LIDIANE COSTA LIMA

DEVELOPMENT OF KRAFT PAPER REINFORCED WITH BLEACHED CELLULOSIC NANOFIBRILS FOR APPLICATION IN PACKAGING

LAVRAS–MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-graduação em Ciência e Tecnologia da Madeira, área de concentração Madeira como Matéria-prima, para a obtenção do título de Doutor.

Profa. Dra. Maria Lúcia Bianchi
Orientadora

Prof. Dr. Gustavo Henrique Denzin Tonoli
Prof. Dr. Paulo Ricardo Gherardi Hein
Coorientadores

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LIDIANE COSTA LIMA

DESENVOLVIMENTO DE PAPEL KRAFT REFORÇADO COM NANOFIBRILAS CELULÓSICAS BRANQUEADAS PARA APLICAÇÃO EM EMBALAGENS

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Dra. Maria Lúcia Bianchi	UFLA
Dr. Paulo Fernando Trugilho	UFLA
Dr. José Benedito Guimarães Júnior	UFLA
Dra. Franciane Pinheiro Cardoso Campos	UFLA
Dr. Mário Guimarães Júnior	CEFET-MG

_____
Profa. Dra. Maria Lúcia Bianchi
Orientadora

Prof. Dr. Gustavo Henrique Denzin Tonoli
Prof. Dr. Paulo Ricardo Gherardi Hein
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À minha mãe Maria Grassidnei (sempre presente), ao meu pai Benedito, à minha irmã Dayanne e aos queridos amigos, que permaneceram comigo ao longo do caminho.

Dedico

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RESUMO

O primeiro estudo teve como objetivo estabelecer a contribuição física e mecânica das nanofibrilas celulósicas para a resistência dos papéis para embalagem, determinar a interação das nanofibrilas com a matriz fibrosa e seu potencial para permitir a redução da gramatura sem redução da resistência do papel. Folhas de papel foram preparadas misturando fibras de eucalipto não-branqueadas e nanofibrilas de celulose produzidas via desfibrilação mecânica, seguindo os passos: homogeneização, filtragem a vácuo, prensagem e secagem à temperatura ambiente. Os doze tratamentos resultantes da combinação das gramaturas finais 75, 85, 95 e 105 g/m² com as concentrações de nanofibrilas de 1, 5 e 10% em massa foram analisados para determinar propriedades físicas e mecânicas do papel, juntamente com imagens FEG-SEM para investigar a formação da folha e acomodação das nanofibrilas dentro do papel. As micrografias mostraram a formação de nanofilmes e a agregação entre nanofibrilas e fibras/microfibras dentro do papel, causando redução na porosidade e aumento na resistência à passagem do ar do papel. O reforço das nanofibrilas contribuiu para a melhora de todas as propriedades analisadas, com exceção do teste de compressão em ondas, influenciado apenas pela gramatura, da permeabilidade ao vapor d'água e da taxa de transmissão de vapor d'água. Resistência à passagem do ar, índice de tração, alongamento e módulo de elasticidade destacaram-se por seu aumento ser responsabilidade apenas das nanofibrilas de celulose, sem influência da gramatura, comprovando a eficácia das nanofibrilas de celulose em potencializar as propriedades do papel mesmo com redução de gramatura. O segundo estudo teve como objetivo investigar a capacidade da espectroscopia no infravermelho próximo para estimar o conteúdo de nanofibrilas, as propriedades físicas e mecânicas dos papéis. Análise de componentes principais (PCA), mínimos quadrados parciais (PLS) e análise discriminante de mínimos quadrados parciais, baseadas em informações laboratoriais e espectrais foram utilizadas. Na PCA não houve separação entre amostras relacionada ao conteúdo de nanofibrilas. A PLS gerou modelos para concentração de nanofibrilas, índice de tração, alongamento e resistência à passagem de ar com R^2cv de 0,73 a 0,98, indicando que a técnica NIRS é adequada para predizer propriedades físicas e mecânicas de papéis para embalagem e pode detectar a presença de nanofibras celulósicas no papel. Os modelos de PLS-DA classificaram corretamente mais de 98% das amostras em relação ao conteúdo de nanofibrilas.

Palavras-chave: Nanocelulose. Resistência mecânica. Espectroscopia no infravermelho próximo.

ABSTRACT

The first study aimed to establish physical and mechanical contribution of cellulose nanofibrils to the resistance of packaging papers, determine nanofibrils interaction with the fibrous matrix and its potential to allow grammage reduction without paper resistance downsizing. Paper sheets were prepared by mixing unbleached Eucalyptus fibers and cellulose nanofibrils from mechanical defibrillation, following the standardized steps: homogenizing, vacuum filtration, pressing and room temperature drying. The twelve treatments resultants from the combination of the final grammages 75, 85, 95 and 105 g/m² with the nanofibril concentrations of 1, 5 and 10 wt% were analyzed to determine physical and mechanical properties, along with FEG-SEM images to investigate paper formation and nanofibrils accommodation within the paper. Micrographs showed the formation of nanofilms and aggregations between nanofibrils and fibers/microfibers within the paper, causing reduction in paper porosity and consequent increase in resistance to air passage. Results showed that nanofibrils reinforcement contribute to enhance all properties analyzed, except for corrugating medium test, only influenced by grammage, water vapor permeability and water vapor transmission rate, that presented no tendency. Resistance to air passage, tensile index, stretch and modulus of elasticity stand out for improvements being result only of the cellulose nanofibril reinforcement, with no influence of grammage, proving the effectiveness of cellulose nanofibrils to enhance barrier properties and mechanical resistance even with grammage reduction. The second study aimed to investigate near infrared spectroscopy capability to estimate nanofibrils content, physical and mechanical properties of packaging papers reinforced with cellulose nanofibrils. Principal component analysis (PCA), partial least squares (PLS) and partial least squares discriminant analysis (PLS-DA) based on laboratorial and spectral information were utilized. At PCA there was no separation between specimens related to nanofibril content. PLS generated models for nanofibrils content, tensile index, stretch and resistance to air passage with R^2cv range from 0.73 to 0.98, indicating that NIRS technique is suitable for predicting physical and mechanical properties of packaging papers and can detect cellulose nanofibril into the paper matrix. PLS-DA models correctly classify more than 98% of the samples according to nanofibril content.

Keywords: Nanocellulose. Mechanical resistance. Near infrared spectroscopy.

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PRIMEIRA PARTE

1 INTRODUCTION

The rising concern of the population about the environment has sent researchers and several industry segments in a search for recyclable, biodegradable and renewable materials, as well as more efficient, economically reasonable and less polluting production methods, avoiding wastes and a ensuring the production of quality goods.

The pulp and paper industry has great importance to the world's economy and large investments, technology and studies are devoted to find new raw materials, innovative techniques of growth, harvest, pulping and quality control.

With the advent of the use of nanoscale materials, many studies were developed using this technology in pulp, papers and paperboards, aiming to improve characteristics such as mechanical resistance, permeability, antimicrobial and barrier properties, hydrophobicity, printability and durability.

Among nanomaterials, cellulose nanofibrils stand out for its biodegradability, biocompatibility, renewability, barrier properties, dimensional stability, high specific strength and stiffness associated with low weight, high reinforcing potential, high specific surface area and high aspect ratio.

Packaging are a segment of paper industry that looks for higher mechanical strengths and better barrier properties, in order to guarantee the integrity of the product storage in it, which made cellulose nanofibrils an excellent application alternative to improve both properties.

Although many studies involving paper and cellulose nanofibrils has been developed, the consequences of the reduction in paper grammage associated with nanofibril reinforcement to the physical, mechanical and barrier properties of packaging papers is still little approached. To which point it is possible to reduce paper grammage and add cellulose nanofibrils without occasioning resistance / barrier properties loss? This is the subject matter addressed in the first article.

Since the first study investigates the paper raw material, the second study addresses paper quality assessment methods, which are time consuming and expensive activities, with each property measured frequently requiring a specific instrument and sample preparation, highlighting the necessity to find alternatives to fast and reliable measurements at a low cost.

The near infrared spectroscopy (NIRS) is a fast, non-destructive, non-invasive, minimum sample preparation technique that aims to examine a sample in order to acquire qualitative/quantitative information by measuring the interaction between near infrared electromagnetic waves and the chemical bonds of the material constituents.

The NIRS technique is applied to the pulp and paper segment since 1980, in studies involving pulp yield, cellulose content, lignin content and fiber morphology. The technique was also used to determine non-chemical properties of wood, such as density, mechanical strength and microfibril angle, which is possible because the expression of these properties is influenced by the chemical composition of the wood.

Starting from the same principle, the NIRS technique has been applied in a feel studies to determine physical and mechanical properties of papers, with different degrees of success. However, little is known about NIRS capability to predict the cellulose nanofibril content in a blend, which motivated the second study.

