrofibrils (%)	Fines Elements (% in Length)	°SR	WRV (%)
1	0.780±0.000	19.0±0.1	6.82±0.02	0.543±0.013	36.4±0.6	21±0	85.0±2.1
2	0.778±0.002	19.0±0.1	6.72±0.19	0.550±0.010	38.0±0.3	22±0	96.2±2.6
3	0.775±0.002	18.7±0.1	6.08±0.09	0.551±0.008	40.1±1.3	26±1	141.1±6.1
4	0.773±0.001	18.5±0.5	6.01±0.19	0.567±0.017	40.2±0.9	28±0	181.8±2.1
5	0.777±0.001	19.0±0.1	6.77±0.04	0.520±0.002	37.6±0.5	20±1	144.0±5.1
6	0.776±0.002	18.8±0.1	6.75±0.16	0.532±0.009	38.9±0.1	21±0	180.8±1.2
7	0.776±0.002	18.7±0.1	6.73±0.05	0.537±0.003	39.4±0.4	27±1	204.3±4.0
8	0.769±0.002	18.7±0.1	6.48±0.13	0.553±0.015	39.6±0.9	28±0	291.0±4.1

Values reported are the mean ± standard deviations.

* Conditions specified in Table III.13. Assays 1-4 correspond to mixtures of 80% enzyme-treated kraft pulp, with different enzyme dosage and reaction time conditions with 20% sulfite pulp without treatment. Assays 5-8 correspond to mixtures 80:20 of both enzyme-treated pulps under the same conditions.

Differences in the structure of the 3D networks were also observed in the pulp mixtures (Figure III.16). For example, mixture 4 showed fibrils on the fiber walls, exposing external fibrillation (Figure III.16a). In mixture 8, external fibrillation on the fiber walls as well as inter-fiber bonds were more visible (Figure III.16b).

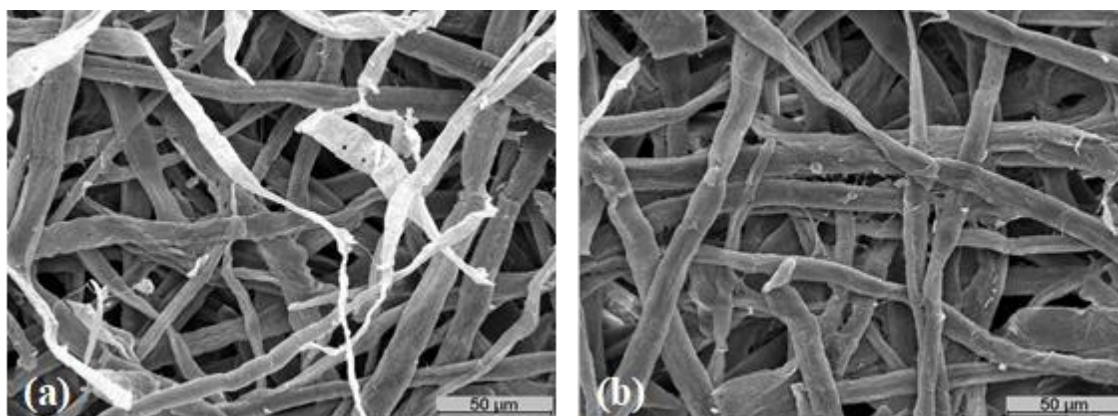


Figure III.16. The SEM images of a) pulp mixture 4 and b) pulp mixture 8.

Figure III.17 presents the tissue properties of the handsheets produced with the studied mixtures. According to the structural properties, the pulp mixtures influenced the handsheet porosity and the bulk (Figure III.17a). Very similar properties were observed. The porosity was between 87.0% and 88.2% and the bulk was between 4.72 cm³/g and 5.21 cm³/g.

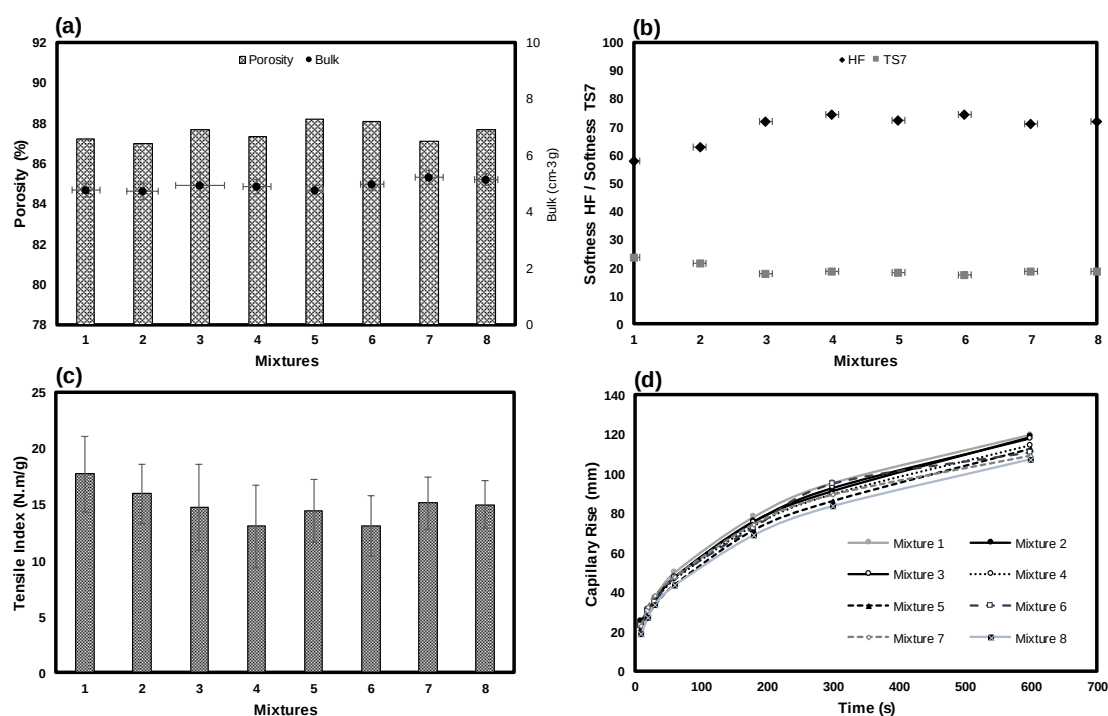


Figure III.17. The evolution of the tissue properties for the pulp mixtures, namely, (a) porosity and bulk, (b) softness HF and TS7, (c) tensile index, and (d) water capillary rise.

The handsheet mixtures had a softness HF that ranged from 57.8 to 74.4 (Figure III.17b). Values in this range are found in commercial tissue papers. The inverse relationship between the softness HF and the TS7 was also verified. The tensile index of the handsheet mixtures showed values between 13.0 and 17.7 Nm/g (Figure III.17c). Stronger structures were produced with the different mixtures, along with good levels of softness, compared to the enzyme-treated pulps separately.

Mixtures 4 and 6 presented the maximum values of the softness HF and minimum values of the tensile index. The compatibility of these two opposing properties will depend on the type of tissue paper to be produced.

Additionally, the inverse relationship of the softness HF and the tensile index properties were verified in both the separate and combined enzymatically treated pulps (Figure III.18). The relationship of these two variables in modified the kraft pulp, the sulfite pulp, and the pulp mixtures can be explained, respectively, by the models $HF = -1.08 \text{ Tensile} + 72.01$ ($R^2 = 0.820$), $HF = -1.62 \text{ Tensile} + 92.19$ ($R^2 = 0.758$), and $HF = -3.68 \text{ Tensile} + 124.36$ ($R^2 = 0.858$). Previous studies reported that untreated hardwood pulps have also shown an inverse tendency for these two variables (Morais et al., 2019, 2020). For these untreated hardwood pulps, for every 2.4 units of increased softness, one unit of the tensile index was reduced. However, for the kraft pulp, the enzymatically modified sulfite pulp, and the pulp mixtures, for each 1.1, 1.6, and 3.7 units of increased softness, respectively, one unit of the tensile index was reduced.

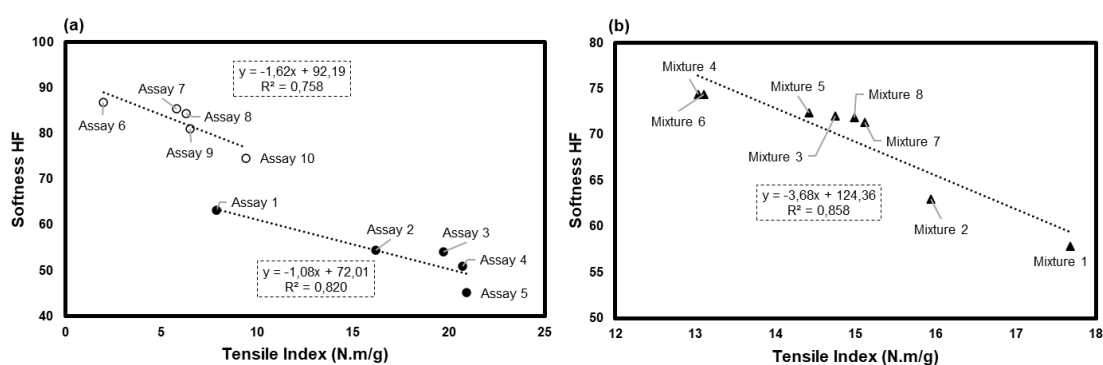


Figure III.18. Correlation of the tensile index and the softness HF for the a) enzymatically treated kraft and sulfite pulps and the b) pulp mixtures.

Regarding the water absorption properties, the capillary rise of the handsheets were between 107 mm and 120 mm (Figure III.17d). Similar capillary rise profiles for the different mixtures were observed. The mixtures of both enzymatically treated pulps (mixtures 5 through 8) showed lower capillary rise values than the mixtures with the untreated sulfite pulp (mixtures 1 through 4). The structure capillarity decreased as the enzyme dosage and reaction time increased. However, despite these small differences found, the different levels of enzymatic treatment did not show significant differences in the capillary rise properties in eucalyptus fiber pulp mixture furnishes ($t(8) = 0.558$, $p > 0.05$). The critical value of student's t distribution with 8 degrees of freedom is 1.860, with a 95% confidence level.

A fundamental step in tissue paper production is the creping process. This process promotes paper structural changes when it is scraped from the Yankee cylinder by the action of a creping blade. This results in fiber orientation changes and paper creping. This process contributes to elongation and softness properties, and therefore it is extremely important for the final quality of tissue papers (Raunio and Ritala, 2012; Pan et al., 2019; Mendes et al., 2020).

The present research work did not involve the creping process of the isotropic laboratory handsheets, so the prediction of the tissue functional properties did not include the creping step of tissue making. If the strategy presented in our work is feasible to be implemented industrially, it is important to understand how the creping process can influence the results. We believe that the creping process will decrease the mechanical properties of the tissue papers produced with the eucalyptus pulps maximization since the softness and strength properties are inversely related. From this perspective, we also believe that the investigation of the creping and embossing processes quantification in the softness, strength, and, also, absorption properties is necessary for advanced predictions.

III.2.1.5. Conclusions

1. The results achieved in this work showed that biorefining with enzymes contributed to changes in the tissue properties of kraft and sulfite industrial pulps. The enzymatic treatment of pulp contributed to a more efficient fiber fibrillation, increased fines formation, and improved fiber bonding. Additionally, the individualized enzymatic treatment for both pulps promoted the maintenance of the strength and softness properties for the kraft and sulfite pulps, respectively, as verified in Figure III.15.
2. In order to balance the inverse relationship between softness and strength properties, different furnish combinations of enzymatically treated eucalyptus pulps were studied. The combination of the enzymatically treated kraft and sulfite eucalyptus pulps allowed the fiber furnish adjustment to develop the key properties of tissue paper materials. The softness, strength, and absorption properties of the low basis weight structures improved, compared to the pulp samples that were treated separately, as shown in Figure III.17.
3. Overall, this study identified the different conditions of the pulp mixtures that facilitate the best compromise between softness, strength, and absorption properties for different types of tissue papers. For example, premium toilet or facial papers can be produced with pulps that have good softness properties, such as mixtures 4 and 6, and premium towel papers or napkins can be produced with pulps that have good strength and absorption properties, such as mixtures 1 and 2.

III.2.1.6. References

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III.2.2. Micro/Nano-fibrillated Cellulose (MFC/NFC) Fibers as an Additive to Maximize Eucalyptus Fibers on Tissue Paper Production

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III.2.2.1. Abstract

Tissue furnish optimization plays a key role in enhancing tissue properties, making the process cost-effective. Typically, this furnish is composed of a mixture of hardwood eucalyptus fibers (HW) and softwood (SW) fibers, which ensure strength and tissue machine runnability. However, the tissue paper production with the maximization of eucalyptus fibers achieves softer papers at less cost, since SW fibers are often more expensive than HW fibers. From this perspective, this study aims to investigate the effect of micro/ nano-fibrillated cellulose (MFC/NFC) as an additive, on structural, softness, strength, and water absorption properties of tissue papers, promoting partial or total removal of SW fibers to produce 100% eucalyptus materials. MFC/NFC was characterized in terms of morphological, chemical, and water interaction properties. The results showed that MFC/NFC presents a high bonding surface area, high carboxyl group content and, when incorporated into tissue furnishes, it promotes strong inter-fiber bonds. This evidence was also supported by SEM image analysis methods and FTIR. Additionally, laboratory tissue handsheets with low basis weight were produced and used in the characterization assays. Overall, the results indicated that MFC/NFC improved strength, at the expense of bulk, porosity, softness, and absorption properties. Compared to typical industrial furnish mixtures (75%HW+25%SW), MFC/NFC enhanced the production of bulkier, porous, and softer structures, but with reduced strength and absorption. It was possible to optimize the furnish composition by using fiber modeling to obtain 3D structure computation simulations with predictive capability. The MFC/NFC proved to be a high-quality additive to improve softness and strength properties.

Keywords

Eucalyptus fibers; Softwood reinforcement fibers; Micro/nano-fibrillated cellulose; Tissue computational simulator; Tissue products and properties

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III.2.2.2. Introduction

Tissue materials are low-basis weight paper materials with functional purposes, including toilet papers, towel papers, napkins, facial papers, tissue masks, among others. The quality requirements of tissue papers differ according to their purpose and consumer expectations (de Assis et al., 2018a). The final properties of these papers are obtained with an optimized combination of bulk, softness, strength, and absorption (Hollmark and Ampulski, 2004; Beuther et al., 2010; Raunio and Ritala, 2013; Wang et al., 2019a). In some products, softness can be the key property, while in others strength or/and absorption properties are decisive to the paper function. It is also important to consider consumer demand when combining these properties, for the development of each type of tissue product (Morais et al., 2019). An approach to improve processes and products includes furnish and additives management in the tissue paper machine. In tissue paper production, a mixture of hardwood cellulose fibers, such as Eucalyptus, and softwood cellulose fibers, such as Pinus or Picea Abies, is used. The key fiber properties and fiber modification process steps influence the tissue paper structural and functional properties (Kullander et al., 2012; Stankovská et al., 2018; Fišerová et al., 2019; Morais et al., 2019). Therefore, the paper quality can be achieved or improved by selecting different fibers.

Hardwood fibers develop properties of bulk, softness, water absorption, homogeneity of paper formation, among others, while softwood fibers are frequently introduced to ensure strength properties and paper machine runnability (de Assis et al., 2018a). Therefore, an impact is expected on the effectiveness of tissue paper production by the partial or total removal of softwood fibers, aiming at tissue papers with maximization of eucalyptus fibers. An approach to modifying eucalyptus fibers and improve their strength usually includes refining methods (Gigac and Fišerová, 2008). However, this treatment has negative impacts on fibers and key tissue properties such as softness and absorption (Laine et al., 2004; Gigac and Fišerová, 2008; Gharehkhani et al., 2015; Chang et al., 2017). Besides, biorefining or enzymatic treatments reduce the need for mechanical refining to achieve the desired fiber properties. This process also reduces production and energy costs, aiming for new products with high added value (Lin et al., 2018; Morais et al., 2021). Nevertheless, an alternative to produce papers with maximization of eucalyptus fibers and partial or total substitution of softwood fibers can be the incorporation of additives. The tissue paper properties are modified with the addition of chemical additives, such as dry strength agents, wet strength agents, softeners, etc. (Ginebreda et al., 2011). Park et al. (2019) have proved that dry strength agents, such as polyvinyl amine (PVAm) and polyacrylamide (G-PAM), and wet strength agents, such as polyamideamine-epichlorohydrin (PAE), do not affect the softness properties at dosages of 0.4% and 4%, respectively. The wet strength agent also increased the dry strength. These additives promoted hydrogen bonds and covalent bonds between fibers as a crosslinking mechanism, without affecting the surface friction. Additionally, the combination of softeners and wet strength agents improves the surface softness of tissue papers (Park et al., 2019).

However, some strength additives, such as cationic starches and carboxymethylcellulose, can be used to meet the strength requirements of tissue products, which may present adverse effects on the absorption and softness properties (Shannon and Soerens, 2004; Hubbe, 2006; Uematsu et al., 2011; Siqueira et al., 2015). Therefore, the development and optimization of new strategies for incorporating additives in tissue furnishes will enhance the design of different tissue products with improved end-use properties. One of the proposals is the incorporation of micro and nanofibrillated cellulose (MFC/NFC) as an additive in cellulose-based tissue paper biomaterials (Klemm et al., 2018; Zambrano et al., 2020).

Over recent years, MFC/NFC has attracted great interest in the paper industry. MFC/NFC has unique characteristics such as high specific surface area, rheological properties, liquid crystalline behavior, specific orientation, chemical surface reactivity, biocompatibility, biodegradability, low toxicity, among others (Lavoine et al., 2012; Lin and Dufresne, 2014; Nechyporchuk et al., 2016; Hubbe et al., 2017). The MFC/NFC materials can present a shear-thinning behavior since the fibrils tend to orient themselves and partially detangle due to the flow leading to a lower viscosity as the shear rate increases. That is why the MFC/NFC rheological properties depend significantly on the manufacturing technique (Moberg et al., 2017; Costa et al., 2019). MFC/NFC can be produced from enzymatic, chemical, and mechanical treatments (Nasir et al., 2017; Nie et al., 2018; Zhang et al., 2018). These treatments enhance the production of MFC/NFC due to the strong increase of specific surface area and, consequently, to the higher amount of hydrogen bonds compared to native cellulosic fibers (Missoum et al., 2013; Abdul Khalil et al., 2014). The use of MFC/NFC as an additive in paper industry applications has become a notable research field. Studies have revealed that MFC/NFC can also be used in packaging with antibacterial properties (Lavoine et al., 2015; Martins et al., 2018), but it can be used mainly to improve the strength and printability properties of office papers (Taipale et al., 2010; González et al., 2012; Tarrés et al., 2016; Lourenço et al., 2019a; Lourenço et al., 2019b; Lourenço et al., 2020). The main cost factors to produce MFC/NFC at the industrial scale are energy consumption and fiber pulp sources, which represent more than 60% of the total manufacturing cost. Therefore, the minimization of MFC/NFC manufacturing costs can be achieved by fiber selection (de Assis et al., 2018b; Zambrano et al., 2021). As bleached eucalyptus kraft pulps present lower costs than bleached softwood kraft pulps (Zambrano et al., 2021), the production of MFC/NFC from eucalyptus pulp at the industrial level is a strategy of commercial interest and can be used as an additive in tissue papers. To the best of our knowledge, the use of MFC/NFC as an additive in tissue papers based on cellulose fibers has been slightly investigated. Studies are already beginning to arise from the application of MFC/NFC as an additive in the production of hygiene tissue papers (Zambrano et al., 2021), superabsorbent diapers (Patiño-Masó et al., 2019), or tissue papers produced from bamboo fibers (Guan et al., 2019), and with efficient separation membrane applications (Roy et al., 2018). MFC/NFC has been also proposed to be used as a driver to reduce the fiber content of tissue products while maintaining the tensile strength and softness performance of different products (Gonzalez et al., 2020; Zambrano et al., 2020).

The main goal of this work was to investigate the influence of MFC/NFC as an additive in tissue paper production, to substitute partially or totally softwood reinforcement fibers in a tissue paper conventional furnish mixture. The aim was to obtain eucalyptus enriched papers, with minimal to zero softwood fibers, while preserving or even improving the end-use tissue paper characteristics. For this purpose, the morphological, chemical, and water interaction properties of the raw materials were evaluated. Handsheets with a basis weight of 20 g/m² were produced and the bulk, porosity, softness, strength, and absorption properties were measured. A tissue computational simulator was used to predict the evolution of these tissue properties from different scenarios to those studied experimentally.

III.2.2.3. Materials and Methods

III.2.2.3.1. Pulp Samples

An industrial never-dried, total chlorine-free (TCF) bleached Eucalyptus kraft pulp (a different pulp than those presented in previous subchapters, designed by HW), and an industrial, dried, elemental chlorine-free (ECF) bleached Pinus kraft pulp (S_A) were used in this work. This HW pulp, supplied by a Portuguese tissue paper manufacturer, is a suitable sample for tissue products, with a 25 °SR (Shöpper-Riegler degree). Furthermore, to mimic industrial conditions, only the S_A pulp was refined in a PFI-mill, to reach this target °SR (1500 PFI revolutions, under a refining intensity of 3.33 N/mm), now being designated by SW. The MFC/NFC sample was supplied by a research institute and was obtained from an industrial, never-dried, ECF bleached, with DEpDD sequence, Eucalyptus kraft pulp via cellulase treatment, and mechanical treatments including refining and homogenization treatments. All of the reagents in the experiments were of analytical grade.

III.2.2.3.2. Pulp Samples Characterization

The morphological properties of HW, SW, and MFC/NFC samples were evaluated by a system based on image analysis, the MorFi Analyzer (TECHPAP, Grenoble, France). Diluted suspensions of 20 mg/L for HW and MFC/NFC samples and 30 mg/L for SW samples were analyzed. Different morphological parameters such as the number of fibers, length weighted by length, width, coarseness, kinks, curl, rate of macrofibrils, and fine elements, were determined. All the elements longer than approximately 10 mm were excluded from the analysis. The fibers are defined by lengths between 200 µm and 10 mm, and widths between 5 and 75 µm. The fine elements present lengths and widths less than 200 and 15 µm, respectively. The rate of macrofibrils is the ratio of total fiber length to the sum of total fiber length and total macrofibrils length (Tourtollet et al., 2003). The results were determined in triplicate.

The sample drainability was evaluated by the °SR method according to ISO 5267-1. Triplicate assays were performed.

To evaluate the water retention value (WRV), the samples were centrifuged at a speed of 5000 revolutions per minute (centrifugation force: 3000 g) for 10 minutes, according to the method reported to Silvy et al. (1968). The samples were removed, weighed, and oven-dried at 105 ± 2 °C for 24 or more hours. The samples were again weighed. The assay was performed in triplicate, and the WRV index (%) was calculated as $WRV = ((M_1 - M_2) / M_2) * 100$, where “M1” was the wet sample mass after centrifugation and “M2” was the mass of wet sample drying at 105 °C.

The samples' intrinsic viscosity $[\eta]$ was measured by solubilization in a cupriethylenediamine (CED) solution, according to the SCAN-CM 15:88 standard, and the degree of polymerization (DP) was calculated using the Mark-Houwink-Sakurada equation $[\eta] = 0.57 * DP$, as described elsewhere (Smith et al. 1963).

The samples' carboxyl group content (C_{COOH}) was determined according to the TAPPI T 237 om-93 standard. Briefly, the samples were initially acidified with 0.1 M HCl, filtered with distilled water, mixed with $NaHCO_3/NaCl$ aqueous solution, and finally, titrated with 0.01 M HCl. The HCl volume spent in the titration of the sample and the standard assay, the mass of water retained in the sample after filtration, and the sample dry mass allowed the determination of the millimoles of acid groups per 100 grams of pulp.

III.2.2.3.3. Pulp Sample Mixtures Combination

Table III.16 summarizes the various sample mixtures studied, being the 75%HW+25%SW mixture a reference for the combination of eucalyptus fibers and SW reinforcement fibers at typical tissue mills. Different furnish mixtures of cellulose pulps were performed to understand the effect of MFC/NFC as an additive in the tissue paper properties compared to SW reinforcement fibers frequently used. A furnish mixture combining the HW, MFC/NFC, and SW samples was also studied in order to understand not only its effect on key tissue properties but also to confirm if it is a good alternative approach to the partial replacement of softwood reinforcement fibers. The MFC/NFC and SW fibers were incorporated in the fiber slurry, according to the loads described in Table III.16, and disintegrated following the ISO 5263-1.

Table III.16. Pulp sample mixtures combination used in the studies.

Assays	HW	MFC/NFC	SW
1	100 %	-	-
2	99 %	1 %	-
3	95 %	5 %	-
4	90 %	10 %	-
5	99 %	-	1 %
6	95 %	-	5 %
7	90 %	-	10 %
8	90 %	5 %	5 %
9	75 %	-	25 %

III.2.2.3.4. Pulp Sample Mixtures Characterization

The morphological, drainability, and WRV properties were evaluated for all assays, according to the procedures described above. Additionally, Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) was performed, at a wavelength of 600-4000 cm⁻¹, with a resolution of 4 cm⁻¹, for chemical functional groups identification.

III.2.2.3.5. Isotropic Laboratory Handsheets Preparation and Characterization

Never-pressed, low-basis weight (20 g/m²) isotropic laboratory handsheets were produced according to the method described by Morais et al. (2019, 2020a), in a batch laboratory sheet former (adaption of ISO 5269-1). The handsheets were prepared with the different mixtures described in Table 1. The handsheets were conditioned at (23±1) °C with a relative humidity of (50±2) %, according to ISO 187.

Scanning electron microscopy (SEM) was performed in the never-pressed, low-basis weight handsheets using a Hitachi S-2700 microscope (Tokyo, Japan) (accelerating voltage of 20 kV), after coating the samples with gold, using a Sputter Quorum Q 15 OR ES (Laughton, East Sussex, UK). SEM images were processed and analyzed using image analysis software, the “ImageJ”, for pore size distribution characterization. SEM images were processed using a methodology with defined criteria for the stabilization of the average of the measured values (Hotaling et al., 2015). Figure III.19 shows the process of the SEM image processing procedures using the “ImageJ”. SEM images were segmented into binary images for further processing. Different morphological processing algorithms were applied to process the binary images. These algorithms include correcting the shadow gradient, reducing noise, obtaining an image detail, improving edges, creating higher contrast between light and dark areas, among others. Subsequently, an integrity check of the processed image was performed to remove isolated fibers. A systematic method was used to generate fiber diameter, porosity, pore dimension, and distribution statistics (Martins et al., 2018; Xi et al., 2019). About 260 fibers and 1500 pores were measured from at least three SEM images per sample.

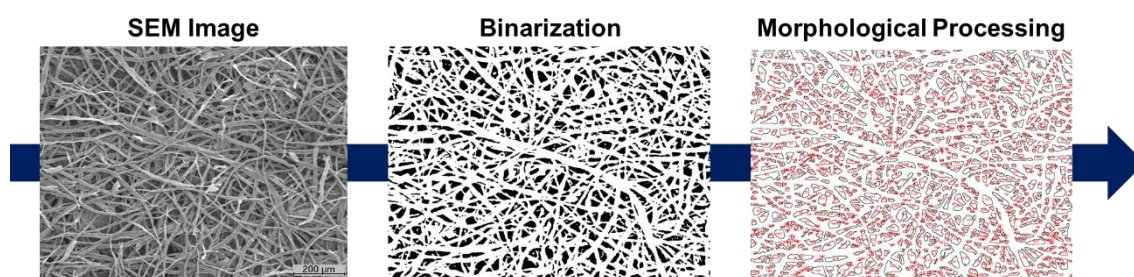


Figure III.19. SEM image processing procedures using the “ImageJ” software.

The handsheet structural properties, such as basis weight, thickness and bulk, and porosity were determined, following ISO 12625-6 and ISO 12525-3 standards. The handsheet solid volume, essential to calculate the porosity, was measured using a helium-gas displacement pycnometer (AccuPyc II), in a 10 cm⁻³ sample chamber.

The experimental results of this method were validated through the porosity calculated theoretically ($\text{Porosity} = 1 - (\text{density of the sheet} / \text{density of cellulose})$), obtaining the same porosity range values. According to the corresponding ISO standards, the handsheet tissue paper properties, such as tensile index (ISO 12625-4), water absorption capacity (ISO 12625-8 adaptation), and capillary rise (ISO 8787 adaptation), were measured. The standard adaptation to determine the water absorption capacity consisted of immersing 2.5 g of handsheets for 30 seconds. At the end of this time, the basket containing the sample was removed from the water, running on the support, with 30° of amplitude, for 60 seconds. Finally, the amount of water that the tissue sample was able to absorb at this time was determined. The assays were carried out in triplicate. The standard adaptation to measure the capillary rise consisted of collecting the water rise in a tissue sample 50 mm wide, for 10, 20, 30, 60, 180, 300, and 600 seconds. Four tests were carried out. The handsheet softness was evaluated using a Tissue Softness Analyzer (TSA Emtec), with QA1 algorithm for measurements of handfeel (HF) and TS7 (parameter related to the surface softness from the fibers and the paper material). All assays were performed at a temperature of $(23 \pm 1)^\circ\text{C}$ and a relative humidity of $(50 \pm 2)\%$, according to ISO 187.

III.2.2.3.6. Computational Studies

The computational studies were carried out to obtain different relationships between the MFC/NFC and SW percentages and the final tissue properties, using a tissue computational simulator developed from scratch, the *SimTissue* (FibEnTech-UBI, Covilhã, Portugal) for furnish management and optimization. The experimental results were evaluated with robust linear regressions. The ability to predict different scenarios from those obtained experimentally was performed using interpolation and extrapolation methods and a 3D simulator of fibrous materials, the *voxelfiber* (<https://github.com/eduardotrincaoconceicao/voxelfiber>) in order to simulate the different 3D structures (Conceição et al., 2010; Curto et al., 2011). This simulator allows the modeling of porous tissue materials as planar random networks, through the fiber dimensions and properties (Morais et al., 2020b). Computational studies were carried out using Matlab® (R 2020a, 9.8.0.1323502, MathWorks, Natick, MA, USA). All variables were normalized to present the same scale range.

III.2.2.4. Results and Discussion

III.2.2.4.1. Pulp Samples Characterization

The HW and SW were selected to be representative of hardwood fibers with 0.7 mm lengths and 19.1 μm widths, and softwood fibers with 1.7 mm lengths and 33.1 μm widths, respectively. The enzymatic and mechanical modification processes of a eucalyptus fiber also allowed to obtain MFC/NFC fibers with 0.5 mm lengths and 21.3 μm widths. Table III.17 shows the morphological, water interaction, and chemical properties of these three samples.

Table III.17. Morphological, water interaction, and chemical properties of HW, MFC/NFC, and SW samples.

Properties	HW	MFC/NFC	SW
Morphological properties			
FN (million/g)	25.3±0.1	20.8±0.3	5.7±1.3
L (mm)	0.7±0.0	0.5±0.0	1.7±0.0
W (µm)	19.1±0.0	21.3±0.1	33.1±0.3
C (mg/100m)	6.3±0.0	10.7±0.2	14.9±1.2
KF (%)	44.2±0.3	15.9±0.2	37.8±2.0
Curl (%)	9.7±0.0	5.5±0.0	10.6±0.3
MF (% in length)	0.545±0.010	1.269±0.023	0.716±0.013
FE (% in length)	38.5±0.4	67.4±0.2	40.3±1.1
Water interaction properties			
°SR	25	> 80	25
WRV (%)	110.3±0.7	1185.1±9.4	113.4±1.4
Chemical properties			
Viscosity (mL/g)	453±0	899±0	844±0
DP	794±0	1577±0	1481±0
C_{COOH} (mmol/100g)	5.1±0.1	8.4±0.2	7.2±0.3

Values reported are the mean ± standard deviations. FN: number of fibers; L: length weighted by length; W: width; C: coarseness; KF: kinked fibers; MF: rate of macrofibrils; FE: fine elements

The MFC/NFC is composed of a fibrillary (FE) and a non-fibrillary fraction, and MFC/NFC presented a fiber length almost similar to the HW fibers, and higher fiber widths (Table III.17). The fiber fraction in the MFC/NFC presented a low slenderness ratio (23) (fiber length to width ratio) followed by HW (37) and SW (51) samples. The short fibers of the MFC/NFC produced a good slenderness ratio, which is related to the production of a good aspect ratio and inter-fiber bonding (Dutt and Tyagi, 2011). According to the MorFi analyzer characteristics that define fibers with lengths between 200 µm and 10 mm, and widths between 5 and 75 µm, the HW sample presented a fiber population higher than MFC/NFC. These results correspond to the fiber fraction remaining in the sample after mechanical and enzymatic treatments applied for MFC/NFC production, which corresponds to 32.6% (100% - FE) of the fibers that were not fully fibrillated. For this reason, the MFC/NFC presented a lower FN than the HW. Due to the limitations regarding the detection limit of fiber quality analyzers, determining the length and width dimensions of micro/ nanofibrils is challenging and it requires very careful microscopic analysis (Chen et al., 2015), viscosity measurements (Tanaka et al., 2014), or image analysis treatments with well-defined criteria (Zhang et al., 2012; Ang, Haritos and Batchelor, 2020; Zambrano et al., 2020). Therefore, the analysis of the micro/ nanofibrils diameter was also determined by image analysis (Figure III.20). The results indicated that the diameter of the fibrils for MFC/NFC are in the range between 0.09 and 4.7 µm, with an average diameter of (2.4±1.5) µm. The mechanical and enzymatic treatments applied to a bleached eucalyptus kraft pulp made it possible to produce an MFC/NFC with 56% of particles below 1000 nm, representing 10% of particles below 200 nm.

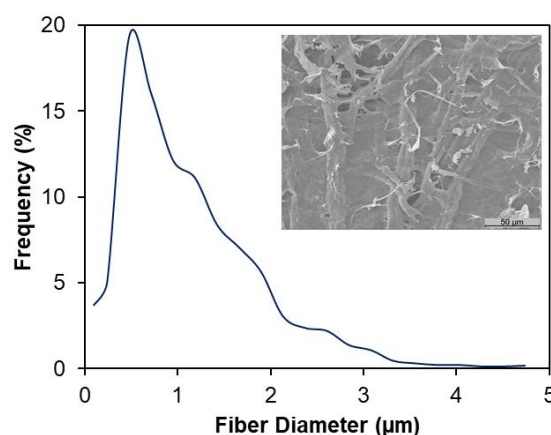


Figure III.20. Distribution of fiber diameters for MFC/NFC sample, highlighting a SEM image of MFC/NFC sample.

The raw materials coarseness, related to the fiber wall thickness and fiber width, influences the fiber collapse degree (Kibblewhite and Riddell, 2000) and consequently the bulk, strength, and absorption properties. Tissue papers require hardwood fibers with high coarseness to develop bulk and softness, and softwood fibers with low coarseness to ensure strength and paper machine runnability (Foelkel, 2007). The fiber deformations (kinks and curl), that arise throughout the pulping process, influence tissue paper bulk, porosity, and softness properties as they enable a more open fibrous network, with low inter-fiber bonds (Foelkel, 2009). The use of MFC/NFC as an additive in eucalyptus pulps can allow the strength properties improvement since this sample presented low kinks and curl values (Morais et al., 2020a). The pulp macrofibrils and fine elements also increase strength properties, improving the inter-fiber bonds. In the SW sample, the high fines content might correspond to the degraded fibers, less rigid, with less intrinsic strength (Muneri, 1997), due to the refining process carried out to obtain a 25°SR. In the MFC/NFC sample, the fiber surfaces were removed from the primary wall during the enzymatic treatment, increasing macrofibrils and fines content amounts (Jones et al., 2013).

The drainability of the HW and SW samples presented the target °SR of 25 (typical value at a tissue mill). However, MFC/NFC sample showed a °SR higher than 80°SR. The MFC/NFC sample final °SR value was not possible to obtain experimentally due to the high flow time. In addition, MFC/NFC sample showed a high WRV and consequently a higher water affinity, followed by SW and HW samples. The water affinity is related to the fiber modification treatment increase applied to the MFC/NFC and SW samples (Gu et al., 2018).

The intrinsic viscosity is related to the cellulose DP, and consequently to its degradation and intrinsic strength. On the other hand, carboxyl groups act as interaction points with water, providing more local binding (Neiva et al., 2015). MFC/NFC showed higher viscosity, DP and C_{COOH} compared to HW and SW samples. The most degraded fibers in the HW sample, due to the low intrinsic viscosity obtained, are possibly related to the oxygen and ozone bleaching stage process which it was submitted.

The use of MFC/NFC as an additive can also be advantageous to increase the tissue paper strength properties due to the formation of more interfiber bonds. However, compared to other MFC/NFC produced with enzymatic pre-treatments with xylanases, followed by mechanical treatments and high-pressure homogenization (Nie et al., 2018; Zhang et al., 2018), the MFC/NFC used in our experiments presents a low carboxyl group content (approximately 50% lower). These differences depend on the type of equipment used, the energy consumption, the slurry consistency, the type and loading of the enzyme, among other parameters.

III.2.2.4.2. Pulp Sample Mixtures Characterization

Table III.18 shows the morphological and water interaction properties of different furnish mixtures. The fiber length weighted by length, curl, and kinks in the mixtures decrease with increasing percentages of MFC/NFC. The greater swelling of the MFC/NFC fibers together with a higher carboxyl group content may explain the decrease in fiber deformations (kinks and curl), i.e., the MFC/NFC incorporation in the slurry results in straighter fibers than the pulps without this additive (Brodin and Theliander, 2013). However, the coarseness, macrofibrils, and fines content properties were increased with the addition of MFC/NFC. Normally, depolymerization and fibrillation of micro/ nanofibers decrease the coarseness properties, enhancing the fiber flexibility and, consequently, structures with high density (Paavilainen, 1990; Curto et al., 2009). The increase in fiber coarseness with the incorporation of MFC/NFC in the furnish can be explained by the decrease in fiber length. The coarseness, mass per unit length, is calculated on the MorFi analyzer by the ratio between the mass of all fibers and the total length. This mass is measured by the number of processed images, the imaged volume, and the pulp fiber consistency (Tourtollet et al., 2003). The MorFi fiber analyzer may not accurately determine these results due to the fiber kinks and curl. It can also be considered that some fine elements were not counted in the measurement due to the presence of nanofibers in the slurry. Joutsimo and Asikainen (2013) also reported results like those presented in this work. These authors reported that after refining different pulps, at different PFI revolutions, the fiber coarseness increased. Some fine elements may not be accounted for in the fine's measurement, decreasing the fiber length and, consequently, generating a higher fine content, despite the fact that the measurement showed higher fiber coarseness (Joutsimo and Asikainen, 2013). The SW addition promoted an increase of fiber length, coarseness, macrofibrils, and fines content in pulp mixtures. The slight increase of fiber length and coarseness properties are in accordance with the PFI revolutions applied to the SW sample (Chauhan et al., 2011). As PFI causes less damage to the SW fibers properties as opposed to industrial refining (González et al., 2012), a small increase in the macrofibrils and fines content was observed. Nevertheless, the deformation properties (fiber kinks and curl) were also increased with the SW addition. The fiber widths were not evidently modified with the addition of MFC/NFC and SW samples. The mixture 90%HW+5%MFC/NFC+5%SW presented morphological properties similar to those of mixtures 95%HW+5%MFC/NFC and 99%HW+1%SW. The typical industrial furnish mixture (75%HW+25%SW) showed fiber length, width, and coarseness properties higher than the mixtures with MFC/NFC properties.

The °SR properties increased from 4 to 76%, with the incorporation of 1% to 10% of MFC/NFC. Under the same conditions, the WRV values increased from 5 to 46%. This water interaction increase can be related to the MFC/NFC binding surface area along with the carboxyl group content (Gu et al., 2018). High °SR values cause drainage difficulties, which may represent some issues for the paper machine runnability and efficiency (Hubbe and Heitmann, 2007); however, de Assis et al. (2018a) have reported that eucalyptus fibers with light refining in a range between 22 and 35 °SR are suitable to produce high-quality tissue papers. On the other hand, higher SW content also increased the WRV properties from 2 to 18%. Compared to MFC/NFC incorporation, the WRV increase in furnish with SW fibers was not so significant. However, the fines of the refined SW pulp also play a fundamental role in water retention, enabling inter-fiber and fiber-water bonding. The mixture 90%HW+5%MFC/NFC+5%SW presented °SR and WRV properties similar to those of mixture 95%HW+5%MFC/NFC.

Table III.18. Morphological and water interaction properties of pulp mixtures.

Properties	99%HW+1% MFC/NFC	95%HW+5% MFC/NFC	90%HW+10% MFC/NFC	99%HW+1% SW	95%HW+5% SW	90%HW+10% SW	90%HW +5%MFC/NFC +5%SW	75%HW+25% SW
Morphological properties								
FN (million/g)	23.2±0.5	23.3±0.2	23.1±0.2	23.4±0.4	23.4±0.4	22.2±0.1	22.0±0.3	21.8±0.1
L (mm)	0.728±0.003	0.725±0.001	0.716±0.003	0.734±0.002	0.745±0.002	0.760±0.006	0.737±0.001	0.815±0.004
W (µm)	19.1±0.1	19.3±0.1	19.3±0.1	19.2±0.0	19.3±0.1	19.5±0.1	19.4±0.0	20.1±0.1
C (mg/100m)	6.9±0.1	7.0±0.1	7.2±0.1	6.8±0.1	6.8±0.1	7.1±0.1	7.3±0.1	7.7±0.0
KF (%)	44.2±0.1	43.5±0.3	43.2±0.4	43.7±0.3	42.8±0.1	42.1±0.3	43.1±0.4	41.4±0.2
Curl (%)	9.5±0.1	9.4±0.1	9.4±0.1	9.5±0.1	9.2±0.1	9.1±0.1	9.4±0.1	9.1±0.1
MF (% in length)	0.588±0.005	0.595±0.009	0.640±0.011	0.548±0.017	0.563±0.018	0.572±0.009	0.591±0.017	0.574±0.005
FE (% in length)	40.2±0.1	42.4±0.5	43.4±0.4	39.3±0.2	39.3±0.5	40.0±0.2	41.7±0.1	41.2±0.7
Water interaction properties								
°SR	26±0	32±0	44±0	25±0	25±0	25±0	33±1	25±0
WRV (%)	116.3±1.3	144.8±10.4	160.8±15.0	112.1±1.1	115.4±2.4	121.9±1.4	153.5±10.4	130.1±1.5

Values reported are the mean ± standard deviations.

Additionally, the identification of chemical functional groups in the mixtures was performed using the FTIR-ATR technique. Figure III.21 showed FTIR-ATR spectrum of 100% HW sample and 90%HW+10%MFC/NFC and 75%HW+25%SW pulp mixtures. The typical absorption bands of hydroxyl groups, related to the intra and intermolecular interactions of hydrogen bonds, were verified for the HW sample, 90%HW+10%MFC/NFC, and 75%HW+25%SW mixtures at 3332, 3329, and 3331 cm^{-1} , respectively. The FTIR spectrum of the mixture 90%HW+10%MFC/NFC indicated a -OH band with higher area, followed by the mixture 75%HW+25%SW and the 100% HW sample, which following the results of carboxyl groups content. Mixtures with MFC/NFC showed a higher amount of -OH groups and the same trend has been reported in the literature (Guan et al., 2019; Maaoui, et al., 2017). The bands at 2981 cm^{-1} and 2889 cm^{-1} correspond to the C-H groups' angular deformation vibration of the three samples. A higher intensity of these bands was verified for the mixture 90%HW+10%MFC/NFC. In the FTIR spectrum, all bands characteristic of the cellulose molecule between 1300 and 900 cm^{-1} were also observed. These bands correspond to the angular deformations of the C-H groups and the primary alcohols C-O bonds, the primary alcohols C-O-C bonds absorption, and β -glycosidic bonds between glucose units.

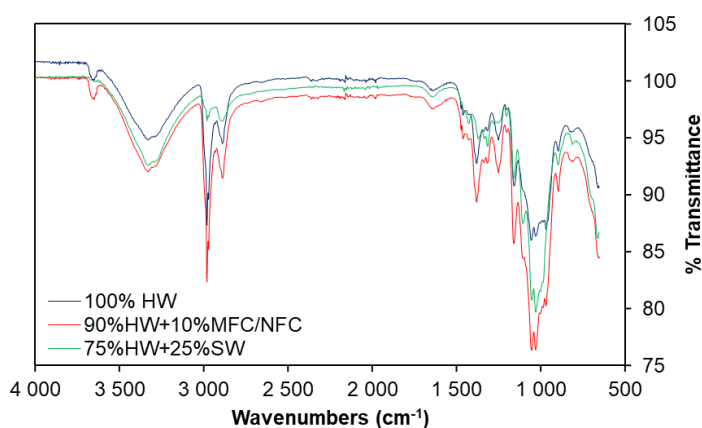


Figure III.21. FTIR spectrum of 100% HW sample (blue) and 90%HW+10%MFC/NFC (red) and 75%HW+25%SW (green) mixtures.

III.2.2.4.3. Effect of MFC/NFC and SW Fibers Incorporation on Laboratory Tissue Handsheet Properties

As previously mentioned, SW fibers are used in tissue paper materials production for reinforcement and runnability purposes. Its replacement by additives such as MFC/NFC has implications in the tissue end-use properties. At very low coverage, a connected fiber network is formed only if there are enough fiber bonds. The limit is at the percolation point. Below this limit, the network consists of several disconnected parts. Although the 2D approach overestimates the real fiber network bonding in the paper, the 2D percolation threshold has high relevance to the tissue paper properties. Tissue materials sheets correspond to 2D networks of springs close to a percolation threshold, or with central forces (Alava and Niskanen, 2006; Bloch et al., 2019).

Figure III.22 presented the SEM images of the 100% HW sample and 90%HW+10%MFC/NFC and 90%HW+10%SW mixtures, as well as the pore size distribution in the 3D cellulose network surface structure of these samples. The addition of MFC/NFC in the tissue handsheets favored the inter-fiber bonding with the HW cellulose fibers, filling in the empty spaces between fibers and, consequently, reducing the pore dimension and distribution in the structures (Figure III.22b). The higher bonding surface area can result in a lower water absorption capacity, but also in an increase in strength properties (González et al., 2012; Roy et al., 2018). On the contrary, the SW incorporation did not promote the filling of pores in the HW structure. A different 3D cellulose network was formed with the two fibers used in the mixture. The presence of fibrillation was also visible in the SW fibers, due to the refining process (Figure III.22c), which also contributes to the bonding between HW fibers and SW fibrils.

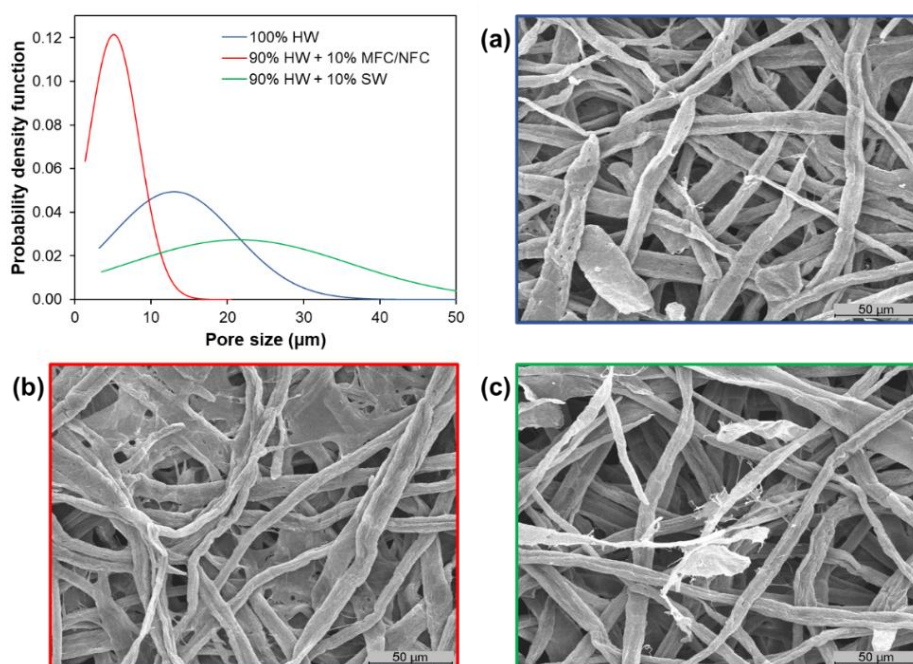


Figure III.22. SEM images of 100% HW sample (a) and 90%HW+10%MFC/NFC (b) and 90%HW+10%SW (c) mixtures and pore size distribution in the 3D network structure of these samples. The 100% HW, 90%HW+10%MFC/NFC, and 90%HW+10%SW samples showed average pore sizes of 13, 5, and 21 μm , respectively. These features correspond mainly to the tissue handsheet surface and do not necessarily extrapolate the handsheet bulk.

As previously mentioned, the SW fiber removal from the typical furnish formulations at a tissue mill can present benefits/ advantages on the tissue end-use properties, so the comparison of properties with the mixture 75%HW+25%SW becomes essential. Figure III.23 showed the effects of adding MFC/NFC and SW in the bulk, porosity, softness, tensile index, water absorption capacity, and capillary rise properties.

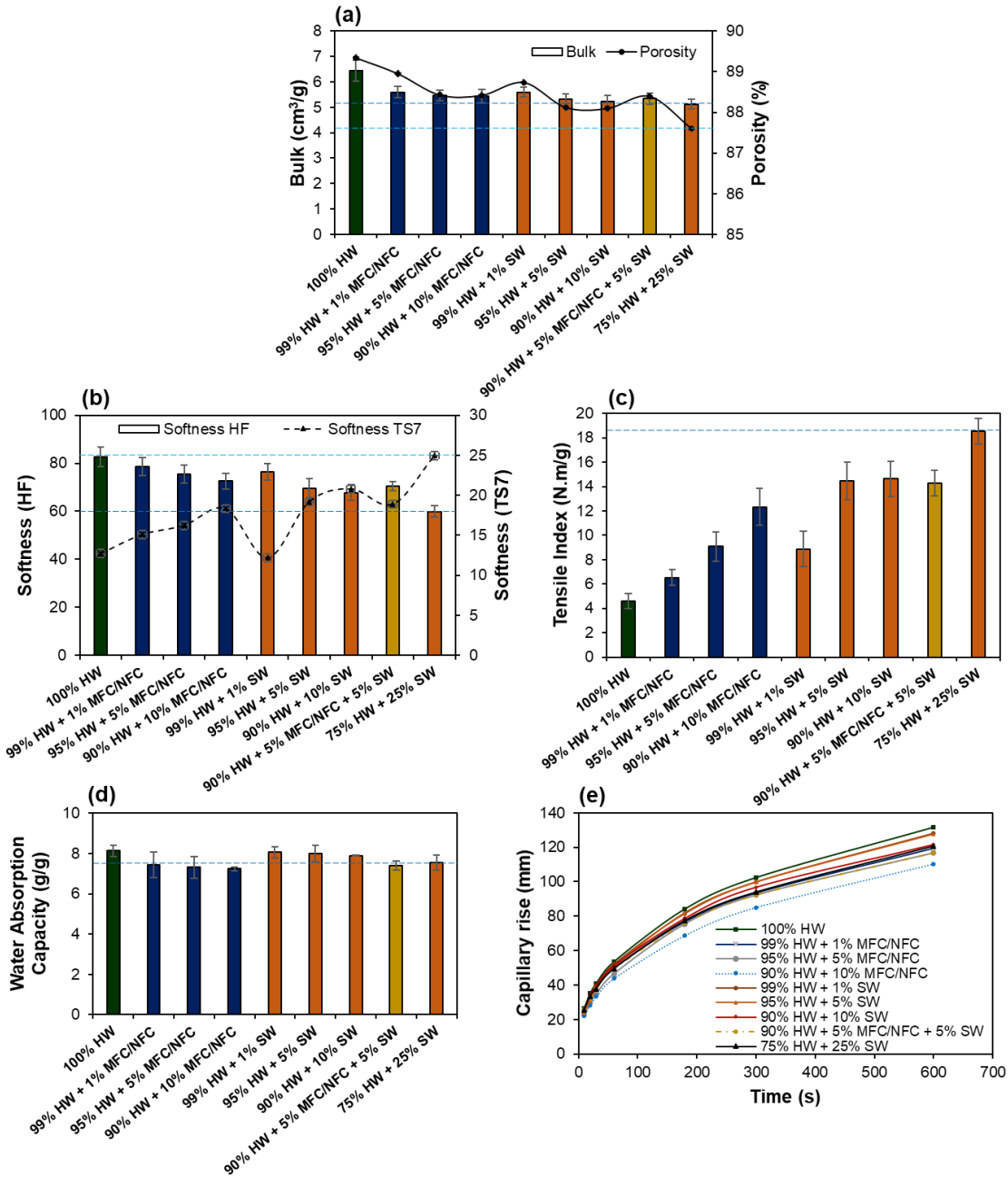


Figure III.23. Bulk, porosity (a), softness (b), tensile index (c), water absorption capacity (d), and capillary rise (e) of tissue handsheets with MFC/NFC and SW at different percentages. The horizontal lines represent the properties obtained for the typical furnish mixture at a tissue mill (75%HW+25%SW).

The results indicated that the decrease of SW fibers incorporation, between 0 and 10%, increased the properties of bulk from 2 to 26% and porosity from 1 to 2%. The replacement of SW fibers by MFC/NFC fibers, in percentages of 0 to 10%, also increased the properties of bulk from 6 to 26% and porosity from 1 to 2% (Figure III.23a). Consequently, these increases are also advantageous for the softness properties, as reported below. Compared to 100%HW structures, the 3D cellulose network formed by MFC/NFC and SW showed a bulk and porosity decrease, which is in agreement with the SEM images (Figure III.22). The high bonding surface area of MFC/NFC also caused this bulk decrease (Dutt and Tyagi, 2011).

Sanchez-Salvador et al. (2020) also studied the effect of using nanocellulose as a reinforcement additive in papers. It was found that the mechanical properties were increased, at the expense of porosity, with the incorporation of MFC/NFC (Sanchez-Salvador et al., 2020), when compared to structures without micro/ nanofibers. The mixture 90%HW+5%MFC/NFC+5%SW presented a bulk (5.34 cm³/g) and porosity (88.39%) comparable to mixtures 95%HW+5%MFC/NFC (bulk of 5.47 cm³/g and porosity of 88.43%) and 95%HW+5%SW (bulk of 5.23 cm³/g and porosity of 88.09%).

Compared to the mixture 75%HW+25%SW, softness HF of tissue handsheets improved from 13 to 38% with the SW fibers incorporation decrease, between 0 and 10% percentages. The replacement of SW fibers by MFC/NFC fibers, in percentages of 0 to 10%, also increased the softness HF from 21 to 38% (Figure III.23b). The production of structures with a low content of SW fibers or by replacing them with MFC/ NFC promotes an increase of softness HF, due to the higher fiber content that contributes to the formation of a fibrous structure with less stiffness (Trepanier, 2017). These results agreed with the higher values of bulk and porosity. The softness TS7 is related to the fiber's softness, being influenced by the presence of fibers on the handsheet surface (Wang et al., 2019b). The softness TS7 has an inverse behavior to the softness HF. Softness TS7 of tissue handsheets decreased by 17% to 49% with the SW fibers incorporation, and 27% to 49% with MFC/NFC fibers incorporation, in percentages of 0 to 10%. The SW fiber removal and their replacement by MFC/NFC fibers allowed to produce a fibrous structure with less attached fibers to the tissue handsheet structure. The mixture 90%HW+5%MFC/NFC+5%SW presented a softness (70.5 HF and 18.9 TS7) comparable only to the mixture 90%HW+10%MFC/NFC (72.5 HF and 18.3 TS7).

Figure III.23c showed that the tensile index of handsheets was decreased from 21 to 75% when the SW fibers dosage between 0 to 10% was incorporated. The replacement of SW fibers by MFC/NFC fibers, in the same percentages, also decreased the tensile index of handsheets from 34 to 75%. This phenomenon can be explained by the carboxyl group content, viscosity, relative bonding area, and consequently higher fibers' intrinsic strength. The presence of a structure with a 3D network with two types of fibers (Figure III.22c) contributed positively to the strength properties development when compared to structures with micro/ nanofibers. The SW fibers removal and their replacement by MFC/NFC fibers resulted in fatalities of strength properties, as expected. The formulations that will present a balance between the softness and strength properties and, therefore, will have more potential to replace the formulation 75%HW+25%SW industrially would be 95%HW+5%MFC/NFC and 90%HW+10%SW. Several authors concluded that the addition of micro and nanofibrils to paper materials, including tissue handsheet papers, increases the tensile index of these materials (González et al., 2012; Guan et al., 2019; Lourenço et al., 2019b; Sanchez-Salvador et al., 2020), as well as the addition of refined softwood reinforcement fibers (Chauhan et al., 2011) when compared to structures without SW fibers or micro/nanofibers.

However, in our case studies, the SW fiber removal and replacement, that play a fundamental role in the strength properties, is performed; so, it is expected to present structures with less strength compared to the industrial reference. Besides, the inverse relationship of softness HF and tensile index properties was verified, as reported by Morais et al. (2019, 2020a). For hardwood fibers without any treatment or additives addition, the softness HF increased by 2.4 units per unit of the decreased tensile index (Morais et al., 2019, 2020a). However, the addition of MFC/NFC and SW fibers in HW samples increased 1.28 and 1.58 units of softness, respectively, for each unit of the decreased tensile index (Figure III.24). The mixture 90%HW+5%MFC/NFC+5%SW presented a tensile index (14.31 Nm/g) similar to the mixture 95%HW+5%SW (14.46 Nm/g).

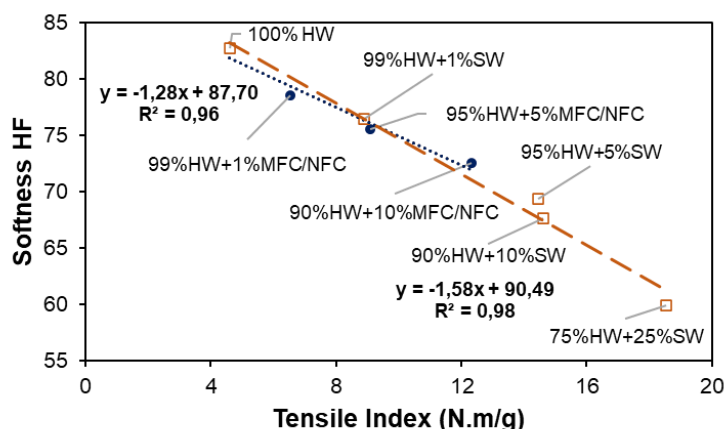


Figure III.24. Correlation between the tensile index and softness HF properties of tissue handsheets with MFC/NFC and SW fibers at different percentages.

Regarding the absorption properties and compared to the mixture 75%HW+25%SW, the water absorption capacity is increased from 5 to 8% with a decrease of SW fibers incorporation at percentages from 0 to 10% (Figure III.23d). On the other hand, their replacement by MFC/NFC fibers, in percentages between 1 and 10%, decreased the water absorption capacity from 2 to 4%. The filling of the pores between HW fibers by micro and nanofibers, as shown in Figure III.22b, can explain this phenomenon. Although the handsheet porosities are slightly higher than that obtained with the SW addition, the dimension and distribution of the pores are lower in the structures with MFC/NFC. In the literature, studies with the addition of MFC/NFC also reported a water absorption capacity decrease in papers made with wood pulp fibers (Lourenço et al., 2019b; Martins et al., 2018; Roy et al., 2018). The mixture 90%HW+5%MFC/NFC+5%SW presented a water absorption capacity (7.41 g/g) comparable to the mixture 99%HW+1%MFC/NFC (7.43 g/g).

The capillary rise of handsheets, another indicator of the absorption properties, presented results that are in agreement with the water absorption capacity (Figure III.23e). The capillary rise at 10 minutes is increased from 1 to 9% with a decrease of SW fibers incorporation at percentages from 0 to 10%, and their replacement by MFC/NFC fibers, in the same percentages, decreased this property from 1 to 9%. Once again, these results were due to the tissue handsheets network structure with the most pronounced fiber bonding caused by MFC/NFC as an additive.

The mixture 90%HW+5%MFC/NFC+5%SW presented a capillary rise (117 mm, at 10 minutes) similar to the mixture 95%HW+5%MFC/NFC (117 mm, at 10 minutes). It is also important to analyze the capillary rise at 30 seconds since it is a time period more adequate for consumer perception of the absorption rate. In this case, the results indicated that the SW fibers incorporation decrease, between 0 and 10%, increased the capillary rise from 4 to 7%, and their replacement by MFC/NFC fibers, in the same percentages, also decreased this property from 1 to 13%. Finally, the mixture 90%HW+5%MFC/NFC+5%SW presented a capillary rise (38 mm) similar to the mixture 99%HW+1%MFC/NFC and 95HW+5%SW (38 mm).

The mixture 90%HW+5%MFC/NFC+5%SW showed relationships between the different combinations with MFC/NFC and SW separately for all tissue properties. This mixture did not show an average relationship with the mixtures 95%HW+5%MFC/NFC and 95%HW+5%SW. Therefore, a good combination of the softness, strength, and absorption properties was obtained, being essential for a high-quality premium tissue paper. An approach of combining the three cellulose sources allowed to obtain a multi-structured material, at different scales, with improved key tissue properties compared to the typical furnish mixture at a tissue mill. Based on this study, formulations 95%HW+5%MFC/NFC and 90%HW+10%SW presented improved softness properties with less possible losses of strength and absorption properties. These were the formulations that allowed the best compromise of the tissue properties, with a saving of 20 to 25% in the consumption of SW fibers in the tissue paper production of industrial references.

In terms of cost-effectiveness, MFC/NFC is more expensive than SW fibers. Zambrano et al., (2020) evaluated the manufacturing cost of MFC/NFC ranging from 764 to 1471 USD/OD ton fiber, depending on the fiber source. MFC/NFC produced from bleached eucalyptus kraft pulps presented costs between 1229 and 1289 USD/OD ton fiber. The cost of HW and SW pulps is approximately 770 and 950 USD/OD ton fiber, respectively. Considering these results reported by the authors, we have proposed an estimate of the cost of the different fiber mixtures used (Figure III.25). Compared to the mixture 75%HW+25%SW, only the 90%HW+10%MFC/NFC mixture presented higher costs (+ 1%). The incorporation of 1 to 5% of MFC/NFC reduced the costs by 2 to 5%, while the incorporation of 1 to 10% of SW fibers decreased the costs by 3 to 5%. The mixture 90%HW+5%MFC/NFC+5%SW showed costs lower by 1% compared to the typical furnish mixture at a tissue mill. The results indicated that MFC/NFC is a potential additive for tissue applications since the trade-off between the fiber mixture costs and the final tissue properties has been desired. The SW decrease in furnish is also achievable in the tissue industry as they continue to provide strength and absorption properties at low costs. The combination of these three cellulose sources also presented economic advantages, supporting the use of different raw materials in tissue materials with innovative and added-value applications.

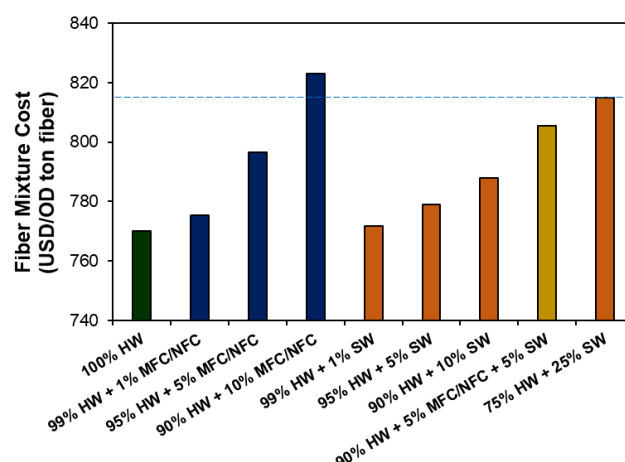


Figure III.25. Costs of fiber mixtures containing MFC/NFC and SW at different percentages. The horizontal line represents the cost obtained for the typical furnish mixture at a tissue mill (75%HW+25%SW).

III.2.2.4.4. Computational Studies to Predict the Variability of Final Tissue Properties

The simulation results (Figure III.26) were represented to study the variation of tissue final end-use properties. Using our tissue computational simulator for furnish optimization and a 3D fiber-based computational simulator to simulate 3D tissue fibrous structures (Morais et al., 2020b), it was possible to predict the influence of the amount of MFC/NFC and SW on the evolution of the softness, strength, and absorption properties. The amount of MFC/NFC incorporated in tissue materials has a different impact on tissue properties compared to the SW incorporation. Throughout the MFC/NFC percentages, as an additive in tissue products, the impact on the softness properties is low compared to the SW percentages. The opposite occurs with the strength properties, measured by the tensile index since these parameters are inversely related (Figure III.26a,c). The differences found in the absorption properties, measured by the water absorption capacity and capillary rise, are related to the 3D matrix in the tissue structures formed by the MFC/NFC incorporation, which fills the spaces between the HW fibers, and SW incorporation, which forms a second network with HW fibers (Figure III.26b,d).

These methods allow selecting the combinations between the different fibrous compositions and MFC/NFC, and the favorable tissue properties for each tissue product. The simulation results allow obtaining the ideal ranges for several properties simultaneously, to identify combinations of fibers and percentages of MFC/NFC that cover a much larger result area, corresponding to all possible computational combinations, and which would not be possible get using only experimental results, with the time and resource they require. The replacement of SW fibers resulted in a favorable improvement in softness, at the expense of reduced strength. However, most tissue products require a minimum tensile strength to ensure the paper machine's runnability, converting operations, and mechanical integrity for consumer use, for example.

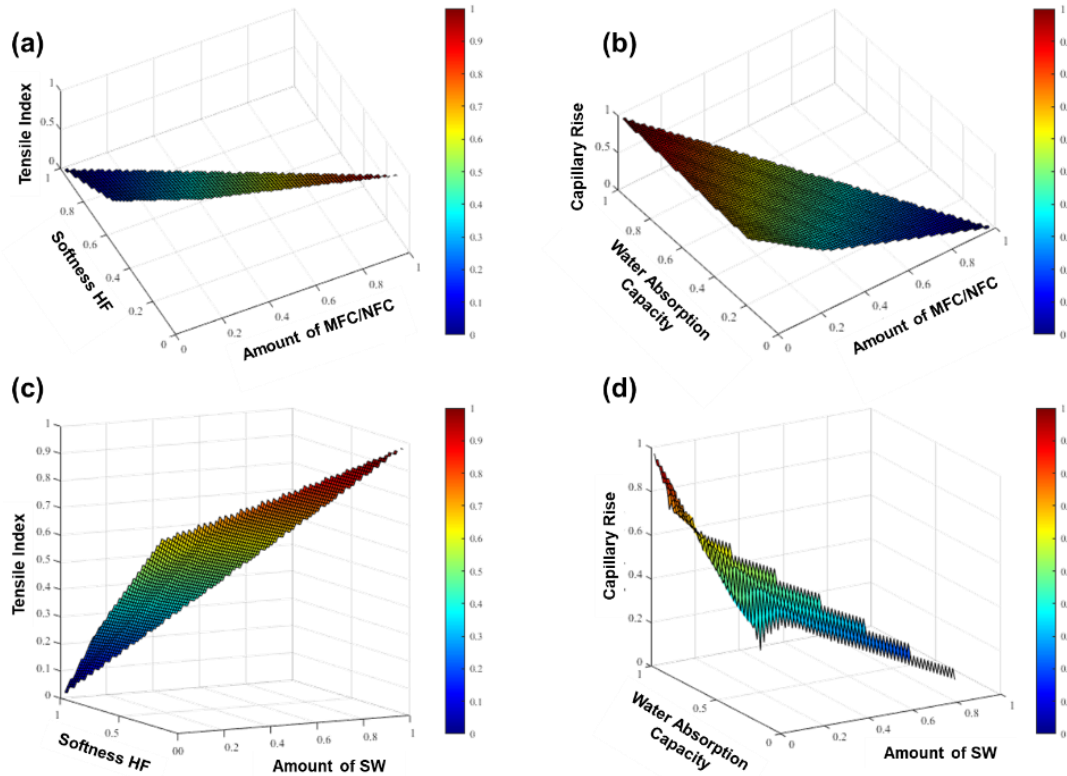


Figure III.26. Evolution of final end-use properties with the amount of MFC/NFC (softness and tensile index properties (a); water absorption capacity and capillary rise at 30 seconds (b)), and with the amount of SW (softness and tensile index properties (c); water absorption capacity and capillary rise at 30 seconds (d)).