The objectives of this study was to establish physical and mechanical contribution of cellulose nanofibrils to the resistance of packaging papers, to determine nanofibrils interaction with the fibrous matrix and its potential to allow grammage reduction without resistance downsizing, to investigate near infrared spectroscopy capability to estimate nanofibrils content, physical and mechanical properties of packaging papers reinforced with cellulose nanofibrils.

2 THEORETICAL REFERENCE

2.1 Cellulose

Cellulose is a linear polysaccharide whose repeating unit is called cellobiose (MCNAMARA; MORGAN; ZIMMER, 2015) and is composed of D-anhydroglucopyranose units linked by β-(1-4)-glycosidic bonds (QIU; HU, 2013). Individual cellulose chains tend to aggregate and form microfibrils. The numerous hydroxyl groups present in the molecule form intra and intermolecular hydrogen bonds, resulting in the crystallization of multiple cellulose chains into insoluble microfibrils and in the formation of two structural regions: crystalline and amorphous (SHAGHALEH; XU; WANGA, 2018).

The complex structure, arrangement and composition of cellulose is responsible for the characteristics and properties that makes this polymer suitable for numerous applications. The presence of crystalline and amorphous regions in the cellulose results in characteristics such as high strength, stiffness, durability, and biocompatibility (LAVOINE et al., 2012). The three

high reactive hydroxyl groups in each monomeric unit is responsible for cellulose properties such as hydrophilicity, biodegradability (KLEMM et al., 2005) and possibility to create cellulose derivatives through chemical modification (SHAGHALEH; XU; WANGA, 2018).

Another possibility for cellulose is to be isolated in fibers at nanoescale, which can be obtained by various isolation methods and from a range of lignocellulosic sources.

2.1.1 Cellulose nanofibrils

In the literature the most commonly used materials for the generation of cellulose nanostructures are commercial bleached Kraft pulps from softwoods and/or hardwoods (TONOLI et al., 2012, VIANA, 2013). However, several studies in the literature have demonstrated the potential of other vegetable sources for this purpose, such as Amazonian woods (BUFALINO et al., 2015), rice fiber and potato tubers (ABE; YANO, 2009), banana fibers (ELANTHIKKAL et al., 2010), wheat (ALEMDAR; SAIN, 2008), pineapple (CHERIAN et al., 2010), kenaf (KARGARZADEH et al., 2012), sugarcane bagasse (GILFILLAN; MOGHADDAM; DOHERTY, 2014), among others.

When choosing raw materials without any kind of chemical or mechanical treatment, in detriment of commercial pulps, one of the most important steps in the production of cellulose nanostructures is the removal of lignin, extractives and hemicelluloses from the cell wall of the material, since these materials hinder the dissociation of the cellular elements and increase the energy expenditure during the process (GUIMARÃES et al., 2008a; MORÁN et al., 2008). Some of the most commonly used methods for removal of these unwanted components are alkaline treatment, mercerizing, pulping, oxidation and bleaching (PHONG et al., 2013).

After pretreating the chosen raw material, two different types of nanomaterials can be obtained from cellulose in a top-down approach: nanocrystals and nanofibrils (SHAGHALEH; XU; WANGA, 2018), the first one containing only crystalline regions and the second containing both crystalline and amorphous regions. Cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) differ in terms of their structures and obtaining processes, and can generally be separated from a cellulose source by mechanical, chemical, a combination of mechanical and chemical or enzymatic processes (MOON et al., 2011).

In the chemical methods, partial hydrolysis of the cellulose chains occurs, beginning in the amorphous regions, due to their greater chemical accessibility. The process results in the formation of purely crystalline structures, CNCs (SIQUEIRA; BRAS; DUFRESNE, 2009; TONOLI et al., 2012).

Between mechanical methods, the mechanical defibrillation uses a microfibrillator grinder, whose mechanism consists in the breaking of hydrogen bonds by means of shear forces, to cause the individualization of bundles of microfibrils of the cell wall structure (SIRÓ; PLACKETT, 2010). This procedure result in nanostructures containing crystalline and amorphous regions, CNFs.

Cellulose nanoparticles have a wide range of potential applications, in several areas, due to their low density, biodegradability, high contact surface, high aspect ratio, high strength and stiffness, reinforcing properties and diameter below the visible light lengths, that allows obtaining transparent materials (BESBES et al., 2011; SHAGHALEH; XU; WANGA, 2018).

2.2 Pulp and paper industry

In Brazil, the area of planted tress for industrial purposes totaled 7.84 million hectares in 2016, with the pulp and paper industry accounting for 34% of this value (IBÁ, 2017).

Brazilian pulp production in 2016 totaled 18.8 million tons, 8% superior to the previous year, bringing Brazil to the position of world's second largest pulp producer. On the other hand, the country paper production in 2016 totaled 10.3 million tons, 0.2% lower than in 2015, probably related to 0.3% retraction of domestic sales. Even so, in 2016 Brazil rose one position, occupying the eighth position in the rankings of the world’s largest paper producers (IBÁ, 2017), which represents a great incentive for industries and researches to invest in studies aiming improvements in quality, from planting to paper production.

2.2.1 Paper

Because it is a biodegradable and environmentally safe material, paper is widely used in the world. The paper is composed of long cellulose chains in the amorphous and crystalline state. The hydrophilic nature of the cellulose is result of the presence of hydroxyl groups in its basic unit ($C_6H_{12}O_6$) and of the fibers porosity, which limit the barrier properties to water vapor, making it necessary for paper to be associated with other materials, such as plastic resins and metals, which can improve several of their properties (KHWALDIA; ARAB-TEHRANY; DESOBRY, 2010).

Polyphenols films are generally associated with paper to improve their barrier properties, but unfortunately, this leads to the loss of their biodegradability and makes recycling

difficult, becoming a negative point in the production of polymers (KHWALDIA; ARAB-TEHRANY; DESOBRY, 2010).

Materials for packaging based on biopolymers from natural sources such as lignocellulosic materials, proteins, resins and lipids offer environmental advantages and are presented as an alternative to the use of synthetic polymers originating from petroleum (KHWALDIA; ARAB-TEHRANY; DESOBRY, 2010).

2.2.2 Packaging paper

The most restrictive properties for the use of packaging papers are high tensile energy absorption (TEA) and relatively low resistance to air passage, because these characteristics allow the paper to withstand impact stress during the bagging process. The high-consistency refinement technique (HCR) is used to treat Kraft pulp fibers, as it induces microcompression and bending in the fibers, improving sheet stretching and increasing tensile and air resistance moderately (SHALLHORN; GURNAGUL, 2010).

2.3 Near Infrared Spectroscopy and the paper

NIRS is a technique based on vibrational spectroscopy, which measures the interaction of light with the material. The technique measures the interaction of radiation (absorption, transmission or reflection) with the chemical bonds of the sample constituents (PASQUINI, 2003).

Infrared radiation is emitted by the equipment in a wavelength ranging from 750 to 2500 ηm (13000 to 4000 cm^{-1}) and is able to interact with the material functional groups, mainly C-H, N-H, S-H or O-H bonds (PASQUINI, 2003). Each material presents a peculiar response of absorbance, reflectance and transmittance, often called spectral signature.

The analysis of spectral information and the development of predictive models based on spectra are possible with the use of multivariate data analysis techniques. Two sets of information are correlated: the matrix of spectral information (obtained in the spectrometer) and the information matrix of the sample properties, which are determined by conventional methods (HEIN, 2008).

One of the objectives of the pulp and paper industry is to obtain a fast and reliable characterization of its raw materials and products. The near infrared spectroscopy (NIRS), with

the aid of multivariate data analysis or chemometrics, has demonstrated great potential to supply this necessity (TSUCHIKAWA; SCHWANNINGER, 2013).

Since then the NIRS technique has been used in several studies to predict the kappa number (ALVES et al., 2007; MONRROY et al., 2008; YANG; HE; SONG, 2008), monitor the residual lignin content (MONRROY et al., 2008), determine the yield of delignification (PU et al., 2008), estimate the yield of bleachable cellulose (WHITE et al., 2009), estimate the chemical properties of the pulp (KIPUPUTWA; GRZESKOWIAK; LOUW, 2010), identify different types of paper (RIBA et al., 2011) and determine Kraft papers resistance to bursting, tearing, tension and compression (SAMISTRARO et al., 2009).

REFERENCES

ALEMDAR, A.; SAIN, M. Isolation and characterization of nanofibers from agricultural residues - Wheat straw and soy hulls. **Bioresource Technology**, Essex, v. 99, n. 6, p. 1664-1671, 2008.

ALVES, A. et al. NIR PLSR model selection for Kappa number prediction of maritime pine Kraft pulps. **Wood Science and Technology**, v. 41, n. 6, p. 491–499, 2007.

BESBES, I.; VILAR, M. R.; BOUFI, S. Nanofibrillated cellulose from alfa, eucalyptus and pine fibres: preparation, characteristics and reinforcing potencial. **Carbohydrate Polymers**, Barking, v. 86, n. 3, p. 1198-1206, 2011.

BUFALINO, L. et al. Nanocellulose films from amazon forest wood wastes: structural and thermal properties. **Key Engineering Materials**, v. 668, p. 110-117, 2015.

CHERIAN, B. M. et al. Isolation of nanocellulose from pineapple leaf fibres by steam explosion. **Carbohydrate Polymers**, v. 81, p. 720–725, 2010.

ELANTHIKKAL, S. et al. Cellulose microfibres produced from banana plant wastes: Isolation and characterization. **Carbohydrate Polymers**, Barking, v. 80, n. 3, p. 852-859, 2010.

GILFILLAN, W. N.; MOGHADDAM, L.; DOHERTY, W. O. S. Preparation and characterization of composites from starch with sugarcane bagasse nanofibres. **Cellulose**, v. 21, p. 2695–2712, 2014.

HEIN, P. R. G. **Avaliação das propriedades da madeira de *Eucalyptus urophylla* por meio da espectroscopia no infravermelho próximo**. 2008. 75 p. Dissertação (Mestrado em Ciência e Tecnologia da Madeira) – Universidade Federal de Lavras, Lavras, 2008.

INDÚSTRIA BRASILEIRA DE ÁRVORES - IBÁ. 2017. **Relatório anual 2017**. São Paulo, Brasília, 2017. 80 p.

KARGARZADEH, H. et al. Effects of hydrolysis conditions on the morphology, crystallinity, and thermal stability of cellulose nanocrystals extracted from kenaf bast fibers. **Cellulose**, v. 19, p. 855–866, 2012.

KHWALDIA, K.; ARAB-TEHRANY, E.; DESOBRY, S. Biopolymer coatings on paper packaging materials. **Comprehensive reviews in food science and food safety**, Chicago, v. 9, p. 82 -91, 2010.

KIPUPUTWA, C.; GRZESKOWIAK, V.; LOUW, J. H. The use of near-infrared scanning for the prediction of pulp yield and chemical properties of *Pinus patula* in the Mpumalanga escarpment area of South Africa. **Southern Forests**, v. 72, n.3, p. 181–189, 2010.

KLEMM, D. Cellulose: fascinating biopolymer and sustainable raw material. **Angewandte Chemie International Edition**, v. 44, p. 3358–3393, 2005.

LAVOINE, N. et al. Microfibrillated cellulose - its barrier properties and applications in cellulosic materials: a review. **Carbohydrate Polymers**, v. 90, n. 2, p. 735–764, 2012.

MCNAMARA, J. T.; MORGAN, J. L. W.; ZIMMER, J. A molecular description of cellulose biosynthesis. **Annual Review of Biochemistry**, v. 84, p. 895–921, 2015.

MONRROY, M. et al. Estimation of hexenuronic acids and kappa number in Kraft pulps of *Eucalyptus globulus* by Fourier transform near infrared spectroscopy and multivariate analysis. **Journal of Near Infrared Spectroscopy**, v. 16, n. 2, p. 121–128, 2008.

MOON, J. et al. Cellulose nanomaterials review: structure, properties and nanocomposites. **Chemical Society Reviews**, v. 40, n. 7, p. 3941–3994, 2011.

MÓRAN, J. I. et al. Extraction of cellulose and preparation of nanocellulose from sisal fibers. **Cellulose**, Bucharest, v. 15, n. 1, p. 149-159, 2008.

PASQUINI, C. Near infrared spectroscopy: fundamentals, practical aspects and analytical applications. **Journal of the Brazilian Chemical Society**, v. 14, n. 2, p. 198-219, 2003.

PHONG, N. T. et al. Enhancement of mechanical properties of carbon fabric/epoxy using micro/nanosized bamboo fibrils. **Materials & Design**, v. 47, p. 624-632, 2013.

QIU, X.; HU, S. "Smart" materials based on cellulose: a review of the preparations, properties, and applications. **Materials**, v. 6, p. 738–781, 2013.

RIBA, J. R. et al. Potential of infrared spectroscopy in combination with extended canonical variate analysis for identifying different paper types. **Measurement Science and Technology**, v. 22, n. 2, 2011.

SAMISTRARO, G. et al. Previsão das propriedades físicas do papel Kraft por espectroscopia no infravermelho próximo (NIR) e regressão por mínimos quadrados parciais (PLS). **Química Nova**, São Paulo, v.32, n.6, p.1422-1425, 2009.

SHAGHALEH, H.; XU, X.; WANGA, S. Current progress in production of biopolymeric materials based on cellulose, cellulose nanofibers, and cellulose derivatives. **RSC Advances**, v. 8, p. 825-842, 2018.

SHALLHORN, P.; GURNAGUL, N. A semi-empirical model of the tensile energy absorption of sack Kraft paper. **BioResources**, v. 5, n. 1, p. 455-476, 2010.

SIQUEIRA, G.; BRAS, J.; DUFRESNE, A. Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. **Biomacromolecules**, v. 10, p. 425–432, 2009.

SIRÓ, I.; PLACKETT, D. Microfibrillated cellulose and new composite materials: a review. **Cellulose**, Bucharest, v. 17, n. 3, p. 459-464, 2010.

TONOLI, G. H. D. et al. Cellulose micro/nanofibres from *Eucalyptus* Kraft pulp: Preparation and properties. **Carbohydrate polymers**, v. 89, p. 80–88, 2012.

TSUCHIKAWA, S.; SCHWANNINGER, M. A review of recent near-infrared research for wood and paper (Part 2). **Applied Spectroscopy Reviews**, v. 48, n. 7, p. 560-587, 2013.

VIANA, L. C. **Desenvolvimento de filmes celulósicos nanoestruturados a partir de fibras de *Pinus* sp**. 2013. 124 p. Tese (Doutorado em Engenharia Florestal) – Universidade Federal do Paraná, Curitiba, 2013.

WHITE, D. E. et al. Effects of specific gravity and wood chemical content on the pulp yield of loblolly pine. **TAPPI Journal**, v. 8, n. 4, p. 31–36, 2009.

YANG, C. J.; HE, C.; SONG, Z. H. The online measurement for pulp kappa number based on near infrared spectroscopy and support vector machine. **Spectroscopy and Spectral Analysis**, v. 28, n. 8, p. 1795–1798, 2008.

SEGUNDA PARTE - ARTIGOS

ARTIGO 1 - INFLUENCE OF CELLULOSE NANOFIBRILS ON PACKAGING PAPERS RESISTANCE

Lidiane Costa Lima, Taiane Oliveira Guedes, Maria Lúcia Bianchi, Lisiane Nunes Hugen, Luiz Eduardo Silva, Pedro Ivo Cunha Claro, Gustavo Henrique Denzin Tonoli

Abstract: The aim of this study was to establish physical and mechanical contribution of cellulose nanofibrils to the resistance of packaging papers, determine nanofibrils interaction with the fibrous matrix and its potential to allow grammage reduction without resistance downsizing. Paper sheets were prepared by mixing unbleached Eucalyptus fibers and cellulose nanofibrils from mechanical defibrillation, following the standardized steps: homogenizing, vacuum filtration, pressing and room temperature drying. The twelve treatments resultants from the combination of the final grammages 75, 85, 95 and 105 g/m² with the nanofibril concentrations of 1, 5 and 10 wt% were analyzed to determine physical and mechanical properties, along with FEG-SEM images to investigate paper formation and nanofibrils accommodation within the paper. Micrographs showed the formation of nanofilms and aggregations between nanofibrils and fibers/microfibers within the paper, causing reduction in paper porosity and consequent increase in resistance to air passage. Results showed that nanofibrils reinforcement contribute to enhance all properties analyzed, except for corrugating medium test, only influenced by grammage, water vapor permeability and water vapor transmission rate, that presented no pattern. Resistance to air passage, tensile index, stretch and modulus of elasticity stand out for improvements being result only of the cellulose nanofibril reinforcement, with no influence of grammage, proving the effectiveness of cellulose nanofibrils to enhance physical and mechanical resistance of paper, even with grammage reduction.

Keywords: Nanocellulose; Mechanical resistance; Bag paper; Kraft paper.

1 INTRODUCTION

Paper is a widely used material, basically composed of cellulose and present in many industries due to their high strength, flexibility, printability, low cost and recyclability (AFRA;

MOHAMMADNEJAD; SARAEYAN, 2016; SAMYN et al., 2018). Paper substrates have a complex structure, present both inside and on its surface, which allows modifications and improvement on their properties. This technology is explored, between others, by the packaging industries, to guarantee the preservation and protection of the good packed, that must reach the consumer without compromising the product quality (EL-SAMAHYA et al., 2017).

Conventionally, paper is reinforced and coated with numerous synthetic or non-organic substances and polymers, such as kaolin, carbonated calcium and polyethylene, resulting in materials that are unlikely to be recycled, do not biodegrade quickly and can lead to environmental pollution, which result in the need to find and improve natural and eco-friendly substances to replace conventional materials (AFRA; MOHAMMADNEJAD; SARAEYAN, 2016).