In order to evaluate the potential of using MFC/NFC to replace SW fibers in terms of strength requirements, a scenario was produced with a furnish containing MFC/NFC whose strength properties match those of 75%HW+25%SW mixture. In these conditions, it was possible to produce a tissue paper with 66.7 softness HF (+11%), 18.5 Nm/g of tensile index, 7.1 g/g of water absorption capacity (-6%), and 30 mm of capillary rise (-20%), when 19-20% of MFC/NFC was incorporated. Although the softness properties are improved, at the expense of the absorption properties, this scenario is 7% more expensive than the typical furnish mixture at a tissue mill (874 vs 815 USD/OD ton fiber). In terms of performance, this computational approach also allowed us to predict that the incorporation of MFC/NFC as an additive between 5% to 15%, and without SW fibers, could be in improved conditions when replacing the 75%HW+25%SW mixture. The use of MFC/NFC as an additive in a range of 5 and 15% can produce tissue structures with softness HF between 69.5 and 75.5, tensile index between 9.1 and 15.6 Nm/g, water absorption capacity between 7.2 and 7.3 g/g, and capillary rise between 32 and 35 mm. However, cost-effectiveness must also be considered. From 10% of MFC/NFC incorporated, the fiber mixture costs increase compared to 25% of SW fibers in slurry (Figure III.25). Therefore, it was found that the trade-off between the final tissue properties and the fiber mixture costs is achieved with the addition of up to 8% MFC/NFC. In these conditions, it is possible to produce a tissue paper with 73.7 softness HF, 11.0 Nm/g of tensile index, 7.3 g/g of water absorption capacity, and 34 mm of capillary rise, with the same costs of the 75%HW+25%SW mixture.

Moreover, different industrial base tissue papers with a basis weight between 15.7 and 19.1 g/m² can present tensile indexes between 6.9 and 12.0 Nm/g (means of the paper machine direction and cross direction) (Veira et al., 2020). Based on these results, the incorporation of 1 to 8% of MFC/NFC presents strength values in the range of industrial base tissue papers. For this reason, MFC/NFC is a potential additive to produce high-quality tissue materials with improved softness and strength properties. The predictive capacity of these computational tools allows optimized furnish management of the cellulose raw materials, allowing the development of innovative formulations, saving laboratory and industrial resources, predicting the behavior of different pulps, and resulting in higher speed and flexibility of response.

III.2.2.5. Conclusions

In this study, tissue handsheets from Eucalyptus pulp, Eucalyptus-MFC/NFC, and Pinus reinforcement pulp were produced. The effects of tissue end-use properties were analyzed using experimental and computational approaches. The use of MFC/NFC as an additive and the use of softwood fibers, in different percentages, were compared with the blend usually used by the tissue industry (75%HW+25%SW). Computational studies were performed to predict the variability of tissue properties with different percentages of MFC/NFC and SW fibers, using a tissue computational simulator developed for furnish management optimization.

Compared to the 75% HW + 25% SW mixture, it was found that the reduction of SW fibers in tissue structures improved structural, softness and absorption properties, and decreased the strength properties. On the other hand, the replacement of reinforcement fibers by micro/nanofiber in tissue structures improved structural and softness properties and decreased the strength and absorption properties compared to the typical industrial blend. This effect can be due to the high bonding surface of MFC/NFC with high carboxyl group content, as well as the filling of the spaces between the Eucalyptus fibers by micro and nanofibers, providing a decreased pore dimensions in the tissue paper structure. The predictive capability of the computational tools used in this study allowed to create different scenarios of the evolution of the softness, strength, and absorption properties with the MFC/NFC and SW incorporation, to develop innovative formulations, saving laboratory and industrial resources. Furthermore, through this experimental and computational approach, the results showed that formulations with MFC/NFC percentages of 1 to 8% and without SW fibers could allow an innovative design of tissue products combined with these micro/ nano cellulose fibers, as an additive, optimizing the tissue end-use properties, with partial or total removal of SW fibers, achieving a trade-off between the final tissue properties and the fiber mixture costs.

From the present work, it was possible to conclude that MFC/NFC has a good potential to be used in tissue products in which the softness and strength properties are crucial, such as toilet and facial papers, produced with maximization of eucalyptus pulps. This maximization is the beginning of positive advantages in terms of product quality, process optimization, and MFC/NFC costs (competitiveness).

Nevertheless, SW fibers remain an important element to confer strength and absorption properties especially in products with high requirements of these properties, such as towel papers or napkins. An approach of combining these three raw materials in tissue papers can also be considered to obtain a high-quality premium tissue paper with a combination of softness, strength, and absorption properties.

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III.2.3. An Innovative Computational Strategy to Optimize Different Furnish Compositions of Tissue Materials Using Micro/Nanofibrillated Cellulose and Biopolymer as Additives

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III.2.3.1. Abstract

The furnish management of tissue materials is fundamental to obtain maximum quality products with a minimum cost. The key fiber properties and fiber modification process steps have a significant influence on the structural and functional properties of tissue paper. In this work, two types of additives, a commercial biopolymer additive (CBA) that replaces the traditional cationic starch and micro/nanofibrillated cellulose (MFC/NFC), were investigated. Different formulations were prepared containing eucalyptus fibers and softwood fibers treated mechanically and enzymatically and both pulps with these two additives incorporated independently and simultaneously with drainage in the tissue process range. The use of these additives to reduce the percentage of softwood fibers on tissue furnish formulations was investigated. The results indicated that a maximum of tensile strength was obtained with a combination of both additives at the expense of softness and water absorbency. With a reduction of softwood fibers, the incorporation of additives increased the tensile strength and water absorbency with a slight decrease in HF softness compared with a typical industrial furnish. Additionally, a tissue computational simulator was also used to predict the influence of these additives on the final end-use properties. Both additives proved to be a suitable alternative to reduce softwood fibers in the production of tissue products, enhancing softness, strength, and absorption properties.

Keywords

Absorbency; Commercial biopolymer additive (CBA); Micro/nanofibrillated cellulose (MFC/NFC); Softness; Strength; Tissue paper materials

Inspired from Paper V:

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III.2.3.2. Introduction

In recent years, there has been great growth potential in the tissue paper market. Factors such as the abundance of fibrous raw materials, the high demand for hygiene and health products and the evolution of socio-economic living standards have promoted this global growth. In addition, advances in manufacturing technologies for these materials have made the market increasingly competitive (Raunio, Löyttyniemi and Ritala, 2018). Tissue paper materials are increasingly used in consumer goods products such as napkins, facial tissues, paper towels, toilet papers, diapers, and tissue masks. Tissue papers are produced to meet the desired properties for a specific application in the market such as a low basis weight, softness, strength, and absorption (de Assis et al., 2018a). To optimize the process, a great deal of effort has been made to improve the properties of the raw materials used in the production of these papers (Boudreau and Germgård, 2014; Raunio, Löyttyniemi and Ritala, 2018; de Assis et al., 2018a; de Assis et al., 2020). The highest quality tissue products are produced with a blend of hardwood and softwood fiber pulps. The production of tissue papers with 100% eucalyptus fibers generally presents a higher softness and absorption; however, the strength is degraded during the creping and converting processes in the tissue manufacture (Boudreau and Germgård, 2014; de Assis et al., 2020). Softwood fibers are introduced because these pulps provide strength to the papers and ensure the paper machine's runnability (Fišerová et al., 2019; Morais et al., 2019, 2020a; Stankovská et al., 2020). The fibers can also be subject to modification processes such as enzymatic and mechanical modifications. Refining is an important process in the development of functional tissue properties; however, it is associated with a large energy consumption (Gigac and Fišerová, 2008; Chang, Yu and Perng, 2018). The application of enzymes enhances not only the development of the tissue properties but also the reduction of energy costs associated with the refining process (Demuner, Junior and Antunes, 2011; Morais et al. 2021a).

In addition to the modification of fiber pulps, chemical additives are used to modify properties or improve the production process for different materials. Different chemical additives used in the tissue paper industry are designed and applied according to different needs such as dry strength agents, wet strength agents, softeners, and lotions (Park et al., 2014; Valencia, Valencia and Tovar, 2020). Usually, these additives are cationic as the fibers carry negative charges and they are also more effective in much lower concentrations than anionic polymers. Nevertheless, these cationic additives normally adhere in excess to the paper, negatively affecting the creping process and the product quality (Valencia, Valencia and Tovar, 2020). The addition of strength agents can ensure that tissue products remain integrated when applied in wet conditions while the addition of debonding agents can improve the softness and bulk of these products (Chan, Woods and Salaam, 2011; Siqueira et al., 2015; Adhikari et al., 2016; Miller et al., 2014, 2016; Chen, Zhang and He, 2018; Zhang et al., 2020). However, reaching a balance between these two properties is a challenge because the conditions that maximize the softness are those that minimize strength properties. This balance can be achieved by selecting fibers, refining treatments, and adding chemical polymers.

Therefore, the tissue manufacturer must balance these factors in terms of cost and effect. The tissue paper industry provides the design, development, and production of many chemical and polymeric additives (Ginebreda et al., 2011).

The application of innovative and versatile additives such as biopolymers and micro/nanofibrillated cellulose (MFC/NFC), replacing synthetic additives currently used, is a sustainable strategy to be considered in order to produce high-quality tissue premium products with innovative features. Biopolymers as additives can be new natural and green approaches to new possibilities and advances in modifying or improving the final end-use tissue properties (Shen, Fatehi and Ni, 2014). The same is true for MFC/NFC as an additive that has been extensively investigated for its application in tissue products due to its high specific surface area, excellent mechanical properties, flexibility, biocompatibility, biodegradability and lack of toxicity, among other properties (Guan, An and Liu, 2019; Patiño-Masó et al., 2019; Zambrano et al., 2021; Morais et al., 2021b). The furnish formation is also affected by the MFC/NFC incorporation as an additive. MFC/NFC decreases porosity and air permeability when added to the tissue structures. MFC/NFC content and structural changes present a proportional behavior. These decreases are caused by the MFC/NFC bonding with the cellulose fibers in the 3D net-work structures, closing the porous structure. Furthermore, this reduction in porosity is also correlated with the increase in the structure's apparent density (Zambrano et al., 2020).

The presence of MFC/NFC can present an impact on the structure porosity because of the increasing number of hydrogen bonds present in this nanocellulose. The increase of these bonds is related to its increase in the surface/volume ratio due to the nanosized scale (Zambrano et al., 2020). By filling the large pores created by the 3D fiber network, the MFC/NFC incorporation contributes to smaller pore dimensions and a narrower distribution of the structures, providing abundant pores with a uniform size and, consequently, a decrease in the properties of water absorption capacity and capillarity penetration (Guan, An and Liu, 2019; Morais et al., 2021b). The flexibility of MFC/NFC can be a filler for large pores in structures (Guan, An and Liu, 2019). Although the mechanical properties of tissue products are improving, MFC/NFC also brings a difficulty to the dewatering of papermaking furnishes. The fibrillation degree influences the dewatering capacity of pulp suspensions. The drainage time increases depending on the MFC/NFC fibrillation degree. Particles resulting from fibrillation are more easily incorporated into the fiber network, partially closing the pores between the fibers and consequently limiting the wet network's ability to drain water. This drainage difficulty is also caused by the increased water retention capacity of MFC/NFC. However, this dewatering of pulp suspensions containing MFC/NFC can be improved with the use of retention aids and also with cationic starch-treated MFC/NFC with colloidal silica (Zambrano et al., 2020). In addition to a negative impact on dewatering, the accumulation of MFC/NFC particles in the closed circuit of the tissue machine can increase the viscosity of the recirculating water, thus affecting processability. Therefore, there is a need to study the feasibility of using MFC/NFC to reduce the fiber content.

Our study (Morais et al., 2021b) confirmed that the use of 1 to 8% of MFC/NFC incorporated into tissue paper formulations, along with a reduction of hardwood and softwood fiber content, achieves a trade-off between the final end-use tissue properties and fiber blend costs, with drainability between 26 and 32°SR (Schopper–Riegler degree). In this range of drainability, the furnish formulations are able to produce high-quality tissue papers without difficulties in tissue paper machine runnability and efficiency (de Assis et al., 2018a; Morais et al., 2021b).

The application of these additives leads to the optimization of strength properties without compromising the softness and absorbency properties of these types of papers. These strategies can allow a reduction of softwood fibers in the production of tissue paper without affecting the strength performance and decrease the overall tissue manufacturing cost (González et al., 2012; de Assis et al., 2018c; Zambrano et al., 2020, 2021; Morais et al., 2021b). The aim of this work was to perform a comparative study between different tissue furnish compositions and the incorporation of two additives, a commercial tissue biopolymer additive (CBA) as a cationic starch substitute and MFC/NFC, and their effect on the properties of the final end-use tissue paper. For this purpose, the fiber and suspension drainability characterizations of different investigated samples were performed. Laboratory isotropic structures with a light basis weight of 20 g/m² were prepared and the softness, tensile strength and absorbency properties were evaluated.

III.2.3.3. Materials and Methods

III.2.3.3.1. Materials

An industrial, never-dried, bleached eucalyptus kraft pulp (HW) and an industrial, air-dried, bleached Pinus kraft pulp (S_G) were used in this work after disintegration according to ISO 5263-1. The additives used in this study were CBA and MFC/NFC. This commercial tissue additive, CBA, is a cationic polymeric solution specially designed as a replacement for cationic starch. CBA presents a viscosity of 500–900 cP, a pH of 2.1–4.0 and a density of 1.030 ± 0.040 g/cm³ at 20 °C (data supplied by a commercial enterprise). MFC/NFC was supplied by a research institute and obtained by mechanical (refining and homogenization) and enzymatic (cellulase) treatments using an industrial bleached eucalyptus kraft pulp. This sample was characterized in our previous work, which can be used for more detailed information (subchapter III.2.2., and Morais et al., 2021b). MFC/NFC (Figure III.27) presents an intrinsic viscosity of 1577 mL/g (ISO 5351), a carboxyl group content of 8.4 ± 0.2 mmol/100 g (TAPPI T 237 om-93), a suspension drainability degree superior to 80°SR (Schopper–Riegler) and 56% of particles below 1000 nm, representing 10% of particles below 200 nm (Morais et al., 2021b).

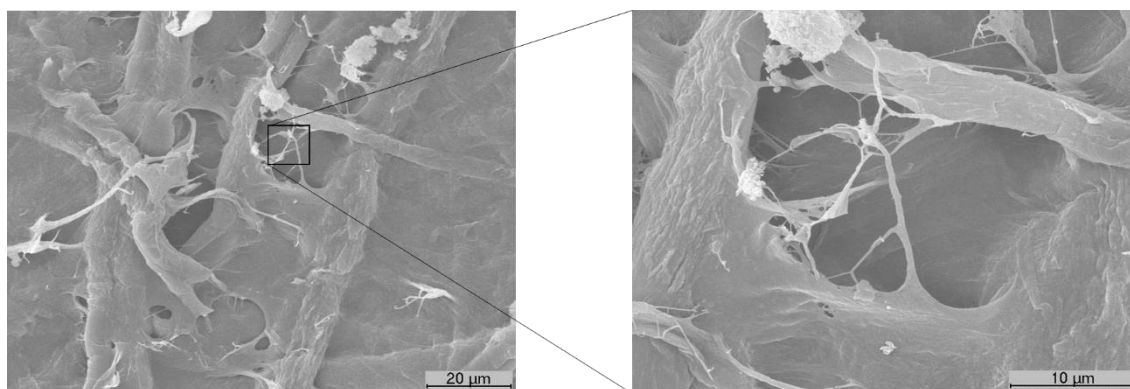


Figure III.27. SEM image of the MFC/NFC additive, highlighting a high magnification image (3000×) where it is possible to verify the micro and nanofibrils of this sample.

III.2.3.3.2. Enzymatic and Mechanical Treatments

The softwood pulp was beaten in a PFI mill at 4000 revolutions under a refining intensity of 3.33 N/mm (ISO 5264-2) followed by an enzymatic treatment. The enzymatic treatment was performed according to the method described by Morais et al. (2021a). The treatment was carried out at a consistency of 4% at pH 7 at 40°C with continuous mechanical agitation to ensure an efficient mass transfer for 60 min and 30 mg of enzyme/g of pulp.

III.2.3.3.3. Tissue Formulations

Table III.19 presents the various tissue formulations (investigated samples) carried out in this study. The different formulations were performed to study the effect of additives in the tissue structure properties and understand their implication in the reduction of softwood pulp usually used in this type of paper. The first formulation presents a similar combination of eucalyptus fibers and softwood fibers typically used in tissue mills. All of the samples presented similar drainability properties around 25 °SR, which is recommended for tissue paper products and means that drainage and processability are in the range for the tissue process and, consequently, processability is not negatively impacted (de Assis et al., 2018a).

Table III.19. Tissue formulations used in the study.

	Eucalyptus Pulp (HW)	Softwood Pulp (S_G) with Mechanical and Enzymatic Treatment	Commercial Biopolymer Additive (CBA)	Micro/ Nanofibrillated Cellulose (MFC/NFC)
Formulation 1	75%	25%	-	-
Formulation 2	75%	25%	2%	-
Formulation 3	75%	25%	-	2%
Formulation 4	75%	25%	2%	2%
Formulation 5	90%	10%	-	-
Formulation 6	90%	10%	2%	-
Formulation 7	90%	10%	-	2%
Formulation 8	90%	10%	2%	2%

III.2.3.3.4. Preparation of Tissue Structures

The tissue structures were produced in a batch laboratory sheet former according to the method described by Morais et al. (2019, 2020a). An adaptation to ISO 5269-1 was used, namely, the suppression of the pressing operation and the production of structures with a basis weight of 20 g/m². The tissue structures were prepared with the different formulations described in Table III.19. Finally, all samples were conditioned at 23±1 °C, with a relative humidity of 50±2 %, according to ISO 187.

III.2.3.3.5. Characterization of the Morphological, Drainability and Chemical Properties

The morphological properties of pulp fibers and formulations were evaluated automatically by an image analysis using a fiber analyzer, the MorFi equipment (TECHPAP, Grenoble, France).

In order to characterize the surfaces of the different formulations, the obtained tissue structures were coated with gold using a Sputter Quorum Q 15 OR ES (Laughton, East Sussex, UK) to be analyzed by scanning electron microscopy (SEM) using a Hitachi S-2700 model (Tokyo, Japan) with an accelerating voltage of 20 kV at different magnifications. ImageJ, an image analysis software, was also used to characterize the pore properties of the samples. The SEM images were processed and analyzed using a methodology with defined criteria for the stabilization of the average of the measured values (Hotaling et al., 2015).

The chemical functional groups were analyzed using Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) at a wavelength of 600–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

The drainability of pulp suspensions and formulations was evaluated by the °SR method (ISO 5267/1). Triplicate assays were performed for both methods.

III.2.3.3.6. Characterization of the Tissue Properties

III.2.3.3.6.1. Structural Properties

The structures produced were characterized in terms of basis weight (ISO 12625-6), thickness and bulk (ISO 12525-3). The basis weight was obtained by the quotient between the average mass of each structure and the respective area (0.02138 m²). The thickness was obtained using a Frank-PTI micrometer. The bulk was obtained by the quotient between the thickness and the basis weight of the structures. Additionally, the porosity (apparent theoretical porosity) of the structure was also calculated according to the following equation:

$$Porosity (\%) = \frac{1 - \rho_{structures}}{\rho_{cellulose}} \times 100 \quad (III.4)$$

where $\rho_{cellulose}$ was the density of the cellulose (1.5 g/cm³) (Morais et al., 2021a) and $\rho_{structure}$ was the apparent density of the structures (g/cm³).

III.2.3.3.6.2. Softness Properties

Softness was assessed using a Tissue Softness Analyzer, the TSA (Emtec). A two-step measurement was used. The first was a noise measurement where the real softness (TS7) was measured. The second step was a deformation measurement where stiffness, plasticity, elasticity and hysteresis were measured. The handfeel (HF) parameter value was calculated using both steps.

III.2.3.3.6.3. Strength Properties

Strength properties were determined according to ISO 12625-4 using the tensile index and calculated according to the following equation:

$$Tensile\ Index\ (Nm/g) = \frac{break/W}{G} \quad (III.5)$$

where *break* was the breaking force (N), *W* was the sample width (50 mm) and *G* was the sample grammage or basis weight (g/m²).

III.2.3.3.6.4. Absorbency Properties

The absorbency properties were determined by the methods of water absorbency capacity per unit of mass and Klemm capillary rise.

The immersion absorption method was used to determine the water absorption capacity per unit of mass of the samples. The assay was carried out according to an adaptation of ISO 12625-8. The sample was immersed for 30 s. At the end of that time, the sample was removed from the water and left to run on a support that guaranteed an amplitude of 30° for approximately 1 min.

Finally, the amount of water that the sample was able to absorb during this time was determined. The assay was performed in triplicate for each sample.

The Klemm capillary rise method was measured through an adaptation of ISO 8787. The assay consisted of the water rising in the sample (50 mm wide) at a certain time. The capillary rise was recorded at 10, 20, 30, 60, 180, 300 and 600 s. Four readings were performed for each sample. All of the assays were performed in a controlled temperature and humidity laboratory.

III.2.3.3.7. Computational Studies

SimTissue, a tissue simulator, was developed specifically for furnish management and optimization by FibEnTech-UBI members, in the scope of Project InPaCTus. This tissue simulator was used to compare different end-use final tissue properties and to access them for the different formulations to those performed experimentally (Morais et al., 2021b).

A 3D fiber-based computational simulator was used to model the tissue structures as planar random networks. This simulator is open-source software, and the code is available on GitHub (<https://github.com/eduardotrincaoconceicao/voxelfiber>, accessed on April, 2021). A more detailed description of this 3D simulator can be found in Conceição et al., (2010) and Curto et al., (2011). The fibers are represented by a voxel chain and modeled according to fiber dimensions and properties such as the fiber length and width ratio, flexibility, fiber wall thickness and lumen dimensions (Morais et al., 2020b). The structural properties were obtained following this computational study and the resulting 3D computational structures. The computational studies were performed using Matlab® (R 2020a, 9.8.0.1323502, Math-Works, Natick, MA, USA).

III.2.3.4. Results and Discussion

III.2.3.4.1. Characterization of Pulp Fibers and Tissue Formulations

In a first approach, the characterization of the raw materials used in the study was carried out. The HW pulp presented a length weighted by length of 0.729 ± 0.003 mm, a width of 19.1 ± 0.0 μ m, a coarseness of 6.31 ± 0.04 mg/100m and fine elements of $38.5 \pm 0.4\%$ in length. The softwood pulp presented a length weighted by length of 1.889 ± 0.052 mm, a width of 30.1 ± 0.2 μ m, a coarseness of 20.52 ± 3.23 mg/100m and fine elements of $36.6 \pm 4.2\%$ in length. In this study, only S_G pulp was subjected to fiber modification treatments, namely, refining and enzymatic treatments, as this eucalyptus pulp is already an industrial pulp suitable for the production of tissue papers. These treatments were carried out in order to improve fiber flexibility and inter-fiber bond properties with a greater strength three-dimensional matrix (de Assis et al., 2018b). Analyzing the treatments separately, the refining effect was more pronounced than the enzymatic treatment. The results indicated that refining decreased the length weighted by length by 8% and coarseness by 30% and increased the fiber width by 7% and the fine content by 17% while the enzymatic treatment decreased the fiber length weighted by length by 2% and the coarseness by 18% and increased the fiber width by 23% and the fine content by 4%. The combination of these two treatments decreased the fiber length weighted by length by 10% and the coarseness by 26% and increased the fiber width by 7% and the fine content by 11% compared with the untreated pulp. Figure III.28 presents an analysis of coarseness as a function of the length/width ratio (slenderness ratio) for the S_G samples. The results indicated that two groups can be considered with the fiber modification treatments applied. In the first one, the softwood fibers without treatment (63 of length/width ratio and 20.52 mg/100m of coarseness) and with enzymatic treatment (61 of length/width ratio and 16.92 mg/100m of coarseness) presented a higher slenderness ratio and higher coarseness. In the second group, the refined softwood fibers (54 of length/width ratio and 15.81 mg/100m of coarseness) and with both treatments (52 of length/width ratio and 15.09 mg/100m of coarseness) presented a lower slenderness ratio and lower coarseness. This suggests that the first group was more susceptible to presenting better tissue properties of softness and absorbency than the second group, which was more susceptible to presenting higher strength properties (Morais et al., 2020a). Additionally, the first group presented °SR between 12–14 and the second group presented 55–66 °SR.

The mechanical refining and the combination of both treatments promoted a more efficient fiber fibrillation and consequently decreased the suspension drainability.

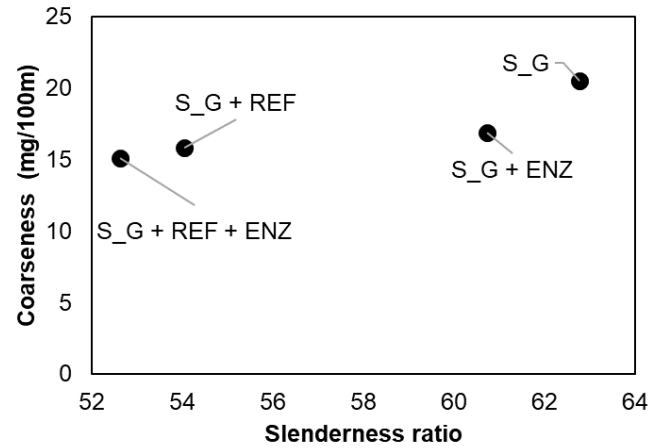


Figure III.28. Coarseness as a function of the slenderness ratio of softwood fiber pulp (S_G) with enzymatic treatment (S_G + ENZ), with refining (S_G + REF), and with the combination of both fiber modification treatments (S_G + REF + ENZ).

The S_G pulp with the refining and enzymatic treatment was also assessed through SEM images (Figure III.29a). This treatment made it possible to modify the properties of the softwood pulp, promoting inter-fiber bonds and the combination of key structural properties such as the pore dimension and distribution. The pore properties depend on the fiber properties and the mechanical and enzymatic processes to which they are subjected (Martins et al., 2018). The results indicated that these treatments had an impact on the fiber dimension and flexibility, resulting in a structure with a surface porosity of $83 \pm 1\%$ and a pore diameter distribution of 35% between 2 and 10 μm and 65% between 10 and 27 μm (Figure III.29b).

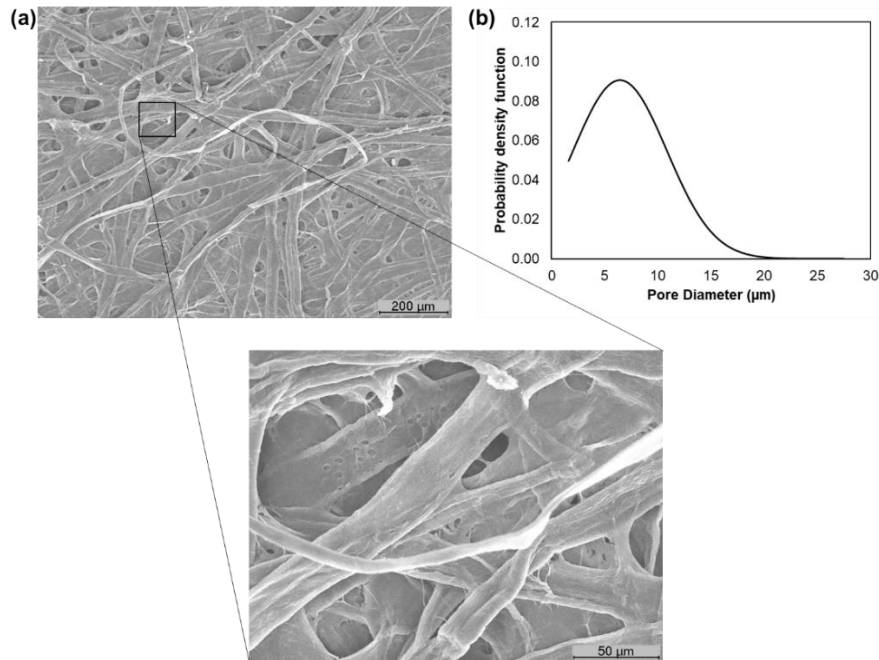


Figure III.29. SEM image of the S_G pulp with refining and enzymatic treatment with a high magnification image (500 $\times$) (a) and its pore diameter distribution (b).

In a second approach, the characterization of the tissue formulations was carried out. As previously reported, this study compares two versatile additives: CBA and MFC/NFC. The MorFi analyzer is only able to evaluate the fiber suspension properties, so the presence of the CBA does not affect its fibrous composition. The formulations with 75% HW pulp and 25% S_G pulp-treated and with incorporated additives presented a length weighted by length between 0.717 and 0.729 mm, a width between 19.4 and 19.9 μm , coarseness between 7.78 and 8.27 mg/100m and fine elements between 32.7 and 35.7% in length. With a reduction of the softwood fibers, the formulations with 90% HW pulp and 10% S_G pulp-treated and with incorporated additives presented a length weighted by length between 0.719 and 0.722 mm, a width between 19.1 and 20.1 μm , coarseness between 6.77 and 7.61 mg/100m and fine elements between 30.4 and 32.8% in length. Additionally, these formulations presented an $^{\circ}\text{SR}$ degree between 20 and 25 $^{\circ}\text{SR}$. Although the softwood pulp presented low drainability, its combination with eucalyptus pulp and with different additives allowed the tissue formulations to present a range of $^{\circ}\text{SR}$ s suitable of producing premium tissue materials (de Assis et al., 2018a) without compromising the processability. Figure III.30 presents the SEM image of the formulation 4 (75% HW pulp + 25% S_G pulp-treated + 2% CBA + 2% MFC/NFC) as well as its pore diameter distribution. The 3D structure matrix resulting from this formulation was presented as a multi-structured material with bonding between MFC/NFC fibrils and pulp fibers. The CBA addition also promoted a more closed structure with a surface porosity of $88 \pm 1\%$ and a pore diameter distribution of 40% between 1 and 10 μm and 60% between 10 and 22 μm (Figure III.30b).

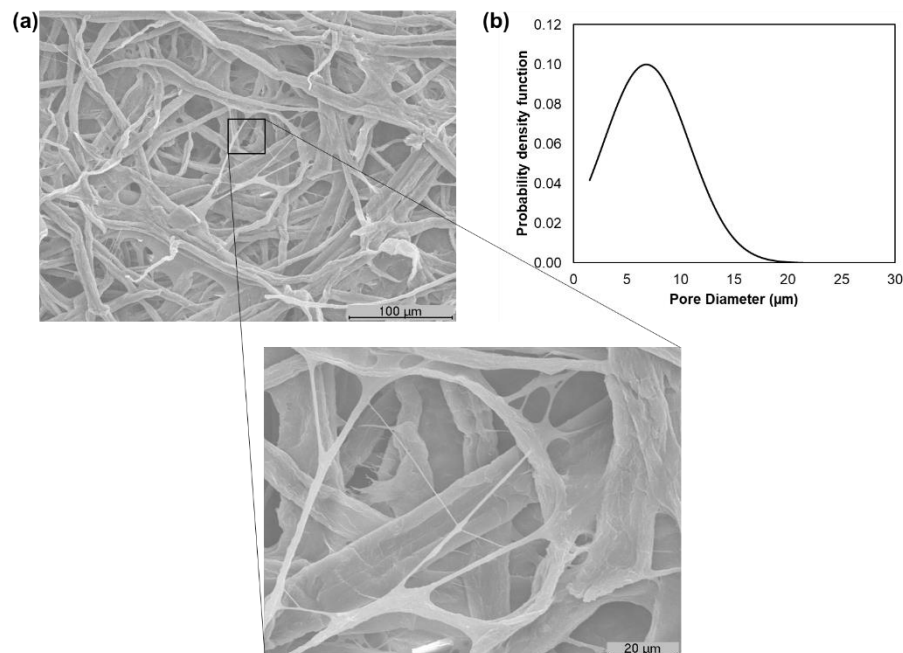


Figure III.30. SEM image of tissue formulation 4 (75% HW pulp + 25% S_G pulp-treated + 2% CBA + 2% MFC/NFC) with a high magnification image (1000 $\times$) where is possible to verify the inter-fiber bonding between MFC/NFC and the structure in more detail (a) and its pore diameter distribution (b).

To complement this study, the FTIR-ATR technique allowed us to chemically characterize, identify and quantify the formulations with CBA and MFC/NFC, evaluating the existence of physical retentions in the structure without new chemical bonds between these additives and the cellulose eucalyptus and softwood fiber 3D matrix. Figure III.31 shows the FTIR spectrum of formulation 1 (a typical furnish mixture at a tissue mill), formulation 2 (with CBA incorporation) and formulation 3 (with MFC/NFC incorporation). The typical absorption bands of hydroxyl groups between 3000 and 3500 cm^{-1} indicative of the $-\text{OH}$ stretching of the intra- and inter-molecular interactions of hydrogen bonds were verified for the three formulations. A $-\text{OH}$ band with a higher area was observed for the structures with CBA. The biggest differences in the FTIR spectrum were found in the bands between 2800 and 3000 cm^{-1} . This range corresponds with the $=\text{C}-\text{H}$ stretching in the methyl groups of cellulose and hemicellulose. The band with the highest intensity in this range was observed for the formulation with MFC/NFC followed by the formulation with CBA and formulation 1. Additionally, the bands between 2200 and 2400 cm^{-1} correspond with the $-\text{OH}$ asymmetrical stretching vibration of the carboxylic acid due to the enzymatic treatment applied to the materials (Morais et al., 2021a). The bands between 1500 to 1700 cm^{-1} were due to the $\text{C}=\text{O}$ stretch of hemicelluloses. Other characteristics of cellulose were also observed between 800 and 1500 cm^{-1} such as the angular deformation of $\text{C}-\text{H}$ and primary alcohol $\text{C}-\text{O}$ bonds, the absorption band of $\text{C}-\text{O}-\text{C}$ bonds, the β -glycosidic bonds between glucose units, $\text{C}=\text{H}$ stretching, $\text{C}=\text{O}$ stretch vibration in the syringyl ring and carboxylate ion group vibration.

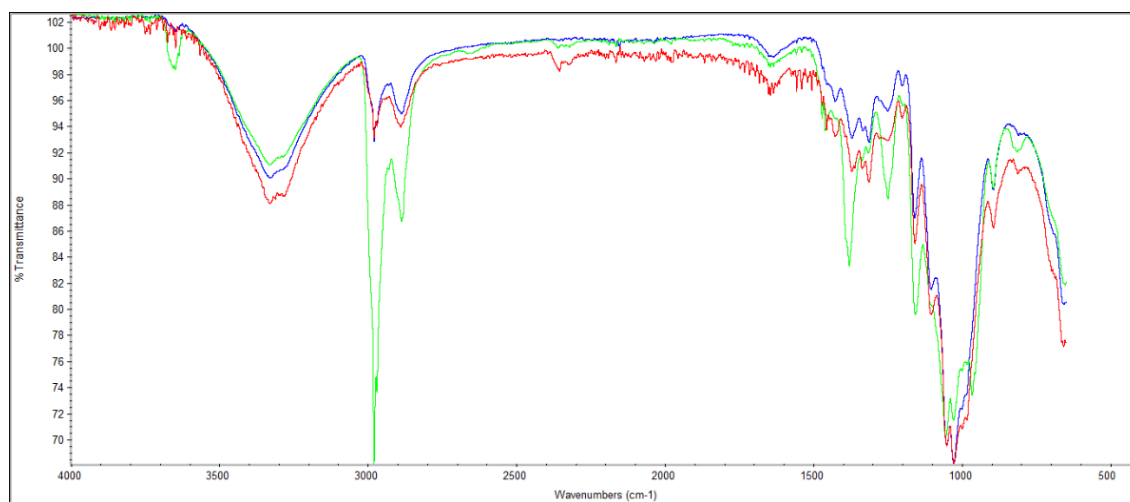


Figure III.31. FTIR-ATR spectrum of formulation 1 (blue), formulation 2 (red) and formulation 3 (green).

III.2.3.4.2. Characterization of the Properties of the Final End-Use Tissue

III.2.3.4.2.1. Structural Properties

Bulk and porosity are essential parameters for the quality of tissue products that influence the softness and liquid absorption properties (Morais et al., 2019,2020a). Figure III.32a shows, for the different tissue formulations, the behavior of the structural properties.

The addition of CBA in formulation 2 promoted a decrease in bulk and porosity by 1% and 0.1%, respectively, compared with formulation 1. The addition of MFC/NFC (formulation 3) showed a tissue structure with lower bulk (<4%) and porosity (<0.5%) compared with formulation 1. The combination of these versatile additives (formulation 4) also promoted an increase of hydrogen and inter-fiber bonds, inducing a decrease of 11% in bulk and 1% in porosity of the tissue structures in comparison with formulation 1. This densification effect can be observed in the cross-section of the structures, as shown in Figure III.33. With the reduction of the reinforcement fibers by 15% in the formulations, bulk and porosity were increased. This reduction promoted an increase of 20% in bulk and 2% in porosity when comparing formulations 1 and 5. The same trend in formulations 1–4 was observed in formulations 5–8; i.e., the combination of both additives presented a higher influence on the structural properties followed by MFC/NFC and CBA. Formulations 6, 7 and 8 promoted a reduction in bulk by 4, 10 and 22%, respectively, and a reduction in porosity by 0.4, 1 and 3%, respectively, compared with the control (formulation 5). The addition of both CBA and MFC/NFC in formulations with a softwood fiber reduction (90% eucalyptus fiber and 10% softwood fiber) allowed the obtaining of structures with increased structural properties compared with typical industrial structures (75% of HW fiber and 25% S_G fiber). The results indicated that formulations 6 and 7 increased the structure bulk by 16% and 9%, respectively, compared with formulation 1 (Figure III.34). However, the combination of these two additives promoted a 6% reduction in bulk compared with this formulation typically used industrially.

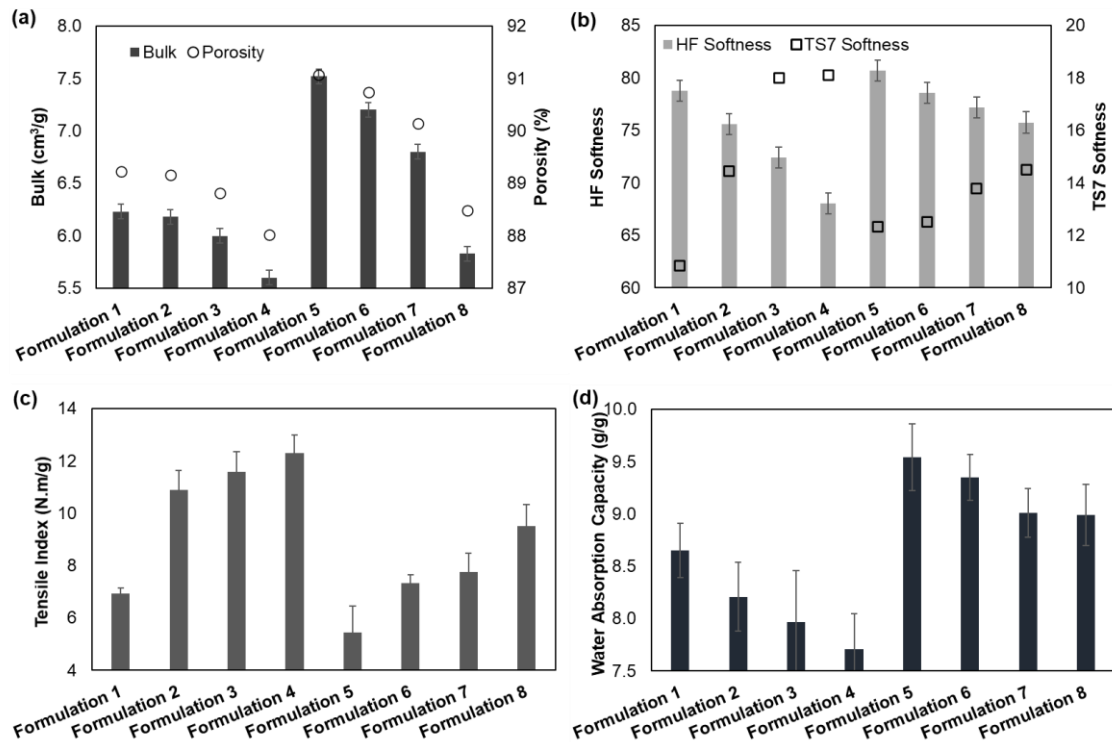


Figure III.32. Properties of bulk and porosity (a), softness (b), tensile index (c), and water absorption capacity per unit of gram (d) of all tissue formulations.

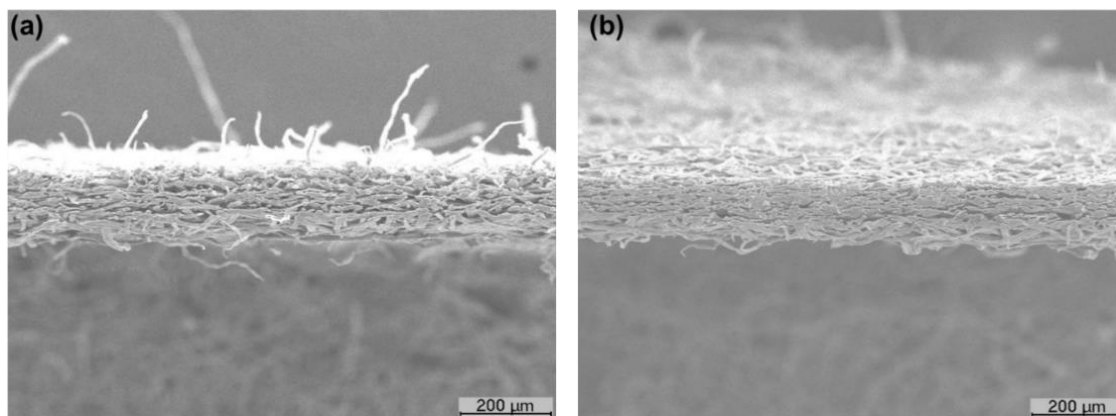


Figure III.33. SEM images of the cross-section of the tissue structures prepared with formulation 1 (a) and formulation 4 (b).

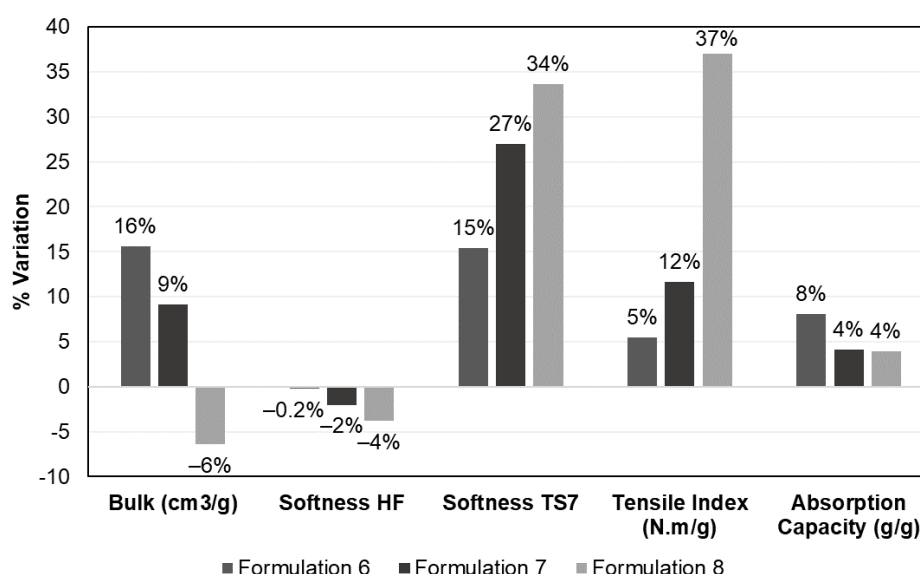


Figure III.34. Percentage of variation in the properties of bulk, softness HF, softness TS7, tensile index, and water absorption capacity of formulations 6, 7, and 8 compared with formulation 1 obtained with *SimTissue*.

III.2.3.4.2.2. Softness Properties

Softness is also a characteristic that is highly appreciated by consumers, resulting in the combination of structure flexibility, bulk, and surface softness. Softness properties of the different formulations are shown in Figure III.32b. The HF (handfeel) values decreased with the additives loaded in the paper 3D matrix. The increase in fiber flexibility, fine elements and, consequently, the number of inter-fiber bonds promoted a more closed and compact 3D matrix with less bulk, resulting in a structure with less softness. The addition of CBA in formulation 2 promoted a decrease in softness HF by 4% compared with formulation 1. The addition of MFC/NFC (formulation 3) showed a tissue structure with lower softness compared with formulation 1 with a decrease of 8%. The combination of these versatile additives (formulation 4) also promoted a decrease of 14% in the softness HF of the tissue structure compared with formulation 1.

The reduction of the reinforcement fibers in the formulations increased softness properties by 2% compared with formulations 1 and 5. As with bulk properties, the same trend was also observed for softness properties. Formulations 6, 7 and 8 promoted a reduction in softness by 3%, 4% and 6%, respectively, compared with formulation 5. Regarding Figure III.34, the softness HF values decreased by 0.2%, 2% and 4% with the incorporation of CBA, MFC/NFC, and the combination of both, respectively. The production of structures with a low content of S_G fibers and versatile additives promoted a small reduction in softness, improving strength properties, as reported below, contributing to the formation of a fibrous structure with less stiffness (Trepanier, 2017).

Softness TS7 is inversely related to softness HF values; therefore, it is influenced by the presence of fibers in the structure surface. TS7 values increased with the addition of additives in the structure (Figure III.32b). This result indicated that the fibers in the structure presented higher bonds, causing structure densification and rigidity. The fibers in the z-direction were more adherent to the paper structure, reducing the number of free fibers on the tissue surface compared with the structures without additives (Figure III.33). Compared with formulation 1, softness TS7 of the tissue structure increased by 33%, 65% and 67% with the incorporation of CBA, MFC/NFC, and both, respectively (formulations 2–4). With the reduction of the reinforcement fibers in the formulations, this property also increased by 13% compared with formulations 1 and 5. Additionally, formulations 6, 7 and 8 promoted an increase in softness TS7 by 2%, 12% and 18%, respectively, compared with formulation 5. Compared with formulation 1 (75:25), softness TS7 increased by 15%, 27% and 34% with the incorporation of CBA, MFC/NFC, and both, respectively, in formulations with a softwood fiber reduction (90:10) (Figure III.34).

III.2.3.4.2.3. Strength Properties

The tensile index is an essential parameter not only for the product quality but also to ensure the paper machine runnability, which depends on the fiber intrinsic strength and the inter-fiber bonds. The results of the tensile index for each tissue formulation are shown in Figure III.32c. The incorporation of additives promoted an increase in the tensile index of the tissue structures. Differences in strength improvements varied with the performance of CBA and MFC/NFC and became more noticeable with the combination of these additives. Formulation 3 with the addition of MFC/NFC showed improvements in the tensile index (+67% compared with formulation 1) related to formulation 2 with the addition of CBA (+57% compared with formulation 1). Formulation 4, with the incorporation of both additives, presented higher structure strength improvements by 77% compared with formulation 1. This result was corroborated by the results of the literature as the addition of MFC/NFC and chemical additives in the tissue structures improve strength properties of these products (Guan, An and Liu, 2019; Park et al., 2019; Zambrano et al., 2021). These additives promoted an increase in the surface area of the tissue structures due to the micro/nanofibrils and consequently formed stronger and more stable structures through inter-fiber interaction and hydrogen bonding (Zambrano et al., 2021). This fact can also be verified by the densification of the tissue structures with the incorporation of both additives (Figure III.33b).

Reinforcement fibers play a fundamental role in strength properties; therefore, the reduction of these fibers in formulation 5 promoted a 21% reduction of the tensile index compared with formulation 1. Additionally, formulations 6, 7 and 8 promoted an increase in the tensile index by 34%, 42% and 74%, respectively, compared with formulation 5. It is important to highlight that the strength gains obtained with the addition of MFC/NFC and CBA and the softwood reduction in the tissue structures were higher when compared with formulation 1. Despite the structures presenting a low basis weight and no pressing, these additives favored strength properties of these tissue structures. Additionally, as shown in Figure III.34, the tensile index increased by 5%, 12% and 37% with the incorporation of CBA, MFC/NFC, and both, respectively.

The commercial biopolymer additive used in this work was a cationic polymeric solution that is especially intended to be a substitute for cationic starch. Generally, cationic starch is used in the printing and writing paper industry with functions of a dry strength additive, emulsification of sizing agents, retention, and drainage. This starch improves the formation, internal bonding, surface strength, tensile strength, writing and printing surface and energy consumption (Maurer, 2009). However, in the tissue paper industry, this starch has several inconveniences as the increase in strength properties promotes an abrupt reduction in softness properties. A solution found in the tissue industry was to design a practically constant biopolymer that would increase strength properties while preserving softness properties with a reduction of softwood fiber content. Furthermore, this additive allows the reduction of the contaminating organic load and costs as a result of reducing the use of cationic starch (Maurer, 2009). Therefore, the results of this work indicated that, compared with formulation 1, a typical industrial mixture can produce tissue structures containing 2% of the CBA and 10% of softwood fibers with 5% tensile index increases while maintaining the softness (Figure III.34). This cationic polymeric solution also improved the inter-fiber bonding and MFC/NFC particle retention. This retention was proven by the 38% increase in strength properties with both additives (formulation 8) compared with formulation 1. The incorporation of MFC/NFC alone (formulation 7) only increased strength properties by 12% compared with formulation 1 (Figure III.34).

In addition, an inverse relationship between the properties of softness and strength can also be observed in these formulations (Figure III.35); i.e., strength improvements present a negative impact on the tissue structure softness. The formulations promoted an increase of 1.52 units of softness HF for each unit with a decreased tensile index ($y = -1.52x + 89.51$; $R^2 = 0.89$). In our previous studies, this relationship was also observed in formulations with only eucalyptus fibers and without additives in which the softness HF increased by 2.4 units per unit of the decreased tensile index (Morais et al., 2019,2020a). This can contribute to the reduction of costs associated with the use of softwood fibers in industrial furnishes as there is a balance between the properties of softness and strength in the tissue structures with the use of these versatile additives.

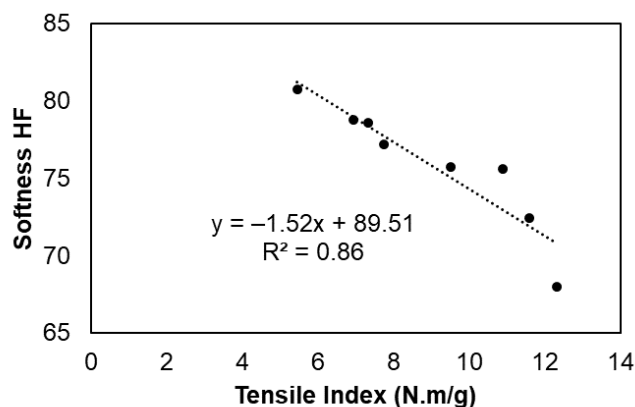


Figure III.35. Correlation between the tensile index and softness HF of tissue formulations.

III.2.3.4.2.3. Absorbency Properties

Absorbency properties are essential in tissue products, mainly in paper towels and napkins, depending on their fibrous structure. Tissue products with a more porous 3D matrix will present better water absorption as empty spaces for water interaction are more available (Morais et al., 2021a). Figure III.32d presents the water absorption capacity of the tissue formulations in the study. Overall, the incorporation of CBA and MFC/NFC into the tissue formulations decreased the water absorption properties compared with the control. This result was also in line with the decrease in bulk and porosity properties (Figure III.32a). This effect was observed from the SEM images in Figures III.30a and III.33b in which the formulations with these additives presented a less porous surface with a more compact cross-section. The addition of CBA and MFC/NFC (formulations 2 and 3) presented a decrease of 5% and 8% of this property, respectively, compared with formulation 1. The incorporation of both additives presented higher absorption decreases by 11% compared with formulation 1. The reduction of the reinforcement fibers in the formulations also increased the absorption properties by 10% compared with the formulations 1 and 5. Additionally, formulations 6, 7 and 8 promoted a reduction in absorption by 2%, 6% and 6%, respectively, compared with formulation 5. Compared with formulation 1, absorption increased by 8%, 4% and 4% with the incorporation of CBA, MFC/NFC, and both, respectively, in formulations with a softwood fiber reduction (90:10) (Figure III.34). In this work, we also found a good linear correlation ($R^2 = 0.78$) between the water absorption properties and the softness of the tissue structures made from these formulations (Figure III.36a). The formulations promoted an increase of 5.39 units of softness HF for each unit of increased water absorption capacity ($y = -5.39x + 29.06$). The same inverse trend observed for the softness and strength properties was also verified for the absorbency and strength properties (Figure III.36b). The tissue formulations promoted an increase of 3.37 units of water absorption capacity for each unit of decreased tensile index ($y = -3.37x + 38.19$; $R^2 = 0.81$).

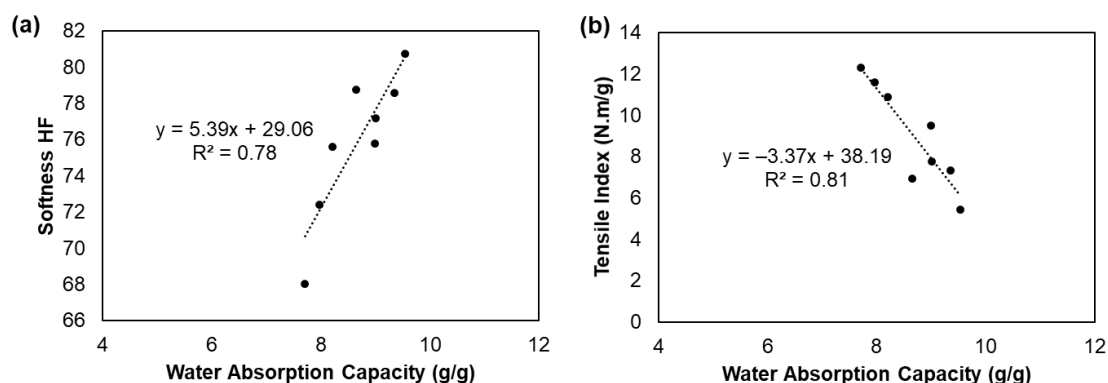


Figure III.36. Correlation between the water absorption capacity and softness HF (a) and tensile index (b) of the tissue formulations.

The capillary rise of the structures depends on the adhesion and cohesion forces of the water molecules that ascend through the fiber walls or between the pores. Therefore, there must be a balance between the pore dimensions to promote the capillary rise efficiency. Inter-molecular bonds between fibers and water molecules in structures with higher pores can impair the capillary rise. On the other hand, in the case of channels that are too narrow, the water progression will be strangled by the limited space for capillary rise (Beuther, Veith and Zwick, 2010). Figure III.37 presents the Klemm capillary rise of the tissue formulations in this study. The same trend in the water absorption properties was observed in the capillary rise of tissue formulations. The formulations with a content of fewer softwood fibers presented better capillary ascents and the additives promoted the capillary rise decrease. The structures with a higher bulk and a more porous 3D matrix promoted a higher capillary rise. Comparatively of both additives, CBA promoted a better water affinity compared with MFC/NFC, corresponding with water capillary rise improvements.

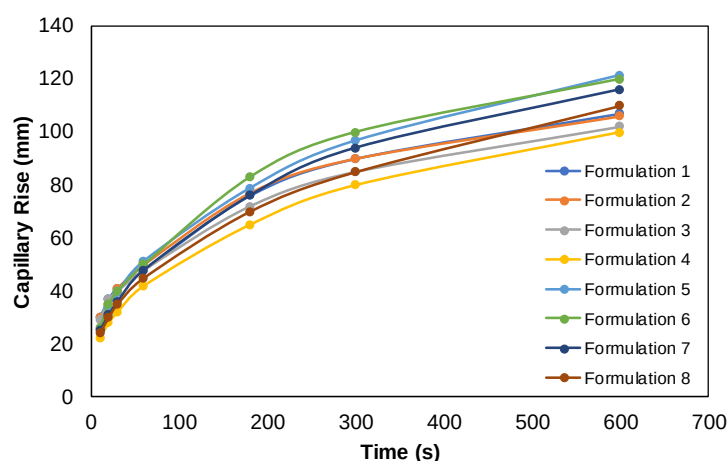


Figure III.37. Klemm capillary rise method as a function of time for all tissue formulations.

These results indicated that a compromise could be found between the properties of softness, strength, and absorbency with the incorporation of versatile additives in tissue formulations, reducing the incorporation of softwood fibers in an industrial furnish.

This effect could promote a reduction in costs associated with the use of these fibers and also the mechanical and enzymatic refining applied to softwood fibers as the incorporation of these additives promoted structure strength improvements while maintaining the softness.

III.2.3.4.3. Computational Prediction of the CBA and MFC/NFC Performance in Formulations with 100% Eucalyptus Fibers

The high manufacturing costs associated with tissue paper materials are due to the market softwood pulp prices and the energy consumption associated with the fiber modification processes such as refining or beating. Finding strategies to reduce these processes is one of the focuses of the research on the management and optimization of the furnish and each type of tissue product. For this reason, we developed a tissue simulator, *SimTissue*, with the ability to predict the final end-use properties of different hypothetical scenarios of industrial interest. Our approach in this study was to estimate improvements in tissue properties with the incorporation of CBA and MFC/NFC, separately, in formulations with 100% eucalyptus fibers compared with formulations containing eucalyptus fibers and softwood fibers (Figure III.38). Note that these simulations were carried out with a reinforcing fiber with high strength properties (SW, presented in subchapter III.2.2), according to a set of pulps studied previously (Morais et al., 2019,2020a). It is important to present the simulations of these fiber mixtures as they represent the limits achievable in the tissue properties.

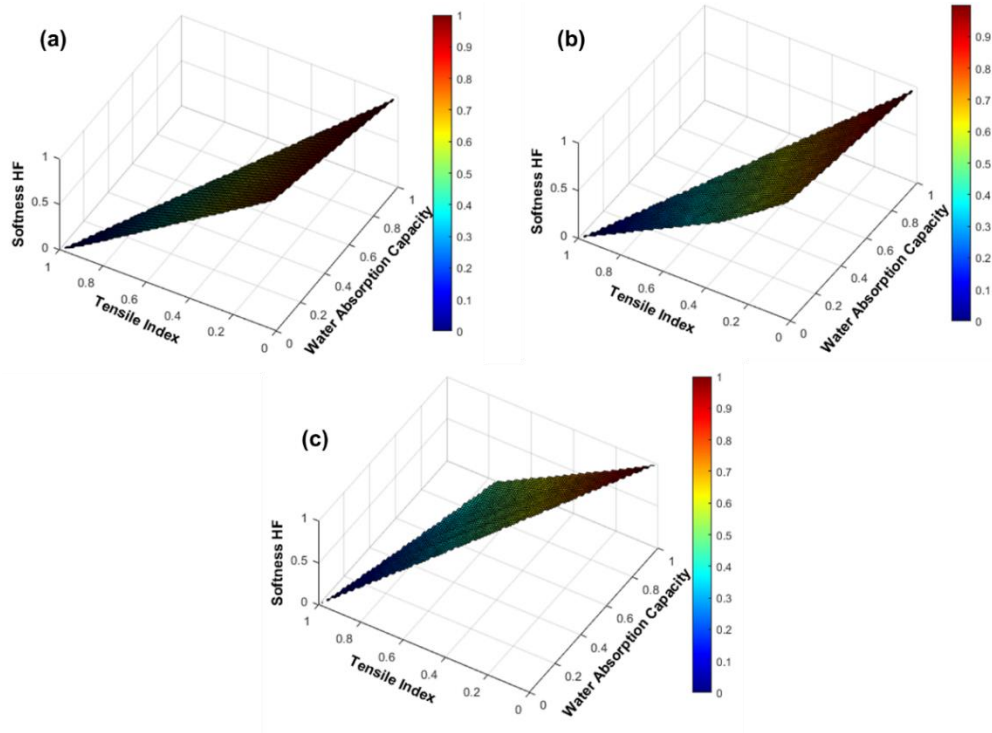


Figure III.38. Evolution of the end-use tissue properties of softness HF, tensile index, and water absorption capacity with the incorporation of CBA (a), MFC/NFC (b), and softwood fibers (c) in formulations with 100% eucalyptus fibers. All variables were normalized to present the same scale range.

As expected, the incorporation of CBA, MFC/NFC and softwood fibers promoted an improvement in strength properties with adverse effects on softness and absorbency. According to the tissue simulator, a formulation with 90% eucalyptus fibers and 10% softwood fibers promoted the production of a tissue product with a 68 softness HF, 15 Nm/g tensile index and 8 g/g water absorption capacity (Morais et al., 2021b). In order to replace this softwood fiber, the incorporation of 3% CBA allowed us to obtain improved tissue properties in the same range (72 softness HF, 15 Nm/g tensile index and 8 g/g water absorption capacity). The same trend was also verified for the incorporation of 14% MFC/NFC, presenting 70 softness HF, 15 Nm/g tensile index and 7 g/g water absorption capacity. However, in a previous work, we found that formulations with more than 10% MFC/NFC incorporation are not economically viable. The trade-off between the cost and the effectiveness of the formulations was achieved with the incorporation of MFC/NFC between 1 to 8%, presenting optimized properties at an industrial range (Morais et al., 2021b).

This approach saves the consumption of softwood fibers in tissue production and is aimed at the use of biocompatible and biodegradable additives in the industrial production process. The simulator's predictive capacity allowed the optimization and development of innovative formulations, saving laboratory and industrial resources.

III.2.3.5. Conclusions

This work presented experimental and computational approaches to evaluate and predict the effects of the incorporation of CBA and MFC/NFC with eucalyptus and softwood fibers on the softness, strength, and absorbency properties of tissue paper materials. Overall, the addition of both additives enhanced tensile strength properties at the expense of reduced softness and absorbency properties, followed by MFC/NFC and CBA. This cationic polymeric solution also improved the inter-fiber bonding and MFC/NFC particle retention. With the softwood fiber reduction in the formulations, the incorporation of additives promoted a strength and absorbency increase with a low softness decrease. It was possible to obtain a trade-off between the tissue end-use properties with CBA and MFC/NFC additions separately. With this work, it was possible to produce tissue furnish formulations using these additives with a reduction of the softwood fiber percentage in a drainage range of the tissue industrial process. This suggested that these additives presented a good potential to be introduced in the production of high-quality tissue materials such as tissue masks or premium napkins and facial papers. These biocompatible and biodegradable additives can promote the maximization of eucalyptus fibers in industrial tissue production, optimizing the process and associated manufacturing costs.

III.2.3.6. References

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III.2.4. A 3D Fiber-based Strategy for Optimization of Tissue Materials using a Combination of Liquid Absorbency/Retention Methods

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III.2.4.1. Abstract

The development of biocompatible polymeric biomaterials, considering the structural hierarchy at the fiber and structure levels through 3D computational simulation is an example of multidisciplinary research in the field of materials science and engineering. The design of biomaterials, such as tissue products, involves the optimization of the 3D network structure and porosity to obtain high liquid retention and improve functional properties. High-quality tissue paper fibrous materials require the use of several types of fibers, fiber modification processes, and additives incorporation. In this work, we present an innovative strategy aiming the optimization of water retention in structures produced with different furnish formulations, and industrial tissue papers. Laboratory structures with basis weight between 20 and 60 g/m² were produced with different eucalyptus fibers, fiber mixtures containing eucalyptus and softwood fibers in different percentages, enzymatic treatments applied to eucalyptus fibers suspensions, and micro/nanofibrillated cellulose incorporation, as an additive. Furthermore, industrial market tissue paper products, including napkins, towel papers, and toilet papers, were also selected. A combination of water absorption capacity, Klemm capillary rise, and liquid droplet spreading kinetics properties was performed. The results indicated that this methodology approach was able to quantify the influence of liquid retention properties for the different formulations, as well as commercial tissue papers. These data were integrated with an innovative simulator for tissue papers that establishes relationships between the fiber properties, the fiber modification processes, and the key properties of tissue papers. In conclusion, a strategy of design, engineering, and simulation of tissue paper materials was performed to support the furnish management that includes the changes in fibrous composition, fiber modification strategies, and micro and nano-scale additives incorporation, aiming the improvement and optimization of the final end-use tissue properties.

Keywords

Kinetics properties; Laboratory and industrial tissue-based papers; Optical Prototype System; Spreading Area; Liquid Absorbency Methods

Inspired from Paper VI:

Morais, F.P., Mendes, A.O., Carta, A.M.M.S., Fiadeiro, P.T., Amaral, A.E., and Curto, J.M.R. A 3D fiber-based strategy for optimization of tissue materials using a combination of liquid absorbency/retention methods. In Andreas Öchsner (Editor), Advanced Structured Materials. Springer. In Press. (Book Chapter)

III.2.4.2. Introduction

The design and development of advanced fiber-based biomaterials, the enhancement of natural resources, and the development of sustainable processes and products are the core of our research. The development of biopolymer-based materials follows the guidelines of EU sustainability societal challenges. The optimization of the 3D network structure, porosity and pore dimensions, and distribution is decisive in the development of porous polymeric biomaterials for liquid retention applications such as tissue products, delivery systems, scaffolds, etc. Cellulose-based fibrous materials have grown over the years in several applications since they present advantages as a renewable, sustainable, and economical resource, and also have shown interesting properties for each type of application (Kurimoto, Niiyama and Ebara, 2016; Hu et al., 2020). These materials present unique characteristics of biocompatibility, biodegradability, safety, controllable porosity, the capacity of being functionalized, ability to incorporate, retain and release molecules (Kurimoto, Niiyama and Ebara, 2016; Hu et al., 2020).

The development of engineering advanced structural materials, such as tissue paper materials, allows the combination of multi-structured materials and their interaction with liquids, achieving better performance and functional properties in quite diverse fields, at the micro and nanoscale. The use of computational tools constitutes an innovative strategy to enhance biopolymeric materials, through the modeling of fibers and structures simultaneously and in three dimensions. The porosity optimization presents a relevant impact on release kinetics, through experimental and computational planning. The design of new materials is done to achieve optimized properties considering the selection of the fibrous material (morphology *vs* properties), the fiber modification treatments, and/or the incorporation of the additive in suspensions (Boucher, 1976). The desired porosity for a specific application of these materials is one of the fundamental properties to be optimized. The porosity and pore size distribution in different fibrous materials presents an essential role in liquid absorption. Besides, the inter-fiber pores and the blind pores of the fiber surface structure play a crucial role in the liquids flow through the fibrous network (Hassan, Cushman and Delleur, 1998; Lang et al., 2013; Gigac, Stankovská and Fišerová, 2017; Stankovská et al., 2019). The complexity of fibrous materials lies in the fact that they do not have a regular pore size distribution, and in the presence of tortuous paths (tortuosity) that the pores provide for the flow-through of liquids or active substances, such as essential oils (Neumann et al., 2020). These molecules need to travel a path higher than a straight line between the original source and its active local (Ghanbarian et al., 2013). The fibrous structures and materials' porosity structure knowledge is important to predict and develop liquid absorption properties (Axelsson and Svensson, 2010). Tissue paper materials are examples of important applications for optimizing the properties of liquid or molecules' absorption, deposition time, spreading area, and kinetics. The liquid interaction properties, through the understanding of liquid transport processes in porous media, are important variables to optimize the performance of tissue paper materials.

Tissue paper materials are recognized for their low basis weight, high bulk, softness, strength, and water absorption capacity, although the priority given to each of these properties varies according to the desired final product, such as napkins, towel papers, toilet papers, among others (Beuther, Veith and Zwick, 2010; de Assis et al., 2018a). Overall, what distinguishes tissue papers from other paper materials is their production, namely, the creping process, used essentially to change tissue properties, and the converting process in which paper is transformed into different types of tissue products. Due to the low basis weight and density of these fibrous materials, the sheets cannot be subjected to drying with multiple cylinders, as it happens for other conventional types of paper. Instead, the tissue paper sheet just goes through a large steel dryer cylinder, called the Yankee dryer. This dryer removes the remaining water, and the sheet adheres to the Yankee's surface through specific additives, which are applied directly to the dryer. The tissue sheet is then removed from the surface of this cylinder with the aid of a creping blade, to be wound in reels (initial industrial base tissue paper) (Raunio and Ritala, 2012; Rezaei-Arjomand et al., 2013; Boudreau and Germgård, 2014; Raunio, Löyttyniemi and Ritala, 2018). These tissue paper reels feed afterward the converting process that includes the following steps: unwinding, embossing, printing, perforating, rewinding, cutting, packaging, and palletizing (Spina and Covalcante, 2018; Mendes et al., 2020; Vieira et al., 2020a). In the laboratory these steps are not easy to replicate, hence the quantification of differences between the finished tissue paper product properties and the laboratory-made structures that were produced from its disintegration becomes essential. Similarly, isotropic structures (laboratory handsheets) using hardwood and softwood pulps were made. In tissue paper materials, liquid absorption properties, such as absorption capacity, absorption rate, and absorption time are the most significant variables to predict the shelf price of napkins and towel papers (de Assis et al., 2018b). These properties are related to fiber type, fine contents, mechanical treatments, additives, creping process, embossing operation, and the stacking sequence of tissue paper sheets, due to their bulk, all have an impact on the liquid absorption capacity (de Assis et al., 2018b; Vieira et al., 2020a, 2020b). Therefore, the know-how and optimization of the tissue paper absorption properties can be carried out using a combination of different types of fibers, with different treatments (mechanical or enzymatic), and additives incorporation (de Assis et al., 2018a; Gigac et al., 2019; Morais et al., 2019, 2021a, 2021b), which consequently affect the porosity and relative bonding area, used to predict the initial liquid absorption (Gigac et al., 2019). The need to reduce costs and increase industrial tissue paper productivity makes furnish optimization and management an important milestone that correlates computational and experimental approaches for the developing and designing of high-quality products with the improved functional properties demanded by the consumers.

Our approach includes the combination of experimental and computational design aiming the optimization of optimize tissue paper materials through advanced computational tools (Raunio and Ritala, 2012; Morais et al., 2020b). An innovative approach of combining different 3D fiber models that define raw materials by a fiber population was used to simulate 3D tissue paper structures, predicting their properties (Morais et al., 2020b).

An experimental planning of fiber characterization and fiber and structure modification process steps, with the development of our own computational simulator, the *SimTissue*, allow us to establish relationships between the process inputs and the tissue end-use properties, to support tissue paper furnish management (Morais et al., 2019, 2020a, 2020b, 2021a, 2021b).

Additionally, a fibrous materials simulator, the *voxelfiber*, allows us to model 3D structures according to the fiber dimensions and properties, such as length and width ratio, flexibility, wall thickness, lumen, among others (Conceição et al., 2010; Curto et al., 2011a), to simulate and optimize different fibrous materials at different scales (Curto, 2012; Curto et al., 2015a, 2015b, 2018; Martins et al., 2018). The laboratory-made structures can be modeled with accuracy using our 3D computational simulations for tissue paper materials, obtaining data of their structural properties such as thickness, intra-, and inter-fiber porosity, relative bonding area, among others. On the other hand, an optical prototype, developed by our research team (Mendes et al., 2013), has been used to collect data of the liquid deposition in the fibrous structures over time, to measure the spreading area and kinetics, through image analysis (Curto et al., 2015b; Fiadeiro et al., 2013; Mendes et al., 2013; Sousa et al., 2014). Hydrophobic and hydrophilic interactions between fibrous structures and liquid droplets are also essential aspects to be considered when studying the absorbency properties (Wågberg and Westerlind, 2000; Modaressi and Garnier, 2002; Kannangara, Zhang, and Shen, 2006; Rosenholm, 2015). Additionally, different studies of deposition and spreading of liquid droplets have indicated that porous structure knowledge is one of the key parameters for optimizing properties, since the pore size distribution and dimensions influence the spreading and equilibrium state of the droplets, contributing to design of these materials for various industrial advanced applications (Senden, Knackstedt and Lyne, 2000; Clarke et al., 2002; Starov et al., 2003; Hilpert and Ben-David, 2009; Curto et al., 2015b; Chen, Nie and Fang, 2020). For these reasons, in future works, the combination of simulations of liquid droplets and 3D fibrous materials is essential for optimization and modeling the spreading area and kinetics, the time of deposition, and other absorption properties, in order to develop products with innovative and advanced features (Curto et al., 2015b; Zhang et al., 2020). To the best of our knowledge, the approach of combining absorbency characterization methods and liquid retention optimization methodologies, that captures the liquid interaction with the structures over time, applied to low basis weight and high porosity materials, such as tissue papers, has not been studied in the literature.

The main goal of this work was to develop a methodology aiming the optimization of liquid retention properties, combining water absorption capacity, Klemm capillary rise, through the experimental characterization of different tissue paper fibrous structures, and liquid spreading area and kinetics measurements, which uses liquid droplets deposition on these structures. Computational simulations of these fibrous materials were also used to present more information about its structural properties and predict their functional properties.

The experimental design plan consisted of the characterization of different industrial tissue papers and different structures, with different treatments that mimic the production of tissue papers, such as the fiber furnish mixture, enzymatic treatments, and additive incorporation, in this case at micro and nanoscales.

III.2.4.3. Materials and Methods

III.2.4.3.1. Materials

The hardwood samples include a never dried, or slush, Total Chlorine Free (TCF) bleached eucalyptus kraft pulp (HW), and two dried bleached eucalyptus pulps, one produced using the Elemental Chlorine Free (ECF) bleaching and kraft cooking processes (H_C) and the other the TCF bleaching and sulfite cooking processes (H_F). The softwood samples include three dried bleached pinus kraft pulps (SW, S_B, and S_F). The nano/ microfibers were obtained by mechanical and enzymatic processes applied to a dried bleached eucalyptus pulp (MFC/NFC). The selected industrial tissue products were napkins, towel papers, and toilet papers, supplied by a Portuguese tissue paper manufacturer.

III.2.4.3.2. Experimental Methods

Different experimental design plans were performed in order to evaluate the influence of liquid retention properties in all the paper samples, as shown in Table III.20. The first four experimental sets included paper samples produced in the laboratory using cellulosic fibers from eucalyptus, fiber mixtures with softwood reinforcement fibers, that differ the type of bleaching from each other, enzymatic treatments, and also the addition of MFC/NFC. To evaluate the impact of the different never dried and dried bleached eucalyptus kraft pulps, isotropic laboratory structures with basis weights of 20, 40, and 60 g/m², without pressing, were produced according to the adaptation of ISO 5269-1. Different mixtures of eucalyptus and softwood fibers pulps, with different percentages, were also prepared and studied, as well as structures with a basis weight of 20 and 60 g/m². To evaluate the enzymatic effect, two mixtures of 80% of kraft eucalyptus enzymatically treated and 20% of sulfite eucalyptus pulp without enzymatic treatment were selected (Morais et al., 2021a). The kraft eucalyptus pulp was treated with 10 g of enzyme per ton of pulp for 30 minutes (E1) and 60 minutes (E2). Finally, to evaluate the influence of micro/ nanofibers, a furnish mixture of eucalyptus fiber, reinforcement fiber, MFC/NFC was carried out (Morais et al., 2021b). For these last two assays, isotropic laboratory structures of 20 g/m² were also produced as reported above. The second experimental set, corresponding to the last three rows in Table III.20, refers to industrial tissue products. These samples were disintegrated according to ISO 5263/1 (named as repulping in Table III.20) to produce isotropic laboratory structures with a basis weight of 20 g/m², without pressing, similarly to the previous ones, where the effect of creping and embossing was attenuated or removed.

Table III.20. Identification and description of all the selected and prepared samples.

Samples ID	Experimental and Design Plan Description
REF_LAB_SS_20	Reference of laboratory-made structures of Eucalyptus slush pulp (HW) with 20 g/m ²
REF_LAB_SS_40	Reference of laboratory-made structures of Eucalyptus slush pulp (HW) with 40 g/m ²
REF_LAB_SS_60	Reference of laboratory-made structures of Eucalyptus slush pulp (HW) with 60 g/m ²
REF_LAB_T_20	Reference of laboratory-made structures of Eucalyptus dried pulp (H_C) with 20 g/m ²
REF_LAB_T_40	Reference of laboratory-made structures of Eucalyptus dried pulp (H_C) with 40 g/m ²
REF_LAB_T_60	Reference of laboratory-made structures of Eucalyptus dried pulp (H_C) with 60 g/m ²
LAB_T_30SW1_20	Laboratory-made structures of a blend of Eucalyptus dried pulp (H_C) (70%) and softwood pulp_1 (S_F) (30%) with 20 g/m ²
LAB_T_30SW1_60	Laboratory-made structures of a blend of Eucalyptus dried pulp (H_C) (70%) and softwood pulp_1 (S_F) (30%) with 60 g/m ²
LAB_T_10SW1_20	Laboratory-made structures of a blend of Eucalyptus dried pulp (H_C) (90%) and softwood pulp_1 (S_F) (10%) with 20 g/m ²
LAB_T_10SW1_60	Laboratory-made structures of a blend of Eucalyptus dried pulp (H_C) (90%) and softwood pulp_1 (S_F) (10%) with 60 g/m ²
LAB_T_30SW2_20	Laboratory-made structures of a blend of Eucalyptus dried pulp (H_C) (70%) and softwood pulp_2 (S_B) (30%) with 20 g/m ²
LAB_80TE1_20S	Laboratory-made structures of 80% enzyme-treated (1) Eucalyptus kraft dried pulp (H_C) and 20% Eucalyptus sulfite pulp (H_F), with 20 g/m ²
LAB_80TE2_20S	Laboratory-made structures of 80% enzyme-treated (2) Eucalyptus kraft dried pulp (H_C) and 20% Eucalyptus sulfite pulp (H_F), with 20 g/m ²
LAB_SS_5SW3_5MFC/NFC	Laboratory-made structures of 90% Eucalyptus slush pulp (HW), 5% softwood pulp_3 (SW), and 5% micro/ nanofibrillated cellulose (MFC/NFC), with 20 g/m ²
NAP_IND_A	Industrial-made napkin A, with 34 g/m ²
NAP_IND_B	Industrial-made napkin B, with 40 g/m ²
NAP_LAB_RP_A	Laboratory-made structures of the repulping of the napkin A, with 20 g/m ²
NAP_LAB_RP_B	Laboratory-made structures of the repulping of the napkin B, with 20 g/m ²
TW_IND_A	Industrial-made towel paper A, with 64 g/m ²
TW_IND_B	Industrial-made towel paper B, with 41 g/m ²
TW_IND_C	Industrial-made towel paper C, with 66 g/m ²
T_IND_I	Industrial base tissue paper (reel) for toilet papers, with 16 g/m ²
T_IND_F	Industrial-made toilet paper, with 33 g/m ²
T_LAB_RP	Laboratory-made structures of the repulping of the toilet paper, with 20 g/m ²

The structural characterization of fibrous structures was carried out using ISO 12625-6 for the basis weight, or grammage, ISO 12625-3 for the thickness, using the universal micrometer (FRANK-PTI – Birkenau, Germany), and the bulk was determined by using these two parameters in accordance with ISO 12625-3. Apparent porosity (theoretical) was calculated according to the following equation:

$$Porosity(\%) = \left(1 - \frac{\rho_{sample}}{\rho_{cellulose}}\right) \times 100 \quad (III.6)$$

Where ρ_{sample} is the sample density (g/cm³) and $\rho_{cellulose}$ is the cellulose density (which is assumed to be 1.5 g/cm³) (Morais et al., 2021a, 2021b).

The fibers morphological properties were determined automatically by image analysis using a diluted suspension of 20 mg/L, in a flow chamber, using the fiber and shive analyzer system LB01 166 (MorFi® TECHPAP – Grenoble, France). The drainability of a pulp suspension in water was measured in accordance with ISO 5267-1 using by Schopper-Riegler (°SR) method.

The surface morphology of the samples was analyzed using scanning electron microscopies S-2700 and S-3400N (SEM Hitachi – Tokyo, Japan), operating at 20 kV and at different magnifications. All paper samples were coated with gold using a sputter coater Q 150 R ES (Quorum - Quorum Technologies Ltd., Ashford, United Kingdom).

Finally, the tensile index was evaluated using ISO 12625-4, the water absorption capacity was measured by the immersion method according to ISO 12625-8, and an adaptation of ISO 8787 was used for the measurement of Klemm capillary rise. Using tissue softness analyzer (TSA Emtec – Leipzig, Germany), the TSA-softness properties were determined, with the QAI algorithm to measure the handfeel (HF) parameter.

The liquid spreading area was studied using an optical system (Fiadeiro et al., 2013; Mendes et al., 2013; Sousa et al., 2014; Curto et al., 2015b) specifically developed to investigate the interaction over time of liquid droplets on different furnish fibrous structures (Mendes et al., 2013) and tissue paper materials. This experimental system works by ejecting microliter droplets, through a syringe filled with dyed water, toward the fibrous structure surface. The droplets spreading images were captured for a given time. We considered the spreading kinetics from 35.7 ms to 3 s. For the different assays, only the spreading images of the initial time (35.7 ms), intermediate time (1 s), and maximum stabilization time (3 s) are shown.

III.2.4.3.3. Computational Methods

Different fibrous structures were modeled in a 3D fiber-based computational simulator, named *voxelfiber*, in which the code is available on GitHub (<https://github.com/eduardotrincaoconceicao/voxelfiber>). This computational tool allows modeling tissue paper materials as planar random networks. The fibers are represented by a voxel chain and modeled according to their dimensions and properties. A more detailed description of the 3D simulator can be found in Conceição et al. (2010) and Curto et al. (2011). The fibers can also be modeled according to different models proposed including the fiber wall thickness and lumen dimensions (Curto et al., 2011a; Morais et al., 2020b). The 3D computational structures are processed to evaluate different structural properties. Computational studies were carried out using the programming platform Matlab® (R 2020a – MathWorks, Natick, United State of America). Additionally, a computational tissue simulator, the *SimTissue*, was developed and used to predict the influence of furnish on TSA-softness, tensile strength, and absorption properties.

III.2.4.4. Results and Discussion

The complete set of results that correspond to each experiment are presented on Tables III.21 to III.24.

Table III.21. Morphological and suspension drainability of laboratory-made structures produced and industrial market tissue products. Values expressed as mean $\pm$ standard deviation.

Samples	LL (mm)	W (μ m)	C (mg/100m)	FC (%)	Kinks (%)	Curl (%)	°SR
REF_LAB_SS_20							
REF_LAB_SS_40	0.729 $\pm$ 0.001	19.1 $\pm$ 0.0	6.31 $\pm$ 0.00	38.5 $\pm$ 0.4	44.2 $\pm$ 0.3	9.7 $\pm$ 0.0	25 $\pm$ 0
REF_LAB_SS_60							
REF_LAB_T_20							
REF_LAB_T_40	0.798 $\pm$ 0.004	19.1 $\pm$ 0.1	6.83 $\pm$ 0.10	37.1 $\pm$ 0.3	35.5 $\pm$ 0.2	8.4 $\pm$ 0.1	20 $\pm$ 0
REF_LAB_T_60							
LAB_80TE1_20S	0.780 $\pm$ 0.000	19.0 $\pm$ 0.1	6.82 $\pm$ 0.02	36.4 $\pm$ 0.6	40.0 $\pm$ 0.1	9.8 $\pm$ 0.1	21 $\pm$ 0
LAB_80TE2_20S	0.778 $\pm$ 0.002	19.0 $\pm$ 0.1	6.72 $\pm$ 0.19	38.0 $\pm$ 0.3	39.2 $\pm$ 0.3	9.7 $\pm$ 0.0	22 $\pm$ 0
LAB_SS_5SW3_5MFC/NFC	0.737 $\pm$ 0.001	19.4 $\pm$ 0.0	7.32 $\pm$ 0.10	41.7 $\pm$ 0.1	43.1 $\pm$ 0.4	9.4 $\pm$ 0.1	33 $\pm$ 1
NAP_IND_A							
NAP_LAB_RP_A	0.767 $\pm$ 0.010	19.7 $\pm$ 0.1	9.61 $\pm$ 1.00	45.6 $\pm$ 2.4	53.0 $\pm$ 0.3	11.6 $\pm$ 0.1	18 $\pm$ 0
NAP_IND_B							
NAP_LAB_RP_B	0.757 $\pm$ 0.002	20.1 $\pm$ 0.1	9.50 $\pm$ 0.37	43.7 $\pm$ 1.1	49.2 $\pm$ 0.1	11.2 $\pm$ 0.0	15 $\pm$ 0
TW_IND_A	0.800 $\pm$ 0.010	25.9 $\pm$ 0.2	55.03 $\pm$ 2.3	78.8 $\pm$ 0.99	51.7 $\pm$ 0.8	12.1 $\pm$ 0.1	15 $\pm$ 1
TW_IND_B	0.850 $\pm$ 0.018	24.8 $\pm$ 0.5	47.79 $\pm$ 4.23	74.1 $\pm$ 2.1	49.1 $\pm$ 1.2	11.4 $\pm$ 0.3	14 $\pm$ 1
TW_IND_C	0.796 $\pm$ 0.001	25.7 $\pm$ 0.3	55.00 $\pm$ 2.90	78.6 $\pm$ 0.8	49.8 $\pm$ 0.1	11.9 $\pm$ 0.0	16 $\pm$ 1
T_IND_I							
T_IND_F	0.813 $\pm$ 0.000	20.8 $\pm$ 0.1	9.02 $\pm$ 0.13	47.8 $\pm$ 0.1	46.0 $\pm$ 0.4	10.3 $\pm$ 0.1	21 $\pm$ 1
T_LAB_RP							

LL: Length weighted by length; W: Width; C: Coarseness; FC: Fines Content (% in length); °SR: Schöpper-Riegler degree.

Table III.22. Structural properties of laboratory-made structures produced and industrial market tissue products. Values expressed as mean $\pm$ standard deviation.

Samples	Basis weight (g/m ²)	Thickness (μ m)	Bulk (cm ³ /g)	Apparent Porosity (%)
REF_LAB_SS_20	20.1 $\pm$ 0.4	114 $\pm$ 2	6.5 $\pm$ 0.0	89.4 $\pm$ 0.1
REF_LAB_SS_40	43.3 $\pm$ 0.4	175 $\pm$ 2	4.1 $\pm$ 0.1	83.6 $\pm$ 0.3
REF_LAB_SS_60	60.9 $\pm$ 0.4	249 $\pm$ 6	4.0 $\pm$ 0.1	83.4 $\pm$ 0.5
REF_LAB_T_20	20.1 $\pm$ 0.1	90 $\pm$ 2	4.5 $\pm$ 0.1	85.2 $\pm$ 0.3
REF_LAB_T_40	40.2 $\pm$ 0.1	160 $\pm$ 3	3.9 $\pm$ 0.1	83.3 $\pm$ 0.3
REF_LAB_T_60	63.1 $\pm$ 0.6	230 $\pm$ 3	3.6 $\pm$ 0.0	81.7 $\pm$ 0.1
LAB_T_30SW1_20	23.6 $\pm$ 0.5	116 $\pm$ 5	5.6 $\pm$ 0.2	87.0 $\pm$ 0.6
LAB_T_30SW1_60	68.6 $\pm$ 1.0	252 $\pm$ 6	3.7 $\pm$ 0.2	81.7 $\pm$ 1.2
LAB_T_10SW1_20	20.4 $\pm$ 0.4	99 $\pm$ 6	4.9 $\pm$ 0.3	86.3 $\pm$ 0.7
LAB_T_10SW1_60	67.5 $\pm$ 1.2	269 $\pm$ 4	3.9 $\pm$ 0.3	83.2 $\pm$ 1.2
LAB_T_30SW2_20	21.5 $\pm$ 0.8	114 $\pm$ 3	5.3 $\pm$ 0.2	87.4 $\pm$ 0.6
LAB_80TE1_20S	21.0 $\pm$ 0.4	100 $\pm$ 5	4.8 $\pm$ 0.2	86.0 $\pm$ 0.7
LAB_80TE2_20S	20.3 $\pm$ 0.4	96 $\pm$ 5	4.7 $\pm$ 0.3	85.9 $\pm$ 0.8
LAB_SS_5SW3_5MFC/NFC	20.1 $\pm$ 0.3	110 $\pm$ 4	5.3 $\pm$ 0.2	88.4 $\pm$ 0.0
NAP_IND_A	33.9 $\pm$ 0.1	225 $\pm$ 3	6.6 $\pm$ 0.1	89.9 $\pm$ 0.2
NAP_LAB_RP_A	20.5 $\pm$ 0.3	122 $\pm$ 4	5.9 $\pm$ 0.2	88.7 $\pm$ 0.5
NAP_IND_B	40.2 $\pm$ 0.1	213 $\pm$ 3	5.3 $\pm$ 0.1	87.4 $\pm$ 0.1
NAP_LAB_RP_B	20.8 $\pm$ 0.6	116 $\pm$ 4	5.6 $\pm$ 0.2	88.0 $\pm$ 0.5
TW_IND_A	64.1 $\pm$ 0.1	755 $\pm$ 3	11.8 $\pm$ 0.2	94.3 $\pm$ 0.1
TW_IND_B	41.4 $\pm$ 0.2	710 $\pm$ 4	17.1 $\pm$ 1.1	96.1 $\pm$ 0.3
TW_IND_C	65.6 $\pm$ 0.9	892 $\pm$ 3	14.3 $\pm$ 0.5	95.3 $\pm$ 0.2
T_IND_I	15.7 $\pm$ 0.1	139 $\pm$ 3	8.9 $\pm$ 0.9	92.4 $\pm$ 0.7
T_IND_F	32.9 $\pm$ 0.2	529 $\pm$ 9	16.0 $\pm$ 0.3	95.8 $\pm$ 0.1
T_LAB_RP	20.6 $\pm$ 0.3	113 $\pm$ 5	5.5 $\pm$ 0.2	87.8 $\pm$ 0.4

Table III.23. Experimental and computational characterization of 3D fibrous structures. Values expressed as mean $\pm$ standard deviation.

Samples	Experimental data			Computational data		
	Thickness (μm)	Bulk (cm^3/g)	Apparent Porosity (%)	Thickness (μm)	Bulk (cm^3/g)	Apparent Porosity (%)
REF_LAB_SS_20	114 $\pm$ 2	6.5 $\pm$ 0.0	89.4 $\pm$ 0.1	100 $\pm$ 2	5.9 $\pm$ 0.3	89.0 $\pm$ 0.3
REF_LAB_SS_40	175 $\pm$ 2	4.1 $\pm$ 0.1	83.6 $\pm$ 0.5	175 $\pm$ 3	4.0 $\pm$ 0.6	78.4 $\pm$ 0.3
REF_LAB_SS_60	249 $\pm$ 6	4.0 $\pm$ 0.1	83.4 $\pm$ 0.3	248 $\pm$ 4	4.1 $\pm$ 0.8	81.4 $\pm$ 0.6
REF_LAB_T_20	90 $\pm$ 2	4.5 $\pm$ 0.1	85.2 $\pm$ 0.3	99 $\pm$ 1	4.8 $\pm$ 0.1	81.5 $\pm$ 0.1
REF_LAB_T_40	160 $\pm$ 3	3.9 $\pm$ 0.1	83.3 $\pm$ 0.3	161 $\pm$ 3	4.0 $\pm$ 0.4	77.4 $\pm$ 0.2
REF_LAB_T_60	230 $\pm$ 3	3.6 $\pm$ 0.0	81.7 $\pm$ 0.1	227 $\pm$ 4	3.6 $\pm$ 0.3	80.8 $\pm$ 0.1

Table III.24. Tissue properties of laboratory-made structures produced and industrial market tissue products. Values expressed as mean $\pm$ standard deviation.

Samples	TSA-Softness HF	Tensile Index (Nm/g)	Water Absorption Capacity (g/g)	Klemm Capillary Rise (mm at 10 min.)
REF_LAB_SS_20	82.7 $\pm$ 4.0	4.60 $\pm$ 0.61	8.13 $\pm$ 0.29	132 $\pm$ 3
REF_LAB_T_20	63.2 $\pm$ 3.0	7.86 $\pm$ 1.58	8.10 $\pm$ 0.36	113 $\pm$ 2
LAB_8oTE1_20S	57.8 $\pm$ 3.3	17.68 $\pm$ 3.34	6.63 $\pm$ 0.32	120 $\pm$ 2
LAB_8oTE2_20S	63.0 $\pm$ 7.1	15.93 $\pm$ 2.64	6.49 $\pm$ 0.28	119 $\pm$ 1
LAB_SS_5SW3_5MFC/NFC	70.5 $\pm$ 1.9	14.31 $\pm$ 1.05	7.41 $\pm$ 0.22	1174
NAP_IND_A	63.7 $\pm$ 2.2	6.09 $\pm$ 0.62	9.23 $\pm$ 0.68	78 $\pm$ 3
NAP_LAB_RP_A	57.3 $\pm$ 3.3	8.77 $\pm$ 1.16	7.12 $\pm$ 0.12	83 $\pm$ 2
NAP_IND_B	72.9 $\pm$ 1.5	4.24 $\pm$ 0.40	7.62 $\pm$ 0.17	90 $\pm$ 1
NAP_LAB_RP_B	65.2 $\pm$ 1.8	7.07 $\pm$ 1.48	6.97 $\pm$ 0.41	91 $\pm$ 3
TW_IND_A	60.8 $\pm$ 2.0	7.96 $\pm$ 3.79	10.87 $\pm$ 0.11	103 $\pm$ 5
TW_IND_B	75.5 $\pm$ 1.8	3.28 $\pm$ 0.25	12.46 $\pm$ 0.22	132 $\pm$ 3
TW_IND_C	64.3 $\pm$ 1.6	4.35 $\pm$ 0.61	10.14 $\pm$ 0.24	90 $\pm$ 1
T_IND_I	69.6 $\pm$ 3.7	11.04 $\pm$ 0.45	9.42 $\pm$ 0.33	43 $\pm$ 1
T_IND_F	71.3 $\pm$ 2.3	5.51 $\pm$ 0.25	12.74 $\pm$ 0.40	75 $\pm$ 5
T_LAB_RP	64.9 $\pm$ 3.0	8.51 $\pm$ 0.99	7.21 $\pm$ 0.35	89 $\pm$ 4

III.2.4.4.1. Laboratory-made Structures

III.2.4.4.1.1. Influence of using Different Types of Eucalyptus Pulps, with Different Basis Weights

Eucalyptus fibers are considered ideal to produce tissue papers due to their morphological and biometric properties that allow improving the properties of bulk, porosity, softness, and absorption (de Assis et al., 2018a). Two eucalyptus pulps were selected for the study since the dried pulp present good strength properties (10 Nm/g of tensile index) and the never dried pulp presented good softness properties, with a HF of 82 units, according to our previous studies (Morais et al., 2019, 2020a). Tissue products can present different basis weights, depending on the type of tissue paper to produce. For this reason, our goal was to produce isotropic laboratory structures of these eucalyptus pulps with different basis weights, in order to evaluate the liquid retention properties. The morphological analysis for the selected eucalyptus pulp fibers presented a fiber length weighted by length range between 0.73 and 0.80 mm, fiber width of 19.1 μm , fiber coarseness between 6.31 and 6.83 mg/100m, fines content between 37.1 and 38.5%, and drainability property accessed by Schopper-Riegler between 20 and 25°SR (Table III.21). Figure III.39 presents the structural properties behavior for the dried eucalyptus pulp (REF_LAB_T) and the eucalyptus slush pulp (REF_LAB_SS) structures with 20, 40, and 60 g/m². The structure thickness increases with their basis weight (Bloch, Engin and Sampson, 2019), in contrast to the bulk and apparent porosity properties. Compared to the REF_LAB_T, the REF_LAB_SS showed, on average, an increase of 15% in thickness, 28% in bulk, and 4% in apparent porosity (Table III.22). REF_LAB_SS structures between 20 and 60 g/m² showed bulk variation between 6.5 and 4.1 cm³/g, and porosities between 89.4 and 83.5%, while REF_LAB_T structures between 20 and 60 g/m² showed bulk variation between 4.5 and 3.7 cm³/g, and porosities between 85.2 and 81.7%. Apart from the fact that these two samples are either dry or never-dried pulp, these differences are also due to the different bleaching procedures applied to produce these eucalyptus pulps. The REF_LAB_T samples was treated with an ECF bleaching sequence, while the REF_LAB_SS sample with a TCF bleaching sequence. For this reason, the REF_LAB_T and REF_LAB_SS samples presented viscosity values in the order of 915 and 453 mL/g, respectively. The laboratory-made structures were simulated computationally in 3D, and the same structural properties were obtained (Table III.23). In 3D fiber modeling, the input variables of fiber properties and structures are considered, including the length/width ratio, fiber population, fiber wall thickness, fiber lumen, grammage, among others. The 3D computational simulation of these tissue structures allows, from experimental and simulated results, the modeling of any type of material by adjusting the parameters of the fiber dimensions and the structures formed by them. This approach is considered a good alternative to model and optimize new innovative materials with a wide field of applications.

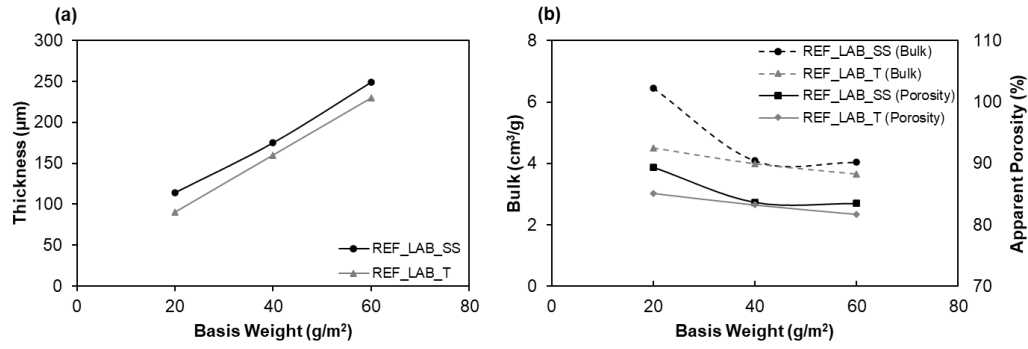


Figure III.39. Basis weight as a function of the thickness (a) and bulk and apparent porosity (b) for the REF_LAB_SS and REF_LAB_T structures.

For the absorbency properties, the REF_LAB_SS structures presented a slightly higher water absorption capacity (8.13 g/g *vs* 8.05 g/g), and Klemm capillary rise at 10 minutes (132 mm *vs* 113 mm), compared to the REF_LAB_T. The kinetics of the liquid droplet spreading area over time for the REF_LAB_SS and REF_LAB_T paper samples with different basis weights is presented in Figure III.40 and Table III.25. The results indicated that the liquid droplet deposition into these fibrous structures showed a smaller spreading area with the basis weight increase, corresponding to a less porous structure, and consequently, a structure bulk decrease with the basis weight, as shown in Figure III.39b. It was also possible to verify that the REF_LAB_SS structures presented a higher liquid droplet spreading area compared with the REF_LAB_T structures. This result is in accordance with the water absorption capacity and Klemm capillary rise properties, as previously mentioned. This result is also due to the fiber hornification in higher basis weights, and structure bulk and porosity differences (Figure III.39b). Furthermore, for these samples (Table III.21), the viscosity, the °SR, and the biometric properties, such as curl and kink deformations and coarseness may also have contributed to these differences. The REF_LAB_SS sample was produced with a more degraded pulp presenting more deformations and higher °SR when compared with the REF_LAB_T sample. REF_LAB_SS fibers present more fibrillation as a consequence of their production process (bleaching sequence), unlike REF_LAB_T pulp.

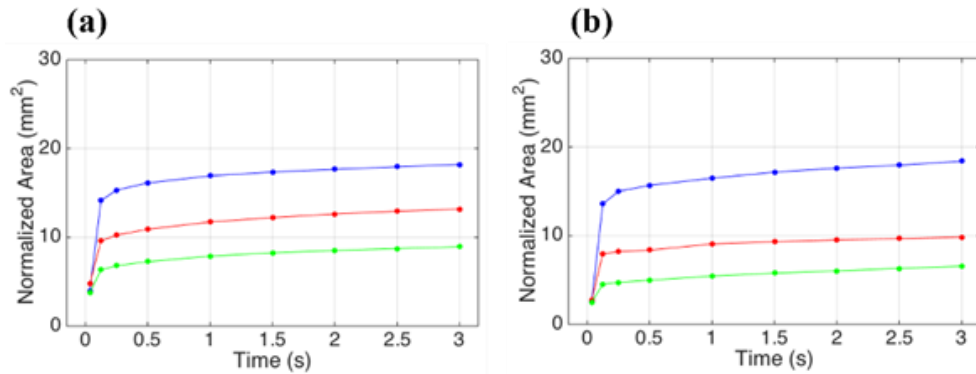
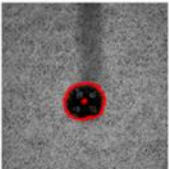
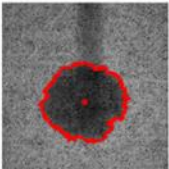
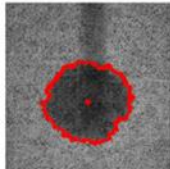
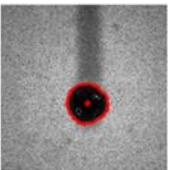
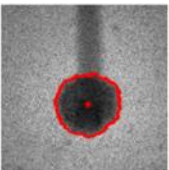
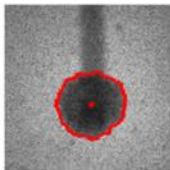
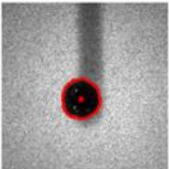
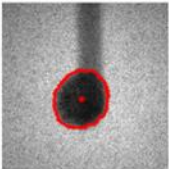
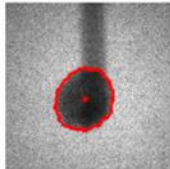
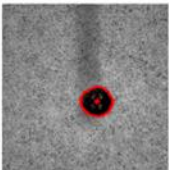
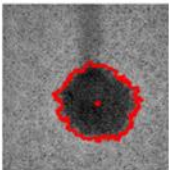
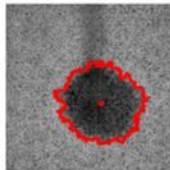
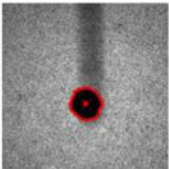
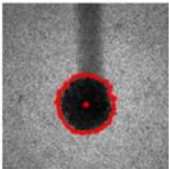
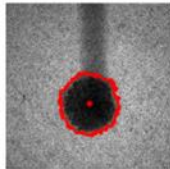
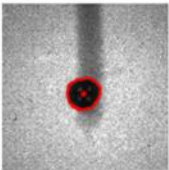
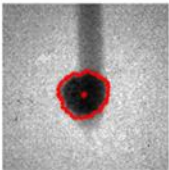
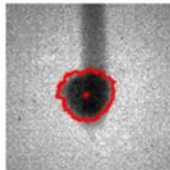


Figure III.40. The normalized spreading area as a function of time for the samples REF_LAB_SS (a) and REF_LAB_T (b). The structures with basis weights of 20, 40, and 60 g/m² are represented in blue, red, and green, respectively.

Table III.25. Evolution of the liquid droplet spreading area over time in laboratory-made structures with two Eucalyptus pulps and different basis weights (20, 40, and 60 g/m²). One set suitable for softness properties (REF_LAB_SS) and the other set for strength (REF_LAB_T).

	t = 35.7 ms	t = 1.0 s	t = 3.0 s
REF_LAB_SS_20			
REF_LAB_SS_40			
REF_LAB_SS_60			
REF_LAB_T_20			
REF_LAB_T_40			
REF_LAB_T_60			

III.2.4.4.1.2. Influence of Fiber Mixtures and Two Different Basis Weights

Tissue products are produced with a high percentage of bleached hardwood pulps, which confer structural, softness, and absorption properties, and with a low percentage of bleached softwood pulps, which provide strength properties and ensure the tissue machine runnability (de Assis et al., 2018a).

Isotropic laboratory-made structures were produced with different softwood reinforcement fibers incorporation in percentages of 10 and 30%, with basis weights between 20 and 60 g/m². Previous studies have proven that mixtures of eucalyptus fibers and reinforcement fibers between these percentages can be suitable to produce tissue papers with high bulk softness, tensile index, absorption, and brightness (Stankovská et al., 2020). The isotropic structures with 20 and 60 g/m² showed, respectively, a thickness of 99 and 269 µm, bulk of 5.30 and 3.66 cm³/g, and apparent porosity of 87.4 and 81.7% (Table III.22).

SEM images were obtained for the different fibrous structures (Figure III.41) to represent, as an example the top view and thickness cross-section of the laboratory-made structures LAB_T_30SW1_20 and LAB_T_30SW1_60. These laboratory-made structures considering the corresponding fiber mixtures were also modeled computationally with the same fibrous elements, and the same structural properties were obtained.

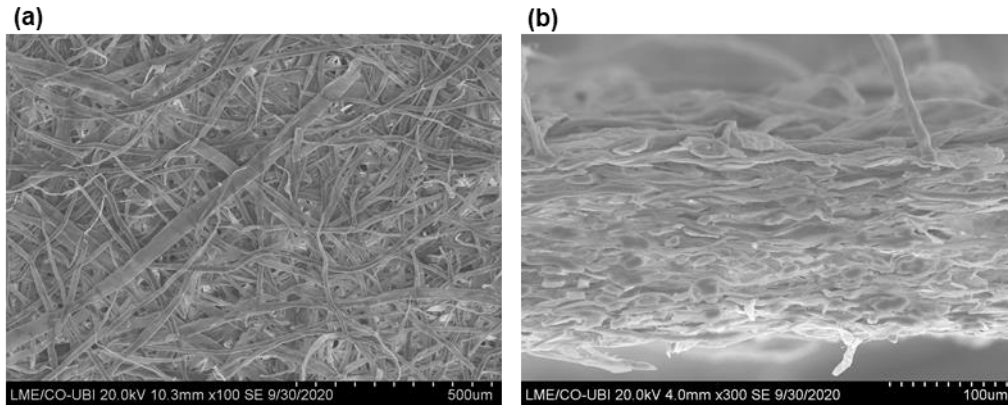


Figure III.41. SEM images of fibrous structures. Top view of sample LAB_T_30SW1_20 (a) and thickness of sample LAB_T_30SW1_60 (b).

The response of the liquid droplet deposition into the fibrous structure made from fiber mixtures having 30% of softwood fibers (LAB_T_30SW1) indicates that the spreading area is smaller compared to 10% of softwood fibers (LAB_T_10SW1), as shown in Figure III.42 a,b and Table III.26. The spreading area decreases when the basis weight increases. Additionally, less porous and bulky structures are produced with a higher percentage of softwood pulp incorporation, also enhancing a decrease spreading area. These structures were produced with a softwood fiber with a water absorption capacity of 8.4 g/g (Morais et al., 2019, 2020a). The change of softwood fibers with higher absorption properties (8.6 g/g) also modifies the liquid droplet spreading area, as shown in Figure III.42c and Table III.26. The sample LAB_T_30SW2_20 showed a higher spreading area when compared with the sample LAB_T_30SW1_20. With this study, it was possible to conclude that not only the percentage of softwood fibers incorporated in tissue materials influences the liquid retention properties but also the type of softwood fibers used.

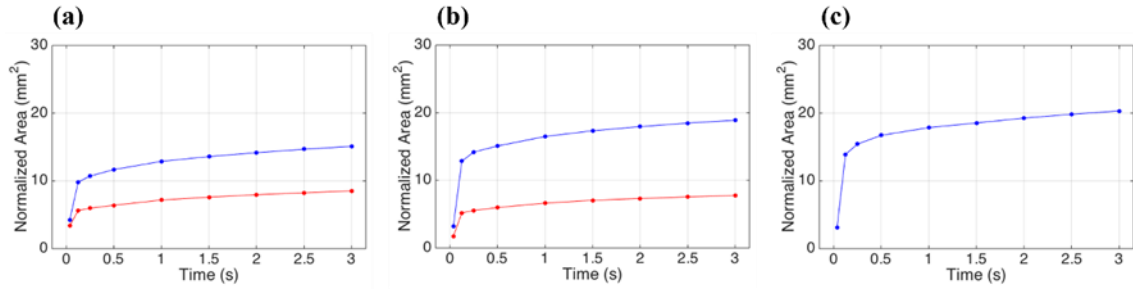


Figure III.42. The normalized spreading area as a function of time for the samples LAB_T_30SW1 (a), LAB_T_10SW1 (b), and LAB_T_30SW2 (c). The structures with basis weights of 20 and 60 g/m² are represented in blue and red, respectively.

Table III.26. Evolution of the liquid droplet spreading area over time in laboratory-made structures of a blend of eucalyptus pulp with a softwood pulp_1 at 30 and 10%, with a basis weight of 20 and 60 g/m², and another softwood pulp_2 at 30%, with 20 g/m².

	t = 35.7 ms	t = 1.0 s	t = 3.0 s
LAB_T_30SW1_20			
LAB_T_30SW1_60			
LAB_T_10SW1_20			
LAB_T_10SW1_60			
LAB_T_30SW2_20			

III.2.4.4.1.3. Influence of Enzymatic Reaction Time Treatments

To enable the great potential of eucalyptus fibers in tissue papers, it is necessary not only to identify the fiber properties, their relationship with the process, and the tissue final properties but also to modify the fibers, minimizing the impact on the functional properties. Biorefining allows modifying the fibers with enzymes, in order to improve the softness by fiber cellulose hydrolysis, producing weak points that make them flexible. The application of enzymes under ideal conditions presents a higher potential to produce materials with high added value, at low costs, being considered environmentally and sustainability friendly (Gil et al., 2009; Morais et al., 2021a). We consider that an innovative feature of biorefining is the mixture of two eucalyptus pulps with different enzymatic treatments, one pulp ensures strength properties (80%) and the other softness properties (20%). Through this methodology, the fibrous structures, that take advantage of all the eucalyptus pulps potential, can be obtained laboratory and computationally. In these two blends, only eucalyptus fibers suitable for strength properties were subjected to two enzymatic treatments with the same enzyme dosage and different reaction times of 30 and 60 minutes, corresponding to the LAB_8oTE1_2oS and LAB_8oTE2_2oS, respectively. The LAB_8oTE1_2oS and LAB_8oTE2_2oS presented, respectively, a fiber length weighted by length range of 0.78 mm, fiber width of 19 μm , fiber coarseness of 6.82 and 6.72 mg/100m, fines content of 36 and 38%, and 21 and 22 °SR (Table III.21). These isotropic laboratory-made structures presented, respectively, a thickness of 100 and 96 μm , bulk between 4.76 and 4.72 cm^3/g , and apparent porosity of 86% (Table III.22). Regarding tissue properties, the isotropic laboratory structures of these structures presented, respectively, a softness HF of 58 and 63 units, tensile strength index of 18 and 16 Nm/g, water absorption capacity of 7.0 and 6.4 g/g, and Klemm capillary rise at 10 minutes of 120 and 119 mm (Table III.24) (Morais et al., 2021a). Additionally, the evolution of the liquid droplet spreading area over time in LAB_8oTE1_2oS and LAB_8oTE2_2oS samples is presented in Figure III.43 and Table III.27. The results indicated that the spreading area decreased as a function of the enzyme reaction time. The sample LAB_8oTE2_2oS presented more flexible fibers, with less porosity and bulk, corresponding to the liquid retention properties decreases, which were also predicted for different furnish scenarios obtained by our tissue simulator, *SimTissue*.

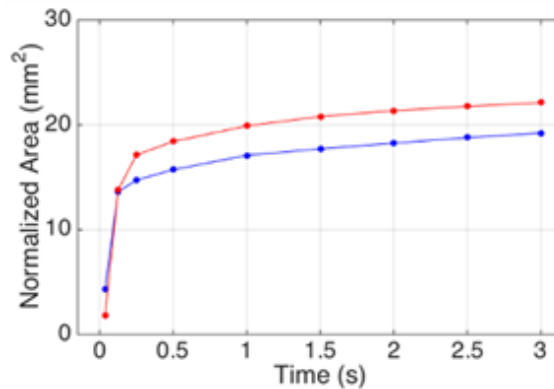
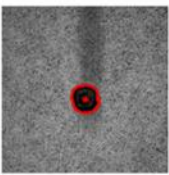
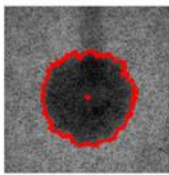
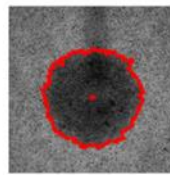
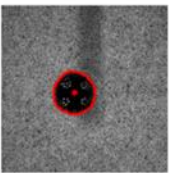
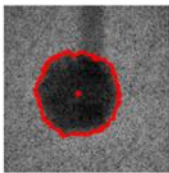
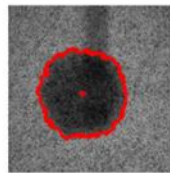


Figure III.43. The normalized spreading area as a function of time for the structures LAB_8oTE1_2oS (red) and LAB_8oTE2_2oS (blue).

Table III.27. Evolution of the liquid droplet spreading area over time in laboratory-made structures of a blend of two Eucalyptus pulp (80:20) with different enzymatic reaction time treatments.

	t = 35.7 ms	t = 1.0 s	t = 3.0 s
LAB_80TE1_20S			
LAB_80TE2_20S			

III.2.4.4.1.4. Influence of Micro/ Nanofibers as an Additive

In addition to the fiber modification processes, it is important to find several solutions that allow obtaining improved tissue properties to introduce innovative formulations on the market and produce premium tissue materials. An example of a raw material that can be used in tissue papers as an additive in order to improve the tissue final properties is the MFC/NFC (Guan, An and Liu, 2019; Zambrano et al., 2021; Morais et al., 2021b). We developed an experimental design to produce multi-structured fibrous structures with eucalyptus fibers (90%), softwood fibers (5%), and MFC/NFC (5%). The morphological characterization shows for this sample a fiber length weighted by length of 0.74 mm, fiber width of 19.4 μm , fiber coarseness of 7.32 mg/100m, fines content of 41.7%, and 33 °SR (Table III.21). The isotropic laboratory-made structures present a thickness of 110 μm , bulk of 5.34 cm^3/g , and apparent porosity of 87.5% (Table III.22). Regarding tissue properties, these structures presented a softness HF of 70.5 units, a tensile strength index of 14.31 Nm/g, water absorption capacity of 7.4 g/g, and Klemm capillary rise at 10 minutes of 117 mm (Table III.24).

From SEM images of the multi-structured fibrous structures, it is possible to identify the different fiber fibrillation degrees, with inter-fiber bonding resulting from MFC/NFC as an additive, as exemplified in Figure III.44.

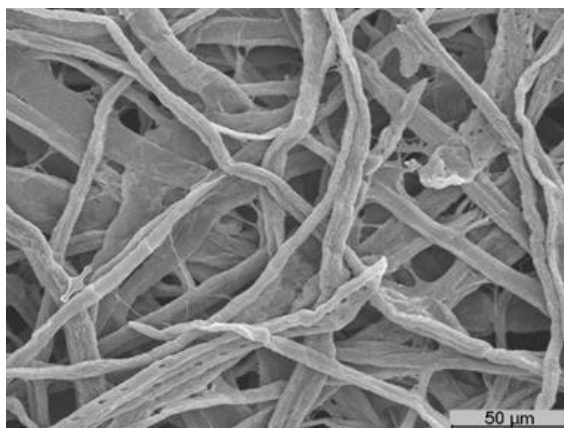


Figure III.44. SEM image of multi-structured fibrous structures of the sample LAB_SS_5SW3_5MFC/NFC.

Furthermore, the incorporation of MFC/NFC, as an additive, enhanced the liquid droplet spreading area, in the formulation of 90% eucalyptus slush pulp, 5% softwood pulp_3, and 5% MFC/NFC, as shown in Figure III.45 and Table III.28. This result was also improved compared to fiber mixtures (section III.2.4.4.1.2.) and enzymatic treatments (section III.2.4.4.1.3.). An approach of combining these three cellulose sources allowed to obtain a multi-structured fibrous material, at different scales, with improved liquid retention properties obtained by *SimTissue*, compared to the processes currently used in the tissue industry. The potential to combine the different properties of commonly used raw materials with the micro/ nanofiber properties could enhance the production of tissue materials with added value and innovative functionalities.

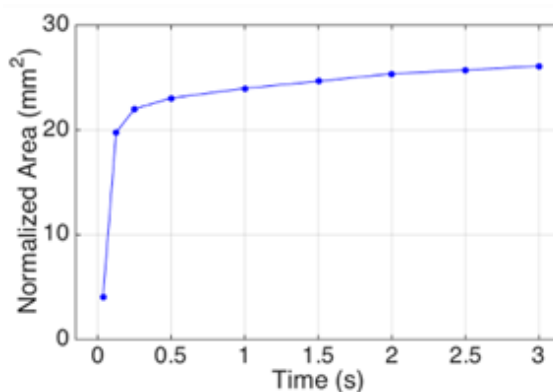
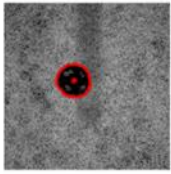
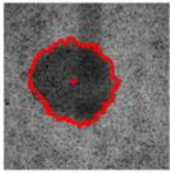
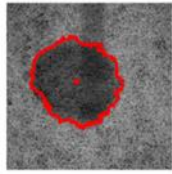


Figure III.45. The normalized spreading area as a function of time for the sample LAB_SS_5SW3_5MFC/NFC.

Table III.28. Evolution of the liquid droplet spreading area over time in laboratory-made structures of a blend of Eucalyptus pulp (90%), softwood fiber pulps (5%), and MFC/NFC (5%).

	t = 35.7 ms	t = 1.0 s	t = 3.0 s
LAB_SS_5SW3_5 MFC/NFC			

III.2.4.4.2. Industrial Market Tissue Products

III.2.4.4.2.1. Influence of Industrial Napkins and Repulping

Industrial napkins are usually produced with a content of eucalyptus pulp between 50 and 60% (de Assis et al., 2018a). Table III.21 in supplementary materials presents slight differences between the morphological and drainability properties of the two napkins used in this work, namely the samples NAP_IND_A, and NAP_IND_B. The fiber curl and kink deformations appear throughout the pulp production process, being directly related to the strength properties (Moraes et al., 2020a). Figure III.46 shows that by the fiber length and width distributions, the presence of reinforcing fibers (softwood fibers) is evident, since fiber lengths and widths higher than 1.2 mm and 20 μm , respectively, were observed, contrary to what happens in eucalyptus fiber pulps (Moraes et al., 2020a). In these industrial napkin samples, the percentage of reinforcement fiber can vary from 30 to 40%. A lower value of $^{\circ}\text{SR}$ implies the presence of reinforcement fibers, being more pronounced in the sample NAP_IND_B.

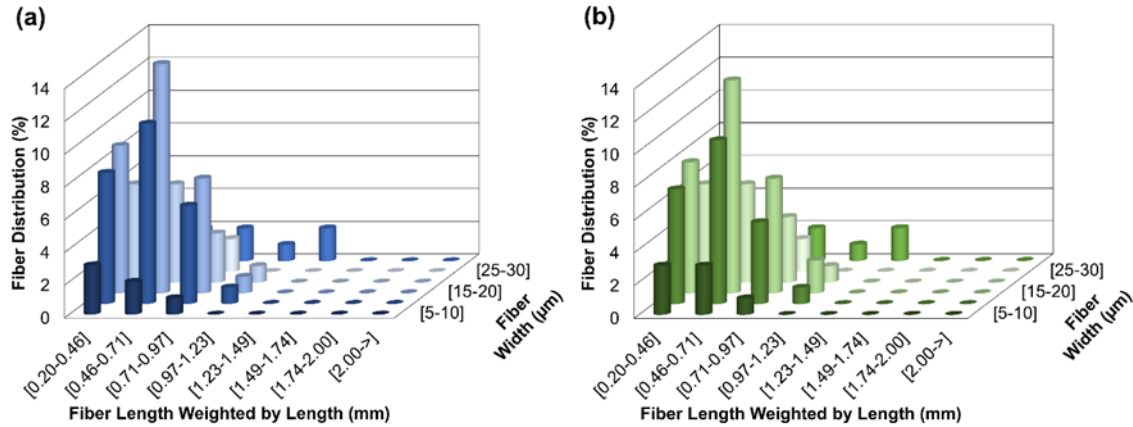


Figure III.46. Fiber length weighted by length and width distributions of samples NAP_IND_A (a) and NAP_IND_B (b).

The production of isotropic laboratory-made structures of 20 g/m^2 , samples NAP_LAB_RP_A and NAP_LAB_RP_B, from the industrial napkin samples allowed quantifying the limits of the creping process conditions. Both napkin samples are made up of 2-ply tissue paper sheets. Each ply of the NAP_IND_A sample (34 g/m^2) presented a basis weight of 16 g/m^2 , while each ply of the NAP_IND_B sample (40 g/m^2) presented a basis weight of 20 g/m^2 (Table III.22).

Then, it was produced laboratory-made structures with 20 g/m² of the disintegrated commercial products, since this basis weight is a standard value used in all previously reported experimental studies to mimic tissue papers. Regarding tissue properties, a combination of absorption and strength properties is required for napkins (de Assis et al., 2019). Overall, under these conditions, the sample NAP_IND_A stood out, presenting additionally less softness properties. The opposite happened for the sample NAP_IND_B. The same trend was observed for isotropic laboratory-made structures. Creping conditions positively affected the softness HF properties by 11% and 12%, and water absorption capacity by 30 and 9%, and negatively affected the tensile strength index properties by 31 and 40% for the samples NAP_IND_A and NAP_IND_B, respectively. Contrary to the water absorption capacity properties, the sample NAP_IND_B showed an improved performance in the Klemm capillary rise properties. Capillarity is related not only to the global porosity of the fibrous structure but also to the pore dimensions and distribution (Mullins and Braddock, 2012; Kolesnikov and Gavrilov, 2020; Bae et al., 2021), together with the presence of fibers with good water affinity. Compared with the isotropic laboratory-made structures obtained by repulping of these napkins, the same behavior was verified for both samples. At 10 minutes, creping conditions negatively affect Klemm capillary rise properties by 6% for the samples NAP_IND_A (Table III.24). However, for sample NAP_IND_B, a variation of only 1% was observed, and consequently, this result does not ensure that it was the creping conditions that affected Klemm capillary rise.

The liquid droplet spreading area of the sample NAP_IND_A was higher than the laboratory-sample NAP_LAB_RP_A, which was structures produced by repulping the original sample, as shown in Figure III.47a, being in accordance with the water absorption capacity properties. However, the opposite was verified for the samples NAP_IND_B and NAP_LAB_RP_B, presenting similar spreading area values, as shown in Figure III.47b. This result is following the capillary rise properties. Additionally, the phenomenon of anisotropy was observed in samples NAP_IND_A and NAP_IND_B, and isotropy in samples NAP_LAB_RP_A and NAP_LAB_RP_B, according to Table III.29. The liquid droplet spreading area was direction-dependent of the creping lines in the napkin samples, presenting an elliptical shape. In the case of NAP_IND_A, the anisotropy of the creping lines enhances a liquid spreading area increase, while the isotropy in the NAP_LAB_RP_A sample can cause higher capillary pressures and lower permeability constants. The creping lines enhance the tortuosity phenomenon, since the liquid droplet presents higher difficulty to intrude into or pass through the cellulosic fibers (Ashari et al., 2010; Coutelieris and Delgado, 2012). This result is also following the structure porosity (Table III.22), as the amount and structure of the void spaces (pores) influence the liquid flow through these porous structures. Regarding the samples NAP_IND_B and NAP_LAB_RP_B, the spreading area variation was not as pronounced. This result is in accordance with the Klemm capillary rise properties, as shown in Table III.24.

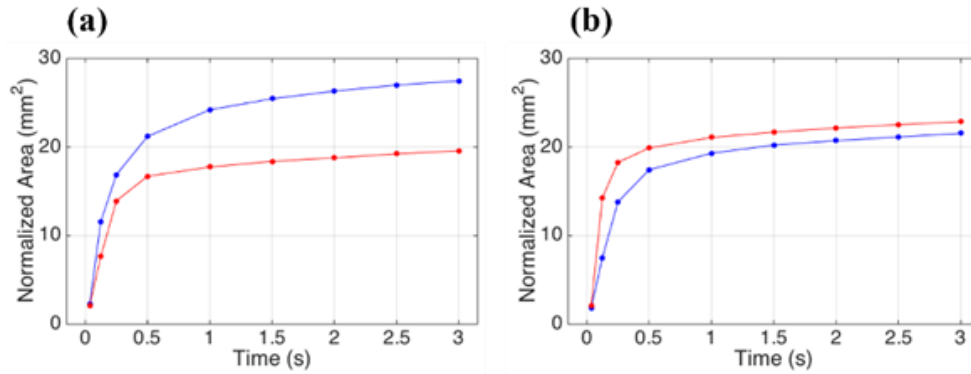


Figure III.47. The normalized spreading area as a function of time for the samples NAP_IND A (blue) and NAP_LAB_RP_A (red) (a), and samples NAP_IND B (blue) and NAP_LAB_RP_B (red) (b).

Table III.29. Evolution of the liquid droplet spreading area overtime in industrial napkins and the corresponding laboratory-made structures.

	t = 35.7 ms	t = 1.0 s	t = 3.0 s
NAP_IND_A			
NAP_LAB_RP_A			
NAP_IND_B			
NAP_LAB_RP_B			

III.2.4.4.2.2. Influence of Industrial Towel Papers

Industrial towel papers, just as napkins, are also produced with a content of eucalyptus pulp between 50 and 60%. Towel papers present a higher percentage of reinforcing fiber compared to other tissue products to confer strength properties. Besides, a peculiarity of these types of papers is the presence of additives, such as wet-strength additives, with a higher capacity of inter-fiber bonding, in order to ensure good absorption and strength properties (de Assis et al., 2018a).

For this reason, the repulping of these industrial papers is a challenge, therefore the preparation of its isotropic laboratory-made structures was not possible. The industrial towel papers selected for this study presented a fiber length weighted by length range between 0.79 and 0.85 mm, fiber width between 24.8 and 25.9 μm , fiber coarseness between 42.79 and 55.03 mg/100m, and fines content between 74.1 and 78.8% (Table III.21). As mentioned before, the fiber curl and kink deformations were directly related to the structure strength properties. The selected industrial towel papers can present 30 to 40% of reinforcement fibers, according to the fiber length and width distributions, as shown in Figure III.48. The sample TW_IND_B had a high content of long fibers, presenting fiber lengths that were longer than 1.74 mm, and the samples TW_IND_A and TW_IND_C presented an intermediate content of long fibers, with lengths measured between 1.23 and 1.47 mm. Additionally, the sample TW_IND_B showed a lower value of °SR, followed by the sample TW_IND_A and the sample TW_IND_C. Figure III.49 also presented an example of a SEM image of the industrial towel paper sample TW_IND_A, where the fiber furnish mixture is visible, with different flexibility degrees due to the beating or enzymatic processes applied to the fibers for the tissue paper production, and the sections of the creping and embossing processes are also visible.

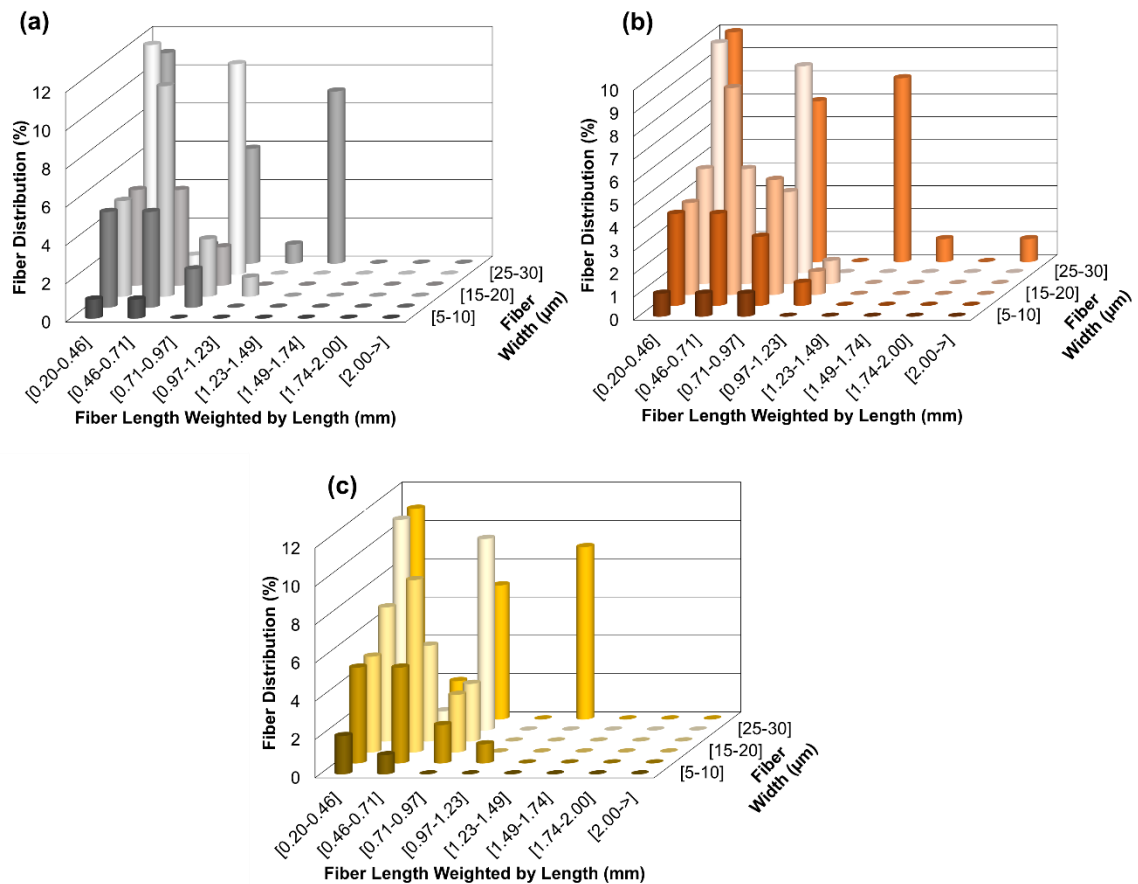


Figure III.48. Fiber length weighted by length and width distributions of samples TW_IND_A (a), TW_IND_B (b), and TW_IND_C (c).



Figure III.49. SEM image of the industrial towel paper sample TW_IND_A.

These samples are made up of 2-ply and 3-ply tissue paper sheets, consequently, their structural properties differ in terms of basis weight, thickness, bulk, and apparent porosity (Table III.22). Regarding tissue properties, the selected industrial towel papers showed softness HF in the range between 60.8 and 75.5 units, tensile index between 3.28 and 7.96 Nm/g and water absorption capacity between 10.14 and 12.46 g/g. The properties of Klemm capillary rise agree with the water absorption capacity properties. The sample TW_IND_B presented higher water absorption capacity and Klemm capillary rise properties, followed by samples TW_IND_A and TW_IND_C. At 10 minutes, the samples TW_IND_A, TW_IND_B, and TW_IND_C showed 103, 132, and 90 mm of water rise, respectively (Table III.24).

The sample TW_IND_B presented the highest liquid spreading area, followed by the samples TW_IND_A and TW_IND_C, as shown in Figure III.50. This result agrees with the water absorption capacity and capillary rise properties. Additionally, for the sample TW_IND_B, the high paper bulk and porosity increased the absorbency properties. The bulk increment resulted from the thickness increase induced by the 2-ply tissue paper sheets and the creping and embossing process. However, the relationship between structural and absorption properties was not observed for the other two samples, because TW_IND_C consists of 3-ply tissue paper sheets and TW_IND_A by 2-ply tissue paper sheets. For this reason, the results indicate that a comparison of tissue absorption properties between paper towel samples can only be performed on papers with the same number of plies. Besides this factor, the major influence on these absorbency results is also the embossing pattern applied to towel papers, as shown in Table III.30. The deeper the embossing pattern is engraved on the towel papers, the higher the water displacement towards these spaces, being more noticeable in the sample TW_IND_B, followed by samples TW_IND_A and TW_IND_C.

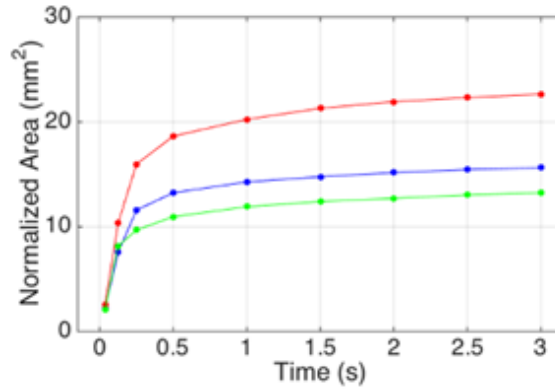
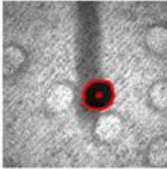
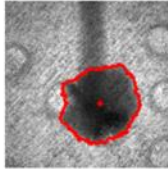
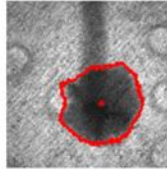
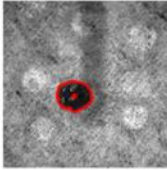
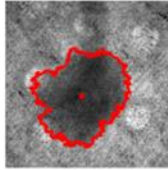
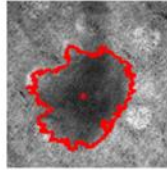
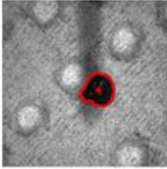
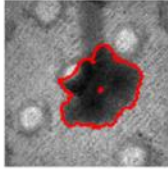
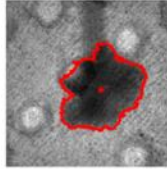


Figure III.50. The normalized spreading area as a function of time for the samples TW_IND_A (blue), TW_IND_B (red), and TW_IND_C (green).

Table III.30. Evolution of the liquid droplet spreading area over time in industrial-made towel papers.

	t = 35.7 ms	t = 1.0 s	t = 3.0 s
TW_IND_A			
TW_IND_B			
TW_IND_C			

III.2.4.4.2.3. Influence of Initial and Final Industrial Toilet Paper and Repulping

Finally, in this section, our approach was to characterize the initial creped industrial base tissue toilet paper (reel), its final creped and embossed industrial toilet paper, and laboratory-made structures prepared with the repulping from the last one. The creped industrial base toilet paper sample T_IND_I and the final creped and embossed industrial toilet paper sample T_IND_F were characterized. The sample T_IND_F has been repulped to produce isotropic laboratory-made structures, identified by T_LAB_RP, without the influence of the creping and embossing processes. Figure III.51 shows a scheme of the methodology used. In SEM images, the creping and embossing operations are visible in the sample T_IND_F, while in the sample T_IND_I, only the creping process is observed. The anisotropy effect of the fibers is also seen in these samples.

The perpendicularity between the creping lines and the fiber orientation is remarkable in these tissue samples. The fiber orientation, creping, and embossing processes were suppressed with the repulping of the final industrial toilet paper. Fiber fibrillation is also present in these products due to the fiber modification processes applied to the tissue paper production.

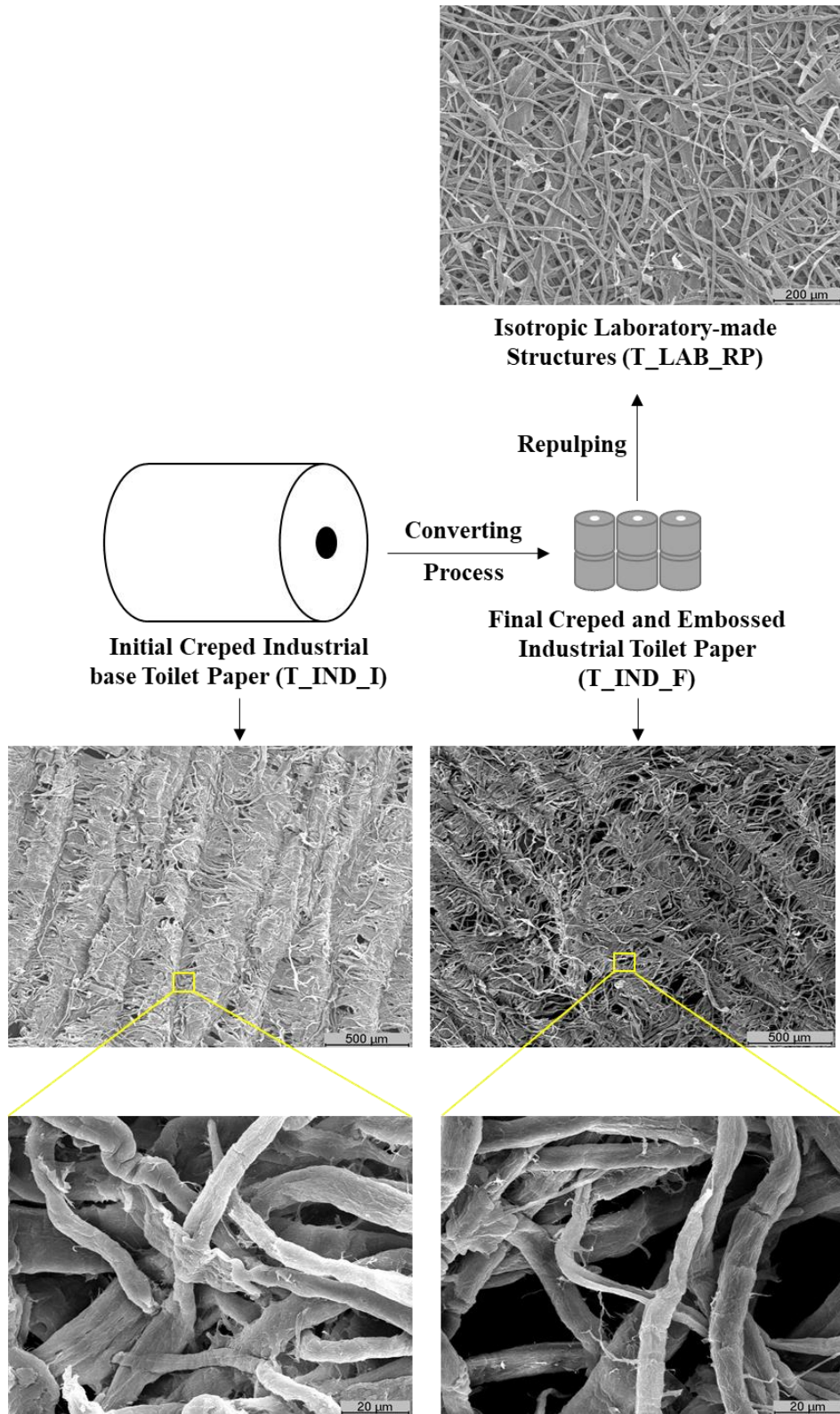


Figure III.51. Scheme of the methodology used for the industrial toilet paper characterization. The SEM images are representative of each paper.