Among bio-based substances, cellulose nanofibrils (CNF) from several types of raw materials has been shown to improve properties of composites and papers when used as a reinforcing agent within the paper and in wet-end applications (BRODIN; GREGERSEN; SYVERUD, 2014), due to the higher specific surface area of cellulose nanofibrils (100-500 m^2/g) compared to cellulose fibers (1-3 m^2/g), which allows the potential properties of cellulose to be achieved (AFRA et al., 2013).

The advantages of the cellulose nanostructures application is attributed to properties like its biodegradability, biocompatibility, renewability, barrier properties, dimensional stability, high specific strength and stiffness associated with low weight, high reinforcing potential, high specific surface area and high aspect ratio (EICHHORN et al., 2010; SIRÓ; PLACKETT, 2010).

Turbak, Snyder and Sandberg published the first study suggesting that cellulose nanofibrils could be used in foods, paints, cosmetics and pharmaceutical products in 1983, since then numerous studies have been developed using CNFs. In the paper improvement field, researches have been made about special functions of paper, such as transparency (ZHU et al., 2014), barrier properties (MIRMEHDI et al., 2018), water repellency (OGIHARA et al., 2012), antimicrobial activity (MARTINS et al., 2012), electrical and thermal conductivity (ANDERSON et al., 2010).

According to Samyn et al. (2018), one of the reasons to apply cellulose nanofibrils in papermaking is to achieve a more efficient use of resources, producing stronger papers with lower grammages, which contemplates the purpose of this study. Osong et al. (2015) stated the importance to implement the use of nanofibrillated cellulose as a strength additive in paper and

board products, once it lends to paper its inherent high strength and stiffness, and its high specific surface area enhance the bond between fibers, by forming fibrillar entanglement.

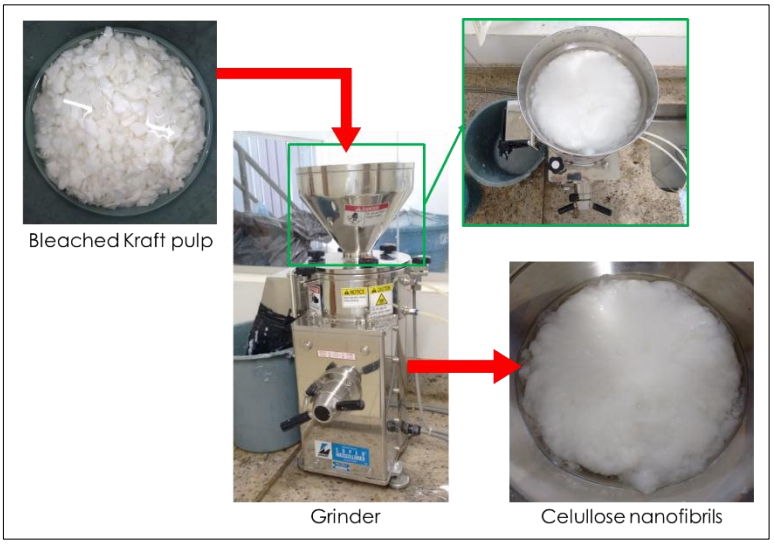
The aim of this study was to establish physical and mechanical contributions of cellulose nanofibrils to the resistance of packaging papers, determine nanofibrils interaction with the fibrous matrix and its potential to allow grammage reduction without resistance downsizing.

2 METHODOLOGY

2.1 Nanofibrils production

Cellulose nanofibrils were obtained from bleached Kraft pulp of eucalyptus (Klabin SA), through mechanical defibrillation. The pulp was soaked overnight in deionized water, disintegrated in a mechanical stirrer (Fisatom 722) and defibrillated in a Masuko Supermascoloider grinder (MKCA-2J, Masuko Sangyo Ltd.), with rotation of 1500 rpm, pulp concentration of 2% (w/v) and 30 cycles. Figure 1 presents the equipment used in this process.

Figure 1 - Bleached eucalyptus Kraft pulp mechanical defibrillation.

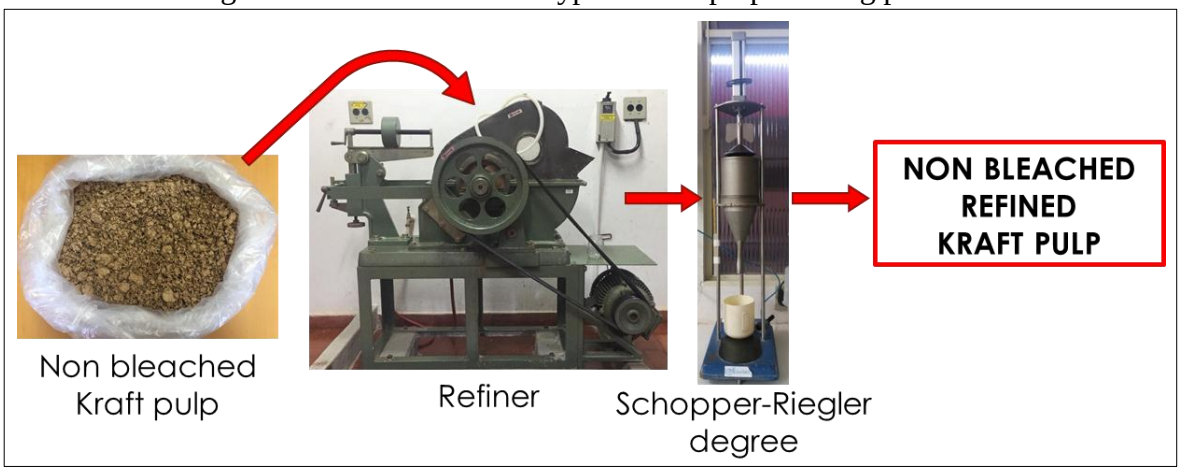


Source: The authors (2019).

2.2 Paper sheets formation

a) Matrix preparation: unbleached Kraft pulp from eucalyptus, provided by Klabin SA, was refined to a Schooper-Riegler degree of 21, aiming to dissociate the fibers but limiting the influence of refining on paper properties, so that the grammage and nanofibrils concentration were the real influences. Figure 2 presents the equipment used in this process.

Figure 2 - Unbleached eucalyptus Kraft pulp refining process.



Source: The authors (2019).

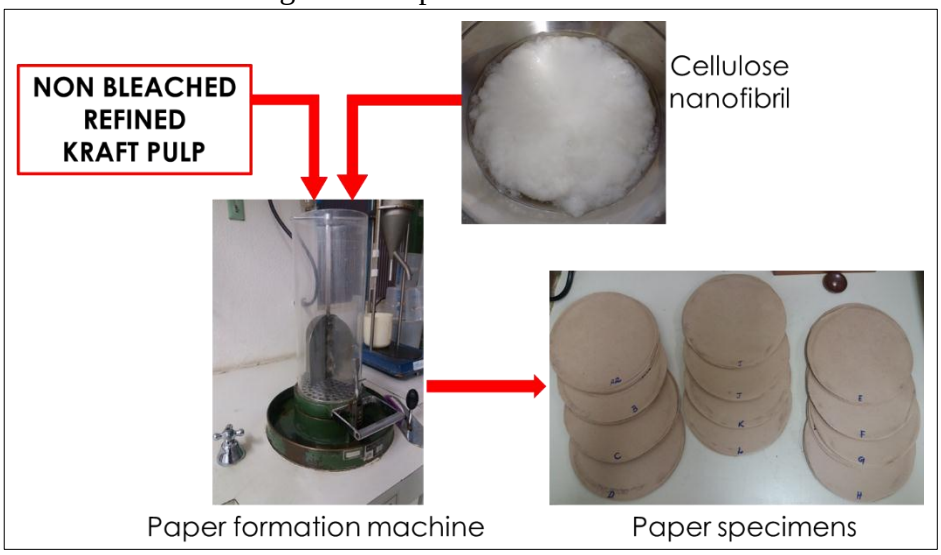
b) Paper preparation: The papers were produced at the Pulp and Paper Laboratory of the Universidade Federal de Viçosa, according to the standard T 205 sp-95 (TAPPI, 2006). The cellulose nanofibrils were sonicated for ten minutes, then mixed up with the refined unbleached cellulose pulp in a homogenizer, respecting the quantities establish in Table 1. The mixture was deposed in a paper forming machine and underwent to a vacuum filtration process, as demonstrated in Figure 3. The wet specimens were pressed in an electronic press and dried at room temperature, producing paper sheets with area of 0,0201 m², compound 12 treatments and 10 paper sheets per treatment, totalizing 120 specimens with final grammages of 75, 85, 95 and 105 g/m² and nanofibril concentrations of 1, 5 and 10% in relation to the paper grammage (wt%).