Industrial toilet papers are produced with a content of eucalyptus pulp between 60 and 100% (de Assis et al., 2018a). The industrial toilet paper samples presented a fiber length weighted in length of 0.81 mm, fiber width of 20.8 μm , fiber coarseness of 9.02 mg/100m, and fines content of 47.8% (Table III.21). The selected industrial toilet paper can present 25 to 30% of reinforcement fibers, according to the fiber length and width distributions, as shown in Figure III.52. From all the studied industrial tissue paper samples, the industrial toilet paper sample was the one with the highest °SR, indicative of the high percentage of hardwood fibers in its composition.

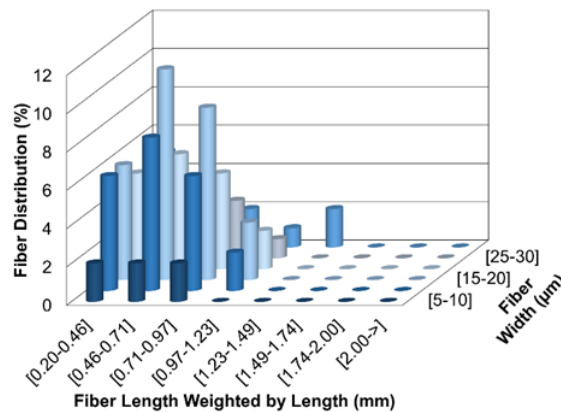


Figure III.52. Fiber length weighted by length and width distributions of industrial toilet paper sample.

Creping and converting conditions increased the structural properties of industrial toilet papers, by comparison with isotropic laboratory structures (Table III.22). The structure thickness, bulk, and apparent porosity were increased by 368, 191, and 9%, respectively. However, the final industrial toilet paper consists of 2-ply tissue paper sheets, each with approximately 16 g/m². Converting conditions increase these properties by 281, 80, and 4%, respectively, by comparing the initial and final industrial tissue papers. Regarding tissue properties, creping and converting conditions positively affected the softness HF properties by 10%, and water absorption capacity by 77%, but negatively affected the tensile strength index properties by 35%, and the Klemm capillary rise by 16% at 10 minutes. Besides, the embossing process increased the properties of softness HF by 2%, tensile index by 29%, and water absorption capacity by 31%, when comparing the samples T_IND_I and T_IND_F. In contrast, the Klemm capillary rise in sample T_IND_I was lower than in the other samples. The creping suppression and the embossing process increase the Klemm capillary rise by 107 and 74%, respectively (Table III.24).

The response of the liquid droplet deposition into the samples is higher for sample T_IND_I, followed by samples T_LAB_RP and T_IND_F, as shown in Figure III.53. In this case, the enhanced anisotropy effect of the liquid droplet spreading area result from the creping operation, as it can be seen in Table III.31. The largest axis of the elliptical shape of the spreading area in the sample T_IND_I is direction-dependent of the creping lines, indicating that this operation influences the tissue paper structure and water spreading. When this sample was subjected to the embossing process, the spreading area was reduced.

Despite the samples T_IND_F having 2-ply tissue paper sheets, higher bulk, and porosity, the water spreading effect was reduced. These structural properties had the most impact on the global water absorption properties. In Table III.31, it is also possible to observe a deformation of the embossing pattern in the sample T_IND_F that promoted the water flow in its direction, conditioning the spreading area by the creping lines, compared with the sample T_IND_I. Regarding the sample T_LAB_RP, the isotropy effect of the fibers promoted a circular shape of the liquid droplet spreading area, as depicted in Table III.31. The process operations suppression gave rise to a less porous structure, conditioning the spreading area, comparing the samples T_IND_I and T_LAB_RP.

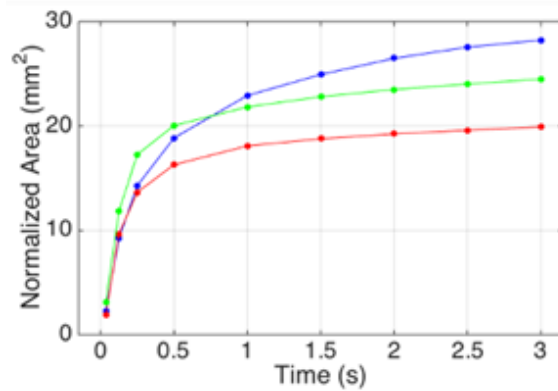


Figure III.53. The normalized spreading area as a function of time for the samples T_IND_I (blue), T_IND_F (red), and T_LAB_RP (green).

Table III.31. Evolution of the liquid droplet spreading area overtime in industrial toilet papers and the corresponding laboratory-made structure.

	t = 35.7 ms	t = 1.0 s	t = 3.0 s
T_IND_I			
T_IND_F			
T_LAB_RP			

III.2.4.5. Conclusions

The purpose of this work was to investigate the liquid retention properties on different fibrous furnish structures. The materials were selected to be representative of the different tissue process stages, including eucalyptus fibers, blend of eucalyptus and softwood fibers, enzymatic treatments, additives incorporation, and even different tissue papers, such as napkins, towel papers, and toilet papers. A combination of experimental and computational approaches aiming the optimization of the absorbency properties was presented. The structures were also modeled according to the 3D simulation model, resulting in a good estimative for the laboratory-made fibrous structures, to be optimized for the desired softness, strength, and absorption properties. The model included the fiber morphology and the behavior in the Z-direction, building a 3D structure with the sequential deposition of individual fibers, and consequently, having representative simulations of the laboratory-made fibrous porous tissue structures.

The integration of liquid droplet deposition data into tissue structures with the data of our tissue simulator (*SimTissue*) proved to be a good tool for studying the influence of fiber properties and process steps, on the spreading area of structured fibrous materials. The spreading area kinetics and its spreading shape is influenced by the type of structure in which the liquid droplet is deposited, being an isotropic or anisotropic structure, and by the process operations, including furnish and fiber modifications, creping, and embossing. This work presented several experimental and computational design plans for the water interaction influence in industrial, and laboratory porous tissue structures produced with different industrial strategies. A combination of absorption methods and spreading area kinetics were applied to measure these functional properties, aiming the optimization of industrial furnish processes for tissue products.

This work is a proof of concept that combines a droplet optical system, a the 3D fiber-based simulator, and *SimTissue* which has a predictive capacity not only of tissue properties but also of trends for changes in the softness, strength, and absorption measurements. This approach contributed to the design of multi-structured, innovative biomaterials with advanced features, at the micro and nanoscale. This strategy was decisive for optimizing the tissue functional properties, with more economical and sustainable resources. Due to the good absorption and retention profiles, tissue products can be used to provide rapid and deep skin hydration, as is the case of facial masks. Sustainable cosmetic substances, such as essential oils, can be incorporated into these single-use materials, promoting their penetration and permeation. The design and development of tissue products with optimized structural and absorption properties can also allow the replacement of plastic-based synthetic filters used, for example, in individual protection masks, being a sustainable and affordable alternative.

III.2.4.6. References

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III.2.5. Embossing Influence on the 3D Structure and Key Properties of Tissue Paper

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III.2.5.1. Abstract

The ability to predict the converting influence on key tissue properties, for different eucalyptus-based materials, constitutes valuable information to manage the furnish and optimize tissue properties. We present an innovative strategy grounded in the development of three major pillars: a laboratory embossing prototype, an optical system that captures the liquid interaction with paper structures, and a tissue paper simulator. The materials are a creped industrial base tissue paper, a disintegrated pulp obtained from the last one, and a never-dried bleached eucalyptus kraft pulp. From these two last samples, unpressed isotropic handsheets were produced with a similar grammage (17 g/m²). All samples were characterized for their morphology, water interactions, and chemistry-related properties. Tissue properties were evaluated on the non-embossed and embossed paper structures. The liquid absorption capacity, water retention value, and Klemm capillarity rise results were complemented with the analysis of the liquid drop spreading area, indicating that the embossing operation has a major influence on the liquid spreading kinetics. The tissue simulator was used to obtain 3D structures with different percentages of eucalyptus and softwood fibers, linking the fibers and the 3D paper structures properties, to obtain predictive capacity for the embossing influence on the softness, strength, and absorbency properties.

Keywords

3D Paper Structure; Laboratory Embossing Prototype; Eucalyptus-based Materials; Optical Liquid Drop System; Tissue Paper Properties; Tissue Paper Simulator

Inspired from Paper VII:

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III.2.5.2. Introduction

The balance between the properties of bulk, softness, strength, and liquid absorption is essential to produce high-quality premium products. Therefore, strategies for their optimization are crucial for the differentiation of these products on market (de Assis et al., 2018a, b; Morais et al., 2019, 2020a). The development of key tissue paper properties is related to the use of raw materials and with the modification processes used to produce tissue structures. Figure III.54 illustrates the principal tissue paper materials and operations considered in this study.

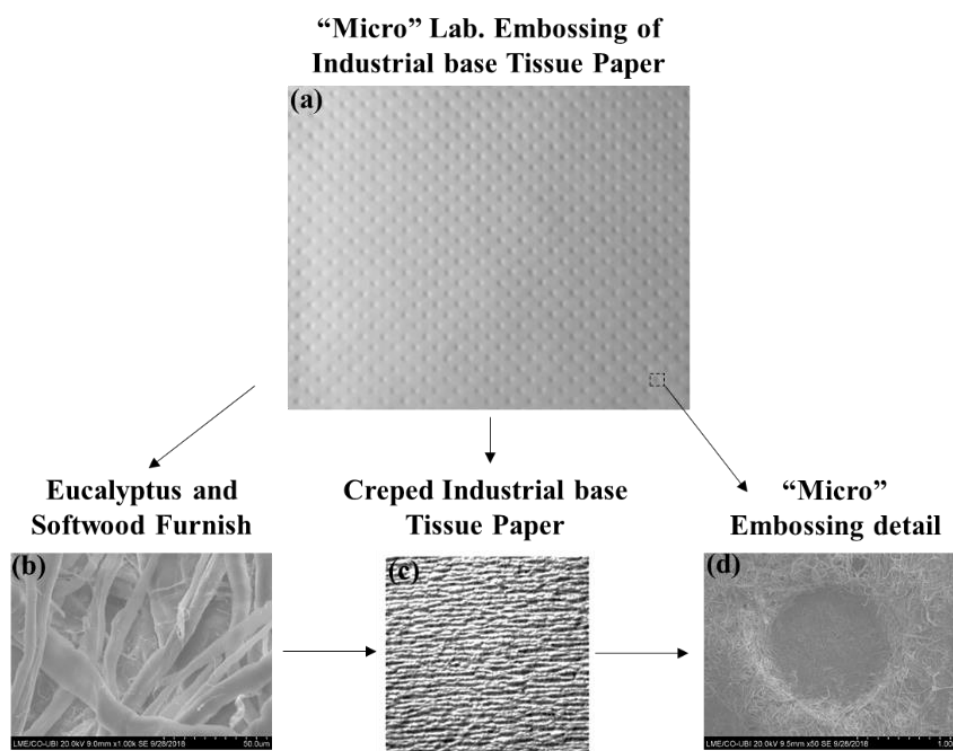


Figure III.54. Representative scheme of materials and process operations considered in this work. (a) industrial base tissue paper with laboratory “micro” embossing image; (b) eucalyptus and softwood furnish SEM image; (c) creped industrial base tissue paper image; (d) “micro” embossing detail SEM image.

The creping and embossing processes are conveyed to the final consumer since these operations are encoded in the final tissue structure (Kortschot, 1997). Therefore, the concept of structural hierarchy applied to tissue papers is fundamental to establish the role of fibers in the structure made by them. Tissue papers are mostly composed of hardwood fibers, specifically *Eucalyptus globulus* fibers, which enhances softness, absorbency, bulk, and porosity properties. Although in lower percentages, softwood fibers are essential to ensure strength properties and runnability of the tissue paper machine (de Assis et al., 2018a, b; Morais et al., 2019, 2020a). Additionally, fibers are subjected to process modification steps to develop strength, flexibility, and inter-fiber bonding ability. Mechanical treatments like beating or enzymatic treatments are essential for the fiber properties development (Spiridon, Duarte and Curto, 2003; Gigac and Fišerova, 2008; Gil et al., 2009; Park et al., 2019; Morais et al., 2021a).

Finally, the incorporation of additives, such as dry and wet strength agents, softeners, lotions, and recently, the possibility of using nano/microfibrillated cellulose as an additive, increases the complexity of the furnish mixture (Guan, An and Liu, 2019; de Assis et al., 2020; Vieira et al., 2020a; Zambrano et al., 2021; Morais et al., 2021b). Therefore, the development of advanced characterization and simulation tools, specifically developed for tissue paper, comes as an advantage for process optimization.

One of the fundamental steps in the tissue paper machine is the creping process that promotes structural changes in the paper sheet when detached from the Yankee dryer surface by the action of a creping blade (Mendes et al., 2020; Vieira et al., 2020a, b). This process promotes changes in the fiber orientation (some fibers in the machine direction change to the z-direction), and the formation of micro and macro wrinkles that form the crepe of the tissue paper (Figure III.54c). The creping process also contributes to properties such as bulk, softness, and liquid absorption capacity, among others, and, therefore, is determinant for the final quality of tissue paper (Mendes et al., 2020; Vieira et al., 2020a, b). In the converting machine, the industrial base tissue paper is subjected to the embossing process. Applying a localized pressure, this process conveys the paper sheets an engraving pattern and promotes the physical bonding between layers. The bonding between layers is usually ensured through glue (lamination glue). The type of embossing varies from product to product. In the case of products such as toilet papers, the embossing pattern designated by "micro" (Figure III.54d) is usually applied in the bottom layer, while the "deco" embossing (decorative patterns) is applied on the top layer (Mendes et al., 2020; Vieira et al., 2020a, b). To the best of our knowledge, there is an absence of scientific data regarding the 3D paper structure before and after the tissue paper embossing operation. The experimental data obtained with a laboratory embossing prototype constitutes valuable information, not only for the study and quantification of the embossing effect on eucalyptus-based papers but also for the 3D representation of these structures and consequently for its 3D modeling and development of predictive capability, to be used in the process optimization and management.

III.2.5.3. Experimental

III.2.5.3.1. Materials

The following materials were used for this study: an industrial never-dried bleached eucalyptus kraft pulp (HW, here designed by LAB_TISSUE), a creped industrial base tissue paper (IND_TISSUE) from the same paper mill, and the disintegrated pulp obtained from the last one (IND_LAB_TISSUE).

III.2.5.3.2. Methods

The samples were disintegrated (ISO 5263-1) and the morphological properties were evaluated using the MorFi analyzer (TECHPAP, Grenoble, France). The samples were chemically characterized in terms of the intrinsic viscosity (ISO 5351) and carboxyl group content (TAPPI T 237 cm-08).

The drainability of the pulps suspensions was determined by the Schöpper-Riegler degree (ISO 5267-1) and the water retention value (WRV) index was evaluated following the method described by Silvy et al. (1968).

To evaluate the tissue paper properties, isotropic laboratory non-pressed structures were produced with an adaptation of ISO 5269-1, with a similar grammage of the creped industrial base tissue paper (IND_TISSUE), with a range between 16.5 and 17.7 g/m². The structures were conditioned at 23 ± 1 °C with a relative humidity of 50 ± 2 %, according to ISO 187. Using an innovative embossing prototype equipment all samples were subject to a “micro” embossing pattern and were designated by IND_TISSUE_MICRO (Figure III.54a), IND_LAB_TISSUE_MICRO, and LAB_TISSUE_MICRO. The structures were characterized by measuring thickness, bulk (ISO 12625-3), grammage (ISO 12625-6). Softness was assessed using a Tissue Softness Analyzer, the TSA (Emtec) and the algorithm QAI. The tensile index (ISO 12625-4), water absorption capacity (adaptation of ISO 12625-8), and capillary rise Klemm method (adaptation of ISO 8787) were measured in a controlled temperature and humidity laboratory. The liquid spreading phenomenon was studied using an optical system specifically developed to study the interaction of different liquids in the surface of various paper structures (Fiadeiro et al., 2013; Mendes et al., 2013; Sousa et al., 2014; Curto et al., 2015). The optical system works by ejecting microliter droplets towards the sample surface, whereas images of the droplets are being captured for a given time. Computational studies were carried out using Matlab® (R 2020a, MathWorks), the fibers and 3D structures were modeled according to their dimensions and properties using *voxelfiber* (<https://github.com/eduardotrincaoconceicao/voxelfiber>) (Conceição et al., 2010; Curto et al., 2011; Morais et al., 2020b). A computational tissue simulator, the *SimTissue*, was developed specifically for tissue paper, integrating the key tissue fiber and structure properties, to predict the influence of furnish and tissue paper process operations, on softness, strength, and absorbency properties. In this work, the *SimTissue* was used to compare the influence of the furnish mixture composition, and different tissue process operations, such as the creping and embossing operations, and to predict the negative and positive trends for different furnish, and process operations scenarios.

III.2.5.4. Results and Discussion

The IND_TISSUE (and IND_LAB_TISSUE) were produced with a mixture of eucalyptus pulps and softwood pulps. These samples presented a fiber length weighted by length of 0.784 mm, fiber width of 20.7 µm, and fiber coarseness of 9.25 mg/100m. The LAB_TISSUE was produced with only eucalyptus pulps and presented a fiber length weighted by length of 0.729 mm, fiber width of 19.1 µm, and fiber coarseness of 6.31 mg/100m. Figure III.55 shows a comparison between the fiber length-weight in length and width distributions of the different samples. The biometry results proved the presence of reinforcement fibers (softwood fibers) in the industrial paper samples (IND_TISSUE) and the ones obtained from their deconstruction (IND_LAB_TISSUE), since the presence of histogram classes with fiber lengths and widths higher than 1.23 mm and 20 µm, respectively, are indicative of the presence of hardwood fibers.

In accordance, the fibers classes with simultaneously higher lengths and widths are absent from the eucalyptus fiber pulps (LAB_TISSUE sample).

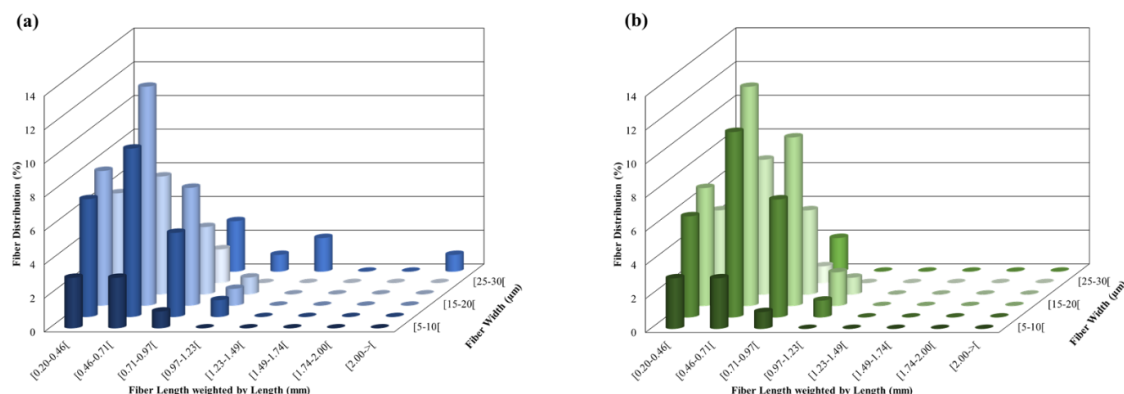


Figure III.55. Histogram of fiber length weighted by length and width distributions for: (a) IND_TISSUE (and IND_LAB_TISSUE) samples; (b) LAB_TISSUE sample.

The fiber dimensions information results were used to simulate 3D structures with different fiber mixtures. Figure III.56 shows a comparison between the LAB_TISSUE and the IND_LAB_TISSUE samples. The different structures were modeled computationally with the same fibrous elements, obtaining a structure with 100% eucalyptus fibers (Figure III.56a) and with a mixture of eucalyptus and softwood fibers (Figure III.56b).

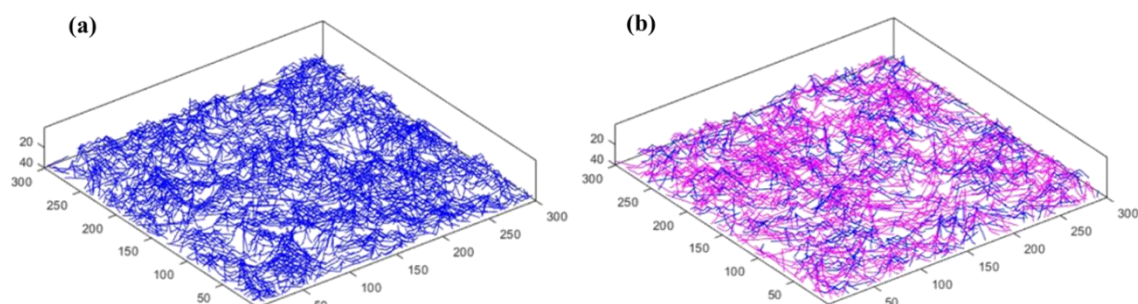


Figure III.56. Examples of 3D structures obtained by simulation with different percentages of eucalyptus and Softwood fibers. (a) Simulated paper structure made from eucalyptus fibers (blue color); (b) Simulated paper structure made from eucalyptus and softwood fibers (magenta color).

Additionally, IND_TISSUE (and IND_LAB_TISSUE) samples exhibit a fines content of 47.0 % in length comparing to the LAB_TISSUE sample, with a fines content of 38.5 % in length. These fine elements cause an increase in the sheet's density, promote better adhesion between the Yankee and paper web, and their presence contributes to gains in the mechanical properties (Boudreau and Germgård, 2014). Regarding chemical characterization, IND_TISSE (and IND_LAB_TISSUE) samples presented intrinsic viscosity and carboxyl group content higher than the LAB_TISSUE sample (607 ml/g vs 469 ml/g and 6.27 mmol/100g vs 5.08 mmol/100g, respectively). LAB_TISSUE sample showed a 27.8% higher amount of water retained by fibers and fibrils measured by WRV compared to IND_TISSUE (and IND_LAB_TISSUE) samples, which may be related to the extent of pulp fiber fibrillation and the hornification effect since the LAB_TISSUE is a never-dried pulp.

The “micro” embossing presents quantitative differences on the tissue properties, so the comparison of the influence of this operation on structures with 100% eucalyptus fibers, with a mixture of fibers, and with creping becomes essential. Figure III.57 presents the percentage of variation caused by the effect of “micro” embossing in the softness properties, such as the TSA Hand Feel (HF) and real softness (TS7) measurements. The TS7 parameter is the softness inherent to the material and progresses oppositely to the global parameter HF. Figure III.57 also integrates the tensile index, absorption capacity, and the Klemm capillary rise kinetics of the samples under study.

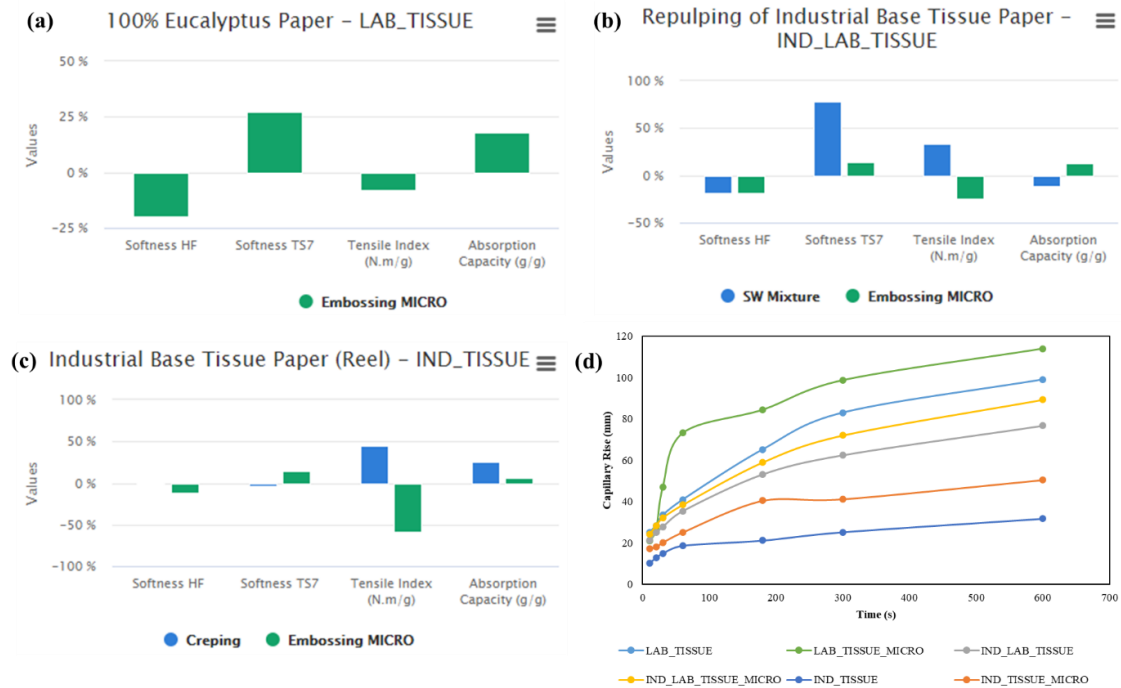


Figure III.57. Percentage of variation in the final end-use tissue properties for (a) LAB_TISSUE structure; (b) IND_LAB_TISSUE structure; (c) IND_TISSUE structure; (d) Klemm Capillary rise properties of the samples with and without “micro” embossing.

The results indicated that the “micro” embossing on LAB_TISSUE structures increase TS7 by 27%, water absorption capacity by 18%, and Klemm capillary rise by 15% and decreases the softness HF by 20%, and the tensile index by 8% (Figure III.57a, d). The IND_LAB_TISSUE sample results from the disintegration of the IND_TISSUE sample, so the influence of the softwood fiber blend (SW mixture) can be studied by comparing it with the LAB_TISSUE structure. The results indicated that the fiber mixtures increase the properties of softness TS7 by 78%, tensile index by 33%, and decrease the softness HF by 18%, water absorption capacity by 11%, and Klemm capillary rise by 22% (Figure III.57b, d). Regarding the “micro” embossing process on IND_LAB_TISSUE, the properties of softness TS7, water absorption capacity, and Klemm capillary rise increased by 14%, 13%, and 16%, respectively, and the softness HF and tensile index decreased by 18% and 25%, respectively (Figure III.57b, d). Additionally, the influence of creping can be quantified by comparing IND_TISSUE and IND_LAB_TISSUE samples.

The results indicated that, in these structures, the creping increases the properties of softness HF by 1%, tensile index by 45%, and water absorption capacity by 25%, however, decreases the softness TS7 by 4% and Klemm capillary rise by 58% (Figure III.57c, d). Regarding the “micro” embossing process on IND_TISSUE, the properties of softness TS7, water absorption capacity, and Klemm capillary rise are increased by 14%, 6%, and 59%, respectively, and the softness HF and tensile index are decreased by 12% and 59%, respectively (Figure III.57c, d).

The evolution of the liquid droplet spreading area over time in samples with and without embossing is presented in Figures III.58 and III.59. The evolution of the spreading area over time is defined by an initial fast kinetics, for spreading times below 0.5 s, followed by a slower kinetics, towards a stabilization value for the spreading area. The effect of the fiber mixture is illustrated when comparing the first two graphics, Figure III.58a and III.58b. The results indicate that having a paper structure made from 100% eucalyptus (LAB_TISSUE), Figure III.58a or the same paper structure with a softwood percentage around 30% (IND_LAB_TISSUE) Figure III.58b, has an impact on both the kinetics and final spreading area, with a larger difference from the embossed and non-embossed structures for the IND_LAB_TISSUE paper structures, which indicates that the presence of a hardwood pulp changes the water interaction differently, for embossed and non-embossed structures. The difference of water spreading behavior for embossed and non-embossed structures is not significant for creped paper, as it is visible in Figure III.58c. Figure III.59 presents a compilation of the images obtained for the liquid drop spreading on the fibrous structure over time, and the red line corresponds to the droplet outline on the structures. The spreading area kinetics, the final spreading area, and the shape of the spreading area are influenced by the type of 3D structure on which the liquid drop is deposited. With this analysis, the effect of isotropic formation, creping, and embossing operation can be analyzed separately. The results of the liquid spreading kinetics presented in Figure III.58 and III.59 constitute valuable information to optimize the embossing operation and to maximize the absorbency properties.

The embossing negative influence on the tensile index comes as a consequence of the fiber and structure deformations, induced by the applied pressure of this operation. The modification of the structure in the z-direction increases the TS7 parameter and, consequently, decreasing the HF softness parameter. The absorption properties are modified due to the creation of 3D effects on these structures, changing the water displacement around, and into the micro pattern circular dots. In Figure III.59 an illustrative example of this effect is visible for $t = 3s$ and LAB_TISSUE_MICRO. Additionally, the paper structure anisotropy effect, resulting from the creping operation is visible in the last two columns of Figure III.59, for both the IND_TISSUE samples, without and with embossing, respectively. In these images, the bigger axis of the elliptical spreading area is located along the creping lines direction, indicating that the creping has an influence on the tissue paper structure and consequently in the water spreading anisotropy.

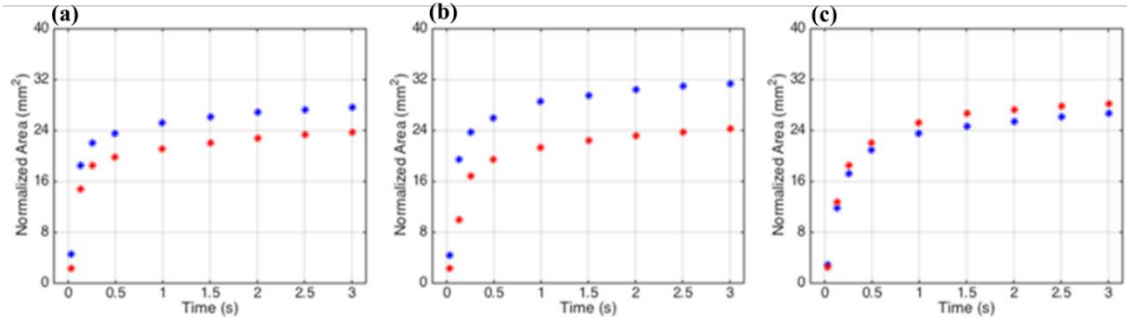


Figure III.58. The normalized spreading area as a function of time for the samples: (a) LAB_TISSUE; (b) IND_LAB_TISSUE; (c) IND_TISSUE. Samples without embossing are represented in blue and with embossing in red.

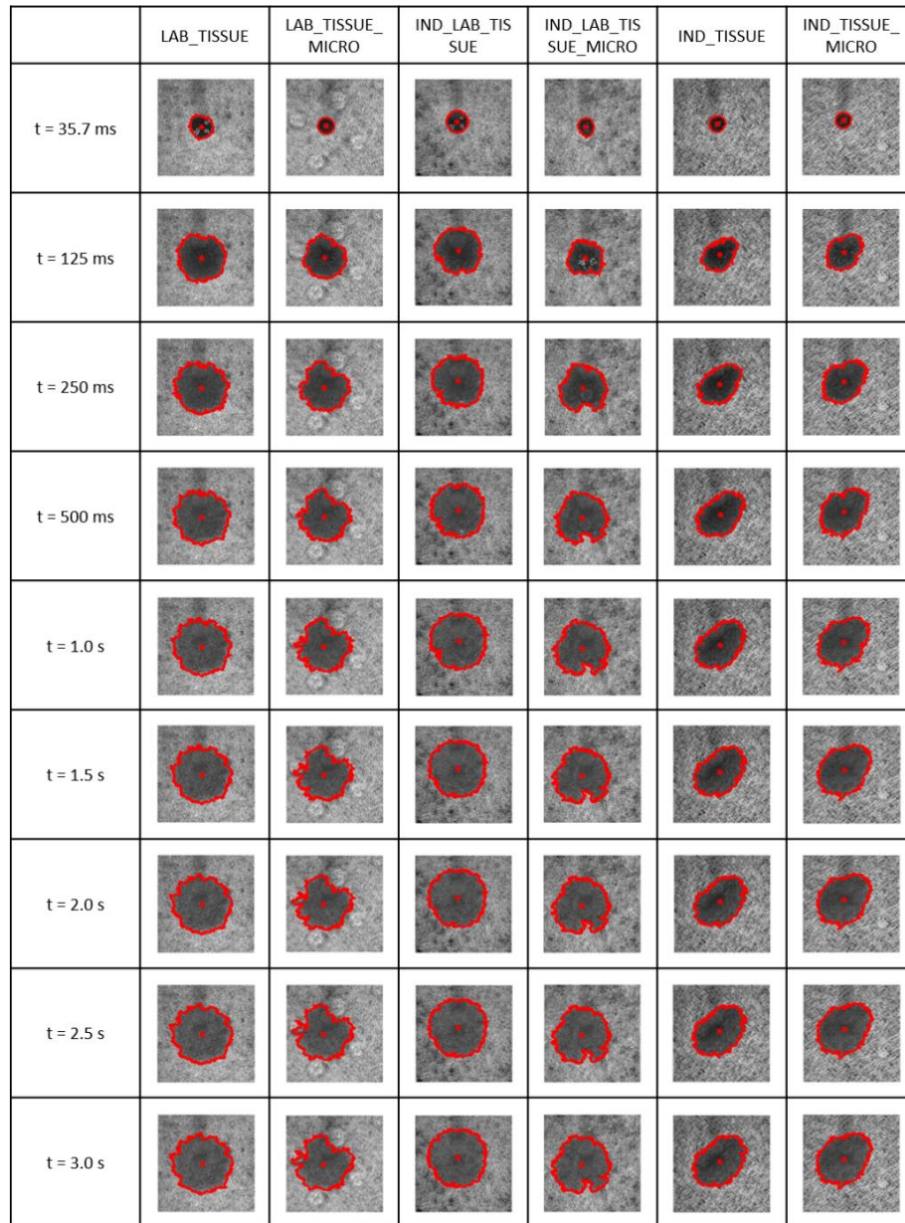


Figure III.59. Evolution of the liquid droplet spreading area over time in samples with and without embossing (field of view of each image $\approx 9.0 \times 9.0 \text{ mm}^2$; time intervals from 35.7 ms to 3.0 s; droplets volume range from 0.30 mm^3 to 0.47 mm^3).

III.2.5.5. Conclusions

Globally, the embossing operation has a negative impact on mechanical properties and softness, on the other hand, increases the thickness in the z-direction and consequently increases the bulk. The creped paper presents a slightly gain in the softness property, when comparing with handsheets with identical fiber mixture composition. Handsheets with 100% eucalyptus present higher softness than similar structures with a fiber composition made from a blend of hardwood and softwood fibers. The spreading area kinetics, the final spreading area, and the shape of the spreading area are influenced by the type of 3D structure in which the liquid drop is deposited, and by the type of process operations. The methodology presented in this work proved that the liquid drop prototype was able to capture the phenomenon of the liquid interaction with the 3D structure for tissue paper, giving valuable information about the water spreading kinetics and its anisotropy. The mixture of fibers, embossing and creping effects were successfully analyzed with this methodology, providing a proof of concept for the importance of the embossing prototype, associated with the optic system and the 3D fiber-based simulator, to predict the trends for the change of softness, strength, and absorbency properties. The experimental data obtained with the laboratory embossing prototype constitutes valuable information, not only for the study and quantification of the embossing effect on eucalyptus-based tissue papers but also for the 3D representation of these structures and consequently 3D modeling with predictive capability, to be used in the process optimization and management.

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III.2.6. Characterization of Absorbency Properties on Tissue Paper Materials with and without “Deco” and “Micro” Embossing Patterns

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III.2.6.1. Abstract

Water absorption is a key property in several tissue paper materials and can be a differentiating factor in terms of consumer choice. The converting modifications applied in the tissue industry can improve absorbency properties. For this purpose, the main goal of the present work is to study the influence of “deco” and “micro” embossing on water absorption capacity, Klemm capillary rise, and liquid spreading kinetics in tissue papers. An industrial never-dried bleached eucalyptus kraft pulp, a creped industrial base tissue paper, and a disintegrated fibrous suspension obtained from the same industrial paper were used to produce structures with and without “deco” and “micro” embossing patterns. The results indicate that the “micro” embossing process promoted bulky and porous structures, enhancing water absorption capacity and Klemm capillary rise properties, while the “deco” embossing pattern decreased water absorption capacity properties. The creping process also increased the water absorption capacity but decreased Klemm capillary rise properties along with the fiber mixtures. Regarding the liquid spreading kinetics, both embossing patterns decreased this property in uncreped isotropic structures, contrary to creped anisotropic structures. The eucalyptus and softwood fibers mixture improved the spreading kinetics compared to the creping process. The performance of structures with and without embossing allowed to quantify the liquid retention properties, combining ISO experimental methods and an optical system that records the liquid interaction with fibrous structures. In conclusion, this laboratory embossing method can be used as an alternative method to optimize converting operations and the final tissue paper characterization, on a laboratory scale.

Keywords

Absorbency Materials Characterization; Creping/ Embossing Operations; Hardwood/ Softwood Fibers; Liquid Spreading Kinetics; Optical Liquid Droplet System; Tissue Papers

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III.2.6.2. Introduction

In the last decades, the tissue paper industry has shown high growth and competitiveness due to the high hygiene products consumption worldwide. Tissue paper materials are creped fibrous structures with a low grammage between 5 and 40 g/m², presenting an elastic and porous structure, with good absorption capacity and softness (de Assis et al., 2018a). These materials are usually used to produce toilet papers, facial papers, towel papers, napkins, among others (de Assis et al., 2018a; Morais et al., 2019). High-quality tissue papers must present factors such as bulk, softness, strength, and absorption. Therefore, it is important to find strategies to produce premium materials to differentiate them in the market, understanding the relationship between their functional properties, and in which sense the modification of one property can affect others (de Assis et al., 2018a, b; Morais et al., 2019, 2020a; Vieira et al. 2020a). The development of optimized tissue paper properties is related to the fiber selection and their modification process steps, including enzymatic treatments, refining, and additives incorporation (Spiridon et al., 2003; Gigac and Fišerová, 2008; Park et al., 2019; Guan et al., 2019; Zambrano et al., 2021; Morais et al., 2021a, b; Debnath et al., 2021). In the production of tissue paper materials, a mixture of eucalyptus fibers is used to enhance bulk, porosity, softness, and absorption properties, meanwhile, softwood fibers are also added to ensure strength properties, and the paper machine runnability. The proportion of this mixture depends on the manufacturer and the desired type of product (de Assis et al. 2018a, b; Morais et al. 2019, 2020a; Stankovská et al., 2020).

One of the fundamental operations in the tissue paper industry is the creping process, which consists of the formation of a uniformly rough structure (de Assis et al., 2020). In the paper machine, the Yankee cylinder is coated with chemical additives to promote both the wet paper sheet adhesion in the Nip, and the dry paper sheet detachment at the Yankee exit (Boudreau and Germgård, 2014). In this phase, the doctor blade scrapes/removes the paper sheet from the Yankee cylinder surface, creating the paper rough folds. The creping process also includes a change in the fiber direction from the machine direction (MD) to the Z-direction, which results in the breaking of inter-fiber bonding, promoting higher softness and elongation capacity (Raunio and Ritala, 2012; Pan et al., 2019). After the production of creped industrial base tissue papers, those are subjected to converting operations to produce the desired type of tissue paper materials. One of these operations is the embossing process in which surface deformations are carried out to the base tissue paper by applying localized pressures. Embossing occurs by placing multiple layers of base tissue paper on top of each other, penetrating a pattern into each layer, and holding them together in a final lamination. Embossing patterns are applied to tissue papers to improve porosity, hygroscopicity, thickness, flexibility, and liquid retention properties. Embossing can result in raised or lowered patterns on the paper, using heat, pressure, and stamping matrices (Spina and Covalcante, 2018; Mendes et al., 2020; Vieira et al., 2020b, c). To the best of our knowledge, there is an absence of scientific data regarding the 3D tissue paper structure characterization and absorbency properties before and after the embossing operation.

As previously mentioned, the type of embossing pattern applied to tissue paper materials has an important impact on product perception. For example, the use of a “deco” pattern gives a decorative effect to the paper, while a “micro” circular pattern gives to the consumer a more absorbent paper perception. For this reason, water absorption properties are differentiating factors in terms of consumer choice. The two fundamental parameters in these properties are the water absorption speed and the global water absorption capacity. The first parameter consists of the time that a structure absorbs a quantity of water, while the second parameter includes the total water content that the paper can absorb in its 3D structure (Beuther et al., 2010; Gigac et al., 2019). The absorption properties depend on factors such as raw materials used, the type of 3D structure, fines content, bulk, porosity, sheet formation, additives, creping, and embossing (Ashari et al., 2010; Mullins and Braddock, 2012; Stankovská et al., 2019). Therefore, different innovative approaches can be considered to optimize the tissue absorption properties, including the 3D simulation of these tissue structures, using 3D computational tools (Curto et al., 2015; Morais et al., 2020b, c). Additionally, an experimental optical prototype system, developed by our research members (Mendes et al., 2013), has been used to collect liquid deposition data over time, to characterize the liquid droplet spreading area and kinetics, through image analysis (Fiadeiro et al., 2013; Mendes et al., 2013; Sousa et al., 2014; Curto et al., 2015). Different studies of liquid droplet deposition and spreading kinetics have indicated that porous structure knowledge is one of the key parameters for optimizing absorption properties since the pore sizes influence the liquid droplet spreading and equilibrium state (Senden et al., 2000; Wågberg and Westerlind, 2000; Clarke et al., 2002; Starov et al., 2003; Kannangara et al., 2006; Wang et al., 2007; Hilpert and Ben-David, 2009; Rosenholm, 2015; Chen et al., 2020).

In this context, the main goal of the present work was to compare the performance of structures with and without embossing made with eucalyptus fibers and a fiber mixture from a disintegrated creped industrial base tissue paper, investigating the effect of fibrous composition, creping, and embossing process on the water absorption properties. To address this objective, a laboratory embossing method was used with two embossing patterns, namely “deco” and “micro” patterns, and an evaluation of water absorption capacity, Klemm capillary rise, and liquid spreading kinetics was performed on uncreped and creped structures before and after embossing.

III.2.6.3. Materials and Methods

Figure III.60 presents the detailed diagram of the experimental plan design executed in this study.

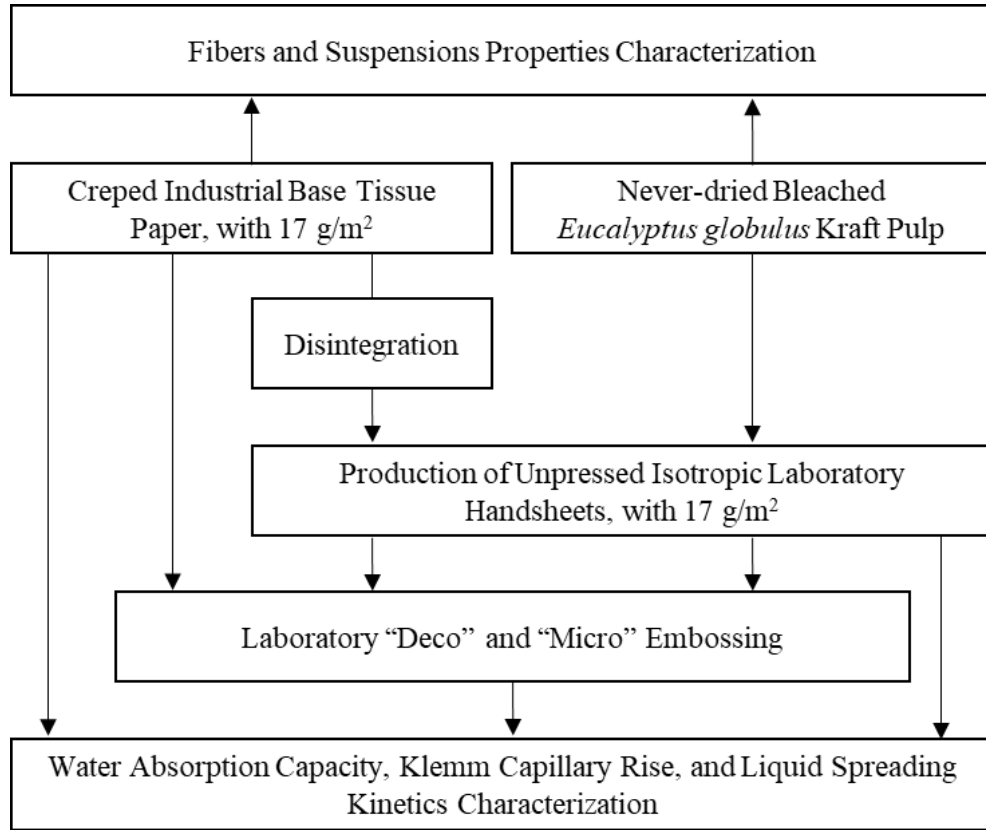


Figure III.60. Diagram of the experimental plan design.

III.2.6.3.1. Materials

A never-dried bleached *Eucalyptus globulus* kraft pulp (HW, here designed by H_h) and creped industrial base tissue paper (I_{hs}) were selected for the present work. The I_{hs} sample was produced, approximately, with 49% of eucalyptus pulps, 27% of softwood pulps, and 24% of broke. The nomenclature of all samples is identified in Table III.32. The $HD_{I_{hs}}$ samples, described in this table, resulted from the disintegration of the I_{hs} sample.

Table III.32. Nomenclature of the tissue paper samples used in this study.

Nomenclature	Composition	Embossing
H_h	Handsheet (hardwood)	none
H_hE_d		“deco”
H_hE_m		“micro”
$HD_{I_{hs}}$	Handsheet of the Disintegration of Industrial Sheet (hardwood + softwood)	none
$HD_{I_{hs}}E_d$		“deco”
$HD_{I_{hs}}E_m$		“micro”
I_{hs}	Industrial Sheet (hardwood + softwood)	none
$I_{hs}E_d$		“deco”
$I_{hs}E_m$		“micro”

III.2.6.3.2. Fibers and Suspensions Characterization

The fiber length/width ratio or slenderness ratio, coarseness, and fines elements properties were determined by image analysis of a diluted sample suspension of 20 mg/L, through a flow chamber, using the MorFi analyzer (TECHPAP, Grenoble, France). The Schöpper-Riegler degree, °SR method was used to measure the sample drainability, according to ISO 5267-1. The water retention value, WRV method was assessed using the method described by (Silvy et al., 1968).

III.2.6.3.3. Handsheets Preparation and Embossing Operation

The samples were disintegrated according to the ISO 5263-1. The isotropic laboratory handsheets were prepared according to an adaptation of the ISO 5269-1. The H_h and HD_{Ihs} samples were produced with 17 g/m² and without pressing. This grammage is similar to the I_{hs} sample. All the produced fibrous structures were conditioned at 23 ± 1 °C with a relative humidity of $50 \pm 2\%$, according to ISO 187.

Meanwhile, samples of the produced fibrous structures were subject to the “deco” and “micro” embossing process using an innovative laboratory embossing prototype equipment. The nomenclature of all samples with these embossing patterns is also identified in Table III.32.

III.2.6.3.4. Tissue Structural and Absorption Characterization

The structural properties, water absorption capacity, Klemm capillary rise, and liquid droplet spreading kinetics of structures with and without embossing were characterized.

The grammage was determined according to ISO 12625-6, and the thickness and bulk were determined following the ISO 12625-3. For thickness measurements, the FRANK-TPI® Micrometer equipment (FRANK-PTI GMBH, Birkenau, Germany) was used. Apparent porosity was calculated using the following equation: $P [\%] = [1 - (\rho_{\text{cellulose}} / \rho_{\text{structure}})] \times 100$, where $\rho_{\text{cellulose}}$ is the cellulose density (1.6 g/cm³) and $\rho_{\text{structure}}$ is the structure density (g/cm³) (Costa et al., 2016).

The water absorption capacity method was determined by the immersion method, using a FRANK-TPI® Tissue Absorption Tester (FRANK-PTI GMBH, Birkenau, Germany), according to an adaptation to ISO 1265-8.

The water capillary rise was determined using the Klemm method, following an adaptation to ISO 8787.

An optical system (Prototype, Universidade da Beira Interior, Covilhã, Portugal), developed by our research members (Mendes et al., 2013) and applied in several materials studies (Fiadeiro et al., 2013; Sousa et al., 2014; Curto et al., 2015) was used to study the liquid droplet spreading kinetics. In this work, the optical system is a unique device to analyze the 3D structures on different tissue papers with and without embossing. This system works by ejecting microliter droplets toward the structure surface, whereas images of the droplets are being recorded for a given period.

The liquid spreading kinetics and spreading dynamics data were collected from 35.7 ms to 3 s, and the snapshot images selected in this work were 35.7 ms (initial time), 250 ms and 1 s (intermediate times), and 3 s (final time).

III.2.6.3.5. Computational Studies

A computational tissue simulator, the *SimTissue* (FibEnTech-UBI, Covilhã, Portugal) was developed specifically for tissue paper furnish materials and used to study different scenarios of the influence of the fiber mixtures, creping, and embossing processes on tissue end-use properties. This simulator works by integrating the key tissue fiber and structure properties, predicting the softness, strength, and absorption properties of different furnish and tissue paper process operations.

III.2.6.4. Results and Discussion

III.2.6.4.1. Fibers and Suspensions Characterization

The eucalyptus sample, H_h , presented a slenderness ratio in the same range as the sample consisting of a mixture of eucalyptus and softwood fibers, HD_{Ihs} / I_{hs} (Figure III.61a), indicating that the H_h sample had fiber lengths and widths lower than the HD_{Ihs} / I_{hs} samples. These morphological properties of the HD_{Ihs} / I_{hs} samples directly contributed to the development of the mechanical properties, improving the tissue paper machine runnability. This ratio is also related to the paper structure density and pulp digestibility (Morais et al., 2020a; Dutt and Tyagi, 2011). Compared to our previous study (Morais et al., 2019, 2020a), the H_h sample showed a low slenderness ratio compared to other eucalyptus pulps. This result indicates that this sample has shorter and thicker fibers, presenting a negative effect on the pulp mechanical properties, not ready for collapse, and providing less surface contact for bonding. Coarseness is influenced by the fiber thickness, width, and fiber pulp population (Morais et al., 2020b). Because this parameter depends on several factors, it should only be compared between fibers of similar species. The samples showed a difference of 48% for coarseness properties (Figure III.61a). This result is due to the presence of softwood fibers in the HD_{Ihs} / I_{hs} samples. Additionally, the HD_{Ihs} / I_{hs} sample presented a higher fine content than the H_h sample, with a difference of 22% (Figure III.61a). This result is due to the presence of refined softwood fibers and broken fibers in the HD_{Ihs} / I_{hs} samples. These broken fibers are obtained by the sheet breakage in the tissue paper machine, which is collected and recirculated to a pulper and introduced again in the blend eucalyptus and softwood pulps process. Regarding the water drainage capacity (Figure III.61b), both samples showed °SR values in the recommended range to produce high-quality tissue papers (de Assis et al., 2018a), between 25 and 26 °SR. The small difference found in these measurements may be due to the presence of refined softwood fibers during the production process of the HD_{Ihs} / I_{hs} sample. Finally, the H_h sample showed a higher WRV (+ 28%) than the HD_{Ihs} / I_{hs} sample (Figure III.61b). This result can be explained by the absence of the hornification effect caused by the drying operation of the H_h pulp sample since this pulp is a never-dried eucalyptus sample (Weise et al., 1996; Giacomozzi and Joutsimo, 2015).

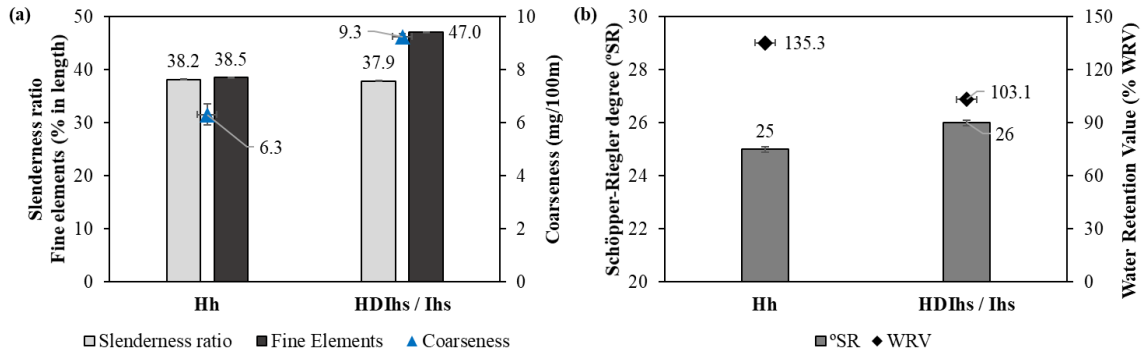


Figure III.61. Pulp fiber morphological properties, namely slenderness ratio, coarseness, and fine elements (a), and pulp suspension properties, such as °SR and WRV (b), of the H_h and HDI_{hs} / I_{hs} samples.

III.2.6.4.2. Tissue Structural and Absorption Characterization

The tissue paper's structural properties, such as bulk and porosity, influence the water absorption properties (Morais et al., 2019; Stankovská et al., 2019). The bulk and porosity properties of the structures with and without embossing are shown in Figure III.62a. The *SimTissue* was used to compare the influence of the furnish mixture composition, and different tissue process operations, such as the creping and embossing operations, and to predict the negative and positive trends for different furnish, properties, and process operations scenarios, as shown in Figure III.63. When comparing the samples without embossing, two effects must be considered: fiber mixing and creping process. The effect of the blend of eucalyptus and softwood fibers is quantified by comparing the H_h and HDI_{hs} samples, indicating that these softwood fibers increase the structure by 5% and the structure porosity by 1%. On the other hand, the creping effect is quantified by comparing the HDI_{hs} and I_{hs} samples, indicating that this operation increases the structure bulk by 30% and the structure porosity by 3%. These results indicate that creping promotes the production of more bulky and porous structures compared to the fiber mixture. The effect of "deco" and "micro" embossing on H_h structures increases, respectively, the bulk by 43% and 246%, and the porosity by 4% and 10%. In HDI_{hs} structures, the effect of "deco" and "micro" embossing increases the bulk by 5% and 78%, and the porosity by 1% and 5%, respectively. Finally, in the I_{hs} samples, the effect of "deco" and "micro" embossing increases the bulk by 5% and 73%, and the porosity by 0.4% and 4%, respectively. Overall, "micro" embossing has a higher influence on structural properties than "deco" embossing. In both patterns, the HDI_{hs} embossed structures showed less bulk and porosity than the H_h and I_{hs} embossed samples. The "micro" pattern promoted bulkier and more porous H_h structures compared to the I_{hs}E_m ("micro" embossed) structures, while the "deco" pattern obtained H_h and I_{hs} embossed structures with the same range of bulk and porosity. It was found that the structural properties of embossed structures are modified not only by the embossing pattern but also by the fiber mixture and creping operation. In this case, eucalyptus fibers were more suitable to produce more bulky and porous structures with embossing. The bulk and porosity of the embossed structures are decreased with the presence of softwood fibers in the mixture and increased with the creping process operation.

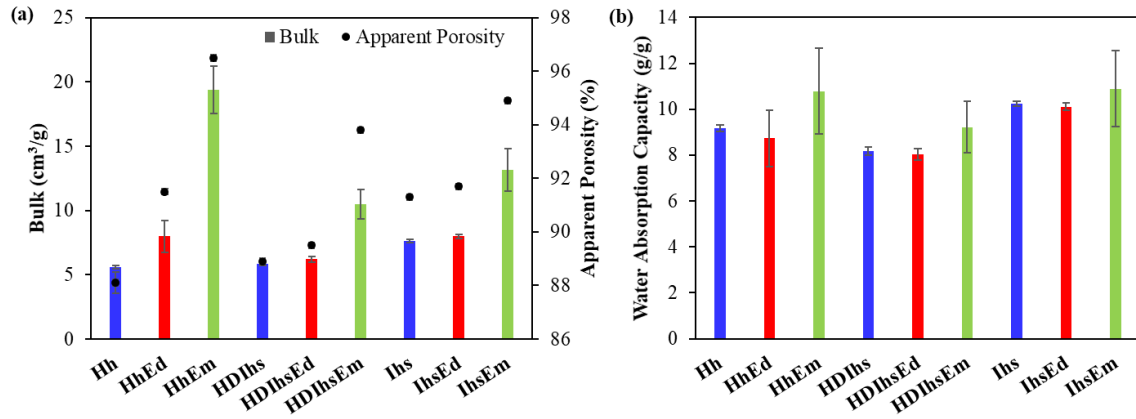


Figure III.62. Structural properties, namely bulk and apparent porosity (a), and water absorption capacity properties (b) of the samples without and with “deco” and “micro” embossing.

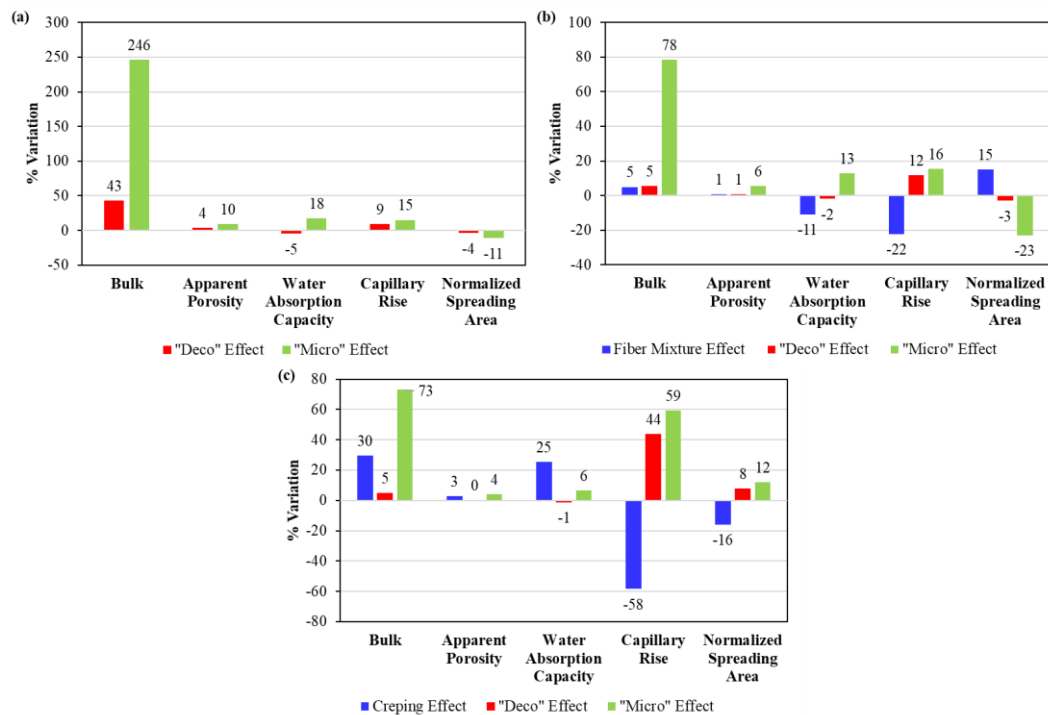


Figure III.63. Percentage of variation in the tissue structural and absorption properties for H_h sample (a), HD_{Ihs} sample (b), and I_{hs} sample (c), predicted using the *SimTissue*.

The water absorption capacity properties of the structures with and without embossing are shown in Figure III.62b, and its percentage of variation is shown in Figure III.63. The fiber mixture effect reduced this property by 11%, comparing H_h and HD_{Ihs} samples. Although the structure bulk and porosity with a blend of eucalyptus and softwood fibers are slightly higher than those obtained with only eucalyptus fibers, the higher fines content of the HD_{Ihs} sample may have contributed to a water absorption capacity decrease, since inter-fiber bonds and low pore size and distribution prevailed in this property. Stankvska et al. (2020) also reported that by increasing the softwood fiber content in tissue formulations, the structure water absorption was decreased. The higher fiber water affinity (WRV, Figure III.61b) of the H_h sample also can explain this behavior.

On the other hand, the creping effect improved this absorption property by 25%, comparing the HD_{Ihs} and I_{hs} samples, which is in accordance with the structural properties. The embossing process modified the absorption of tissue structures. In general, the "deco" pattern had a small negative influence on the water absorption capacity properties, while the "micro" pattern increased these properties. The "deco" embossing decreased the absorption capacity by 5%, 2%, and 1% of the H_h , HD_{Ihs} , and I_{hs} embossed structures. The "micro" embossing increased the absorption capacity by 18%, 13%, and 6% of the H_h , HD_{Ihs} , and I_{hs} embossed structures. As in the structural properties, the HD_{Ihs} embossed structures with both patterns showed less water absorption capacity than the H_h and I_{hs} embossed samples. In this case, the I_{hs} embossed structures with both embossing patterns showed better absorption properties than the H_h embossed structure. This result indicates that the creping process overcomes the water absorption compared to eucalyptus fibers, although the H_hE_m ("micro" embossed) structures were bulkier than the $I_{hs}E_m$ ("micro" embossed) structures. Figure III.64a also presents the relationship between the bulk and the water absorption capacity, in which it is possible to observe two distinct zones in the graphic. From this analysis, it was found that, overall, the structures without embossing and with "deco" embossing are in a range with low bulk (5.6 – 8.0 cm^3/g) and water absorption (8.1 – 10.2 g/g), while structures with "micro" embossing are in a range with high bulk (10.5 – 19.4 cm^3/g) and water absorption (9.2 – 10.9 g/g).

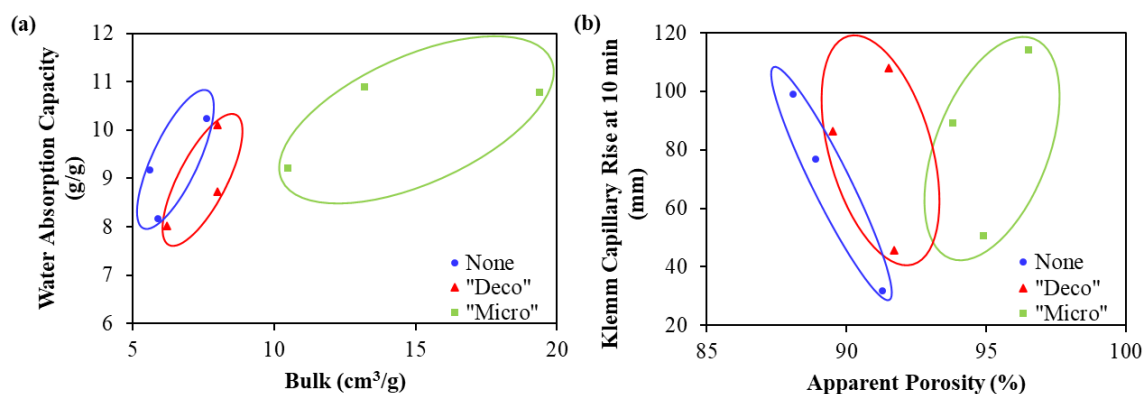


Figure III.64. Water absorption capacity as a function of bulk (a) and Klemm capillary rise at 10 minutes as a function of apparent porosity (b) of the structures without embossing, with "deco" embossing and with "micro" embossing.

The Klemm capillary rise depends on the adhesion and cohesion forces of the water molecules that rise through the fiber walls or between the pores. The Klemm capillary rise properties of the structures with and without embossing and their percentage of variation are shown in Figure III.65 and III.63, respectively. This assay was performed on the machine direction, MD (perpendicular to crepe folds), and cross direction, CD (parallel to crepe folds) of the I_{hs} sample. The results indicated that the CD direction enhanced a better Klemm capillary rise (+ 75% at 10 minutes) compared to the MD direction (Figure III.65a). The crepe lines improved this property. Klemm capillary rise studies for $I_{hs}E_d$ and $I_{hs}E_m$ samples were performed only in the MD direction. The fiber mixture effect decreased this property by 22% (Figure III.63b, III.65b), comparing H_h and HD_{Ihs} samples, which is in accordance with the water absorption capacity properties.

The creping effect also decreased the Klemm capillary rise by 58%, comparing the $HD_{I_{hs}}$ and I_{hs} samples (Figure III.63c, III.65b). The intermolecular bonding between fibers and water molecules in I_{hs} structures with higher pores may have decreased capillary rise. Additionally, in the case of very narrow channels due to creping process, the water progression may have been strangled by the limited space for capillary rise (Mullins and Braddock, 2012). Regarding the embossing effect, capillarity absorption presented a different behavior to immersion absorption. In all samples, both "deco" and "micro" embossing increased capillary rise compared to samples without embossing. The "deco" embossing increased the capillary rise at 10 minutes by 9%, 12%, and 44% of the H_hE_d , $HD_{I_{hs}}E_d$, and $I_{hs}E_d$ embossed structures (Figure III.63, III.65c,d,e). The "micro" embossing also increased the capillary rise at 10 minutes by 15%, 16%, and 59% of the H_hE_m , $HD_{I_{hs}}E_m$, and $I_{hs}E_m$ embossed structures (Figure III.63, III.65c,d,e). These results indicate that the "micro" pattern has a higher influence on the capillary rise properties than the "deco" pattern. In both patterns, capillarity absorption was more pronounced in the H_h embossed structures, followed by $HD_{I_{hs}}$, and I_{hs} embossed structures. It was found that eucalyptus fibers present a higher influence on the water capillary rise than the fiber mixture, followed by the creping process, both in structures with and without embossing. Additionally, Figure III.64b also presents the relationship between the apparent porosity and the capillary rise at 10 minutes, in which it is possible to observe three distinct zones in the graphic. From this analysis, it was found that, overall, the structures without embossing are in a range with low porosity (88.1 – 91.3 %) and capillary rise (32 – 99 mm). The "deco" embossed structures are in a range with intermediate porosity (89.5 – 91.7 %) and Klemm capillary rise (46 – 108 mm), while structures with "micro" embossing are in a range with high porosity (93.8 – 96.5 %) and Klemm capillary rise (51 – 114 mm). Therefore, the pores of the structures should present uniform dimensions, since the contribution of the gravity force should not be higher than the force exerted by the water molecules that allows the molecules to ascend the channels. Hence, there must be a balance between the pore dimensions and distribution to promote the Klemm capillary rise efficiency (Beuther et al., 2010).

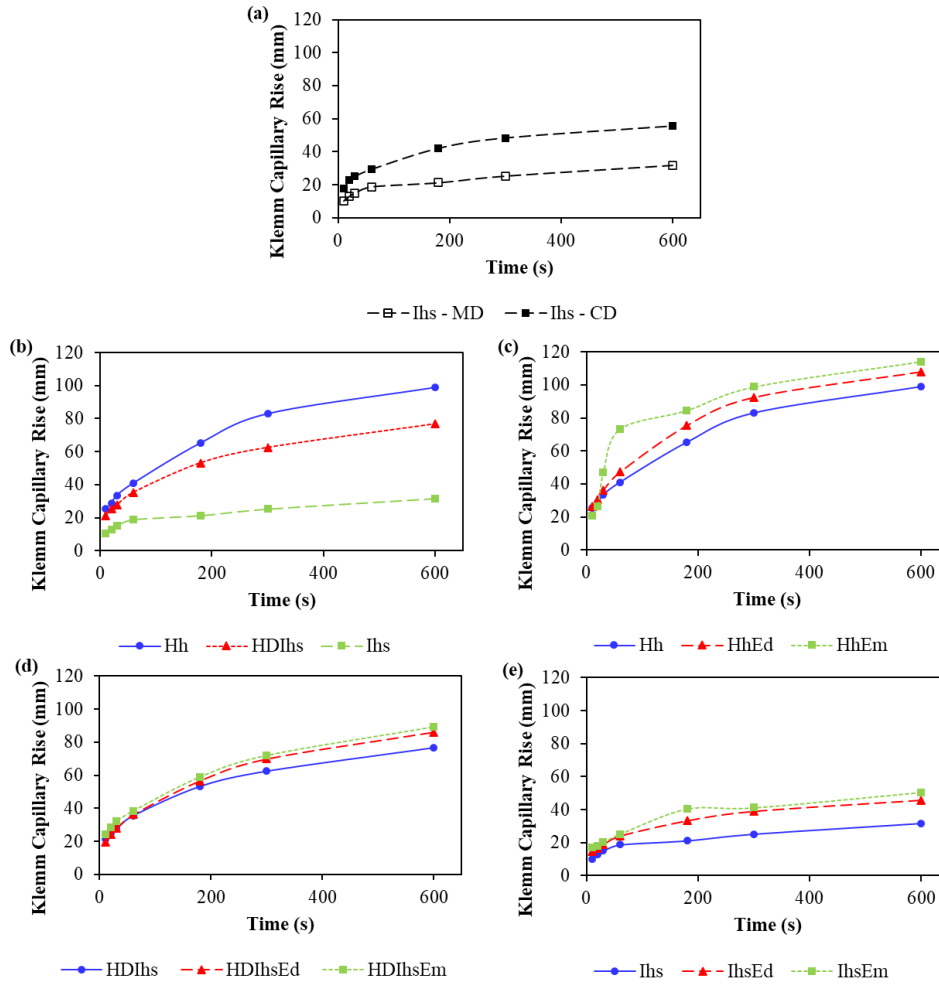


Figure III.65. Klemm capillary rise as a function of time of the I_{hs} structures in MD and CD direction without embossing (a), all handsheets without embossing (b), H_h structures with and without “deco” and “micro” embossing (c), HDI_{hs} structures with and without “deco” and “micro” embossing (d), and I_{hs} structures with and without “deco” and “micro” embossing (e).