Table 1 - Treatments, grammage and nanofibril concentration of paper specimens.

Treatment	Unbleached pulp (g/m²)	Nanofibrils (g/m²)	Final grammage (g/m²)
75-1	74.25	0.75 (1%)	75
75-5	71.25	3.75 (5%)	75
75-10	67.50	7.50 (10%)	75
85-1	84.15	0.85 (1%)	85
85-5	80.75	4.25 (5%)	85
85-10	76.50	8.50 (10%)	85
95-1	94.05	0.95 (1%)	95
95-5	90.25	4.75 (5%)	95
95-10	85.50	9.50 (10%)	95
105-1	103.95	1.05 (1%)	105
105-5	99.75	5.25 (5%)	105
105-10	94.50	10.50 (10%)	105

Source: The authors (2019).

Figure 3 - Paper sheets formation.



Source: The authors (2019).

2.3 Tests

The tests performed in the specimens were realized in a controlled room, with humidity of 50% and temperature of 23°C.

2.3.1 Microscopic characterization

Field-emission gun scanning electron microscopy (FEG-SEM) was applied to the paper specimens and to a cellulose nanofibrils film produced by casting. It was investigate cellulose nanofibrils presence, paper surface and nanofibrils interaction with the paper fibers. The samples were placed on half-moon aluminum stubs, fixed with carbon tape, covered with gold and analyzed in a microscope model JSM-6701F (JEOL®).

2.3.2 Physical properties

Figure 4 presents the equipment used in the thickness, resistance to air passage and capillarity tests. Figure 5 presents the device used to determine water vapor permeability and water vapor transmission rate.

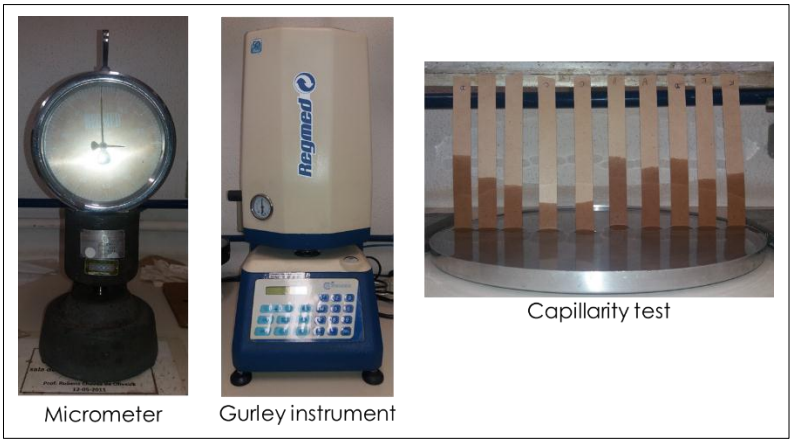
a) Thickness: performed according to the standard T 411 om-97 (TAPPI, 1997);

b) Resistance to air passage (RAP): this method measures the time it takes for 100 cm^3 of air, with a pressure differential of approximately 3 kPa, to pass through the test specimen, along

with any possible leakage of air across the surface. Gurley instrument, standard T 536 om-96 (TAPPI, 2006);

c) Capillarity: determines the water absorptiveness of a paper. Standard T 220 sp-96 (TAPPI, 2001);

Figure 4 - Instruments used to determine thickness, air permeability and capillarity of papers.



Source: The authors (2019).

d) Water vapor permeability: The test allows the determination of paper permeability to water vapor (WVP), which is the amount that will go through a unit area of unit thickness, and water vapor transmission rate (WVTR), which is the actual amount that gets through a unit area of a real sample. Standard E 96-00 (ASTM, 2000), with modifications proposed by Guimarães Jr. et al. (2015). The equations are described by Scatolino et al. (2017).

Figure 5 - Water vapor permeability test.

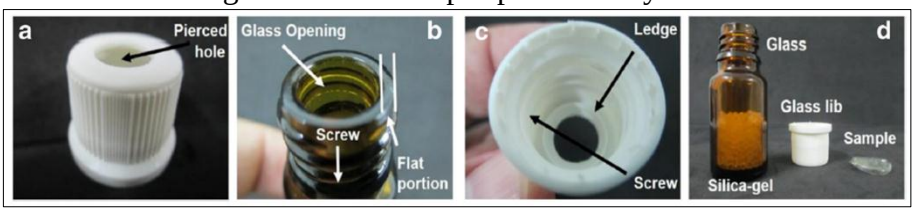


Figure chart: Hole pierced on the cap for diffusion of water molecules in the sample (a); flat portion where the cap ledge rests to avoid interferences between the pressures created, the screw aides sample fixation (b); ledge to press the sample in the flat portion of the glass (c); parts that compose the cell(d). Source: Guimarães et al. (2015).

2.3.3 Mechanical properties

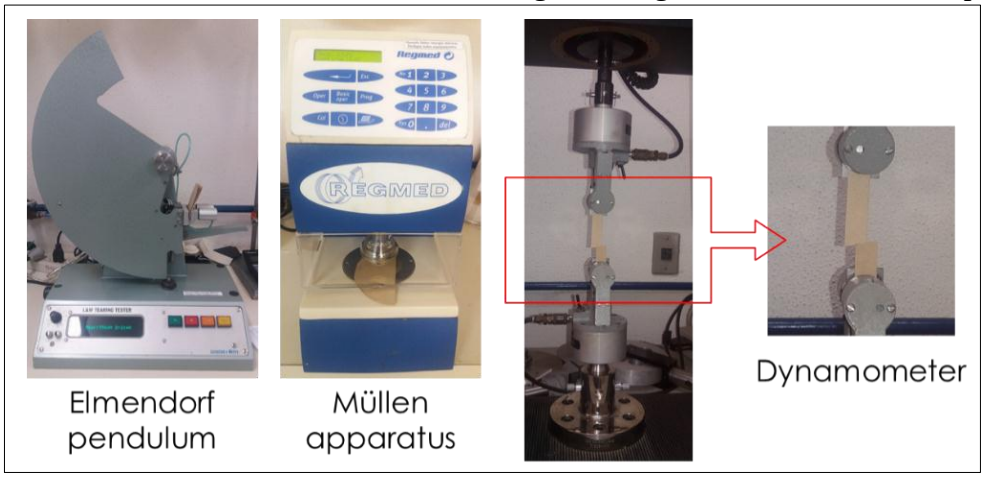
Figure 6 presents the equipment used to determine tearing, bursting and tensile indexes of papers. Figure 7 presents the equipment used to determine paper resistance to compression.

a) Tearing index (TR): the test measure the work required for complete tearing the paper. Elmendorf pendulum, standard T 414 om-98 (TAPPI, 1998);

b) Bursting index (BI): It consists of measuring the applied hydraulic pressure necessary to produce the material overflow. Müllen apparatus, standard T 403 om-97 (TAPPI, 1997);

c) Tensile index (TI): the specimen is subjected to a uniformly increasing tensile stress until its rupture. The test also provide results of Stretch, Tenacity (TEA) and Modulus of elasticity (MOE) of the paper specimens. Dynamometer, standard T 494 om-96 (TAPPI, 1999);

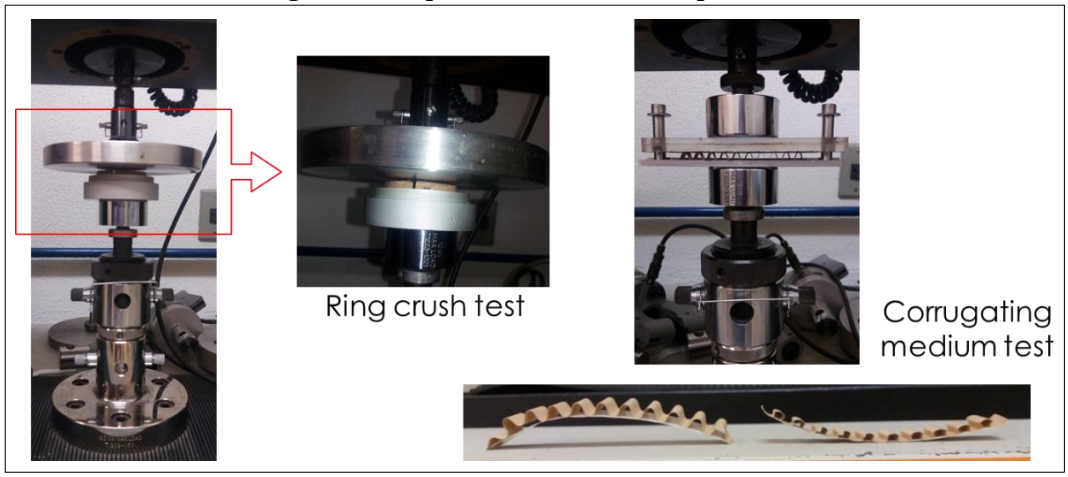
Figure 6 - Instruments used to determine tearing, bursting and tensile indexes of papers.



Source: The authors (2019).

d) Compressive strength: it is measured as the compression force applied to the specimen. Ring crush test (RCT) determines the compression resistance of paper containers, standard T 822 om-93 (TAPPI, 2007). Corrugating medium test (CMT) determines the compression resistance of corrugated boards, standard T 809 om-93 (TAPPI, 1993).

Figure 7 - Paper resistance to compression.



Source: The authors (2019).

2.4 Statistical analysis

To evaluate this study, data was arranged in a factorial scheme with two factors (grammage x nanofibril content). When the variance analysis were significant it was applied the Tuckey test.

3 RESULTS AND DISCUSSION

Figure 8 shows the FEG-SEM micrographs of the papers sheets and a nanofilm produced by casting. Images 8A and 8B represent treatment 75-10 rough and smooth surface, respectively, accompanied by the samples photographs. The different surfaces occur due to paper formation process, in which the material suffers vacuum filtration and pressing in contact with a flat surface, causing a paper surface to be smooth and the other rough.

At Figure 8A it is possible to observe the fibers accommodation and great porosity, that is reduced in the smooth face due to greater fiber collapse and nanofilm formation (FIGURE 8B).

Images 8C and 8D represent treatments 75-5 and 105-10, respectively. The magnification allows the visualization of paper thickness, showing a much more compact and well formed paper with the increase in grammage and nanofibril content, both contributing to reduce porosity and improve fiber-fiber connection.

Figures 8E, 8F and 8G represent treatments 105-10, 105-5 and 105-1, respectively. The higher amounts of nanofibrils are evidenced by the arrows, pointing to zones of nanofilm formation and aggregation between fibers by CNFs. Arrows at Images 8F and 8G point to nanofilms formed within the paper, with translucency evidenced by the fibers visible behind the films. The difference in the continuity of those films between the two images is function of the nanofibril content, five times greater in the sample of Figure 8F.

Image 8H shows the micrograph of a nanofilm produced by casting, where the magnification allows observing the cellulose nanofibrils forming a porous high tangled network, with nanometric diameter and micrometric length.

According to Börjesson and Westman (2015), the hydroxyl groups in the cellulose polymers can form hydrogen bonds between different cellulose polymers (intermolecular hydrogen bonds) or within the polymer itself (intramolecular hydrogen bonds). The intramolecular bonds give stiffness to the polymer chain, while the intermolecular bonds allow the linear polymers to form sheet structures, as can be seen in Figures 8F and 8G.

Figure 8 - FEG-SEM micrographs of papers reinforced with cellulose nanofibrils (A-F) and of a cellulose nanofilm (G).

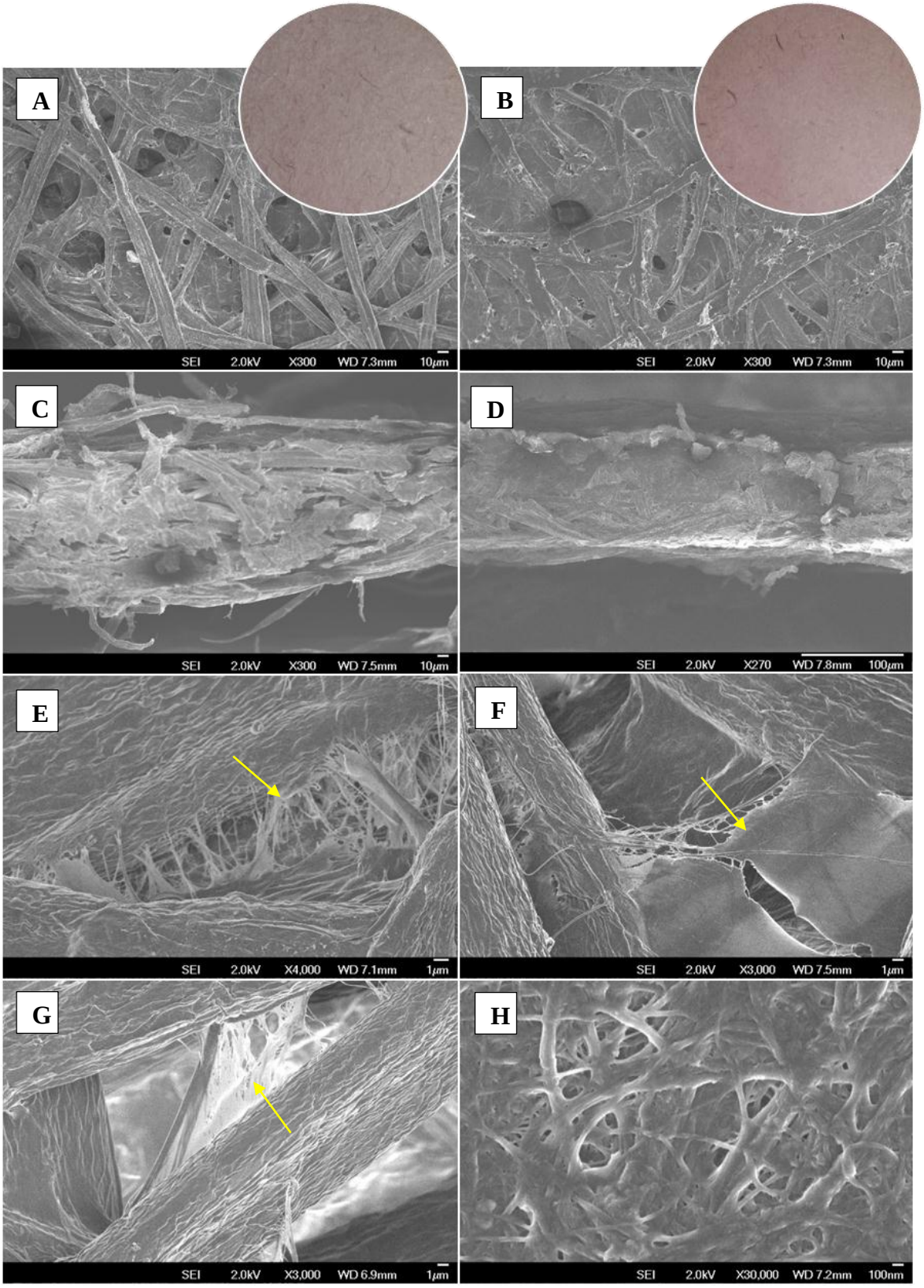
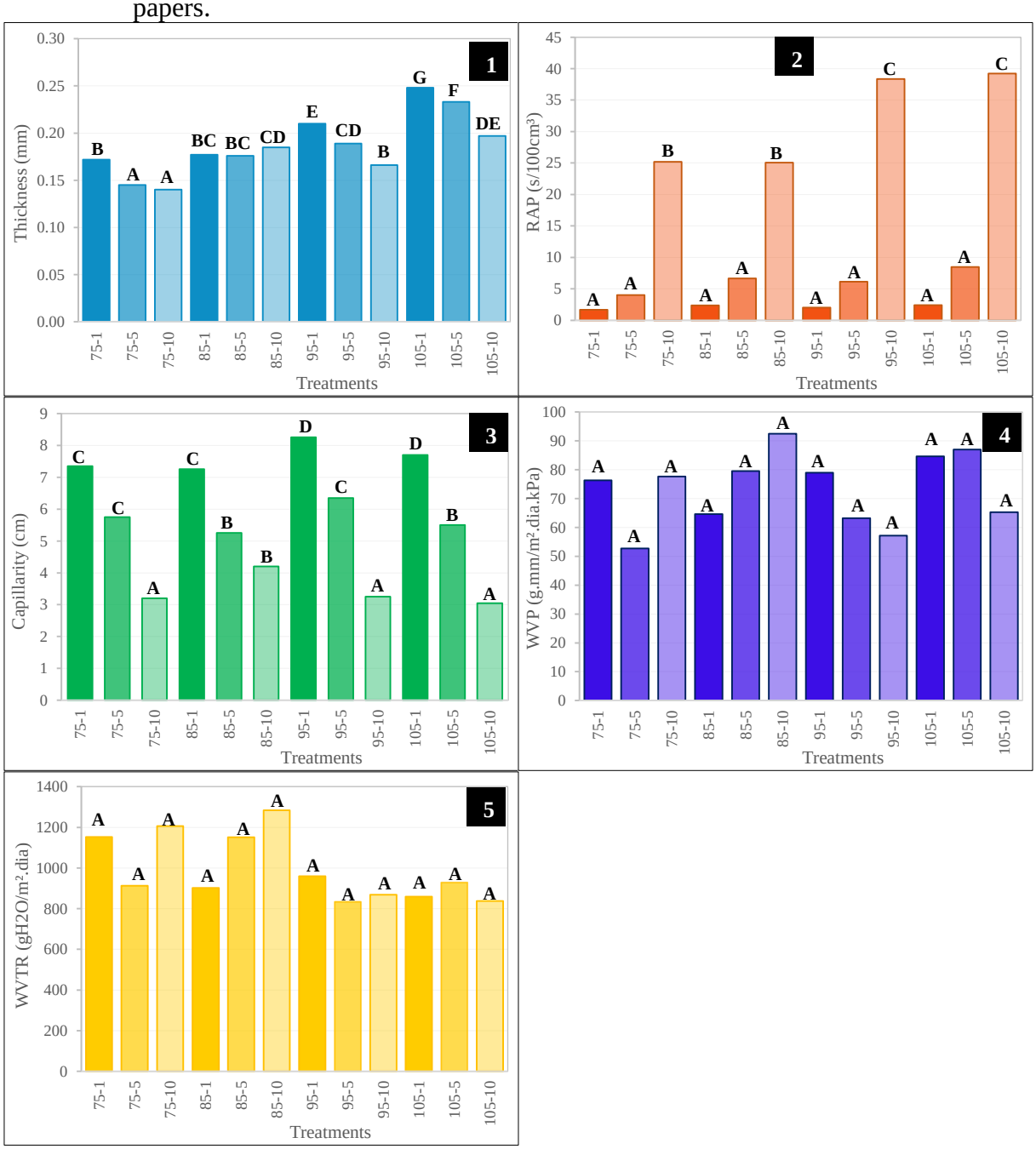