The kinetics of the liquid droplet spreading area over time in papers with and without embossing is presented in Figure III.66 and Table III.33. This liquid spreading area of all samples is defined by initial fast kinetics for times below 0.5 s, followed by slower kinetics, towards a stabilization value for the liquid spreading area. The response of the liquid droplet deposition into the 3D fibrous structure made from fiber mixtures, HDI_{hs}, indicates that the liquid spreading area is higher compared to 100% eucalyptus structure, H_h (Figure III.66a). These results indicated that the eucalyptus and softwood fiber mixture increased the liquid spreading kinetics properties by 15% (Figure III.63b), corresponding to a higher porous and bulky structure (Figure III.62a). However, this result is not in accordance with the immersion and capillary absorption properties (Figure III.62b, III.65b). The liquid droplet spreading area of the creped structure, I_{hs}, was smaller (-16%, Figure III.63c) than the laboratory-made structures produced by disintegration of this sample, HDI_{hs} (Figure III.65a). This result is following the Klemm capillary rise properties. The creping lines enhance the tortuosity phenomenon since the liquid droplet presented higher difficulty to intrude into or pass through the cellulosic fibers, compared to the HDI_{hs} structure.

Additionally, the phenomenon of anisotropy was observed in I_{hs} structures, and isotropy in H_h and $HD_{I_{hs}}$ structures (Table III.33). The liquid droplet spreading area was direction-dependent of the creping lines in the creped industrial base tissue paper sample, presenting an elliptical shape. On the other hand, the liquid droplet spreading area tends to have a circular shape for isotropic laboratory samples without embossing. It was found that the fiber mixture in these structures improved the liquid droplet spreading kinetics over time, followed by eucalyptus fibers and the creping process. The "deco" embossing effect decreased the liquid spreading kinetics in both H_hE_d and $HD_{I_{hs}}E_d$ structures by 4% and 3%, respectively (Figure III.63, III.66b, c), being in accordance with the water absorption capacity properties. However, this decrease is in the same range as structures without embossing. This result was also reported in Figure III.64a. Additionally, the same behavior was also observed for the "micro" embossing in these two samples (Figure III.66b, c). The "micro" embossing also decreased the liquid spreading kinetics by 11% and 23% of the H_hE_m , and $HD_{I_{hs}}E_m$, embossed structures (Figure III.63a,b). The "micro" embossing presented a negative influence on the liquid spreading kinetics compared to the "deco" embossing. This absorption property is modified by the creation of 3D effects of the embossing patterns on the structures, changing the water flow, initially around and then within the "deco" linear pattern and "micro" circular dots. Due to this 3D effect, the liquid has difficulty passing through the cellulose fibers, as seen in creped structures without embossing. This effect can be observed, for example, for $t = 3s$ in H_hE_d and H_hE_m structures (Table III.33). Additionally, the liquid droplet spreading area can yield random and irregular shapes considering the embossing pattern present on the structure surface (Table III.33). Regarding the I_{hs} sample, the structures with embossing showed a higher liquid spreading area than the structures without embossing (Figure III.66d). The "micro" pattern presented a higher influence (+12%, Figure III.63c) on the liquid droplet spreading kinetics compared to the "deco" embossing pattern (+8%, Figure III.63c), being in accordance with the Klemm capillary rise. In this case, the structure bulk and porosity enhanced this property. However, the differences found for both patterns in the creped structure are in the same range. With this study, it was found that the embossing pattern presents higher differences in liquid spreading kinetics of the isotropic laboratory samples than in anisotropy creped industrial samples.

In addition, Table III.34 presents the liquid droplet spreading dynamics of the structures with and without embossing. The blue shaded area corresponds to the red line that circles the droplet outline in each structure, in Table III.33. The number of profiles starts at the largest Euclidean distance between the centroid and the red line and extends in the clockwise direction. In isotropic structures, the blue shaded area is practically a rectangle with few irregularities, which is not the case for anisotropic structures. These differences are due to the circular and elliptical shape of the isotropic and anisotropic samples, respectively. For both "deco" and "micro" embossing patterns, an irregular area of the liquid droplet spreading dynamics for all samples is observed. This result is due to the random and irregular shapes presented in the embossed structures, in Table III.33.

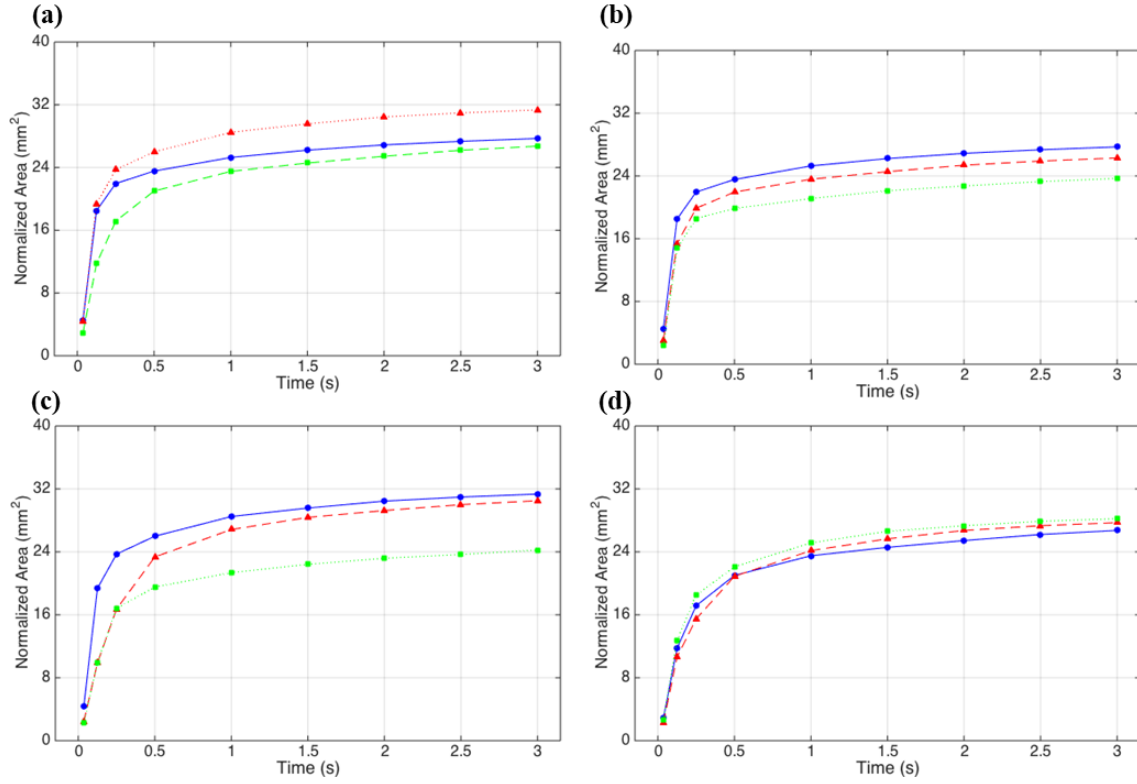


Figure III.66. The normalized liquid spreading area as a function of time for the structures without embossing (a), H_h structures with and without “deco” and “micro” embossing (b), HD_{Ihs} structures with and without “deco” and “micro” embossing (c), and I_{hs} structures with and without “deco” and “micro” embossing (d). In graphic (a), the colors blue, red, and green correspond to the structures H_h , HD_{Ihs} , and I_{hs} , respectively. In graphics (b), (c), and (d), samples without embossing are represented in blue, with “deco” embossing in red, and with “micro” embossing in green.

Table III.33. Kinetics of the liquid droplet spreading area overtime in structures with and without embossing.

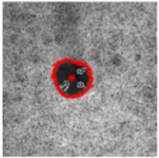
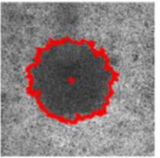
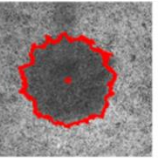
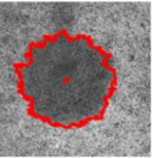
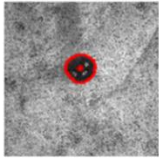
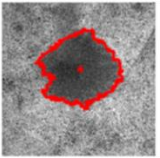
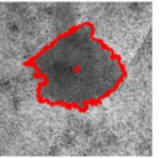
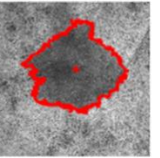
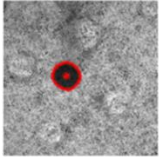
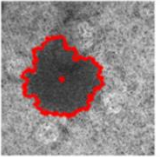
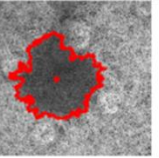
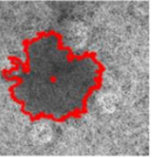
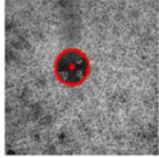
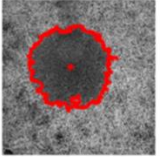
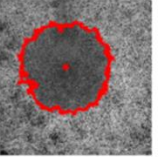
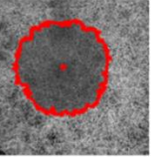
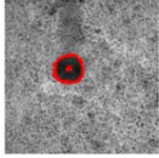
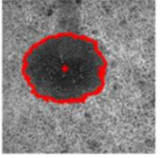
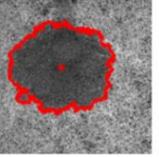
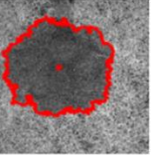
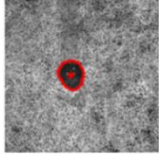
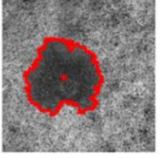
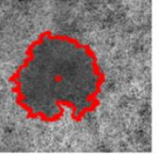
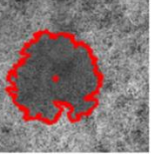
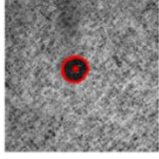
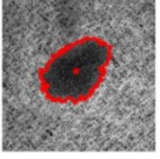
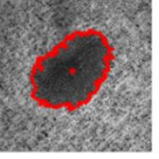
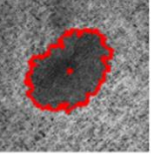
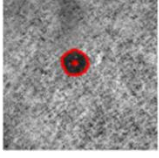
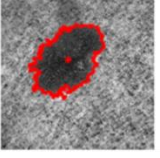
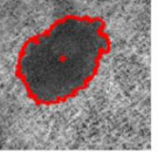
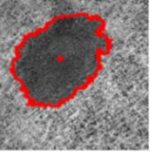
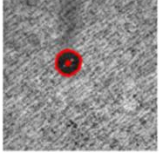
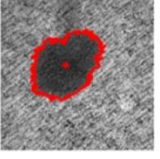
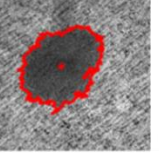
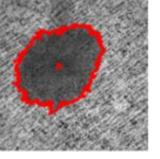
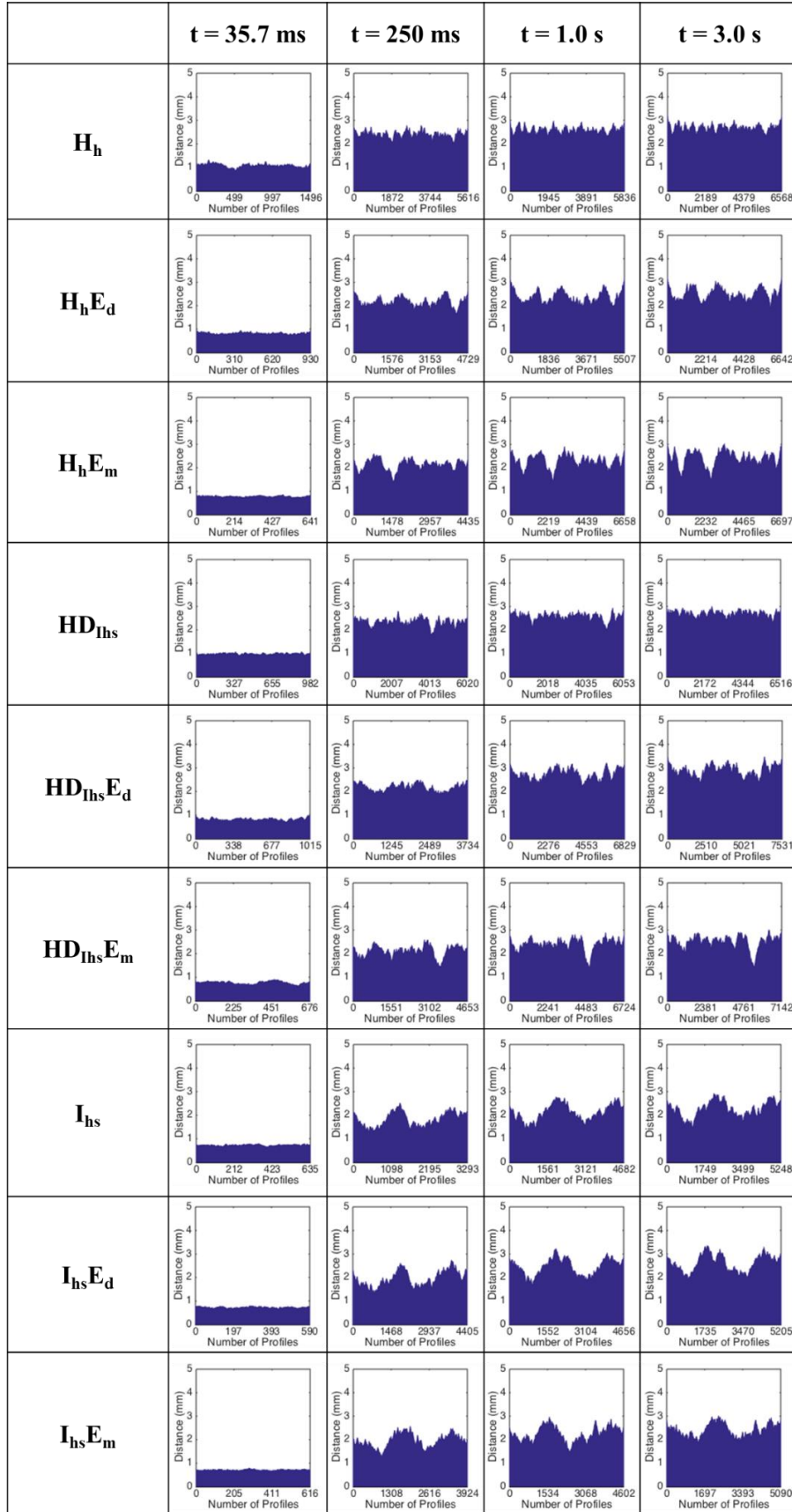
	t = 35.7 ms	t = 250 ms	t = 1.0 s	t = 3.0 s
H_h				
H_hE_d				
H_hE_m				
HD_{Ihs}				
HD_{Ihs}E_d				
HD_{Ihs}E_m				
I_{hs}				
I_{hs}E_d				
I_{hs}E_m				

Table III.34. Evolution of the liquid droplet spreading dynamics overtime in structures with and without embossing.



III.2.6.5. Conclusions

Our research highlights the importance of the absorbency properties characterization of different structures with and without embossing using standard methods, and an innovative optical liquid droplet system to quantify the liquid spreading kinetics. The characterization methodology developed and implemented on this study allowed the quantification of the influence of isotropic and anisotropic tissue papers formation, fiber mixtures, creping, and embossing operations, separately.

Overall, the creping effect has a higher influence on the structural and water absorption capacity properties compared to the fiber mixture; however, the reverse was verified for the Klemm capillary rise and liquid spreading kinetics properties. The “deco” embossing operation decreased the water absorption properties compared to the “micro” embossing. The water capillary rise overtime was higher in structures with “micro” embossing, followed by “deco” embossing. The same behavior was verified for the liquid spreading kinetics in the I_{hs} embossed structures, while an inverse relationship was observed for the H_h and HD_{ths} embossed structures. Considerable insight has been gain using the optical system to obtain the liquid spreading area kinetics and its spreading shape. With these findings it was proved that the type of 3D structure in which the liquid drop is deposited, the isotropic/ anisotropic tissue structures, and the creping/ embossing process operations are key parameters on the liquid/ materials interaction.

The characterization methodology proposed in this work constitutes valuable information to optimize the embossing operation and the absorption properties, combining the water absorption capacity, Klemm capillary rise, and liquid spreading kinetics properties of tissue paper materials. In conclusion, the combination of the laboratory embossing method, 3D modeling, and optical liquid droplet system establishes an innovative approach to quantify and represent the 3D embossing effect of tissue structures, on a laboratory scale, to be used in the process optimization and furnish management, to enhance absorbency materials properties.

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III.3. Optimization using Advanced Computational Tools

The contents of this subchapter are published in the following publications, listed on pages xvii and xviii of the thesis:

- IX. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Computational Simulation Tools to Support the Tissue Paper Furnish Management: Case Studies for the Optimization of Micro/nano Cellulose Fibers and Polymer-based Additives. *Polymers*. **13**: 3982. DOI: 10.3390/polym13223982
- X. **Morais, F.P.** and Curto, J.M.R. (2022). 3D Computational Simulation and Experimental Validation of Structured Materials: Case Studies of Tissue Papers. *BioResources*. **17**: 4206-4225. DOI: 10.15376/biores.17.3.4206-4225
- XI. **Morais, F.P.** and Curto, J.M.R. (2022). Challenges in Computational Materials Modelling and Simulation: A case-study to predict tissue paper properties. *Heliyon*. **8**: e09356. DOI: 10.1016/j.heliyon.2022.e09356
- XII. **Morais, F.P.**, Carta, A.M.M.S., Amaral, M.E.C.C., and Curto, J.M.R. (2022). Development of sustainable cellulose-based tissue materials using an innovative experimental and computational methodology. *KnE Materials Science*. **7**: 34-45. DOI: 10.18502/kms.v7i1.11606

III.3.1. Computational Simulation Tools to Support the Tissue Paper Furnish Management: Case Studies for the Optimization of Micro/Nano Cellulose Fibers and Polymer-based Additives

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III.3.1.1. Abstract

Tissue paper production frequently combines two main types of raw materials: cellulose fibers from renewable sources and polymer-based additives. The development of premium products with improved properties and functionalities depends on the optimization of both. This work focused on the combination of innovative experimental and computational strategies to optimize furnish. The main goal was to improve the functional properties of the most suitable raw materials for tissue materials and develop new differentiating products with innovative features. The experimental plan included as inputs different fiber mixtures, micro/nano fibrillated cellulose, and biopolymer additives, and enzymatic and mechanical process operations. We present an innovative tissue paper simulator, the *SimTissue*, that we have developed, to establish the correlations between the tissue paper process inputs and the end-use paper properties. Case studies with industrial interest are presented in which the tissue simulator was used to design tissue paper materials with different fiber mixtures, fiber modification treatments, micro/ nano fibrillated cellulose, and biopolymer formulations, and to estimate tissue softness, strength, and absorption properties. The *SimTissue* was able to predict and optimize a broader range of formulations containing micro/nanocellulose fibers, biopolymer additives, and treated-fiber mixtures, saving laboratory, and industrial resources.

Keywords

Absorption; Cellulose Fibers; Computational Simulation; Furnish Optimization; Modeling; Polymeric Additives; Softness; Strength; Tissue Papers

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Morais, F.P., Carta, A.M.M.S., Amaral, M.E., and Curto, J.M.R. (2021). Computational Simulation Tools to Support the Tissue Paper Furnish Management: Case Studies for the Optimization of Micro/nano Cellulose Fibers and Polymer-based Additives. *Polymers*. **13**: 3982. DOI: 10.3390/polym13223982

III.3.1.2. Introduction

Furnish optimization is a Multiple-Input Multiple-Output (MIMO) challenge, mainly due to the different fiber and structure properties and the influence of several process operations. The development of multi-structured materials, such as tissue paper products, will benefit from the modeling of raw material characteristics and their functional properties. The use of computational tools constitutes an innovative strategy to enhance this type of polymeric materials, through three-dimensional (3D) modeling of fibers and structures.

Tissue papers, such as toilet paper, paper towels, napkins, and facial tissue masks, are cellulose fibrous materials designed for personal hygiene and utility purposes. Significant growth in the global tissue sector is projected for the next decade, concentrated in the industrialized parts of the world, and a demand for premium products (Wang et al., 2019). The properties required for the tissue materials, such as softness, strength, and absorption, and the production process steps, such as creping and converting, distinguish them from other cellulose-based materials (Hollmark and Ampulski, 2004; de Assis et al., 2018a, 2018b; Raunio, Löyttyniemi and Ritala, 2018; Wang et al., 2020). In general, the creping process consists of the formation of macro and micro folds on the paper, enhancing the properties of bulk, softness, absorption, and elasticity (de Assis et al., 2018a). The converting process includes diverse operations performed on base tissue paper sheets to develop a multi-layer finished product, ready to be placed on the market (de Assis et al., 2018a). The properties of each tissue paper depend on the pulps used for its production, which are influenced by the type of pulp cooking and the applied bleaching sequence. As well as the fibrous raw materials, such as hardwoods like eucalyptus, or softwoods like Norway spruce or pine (de Assis et al., 2019; Fišerová et al., 2019; Morais et al., 2019, 2020a; Stankovská et al., 2020). In the manufacturing of these products, a high percentage of hardwood pulps is employed, which provide structural and softness properties to the materials, with the incorporation of softwood pulps, which provide paper strength and ensure the paper machine runnability (de Assis et al., 2018a; Morais et al., 2019). Eucalyptus fibers present an optimization potential to improve their mechanical properties while maintaining existing benefits. Maximizing the incorporation of these raw materials and the total or partial replacement of softwood pulps present challenges in terms of the final paper properties and paper machine runnability. Obtaining tissue products with the best combination of fibers, and maximizing eucalyptus fibers, requires knowledge of the different pulps available on the market suitable for this type of materials and the consequences on the final end-use properties (Morais et al., 2019, 2020a). The management and optimization of tissue furnish play a key role to maximize eucalyptus fibers without significant losses in strength and runnability (de Assis et al., 2018a; Stankovská et al., 2020). To enable the great potential of hardwood pulps in these materials, it is necessary to identify the fiber properties, their relationship with the processes, and the final end-use properties (Morais et al., 2019). Therefore, the raw material selection, pulp cooking type, and bleaching sequences, fiber modification treatments such as refining and enzymatic processes, and the nature of additives added to the pulp suspension are crucial steps and factors that can affect the tissue key properties and consequently the final product (Kullander, Nilsson and Barbier, 2012).

These factors allow the modification of eucalyptus pulps, minimizing the influence on the strength and stiffness properties that the structure needs for the process operations.

The methods currently used for fiber modification include mechanical refining treatments, enzymatic biorefining treatments, and additive incorporation. These modification process steps are optimized to obtain improved functional properties with the maximization of fibers suitable for tissue papers. Refining is a fiber fibrillation process used to develop wet tensile strength, improve sheet formation, and modify fiber drainability. Consequently, this process decreases the softness and absorption properties by increasing the sheet density and elasticity modulus (Gigac and Fišerova, 2008; Chang, Yu and Perng, 2018). However, refining requires a substantial amount of energy. The use of enzymes reduces the refining time and the applied energy to achieve the desired properties. This green sustainable integrated process increases the paper softness properties, with better tensile strength, which facilitates an increase in machine speed, with a refining energy reduction (An et al., 2020; Morais et al., 2021a). The additives incorporation is also a strategy to optimize the performance of the enzyme in the tissue field, because they improve the enzymatic activity rate, allowing for a lower end-use enzyme application rate. The polymeric additives improve the tissue softness and/ or absorption properties, maintains or increases the paper strength properties, which can provide energy and cost savings (Park et al., 2019; Zambrano et al., 2021; Morais et al., 2021b, 2021c). However, balancing softness and strength properties in tissue paper production is not easy, as actions required to maximize softness are often in conflict with the ones needed to improve strength (de Assis et al., 2018a, 2019; Morais et al., 2019, 2020a). In our previous publications, we have proven that the incorporation of polymeric additives such as micro/nanofibrillated cellulose (MFC/NFC) and a commercial biopolymer into tissue structures enhance the maximization of eucalyptus fibers, optimizing the process and associated manufacturing costs, in order to produce high-quality products (Morais et al., 2021b, 2021c).

Consequently, a detailed level of knowledge is required when manufacturing these products to fulfill the high-quality requirements. It is also important to investigate various modification processes that allow the same or improved final end-use properties by maximizing the eucalyptus fibers incorporation and saving laboratory and industrial resources. An experimental design that included the production of laboratory-made structures to simulate industrial-made structures with enzymatically and mechanically treated-fibers, additives incorporation, and even the physical changes of creping and converting operations, is essential to improve the tissue industrial process (Spina and Covalcante, 2018; Pan et al., 2019; de Assis et al., 2020). These approaches allow the introduction on the market of innovative and value-added formulations, such as antimicrobial tissue papers, individual protection tissue masks, and cosmetic facial tissue masks.

Predicting the tissue material properties from experimental data of pulps used in their production could be an important and interesting milestone to the tissue paper industry. The integration of all important variables for premium tissue materials development with furnish management and optimization can be accomplished using computational tools, modeling, validation, and optimization methods, in order to design new tissue products with innovative features and added value. This approach allowed us to develop mathematical models, based on datasets, with predictive capacity for softness, strength, and absorption. Establishing relationships between fiber properties, process modification steps, and functional tissue properties, as well as the models that describe them, constitute a multifactorial challenge. Over the years, material modeling has become an important tool in the development and design of materials with better performance (Alava and Niskanen, 2006; Axelsson and Syensson, 2010; Conceição et al., 2010; Curto et al., 2011; Lavrykov et al., 2012; Raunio and Ritala, 2012; Dirrenberger, Forest and Jeulin, 2014; Curto et al., 2015; Marulier et al., 2015; Bloch, Engin and Sampson, 2019; Kerekes, McDonald and Zhao, 2020; Morais et al., 2020b; Huang, Sun and Li, 2020; Maghsoudi-Ganjeh et al., 2021). Our strategy also consists of 3D modeling of structured materials, such as tissue papers, considering the structural hierarchy at the fiber and structure level. In our previous work, an innovative 3D voxel approach was used to model the fibers and structures made by them, and consequently, to predict and optimize the properties of various types of tissue materials (Conceição et al., 2010; Curto et al., 2011; Morais et al., 2020b). The computational tools allow us to significantly reduce the experimental work in the new materials development, to have a better synergy between the experimental tests design and the simulation of materials specific properties (Morais et al., 2020b). Despite its importance and the advances achieved in the field of fibrous materials science, engineering, and modeling, to the best of our knowledge, an approach to simulate and optimize the relationships between the key parameters and the functional properties of tissue materials is not presented in the literature. The advanced computational tools development with predictive capacity allows determining which are the most promising pulps for a specified tissue material and which process operations allow obtaining a tissue material with optimized properties. Therefore, we propose a materials design strategy using an innovative computational tool that is applied to develop cellulosic fiber-based materials, including polymeric additives at micro and nanoscale.

The main goal of this work was to present and compare different tissue furnish formulations, using a computational simulation tool with predictive capacity developed by us, named *SimTissue*, valuable to design new tissue multi-structured paper materials with innovative functionalities at the micro and nanoscale and polymer-based additives. This simulator establishes relationships between the key fiber properties, the fiber modifications process steps, and the tissue paper structural and functional properties for furnish management and optimization.

III.3.1.3. Materials and Methods

III.3.1.3.1. Pulp Samples

In this study, different pulps were selected, obtained from hardwood and softwood species and industrial processes relevant to the management of tissue papers. These samples include the hardwood pulps H_A to H_F and HW, and the softwood pulps S_A to S_F, reported in the previous subchapters. The pulps were disintegrated according to the ISO 5263/1. The fibers' morphological properties were determined automatically by image analysis of a diluted suspension (20 mg/L and 30 mg/L for hardwood and softwood samples, respectively) in a flow chamber in MorFi Fiber Analyzer (TECHPAP, Grenoble, France). After their characterization, the HW and SW pulps were mixed in ratios of 99:1, 95:5, 90:10, and 75:25, where this last ratio is taken as an industrial reference.

III.3.1.3.2. Enzymatic Treatments

Two bleached eucalyptus pulps, with different cooking processes, kraft (H_C) and sulfite (H_F), were treated separately, using enzyme dosages of 10 and 100 g per ton of pulp, for 30 and 60 minutes. The assays were carried out at a consistency of 4%, pH 7, and 40°C, with continuous mechanical agitation using an impeller. A minimum amount of sodium hypochlorite was added to the pulp suspension to stop the enzyme reaction. After these enzymatic treatments, the pulps were mixed in a ratio of 80:20. A more detailed description of this study can be found in (Morais et al., 2021a).

III.3.1.3.3. Mechanical Treatments

A bleached eucalyptus kraft pulp (H_B) was subjected to mechanical refining treatments using a PFI mill at 500, 1000, 2000, and 3000 revolutions, and two refining intensities of 3.33 N/mm, according to the ISO 5264-2 standard, and of 1.67 N/mm, which corresponds to half of the normalized value. This study was carried out to simulate processing conditions with different refining energies. The *SimTissue* was used in these studies to reduce energy consumption in the tissue process.

III.3.1.3.4. Combination of Enzymatic and Mechanical Treatments

To study the effect of the combination of both treatments (sections 3.1.3.2 and 3.1.3.3), different enzymatic treatments and a slight mechanical treatment, were applied to the kraft pulp used in section 3.1.3.2 (H_C).

In these assays, enzyme dosages of 0.5 and 1 kg per ton of pulp were used, for 2 hours, with the same process conditions noted in the enzymatic treatment method section. Subsequently, this pulp was beaten in a PFI mill at 500 revolutions, under a refining intensity of 3.33 N/mm. A pre-refining process followed by enzymatic treatment was also carried out under the same conditions.

III.3.1.3.5. Additives Incorporation

Different furnish mixtures were performed to understand the effect of polymer-based additives in the tissue properties compared to the reinforcing fibers frequently used in these types of products. The micro/ nanofibrillated cellulose (MFC/NFC) was incorporated in a never-dry (slush) bleached eucalyptus kraft pulp (HW), according to loads of 1%, 5%, and 10%. A commercial biopolymer additive (CBA) was also incorporated in the same fiber pulp slurry, at the dosage of 2%. A more detailed description of this study can be found in (Morais et al., 2021b, 2021c). This study was designed and predicted using the *SimTissue* to evaluate the potential for reducing or replacing softwood reinforcement fibers with these polymeric additives.

III.3.1.3.6. Handsheets Preparation and Testing

The tissue structures were produced in a batch laboratory sheet former according to an adaptation of ISO 5269-1. The adjustments consisted of the production of structures with a basis weight of 20 g/m² instead of 60 g/m² and suppression of the pressing operation as described in the respective standard. This experimental methodology allowed us to obtain sheet structures similar to tissue papers. The tissue structures were prepared according to the different process steps described above. Additionally, all samples were conditioned at 23±1°C, with a relative humidity of 50±2%, according to ISO 187.

For all assays, the tissue properties for handsheets were measured in terms of structural and functional properties. The basis weight (ISO 12625-6) was obtained by the quotient between the average mass of each structure and the respective area (0.02138 m²). The thickness (ISO 12625-3) was obtained using a Frank-PTI micrometer. The bulk (ISO 12625-3) was obtained by the quotient between the structure thickness and the basis weight. The apparent porosity was calculated according to the method described by Morais et al. (2021c). The softness, namely the handfeel (HF) parameter, was evaluated using a Tissue Softness Analyzer (TSA, Emtec equipment). The tensile index was assessed according to ISO 12625-4. The water absorption capacity was determined with the immersion absorption method, according to an adaptation of ISO 12625-8. The Klemm capillary rise method was evaluated according to an adaptation of ISO 8787. A more detailed description of these adaptations can be found in our referenced and cited publications (Morais et al., 2019, 2020a, 2021a,b,c).

III.3.1.3.7. Computational Simulator

A tissue computational simulator developed from scratch, the *SimTissue* (FibEnTech-UBI members, Covilhã, Portugal) was used to compare and predict different tissue furnish formulations, with different enzymatic and mechanical treatments, and additives incorporation from those studied experimentally. This simulator can establish the correlations between the tissue paper process inputs and the end-use paper properties. The ability to predict different scenarios was facilitated using advanced computational tools, including multiple and robust linear regressions, interpolation and extrapolation methods, and a 3D simulator of fibrous materials named *voxelfiber* (Conceição et al., 2010; Curto et al., 2011).

The *voxelfiber* allows the material modeling and simulation as planar random networks, through the fiber dimensions and properties (Morais et al., 2021b), and it can be accessed in <https://github.com/eduardotrincaoconceicao/voxelfiber> (accessed on September 2021). Computational studies were carried out using Matlab® (R 2020a, 9.8.0.1323502, MathWorks, Natick, MA, USA). All variables were normalized to present the same scale range.

Statistical analysis was performed using cluster analysis with IBM SPSS Statistics 25 (Armonk, NY, USA). The hierarchical cluster analysis was used, with Ward's method and square Euclidean distance measure. In the proximity matrix, a range of solutions of 2 to 3 clusters was used.

III.3.1.4. Results and Discussion

III.3.1.4.1. Pulps Samples Characterization

An experimental set of different hardwood and softwood fiber pulps suitable for tissue materials production was characterized in terms of fibers morphology and suspensions drainability accessed by the Schöpper-Riegler method, °SR (Morais et al., 2019, 2020a). Hardwood fibrous suspensions present ranges between 18 and 25 °SR and softwood suspensions between 12 and 15 °SR. Figure III.67 shows the relationship between the slenderness ratio and coarseness, as well as between the TSA-softness and tensile index properties of the hardwood and softwood fiber samples. The low slenderness ratio values of hardwood fibers (38-44) represent fibers with low flexibility and low chance of forming well-bonded structures, resulting in high softness properties, compared to the high slenderness ratio values of softwood fibers (39-59), resulting in improved strength properties. The hardwood fibers studied can be separated into two clusters of slenderness ratio *vs* coarseness, whereas the softwood fibers are classified into three distinct clusters (Figure III.67a, b). The organization of these clusters corresponds to a similar behavior between pulp fibers, indicating the direct or inverse relationship between properties. In Figure III.67a, for example, the hardwood pulps grouped in the yellow cluster presented a positive correlation. The statistics results indicated that the coarseness increased by 1.4 units per unit of the increased slenderness ratio, with a R-squared (coefficient of determination – R^2) of 0.8. In contrast, in the blue cluster, these pulps presented a negative correlation (Figure III.67a). The statistics results indicated that the coarseness increased by 0.8 units per unit of the decreased slenderness ratio, with a R^2 of 0.3. All this cluster analysis was performed to set similar cases into groups, being distinct from each other. The data were based on our previous work in the analysis of a representative pulp group to produce tissue materials, namely seven hardwood pulps and six softwood pulps. For this reason, there are few points in each cluster. However, these data were adequate to feed our computational simulator, *SimTissue*. These are samples without any enzymatic and/or mechanical treatments or additives incorporation, which does not occur in the industry. It is important to emphasize the importance of these data to select the most suitable raw material to be optimized in the process modification steps.

Hardwood fibers with a slenderness ratio between 38 and 39 and coarseness between 6.31 and 8.22 mg/100m represent the highest softness values (81.7-86.9 HF). In contrast, hardwood fibers with a slenderness ratio between 42 and 43 and coarseness between 6.71 and 9.56 mg/100m represent, on average, the highest values of the tensile index (4.03-9.96 Nm/g). Softwood fibers with a slenderness ratio between 39 and 59 and coarseness between 18.83 and 19.66 mg/100m present high softness (71.3-75.8 HF) and low tensile index (4.49-6.12 Nm/g). Additionally, softwood fibers with a slenderness ratio between 52 and 57 and coarseness between 16.77 and 17.37 mg/100m present high tensile index values (8.36-11.45 Nm/g) and consequently low softness values (63.8-69.3 HF).

Regarding the tensile index *vs* TSA-softness properties, the samples were classified into three clusters (Figure III.67c, d). The results indicate that two hardwood pulps with low tensile index values and high softness values belong to cluster 1 (blue), the four pulps with intermediate values for both properties belong to cluster 2 (red), and one pulp stands out from the rest for being isolated in cluster 3 (green), presenting the highest values of the tensile index. The same analogy was made for softwood pulps, and one pulp also stands out from the rest due to the higher values of the tensile index. Overall, softness and strength properties are inversely related. Hardwood eucalyptus slush pulp was also used for the studies. The particularity of this sample is to present high values of softness (82.7 ± 4.0 HF) and intermediate values of the tensile index (4.60 ± 0.61 Nm/g). Although this classification is not the same in both analyses presented in Figure III.67, there is a relationship between the morphological properties of length/width ratio and coarseness and the tissue functional properties of softness and tensile index.

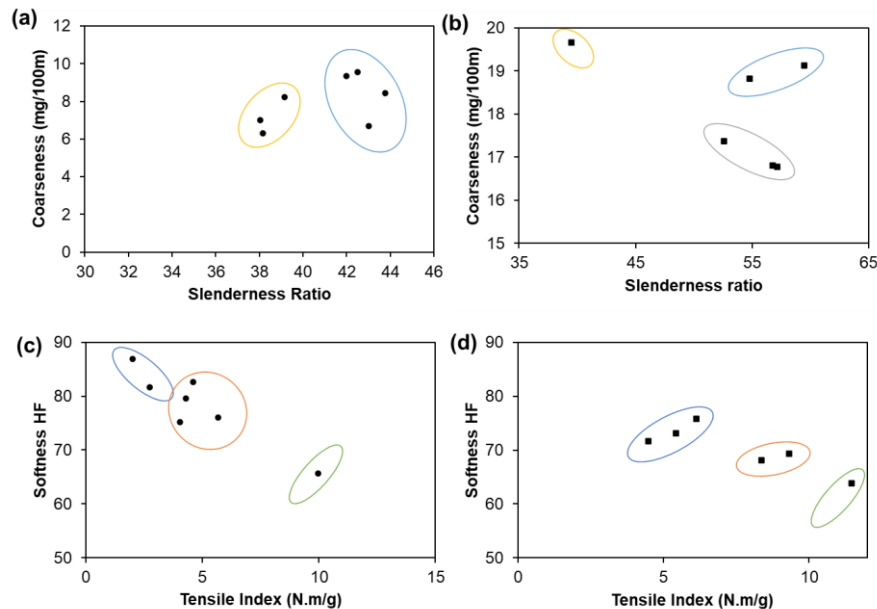


Figure III.67. Coarseness as a function of slenderness ratio of hardwood (a) and softwood (b) fiber pulps, as well as softness HF as a function of tensile index properties of hardwood (c) and softwood (d) fiber pulps.

Water absorbency properties are essential for the good performance of tissue papers and depend on the structural tissue properties, namely the thickness, bulk, and porosity. The characterization of tissue apparent porosity is crucial, as the ability of the liquids to migrate through the tissue paper depends on the pore sizes (Hassan, Cushman and Delleur, 1998; Gigac, Stankovská and Fišerová, 2017). The complexity of these porous materials comes from the fact that they do not have a regular pore distribution, but rather a pore dimension that varies in a wide range and the tortuous paths that the pores provide for the flow of the liquid (Neumann et al., 2020). The molecules need to travel a path higher than a straight line between the original source and its active local (Ghanbarian et al., 2013). Therefore, 3D structural porous materials structure knowledge is important for the prediction of water absorption properties (Axelsson and Syensson, 2010).

Figure III.68 shows the water absorption capacity and capillary rise – Klemm method properties as a function of the apparent porosity properties for hardwood and softwood handsheets. The clusters involved in these relationships are identified as well as their positive and negative correlation. For example, in a yellow cluster of hardwood pulps from Figure III.68a, the statistics results indicate that the water absorption capacity increased by 0.4 units per unit of the increased apparent porosity, with a R^2 of 0.7. In contrast, in a blue cluster, the statistics results indicated that the water absorption capacity increased by 0.04 units per unit of the decreased apparent porosity, with a R^2 of 0.8 (Figure III.68a). The same analogy was made for softwood pulps and capillary rise properties. According to Figures III.68a and III.68c, the results indicated that hardwood fibers with porosities between 81 and 82% present water absorption capacity between 8.08 and 8.83 g/g and capillary rise between 85 and 119 mm. Hardwood fibers with higher porosity (88-89%) presented water absorption capacity between 8.13 and 8.19 g/g and capillary rise between 113 and 132 mm. According to Figures III.68b and III.68d, the results indicated that the softwood fibers with 81% porosity present water absorption capacity between 8.42 and 8.64 g/g and capillary rise between 103 and 105 mm. Softwood fibers with higher porosity (90-92%) present water absorption capacity between 8.34 and 9.48 g/g and capillary rise between 117 and 126 mm.

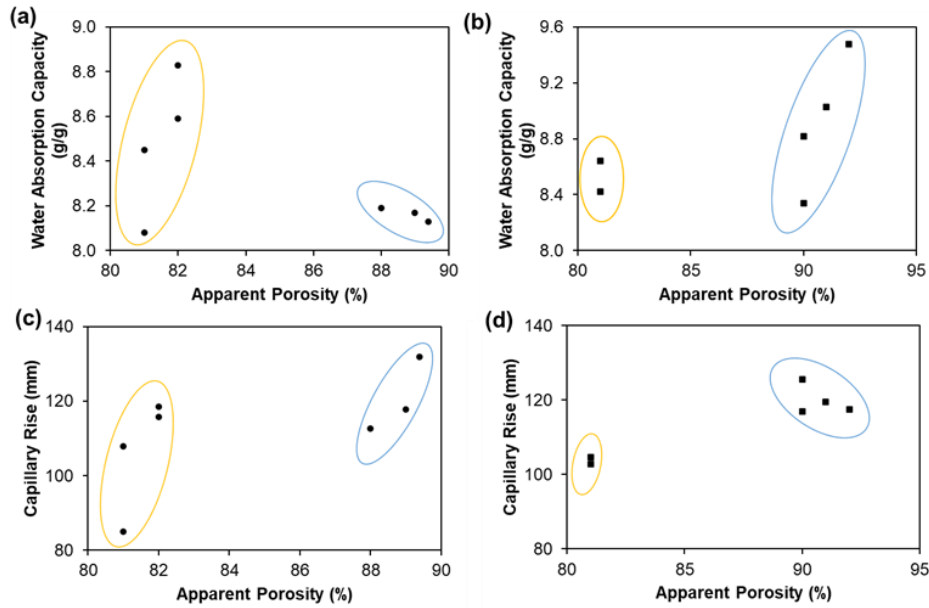


Figure III.68. Water absorption capacity as a function of apparent porosity of hardwood (a) and softwood (b) fiber pulps, as well as capillary rise as a function of apparent porosity of hardwood (c) and softwood (d) fiber pulps.

Considering the previous characterization, different pulp samples were selected for the studies of fiber modification process operations and polymer-based additives incorporation. For the enzymatic modification studies, hardwood fiber samples with extreme values of softness (86.9 ± 3.1 HF) and tensile index (9.96 ± 0.30 Nm/g) properties were selected. For the refining studies, we selected the hardwood pulp with a balance between the properties of softness (81.7 ± 3.3 HF), tensile index (2.73 ± 0.42 Nm/g), and water absorption capacity (8.59 ± 0.22 g/g). For the enzymatic and mechanical treatment combination studies, we selected the hardwood pulp with the highest strength properties (9.96 ± 0.30 Nm/g). Additives were incorporated with the eucalyptus slush pulp. Finally, fiber mixtures were carried out using the latter pulp sample and the softwood pulp with the extreme values of the tensile index (11.45 ± 0.99 Nm/g).

III.3.1.4.2. Predictive Capacity for Furnish Optimization

III.3.1.4.2.1. Fiber Mixtures Ratio

A blend of hardwood pulps with a percentage of softwood pulps is used to produce these materials. The softwood fibers ensure the fibrous structure strength and runnability to the tissue paper machine; however, these fibers present a high cost in tissue production. Therefore, it is essential to find effective strategies for removing or replacing these fibers in the production of these products. In our work, we investigated mixtures of eucalyptus fiber and softwood reinforcement fiber in ratios of 100:0, 99:1, 95:5, 90:10, and 75:25. The experimental results indicated that the strength properties were increased from 93 to 303% and the properties of softness, water absorption capacity, and capillary rise were decreased from 28 to 8%, 7 to 1%, and 7 to 2%, respectively (Morais et al., 2021b).

The *SimTissue* allows us to predict a wide range of scenario variability by quantifying the influence of incorporating other percentages of reinforcement fibers that have not been studied experimentally. The ideal ranges for tissue properties were obtained simultaneously through computational simulation to identify different combinations of fiber percentages. All these computational combinations allow covering a much larger results area, which would not be possible using only experimental results, with the time and resources they require (Morais et al., 2021b). Figure III.69 presents the functional properties of tissue products as a function of fiber mixtures, obtained with the *SimTissue* prediction. For the studies, we considered the softwood maximum incorporation of 30%, as tissue papers are produced in this range. Higher softness values correspond to lower tensile index values. This trend varies with the fiber mixture, where the normalized variable 0 corresponds to a formulation with 100% eucalyptus pulp, and the normalized variable 1 corresponds to a formulation with 70% eucalyptus pulp and 30% softwood fibers, the reasonable maximum incorporation to produce tissue papers.

The computational results indicated that the incorporation of 30% reinforcement fibers in a tissue structure increases the tensile index properties by 330% and decreases the properties of softness by 30%, water absorption capacity by 9%, and capillary rise by 7%. Through our *SimTissue*, we found that the balance between the properties of softness (65.0-69.3 HF), strength (14.5-15.9 Nm/g of the tensile index), and absorption (7.8-8.0 g/g of water absorption capacity and 38.3-39.5 mm of capillary rise) can be found with the incorporation of 5 to 15% of reinforcement fibers in tissue papers. This suggests the possibility of reducing the incorporation of softwood fibers in tissue structures, which translates into financial advantages. The results presented in this section describe structures without process modification steps. Therefore, to balance the absence of softwood pulps, it is also important to select strategies to modify the fibers combining the enzymatic and mechanical fiber modification treatments, as well as the incorporation of polymeric additives in the suspensions.

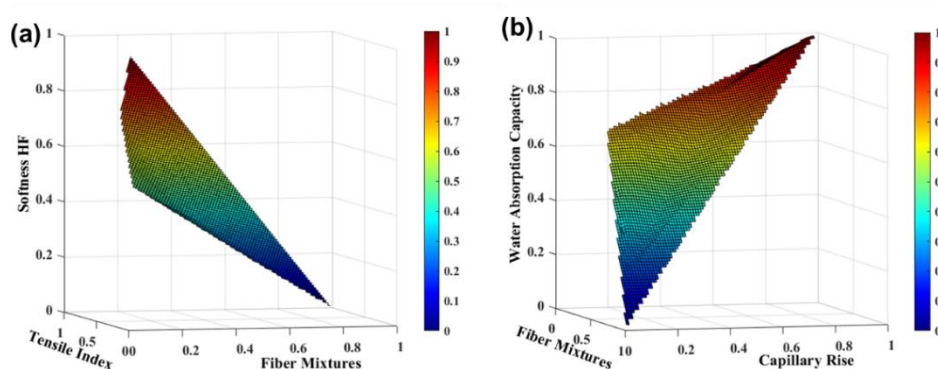


Figure III.69. TSA-Softness HF and tensile index properties (a) and water absorption capacity and capillary rise (b) with eucalyptus fiber and softwood fiber mixtures. The variables were normalized.

III.3.1.4.2.2. Enzymatic Treatment

New enzymatic technologies reduce refining energy and consequently production costs, and could also optimize the tissue functional properties, that one may develop new products with high added value. In our previous work, an approach to optimize two eucalyptus fiber pulps was used through different enzymatic treatments. The sulfite and kraft pulps were treated to obtain optimized softness and strength properties, respectively, to produce tissue structures with 100% eucalyptus fibers (Morais et al., 2021a). Figure III.70a and III.70b presents the TSA softness HF and strength properties as a function of enzyme dosage in eucalyptus kraft pulp at 30 and 60 minutes, obtained with the *SimTissue* forecast. The simulations predicted the functional properties of different formulations with variation in the two process variables: reaction time and enzyme dosage. We considered a maximum enzyme dosage of 100 g/ton. Regarding the enzymatic treatment in the kraft pulp, the results indicated that in a time reaction of 30 and 60 minutes, the softness properties are decreased by 20% and 29%, respectively, and the strength properties are increased by 2%, with increasing enzyme dosage. Through our *SimTissue*, we found that the balance between the properties of softness (53.0 ± 4.0 HF) and strength (18.5 ± 2.0 Nm/g) can be found with an enzyme dosage of 50 g/ton for 30 minutes or 20 g/ton for 60 minutes. In these simulation studies, similar softness and strength properties are obtained with a lower reaction time (30 minutes) and higher enzyme dosage (50 g/ton), or also with twice the reaction time (60 minutes) and an enzyme dosage 2.5 times less (20 g/ton). Additionally, these results indicated that these final properties are in the same variation range as the formulation typically used in the tissue industry, namely 75% eucalyptus pulps + 25% softwood pulps (softness: 59.9 ± 2.3 HF and tensile index: 18.5 ± 1.1 Nm/g).

This analysis is also performed for other suitable pulps in tissue paper production. Regarding the enzymatic treatment in the sulfite pulp, the results indicated that in a timed reaction of 30 and 60 minutes, the softness properties are decreased by 0.1%, and the strength properties are increased by 2% and 4%, respectively, with increasing enzyme dosage (Figure III.70c, d). *SimTissue*'s predictive ability indicated that the balance between softness properties (82.0 ± 5.0 HF) and strength properties (7.0 ± 2.1 Nm/g) can be achieved with an enzyme dosage of 100 g/ton for 30 minutes or 30 g/ton for 60 minutes.

With this approach, strategies were found to decrease the enzyme dosage in eucalyptus fiber modification treatments, increasing the reaction time of the enzyme. These results suggest a decrease in the economic value of the formulations associated with the enzyme costs.

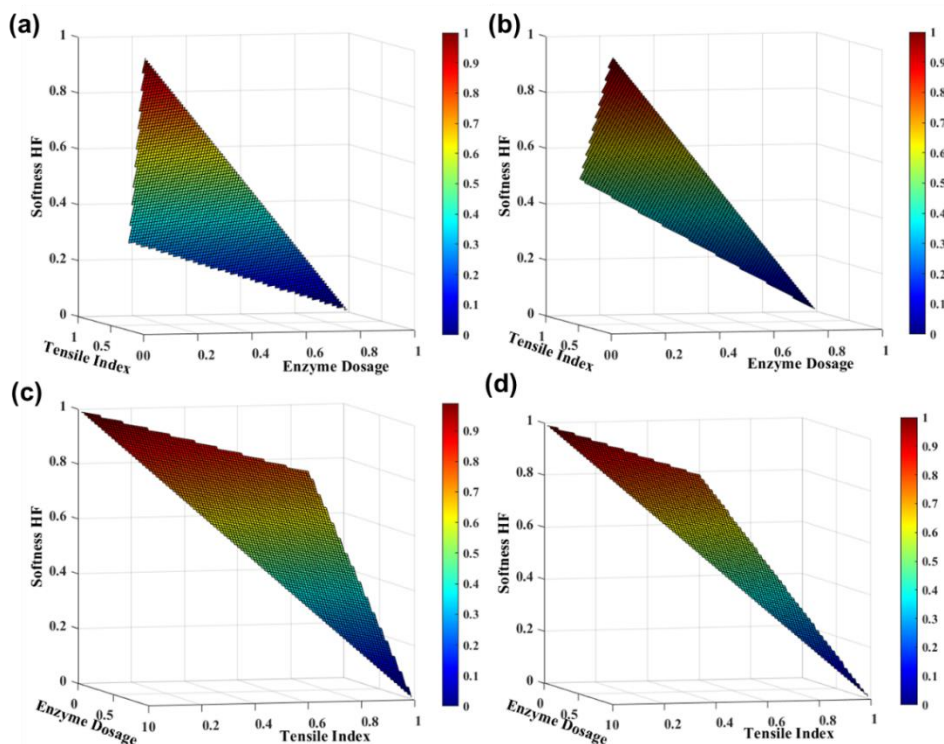


Figure III.70. TSA-softness HF and tensile index properties with enzyme dosages in eucalyptus kraft pulp (a,b) and eucalyptus sulfite pulp (c,d) for 30 minutes (a,c) and 60 minutes (b,d). The variables were normalized.

III.3.1.4.2.3. Mechanical Treatment

The mechanical treatment of refining is also one of the fundamental steps in tissue paper production. The drainage characteristics between 25 and 32°SR to produce high-quality tissue sheets are desirable (de Assis et al., 2018a). As all these characteristics are affected during refining processes, mechanical treatment optimization must be considered. Our strategy was to investigate the influence of the refining intensity on the tissue functional properties of eucalyptus pulp to save energy resources from refining. Figures III.71 present the evolution of the final end-use tissue properties as a function of the PFI revolutions at 3.33 N/mm and 1.67 N/mm, obtained by *SimTissue*. These results indicated that similar tissue properties are achieved in 1000 PFI revolutions at 3.33 N/mm and 600 PFI revolutions at 1.67 N/mm. In these conditions, the strength properties are increased by 140%, and softness HF, water absorption capacity, and capillary rise are decreased by 60%, 15%, and 20%, respectively. Simulation studies were used to optimize the mechanical treatments, with different refining energies, obtaining similar tissue properties with higher or lesser refining times and intensities. A strategy of reducing the refining intensity can be implemented in the industry, saving energy costs and consumption in tissue products production. This computational tool allows predicting the final properties, according to the pulp input characteristics, and therefore requires reliable databases. Different scenarios of industrial interest can be accurately evaluated, without extensive experimental planning design, to optimize raw material management and associated formulation costs.

The integration of all the variables of an industrial tissue process will dynamically model the evolution of the tissue process and study the effect of changes and disturbances over time in this industrial process for forecasting and decision-making. This allows assessing expenses and operational implications in each scenario simulated by *SimTissue*.

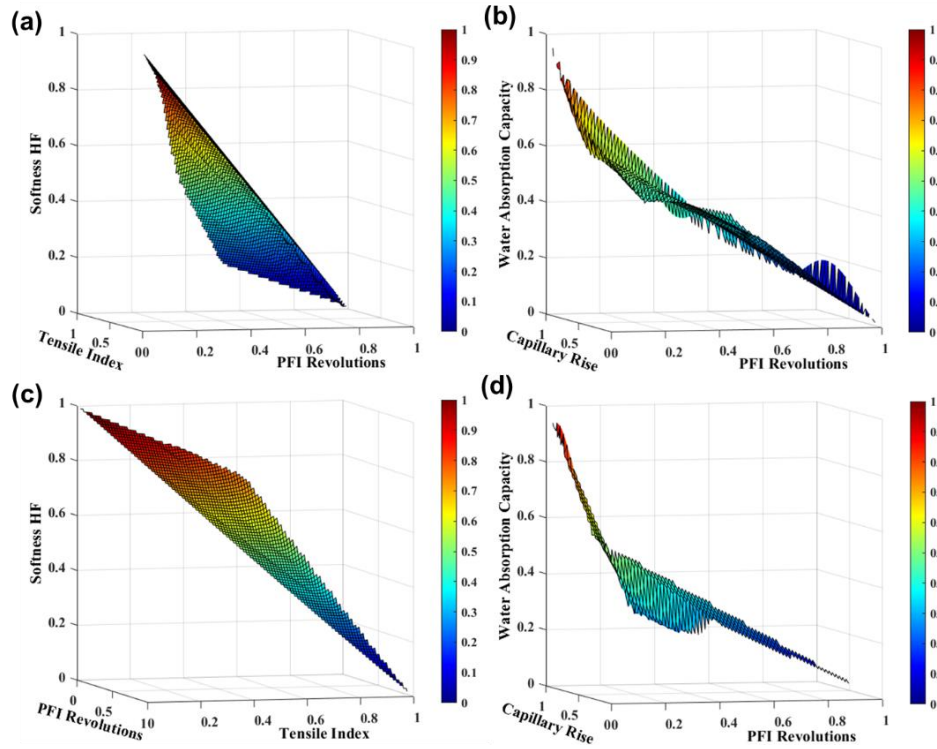


Figure III.71. TSA-softness HF and tensile index properties (a,c) and water absorption capacity and capillary rise (b,d) with PFI revolutions at 3.33 N/mm (a,b) and 1.67 N/mm (c,d). The variables were normalized.

III.3.1.4.2.4. Combination of Enzymatic and Mechanical Treatments

Innovative methodologies and the optimization of the tissue paper production process are crucial strategies for managing tissue furnish. The application of an enzymatic pretreatment followed by a mechanical refining process is commonly used in the tissue industry. However, to the best of our knowledge, a mechanical pre-treatment followed by enzymatic treatment is not used industrially. The investigation and comparison of these two processes in eucalyptus pulp are essential to optimize the enzyme dosage in the production process as well as the savings of refining energy consumption and costs. Figure III.72a and III.72b presents the tissue functional properties as a function of enzyme dosage, in an enzymatic pretreatment process followed by 500 PFI revolutions at 3.33 N/mm, according to the *SimTissue* prediction. The results indicated that this process increased the strength properties by 6% and decreased the softness HF, water absorption capacity, and capillary rise by 15%, 8%, and 15%, respectively. The reverse process of pre-refining at 500 PFI revolutions at 3.33 N/mm, followed by enzymatic treatment increased the strength properties by 314% and decreased the softness HF, water absorption capacity, and capillary rise by 69 %, 17%, and 41%, respectively (Figure III.72c,d).

These results indicate that a pre-refining followed by an enzymatic treatment is not advantageous to produce tissue papers with desired softness and absorption properties. However, this treatment is an innovative strategy to enhance strength properties. Therefore, a eucalyptus pulp with improved strength characteristics can be obtained through this fiber modification process. A planning design that combines this eucalyptus pulp with other pulps with good softness and absorption characteristics can be proposed. To this extent, formulations with 100% eucalyptus pulps and with optimized tissue properties can be used to produce high-quality products.

Additionally, to optimize the tissue furnish management, this tissue simulator predicted that the same tissue properties are achieved with an enzymatic pre-treatment using an enzyme dosage of 350 g/ton, followed by refining and with a pre-refining followed by enzymatic treatment with an enzyme dosage of 50 g/ton. This indicates that a potential savings of 85% in the enzyme dosage consumption can be achieved with the same energy consumption, obtaining properties of the softness of 60 ± 3 HF, tensile index of 8 ± 2 Nm/g, the water absorption capacity of 8 ± 1 g/g, and capillary rise of 95 ± 3 mm, which can be viably implemented in the tissue industry.

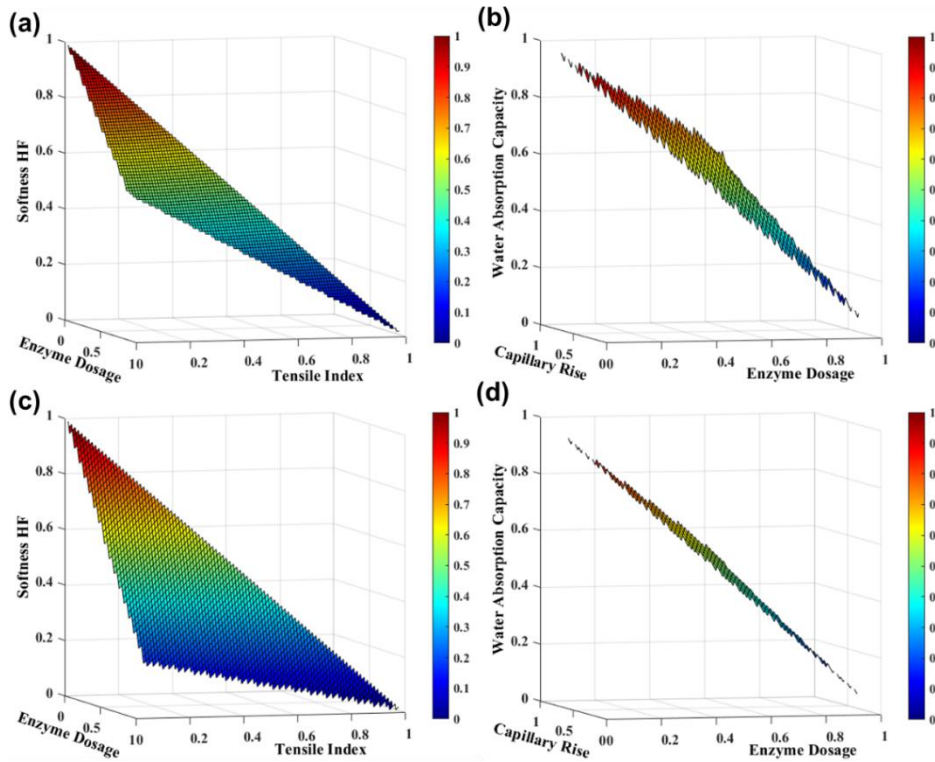


Figure III.72. TSA-softness HF and tensile index properties (a,c) and water absorption capacity and capillary rise (b,d) with enzyme dosage in an enzymatic pretreatment process followed by 500 PFI revolutions at 3.33 N/mm (a,b) and pre-refining at 500 PFI revolutions at 3.33 N/mm, followed by enzymatic treatment (c,d). The variables were normalized.

III.3.1.4.2.5. Additives Incorporation

There is also a great diversity of additives in tissue paper production used to improve the tissue final end-use properties. Currently, additives such as softeners, wet strength agents, dry strength agents, retention agents, among others, are used. However, the use of more promising additives, as is the case of micro/ nanofibrillated cellulose (MFC/NFC), is still not widely considered industrially for this type of daily use papers. Gonzalez et al. (2020) proved that highly fibrillated cellulose fibers enhanced significant strength increases in tissue structures that are strategically used to reduce the fiber content in formulations, maintaining the minimum functional strength and softness required for adequate performance and consumer satisfaction. Therefore, to produce an innovative tissue product with 100% eucalyptus fibers, we investigated and quantified the influence of the MFC/NFC incorporation, as an additive, in a eucalyptus slush pulp (Morais et al., 2021b). Figure III.73 presents the final tissue properties as a function of the MFC/NFC incorporation at different dosages, through the *SimTissue* prediction. For these studies, we considered maximum incorporation of 15%, as MFC/NFC only had an additive function. These results indicated that the MFC/NFC incorporation in tissue structures increased the strength properties by 238% and decreased the softness HF, water absorption capacity, and capillary rise by 16%, 12%, and 22%, respectively.

Through our *SimTissue*, we found that the balance between the properties of softness (74-79 HF), strength (7-11 Nm/g of the tensile index), and absorption (7.3-7.4 g/g of water absorption capacity and 34-38 mm of capillary rise) can be found with the MFC/NFC incorporation of 1 to 8% in tissue papers (Morais et al., 2021b). This additive can also be used as a substitute for softwood reinforcement fibers in tissue paper production, as improved properties are achieved in a tissue structure with 100% eucalyptus fibers at the micro and nanoscale, compared to structures with fiber mixtures as previously reported (Figure III.69).

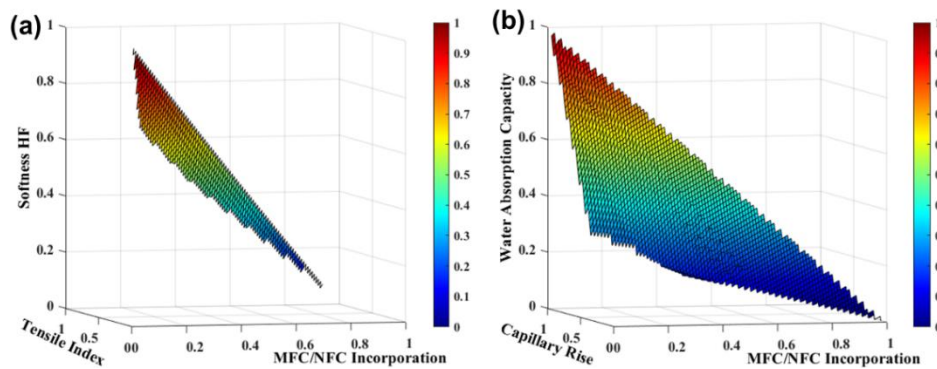


Figure III.73. TSA-softness HF softness and tensile index properties (a) and water absorption capacity and capillary rise (b) with MFC/NFC incorporation in a eucalyptus slush pulp. The variables were normalized.

Dry strength agents, such as cationic starch, are used to increase the paper's physical strength, increasing the polarity and affinity for anionic materials. However, this agent decreased the paper softness properties. Gonzalez et al. (2020) also showed that the use of a cationic polymer in tissue formulations counteracts the adverse effects on drainability of high fibrillated fiber furnishes, ensuring that tissue paper machine runnability is not affected and that production rates remain at normal levels. Therefore, the use of a commercial biopolymer additive as a substitute for cationic starch that increases the strength properties while maintaining the softness properties by removing or replacing the softwood reinforcing fibers is also a good strategy to be considered industrially (Morais et al., 2021c). Figure III.74 presents the tissue functional properties as a function of the biopolymer incorporation at different dosages in eucalyptus slush pulp, through the *SimTissue* forecast. For these studies, we considered maximum incorporation of 5%. The results indicated that the biopolymer incorporation increased the strength properties by 390% and decreased the TSA-softness HF, water absorption capacity, and capillary rise by 24%, 12%, and 42%, respectively.

The tissue paper simulator for furnish management optimization predicted that the balance between the softness (72 ± 2 HF), the strength (15 ± 2 Nm/g of the tensile index), and the absorption (8 ± 1 g/g of water absorption capacity and 97 ± 4 mm of capillary rise) can be found with the biopolymer incorporation of 3% in tissue papers, replacing the use of reinforcement fibers in these structures. The biopolymer incorporation of 4% still allows obtaining the same strength properties (18.7 ± 1.3 Nm/g) as the typical mixture used industrially (75 HW : 25 SW) (18.5 ± 1.1 Nm/g), improving the softness (67.3 ± 1.9 HF vs 59.9 ± 2.3 HF) and absorption (7.3 ± 0.6 g/g vs 7.5 ± 0.4 g/g; 86 ± 4 vs 38 ± 4 mm). The simulator's predictive capacity allowed us to define several scenarios for the replacement or reduction of the softwood fiber using innovative polymer-based additives.

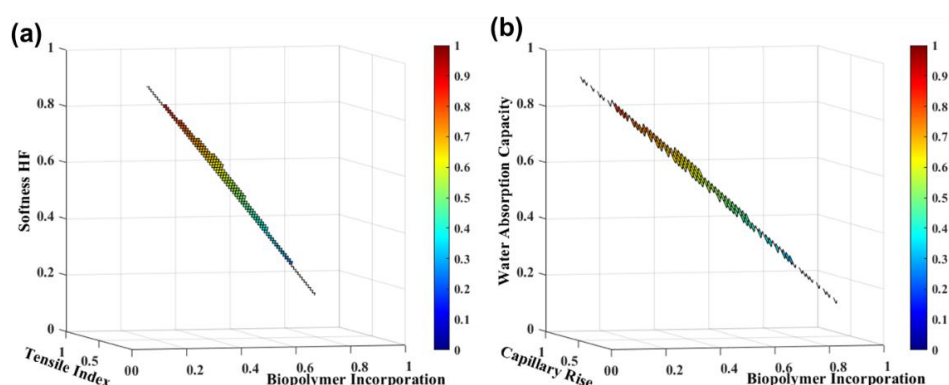


Figure III.74. TSA-softness HF and tensile index properties (a) and water absorption capacity and capillary rise (b) with biopolymer incorporation in a eucalyptus slush pulp. The variables were normalized.

III.3.1.4.3. Furnish Formulations to Develop Premium Tissue Materials

The development of premium tissue products requires the optimization of furnish formulations and, consequently, the functional tissue properties. The planning and management of innovative furnish formulations allow the choice of different fiber combinations, process steps, and additive incorporation using *SimTissue*'s predictive ability. Table III.35 presents different scenarios with an interest to produce various tissue papers, aiming at maximizing the trade-off between the softness, strength, and absorption properties.

Table III.35. Examples of case studies of different furnish scenarios to design new multi-structured innovative tissue paper materials.

Formulations	Hardwoods	Softwoods	Fiber Modification Process	Additives Incorporation
1	80% Eucalyptus kraft pulp + 20% Eucalyptus sulfite pulp	-	Both with enzymatic treatment of 10 g/ton, at 60 minutes	-
2	80% Eucalyptus kraft pulp + 20% Eucalyptus sulfite pulp	-	First with enzymatic treatment of 10 g/ton, at 30 minutes + Second without treatment	-
3	90% Eucalyptus kraft slush pulp	5% softwood kraft pulp	Beating process of softwood pulp achieving 25 °SR	5% MFC/NFC

This tissue simulator for furnish management and optimization allows the design of new innovative products, which can be achieved with the combination of two enzyme-treated eucalyptus kraft and sulfite pulps, in a ratio of 80:20 (Morais et al., 2021a). In formulation 1, both pulps were treated enzymatically with an enzyme dosage of 10 g/ton for 60 minutes. In formulation 2, only the eucalyptus kraft pulp was treated enzymatically with the same enzyme dosage for 30 minutes. Formulation 1 showed softness of 74±5 HF and a tensile index of 13±4 Nm/g. Compared to industrial reference mixtures (75% hardwood fibers + 25% softwood fibers), this formulation presents a 23% increase in softness HF and a 28% decrease in tensile index properties. Formulation 2 showed softness of 58±3 HF and a tensile index of 18±3 Nm/g. Compared to the same reference mixture, this formulation presents the same tensile index properties and a decrease of only 3% in the softness. The results can indicate that formulation 1 can be used to produce toilet papers or facial papers, where softness properties are essential, whereas formulation 2 can be used to produce towel papers or napkins, where strength properties are essential. These innovative formulations allow the production of tissue materials with 100% eucalyptus fibers, reducing the costs associated with softwood fibers.

Another approach may allow the design of new products with the combination of hardwood, softwood, and MFC/NFC cellulose fibers (Morais et al., 2021b) (formulation 3 in Table III.35). Formulation 3 showed softness of 71 ± 2 HF, tensile index of 14 ± 1 Nm/g, and water absorption capacity of 7 ± 0 g/g. Compared to industrial reference mixtures, this formulation presents an 18% increase in softness HF, a 23% decrease in tensile index properties, and a 2% decrease in water absorption capacity properties. The results indicate that formulation 3 can be used to produce a premium high-quality product where the compromise between the softness, strength, and absorption properties is optimized. This innovative formulation allows designing innovative tissue materials at the micro and nanoscale (Morais et al., 2021b).

III.3.1.5. Conclusions

Computational simulation tools were applied to optimize tissue paper materials. The simulator allowed the integration of all the important variables for the tissue paper structures development. This innovative tool allowed the valorization of different cellulose fibers from renewable sources and polymer-based additives, resulting in possible financial improvements. *SimTissue's* predictive capacity also allowed the development of innovative furnish formulations, containing micro/nanofibers and biopolymer additives, saving laboratory and industrial resources. In this study, different fiber mixing and modification process strategies were evaluated considering the desired softness, strength, and absorption properties, including maximizing the eucalyptus pulp incorporation, with the addition of MFC/NFC, biopolymer, different eucalyptus pulps, or softwood pulps, among others.

The results indicated that *SimTissue* evaluates the potential of raw materials for each type of tissue paper materials, considering the characteristics of fibers and structures made by them. The reduction of softwood fibers incorporation presented economic advantages, improving the functional properties. The simulations also predicted the properties of formulations with different enzyme reaction times and dosage, obtaining more economical scenarios associated with enzyme costs. The results also exemplified the possibility of using the simulator to reduce refining energy consumption, obtaining similar tissue properties with different refining times and intensities. With this computational approach, several scenarios for enzymatic and mechanical treatments with equivalent energy consumption were also foreseen. Finally, the *SimTissue* also allows us to predict scenarios in which the incorporation of additives such as MFC/NFC and biopolymers can be considered to replace softwood fibers to produce tissue products. The results indicated that formulations with 100% eucalyptus, when optimized with fiber modification treatments and polymer-based additives, can present improved properties over formulations with softwood fiber pulps.

In conclusion, the *SimTissue* is a useful tool not only to support industrial production in furnish management and process optimization but also to design innovative tissue materials, at the micro and nanoscale, establishing the correlations between tissue process inputs and the end-use properties.

III.3.1.6. References

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III.3.2. 3D Computational Simulation and Experimental Validation of Structured Materials: Case Studies of Tissue Papers

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III.3.2.1. Abstract

The development and optimization of structured materials, such as tissue paper materials, benefit from modeling strategies that take into consideration its structural hierarchy at the fiber and the paper levels. The use of an innovative three-dimensional voxel approach to model both the fiber and the 3D paper structure were validated by comparison of the computational structures with the laboratory-made structures. The main goal of this work was to model tissue structures and obtain a computational implementation adapted for tissue products. The fibers were modeled in 3D according to their dimensions, and the structures produced by them were characterized using the Representative Elementary Volume (REV) and image analysis computational tools. This methodology made it possible to model the fibers according to their morphology, flexibility, and collapse, resulting in a tissue structure with thickness, porosity, relative bonding area, coverage, among other properties. The experimental design plan included the production and characterization of isotropic laboratory structures with basis weights of 20, 40, and 60 g/m² with different eucalyptus fibers and beating degrees. With the aid of these advanced computational tools, mathematic models with predictive capacity for tissue properties such as softness, strength, and absorption can be developed.

Keywords

3D Fiber Models; Eucalyptus Pulp Fibers; Representative Elementary Volume (REV); Structural Properties; Tissue Paper Materials; Validation

III.3.2.2. Introduction

Fibrous paper materials, such as tissue products, for their multiplicity, cost-effectiveness, cleanliness, and convenience, play an important role in society. The study and validation of computational methods to optimize these materials play an important role in the ability to improve them. Our approach combines an experimental and computational plan design for the development of three-dimensional (3D) paper networks models able to correlate the influence of 3D fiber dimensions and properties and the structures formed by them (Conceição et al., 2010; Curto et al., 2011), and to optimize these types of materials (Lavrykov et al., 2012; Morais et al., 2020a, 2020b). 3D paper images are also used to create databases of microstructural descriptors for a complex fiber network (Marulier et al., 2015), and model their properties, combining a realistic configuration of cellulosic fibers by macroscale methods (Kettil et al., 2018).

Paper materials' multi-scale structural characterization constitutes an ongoing challenge that could be accessed using a combination of different analysis methods (Chinga-Carrasco, 2009). Due to the complexity and non-uniformity of these materials, their quantification may be difficult. To investigate the properties and structures of different tissue paper materials, numerical simulations of material features are needed (Wiltche et al., 2011; Sun et al., 2021). Several methods are used to characterize pores at nano, micro, and macroscale (Lawrence and Jiang, 2017; Morais et al., 2021a). Image analysis methods using computational tools are effective in pore properties characterization in processed images from SEM, for example (Chinga-Carrasco and Helle, 2002; Raunio and Ritala, 2013). To use an image fraction for this type of analysis, the image fraction must be representative of the original image. This fraction must represent the material for a respective property and be wide enough to contain satisfactory information about the porous structure to be statistically representative (Bloch and Roscoat, 2009; Xie et al., 2019). It is necessary to prove that the representative elementary area (REA) or volume (REV) is satisfactory to allow the quantification of porosity and pore size and distribution (Kanit et al., 2003; Bloch and Roscoat, 2009; Dirrenberger, Forest and Jeulin, 2014).

Tissue paper materials are optimized according to their intended use, including toilet papers, towel papers, napkins, facial papers, tissue masks, among others. The key properties to evaluate tissue product performance are bulk, porosity, softness, strength, and absorption (Raunio and Ritala, 2012; de Assis et al., 2018; Morais et al., 2019, 2021b, 2021c). These properties depend especially on the fiber properties (Figure III.75), especially the fiber transverse dimensions (fiber wall and lumen), and densification (fiber flexibility and collapsibility) (Paavilainen, 1993a, 1993b). In addition to these fiber characteristics, tissue properties are also affected by fiber chemistry, fiber orientation, papermaking chemistry, and technologies used to produce these materials, among other aspects; however, the present work is focused on the fiber morphological/physical properties, as well as the paper structural properties.

Establishing relationships between fiber properties and the structures formed by them, based on experimental data, is very complex due to the variability of fiber dimensions in each raw material used in its production. Furthermore, fiber flexibility and collapse are two mechanisms that occur simultaneously when studying the densification of paper structures (Bloch, Engin and Sampson, 2019). For this reason, 3D paper modeling has been considered a useful computational tool to overcome these experimental limitations. To the best of our knowledge, there has been a deficiency of research to relate the 3D fiber dimensions with low basis weight and high porosity structures, such as tissue materials, with the aim not only to improve their properties but also to model these structures with 3D fiber-based simulators. However, 3D fiber-based simulation studies arise for other low-density fibrous materials such as nonwovens.

Nonwoven are materials applied to surgical, cosmetic masks, *etc.*, produced by the random deposition of short (staple fibers) or infinitely long fibers (continuous filaments) on top of each other, bonding them by mechanical, thermal, or chemical processes (Pourdeyhimi et al. 2006). Numerical models used allowed the modeling and simulation of the 3D geometry of fiber webs, to optimize the performance of these materials at a laboratory and industrial level (Pourdeyhimi et al., 2006; Grothaus et al., 2014; Jirsák et al., 2022; Xie et al., 2022). This motivated us to design an innovative methodology for model tissue structures and predict the structural and functional properties, optimizing the various tissue materials (Morais et al., 2020a, 2020b).

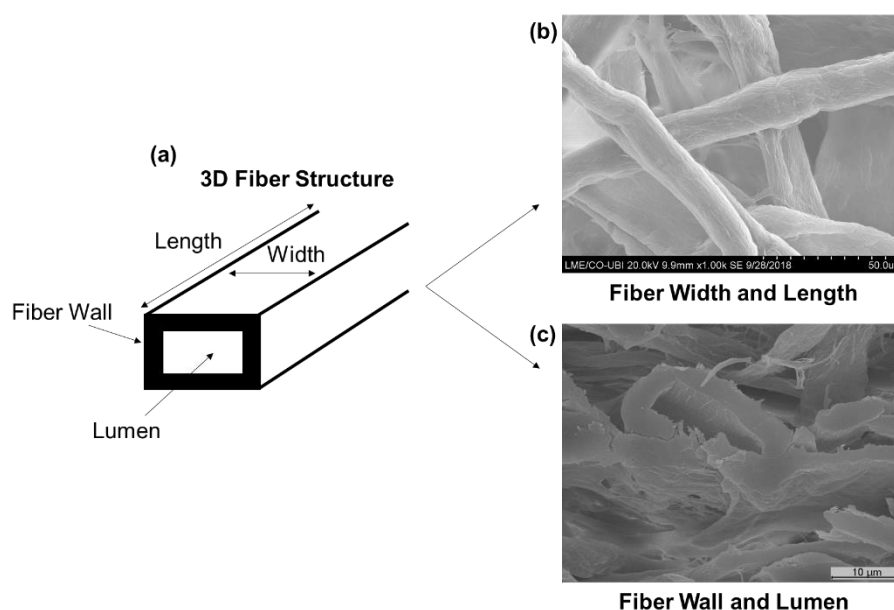


Figure III.75. Illustration of the (a) fiber morphology. Scanning electron microscopy (SEM) images of (b) fiber length and fiber width and (c) fiber wall and lumen. These are images of isotropic laboratory paper structures obtained using SEM.

Over the years, material modeling has become an important tool in the development and design of materials with better performance. The computational tools make it possible to significantly reduce the experimental work in the new materials development, to have a better synergy between the experimental tests design, and to carry out the simulation of materials specific properties (Niskanen et al., 1997; Dodson, et al., 2001, 2002; Alava and Niskanen, 2006; Sampson, 2009).

An approach to modeling the relationships between the key parameters and the functional properties of tissue materials is essential for the advances achieved in the field of fibrous materials science, engineering, and modeling. The authors' previous work involved the design of 3D fiber models for each fiber population from different types of raw materials, in order to simulate and optimize tissue papers (Morais et al. 2020a, 2020b). The tissue structure modeling is achieved using a fibrous material simulator, implemented, and validated by Conceição et al. (2009) and Curto et al. (2011), designated by *voxelfiber*. This simulator was previously validated for printing and writing paper (Curto, 2012); however, it was not applied to low basis weight and high porosity materials. The structures are simulated and compared with the real structures. *Voxelfiber* is based on a cellular automata, in which there is a Cartesian division of cells so that each fiber is represented as a sequence of voxels, each occupying a pre-established volume (Conceição et al., 2009; Curto et al., 2011). The fibers are also deposited one by one, each fiber occupying its space. Depending on its position, dimension, and flexibility, the fiber obeys the underlying structure (Fig. III.76a,b,c). This fiber model includes the fiber internal structure and the possibility to change it and have collapsibility in the material Z-direction (Curto et al., 2011; Morais et al., 2020b). This innovative 3D voxel approach considers the modeling at the fiber level and the paper structure level. The *voxelfiber* can also be extended to incorporate other fiber sedimentation possibilities and for other fibrous materials, such as micro/nanocellulose-derived products (Curto, 2012; Martins et al., 2018; Morais et al., 2020c).

To achieve these goals, it is necessary to introduce 3D fiber data, to obtain a computational implementation adapted for tissue products, as well as to validate structures developed in the 3D computational simulator by comparison with structures produced in the laboratory. This simulation approach can also be applied to real tissue papers by adjusting the simulator by introducing the physical processes used in these materials such as fiber orientation, creping, and embossing processes (Raunio and Ritala, 2012; Raunio et al., 2018). These advanced computational tools developed with predictive capacity can determine the most promising raw materials for a specified tissue paper and which process operations are needed to obtain a material with optimized properties. The novelty of this work is to demonstrate an experimental and computational approach to 3D fiber characterization and modeling to forecast tissue characteristics, optimizing the performance of tissue materials. Figure III.76 presents an outline of this work. The first part of this work presented 3D fiber and structure characterization, and the second part demonstrated a 3D modeling approach to include key fiber and structure parameters and simulate a concrete fibrous material. For this purpose, the computational model was applied to eucalyptus-based tissue papers. As these types of products are mainly produced from eucalyptus pulps, it is important to assess the contribution of this raw material with different biometry and morphology to the final properties. Therefore, two different eucalyptus pulps were subject to a refining treatment to implement the behavior in the Z-direction (thickness) and different flexibilities and fiber collapse degrees into the model. Additionally, these computational studies were validated by comparing laboratory-made structures with different basis weights.

The measured properties, such as the thickness and porosity, were compared with the estimated properties. Therefore, the influence of fiber and structure properties was evaluated and investigated to study and predict the properties of tissue paper materials.

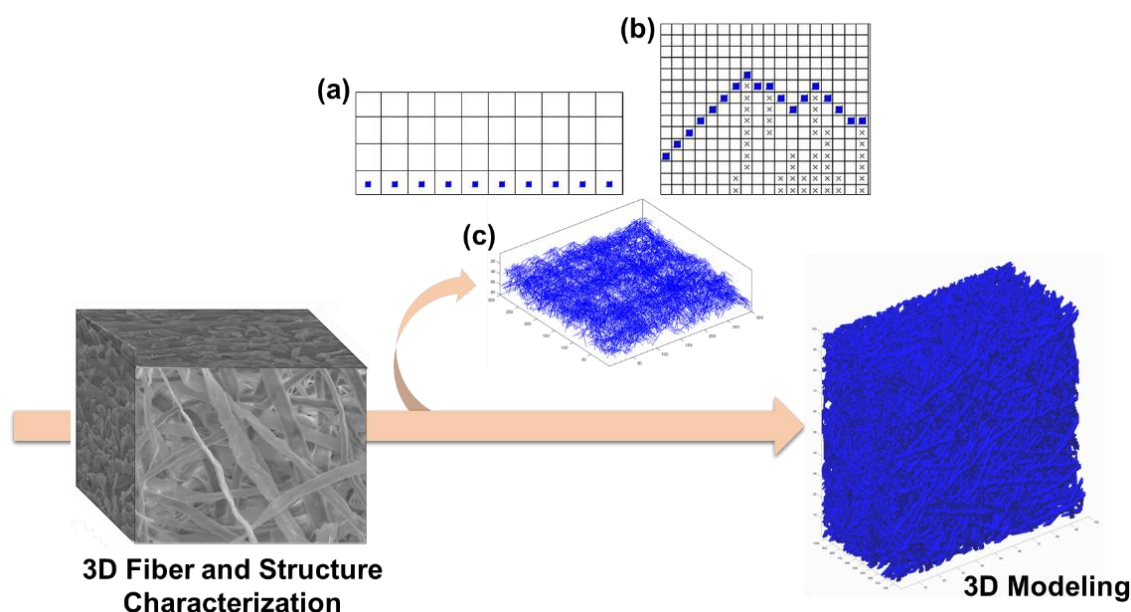


Figure III.76. Outline of the different steps for the development of this work. The first part includes a 3D fiber and structure characterization, and the second part presents a 3D modeling approach. To achieve these computational simulation studies, fibers are modeled with realistic parameters based on experimental analysis. The 3D computational structure is produced with the random deposition of fibers, (a) one by one, (b) not depositing on others since the space occupied by the fibers will not be overlaid, (c) under a spatial organization in the 3D matrix.

III.3.2.3. Experimental

III.3.2.3.1. Materials

Two industrial bleached eucalyptus kraft pulps were used in this work after disintegration according to ISO 5263-1. These samples differed in the bleaching steps (ECF – Elemental Chlorine Free and TCF – Total Chlorine Free) and one was air-dried (H_C) and the other was never-dried (HW). Both pulps were selected as they are representative eucalyptus pulps in tissue paper manufacture.

III.3.2.3.2. Methods

An experimental design was conceived to characterize the samples to quantify the fiber influence and beating degree. The pulps were beaten in a PFI mill at 500, 1000, and 1500 revolutions under a refining intensity of 3.33 N/mm, according to ISO 5264-2. The isotropic laboratory-made handsheets were produced from an adaptation to ISO 5269-1, including the suppression of the pressing operation and the production of structures with different basis weights.

The samples were conditioned at $23 \pm 1^\circ\text{C}$, with a relative humidity of $50 \pm 2\%$, according to ISO 187. Although some functional properties would vary depending on the fiber orientation in the structures (anisotropy phenomenon), it should be noted that in this work, only isotropic structures were considered in order to follow a standardized method. Additionally, the simulator used in the studies, *voxelfiber*, was developed and implemented to simulate the random deposition of fibers, as isotropic laboratory structures are produced. Therefore, computational simulation of 3D fiber networks is more realistic and comparable to real structures.

The morphological properties of pulp fibers were determined automatically by image analysis of a diluted suspension (20 mg/L) in a flow chamber in the fiber analyzer MorFi (TECHPAP, Grenoble, France). This data included the fiber length weighted by length, fiber width, coarseness, and fines content. The fibers are defined by lengths between 200 μm and 10 mm, and widths between 5 and 75 μm . The fine elements present lengths less than 200 μm and widths less than 15 μm . The fiber coarseness is measured according to the ratio of the mass of all fibers to the total length, considering the number of processed images, the imaged volume, and the pulp fiber consistency (Tourtollet et al., 2003). The assays were performed in triplicate, and the values presented are the mean and standard deviation of these three measurements. The pulp suspension drainability was evaluated, in triplicate, by the Schopper–Riegler degree method, according to ISO 5267-1.

Scanning electron microscopy (SEM) was used to characterize the 3D network surface (XY direction) and cross-sections (Z-direction) of handsheets. The samples were gold plated using a Sputter Quorum Q 15 OR ES equipment (Laughton, East Sussex, UK), and analyzed by Hitachi S2700 SEM (Tokyo, Japan), with a Bruker detector (Karlsruhe, Germany) operating at +20 kV and different magnifications. In the cross-section of the handsheets, the effective thickness of each fiber (cell wall fiber + lumen fiber) was measured, according to the method described by Morais et al. (2020a). The vector placement method was used to measure about 300 to 400 different fibers, along the entire handsheet cross-section. To ensure that each fiber was measured only once, without duplication, all fibers were identified, numbered, and measured. Additionally, SEM images were processed and analyzed using image analysis software, the *ImageJ*, for surface pore size distribution characterization, with defined criteria for the stabilization of the average of measured values (Hotaling et al., 2015). An image fraction of the 3D network was selected to contain an elementary area representative of the structure's pores. This area represented the overall structure for pore properties and contained satisfactory 3D network information to be statistically representative (Hotaling et al., 2015; Morais et al., 2020b). Binary images were segmented, processed, and analyzed, generating summary statistics for pore properties. Additionally, several morphological processing algorithms were used to process these binary images, including correcting the shadow gradient, reducing noise, obtaining an image detail, improving edges, creating higher contrast between light and dark areas, and removing isolated fibers (Morais et al. 2021a). A systematic method was used to generate pore dimension and distribution statistics.

About 500 to 1500 pores were measured from at least three SEM images per sample. This analysis was carried out for the different samples presented in this work; however, as a proof of concept, in the results and discussion section, only the results for the samples without beating, with a basis weight of 20 g/m² are presented.

The structural properties of the handsheets, such as basis weight, thickness, using a micrometer (FRANK-PTI GMBH, Birkenau, Germany), and bulk, were determined according to ISO 12625-3 and ISO 12525-3. The handsheet apparent porosity (%) was also calculated theoretically as $\text{Porosity} = 1 - (\text{density of the handsheet} / \text{density of cellulose, } 1.5 \text{ g/cm}^3)$ (Morais et al., 2020b, 2021a).

III.3.2.4. Computational Studies

A 3D simulator of fibrous materials, the *voxelfiber* (<https://github.com/eduardotrincaoconceicao/voxelfiber>), was used to simulate the 3D structures with the fiber dimensions obtained experimentally. A more detailed description of the 3D simulator can be found in Conceição et al. (2009) and Curto et al. (2011). This simulator allows the modeling of porous structures as planar random networks (Figure III.76). The 3D simulator uses fiber dimensions and properties as input parameters and produces the resulting 3D structure made from these fibers. The input parameters are length/width ratio, fiber wall thickness, lumen thickness, fiber flexibility, and resolution (number of layers in the thickness direction, up to 0.05 μm). Curto (2012) established relationships between fibers and structural properties of paper-based materials, developing and validating this 3D model. In Curto's studies, the fiber flexibility was determined experimentally, in which the values determined corresponded to the extreme values of different fibers. Therefore, that study constituted valuable information in order to be applied to other fibers with fiber dimensions and properties in the same range. In the present work, the fiber flexibility was estimated according to these works developed previously simultaneously with a methodology of SEM image analysis, described above, to be inputted in the model. The 3D computational structures will be processed to obtain important properties, such as thickness (local and average), porosity (interfiber and global), relative bonded area (RBA), coverage, number of crossings per fiber, among others (Morais et al., 2020a, 2020b). RBA corresponds to the fraction of fiber surface in contact with other fibers and is described as the ratio between the fibers' bonded area and the total surface area of the fibers. Coverage is the number of fibers covering a given point on the surface of the paper material. In the present work, average thickness, interfiber porosity, RBA, and coverage were evaluated to determine the REV, and the estimated properties of average thickness and global porosity were compared to the same experimental measured properties. The adjustments of uniform model parameters were performed, so that it reproduces realistic results, according to experimental datasets independent of the laboratory-made structures. Under conditions other than calibrated, the computational model was verified, examining its ability to realistically represent the desired properties. Computational studies were performed using Matlab® (R 2020a, 9.8.0.1323502, MathWorks, Natick, MA, USA).

III.3.2.5. Results and Discussion

III.3.2.5.1. Pulp Fiber and Structure Experimental Characterization

Eucalyptus fibers present high homogeneity as well as other characteristics such as high fiber wall thickness, resistance to collapse, fibrous population, low fines content, among others when compared with other fibers used in tissue products, which results in good drainage, formation, runnability, high bulk, absorption, and softness (de Assis et al., 2018). The two investigated raw materials with different beating degrees presented different fiber morphology (Table III.36). The changes were more visible in the HW sample, since this pulp was a more degraded pulp with lower drainability (25°SR), more deformations, and fibrillation as a result of its bleaching sequence (TCF), compared to the H_C sample. In the hornification process during the drying of the EUC sample, a fraction of the pores in the cell wall collapsed and closed irreversibly due to the formation of hydrogen bonds between adjacent surfaces, leading to fibril aggregation or coalescence (Giacomozzi and Joutsimo, 2015). It would be expected that this sample presented high deformations (Giacomozzi and Joutsimo, 2017). However, the oxygen and ozone bleaching stage process promote a more intense degradation of polysaccharides and consequent loss of yield and pulp properties, such as decreased intrinsic viscosity and high fine content (Masrol et al., 2017; Morais et al., 2021a).

Table III.36. Fiber morphology and pulp drainability of H_C and HW samples.

Fiber Types	PFI refining revolutions	FL* (mm)	FW* (μm)	C* (mg/100m)	FC* (%)	°SR
H_C	0	0.798 ± 0.004	19.1 ± 0.1	6.83 ± 0.11	37.1 ± 0.3	20 ± 0
	500	0.770 ± 0.002	19.3 ± 0.1	6.86 ± 0.10	40.7 ± 0.9	23 ± 0
	1000	0.764 ± 0.002	19.5 ± 0.1	6.67 ± 0.07	41.5 ± 0.2	27 ± 0
	1500	0.757 ± 0.002	19.6 ± 0.1	6.77 ± 0.07	42.3 ± 0.6	32 ± 0
HW	0	0.729 ± 0.003	19.1 ± 0.0	6.31 ± 0.04	38.5 ± 0.4	25 ± 0
	500	0.701 ± 0.002	20.2 ± 0.2	6.62 ± 0.10	45.7 ± 0.6	32 ± 0
	1000	0.683 ± 0.002	20.6 ± 0.2	6.84 ± 0.07	46.8 ± 0.9	47 ± 0
	1500	0.665 ± 0.003	20.7 ± 0.2	7.06 ± 0.07	50.4 ± 0.9	70 ± 0

* FL: fiber length weighted by length; FW: fiber width; C: coarseness; FC: fines content; °SR: Schopper–Riegler degree

The fiber length weight by length (FL) decreased over the PFI revolutions, contrary to the fiber width (FW), coarseness (C), and fines content (FC). Fiber fibrillation after beating decreases coarseness; however, the coarseness increase can be explained by the decrease in fiber length, since is described as the mass per length unit. These results can be explained by the presence of some fine elements that were not accounted for in the measurements. This evidence reduces the fiber length and, consequently, increases fine content, despite the high fiber coarseness (Joutsimo and Asikainen, 2013; Morais et al., 2021a). The beating process increased the fines content corresponding to a higher degradation of the cellulosic chains (degraded and less rigid fibers), and consequently to a loss of the fiber intrinsic strength (Muneri, 1997; Morais et al., 2021a).

The effect of mechanical refining enhanced efficient fibrillation, which negatively affected the drainability, as verified by the °SR values increase (Table III.36). This property is influenced by fiber external fibrillation and the amount of fine elements and related with the fibers' flexibility and the improvement of their bonding capacity. This effect was especially noticeable for the HW sample, where a maximum increase of 180% can be observed, while for H_C sample a maximum increase of 60% can be observed. Dry H_C fibers can become more conformable when refined, producing fines and, consequently, increasing drainage resistance, requiring considerable energy expenditure. Furthermore, the changes caused by drying are not fully reversible (Seth, 2001). Considering also that both pulps have different bleaching stages, the never-dried fibers of HW were fibrillated to a much higher extent than the dry fibers of H_C, increasing the fines content and consequently the °SR values. Light refining between 22 and 35 °SR is recommended for eucalyptus pulps to produce high-quality tissue papers (de Assis et al., 2018). Therefore, it is considered that the H_C pulp must be refined up to 1500 revolutions and the HW pulp must be refined up to 500 revolutions.

Suspended fibers are not subjected to the tensions found in the handsheets, so the fiber morphology may be different when fibers are in water suspension or the paper structure. Only SEM is a method that provides information about the fibers in the paper structure. The fiber dimensions and the collapse degree can be measured and estimated in the handsheet cross-section, using this methodology. Kallmes and Bernier (1963) stated that the best representation of the effective fiber thickness cross-section is a rectangle to accurately determine measurements of this 3D fiber dimension, which includes the fiber wall and lumen, in the paper structure. They also stated that in the handsheets formation, pressures are applied to the fibers causing fiber collapse, with considerable variations in cross-sectional thickness (Kallmes and Bernier, 1963). In previous work, the authors analyzed the effective fiber thickness, the third fiber dimension of eucalyptus pulp fibers without beating, through the vector placement method on a significant number of fibers in the handsheet cross-section (Morais et al., 2020a). The experimental results for effective fiber thickness distribution were obtained using this approach (Figure III.77). The effective fiber thickness of H_C and HW samples presented values, on average, of $3.92 \pm 1.57 \mu\text{m}$ and $5.65 \pm 1.23 \mu\text{m}$, respectively. This suggests that HW fibers present a thicker cell wall compared to H_C fibers. This evidence can also be explained by fiber length weighted by length and coarseness (Table III.36). The effective fiber thickness (fiber wall plus lumen) data are essential to predict handsheets properties of eucalyptus pulp fibers, such as thickness, bulk, and porosity (Pulkkinen, Ala-Kaila and Aittamaa, 2006). By following these fiber modifications in the 3D structure, together with the coarseness properties, a realistic approach of the dimensions in the paper Z direction can be performed, to accurately model the fibers in simulators based on 3D modeling of these structural elements (Morais et al., 2020b).

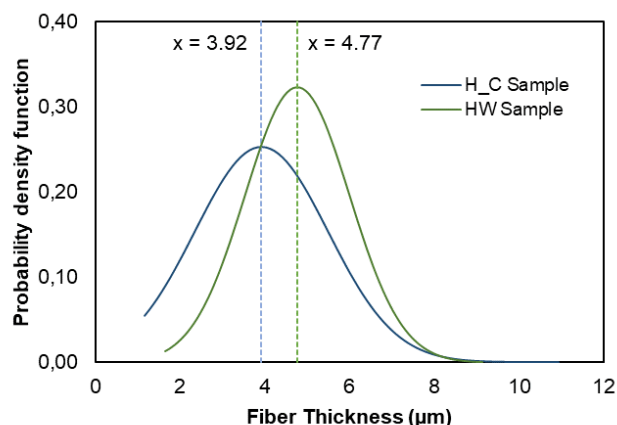


Figure III.77. Fiber effective thickness normal distribution of H_C and HW samples, in comparison to the arithmetic mean (vertical line).

This approach of measuring the effective fiber thickness in paper structure is only possible to be carried out in structures without refining operation since the densification that occurs from changing the fiber flexibility and collapse with beating is evident. Figure III.78 showed an example of this densification effect on the handsheet cross-section of HW sample with zero and 1500 revolutions.

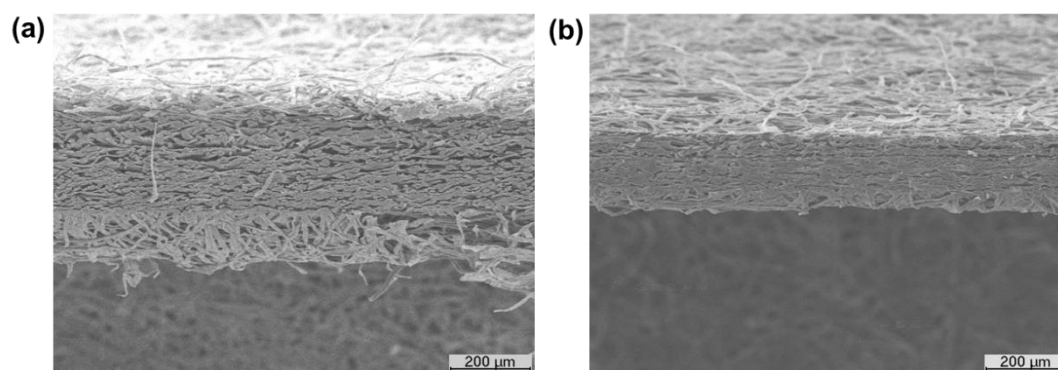


Figure III.78. SEM images of HW sample handsheet cross-section, with (a) zero PFI revolutions (basis weight of 60 g/m² with a thickness of 249 μm) and (b) 1500 PFI revolutions (basis weight of 60 g/m² with a thickness of 138 μm) (magnification: 100x).

Additionally, Figure III.79 presents the SEM images of the H_C and HW samples without beating, as well as the pore size distribution in the 3D network surface handsheets. These multi-structured materials presented a 3D network of non-oriented cellulosic fibers and an irregular porous structure. The optimization of these structures is essential to produce optimized tissue papers with improved functional properties, such as softness, strength, and absorption. The porous structure and the pore surfaces of these types of materials are essential for absorption properties, especially by paper towels. Also, the pores allow the penetration of additive agents, such as softeners or lotions that are sprayed on the sheet surface, providing space for their deposition, improving the final strength and softness properties of toilet papers and napkins, for example (Rowland 1977; Neumann et al. 2016).

This ability of additives to migrate through the material depends on the irregular pore distribution, pore size that varies over a wide range, and the tortuous paths that the pores provide for the flow of the liquids (Neumann et al. 2016). The H_C and HW samples showed average pore sizes of $14.20 \pm 13.02 \mu\text{m}$ and $12.98 \pm 8.05 \mu\text{m}$, respectively. The characteristics of the HW sample, such as TCF bleaching stage, lower fiber length, and higher fine content and °SR, benefited the inter-fiber bonding, filling in the empty spaces between fibers and, consequently, reducing the pore dimension and distribution in the structures (Morais et al., 2021a). These features correspond mainly to the handsheet surface and do not necessarily extrapolate the handsheet bulk. This analysis demonstrated the heterogeneity of 3D networks from the high standard deviation due to the presence of numerous deep pores in contrast to the larger pores on the surface. In addition, the global porosity, across the sheet thickness, was calculated, and the results are shown in Figure III.80. These computational image analysis tools also allow to analyze the pore properties of computationally simulated structures. An analysis of the pore dimension and distribution can be performed in the 3D computational structure network and compared with the experimental structure.

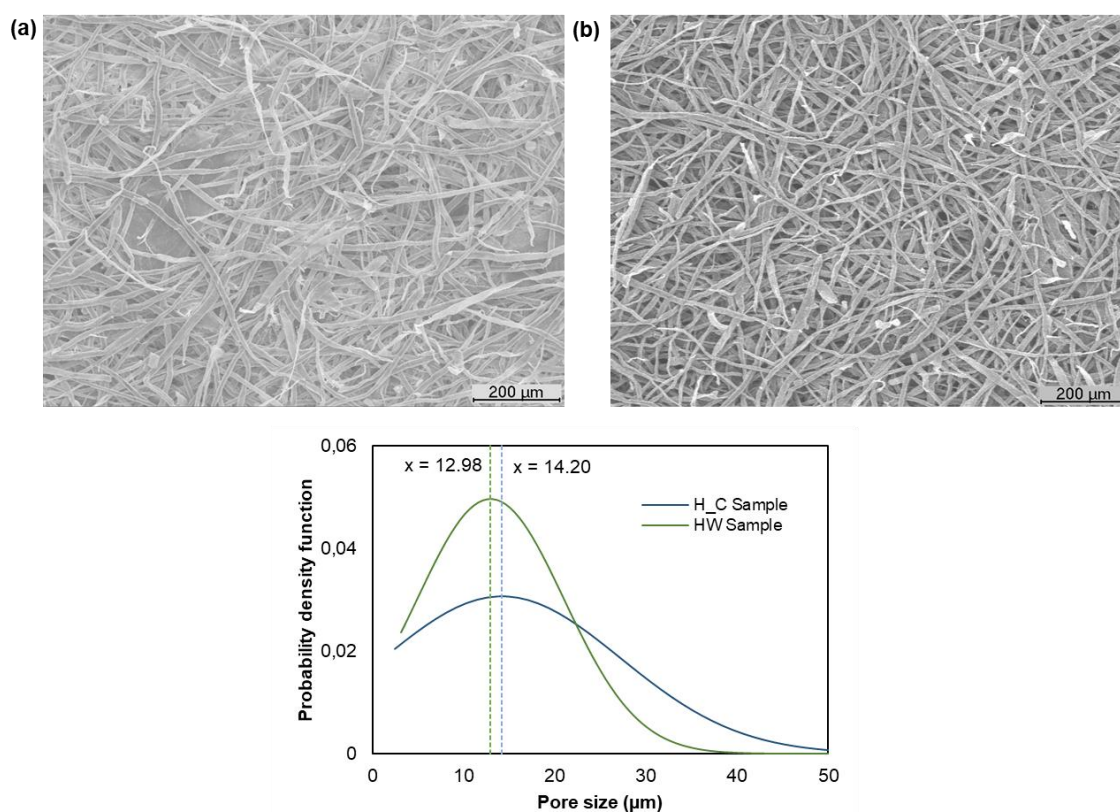


Figure III.79. SEM images of (a) H_C and (b) HW samples (magnification: 100x), and pore size distribution in the 3D network surface handsheets.

Tissue papers have structural characteristics of low basis weight paper materials. In the production of these types of materials, different individual sheets are used. Therefore, the basis weight and thickness properties of tissue papers directly depend on the number of sheets in their composition.

For this reason, three different basis weights were investigated to mimic these individual sheets in tissue papers. A structure with 20 g/m² can correspond to a tissue base industrial sheet, a structure with 40 g/m² can correspond to a product made up of 2-ply sheets of 20 g/m², and a structure with 60 g/m² can correspond to a product made up of 3-ply sheets of 20 g/m² or even 2-ply sheets of 30 g/m². It should also be noted that in this work the creping stage was not considered, in order to separate the effects of this operation, as it constituted a multifactorial challenge (multiple-input multiple-output (MIMO) approach), mainly due to relationships between pulp fibers, the multiple changes resulting from the different processes, and the functional tissue properties (Morais et al., 2021c).

The evolution of structural properties against PFI revolutions for H_C and HW handsheets with different basis weights are presented in Figure III.80. The pulp fibers were beaten in four beating levels (0, 500, 1000, and 1500 PFI revolutions). As to be expected, the results indicate that the handsheets thickness increased with the basis weights and decreased with the PFI revolutions. Inversely, the bulk and porosity decreased with the basis weights and PFI revolutions. This evidence is explained by the definitions of basis weight (weight per unit area), thickness, bulk, and porosity. For a given basis weight, thickness determines how bulky or dense paper is, since a structure produced with a refined pulp presents lower thickness. Bulk, reciprocal of density, indicates the volume or thickness in relation to weight, and it is calculated from thickness and basis weight. Porosity is the volume fraction not occupied by the fibers within a paper sheet, and it is simply obtained by dividing the volume of all the voids by the total volume of the sheet. Considering these definitions, structures with higher basis weight are thicker, denser, and, consequently, less porous. Additionally, the differences found in these structural properties are due to the different eucalyptus pulps, with different production processes, used to produce the handsheets.

Fiber flexibility changes during the beating. The possibility of modeling this parameter is very important for the model performance evaluation. When comparing these two eucalyptus pulps, the information about fiber flexibility and biometry is determinant to predict structural properties. The extreme values of fiber wall thickness, beating ability, and flexibility correspond to the different eucalyptus used in tissue paper manufacture. Fiber flexibility and conformability are related to the structure density and porosity, and consequently to the fiber morphology and the modulus of the cell wall, which also present an effect on fiber bonding (Paavilainen, 1993a). HW presented higher values of effective fiber thickness (Figure III.77) and consequently, it was less flexible (Figure III.80) than the thinner fibers of H_C sample. This provides HW fibers with higher resistance to collapse and individual fiber stiffness than H_C fibers, to produce bulky structures with loosely bonded fibers (higher porosity). These experimental results for the evolutions of structural properties, together with fiber thickness and flexibility, constitute valuable information, also applicable for other eucalyptus fiber pulps, with fiber dimensions in this range. After this quantification, the key property of flexibility is included in the structural model, with fiber bending in the Z-direction as an important parameter.

The implementation presents full discretization of space in both the in-plane and out-of-plane directions, and an approach using cellular automata to drive fiber bending (Curto 2012).

Depending on the specific use of each tissue product, the control of the bulk and porosity, which are thickness' dependent, may be particularly relevant. For tissue papers, a high bulk is required to ensure the development of the final end-use properties (Morais et al., 2019). The experimental study of paper structures with different basis weights also provides important data for 3D paper model calibration and validation processes to obtain a paper simulator with a predictive capacity.

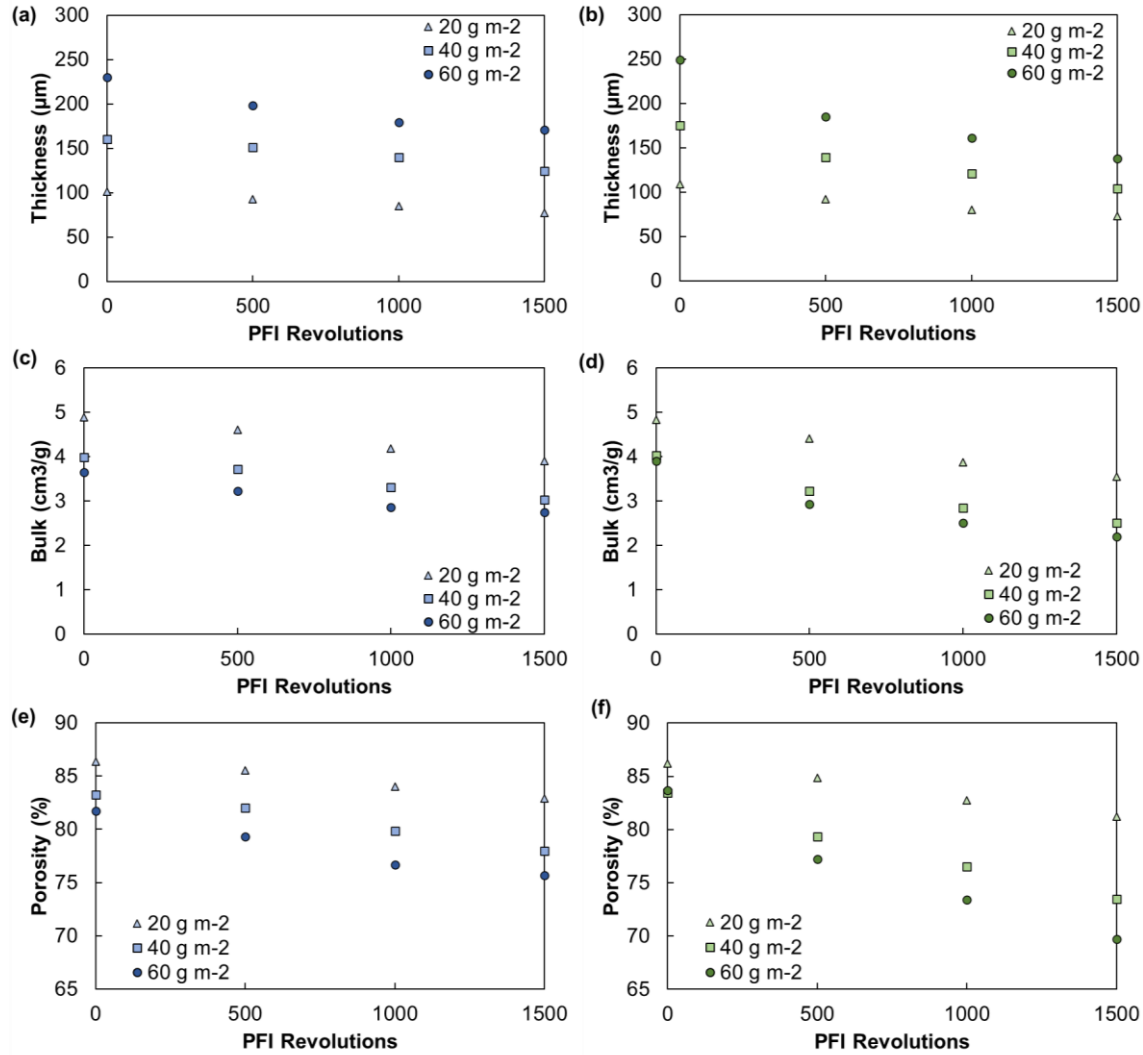


Figure III.80. Structural properties, such as (a, b) thickness, (c, d) bulk, and (e, f) porosity as a function of PFI revolutions of (a, c, e) H_C and (b, d, f) HW handsheets with 20, 40, and 60 g/m².

III.3.2.5.2. Computational Simulations and Representative Elementary Volume (REV)

The structures produced with different basis weights and beating degrees can be simulated computationally to optimized tissue paper materials. Beating presents a major effect on the fiber flexibility, and consequently on its collapse in the paper structure. Figure III.81 shows an example of the computational simulations that can be obtained for the H_C sample. The computational simulation model was used to perform simulation studies. In these case studies, it was used to investigate the relative influence of fiber flexibility, dimensions, and collapsibility. The model includes these key fiber properties as well as process operations such as fiber deposition, network formation, and densification. Therefore, simulation studies allow one to separate the influence of these papermaking fiber properties on the structure densification, for example, which occurs with beating.

The multiscale model gave realistic predictions and enabled us to link fiber microstructure and structural properties. The computational model simulates a structure similar to the real one obtained experimentally, with a distinction between the XY plane (Figure III.81a,b) and the Z plane (Figure III.81c,d). The fibers' properties and dimensions obtained by the fiber analyzer, MorFi, as well as the data of fiber morphology and behavior in the z-direction, obtained by the vector placement method in SEM images, are considered to promote a more realistic computational representation (Morais et al., 2020a).

The uniform model parameters were adjusted to reproduce realistic results according to experimental datasets independent of the laboratory-made structures (Morais et al. 2020a). Under conditions other than calibrated, the computational model was verified, examining its ability to realistically represent the properties. To increase the reliability of the computational model, an independent set of the initial structures produced was used to validate the 3D computational model. The fibers were randomly positioned and oriented in the XY plane to simulate the formation of isotropic laboratory handsheets (the ones used to validate the model). The model output is a 3D fiber network structure formed with occupied and empty voxels, in which the information concerning each fiber is kept. At this stage, this formed structure can predict several structural properties such as thickness (local and average), porosity (interfiber and global), RBA, coverage, and the number of crossings per fiber.

The fibers are modeled and simulated three-dimensionally by their random deposition, representing a good estimative of the real handsheets network. The model includes key fiber properties such as morphology, flexibility, and collapsibility, and process operations such as fiber deposition, network forming, or densification. Additionally, the model considers the fiber microstructure level, including lumen and fiber wall thickness, with a resolution up to 0.05 μm (Curto, 2012). 3D computational simulations with this 3D data are essential to optimize the final end-use properties of tissue paper materials.

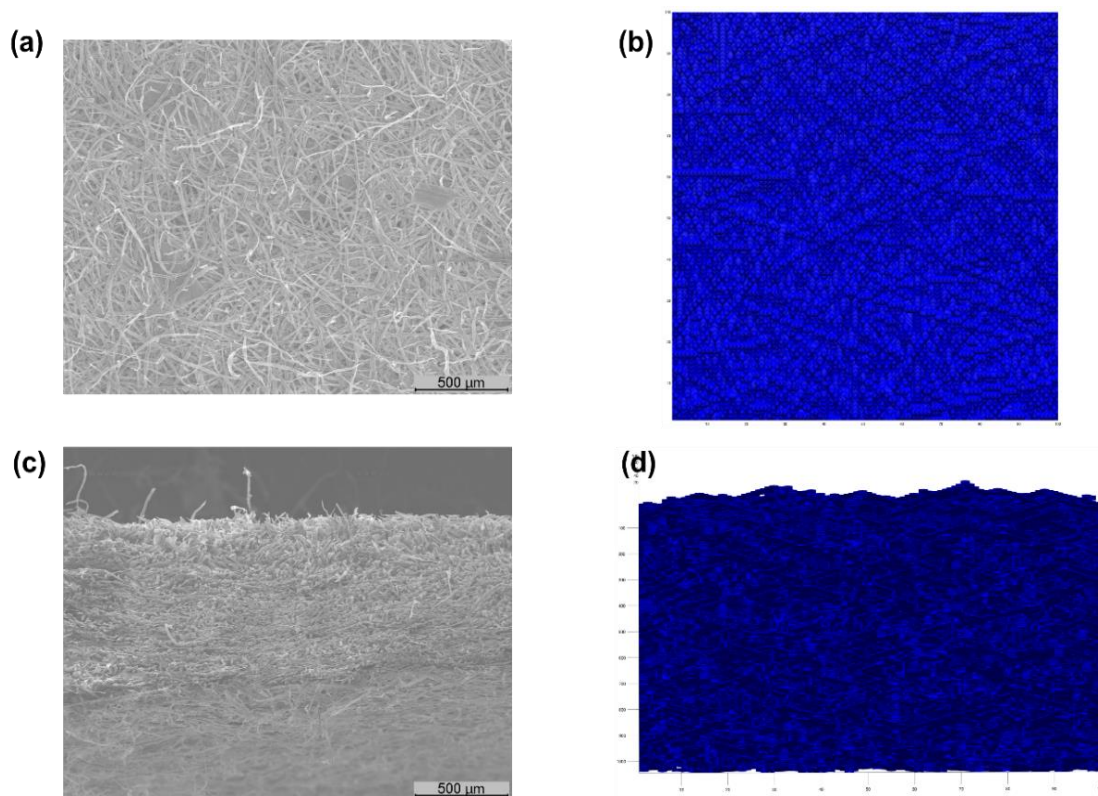


Figure III.81. SEM images of the experimental structure of the H_C sample with a basis weight of 40 g/m² in the XY plane (a) and Z plane (c), and the respective computational images in the XY plane (b) and Z plane (d), using the 3D computational simulator described in (Conceição et al., 2010; Curto et al., 2011; Morais et al., 2020b).

The REV is the key concept in determining and modeling the different properties of heterogeneous materials (Doškář et al., 2018; Hu et al., 2018). A REV should be large enough to accommodate sufficient properties information from the structures and, at the same time, small enough to comply with scales separation (du Roscoat et al., 2007; Mirkhalaf, Pires and Simões, 2016). For this purpose, the REV was determined for different properties in the computational structure. A systematic analysis was performed of the influence on the thickness, interfiber porosity, RBA, and coverage of the XY plane (Figure III.82). The structures were formed by the random deposition of single fibers in this plane to simulate the formation of handsheets. The fibers were modeled according to their length/width ratio (38), fiber flexibility (1), wall thickness (2), lumen thickness (0), and the number of fibers (24500). The information in parentheses corresponds to the values used in the simulations to represent each parameter. The length/width ratio was obtained from the experimental data; fiber flexibility, wall thickness, and lumen are represented in computational voxel units; and the number of fibers was automatically defined by establishing the basis weight of the structures in the model. A fiber flexibility equal to one corresponds to a less flexible fiber, and a wall thickness equal to two and a lumen equal to zero corresponds to a fully collapsed fiber, with an effective fiber thickness of four voxels.

The proposed fiber models based on an experimental analysis, with differences between fiber morphology and dimensions, collapse degrees, and flexibility, result in structures with different structural properties (Morais et al., 2020b). These input parameters were kept constant, and the dimensions of the XY plane (between 10 to 300) were changed through the simulations. According to Figure III.82, the structural properties become more stable and tend towards experimental values while XY plane dimensions increase. For a given XY plane dimension superior to 200, the structural properties reach a practically constant value. The results indicated that these properties depend on the size of the volume in the XY plane. Therefore, to carry out the different computational simulations, we decided to use an XY plane with dimensions of 300x300.

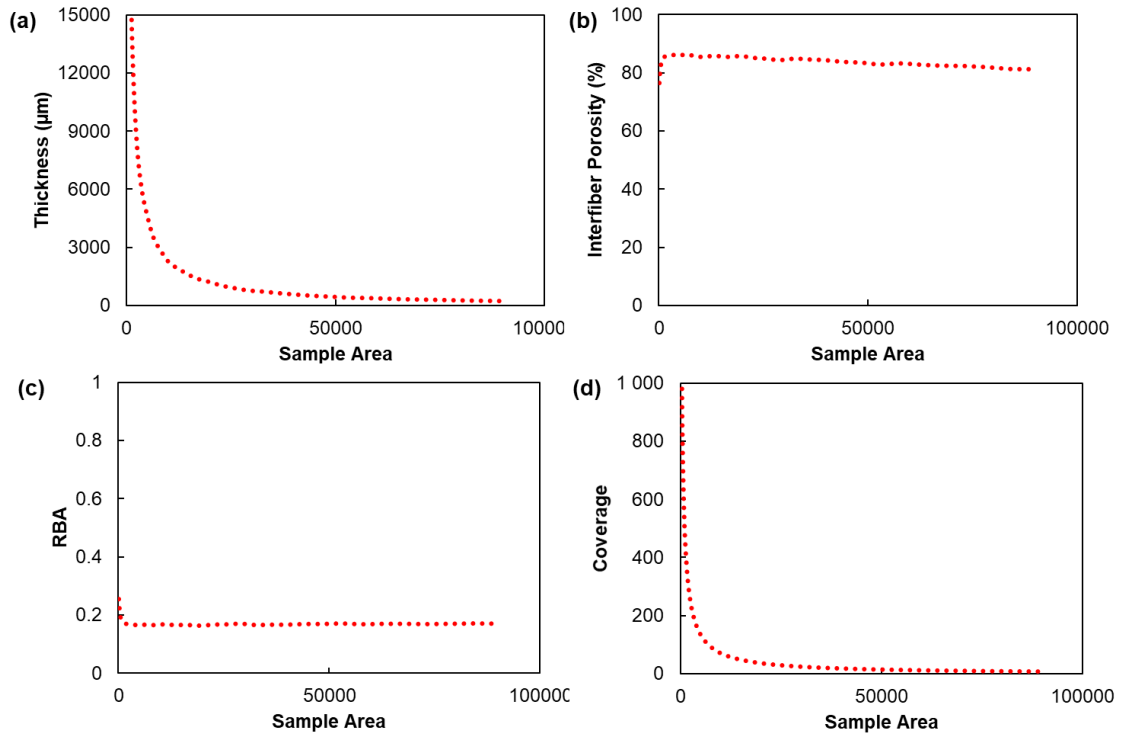


Figure III.82. Evolution of the (a) thickness, (b) interfiber porosity, (c) RBA, and (d) coverage of the XY plane for a eucalyptus structure.

III.3.2.5.3. Validation of Computational Structures

To validate the predictive capacity of the structural properties of tissue structures, a comparison of the computational and experimental structures was performed. Figure III.83 presents the beating influence on the paper thickness and porosity for computational simulated structures, validated with the experimental results presented in Figure III.80. Following our experimental results, a similar impact for the influence of computational structures was verified. Furthermore, the model proves to adjust to the experimental data. To relate simulations with experimental data, the fiber parameters needed to be defined. For the simulated structures, the H_C and HW pulps were defined as a fiber population that was the combination of four fiber models proposed by us in a previous publication (Morais et al., 2020b).

Beating levels are implemented in the 3D model through the influence of fiber collapse. It was evident that different fiber collapse degrees influenced the structural properties. For each beating level, different fiber wall thickness and lumen dimensions were tested, and structural properties were determined. The simulated computational structures were obtained for a fixed basis weight of 20, 40, and 60 g/m², identical to the experimental data.

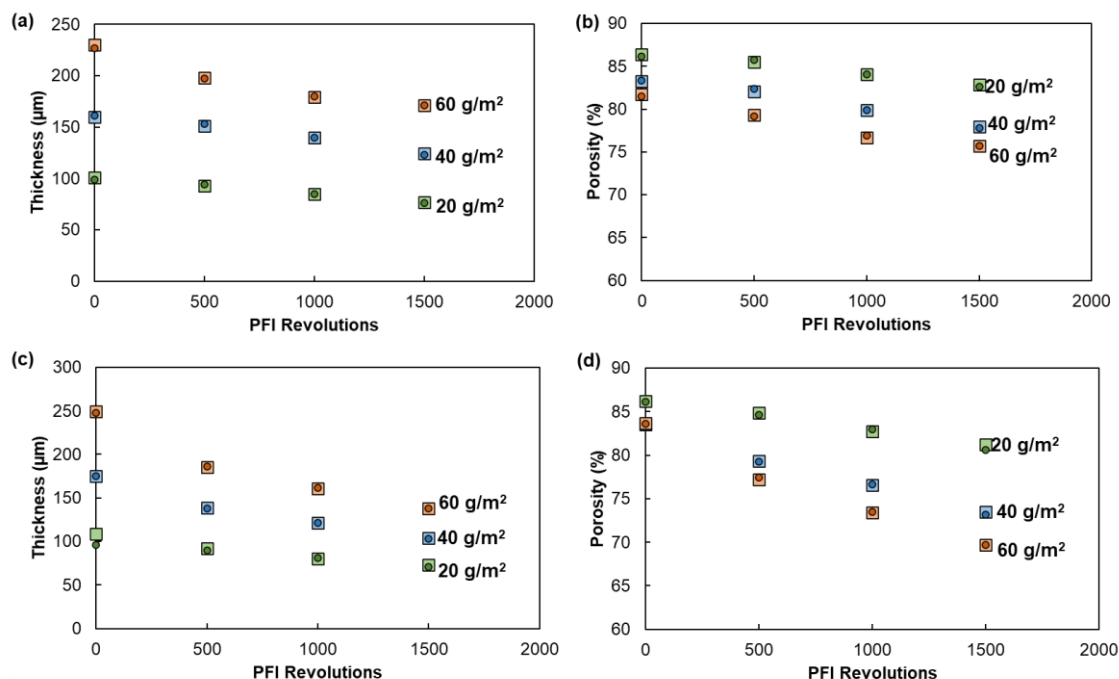


Figure III.83. Comparison of computational and experimental (a, c) thickness and (b, d) porosity as a function of PFI revolutions of (a, b) H_C and (c, d) HW handsheets with 20, 40, and 60 g/m². The computational results are presented with a circle symbol and the experimental results with a square symbol.

This entire process makes it possible to model the structures in 3D and predict the structural properties of a material with low basis weight and high porosity as in the case of tissue papers. Posteriorly, this strategy allows optimizing the various tissue materials, defining different furnish tissue scenarios. This is possible with the combination of an approach presented in the authors' previous publications (Morais et al., 2021a, 2021b, 2021c), in which mathematical models of multiple linear regression, artificial neural networks, robust linear regressions, and interpolation and extrapolation methods were used. These proposed mathematical models consider the fiber morphological, suspension, and structural properties to forecast functional tissue properties (Morais and Curto, 2022). Using these computational simulation methods, different fiber mixing and modification process strategies were evaluated considering the desired softness, strength, and absorption properties, including maximizing the eucalyptus pulp incorporation, with additives such as micro/nanofibrillated cellulose and biopolymer, and different eucalyptus pulps (Morais et al., 2021c). The results of the 3D fiber modeling, using the *voxelfiber*, were used to investigate the influence of fibers on the structural properties due to the good estimative of the simulated results with the experimental ones.

Therefore, the bulk and porosity values predicted by the simulator, which are directly related to the paper thickness, are used in the models developed by the authors to predict the tissue functional properties, resulting in higher speed and flexibility of response, without the need to produce extensive laboratory structures (Morais and Curto, 2022).

III.3.2.6. Conclusions

1. The purpose of this article was to present a computational approach to model fibers and tissue structures using a 3D fibrous material simulator, predicting their structural properties. These simulations were based on an initial experimental characterization of beaten and unbeaten eucalyptus fiber pulps, implementing these datasets in the model in order to benefit from modeling strategies considering the structural hierarchy at the fiber and structure level. The samples to build this model (Morais et al., 2020a) were independent of the samples to test the model. The 3D model includes key papermaking fiber properties and process operations, with a detailed fiber model. The model has shown good forecast capability for structural properties like paper thickness and porosity. It was found that this simulation studies approach constitutes a valuable tool to distinguish the influence of fiber characteristics like fiber flexibility and collapse on the structure densification, for example, that occurs with beating.
2. The computational results were validated with experimental structures produced in the laboratory, and the simulated results represented a good estimative of this real tissue paper network. The tissue structures were built by the random deposition of individually 3D fibers. The fibers were modeled using fiber dimensions and the structures made by them, according to image analysis methods. These parameters were changed independently, and the raw materials were defined as a fiber population with a combination of different fiber models, to allow the implementation of different degrees of fiber flexibility and collapse.
3. The possibility of modeling tissue materials, at the fiber level and 3D structure level, is crucial to predict the structural and functional properties and therefore optimize these types of products. The integration of the predicted and validated results of this 3D fiber-based simulator with the mathematical models built in the authors' recent work (Morais and Curto, 2022), will make it possible to forecast and optimize the softness, strength, and absorption properties of tissue products. The combination of advanced computational tools and experimental design in the development of a simulator that mimics tissue products is an important milestone not only to support industrial production in furnish management and process optimization but also to design innovative tissue materials.

III.3.2.7. References

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III.3.3. Challenges in Computational Materials Modelling and Simulation: A Case-Study to Predict Tissue Paper Properties

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III.3.3.1. Abstract

The growing demand for tissue papers worldwide encourages the paper industry to find new approaches to optimize the raw materials furnish management, and simultaneously to improve tissue paper performance. Softness, strength, and absorption are the key tissue properties that enhance the attention of both industry and consumers. Fiber morphology, fiber modification process steps, and structural properties affect these functional properties, and, therefore, the efforts to evaluate them and establish the relationship or models that describe them constitute a multifactorial challenge. For this purpose, we aimed to investigate the trade-off between the input variables (morphological, suspension, and structural properties) and the final properties. Key variables like the type of furnish raw materials, including the fiber mixture, mechanical and enzymatic treatments, additives incorporation, and the type of industrial base tissue papers were taken under consideration. To achieve these relationships, we used different data-driven modeling approaches including multiple linear regression (MLR), artificial neural networks (ANN), and a 3D fiber-based simulator. The MLR and ANN models were built by data collected from an experimental design, and isotropic laboratory structures were prepared and tested for changes in structural and functional properties. Moreover, a 3D fiber-based simulator was used to investigate the influence of fibers on structural properties. These results indicated that the realistic predictions enabled us to link fiber and tissue structure characteristics. In conclusion, this work has revealed that this computational modeling approach can be used to model the effect of fiber pulps parameters with final end-use tissue properties, allowing to design innovative tissue products.

Keywords

3D Fiber-based Simulator; Artificial Neural Network; Multiple Linear Regression; Tissue Functional Properties; Tissue Paper Materials

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III.3.3.2. Introduction

The identification of challenges and improvements in the field of material computer science, in particular its applications to structured materials, such as the case of tissue papers, constitutes the motivation for this work. The need within this industry for methods for the rational analysis of the fiber materials behavior has been emphasized, and meaningful work has been done in the modeling of fiber materials. The morphology of fiber-based materials has a deep impact on their functional properties, therefore detailed structural and morphological investigations are needed (Gaiselmann et al., 2012). The analysis of the fiber properties with an impact on the tissue properties is complex since it presents a series of dependencies between them. Not only the raw material but also the conditions of the overall process determine the suitability of the fibers to produce tissue products. Moreover, the tissue's final end-use properties are dependent on the final application. All these tissue properties are fundamental to obtain a product of high quality. The main limitation in the prediction of tissue paper properties is the absence of mathematical descriptors to describe the trade-off between fiber features and materials properties. The possibility of having computational tools with predictive capacity for these properties would be essential to define which are the key pulp fiber parameters that influence the type of tissue paper desired (Kerekes, McDonald and Zhao, 2020; Wange et al., 2019; Jacobs et al., 2020; Yao, Shao and Feng, 2020).

With the development of several computer-based papermaking simulations, the impact of fiber characteristics on paper properties has been a focus of research interest (Alava and Niskanen, 2006; Conceição et al., 2010; Curto et al., 2011; Lavrykov et al., 2012; Simon, 2020). Computational simulations of paper structures predict and determine the structural and mechanical properties according to the constituent fibers, which are deposited independently and randomly, and the structure of the fibrous architecture (Sampson, 2009; Borodulina, Motamedian and Kulachenko, 2019; Motamedian, Halilovic and Kulachenko. Different computational models of tissue materials predicted a non-linear relationship between sheet basis-weight and thickness, with higher density variation (Dodson, Oba and Sampson, 2001; Bloch, Engin and Sampson, 2019). Furthermore, many investigations have emerged to predict the softness, strength, and absorption properties of tissue products (Gigac et al., 2019; Park et al., 2020; Prinz et al., 2021); however, the different authors have not proposed any mathematical model that relates the fiber morphological properties with these functional properties. Page (1969) proposed a general mathematical equation that assesses the relative bond strength compared to the fiber strength, describing the strength properties of paper sheets with uniform random fiber orientation, such as tensile index (T), as follows:

$$\frac{1}{T} = \frac{9}{8 \cdot Z} + \frac{12 \cdot g \cdot C}{P \cdot l \cdot b \cdot RBA} \quad (\text{III.7})$$

where the contribution of fibers is described by the zero-span tensile index (Z), and the contribution of bonding is merged into a gravitational constant (g), fiber coarseness (C), fiber perimeter (P), fiber length (l), fiber-fiber bond strength (b), and relative bonded area (RBA). At a low level of bonding (low Page RBA), bonding is the controlling factor for strength, as is the case of tissue paper materials. Therefore, when fiber strength is higher than bond strength, the assumption approaches the value where fibers do not fracture ($g/8Z = 0$) (Pawlak, 2021). However, some of these parameters are difficult to determine due to the complexity of analyzing highly nonlinear problems. For this reason, over the years, data-driven models have been considered alternatives to forecast and optimize advanced processes. Examples of these modeling methods are multiple linear regressions (MLR) and artificial neural networks (ANN).

MLR model's application has demonstrated great benefit in the pulp and paper industry. Risén, Hultén, and Paulsson (2004) reported that network strength is influenced by fiber length, lignin content, specific surface area, and total charge, for a given pulp. Another approach proposed by Chagaev and Zou (2007) proved that strength development during mechanical pulp refining can be monitored through indexes based on the fine content/ coarse fibers ratio, considering pulp quality and fiber development. The relationship between the fiber pulps' morphological and chemical characteristics and the paper's structural and mechanical properties has been constantly investigated using these mathematical models, concluding that the quantitative assessment of different types of fibers for paper applications is effective through theoretical-experimental methods (Carvalho, Ferreira and Figueiredo, 2001; Joutsimo, Wathén and Tamminen, 2005; Neagu, Gamstedt and Berethold, 2006; Pereira, Santos and Anjos, 2016). Similarly, the application of ANN models in the paper industry has been investigated (Scharcanski and Dodson, 1997; Edwards et al., 1999; Nieminen et al., 2011). Ciesielski and Olejnik (2014) proved that an additional ANN approach can be applied in a quality control system in a paper mill, predicting different properties including apparent density, breaking length, tear strength, water retention value (WRV), fine content, and fiber length. Additionally, Almonti et al. (2019) also developed an ANN model to optimize a fiber refining system. It was found that additives' incorporation and process parameters can be optimized through fiber length prediction, in order to obtain detailed properties of the final end-used products (Almonti et al., 2019). Overall, a neural network provides a predictive model, but not a fundamental understanding of the underlying process mechanism that produced the data, which is not superior to the prediction obtained from a well-designed MLR study (Myers, Montgomery and Anderson-Cook, 2016). Neural networks can be a complement to the statistical tools of regression analysis to model the effects of fibers on paper parameters (Monga et al., 2017a, 2017b).

Tissue paper materials are lightweight creped papers used for cleaning, hygiene, and cosmetic purposes, and examples of tissue products include facial papers, toilet papers, towel papers, napkins, diapers, facial masks, among others. The properties required for these materials, such as softness, strength, and absorption, depend on fiber properties and their relationship with the process (de Assis et al., 2018).

The tissue materials production requires several steps that can affect the tissue key properties, such as the selection of raw materials, the method and conditions of pulps used, the refining degrees, the pulp enzyme performance, and the amount of additives added (Morais et al., 2019, 2020a, 2021a, 2021b, 2021c). As the optimization of tissue paper materials requires the use of several computational tools, our approach is to combine experimental and computational planning to model the fibers and establish relationships between fiber and structural properties, process modification steps, and functional tissue properties. To the best of our knowledge, the development of models for tissue paper materials based on the influence of pulp fiber and structure characteristics for different process steps has not been reported in the literature.

The main goal of this work was to present an innovative strategy for computer materials simulation and to identify the main achievements and challenges. The strategy to predict softness, strength, and absorption properties of several process steps, such as fiber furnish, mechanical and enzymatic treatments, and additives incorporation, uses a combination of computational tools, including MLR, ANN, and a 3D fiber-based simulator. The models were built by data collected from fiber morphological, suspension, and paper structural properties. The 3D fiber-based simulator, the *voxelfiber*, was used to model the fibers, obtaining 3D structure computational simulations with the predictive capability of the tissue paper structural properties.

III.3.3.3. Experimental

III.3.3.3.1. Materials

A wide range of samples from our previous works (Morais et al., 2019, 2020a, 2020b, 2020c, 2021a, 2021b, 2021c), and presented in all previous subchapters, was selected for the present study. These samples include eucalyptus pulps and softwood pulps, which were subjected to mechanical and enzymatic treatments. These industrial pulp samples present different cooking and bleaching histories. Nano/ microfibrillated cellulose (MFC/NFC) (Morais et al., 2021b), a biopolymer designed to substitute cationic starch (CBA) (Morais et al., 2021c), and carboxymethylcellulose (CMC) were used as additives. A set of industrial base tissue paper samples were also selected for the studies, using data from ours (subchapter III.2.4) and other previous studies (Vieira et al., 2020). These samples included industrial reels, toilet papers, paper towels, and napkins.