Figure chart - FEG-SEM micrographs showing paper surfaces rough (A) and smooth (B) with respective samples, paper thickness (C, D), formation of nanofilm within the paper (E, F, G) and a cellulose nanofilm (H). Arrows pointing to zones of nanofilm formation.
Source: The authors (2019).

Figure 9 introduces the mean results for each physical property and comparisons between treatments. In general, between treatments with the same grammage, it is possible to notice a pattern of improvement in paper performance according to the increase of nanofibrils added to the mass.

Figure 9 - Mean values and multiple comparison test for physical properties of packaging papers.



Means followed by the same letter do not differ from one another by the Tuckey test, at 5% probability.
Source: The authors (2019).

Average thickness varied between 0.140 and 0.248 mm, the variation in this property is normal and can be associated with fiber/nanofibril accommodation during paper sheet formation, along with fiber structure and collapse occasioned by the processes of pulping, refining, vacuum filtration ant pressing, which influence the binding between fibers within the paper sheet. Apart from treatments with 85 g/m², it is possible to notice a behavior of reduction in thickness with the increase of nanofibril content (FIGURE 9.1).

For each grammage it is possible to observe an increase in the resistance to air passage according to the addition of nanofibrils to the paper (FIGURE 9.2). Statistically there was no difference between the papers with addition of 1 and 5% of nanofibrils, independent of the grammage, which is important because increasing the nanofibril concentration by five times there was a gain in other mechanicals properties without a loss in the RAP, highlighting the sample 105-5, that presented great performance in tearing index, RCT, CMT and good performance in burst index, stretch and TEA (visible in FIGURE 10). The samples with 10% of nanofibrils presented an expressive enlargement of RAP, possibly caused by the formation of nanofilms within the paper that significantly reduced its porosity.

According to Shallhorn and Gurnagul (2010), critical properties for sack papers, those used for storing powder substances as cement and flour, are high TEA e low resistance to air flow, because this combination of properties allow a paper to resist to impact stress during its filling and handling, which makes papers with 10% of nanofibrils unsuitable for this type of package, compared to those with 1 and 5% of nanofibrils.

Afra, Mohammadnejad and Saraeyan (2016), studying papers coated with double-layers of 1.5 wt% and single-layers of 3 wt% CNFs, found an increase in resistance to air passage from uncoated to coated papers, which the authors associated with the reduction in the number of pores in paper surface, same behavior observed in this study, although the processes were different. El-Samahya et al. (2017) also found that increasing CNF coating from 0.4 to 1.6 g caused paper air permeability to increase dramatically from 3.1 to 26.3 s, which consists with the results found in this study.

A clear reduction in paper capillarity is visible in Figure 9.3, in function of nanofibril increasing in the blend, that reduces the paper porosity. Although using the Cobb 60 water absorption test (TAPPI standard T 441 om-04), Afra, Mohammadnejad and Saraeyan (2016) found that for CNF coated papers there was a reduction in water absorption compared to non-coated papers. According to the authors, the effect was caused by the continuous layer with fewer pores formed by the CNF coat, where less water was able to penetrate the surface.

The permeability of packaging and coatings influences the shelf life of the product due to absorption or moisture loss, loss of volatile compounds and gas in aerated drinks (MARSH; BUGUSU, 2007). The paper WVP (FIGURE 9.4) and WVTR (FIGURE 9.5) presented no difference between treatments at 5% of significance, although for grammages 95 and 105 g/m² it is possible to observe a reduction in variation of WVTR between treatments with different CNF concentrations.

Figure 10 introduces the mean results for each mechanical property and comparisons between treatments.

The tearing index also presented a behavior of increase with the addition of nanofibrils for all grammages (FIGURE 10.1). Except for the grammage 75 g/m², all the specimens with 5 and 10% of nanofibrils showed good TR. Although sample 105-10 presented the grater TR, sample 85-10, with a 20% reduction in grammage, statistically showed the same TR as 105-10, demonstrating the potential of cellulose nanofibrils to enhance a product performance even with reduced raw material.

Figure 10 - Mean values and multiple comparison test for mechanical properties of packaging papers. (To be continued)