III.3.3.3.2. Methods

The fiber furnishes included different mixtures of eucalyptus fibers and softwood fibers, in different percentages (0-100%). More detailed information about these studies can be found in (Morais et al., 2021 b, c).

Regarding mechanical treatments, different eucalyptus pulps were beaten in a PFI mill at different revolutions, under two refining intensities of 3.33 and 1.67 N/mm. To accomplish the enzymatic processes, eucalyptus fiber pulps were treated, using enzyme dosages between 10 and 100 g per ton of pulp, for 30 and 60 minutes.

The assays were carried out at a consistency of 4%, pH 7, and 40°C, with continuous mechanical agitation using an impeller. More detailed information about these studies can be found in Morais et al. (2021a). Additionally, eucalyptus fiber pulps were also subjected to enzymatic and mechanical combination treatments. In these assays, enzyme doses between 0.25 and 1 kg per ton of pulp were used, from 30 to 120 minutes, with the same process conditions mentioned above. Subsequently, these pulps were beaten in a PFI mill at different revolutions, under a refining intensity of 3.33 N/mm. A pre-refining process followed by enzymatic treatment was also carried out under the same conditions.

The additives incorporation was performed with NMFC, at dosages between 1 to 10 %, a biopolymer, at 2%, and CMC, at 5%, in different fiber furnish formulations consisted of eucalyptus and softwood pulps. More detailed information about these studies can be found in (Morais et al., 2021 b, c).

Each sample was analyzed for morphological properties using MorFi Fiber Analyzer (TECHPAP, Grenoble, France). The morphological characteristics evaluated were fiber length weighted by length, fiber width, coarseness, kinks, curls, and fine elements.

Additionally, the drainability suspension properties of each sample were also measured according to the Schopper-Riegler degree (°SR) method (ISO 5267/1).

Isotropic laboratory structures of 20 g/m² were prepared without pressing, according to an adaptation of ISO 5269-1. These structures were air-dried under atmospheric conditions, preconditioned at (23±1)°C at a relative humidity of (50±2) %, and evaluated for structural properties, such as bulk (ISO 12625-3), and porosity, according to the equation: Porosity = 1 – (density of the sheet/ density of cellulose), and functional tissue properties, such as softness HF (calculated considering softness, smoothness and stiffness parameters with basis weight and thickness) and softness TS7 (superficial softness influenced by the presence of fibers in the Z-direction on paper) using Tissue Softness Analyzer (TSA Emtec) equipment, tensile index (ISO 12625-4), water absorption capacity (ISO 12625-8 adaptation), and capillary rise (ISO 8787 adaptation). The range of values for morphological, suspension, structural and functional tissue properties, for the furnish process and industrial base tissue papers, can be found in Table III.37.

Table III.37. Range of values for morphological, suspension, structural, and functional tissue properties, for furnish process that included fiber mixture, mechanical and enzymatic treatments, and additives incorporation, and industrial base tissue papers.

		L*, mm	W*, µm	C*, mg/100m	K*, %	Curl, %	F*, %	°SR	Bulk, cm³/g	Porosity, %	HF	TS7	TI*, Nm/g	WAC*, g/g	CR*, mm
Furnish (n=114)	Min.	0.529	18.0	5.46	17.5	5.6	23.7	12	3.46	80.67	-97.5	10.9	2.0	5.16	27
	Máx.	1.852	30.9	19.66	55.5	14.4	61.3	82	8.04	92.00	86.9	107.9	52.3	9.54	132
	Av.	0.848	20.1	8.04	38.5	9.4	38.2	26	5.00	86.26	59.0	25.0	16.1	7.47	104
	STDV	0.260	3.1	3.03	8.9	2.0	5.9	9	0.92	2.39	29.4	15.7	10.1	0.97	20
Industrial base Tissue Papers (n=23)	Min.	0.732	19.3	7.14	39.8	9.0	78.8	-	5.3	87	54.20	12.10	3.3	6.9	-
	Máx.	0.930	25.9	55.03	130.8	12.1	43.7	-	17.1	96	75.50	27.90	15.5	12.7	-
	Av.	0.807	20.7	14.11	54.5	10.5	57.8	-	8.6	92	69.04	19.36	9.1	8.8	-
	STDV	0.057	2.0	14.75	24.3	0.85	16.2	-	3.3	2	5.60	3.34	3.1	1.5	-

* Properties: L – Length weighted by length; W – Width; C – Coarseness; K – Kinks; F – fines elements; TI – Tensile index; WAC – water absorption capacity; CR – Capillary Rise.

III.3.3.4. Computational Modeling

III.3.3.4.1. Multiple Linear Regression (MLR)

MLR modeling was used to predict the functional tissue properties of structures made from furnish process and industrial base tissue papers. Statistical software IBM SPSS Statistics 25 (Armonk, NY, USA) was used for MLR analysis. Tissue properties of softness HF, softness TS7, tensile index, water absorption capacity, and capillary rise were used as dependent variables (output variables, Y), and the morphological, suspension, and structural properties as independent variables (input variables, X), as shown in Table III.38. Additionally, the backward elimination procedure was used to build the models, since this method rejects statistically insignificant terms in the model. Only statistically significant linear regression equations (ANOVA, p -value ≤ 0.5 %) were reported.

Table III.38. Dependent and independent variables used for MLR analysis.

Dependent Variables (Outputs)	
Y ₁	Softness HF
Y ₂	Softness TS7
Y ₃	Tensile Index (Nm/g)
Y ₄	Water Absorption Capacity (g/g)
Y ₅	Capillary Rise (mm at 10 minutes)
Independent Variables (Inputs)	
X ₁	Length weighted by length (mm)
X ₂	Width (μm)
X ₃	Coarseness (mg/100m)
X ₄	Kinks (%)
X ₅	Curl (%)
X ₆	Fines content (% in length)
X ₇	Schopper-Riegler degree (°SR)
X ₈	Bulk (cm ³ /g)
X ₉	Porosity (%)

Through a collection of statistical techniques, MLR allows building different empirical models needed in response surface methodology. In general, these models fit a linear equation to the experimental data, relating different independent variables with a dependent variable. Considering a set of n independent variables, namely $x_1, x_2, \dots, x_n$, associated with a value of the dependent variable y , the linear regression model that describes this relationship is seen as follow:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_n x_n + \varepsilon \quad (\text{III.8})$$

Where the regression coefficients are the parameters $\beta_j, j = 0, 1, \dots, n$, and ε is a random error. In the n -dimensional space of the regressor variables (x_j), a hyperplane is described.

When all the remaining independent variables x_i ($i \neq j$) are kept constant, the estimated change in response y per unit change in x_j is represented by the parameter β_j (Myers, Montgomery and Anderson-Cook, 2016).

III.3.3.4.2. Artificial Neural Networks (ANN)

Statistical software IBM SPSS Statistics 25 (Armonk, NY, USA) was used for the configuration of the ANN models. The data of dependent variables considered (softness HF, softness TS7, tensile index, water absorption capacity, and capillary rise) were randomly divided into training (approximately 70%) and test (approximately 30%) sets. Morphological, suspension and structural properties were used as input variables and functional tissue properties as output variables in the models.

Overall, in order to approximate the output data, ANN models perform a non-linear transformation of the input data. This modeling learns from examples of experimental data and exhibits some generalizability beyond the training data. A multilayer feedforward artificial neural network is the most commonly used ANN. Each variable in a layer, the so-called nodes, involves the input layer, which are the original predictors, the hidden layer, composed of a set of constructed variables, and the output layer, consisting of the responses. Additionally, an activation or transfer function achieves the output value of each node. This function can be presented as a sigmoid, a hyperbolic tangent, or an exponential (Myers, Montgomery and Anderson-Cook, 2016). Each of the n hidden layer nodes, a_u can be a linear combination of the input variables, as follow:

$$a_u = \sum_{j=1}^p w_{1ju} x_j + \theta_u \quad (\text{III.9})$$

where the w_{1ju} are unknown parameters that must be estimated (weights), and θ_u is a parameter that plays the role of an intercept in linear regression (bias node) (Myers, Montgomery and Anderson-Cook, 2016).

III.3.3.4.3. 3D Fiber-based Modeling Simulation

A 3D fiber-based simulator, the *voxelfiber*, developed, implemented, and validated by Conceição et al. (2010) and Curto et al. (2011), was adapted and used to simulate different tissue structures with the fiber dimensions obtained experimentally. The simulator is based on a cellular automata, in which there is a cell Cartesian division, making each fiber represented as a sequence of voxels, where each one occupies a pre-established volume (Curto et al., 2011). This is open-source software, and the code is available at <https://github.com/eduardotrincaoconceicao/voxelfiber>. In general, this simulator allowed the modeling of tissue structures as planar random networks, through the fiber dimensions and properties, such as length/width ratio, fiber flexibility, fiber wall thickness, lumen thickness, and resolution (Morais et al., 2020b, 2020c), as shown in Figure III.84.

The models proposed to predict the functional tissue properties were validated through the structural properties results of 3D computational modeled structures with this simulator. These computational studies were carried out using Matlab® (R 2020a, 9.8.0.1323502, MathWorks, Natick, MA, USA).

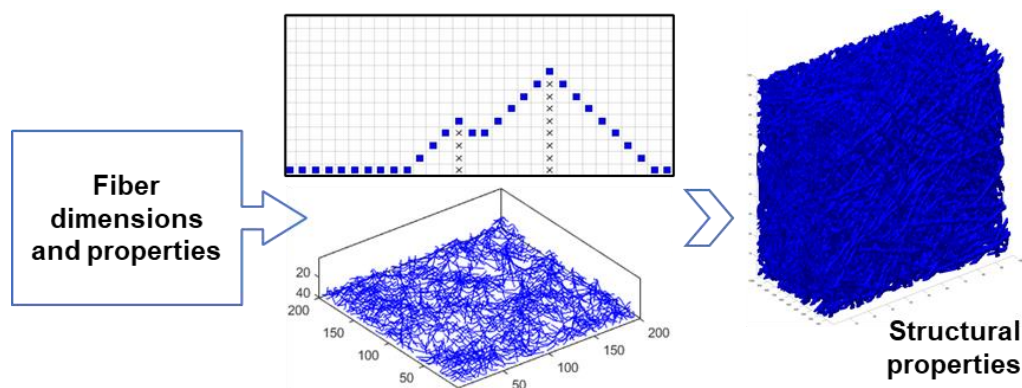


Figure III.84. Schematic diagram of the 3D modeling of tissue structures using the 3D fiber-based simulator. The fibers, modeled with different dimensions and properties, are randomly deposited in the 3D matrix. The fiber deposition model is achieved using a cellular automata mechanism since the space occupied by other fibers is not overlapped. The 3D computational tissue structures are assembly using the 3D fiber models that better describe the population of fibers.

III.3.3.5. Results and Discussion

III.3.3.5.1. Multiple Linear Regression (MLR) Analysis between Morphological, Suspension, and Structural Properties and Functional Properties of Tissue Furnish and Papers

An MLR was run to predict softness HF, softness TS7, tensile index, absorption capacity, and capillary rise properties from different morphological, suspension, and structural properties, for tissue furnish process and industrial base tissue papers. All variables added statistically significantly to the prediction, $p < 0.05$. The higher the multiple coefficients of determination (R^2) value, the better the models fit the data. The adjusted multiple coefficients of determination (adjusted R^2) explain how much variance in the results would be considered if the model had been derived from the samples, the population used to create the model. The higher the value, the better the adjustment data.

III.3.3.5.1.1. Tissue Furnish Process

Our experimental studies of the tissue furnish process were composed of a mixture of eucalyptus and softwood fiber pulps, fibers subjected to refining and enzymatic treatments, and additives incorporation, and their key fiber properties can influence the tissue's functional properties. Therefore, the mathematical models developed can predict the softness, strength, and absorption properties of isotropic laboratory structures of 20 g/m², based on the fiber and structure modification furnish processes.

The MLR analysis showed that the width, curl, °SR, and porosity variables statistically significantly predicted softness HF, $F(4, 109) = 89.677, p < 0.005, R^2 = 0.767$, adjusted $R^2 = 0.758$. The most significant MLR model developed between these variables is:

$$Y_1 = -31.616 - 2.708 X_2 + 2.376 X_5 - 2.365 X_7 + 2.134 X_9 \quad (\text{III.10})$$

Additionally, the same variables (width, curl, °SR, and porosity) statistically significantly predicted softness TS7, $F(4, 109) = 94.428, p < 0.005, R^2 = 0.776$, adjusted $R^2 = 0.768$. The most significant MLR model developed between these variables is:

$$Y_2 = 83.955 + 1.459 X_2 - 1.199 X_5 + 1.261 X_7 - 1.272 X_9 \quad (\text{III.11})$$

The softness of tissue paper sheets is achieved with the use of curly fibers, obtaining structures with higher porosity (or bulk) in which the bonding strength and bonding area among the fibers are not fully developed. Furthermore, the degree of refining expressed in °SR, influences this fiber bonding capacity (de Assis et al., 2018).

The MLR models also reveal that the key factors which affect tensile index are all independent variables except the curl, $F(8, 105) = 47.255, p < 0.005, R^2 = 0.783$, adjusted $R^2 = 0.766$. The most significant MLR model developed between these variables is:

$$Y_3 = -92.882 + 11.860 X_1 - 1.402 X_2 + 1.317 X_3 - 0.404 X_4 - 0.273 X_6 \\ + 0.764 X_7 - 6.543 X_8 + 1.802 X_9 \quad (\text{III.12})$$

The strength of sheets is promoted by long fibers that present a higher capacity to form bonds with multiple fibers (de Assis et al., 2018). Coarseness is related to the fiber wall thickness, diameter, and density. Therefore, strengths are improved with the conformation/collapse degree of the fibers, and consequently, with the amount of fiber bonding. Fibers with higher diameter and smaller thickness collapse more easily, resulting in denser structures, with less bulk and improved strength. To develop this property, enzymatic treatment and/or refining processes are used, which subsequently improve the sheet formation and fiber drainability (°SR), with fine element formation (Gigac and Fišerova, 2008). On the other hand, fibers with a higher kink index negatively influence tensile strength (Page et al., 1965).

The MLR analysis showed that the width, kinks, curl, °SR, bulk, and porosity variables statistically significantly predicted water absorption capacity, $F(6, 107) = 25.227, p < 0.005, R^2 = 0.586$, adjusted $R^2 = 0.563$. The most significant MLR model developed between these variables is:

$$Y_4 = 28.473 - 0.067 X_2 - 0.057 X_4 + 0.316 X_5 - 0.047 X_7 \\ + 1.125 X_8 - 0.288 X_9 \quad (\text{III.13})$$

Finally, the coarseness, curl, °SR, and bulk variables statistically significantly predicted capillary rise, $F(4, 109) = 49.364, p < 0.005, R^2 = 0.644, \text{adjusted } R^2 = 0.631$. The most significant MLR model developed between these variables is:

$$Y_5 = 139.284 - 2.044 X_2 - 1.841 X_5 - 1.500 X_7 + 7.427 X_8 \quad (\text{III.14})$$

The coarse, curly, and kinked fibers enhanced the formation of bulkier, porous, and absorbent sheets. The fiber and structure modification processes influence the drainability, promoting efficient fiber fibrillation and, consequently, a higher availability and accessibility for establishing water bonding and, consequently, a higher water retention capacity.

In general, the fiber deformations (curl and kinks), °SR, and the structural properties of bulk and porosity were the dominating factors that influence all the tissue functional properties for the tissue furnish process.

III.3.3.5.1.2. Industrial base Tissue Papers

The quality requirements of tissue papers differ according to their purpose and consumer expectations, and the creping and converting processes are conveyed to the final consumer since these operations are encoded in the final tissue structure (Raunio and Ritala, 2012; de Assis et al., 2018; Spina and Covalcante, 2018).

The MLR analysis between softness HF and morphological, suspension and structural properties of industrial base tissue papers have shown non-significant correlation, and no regression model could be suggested. However, the length weighted by length, kinks, bulk, and porosity variables statistically significantly predicted softness TS7, $F(4, 18) = 3.304, p < 0.005, R^2 = 0.423, \text{adjusted } R^2 = 0.295$. The most significant MLR model developed between these variables is:

$$Y_2 = -161.562 + 24.248 X_1 - 0.050 X_4 - 1.487 X_8 + 1.929 X_9 \quad (\text{III.15})$$

This evidence can be explained by the different process operations used to produce each industrial base tissue paper. The creping process improves the product's softness, bulk, absorption, and stretch. During this process, the doctor blade scrapes the sheet off from the Yankee dryer surface, consisting of the formation of macro and micro wrinkled on the paper web. Creping delaminates the fiber network and changes the fibers from machine direction to Z-direction, resulting in a breaking of inter-fiber bonding, and consequently, a higher softness and elongation capacity. Therefore, these changes that occur in each tissue paper depend on the process conditions used, which can be different in each situation, since the creping process is influenced by the sheet adhesion to the Yankee, the blade geometry, and the difference between the Yankee and the paper reel speed (de Assis et al., 2018; Raunio and Ritala, 2012).

The MLR models also reveal that the key factors which affect tensile index are curl, bulk, and porosity, $F(3, 19) = 15.331$, $p < 0.005$, $R^2 = 0.708$, adjusted $R^2 = 0.661$. The most significant MLR model developed between these variables is:

$$Y_3 = -79.336 - 1.804 X_5 - 1.222 X_8 + 1.287 X_9 \quad (\text{III.16})$$

As reported above, collapsed fibers with less bulk, porosity, and curl, enhanced the tensile strength properties. The creping process also contributes to the tissue paper's mechanical properties, since it promotes elongation. These mechanical properties can also be influenced by raw materials, stock preparation, sheet formation, pressing, humidity content, and paper adhesion on the Yankee cylinder, and be developed by optimizing fiber modification processes and changing furnish stocks (de Assis et al., 2018; Page et al., 1965).

The MLR analysis showed that only bulk variable statistically significantly predicted water absorption capacity, $F(1, 21) = 109.580$, $p < 0.005$, $R^2 = 0.839$, adjusted $R^2 = 0.832$. The most significant MLR model developed between these variables is:

$$Y_4 = 5.107 + 0.426 X_8 \quad (\text{III.17})$$

The creping and converting operations influence absorbency properties, enhancing a bulkier structure. The converting operations, including embossing, are performed on base tissue paper sheets to form a single layer or multilayer finished product. Embossing patterns are applied to tissue materials to improve bulk, and consequently, absorption (Spina et al., 2018; Morais et al., 2021d).

The MLR analysis was unable to predict any model with significance for the capillary rise properties due to the data absence. In general, the fiber deformations and structural properties were the dominating factors that influence all the tissue functional properties for industrial base tissue papers, with creping and converting operations.

III.3.3.5.2. Artificial Neural Network (ANN) Analysis between Morphological, Suspension and Structural Properties and Functional Properties of Tissue Furnish and Papers

The ANN models were built by specifying the minimum (1) and maximum (50) number of units accepted in the hidden layer by default. ANN's automatic architecture selection procedure identified the best prediction of the number of units in this layer through the hyperbolic tangent function, and in the output layer through the identity function. Morphological, suspension, and structural properties are represented as “covariates”, the predictor variables. The network training was improved with the choice of the standardized method for the covariates rescaling, since the batch training method minimizes the total error directly, on “smaller” datasets. Additionally, the stopping criteria of the network training allowed for a maximum step if the error was not further reduced. The ANN models accurately replicated the results using the same initialization value for the random number generator, the same order of data and variables, and the same procedural settings. The results of the ANN architecture analysis can be found in Tables III.39 and III.40.

The model summary of Table III.41 presents the results of the ANN training and testing for tissue furnish and papers. The relative error of each scale-dependent variable is associated to the sum-of-squares, where the predicted value for each case is the average value of the dependent variable. This relative error is defined as the error of the sum-of-squares of the dependent variable divided by the error of the sum-of-squares of the “null” model.

Table III.39. The architecture of ANN model for the tissue furnish process.

		Hidden Layer 1						Output Layer				
		H(1:1)	H(1:2)	H(1:3)	H(1:4)	H(1:5)	H(1:6)	Softness HF	Softness TS7	Tensile Index	Water Absorption Capacity	Capillary Rise
Input Layer	Bias	-0.669	-0.754	0.397	-0.457	1.495	0.835					
	Length	0.220	0.097	-0.328	0.584	-0.897	-0.001					
	Width	0.548	0.297	-0.767	0.699	0.673	-0.317					
	Coarseness	-0.034	-0.137	-0.974	0.525	-0.011	0.064					
	Kinks	0.383	-0.322	-0.175	-0.932	0.688	-0.520					
	Curl	0.428	-0.556	0.347	-0.570	0.431	0.609					
	Fines	0.824	-0.375	0.094	-0.237	0.685	-0.175					
	°SR	0.067	0.333	-0.237	0.271	0.172	0.797					
	Bulk	-0.760	-0.006	0.219	0.923	0.781	-0.606					
Porosity	-1.204	-0.177	-0.146	0.074	-0.017	0.588						
Hidden Layer 1	Bias							-0.385	0.469	0.419	-0.320	0.141
	H(1:1)							-0.171	0.187	0.024	0.126	-0.534
	H(1:2)							-2.574	2.552	1.305	-1.209	-0.773
	H(1:3)							0.531	-0.553	-0.883	1.177	0.959
	H(1:4)							0.471	-0.462	-0.440	1.182	0.091
	H(1:5)							-1.549	1.505	-0.038	0.027	-0.689
	H(1:6)							-9.325E-5	-0.056	1.016	-1.084	-1.296

Table III.40. The architecture of ANN model for the industrial base tissue papers.

		Hidden Layer 1			Output Layer			
		H(1:1)	H(1:2)	H(1:3)	Softness HF	Softness TS7	Tensile Index	Water Absorption Capacity
Input Layer	Bias	-1.415	0.215	-0.129				
	Length	0.783	-0.100	0.365				
	Width	0.233	-0.614	0.346				
	Coarseness	0.891	-0.799	0.549				
	Kinks	-0.393	0.615	-0.329				
	Curl	-1.111	0.250	0.309				
	Bulk	-0.811	-0.459	-0.130				
	Porosity	-0.032	-0.263	-0.797				
Hidden Layer 1	Bias				-0.489	0.726	0.540	0.076
	H(1:1)				-0.630	1.176	1.186	-0.570
	H(1:2)				0.310	-0.144	0.418	-1.172
	H(1:3)				-0.634	-0.574	-0.529	-0.123

Table III.41. Model summary of the ANN training and testing for all tissue process steps.

		Softness HF	Softness TS7	Tensile Index	Water Absorption Capacity	Capillary Rise
Tissue Furnish Process						
Training	Sum of Square Error	31.789	31.789	31.789	31.789	31.789
	Relative Error	0.097	0.089	0.160	0.261	0.179
Testing	Sum of Square Error	29.868	29.868	29.868	29.868	29.868
	Relative Error	0.174	0.158	0.391	0.428	0.332
Industrial base Tissue Papers						
Training	Sum of Square Error	12.055	12.055	12.055	12.055	-
	Relative Error	0.616	0.377	0.227	0.198	-
Testing	Sum of Square Error	9.904	9.904	9.904	9.904	-
	Relative Error	0.637	0.897	0.573	0.216	-

III.3.3.5.2.1. Tissue Furnish Process

The maximum relative error of all dependent variables (tissue functional properties) was 0.261 and the average relative error was 0.157, for the ANN training model of fiber furnish. Regarding the ANN testing model, the maximum relative error was 0.428 and the average relative error is 0.306 (Table III.41). From the architectural point of view, there was a total of 9 independent variables in the input layer, 6 neurons in the hidden layer, and 5 dependent variables in the output layer (Table III.39). Figure III.85 shows this architecture of the ANN model for tissue furnish.

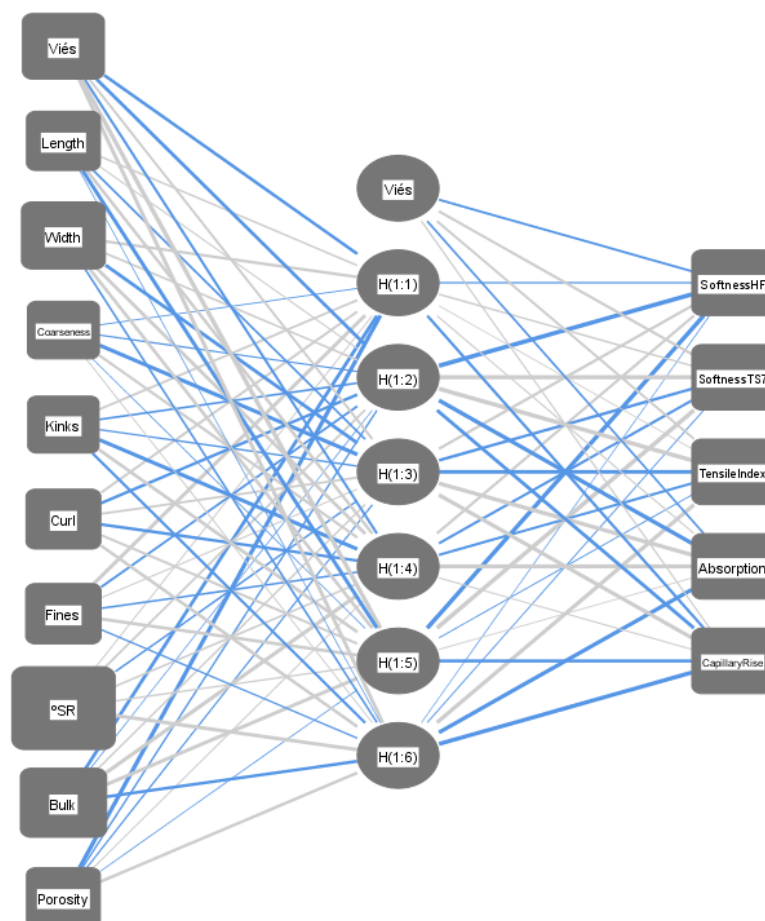


Figure III.85. The architecture of ANN model for the tissue furnish process, in which the hidden layer activation function was a hyperbolic tangent, and output layer activation function was identity. The grey lines represent synaptic weight > 0 and the blue lines represent synaptic weight < 0 .

Figure III.86 presents the relationship between the experimental values and predicted values for the ANN model of tissue furnish. The results indicated that the neural network prediction was very close to the measured values. The accuracy of the prediction models for functional properties was proved by the correlation coefficient values. As R^2 approaches 1, prediction accuracy increases. The developed model includes a coefficient of determination of 0.880 for softness HF, 0.891 for softness TS7, 0.779 for tensile index, 0.680 for water absorption capacity, and 0.769 for capillary rise. These results found a good linear correlation between the measured and predicted values. Compared to MLR models, ANN models were better suited to predict softness and absorption properties, and these models were in the same range to predict strength properties. This suggested that the ANN results also complement the MLR analysis results.

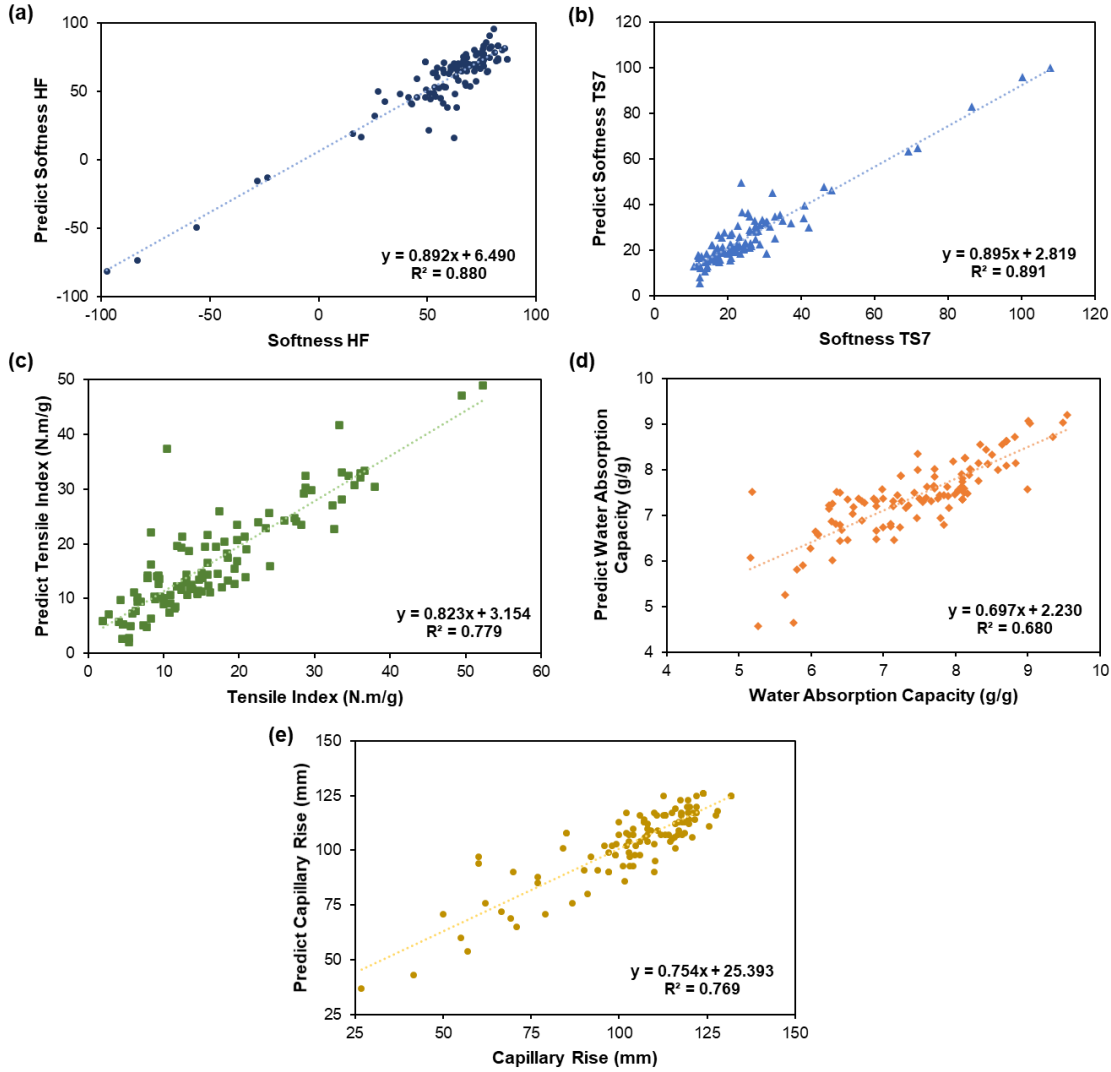


Figure III.86. Predict values as a function of experimental values of (a) softness HF, (b) softness TS7, (c) tensile index, (d) water absorption capacity, and (e) capillary rise, using ANN models for tissue furnish process.

Figure III.87 presents the importance and normalized importance of each independent variable to determine the ANN model, based on the training and testing samples. The importance of an independent variable is quantified by changing the different values of the independent variable achieved by the ANN's model-predicted value. Furthermore, the normalized importance, expressed in percentages, is the ratio between the obtained importance values and the maximum importance values. However, these results do not identify the relationship between the independent variables and the predicted probability of default. This is why predictions from ANN models are complementary to well-designed MLR studies, despite the neural network's most noticeable limitations. For the tissue furnish process, the results revealed that °SR, bulk, and width contribute most to the ANN model construction. Comparing both statistical models, °SR and structural properties are essential for the development of mathematical models.

The furnish of different fibrous compositions, enzymatic and mechanical treatments, and additives incorporation modified the fiber refining degree, expressed in °SR, and consequently the structure' bulk. Hence, these characteristics influenced the tissue functional properties.

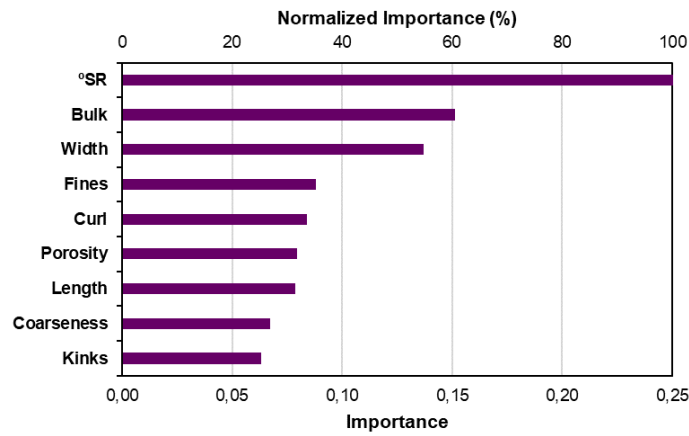


Figure III.87. Quantitative assessment of the importance of independent variables on the tissue furnish process, using an ANN model.

III.3.3.5.2.2. Industrial base Tissue Papers

The maximum relative error of all dependent variables was 0.616 and the average relative error was 0.355, for the ANN training model of industrial base tissue papers. Regarding the ANN testing model, the maximum relative error was 0.897 and the average relative error was 0.573 (Table III.41). From the architectural point of view, there was a total of 7 independent variables in the input layer, 3 neurons in the hidden layer, and 4 dependent variables in the output layer (Table III.40 and Figure III.88).

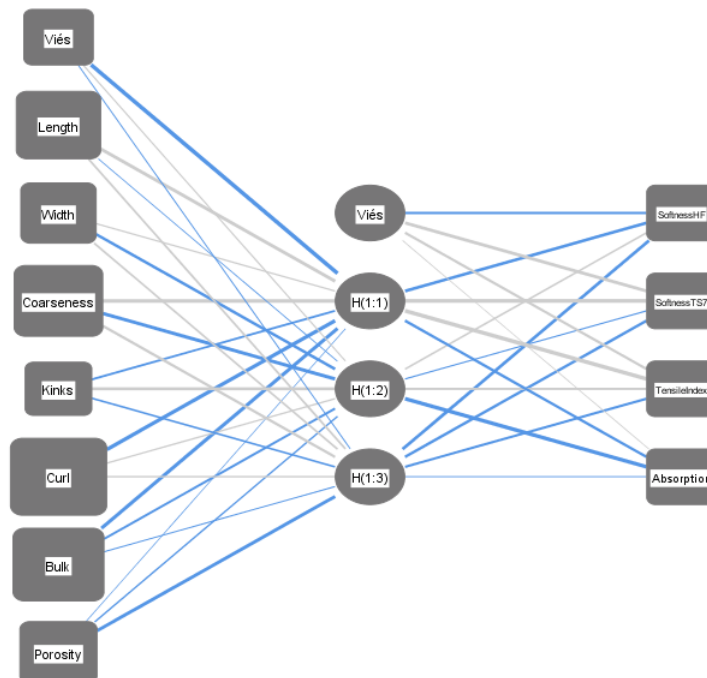


Figure III.88. The architecture of ANN model for the industrial base tissue papers, in which the hidden layer activation function was a hyperbolic tangent, and output layer activation function was identity. The grey lines represent synaptic weight > 0 and the blue lines represent synaptic weight < 0.

Figure III.89 presented the relationship between the experimental values and predicted values for tissue functional properties. Results indicated that the neural network prediction is very close to the measured values for tensile index and water absorption capacity, while for softness HF and softness TS7 it was not verified. Moreover, this analysis could not develop a model for capillary rise properties, as observed for MRL models. Regression analysis presented a coefficient of determination of 0.431 for softness HF, 0.517 for softness TS7, 0.743 for tensile index, and 0.807 for water absorption capacity. As mentioned above, the MLR analysis was unable to predict any model with significance for the softness HF properties, and the R² obtained with the ANN models was also very low. The same trend has also occurred for softness TS7. Additionally, both MLR and ANN models showed a good forecast accuracy to predict the tensile index and water absorption capacity. These results suggest that it was not possible to find any statistically accurate model to predict the softness properties for industrial base tissue papers. Additionally, the results also explained the importance of curl, bulk, coarseness, length, porosity, and width in tissue functional properties of industrial base tissue papers (Figure III.90). The structural properties were the key independent variables to develop the MLR and ANN models. The creping and converting processes improve bulk and porosity properties, which influence tissue functional properties.

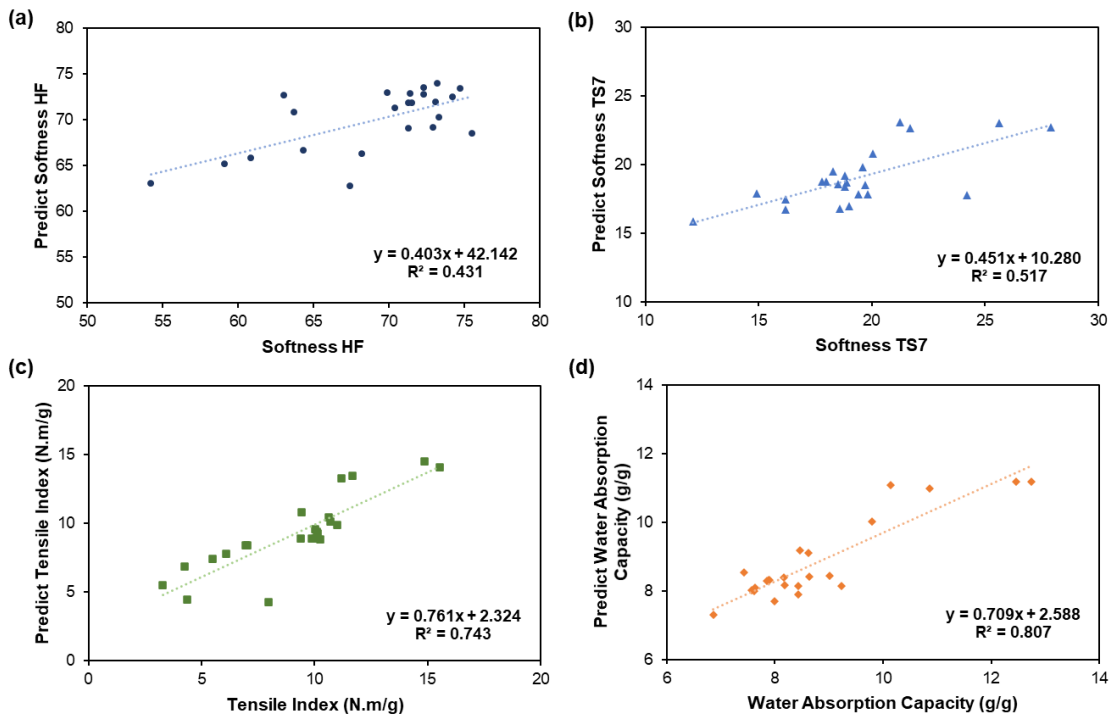


Figure III.89. Predict values as a function of experimental values of (a) softness HF, (b) softness TS7, (c) tensile index, and (d) water absorption capacity, using ANN models for industrial base tissue papers.

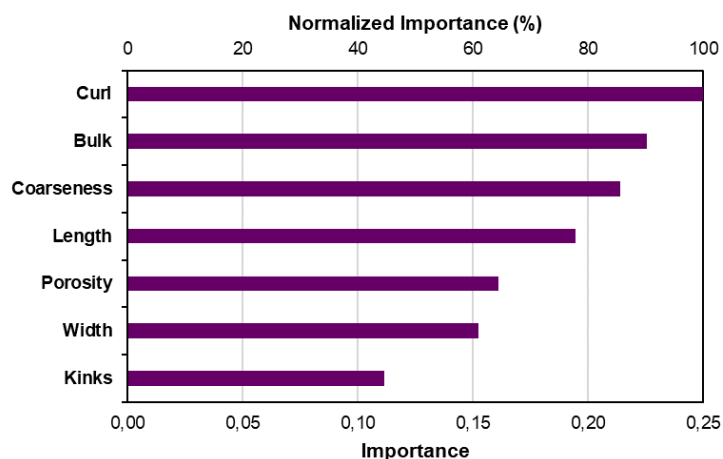


Figure III.90. Quantitative assessment of the importance of independent variables on the industrial base tissue papers, using an ANN model.

III.3.3.5.3. Validation of Models using Experimental and 3D Fiber-based Modeling Simulation Approaches

The regression models of the relationship between softness HF, softness TS7, tensile index, water absorption capacity, and capillary rise (dependent variables) and morphological, suspension, and structural properties (independent variables) were validated using experimental and computational data. We presented an example of the tissue furnish process and industrial base tissue paper models' validation. For this purpose, we selected a bleached eucalyptus kraft pulp, a biopolymer as additives, and an industrial base tissue paper for these studies. Note that these samples were not used to build the models. Additionally, the eucalyptus pulp was beaten in a PFI mill at 500, 1000, and 1500 revolutions under a refining intensity of 3.33 N/mm. The morphological properties of pulp fibers were determined using the MorFi Analyzer. To evaluate the impact of different fibers on paper properties, isotropic laboratory structures of 20 g/m² were prepared and tested regarding structural and tissue functional properties (ISO standards).

Using the 3D fiber-based simulator, it was possible to model the fibers individually, resulting in the 3D tissue computational structure. This approach is important to investigate the relationship between fibers and structures formed by them, predicting the influence of these fibers on the design of innovative tissue products and furnish optimization, saving laboratory and industrial resources (Morais et al., 2020b, 2020c). For example, a comparison of the simulated and experimental structures was performed to validate the predictive character of the structural properties of tissue papers (Table III.42). The pulp fibers have been beaten in four beating levels (0, 500, 1000, 1500 PFI revolutions), and laboratory structures corresponding to a thickness of 101, 93, 85, and 77 μm , respectively. Following our experimental verification, the fiber flexibility and fiber effective thickness, related to the fiber coarseness, presented a crucial impact on the paper structure (Curto et al., 2011; Morais et al., 2019, 2020a, 2020b, 2020c, 2021a).

A similar impact for the influence of these fiber properties on simulated structures was verified. This 3D fibrous material computational simulator simulates the structure's effective thickness and apparent porosity, among other structural properties. The model proves to adjust to the experimental data. The bulk properties were obtained through the experimental and computational thickness. Through this methodology, it is possible to model the fibers and, consequently, predict the structural properties of tissue structures. Without the need for extensive experimental planning, the simulator evaluates different scenarios of interest quickly and accurately. Structural properties, such as the bulk, obtained indirectly by the computational effective thickness, and the computational apparent porosity, obtained directly from simulation, can be introduced into the mathematical models to predict the functional properties, saving laboratory resources. These results suggested that 3D fiber modeling proved to be an essential tool to investigate the influence of fiber properties on the structural properties of tissue products due to the good estimative of the simulated results with the experimental ones. This innovative approach results in higher speed and flexibility of response, without the need to produce laboratory structures.

Table III.42. Structural properties of the experimental and simulated structures with 20 g/m².

Experimental Data				Computational Data		
PFI Revolutions	Thickness (μm)	Bulk (cm^3/g)	Apparent Porosity (%)	Effective Thickness (μm)	Bulk (cm^3/g)	Apparent Porosity (%)
0	101	4.89	86.37	99	4.81	86.13
500	93	4.61	85.53	94	4.68	85.74
1000	85	4.18	84.03	85	4.19	84.08
1500	77	3.90	82.89	76	3.84	82.06

Posteriorly, the developed models were validated. The percent deviation between experimental and the predicted values of softness HF, softness TS7, tensile index, water absorption capacity, and capillary rise were found to be within the acceptable limits for tissue furnish process and industrial base tissue papers (Figure III.91) MLR models. The predicted data is within the experimental error.

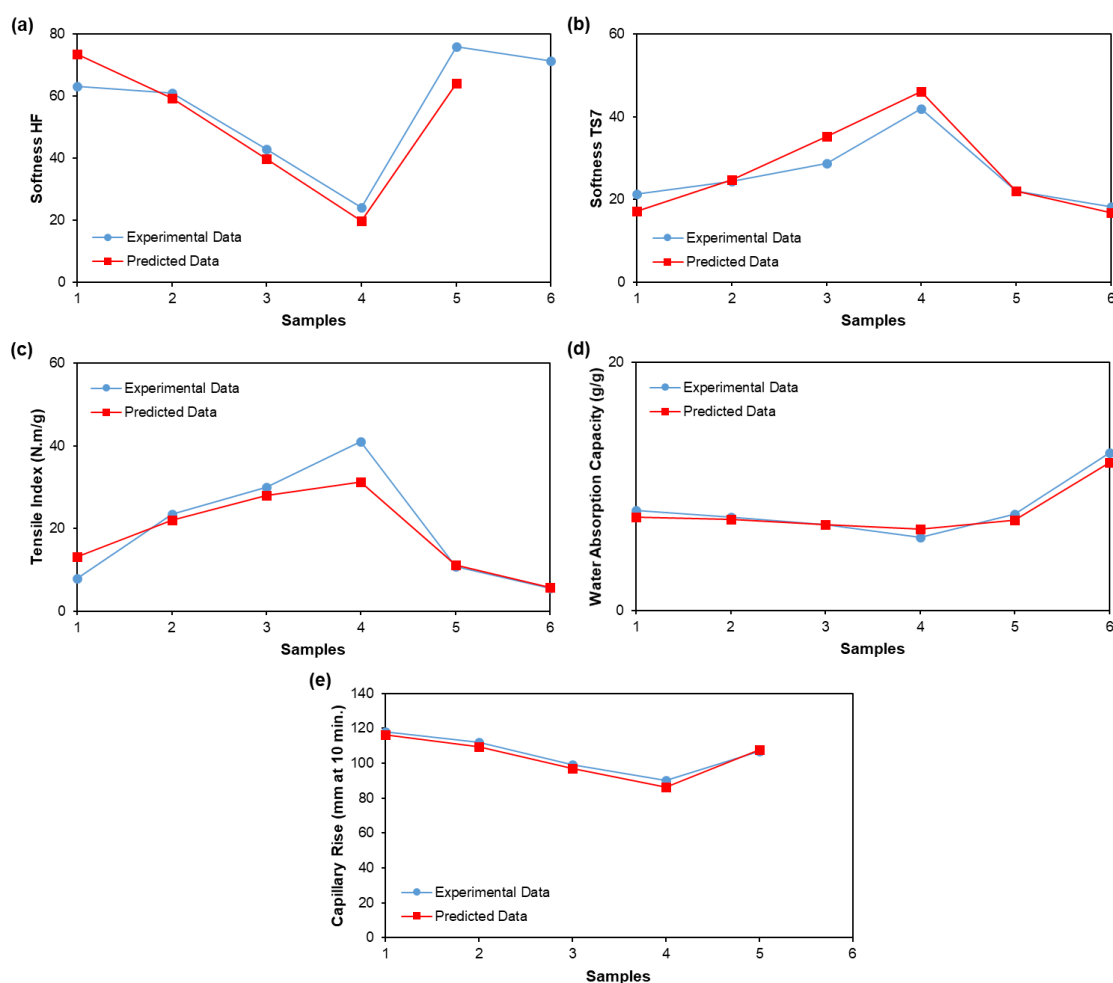


Figure III.90. Relationship between experimental and predicted values for (a) softness HF, (b) softness TS7, (c) tensile index, (d) water absorption capacity, and (e) capillary rise of tissue furnish process and industrial base tissue papers using MLR models. The sample caption is as follows: Sample 1 – eucalyptus kraft pulp with 0 PFI revolutions; Sample 2 – eucalyptus kraft pulp with 500 PFI revolutions; Sample 3 – eucalyptus kraft pulp with 1000 PFI revolutions; Sample 4 – eucalyptus kraft pulp with 1500 PFI revolutions; Sample 5 – eucalyptus kraft pulp with biopolymer incorporation; Sample 6 – industrial base tissue paper.

III.3.3.6. Conclusions

Through the combination of an experimental and computational design, relationships between the variables of fiber and tissue properties were established. The models were essential to obtain predictive capacity, quantifying the changes that occur due to the use of different raw materials and tissue paper production process operations. The development of statistical models allowed the correlation between tissue functional properties and morphological, suspension, and structural characteristics. The simulations were based on a tissue furnish process that included data from fiber mixtures, mechanical and enzymatic treatments, and additives incorporations, and industrial base tissue papers.

The predicted results of the relationship between these dependent and independent variables using MLR and ANN modeling were found to be highly satisfactory in terms of explanatory characteristics and validity of all models, except for softness and capillary rise properties of industrial base tissue papers. Additionally, using 3D fiber modeling to obtain 3D tissue structure computational simulations, it was possible to study the influence of fiber properties on the structural properties of tissue papers. The results indicated that these three approaches can be successfully used to model the effects of key fiber properties, fiber modification process steps, and tissue structural properties on softness, strength, and absorption parameters.

The developed models allow evaluating preliminary decisions regarding the usability of different pulp samples and process steps in which the final end-use tissue properties are important. This computational modeling approach can be used to design innovative tissue products with added value, meeting specific requirements, by changing the pulp fiber morphological characteristics. Furthermore, these methods are important tools to evaluate different scenarios of industrial interest, without the need for extensive experimental planning, contributing to raw-materials furnish management by predicting the associated formulation costs.

III.3.3.7. References

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III.3.4. Development of sustainable cellulose-based tissue materials using an innovative experimental and computational methodology

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III.3.4.1. Abstract

In recent years, the tissue industry has been exposed to several challenges related to the growing demand for high-quality materials and sustainable furnish. An approach that combines experimental and computational planning was implemented and presented in this work. For this purpose, a simulator that establishes relationships between the key fibre properties, the process steps that modify them, and the functional properties, the *SimTissue*, was developed and validated. Different scenarios and a summary of the *SimTissue* research strategy are presented. The experimental planning design consisted of the influence of refining, enzymatic treatment, and incorporation of additives such as micro/ nanofibrillated cellulose and biopolymer. The correlations between these tissue process inputs, and the softness, strength, and absorption properties were established using the *SimTissue*. Overall, the *SimTissue* predicted and optimized several case studies for the management and optimization of sustainable furnish formulations.

Keywords

3D Computational Simulation; Cellulose-based Materials; Furnish Optimization; Tissue Materials.

Inspired from Paper XII:

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III.3.4.2. Introduction

Sustainable cellulose-based fibrous materials, such as tissue papers, are designed for personal hygiene and utility purposes. Examples of tissue papers include toilet papers, towel papers, napkins, facial tissue papers, among others. These materials are recognized for their creped and embossed structures, with low basis weight and high porosity. Their key properties include bulk, softness, strength, and absorption properties, whose contribution and importance differ and depend on the type of final product (de Assis et al., 2018). Significant global growth in this sector is projected into the next decade, also related to the current outbreak of COVID-19. Consumption of tissue materials was estimated to grow by around 55% in Eastern Europe and 45% in Western Europe between 2012-2022 (Tissue World Magazine, 2014). The tissue industry is exposed to several challenges related to the growing demand for sustainable products and furnish, namely the raw materials, process operations steps, and additives incorporation (de Assis et al., 2018). A commitment to sustainable development is necessary to guide process decisions, as well as to search for simultaneous strategies of economic prosperity, environmental responsibility, and social equity (The Navigator Company, 2021). Raw materials, such as cellulose fiber pulp, are the main factor in tissue paper manufacture, accounting for 45% to 59% of the total manufacturing cost (Zambrano Gotera, 2021). Therefore, finding strategies to optimize the use of these raw materials on the final product and offset the cost-effectiveness offers substantial opportunities to drive consumer demand for optimized tissue products with innovative functionality and added value.

Eucalyptus fiber pulps are traditionally used in tissue production because of their ability to provide formation and softness to the materials, while softwood fiber pulps are used to ensure strength and paper machine runnability (de Assis et al., 2018). Eucalyptus fibers present the potential to be optimized to improve their mechanical properties while maintaining existing benefits. A more recent example is the extended impregnation cooking process which has shown the potential to increase tensile strength, reduce refining energy through its physical and chemical properties, increase pulp production yield, with higher product quality, lower consumption of chemical products in cooking, and cost reduction (Tissue World Magazine, 2020). In addition to these strategies in the pulping process development, fiber modification strategies along the process steps have also been extensively investigated in recent years (de Assis et al., 2018; Zambrano Gotera, 2021; Morais et al., 2019, 2020a, 2020b, 2020c, 2021a, 2021b, 2021c). Maximizing the *Eucalyptus globulus* fibers incorporation, and the total or partial replacement of softwood pulps consists of a challenge since the required adjustments represent consequences on the runnability of the paper machine and converting lines. Obtaining tissue products with the best combination of fibers, and maximization of *Eucalyptus globulus* fibers suggests knowledge of the different pulps on the market and the consequences on the finished product properties (Morais et al., 2019, 2020a).

Due to the fibers' properties, such as high coarseness, the eucalyptus fiber's structure can be modified through enzymatic treatment processes (Morais et al., 2021a), refining, and incorporation of additives such as micro/nanofibrillated cellulose (MFC/NFC), and biopolymers (Morais et al., 2021b, 2021c), minimizing the influence on the strength and stiffness properties that the structure needs for the process operations (Ramezani and Nazhad, 2004; Alava and Niskanen, 2006).

This entire tissue furnish optimization process requires extensive research and methodologies to overcome the issues, which involves the design and analysis of laboratory and computational experiences. Computational methods for integrating all important variables for analyzing the behavior and modeling of fiber materials, process modification steps, and functional properties have been increasingly investigated in recent decades (Morais et al., 2020b; Morais et al., 2020c; Alava and Niskanen, 2006; Conceição et al., 2010; Curto et al., 2011; Lavrykov et al., 2012; Raunio and Ritala, 2012; Simon, 2020). Computational tools allow us to significantly reduce experimental work in the development and optimization of new materials, to present a better synergy between experimental tests and simulation of specific properties. The development of advanced computational tools with predictive capability for furnish is a major milestone soon as it allows us to estimate which raw materials are most promising for a particular tissue product and which process operations allow us to obtain tissue with desired and optimized properties (Simon, 2020).

Therefore, an innovative design approach was implemented to create product differentiation. To develop and optimize these premium materials, we designed a simulator that allows us to compare various scenarios of furnish formulations, the *SimTissue*. This simulator establishes relationships between key fiber properties, the fiber modification process steps, and the tissue structural and functional properties. In this work, we present different scenarios and a summary of all the research that is based on the development of *SimTissue* for the management and optimization of sustainable furnish materials, using experimental and computational methodology approaches.

III.3.4.3. Materials and Methods

To implement the computational studies, initially, a characterization of the fiber dimensions in the paper structure was carried out, in the three dimensions, through the development of methodologies using SEM image analysis and advanced computational tools for fiber and structure modeling (Morais et al., 2020b, 2020c). The experimental planning also consisted of the selection and characterization of hardwood and softwood pulp species with different pulping processes of industrial interest, reported in previous subchapters (Morais et al., 2019, 2020a). The effect of fiber modification was also investigated, either by mechanical (refining) process, either by enzymatic treatment, or a combination of both (Morais et al., 2021a), and the incorporation of additives such as MFC/NFC and commercial biopolymer (CBA) (Morais et al., 2021b, 2021c).

All experimental conditions of these fiber and structure modification processes can be found in the previous subchapters and our referenced and cited publications. The properties of bulk (ISO 12625-3), softness (using Tissue Softness Analyzer (TSA, Emtec) equipment), tensile strength index (ISO 12625-4), water absorption capacity (ISO 12625-8 adaptation), and capillary rise (ISO 8787 adaptation) were evaluated on laboratory structures of 20 g/m² (ISO 5269-1 adaptation). This was a proposed methodology to mimic the tissue-based sheets. The relationships between these properties were established, using different innovative computational tools, such as Lasso regression, robust multi-linear regressions (MLR), artificial neural networks (ANN), among others, and using simulation and experimental data, to obtain predictive capacity. Then, the structures were 3D computationally simulated, to calibrate the tissue model and validate its predictive character (Morais et al., 2020b, 2020c, Conceição et al., 2010; Curto et al., 2011). This entire process allowed the computational implementation of the *SimTissue* through the calculation engine algorithm programming, database, and user interface integration, to be used in specific cases to support furnish's industrial management.

III.3.4.4. Results and Discussion

For the *SimTissue* development, a methodology that combines an experimental and computational approach was designed (Figure III.92). *SimTissue* establishes relationships between input variables of fiber properties and output variables of tissue functional properties. Through experimental and computational data, *SimTissue* quantifies the changes that occur due to the use of different pulps and process operations of tissue paper production. The validation of the final end-use properties' prediction was carried out with experimental and simulated structures, to develop this simulator for the fibrous materials and furnish optimization (Morais and Curto 2022). Different furnish scenarios are proposed that include different fiber combinations and the design and optimization of each tissue product. In our previous works, this simulator was also used to obtain predictive capacity for the creping and embossing influence on the softness, strength, and absorption properties of industrial and laboratory structures produced with eucalyptus and softwood fibers (Curto et al., 2021). Therefore, the computational implementation of *SimTissue* also supports industrial furnish management considering structures with creping and converting operations. In the present work, we are presenting only a furnish optimization approach, not considering these operations.

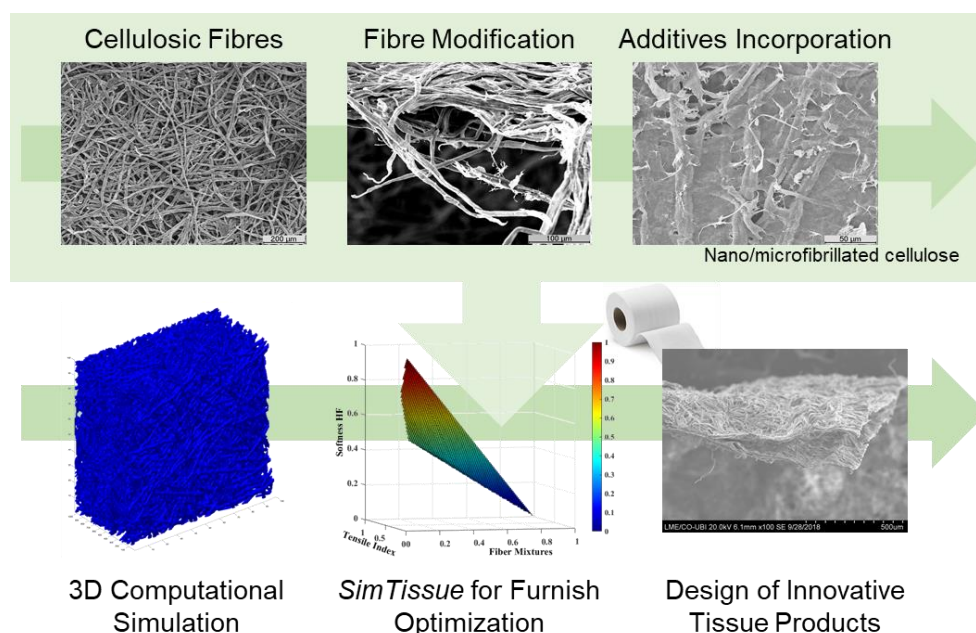


Figure III.92. Outline of the methodology used in this work to develop the *SimTissue* for furnish management and optimization.

The results indicate that *SimTissue* predicts the influence of various types of raw materials used to produce tissue products, process operations, and additives at the micro and nanoscale. An important achievement is the comparison of structures produced with 100% eucalyptus fibers, with different percentages of other fibers, and additives. In this work, we present different comparative scenarios of case studies predicted by *SimTissue* to design new tissue paper formulations, compared to typical industrial formulations (75%HW+25%SW) with typical mill drainability values ($\approx 25^\circ\text{SR}$). These formulations presented a softness of 59.9 HF, a tensile index of 18.5 Nm/g, a water absorption capacity of 7.5 g/g, and a capillary rise of 121 mm.

Figure III.93 presents the percentage of variation in the final end-use tissue properties for formulations with different fibrous compositions and MFC/NFC incorporation. Formulations were simulated with a eucalyptus pulp (HW), and a softwood pulp (SW) with higher strength properties, in percentages of 1%, 5%, and 10% (Figure III.93a). Formulations with MFC/NFC incorporation were also simulated, at the same percentages (Figure III.93b). A formulation was further proposed that contained these three fibrous elements, namely, 90%HW+5%MFC/NFC+5%SW (Figure III.93b). All formulations with HW and SW presented 25°SR , and formulations with MFC/NFC presented drainability between 26 and 44°SR .

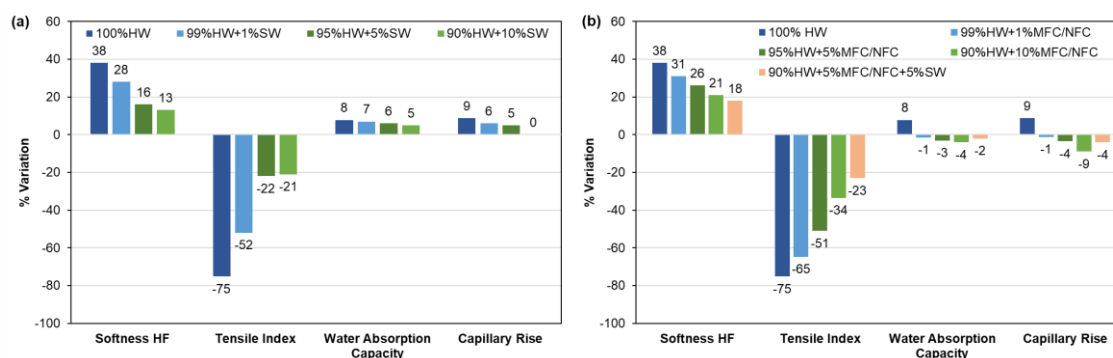


Figure III.93. Percentage of variation in the tissue final end-use properties for formulations with (a) HW and SW; and (b) HW and MFC/NFC, compared to the typical industrial structures (75%HW+25%SW), and predicted using the *SimTissue*.

From these scenarios, the results indicated that the production of tissue structures with reduced SW incorporation or its replacement by MFC/NFC promoted an increase in softness properties. Structures with HW and SW contributed positively to the strength development compared to structures with MFC/NFC. The formulations whose balance between the softness and tensile index properties, and with the highest potential to replace this industrial reference, were 90%HW+10%SW and 95%HW+5%MFC/NFC. This evidence is suggested by comparison with industrial base tissue papers. Despite the 51% loss in the tensile index, structures with 5% MFC/NFC showed strength values in the range of these industrial tissue papers (6.9 - 12.0 Nm/g), and consequently, unsustainable breaks are expected to be unlikely to occur. The results also indicated that SW fibers remain an important element to confer strength and absorption properties, especially in products such as wet strength papers. MFC/NFC presents a good potential to be used in tissue products such as toilet and facial papers, produced with the eucalyptus maximization. The 90%HW+5%MFC/NFC+5%SW formulation also presented a good combination between softness, strength, and absorption, essential to produce premium materials (Morais et al., 2021b).

Regarding fiber modification studies, a kraft eucalyptus pulp with higher tensile index values (H_C) and a sulfite pulp with higher softness values (H_F) were separately subjected to enzymatic treatments (Morais et al., 2021a). The information about fiber flexibility and biometry is determinant to predict tissue paper properties. These two raw materials correspond to the two extremes of eucalyptus pulps, regarding fiber wall thickness, degree of collapse, refining ability, flexibility values, and softness and strength properties. All these fiber properties and dimensions are essential to model them in 3D, resulting in a structure with optimized bulk, for example. Therefore, the results constitute valuable information applicable for other pulps of interest, with fibre dimensions in this range. Through this optimization, the variation of time and enzyme dosage can be predicted, using data-driven statistical mathematical models. Table III.43 presents examples of simulated scenarios for the enzymatic treatment of these pulps. First, and regarding kraft pulp, *SimTissue* predicted softness and tensile index values in the same range as typical industrial formulations (softness: 60 HF; tensile index: 19 Nm/g; capillary rise: 121 mm).

Therefore, *SimTissue* predicts the formulation properties with variation in these two process variables: reaction time and enzyme dosage. In these simulation studies, similar softness and strength properties are obtained with an enzyme reaction time of 30 minutes, and with a dosage of 50 g/ton, or also with twice the enzyme reaction time, and with a lower dosage of 20 g/ton. The same analysis can also be performed for other pulps of interest.

Table III.43. Scenarios for the enzymatic treatments of kraft (H_C) and sulphite (H_F) pulps, predicted by *SimTissue*.

	Enzyme Dosage (g/ton)	Reaction Time (minutes)	Softness HF	Tensile Index (Nm/g)	Capillary Rise (mm)
Simulation 1 (Kraft pulp, H_C)	50	30	53	18	108
Simulation 2 (Kraft pulp, H_C)	20	60	53	20	108
Simulation 3 (Sulfite pulp, H_F)	100	30	81	7	117
Simulation 4 (Sulfite pulp, H_F)	30	60	82	7	116

To obtain new formulations with 100% eucalyptus pulps, it is important to select the process conditions that allow a good trade-off between them, to adjust the furnish for the tissue properties development. A design was proposed that combines 80% of the enzymatically treated H_C eucalyptus pulp and 20% of the H_F pulp with and without enzymatic treatment (Morais et al., 2021a). Figure III.94a presents the percentage of variation in the final end-use tissue properties for formulations with different combinations, compared to formulations with 75%HW+25%SW. Overall, the simulated combinations contributed to increased softness with good tensile and absorption properties, ensuring the necessary strength to obtain premium tissue papers. Considering the inverse progression of softness HF and tensile index, the identification of different mixture conditions that allow the best balance between these two properties can be identified for different types of tissue papers. Despite the difference found between the strength of the combinations and the industrial reference, the tensile index values of the combinations (14 – 17 Nm/g) were higher than the range of values for industrial base creped tissue papers (6 – 11 Nm/g) (Curto et al., 2021).

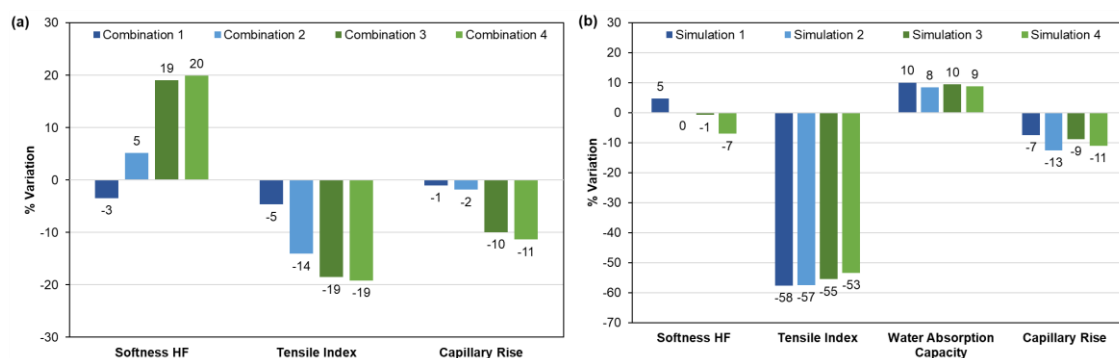


Figure III.94. Percentage of variation in the tissue final end-use properties for fiber modification formulations, compared to the typical industrial structures (75%HW+25%SW) and predicted using the *SimTissue*. (a) Combination 1: 80% H_C pulp with 10 g/ton, 30 minutes + 20% H_F pulp without treatment; Combination 2: 80% H_C pulp with 10 g/ton, 60 minutes + 20% H_F pulp without treatment; Combination 3: 80% H_C pulp + 20% H_F pulp, both with 100 g/ton, 30 minutes; Combination 4: 80% H_C pulp + 20% H_F pulp, both with 100 g/ton, 60 minutes. (b) Simulation 1: H_C pulp treated with 50 g/ton, 120 minutes followed by mechanical treatment (500 PFI revolution); Simulation 2: H_C pulp treated with 350 g/ton, 120 minutes followed by 500 PFI revolution; Simulation 3: H_C pulp with 500 PFI revolution followed by 50 g/ton, 120 minutes; Simulation 4: H_C pulp with 500 PFI revolution followed by 100 g/ton, 120 minutes.

One of *SimTissue*'s features is also to allow the simulation of scenarios that combine different process operations, such as mechanical and enzymatic treatments. To this end, the same kraft pulp, H_C, was subjected to enzymatic pre-treatment followed by refining, and vice versa. Examples of these simulations, compared to the industrial reference (75%HW+25%SW), are shown in Figure III.94b. From this study, *SimTissue* predicted that similar properties were obtained with an enzymatic pre-treatment with an enzyme dosage of 350 g/ton, followed by refining (simulation 2) and a pre-refining followed by enzymatic treatment with an enzyme dosage 7 times less, 50 g/ton (simulation 1). With this approach, several scenarios for enzymatic and mechanical treatments with equivalent energy consumption can be foreseen. Overall, formulations were obtained with improved softness and absorption properties compared to the industrial reference, and with strengths in the commercial tissue paper range. Although a pre-refining followed by an enzymatic treatment presents a negative impact on the fibers, namely the decrease of fiber length and the increase of fines content, this procedure can be advantageous in obtaining pulps with strength characteristics. Therefore, a pulp with this fiber modification process can be used as an additive in pulps with good softness and absorption properties. Consequently, the production of tissue papers with a composition of 100% eucalyptus pulp and with optimized tissue properties can be achievable.

Regarding the incorporation of additives, in addition to MFC/NFC, *SimTissue* also allows the study of other additives such as CBA (Morais et al., 2021c). This computational platform predicted the tissue properties as a function of the CBA incorporation in eucalyptus pulps and compared with the industrial reference (Figure III.95a). Overall, the incorporation of this additive increased the softness and absorption at the expense of decreasing strength, up to 3% incorporation.

On the other hand, after the 4% incorporation, the softness and strength properties increased at the expense of absorption. Note also that the 4% CBA incorporation has practically the same tensile index value as the industrial reference. This means that this incorporation can allow the replacement of SW in terms of strength properties compared to 75%HW+25%SW.

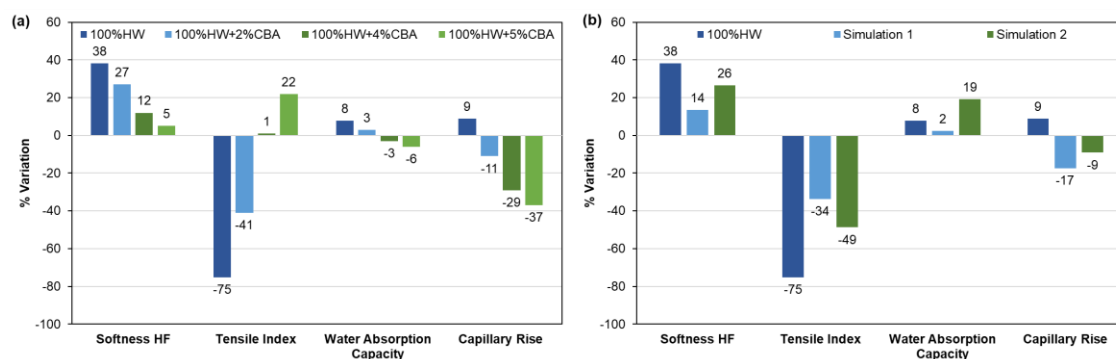


Figure III.95. Percentage of variation in the tissue final end-use properties for formulations with (a) HW and CBA; and (b) HW, SW, MFC/NFC, and CBA, compared to the typical industrial structures (75%HW+25%SW), and predicted using the *SimTissue*. Simulation 1: 75%HW +25%S_G +2%MFC/NFC +2%CBA; Simulation 2: 90%HW +10%S_G +2%MFC/NFC +2%CBA.

Another planning design that included the selection of eucalyptus and softwood pulps, a combination of process operations and incorporation of two additives was carried out and foreseen by *SimTissue*. Two scenarios were simulated on our computational platform and compared to the industrial reference (Figure III.95b). The simulations were carried out to study the effect of the conjugation of two additives on tissue properties and to study their implication in softwood pulp reduction (Morais et al., 2021c). In Simulation 1, the scenario of selecting 75%HW, 25%S_G with mechanical refining treatment followed by enzymatic treatment of 30 g/ton for 60 minutes, and incorporation of 2% MFC/NFC and 2%CBA, as additives, was proposed. In Simulation 2, the same previous conditions of process operation and additives were proposed, but with a selection of 90%HW and 10%S_G. Compared to 100%HW formulations, the addition of both additives improved strength at the expense of decreased softness and absorption. With the softwood pulp reduction, the additives' incorporation promoted an increase in softness and absorption, with good strength properties similar to commercial tissue papers. The understanding of the possibility of producing tissue structures with different additives, softwood pulp reduction, and fiber modification treatments, in the range of industrial drainage, was possible through these simulations.

III.3.4.5. Conclusions

With this research work, we present an experimental and computational methodology to develop sustainable cellulose-based tissue materials. A simulator with predictive capability, the *SimTissue*, was developed and validated to optimize innovative furnish formulations, saving laboratory, and industrial resources. *SimTissue* was applied to identify the more adequate eucalyptus and softwood pulps from a set of raw material pulps. The results indicated the optimized combination of pulps to produce toilet and facial papers, in which softness is the key property, as well as towel papers and napkins, in which strength and absorption are essential. Simulation studies were used to optimize different furnish formulations, predicting different scenarios with enzyme dosages reduction, extending its reaction time, translating into refining energy gains. The effects of incorporating additives, such as MFC/NFC or CBA, were also estimated by *SimTissue*. Several hypotheses of industrial interest were simulated, and the trade-off between softness, strength, and absorption properties was quantified in different scenarios. In conclusion, the *SimTissue* is a computational tool with predictive capacity useful for furnish management and sustainable process optimization.

III.3.4.6. References

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Chapter IV

Conclusions and Future Perspectives

IV.1. Conclusions and Future Perspectives

The research and development of this Ph.D. thesis in the tissue field focused on defining and evaluating innovative computational strategies to optimize furnish, improving the properties of the most suitable raw materials for tissue products, such as eucalyptus pulps, as well as in the development of new differentiating tissue papers, with enhanced key properties such as softness, strength, and absorption. Furnish optimization is a Multiple-Input Multi-Output (MIMO) challenge, mainly due to the different fiber and structure properties, and the influence of several process operations. A blend of hardwood pulps with a percentage of softwood pulps is used to produce these materials. Maximizing the incorporation of eucalyptus pulps and reducing the incorporation of softwood pulps has consequences not only on the properties of the final product but also on the runnability of the paper machine. To use the full potential of this raw material, it was necessary to identify the fiber properties, their relationship with the process, and their functional properties. To balance the absence of softwood pulps, it was important to select strategies to modify the fibers combining enzymatic and mechanical treatments, as well as the incorporation of chemical additives and MFC/NFC in suspensions. The relationships between the properties and the important variables for furnish optimization were established and integrated using computational tools, modeling, validation, and optimization methods, resulting in a differentiating simulator in the tissue field, the *SimTissue*. Therefore, this research explored a furnish optimization approach through the design, development, and application of computational tools, comparing various scenarios with different formulations.

IV.1.1. 3D Fiber Characterization and Modeling

The first strategy developed involved the design of 3D fiber models for each fiber population from different types of raw materials. These models were detailed to the point where fiber wall thickness, fiber lumen, flexibility, and collapse degree are considered. The tissue paper development and optimization benefit from modeling strategies that take into consideration its structural hierarchy at the fiber and structure levels. These 3D fiber data were obtained through a methodology that included measuring the third fiber dimension in the paper structure, the effective fiber thickness, using SEM images cross-section of the unpressed isotropic laboratory structures. It was demonstrated that fiber thickness influences the structural properties of bulk and porosity as well as the final end-use properties. This third fiber dimension is related to fiber wall and lumen dimensions, and consequently, directly correlated to fiber coarseness. This morphological analysis of different pulp fibers was essential for realistic 3D fiber modeling, to simulate tissue paper materials. The combination of a computational 3D modeling approach, using the morphological simulator *voxelfiber*, together with an experimental plan for obtaining 3D fiber data was essential to propose the different fibrous models. This first step of 3D fiber data collection benefited from the classification of pulp fibers into different categories, according to fiber wall thickness, collapse degree, refining ability, and flexibility.

These results were applied to other samples of interest, to simulate fibers with biometric properties, such as coarseness, within this categories range. The development of a network fibrous materials model using these fiber properties was an important achievement to predict, validate, and optimize tissue properties.

Additionally, an experimental plan was designed to characterize and establish relationships between the properties of fibers and the structures formed by them. A representative group of eucalyptus and softwood pulps was used in the morphological, chemical, and water interaction characterization assays, and in the production of low basis weight laboratory isotropic structures (20 g/m²). The contribution of different pulp fibers with different biometry and coarseness to the final end-use tissue paper properties was accessed. The key factors that influence these properties were identified through several correlations. In addition to the previously identified parameters such as fiber wall thickness, flexibility, and fiber coarseness, the fiber curl and kink are inversely related to tensile index properties. The absorption is also related to the pulp chemical properties, besides the bulk and porosity. For example, the type of hemicelluloses is distinct for hardwood and softwood pulps which significantly contributed to the production of different structures, influencing the absorption properties. The establishment of relationships also allowed to identify that the softness was directly influenced by the structural properties, and inversely influenced by the strength measured by the tensile index. It was found that, for untreated hardwood and softwood pulps, for every two and one unit of increased softness, one unit of the tensile index was reduced, respectively. Therefore, the correlations obtained were used to identify which pulps present the trade-off between softness, strength, and absorption properties and which were the most suitable to be used in each tissue product, namely toilet papers, paper towels, napkins, and facial papers.

IV.1.2. Fiber and Structure Modification Processes

The second strategy explored relied on engineering fiber and structure modification processes using experimental and computational approaches. Initially, the effects of enzymatic modification in different eucalyptus pulps were evaluated separately, to improve the key tissue properties and design new applications of this raw material. To address this goal, different furnish combinations with a blend of these two enzymatically treated eucalyptus pulps were designed to achieve a trade-off between softness and strength properties. The information about fiber flexibility and biometry is determinant to predict tissue paper properties. The values presented correspond to the two extremes of eucalyptus pulps, regarding fiber wall thickness, degree of collapse, refining ability, flexibility values, and softness and strength properties. Drainability values are also influenced by fiber modification treatments. The fines content, the fiber fibrillation level, the length/ tendency to flocculate and aggregate, and the functional groups such as carboxyl and hydroxyl groups contribute to the differences in drainability, and consequently to the °SR values. Therefore, the experimental results constitute valuable information applicable for other pulps of interest, with fiber dimensions in this range.

Overall, the tissue structures showed softness in the commercial range, improved absorption properties, and strength in the range of typical industrial formulations (75%HW+25%SW). It was also found that the inverse relationship between softness and strength properties change with the type of fiber modification treatment. This ratio is twice as high in enzymatically treated pulp mixtures compared to untreated hardwood pulps. The findings of this study showed how fiber furnishes can be adjusted to tissue industry standards, using one type of eucalyptus fiber that provides strength and another that provides softness, also identifying the different conditions that enable the best compromise between softness, strength, and absorption properties for different types of tissue papers.

Subsequently, in the same perspective of maximizing the use of eucalyptus fibers, the effect of incorporating MFC/NFC as an additive was investigated on the structural, softness, strength, and water absorption properties, promoting partial or total removal of softwood fibers. Compared with the mixture 75%HW+25%SW, it was shown that the reduction of softwood fibers in tissue structures improved the structural, softness, and absorption, and decreased the strength properties, while its replacement by MFC/NFC improved structural and softness and decreased strength and absorption properties. Additionally, with the use of *SimTissue* it was possible to design scenarios of the property's evolution with the incorporation of softwood fibers and MFC/NFC to develop innovative formulations, saving laboratory and industrial resources. Formulation scenarios with the incorporation of 1 to 8% of MFC/NFC and without softwood fibers were simulated and it was concluded that these hypotheses can be used for the innovative design of tissue products with micro and nanofibers, optimizing the end-use properties and the fiber mixture costs. MFC/NFC has proven to be a high-quality additive to improve the softness and strength of tissue products such as toilet and facial papers, while softwood fibers have proven to be an important element to confer strength and absorption properties, especially in products such as towel papers and napkins. An approach of combining MF/NFC, eucalyptus fibers, and softwood fibers can also be considered to obtain a high-quality premium tissue product with a balance of functional properties.

Ultimately, this strategy presented experimental and computational approaches to evaluate and predict the effects of incorporating a commercial biopolymer and MFC/NFC, as additives, into eucalyptus and softwood fiber pulps on tissue end-use properties. The combination of these raw materials and additives promoted the production of formulations with drainage in the tissue industrial process, and the use of biopolymer neutralized the adverse effects of micro/nanofibers on the drainability properties. It was demonstrated that maximum strength was obtained by combining both additives at the expense of softness and water absorption. It was concluded that these additives presented a good potential to produce high-quality products such as tissue masks or premium napkins and facial papers. These biocompatible and biodegradable additives can promote the maximization of eucalyptus fibers in the production of industrial tissue, optimizing the process and associated manufacturing costs.

Finally, the findings of this second strategy also showed how the combination of innovative experimental methods with *SimTissue* can be used to investigate the liquid retention properties of different furnish structures and tissue papers, evaluating the influence of fiber properties and process stages, on the kinetics of the droplet spreading area and its shape in the 3D network of multi-structured fibrous materials.

IV.1.3. Optimization using Advanced Computational Tools

The third and last strategy developed focused on experimental and computational planning to optimize tissue products, using innovative computational tools. The different experimental sets were designed to reduce the percentage of softwood pulps into the furnish, and, consequently, produce a tissue material with maximization of eucalyptus fibers. *SimTissue* was developed and implemented by organizing the results into database structures, which correspond to more than 200 different structures and 6000 paper sheets produced, allowing the use of computational tools for modeling and optimization. This simulator with predictive capability was also validated to optimize innovative furnish formulations, saving laboratory, and industrial resources. The important process variables to develop tissue structures were integrated into *SimTissue*, enhancing different cellulose fibers from renewable sources and additives. Different formulations with fiber blending and modifications were evaluated and predicted, considering the desired softness, strength, and absorption properties, including the maximization of the eucalyptus pulps incorporation, with the addition of MFC/NFC, biopolymer, different eucalyptus pulps, or softwood pulps, among others. These findings indicated that *SimTissue* is a useful tool to compare and optimize various interest scenarios, supporting industrial production process management and optimization. The computational implementation of *SimTissue* was achieved through the programming of calculation engine algorithms and database integration, and computational tools of 3D modeling and mathematical models, establishing relationships between the properties. *Voxelfiber* was used to model tissue structures by inputting fiber and structure properties, and these computational structures were validated with laboratory-made structures. Fibers were modeled in 3D using fiber dimensions including fiber wall thickness and lumen. These 3D network fibrous materials were simulated by the random deposition of individual fibers, allowing the fiber modeling according to its morphology, flexibility, and collapse, resulting in a structure with thickness, porosity, RBA, coverage, among other properties. These parameters were changed independently, and the raw materials were defined as a fiber population with a combination of different fiber models, to allow the implementation of different flexibility and fiber collapse degrees. In this study, it was demonstrated that it is fundamental to model tissue structures to predict the structural and functional properties, optimizing the various products. Furthermore, the development of statistical models allowed the correlation of tissue functional properties with morphological, suspension, and structural characteristics, considering data from the furnish process, which included fiber mixtures, mechanical and enzymatic treatments and additives incorporation, and industrial-based and single-used tissue papers.

It was concluded that these computational tools can be used successfully to model the effects of key fiber properties, fiber modification process steps, and structural properties on softness, strength, and absorption parameters, evaluating preliminary decisions regarding the usability of different raw materials and operation processes steps where functional properties are important.

Both experimental characterization and computational modeling contributed to investigating the relationship between fibers and the network structure formed, optimizing the furnish and the functional tissue properties. The identification of key fiber properties, the establishment of numerical relationships between the tissue properties, and the experimental and computational results were used to estimate ideal scenarios of pulp and process combination operations, using computational tools. The approach proposed in this Ph.D. thesis can be used to design innovative tissue products with added value, meeting specific consumer requirements and changing the furnish characteristics. *SimTissue* allowed the design of innovative tissue products, at micro and nanoscale, establishing correlations between the input process variables and the output tissue properties. These input process variables included fibrous compositions, use of enzymes, the combination of mechanical and enzymatic treatments, and additives incorporation. Moreover, these methods evaluated different scenarios of industrial interest quickly and accurately, without the need for extensive experimental planning. The *SimTissue* is a computational tool with predictive capacity useful to optimizing the furnish management and the associated formulation costs.

IV.1.4. Future Perspectives

The work developed in this Ph.D., in the scope of Project InPaCTus, will continue to be used to support the industrial tissue paper production process through computational interface tools. *SimTissue* can be extended to the industrial production of new added-value materials with low basis weight and high porosity and applied to brand-new tissue fields. To ensure the robustness of *SimTissue* in its translation from laboratory-scale to industrial-scale, upscaling strategies are being considered and implemented by the University of Beira Interior and The Navigator Company R&D teams.

Appendix

Complementary Publications

Conceição, E.L.T., **Morais, F.P.**, and Curto, J.M.R. (2022). Calibration of a geometric computer model for planar stochastic fibre networks with application to tissue paper. *ChemRxiv*, Publication Date: 2022-04-04. DOI: 10.26434/chemrxiv-2022-9mcvk

Other Scientific Communications/ Presentations

Morais, F.P., Curto, J.M.R., and Amaral, M.E.C.C. (2018). Presentation of InPaCTus R&D Project: *Eucalyptus globulus* Pulp Suitability for Tissue Paper. In *Proceedings of the III Symposium of the Fiber Materials and Environmental Technologies – FibEnTech Research Unit*, Universidade da Beira Interior, Covilhã, Portugal, 21 September 2018, pp. 38-40. ISBN: 978-989-654-486-7. (Poster Communication)

Morais, F.P., Carta, A.M.M.S., Amaral, M.E.C.C., and Curto, J.M.R. (2021). Design and Engineering of Tissue Papers using Cellulose-based Fibrous Materials 3D Simulations: an approach for Furnish Optimization. In *3 minutos, 1 slide, a TUA tese! Contest*, Universidade da Beira Interior, Covilhã, Portugal, 26 November 2020. (Oral Communication)

Morais, F.P., Carta, A.M.M.S., Amaral, M.E.C.C., and Curto, J.M.R. (2021). Design and Engineering of Tissue Papers using Cellulose-based Fibrous Materials 3D Simulations: an approach for Furnish Optimization. In *Proceedings of the VII Ciclo de Conferências da Faculdade de Ciências 2021*, Online Conference, 24-25 September 2021. (Poster Communication)

RESEARCH ARTICLE

Calibration of a geometric computer model for planar stochastic fibre networks with application to tissue papers

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Summary

A stochastic morphology model for constructing random fibre networks can be used to gain insight into tissue paper, more specifically laboratory-made paper sheets mimicking it. Geometry based models of heterogeneous materials pose unique challenges of their own that need to be considered in the respective calibration procedure. This means that detailed accounts would be quite valuable for the identification and evaluation of potential solutions which can be of general interest. We describe a calibration method for a single parameter which is a rational number between 0 and 1 that specifies the flexibility of individual fibres in a network. Of particular interest here is an alternative to least squares estimation to eliminate the influence of constant bias. Errors resulting from measurement and model bias were corrected using the so-called discrepancy function making use of a frequentist two-step procedure for computer model calibration. The procedure is validated by cross-validation.

KEYWORDS:

Computer model calibration; Measurement bias; Model inadequacy; Stochastic morphology model; Stochastic fibre network; Tissue paper

1 | INTRODUCTION

Calibration (also called as parameter estimation in the context of regression analysis) is defined as finding appropriate values for a simulation model parameters such that the simulation output reproduces some given experimental data (for a thorough discussion see (Trucano et al., 2006)). Typically, a full calibration of a computer model incurs in considerable effort performing physical experiments to gather data that imposes a substantial cost and time burden. Of course obtaining the required type and amount of data is unavoidable when using the model for prediction, where output accuracy is paramount. However, in the initial phase the focus is more on running simulation experiments to obtain insight and understanding—in this case specifically into the microstructure of a material. At this stage, most probably the kind and amount of data are severely limited. Therefore, especially in industrial practice, it is often useful to start only with a subset of the parameters amenable

to calibration with readily available routine experimental data; the remaining ones have to be chosen via trial and error from a range of plausible values or taken from the literature.

A drawback of the classical regression framework is the assumption of no systematic discrepancy in the model output predictions relative to physical measurements (no model bias). This is, however, almost never the case with simulation models for complex problems, such as in our case, mimicking the morphology of a heterogeneous material. Or, to put it in another way, imperfect (computer) models are a fact of life. This has been first addressed in the seminal paper by Kennedy and O'Hagan (2001) which presents a methodology based on the Bayesian paradigm, and given rise to the field of *computer model calibration*. The recent works by Plumlee (2017); Tuo (2019); Xie and Xu (2020) shed some light on unidentifiability problems that have been somewhat overlooked in the Bayesian literature and present and discuss some approaches to mitigate them. In the frequentist perspective, Tuo and Wu (2015) showed

that even with model bias the ordinary least squares estimator is consistent but less efficient than the method proposed therein, called the L_2 calibration. Of particular practical interest is the approach developed by Wong et al. (2017) because it can be implemented very easily using off-the-shelf software. The methodology can be summarised succinctly as two sequential steps: following a conventional estimation procedure for calibration of the computer model parameters, any discrepancy between computer model output and experimental data (*discrepancy function*) is represented by a suitable non-parametric statistical model. To conclude this very concise description and for the sake of completeness we mention also the recent approach of Plumlee (2019).

We have developed from scratch a computer code (a simulator) that simulates planar networks of fibres (Conceição et al., 2010) implementing the mechanism for fibre flexibility proposed in Niskanen and Alava (1994). These structures can represent certain *porous heterogeneous* materials of the non-woven type. It belongs to the class of *geometric* or *stochastic morphology* models which are characterised by “concentrating solely on mimicking the morphology (ignoring the physical basis of the microstructure formation process)” (Bargmann et al., 2018) of heterogeneous materials. Indeed, because of their wide range of production processes—dry-laid, wet-laid, spunbond, and electrospun processes—, from a material design perspective (Jain et al., 2014) it is sensible that the modelling of non-wovens should be *abstracted* from a particular fabrication method. The model consists of a *idealised* deposition sequence (assembly process) in which fibres (building blocks) are stacked one above the other along the thickness direction.

Within the above context, we argue that data obtained from simple measurement techniques of bulk or overall properties should be used as extensively as possible for calibration. We investigate the calibration of the fibre “flexibility” parameter considering areal mass density (grammage) as the explanatory variable for hand-made laboratory tissue paper sheets from chemical pulp. Porosity is a key material property and can be regarded as the natural choice for the response variable. However, despite the many techniques available to measure this parameter (Lawrence and Jiang, 2017), the experimental determination of porosity for paper is still a challenge (Charry et al., 2018), and it is thus more convenient to use the conventional measurement of apparent sheet thickness within a range of grammages (Bloch et al., 2019), especially in an industrial setting.

As can be seen from a few works dedicated to developing geometric computer models (Altendorf and Jeulin (2011); Gaiselmann et al. (2013); Neumann et al. (2016)), the issues faced in parameter estimation are quite varied and often specific for a given material model. In our case, we take advantage of

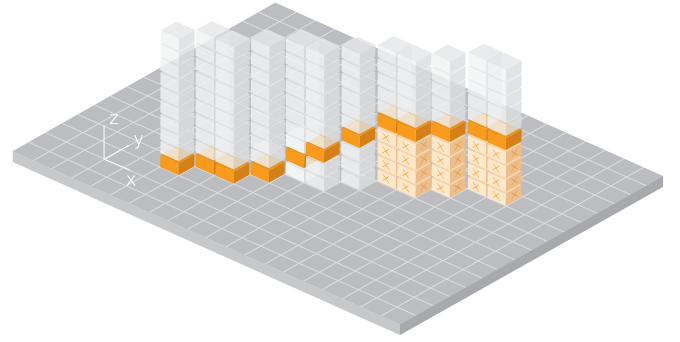


FIGURE 1 Three-dimensional view of a discretised fibre. The darker voxels represent the fibre; those marked with a cross belong to other fibres; the white voxels correspond to empty or void space; the translucent voxels represent cells in a discrete three-dimensional space.

the fact that some biases have *constant magnitudes* and eliminate their influence in the “flexibility” estimate by minimising a scale measure of residuals instead of the least squares criterion. In a nutshell, the calibration task boils down to the resolution of a stochastic optimisation problem in a single variable which is a rational fraction between 0 and 1. We describe an *ad hoc* procedure which allows the use of any conventional *deterministic* derivative-free one-dimensional minimisation technique. Finally, we assess the quality of predictions using the schumaker shape preserving spline (Schumaker, 1983) for the discrepancy function by means of the leave-one-out cross-validation method (see Chapter 5 of James et al., 2013; Arlot and Celisse, 2010).

The article is organised as follows. Section 2 briefly describes the sedimentation-like simulation process resulting in a sheet of fibrous material. Model parameters are presented and classified as *tuning* and *calibration* according to Han et al. (2009). Next, the formulation of the calibration problem is given in Section 3 and Section 4 describes the details of the calibration process. Section 5 gives a brief account of the experimental and computational setups and dataset used for cross-validation. The results are presented and discussed in Section 6.

2 | SIMULATOR

2.1 | Some details

Our implementation fully discretises the 3D space into a Cartesian regular grid. In it, each fibre is represented by a sequence of chained parallelepipeds (voxels) with square base, as depicted in Figure 1. A web is grown by successively laying down *straight* fibres, one after another, onto a horizontal flat substrate. Each one is positioned and oriented uniformly at random in the

horizontal (or in-plane) x and y directions and placed parallel to the substrate on top of the underlying network. These fibres are *flexible* and thus undergo deformation in the vertical (or out-of-plane) z direction by which their initial flat shape is subsequently conformed to the top surface of the previous deposited fibres located just below. Pores arise from voids formed as fibre stiffness most likely will prevent a perfect contact everywhere along the web top surface.

Modelling fibre *flexibility* is accomplished by placing an upper limit on the number of out-of-plane voxels allowed between any pair of adjacent voxels comprising a fibre. To be more precise, let us consider the case of a fibre represented by a vertical strip one voxel wide and n_t^f vertical voxels thick. Any two neighbouring voxels in the same layer of the fibre can be vertically separated at most by an allowed distance of T^f voxels. This is described mathematically as

$$|z(j) - z(j')| \leq T^f,$$

where $z(j)$ and $z(j')$ are the elevations of two adjacent voxels j and j' occupied by the same layer of the fibre and T^f , which can be any positive integer, is the model representation of the physical fibre flexibility. Note that Figure 1 shows a representation of a one voxel thick and wide fibre for which $T^f = 1$. Incidentally, note also that for $T^f > n_t^f$ the fibre representation becomes discontinuous in the z direction.

However, a more homogeneous microstructure than that obtained with this random deposition model (see Figure 2) might be needed to properly handle specific phenomena. One such example is the mechanism of hydrodynamic smoothing on paper sheet formation. This is simulated favouring the deposition into valleys of the surface by the particle deposition rule of Provatas and Uesaka (2003). It compares the mean height of the section of the web where a trial fibre lands, h , with a fraction, α , of its counterpart of the entire fibrous mat, H . The attempt is always accepted if $h \leq \alpha H$, where $0 \leq \alpha \leq 1$ is a constant; otherwise, the attempt is accepted with acceptance probability p .

In overview, our growth process of a 3D fibrous network consists of the following basic steps (see Figure 3):

- (a) Generation of the in-plane coordinates for a trial fibre. Its length is a random variable drawn from a Poisson distribution (Provatas and Uesaka, 2003).
- (b) Particle deposition rule. If not accepted the previous step is repeated.
- (c) Extraction of the out-of-plane slice (defined by the in-plane coordinates) from the 3D network.
- (d) Fibre deformation.
- (e) Reinsertion of the modified slice into the 3D network.

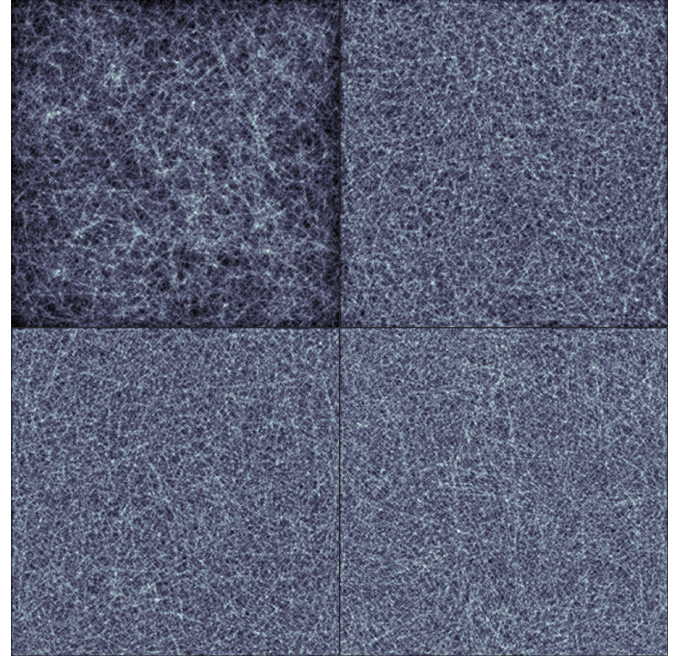


FIGURE 2 Simulated X-ray-like image of the (x, y) plane for a mat as generated from the particle deposition rule, with formation control parameters set to $p = 1$, $\alpha = 1$ (upper left); $p = 0.1$, $\alpha = 1$ (upper right); $p = 0.01$, $\alpha = 0.94$ (lower left); and $p = 0.001$, $\alpha = 0.94$ (lower right). As the acceptance probability p decreases the network surface gets progressively smoother.

This process continues until a termination criterion such as the total number of fibres or the areal mass density (also called basis weight or grammage) of the material is attained. It is important to notice that both the first two steps are of *random nature*, giving rise to changes in different simulation *replications*. The simulator code has been developed using MATLAB® (The MathWorks, Natick, MA, USA) as the implementation language. Further details can be found in Conceição et al. (2010).

2.2 | Model parameters

Here we list the parameters of our computer code classified as either *tuning* parameters or *calibration* parameters. According to Han et al. (2009) the main distinction between these is that “tuning parameters have *no* meaning in the physical experiment”. Calibration parameters define an instance of a model used to simulate an associated physical experiment, whereas tuning parameters control the solution of an algorithm implemented to solve the model. In passing, note that tuning is one of the tasks in the problem of *verification* as discussed in Trucano et al. (2006).

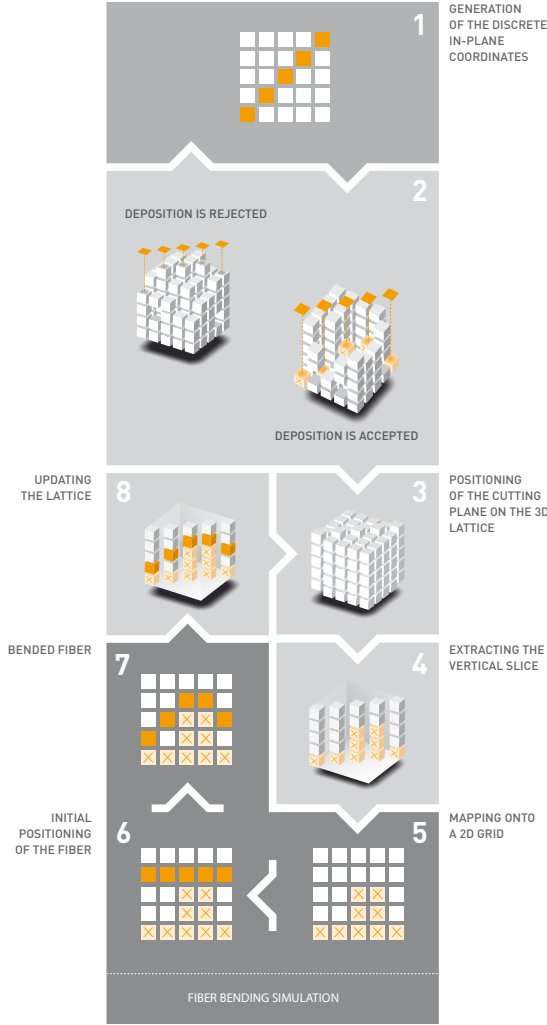


FIGURE 3 Data flow diagram that illustrates the core of the sequence of computations for the fibre deposition model.

2.2.1 | Calibration parameters

p, α

Acceptance probability and constant, respectively, in the particle deposition rule. These mainly determine the 2D spatial distribution of the local areal mass density in the in-plane orientation, meaning they also have a minor effect on porosity. Their calibration would therefore only be possible with a map of the local mass density obtained experimentally (see, for example, [Provatas et al., \(1996\)](#) for a study on the local mass density in paper sheets). Hence, we fix beforehand the values for those parameters making an educated guess based on our experience with the simulator.

$$F = T^f / n_t^f$$

For a fixed discrete fibre width the flexibility normalised by the discrete fibre thickness determines the resulting network

structure ([Hellén et al., 1997](#)). It should be noted that F is a *rational number*. Naturally, there arises the need to impose an integer upper bound U_t^f to n_t^f in order to remain within the memory limits of the hardware. Thus, in practice, the search space is represented by an ascending sequence of *irreducible* fractions whose denominators do not exceed U_t^f such that

$$1 \leq T^f < n_t^f \leq U_t^f;$$

the number 0 is not included since it corresponds to stiff fibres in the fibre representation. For example, with $U_t^f = 10$, we have

$$\mathcal{F}_{10} = \left\{ \frac{1}{10}, \frac{1}{9}, \frac{1}{8}, \frac{1}{7}, \frac{1}{6}, \frac{1}{5}, \frac{2}{9}, \frac{1}{4}, \frac{2}{7}, \frac{3}{10}, \frac{1}{3}, \frac{3}{8}, \frac{2}{5}, \frac{3}{7}, \frac{4}{9}, \frac{1}{2}, \frac{5}{9}, \frac{4}{7}, \frac{3}{5}, \frac{5}{8}, \frac{2}{3}, \frac{7}{10}, \frac{5}{7}, \frac{3}{4}, \frac{7}{9}, \frac{4}{5}, \frac{5}{6}, \frac{7}{8}, \frac{9}{10}, \frac{1}{1} \right\}.$$

In number theory this is known as the Farey series ([Hardy and Wright, 2008](#), Chapter 3) (of order 10).

2.2.2 | Tuning parameters

n_w^f

Discrete width of a fibre expressed as number of horizontal voxels. When using a single fibre type a one voxel wide strip obviously has the minimum memory requirements.

U_t^f

Upper limit for the discrete thickness of a fibre expressed as number of vertical voxels. From a practical viewpoint, this is chosen as large as possible within the limitations of memory and computation time of the machine available to run jobs.

n_x, n_y

Dimensions of the substrate expressed as number of horizontal voxels for the x and y directions. We use a square shape region.

3 | CALIBRATION FORMULATION

As mentioned before, conventional measurements of grammage (areal mass density) and thickness of a single sheet are employed for the model calibration due to their ubiquity in industry. [Bloch et al., \(2019\)](#) developed the following semi-empirical expression for the sheet thickness, z , as a function of the grammage, G ,

$$z = \begin{cases} 2\sqrt{\frac{Gz_b}{(1-\phi_b)\rho_f}} & \text{for } 0 \leq G < G_b \\ z_b + \frac{G}{(1-\phi_b)\rho_f} & \text{otherwise,} \end{cases} \quad (1)$$

with

$$G = \frac{m}{A}$$

and

$$G_b = (1 - \phi_b)\rho_f z_b,$$

where z_b is the distance from the sheet surfaces that marks the beginning of the central bulk region with constant inter-fibre porosity, ϕ_b , ρ_f is fibre density, and m and A denote respectively the mass and area of the sheet. According to their data, the transition from the nonlinear region observed at lower grammages to a linear relationship occurs approximately in the range 10 g/m^2 to 20 g/m^2 .

Within this context, there are three sources of *constant* systematic bias. The first, *measurement bias*, arises when using a standard, caliper-based, physical measurement of thickness: the paper sheet is pressed between two metal plates and because of the corrugation on both surfaces of the sheet, there is a marked difference between (apparent) measured thickness and the true average value of local thicknesses (Sung and Keller, 2008; Fellers, 2009). Nevertheless, according to the ISO standard 12625-3:2014 it is important to recognise that this way of measuring thickness is particularly appropriate for uses involving commerce and industry “at any stage of their manufacture”. The second source of bias arises from a particular form of *model inadequacy* for the computer model: the predicted value of sheet thickness as a function of grammage is *linear* for any grammage, thus failing to reproduce the behaviour below G_b . As explained below, because the experimental data were collected in the linear region above G_b , this bias can be made constant by assuming an appropriate loss function allowing the recovery of the true slope. The third concerns another form of model inadequacy, where the output of the computer model (designated by the superscript s) only gives an empirical approximation to some physical measurement (designated by the superscript p), namely, the thickness of a sheet.

Then the relationship between the experimental data (z_i^p, G_i) and the computer model (simulator) output $z^s(\cdot)$ expressed as number of voxels becomes

$$z_i^p = z^s(G_i, T^f/n_i^f; p, \alpha, n_w^f, n_x) \Delta_z + \delta_1 + \delta_2(G_i) + e_i, \quad (2a)$$

and the voxel height, Δ_z , is given by

$$\Delta_z = \frac{t^f}{n_i^f} \quad (2b)$$

where t^f is the thickness of a fibre, e is the measurement error, and the subscript i refers to the i th physical experiment. The constant δ_1 is a discrepancy function which accounts for the constant biases, whereas $\delta_2(G)$ is a discrepancy function to account for other sources of uncertainty.

We will compare two different ways to compute the thickness of a single simulated sheet, namely, “box” and “percentile”; “box” makes use of the quantiles of the empirical distributions of the elevations of the top, z_{top} , and bottom, z_{bottom} , surfaces, whereas the quantiles of the empirical distribution of local

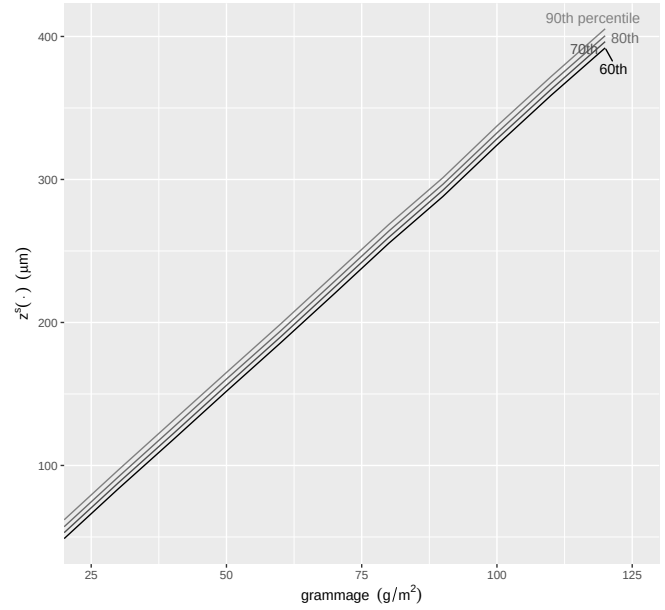


FIGURE 4 Thickness obtained by the “percentile” method for simulated paper sheets of different grammages.

thicknesses are used in “percentile”. The local thickness is the distance between the top and bottom surfaces at each position in the xy -plane of a sheet. The difficulty in the calculation of these distributions lies in being able to unambiguously define the geometry of the paper surface in the absence of a standard definition (Charry et al., 2018). To do this we use the so-called “visibility depth approach” as described in Charry et al. (2018) to determine z_{top} and z_{bottom} at each position (x, y) . Then we take for the apparent thickness of the simulated sheets $z^s(\cdot)$

percentile the 80th percentile of local thickness values, $q_{0.80}(z_{\text{top}} - z_{\text{bottom}})$, as done in Hellén et al. (2002) and

box the difference between the 95th and 5th percentiles of the top and bottom surfaces respectively, $q_{0.95}(z_{\text{top}}) - q_{0.05}(z_{\text{bottom}})$, as proposed by Charry et al. (2018).

A multitude of different variants can be formulated by choosing other values for q that will differ only by a constant shift in $z^s(\cdot)$. This is illustrated in Figure 4 that depicts the thickness obtained by the “percentile” method as a function of grammage. Here, by using the translation invariant loss function described in the following paragraph, the calibration procedure is made independent of the specific choice of q .

In Wong et al. (2017) the actual calibration is performed using a conventional nonlinear regression procedure

$$\begin{aligned} \widehat{T^f/n_i^f} &= \arg \min_{T^f/n_i^f} L(T^f/n_i^f) \\ &= \arg \min_{T^f/n_i^f} L(z^p(G_i) - z^s(G_i, T^f/n_i^f) \Delta_z), \end{aligned} \quad (3)$$

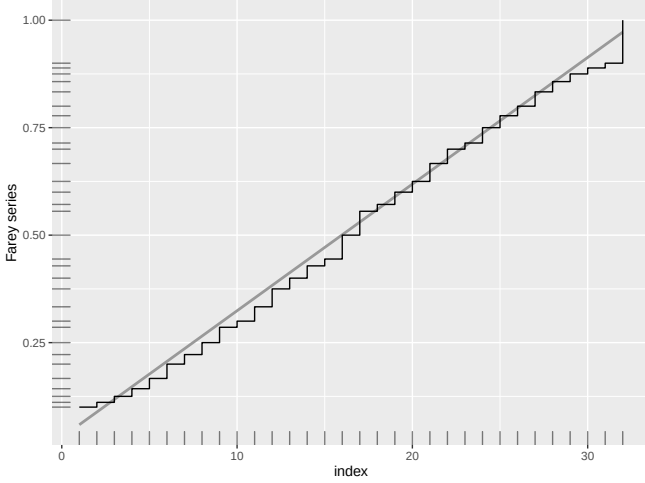


FIGURE 5 Plot of the terms in the Farey series of order 10 versus their respective index together with the individual values displayed on the sides.

where a circumflex above a variable denotes its estimate, and L is the loss function of the estimator. However, instead of using the usual least squares criterion for the loss function L , in this particular situation it is more convenient to minimise a scale measure of the residuals. The ordinary variance σ^2 or standard deviation is one such possibility, but a variety of other *robust* residual scales are available (see Section 5.4 of [Maronna et al., 2019](#)). We note that

$$\sigma(\{z^p(G_i) - z^s(G_i, T^f/n_i^f)\Delta_z\}_{i=1}^n) = \sigma(\{\delta_1 + \delta_2(G_i) + e_i\}_{i=1}^n) \\ = \sigma(\{\delta_2(G_i) + e_i\}_{i=1}^n)$$

since it is well known that σ is invariant under a shift transformation. So this allows the procedure to be invariant to constant biases δ_1 . In the last step, the resulting residuals $z^p(G_i) - \hat{z}^s(G_i, T^f/n_i^f)\Delta_z$, are used to compute the sum of the discrepancy functions $\hat{\delta}_1 + \hat{\delta}_2(G) = \hat{\delta}(G)$ by interpolation with a schumaker shape preserving spline ([Schumaker, 1983](#)).

4 | METHODOLOGY FOR CALIBRATION

The basic idea is to replace the optimisation on the fractions in the Farey series with an optimisation on their *index* sequence. But that implies that this change of variable preserves the overall shape of the loss function L . In [Figure 5](#) we represent the terms in the Farey series of order 10 against their index, which is also representative for higher orders. We can see that the transformation is almost linear, so we speculate that the shape will be retained in general. A point generated by the optimiser in the continuous interval $[1, \text{card } \mathcal{F}_{U_f}]$ is converted into an integer index by discarding the fractional part, where card denotes the cardinal number of a set.

Now, since in this case the computer model is *stochastic in nature*, in order to allow the optimisation to be carried out with a single variable deterministic procedure such as interval elimination, the variation in successive runs is expected to be reduced to near zero through the notion of *statistical* representative volume element (RVE).

Remember that in the following *stochastic optimisation* ([Homem-de-Mello and Bayraksan, 2014](#)) formulation of [\(3\)](#)

$$\min_{T^f/n_i^f} \left\{ g(T^f/n_i^f) = E[L(T^f/n_i^f, \xi)] \right\},$$

the original objective function is replaced by a *sample average* approximation

$$g(T^f/n_i^f) \approx g_N = \frac{1}{N} \sum_{k=1}^N L(T^f/n_i^f, \xi^k)$$

at each iteration of an optimisation algorithm. Here, E denotes the expectation operator and $\{\xi^1, \dots, \xi^N\}$ is a sample from the distribution of a random variable ξ which represents a set of replications of the simulated fibrous material. Note that for the approximating problem $\min_{T^f/n_i^f} g_N(T^f/n_i^f)$, a new sample is drawn independently at every iteration and the in-sample realisations ξ^j are also mutually independent. See [Choirat and Seri \(2012\)](#) for a discussion of the statistical asymptotic properties of this estimator.

For any heterogeneous material it is possible, in principle, to determine the number of realisations, N , of a given volume, V , required for a desired precision in the estimation of any physical property ([Kanit et al., 2003](#)) and *vice versa*. Regarding porosity ϕ , the size of the RVE is given by

$$V_{\text{RVE}} = \frac{4\phi(1-\phi)A_3}{\epsilon_{\text{abs}}^2 N},$$

where A_3 is the integral range and ϵ_{abs} is the absolute sampling error. The value of A_3 can be calculated from 3D image data of the microstructure of paper materials with the procedure presented in [du Roscoat et al. \(2007\)](#) (see also [Kanit et al., 2003](#)). We recall the relationship

$$\phi = 1 - \frac{G/z}{\rho_f}, \quad (4)$$

following directly from the definition of porosity as the ratio between void volume (inter-fibre pores) and total volume that will be used for calculating the porosity of a sheet. To correct for the overestimation caused by the surface unevenness, the intercept of the regression line of the measured thickness values z^p on G was subtracted from z^p to obtain the so called *intrinsic* thickness ([Fellers, 2009](#); [Bloch et al., 2019](#)) that is used in equations [\(4\)](#) and [\(5\)](#).

Under the reasonable assumption that the value of A_3 obtained on a physical sheet can be extended to a simulated similar one, we determine a pair (n_x^{RVE}, N) for the desired precision

ϵ_{abs} from

$$n_x^{\text{RVE}} = \left\lfloor \frac{1}{\Delta_{xy}} \sqrt{\frac{4\phi(1-\phi)A_3}{\epsilon_{\text{abs}}^2 N z}} \right\rfloor, \quad (5)$$

where $\lfloor x \rfloor$ denotes the integer part of the real number x and Δ_{xy} is the size of the square base of the voxels. Since the industry standards for the preparation of laboratory handsheets calls for averaging over replicates, a natural upper bound for ϵ_{abs} is provided by

$$\epsilon_{\text{abs}} \ll \frac{2\sigma(\phi)}{\sqrt{J}},$$

where σ is the standard deviation over J replicate measurements.

Finally, let us consider laboratory handsheets that have been replicated J times ($j = 1, 2, \dots, J$) for each G_i ($i = 1, 2, \dots, n$). Then, the loss function based on the mean of the weighted residuals, $\bar{r}_{i\cdot}$, now takes the form

$$L(T^f/n_t^f, \xi^k) = \sqrt{\frac{1}{n-1} \sum_i (\bar{r}_{i\cdot} - \bar{r}_{\cdot\cdot})^2}, \quad (6)$$

where

$$\bar{r}_{i\cdot} = w_i \left[\bar{z}_{\cdot}^p(G_i) - z^s(G_i, T^f/n_t^f, n_x^{\text{RVE}}, \xi^k) \Delta_z \right],$$

$$\bar{r}_{\cdot\cdot} = \frac{1}{n} \sum_i \bar{r}_{i\cdot},$$

$$\bar{z}_{\cdot}^p(G_i) = \frac{1}{J} \sum_j z_j^p(G_i),$$

and the weights are the reciprocals of the sample standard deviation within each grammage

$$w_i = \left[\frac{1}{J-1} \sum_j (z_j^p(G_i) - \bar{z}_{\cdot}^p(G_i))^2 \right]^{-1/2}.$$

5 | EXPERIMENTAL

We give here a rather succinct description of the experimental methods and data; further details can be found in [Morais et al. \(2020\)](#).

5.1 | Methods

Samples. The procedure given in the ISO 5269-1 standard was adapted with the purpose of preparing isotropic laboratory paper sheets (handsheets) mimicking a single ply of tissue paper. These were fabricated using an *unbeaten* pulp in a ISO-compliant conventional sheet former with circular cross section (0.02138 m^2), *without pressing*. Sheets were formed at seven different grammages, each replicated 10 times: 21.1 g m^{-2} , 42.4 g m^{-2} , 63.9 g m^{-2} , 87.0 g m^{-2} , 109.1 g m^{-2} , 129.0 g m^{-2} and 150.9 g m^{-2} . All the samples were conditioned at 23°C

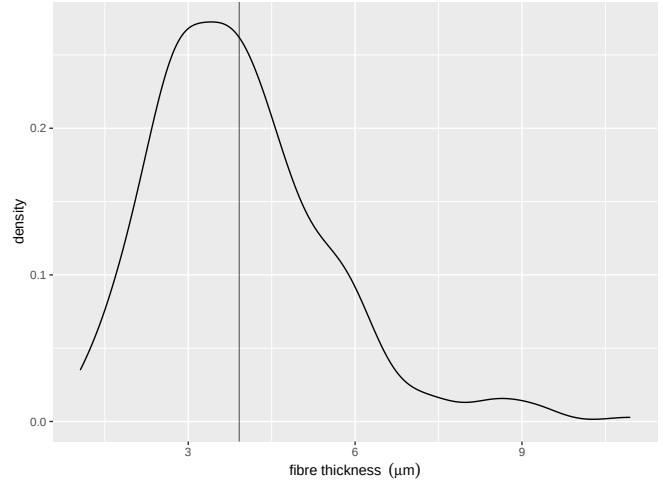


FIGURE 6 Fibre thickness distribution in the handsheets obtained by SEM in comparison to the arithmetic mean (indicated by a vertical line).

and 50 % relative humidity in a climate-controlled room before measuring the thickness z and the mass m of each handsheet.

Sheet thickness. The single-ply thickness was determined using a micrometer (FRANK-PTI GMBH, Birkenau, Germany) according to ISO 12625-3.

Fibre properties. Some morphologic properties of the fibres, namely length, width and coarseness, were measured using a MorFi fibre analyser (Techpap SAS, Grenoble, France). From a sample slice in the z -direction, the distribution of the thickness of individual fibres was evaluated using scanning electron microscopy (SEM) measurements of approximately 300 distinct fibres.

5.2 | Data

Handsheets. The experimental results for fibre thickness distribution and apparent sheet thickness are presented in Figures 6 and 7 respectively. It is evident from the observed linear relationship for the apparent sheet thickness values across the range of grammage that the data is well above the threshold grammage G_b .

Table 1 shows the experimental mean values of apparent thickness used for calibration. The correction term used to calculate intrinsic thickness is $35.79 \mu\text{m}$ and was obtained through the intercept of a weighted linear regression with weights $1/\sigma^2(z^p(G_i))$.

Fibre properties. The shape of cellulose fibres found in paper materials is essentially that of a flat ribbon. In our case fibres have a mean length (length-weighted average fibre

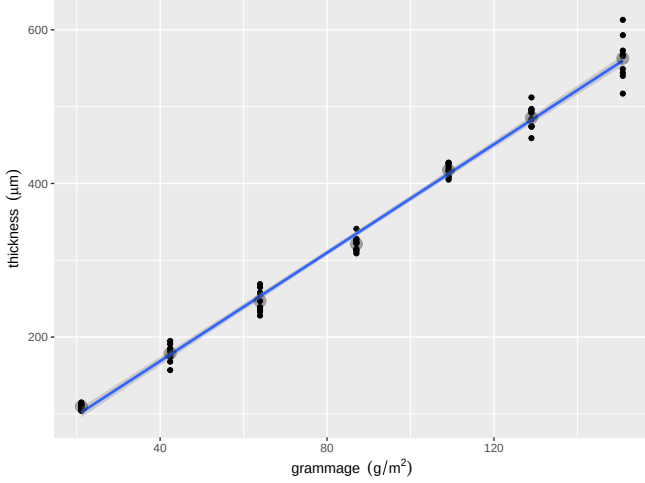


FIGURE 7 Apparent sheet thickness z^p as a function of grammage G . The black circles represent the experimental points; the larger grey circles represent the mean values for each grammage. A regression line is drawn including point-wise 0.95 confidence intervals shown as a grey band.

TABLE 1 Mean values of thickness for laboratory handsheets

Point	Grammage/ g m^{-2}	$\bar{z}^p/\mu\text{m}$	$\sigma(z^p)/\mu\text{m}$
1	21.1	110	3.79
2	42.4	179	11.2
3	63.9	247	14.4
4	87.0	321	9.47
5	109.1	417	8.04
6	129.0	486	15.4
7	150.9	563	27.4

length), mean width and mean thickness of $799 \mu\text{m}$, $18.8 \mu\text{m}$ and $3.918 \mu\text{m}$, respectively, with a coarseness (mass per unit length of fibre) of 0.0956 mg m^{-1} .

We can obtain a rough estimate of fibre density ρ_f from

$$\rho_f = \frac{a}{w^f t^f},$$

where a is the fibre coarseness and w^f is the fibre width.

5.3 | Computational setup

We recall that we assume that the fibre length distribution follows a Poisson distribution whose parameter value equals the experimental mean fibre length determined with a fibre analyser, as done by [Provatas and Uesaka \(2003\)](#). Since there is only one type of fibres, there is no need to use more than a single voxel to define the width of the ribbon in the discrete representation ($n_w^f = 1$) and, thus, the size of the square base of the

TABLE 2 Size of the deposition area for the different grammages

Point	1	2	3	4	5	6	7
$n_x^{\text{RVE}}/\text{voxel}$	326	234	193	166	143	132	122

voxels is $\Delta_{xy} = 18.8 \mu\text{m}$. The region ($n_x \times n_x$) where deposition occurs has dimensions calculated according to Equation (5) for $\epsilon_{\text{abs}} = 2 \times 10^{-4}$ and $N = 5$ (number of simulation replications) which are tabulated in Table 2. The value of $A_3 = 800 \mu\text{m}^3$ for the integral range is taken from [du Roscoat et al. \(2007\)](#), Table 4) for paper “hard”, an in-plane isotropic handsheet which is most similar to our handsheets since the remaining three “reference papers” therein are industrial samples. Evidently, this value will be only a rough approximation of the true one. Nevertheless, it allows to establish a “base case” for future investigations. The deposition parameters are set to $p = 0.1$ and $\alpha = 1$.

The advantage of using a high number of voxel layers for fibre thickness is that a higher resolution discretisation can be achieved for the computer model flexibility T^f . This is, however, done at the cost of increased computational effort. We found that a maximum of 20 layers ($U_t^f = 20$) is within an acceptable computation time with the available computational resources.

For reasons that will not be elaborated upon here, two is the minimum number of layers possible in the simulator. Therefore, $T^f/n_t^f = \frac{1}{1}$ will be replaced by the equivalent fraction $\frac{2}{2}$.

The optimiser used is the MATLAB function `fminbnd` based on golden section search and parabolic interpolation and the R package `schumaker` ([Baumann and Klymak, 2019](#)) was used for approximating the discrepancy function $\hat{\delta}(G)$.

6 | RESULTS AND DISCUSSION

The validity of the proposed calibration procedure is assessed by a leave-one-out cross-validation analysis (LOOCV). We first address the question if the imposed values for ϵ_{abs} and N allow the discrimination between consecutive terms of the Farey fractions in the vicinity of the optimal point. We take advantage of the fact that the optimisation search on the real line may sometimes incur in the repeated evaluation of the optimal fraction and some of its neighbours as depicted in Figure 8; the comparison of the values of $g_N(\cdot)$ will serve as a first step towards a formal approach.

We can observe from Figure 8 that notwithstanding the very flat objective function around the optimum, the repetitions are basically indistinguishable with respect to the value of $g_N(\cdot)$ for the vast majority of the depicted panels (box leave-out point 4 and 6 being the exception). Thus the fixed values of ϵ_{abs} and N

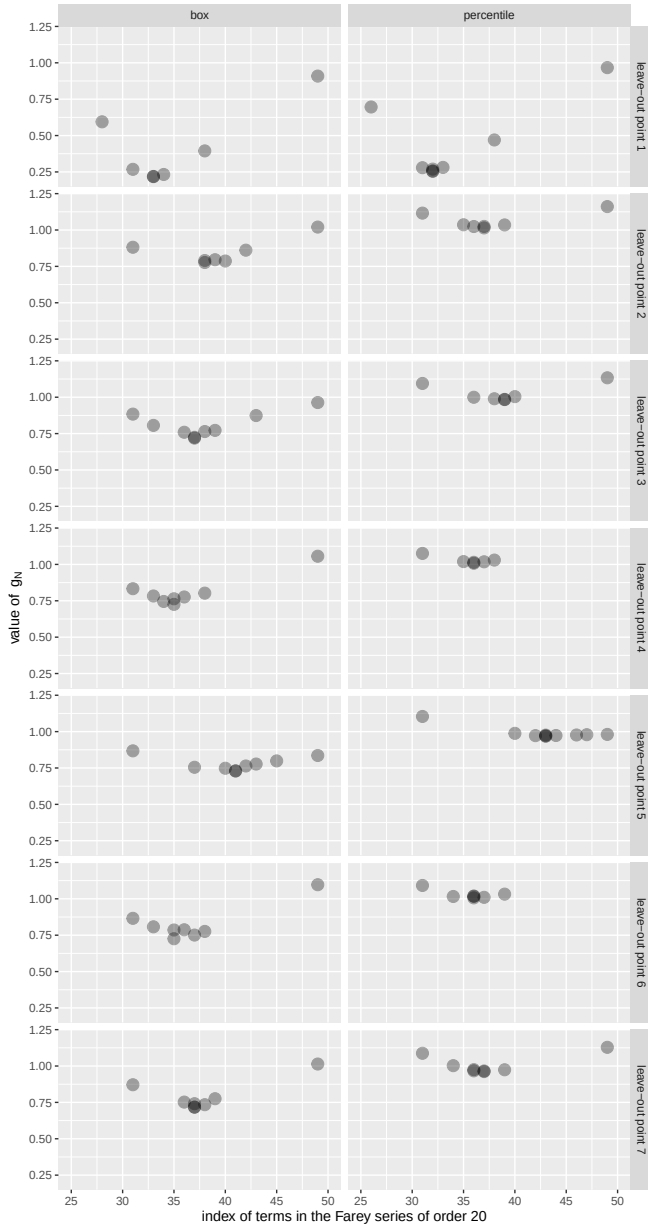


FIGURE 8 Subset of the fractions T^f/n_t^f searched by the optimiser `fminbnd`. The repetitions (semi-transparent circles with darker zones) allow a first rough evaluation of the discrimination power of the values chosen for ϵ_{abs} and N regarding the value of g_N .

may be taken as adequate. The results for the seven splits of LOOCV are shown in Table 3.

Next, we will examine the accuracy of the predictions of the computer model with the obtained parameters in LOOCV by comparison with experimental data, as exhibited in Figure 9. A few observations can be made from these results:

(a) The model predictions are always greater for the “box” approach.

TABLE 3 LOOCV estimates of T^f/n_t^f

Leave-out point	box		percentile	
	index in $\mathcal{F}_{20}$	$\widehat{T^f/n_t^f}$	$\widehat{T^f/n_t^f}$	index in $\mathcal{F}_{20}$
1	33	$\frac{4}{15}$	$\frac{5}{19}$	32
2	38	$\frac{3}{10}$	$\frac{5}{17}$	37
3	37	$\frac{5}{17}^\dagger$	$\frac{4}{13}^\dagger$	39
4	35	$\frac{5}{18}$	$\frac{2}{7}$	36
5	41	$\frac{6}{19}$	$\frac{7}{20}$	43
6	35	$\frac{5}{18}$	$\frac{2}{7}$	36
7	37	$\frac{5}{17}^\dagger$	$\frac{5}{17}$	37

† full-data estimate

- (b) The computer model reproduces fairly well the intrinsic thickness with an advantage to the “box” approach.
- (c) The correction made by the discrepancy function provides a good combined prediction of the (biased) experimental data.

Wong et al. (2017) recommended caution when using their method in extrapolation, especially if $\hat{\delta}(\cdot)$ is large. In order to better address this point, the discrepancy functions for all seven cross-validation cases are displayed in Figure 10. Note that an extrapolation is made to the lowest grammage for leave-out point 1 and another one to the highest grammage for leave-out point 7. Considering that measurements overestimate the thickness by about 35 μm , we find that these corrections of acceptable magnitude relative to the corresponding sheet thickness for the “box” method, but less so for the “percentile” approach.

6.1 | Concluding remarks

The approach described in this article tackles a problem of calibration with the minimum of formality when dealing with a scenario where only conventional measurements of sheet thickness and grammage are available. Of special note is that our results show that it is preferable to use the “box” method for determining the thickness of a simulated paper sheet. Here, the same data has been used for calibration and model validation via LOOCV. Subsequent steps in the validation process with other evaluation criteria—a notable one being the comparison of the simulated microstructure to 3D image data—are needed to provide guidance “about when and how the model should be used in prediction” (Bayarri et al., 2007).

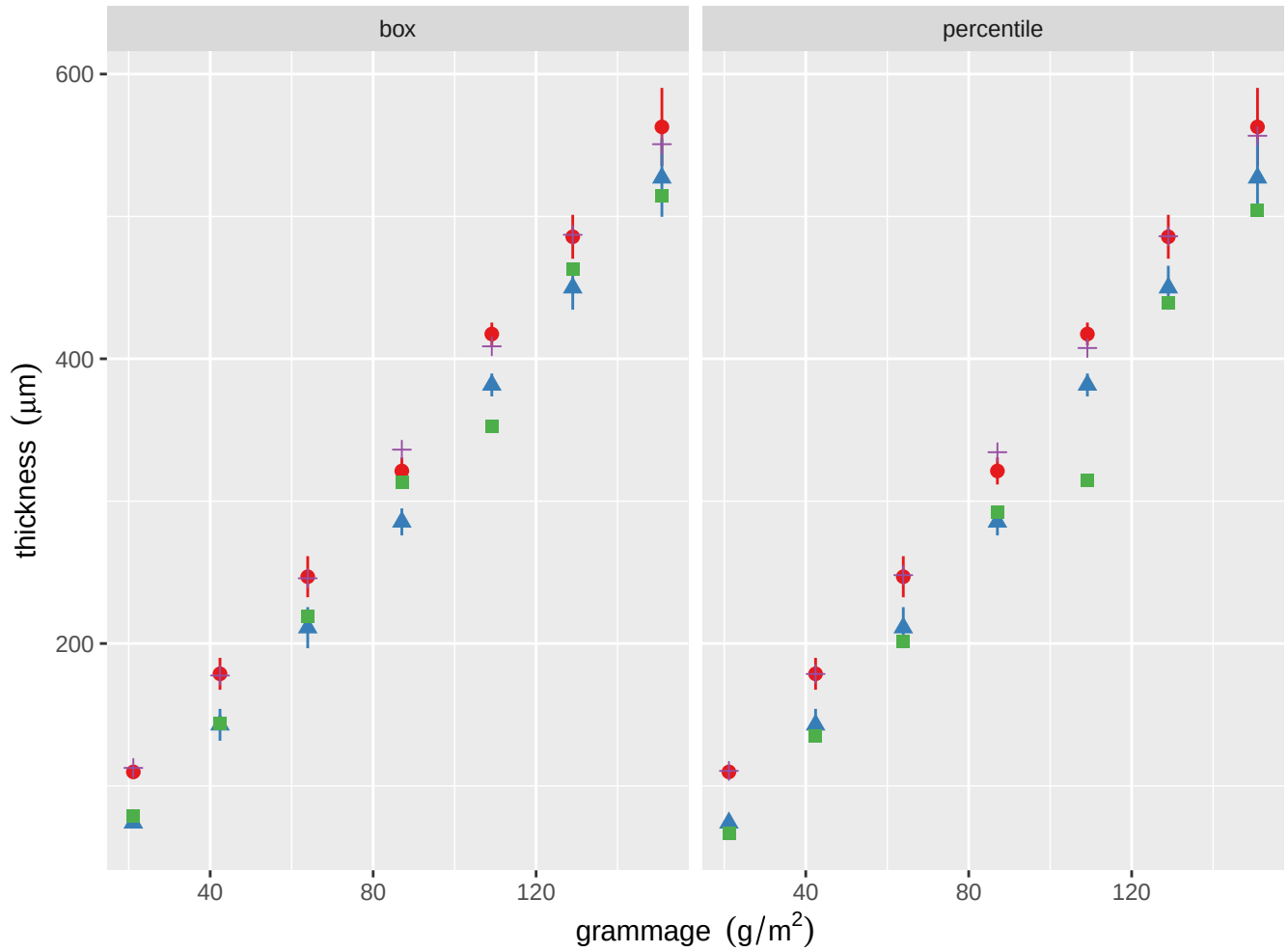


FIGURE 9 Comparison of model prediction with (+) and without ($\square$) bias correction discrepancy function $\hat{\delta}(G)$ and experimental data ($\circ$) expressed as the mean plus/minus the standard deviation of the measurements indicated with an error bar along with intrinsic thickness ($\triangle$). Each single point was excluded in turn from the experimental dataset and a calibration was carried out on the remaining six points. Then, the estimate obtained for T^f/n_l^f was used for prediction at the excluded point.

A measure of the uncertainty for $\widehat{T^f/n_l^f}$ and $\hat{\delta}(G)$ is needed. A crude assessment might be made by looking at the variability of the LOOCV estimates. The inferential issues are quite challenging because the approach combines a *stochastic* computer model, a *discrete* model parameter, *quantile* regression, and minimises a *scale* measure of the residuals. The possibility of using bootstrap (Wehrens et al., 2000) as pointed out in Wong et al. (2017) for a computer simulation model of moderate computational expense such as the one used here will be explored in future research.

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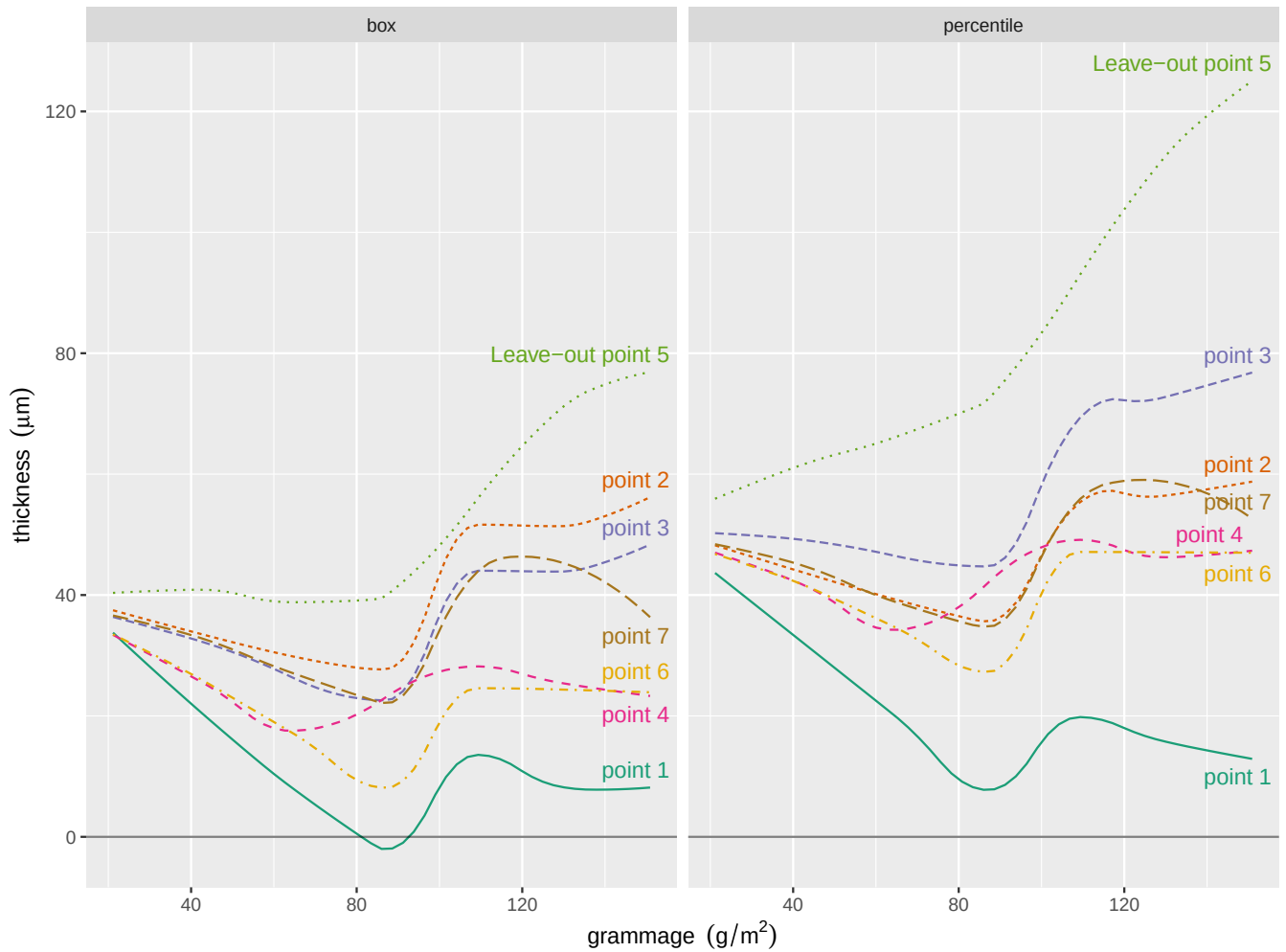


FIGURE 10 Discrepancy functions $\hat{\delta}(G)$ in the cross-validation cases.

SUPPORTING INFORMATION

The simulator, named voxelfiber, is open source software and the code is available on GitHub: <https://github.com/eduardotrinciaoconceicao/voxelfiber>.

Moreover, the following supporting information is available on GitHub: <https://github.com/eduardotrinciaoconceicao/calibration-for-tissue-paper> as part of the online article:

`exptdata+figs-supinfo.R` An R script containing the experimental raw datasets and code used to generate the associated figures [6](#) and [7](#) in the published paper.

`calibration_supinfo.m` A MATLAB script with the implementation of the calibration technique.

`thicknessdist_supinfo.m` A MATLAB script with the code for computing the local sheet thickness for simulated sheets of different grammages.

`discrepancy+figs-supinfo.R` An R script implementing the calculation of the discrepancy function and the analysis code used to generate figures [4](#), [5](#), [8](#), [9](#) and [10](#) in the published paper.

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