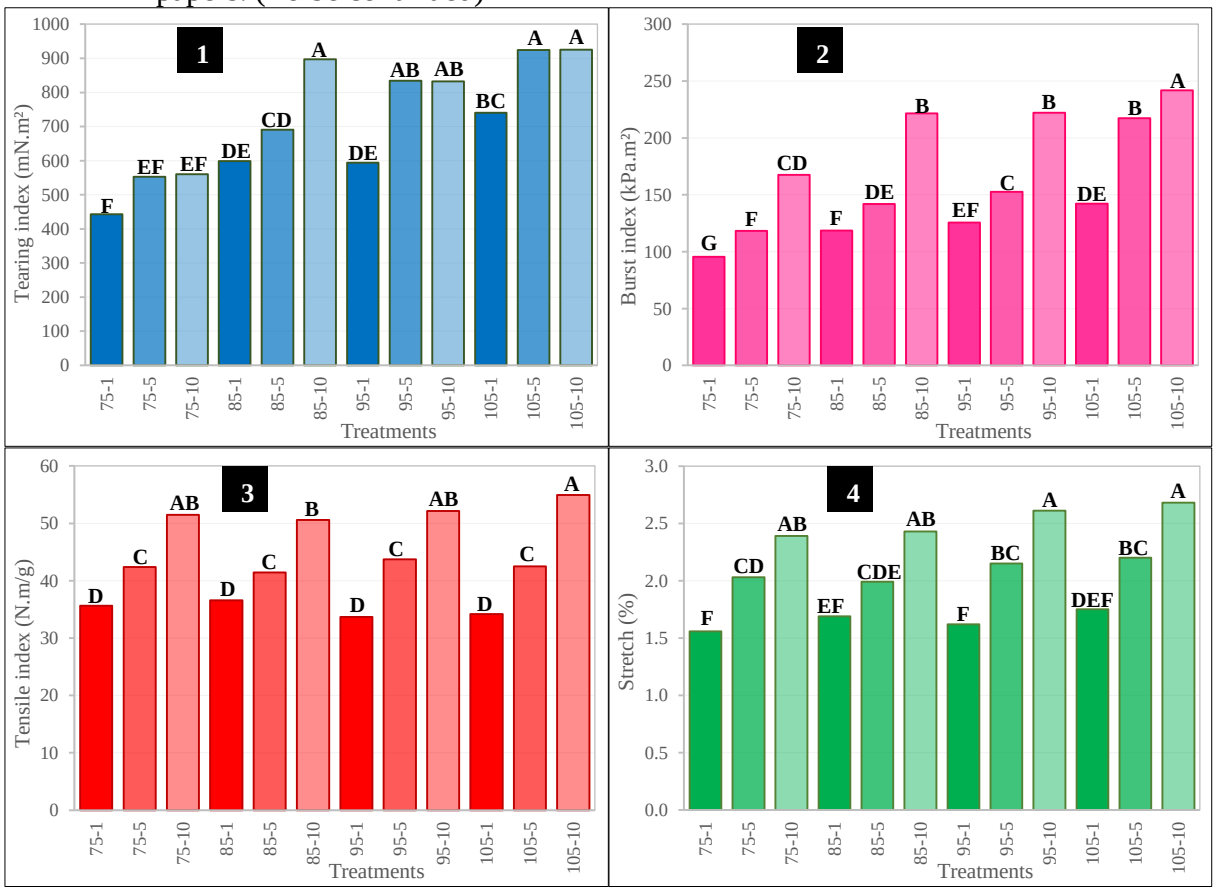
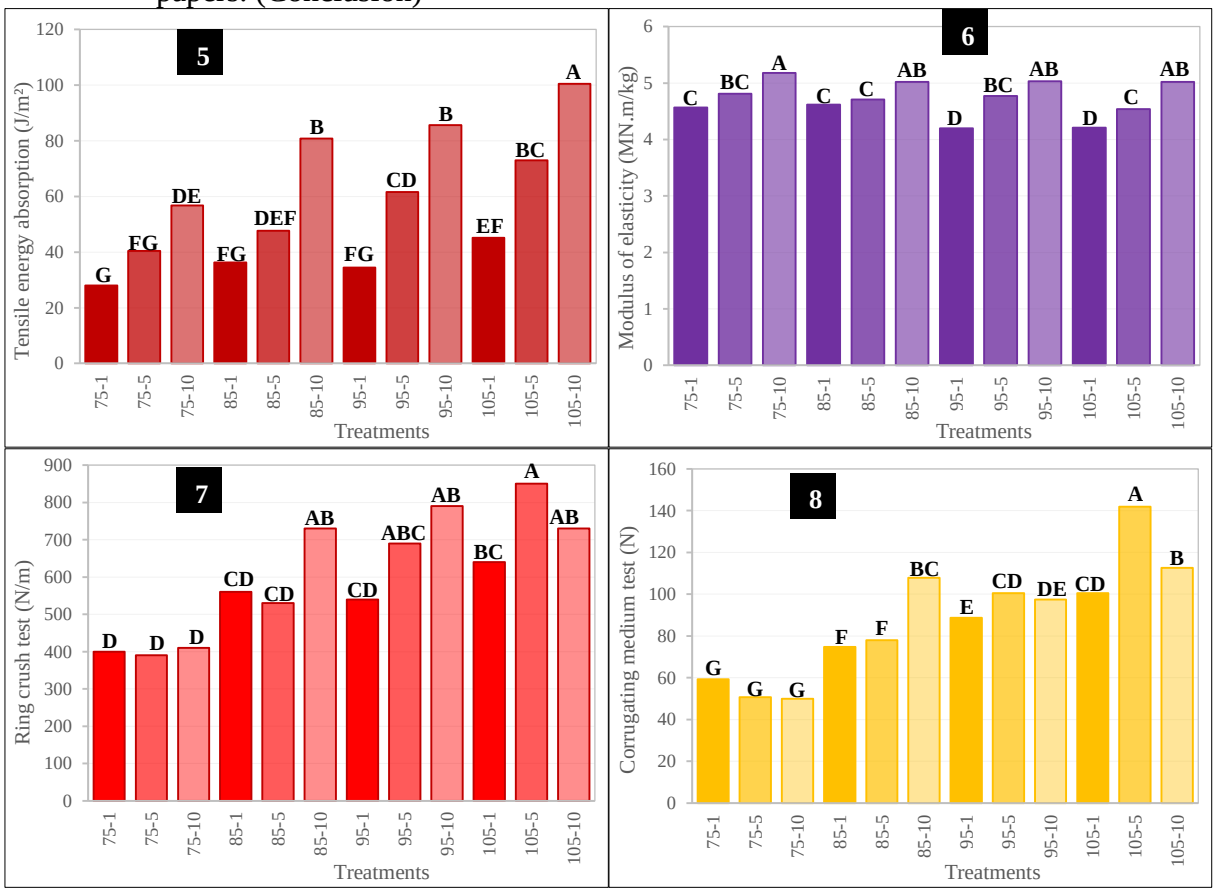


Figure 10 - Mean values and multiple comparison test for mechanical properties of packaging papers. (Conclusion)



Means followed by the same letter do not differ from one another by the Tuckey test, at 5% probability.
Source: The authors (2019).

The greater bursting index was presented by the sample 105-10 (242 kPa.m²), followed by samples 95-10, 85-10 and 105-5 (FIGURE 10.2), statistically equal, over again demonstrating nanofibril potential, once sample 85-10 presented BI of 222 kPa.m², while sample 105-5 resistance was 217 kPa.m², a raw material reduction of 20% without loss in resistance to burst. The increase in the resistance also accompanied the increase in nanofibril content for all grammages.

The treatments that performed better in the tensile index test (FIGURE 10.3) were the ones with 10% nanofibrils for all grammages, same behavior observed in the stretch test (FIGURE 10.4) and in the MOE (FIGURE 10.6), demonstrating that the nanofibrils had more impact on the TI, ST and MOE of the papers than grammage, once samples 75-10 and 105-10 presented statistically the same resistance even though there is a 30% difference in fiber quantity between then.

Although the influence of preparation conditions on nanofibrils arrangement in films is not fully established, according to Benítez and Walther (2017A), in films produced by vacuum

filtration, the nanofibrils concentrate at the bottom forming a densely packed network owing to the aggregation of nanofibrils. Sehaqui et al. (2010) demonstrated that vacuum filtration leads to better mechanical properties by increasing the orientation of the nanofibrils in a horizontal plane with the filter and, when it is followed by a pressing step, the constrained drying also leads to in-plane orientation of the nanofibrils and lower porosity, which can increase film strength (TI) and elongation (ST) (BENÍTEZ et al., 2016; BENÍTEZ; WALTHER, 2017B).

At the tensile energy absorption test (FIGURE 10.5), although the samples had presented the same general behavior of other tests, with nanofibril addition causing an improvement in paper performance, there was a balance in the contribution of grammage and concentration of nanofibrils in the results obtained, once there were larger differences between TEA of papers with same nanofibril concentration and between papers with same grammage, which can be proved by Table 2.

According to the Figure 10.7 and Table 2, papers with higher grammages and nanofibril concentration in general presented greater resistance to compression in the ring crush test, showing that the cellulose nanofibrils could not overcame the fiber reduction, because the property has grater dependence on grammage.

At the corrugating medium test (FIGURE 10.8) the influence of grammage was even more distinguishable, with samples with lower grammages presenting lower resistance to compression regardless the nanofibril concentration present.

Table 2 presents the contribution of nanofibrils and grammage separately to each property. It was possible to observe that for RAP, TI, stretch and MOE the grammage had no influence in the resultant resistance, proving the effectiveness of the nanofibrils alone to improve physical and mechanical properties of paper, even with 30% reduction in grammage.

As expected, for most properties analyzed the reinforcement with 10% of nanofibrils was the most effective. The reinforcement of 5% nanofibrils was statistically equal to 10% only for properties TR and RCT, the last one, as discussed previously, was more influenced by grammage. The only exception to CNF contribution as reinforcement was at CMT, there was no significant difference in the resistance between CNF concentrations for this property, which was affected only by paper grammage.

Table 2 - Mean values and multiple comparison test for the deployment of the interactions between grammage and cellulose nanofibril content of packaging papers.

		Capillarity (cm)	RAP (s/100cm³)	TR (mN.m²)	BI (kPa.m²)	TI (N.m/g)
CNF	1	7.64 C	2.12 A	594.13 B	120.44 C	35.02 C
	5	5.71 B	6.33 A	750.50 A	161.32 B	42.52 B
	10	3.43 A	31.95 B	803.63 A	209.50 A	52.28 A
Gram.	75	5.43 A	10.29 A	518.58 C	122.08 C	43.17 A
	85	5.57 A	11.36 A	728.75 B	160.71 B	42.87 A
	95	5.95 B	15.50 A	753.25 AB	171.79 AB	43.19 A
	105	5.42 A	16.72 A	863.75 A	200.43 A	43.88 A
		Stretch (%)	TEA (J/m²)	MOE (MN.m/kg)	RCT (N/m)	CMT (N)
CNF	1	1.65 C	35.99 C	4.40 C	533 B	80.81 A
	5	2.09 B	55.68 B	4.71 B	613 AB	91.94 A
	10	2.53 A	80.93 A	5.06 A	665 A	92.79 A
Gram.	75	1.99 A	41.76 C	4.59 A	400 C	53.29 C
	85	2.04 A	54.9 BC	4.67 A	600 BC	86.84 B
	95	2.13 A	60.58 AB	4.78 A	670 B	95.59 B
	105	2.21 A	72.85 A	4.85 A	740 A	118.34 A

Gram. - Grammage (g/m²); CNF - Cellulose nanofibrils (%); RAP - Resistance to air passage; TR - Tearing index; BI - Bursting index; TI - Tensile index; ST - Stretch; TEA - Tensile energy absorption; MOE - Modulus of elasticity; RCT - Ring crush test; CMT - Corrugating medium test. Means followed by the same letter do not differ from one another by the Tuckey test, at 5% probability.
Source: The authors (2019).

4 CONCLUSION

- The formation of nanofilms and aggregations between nanofibrils and fibers/microfibers within the paper caused reduction in paper porosity and consequent increase in resistance to air passage and reduction in capillarity;
- Nanofibrils reinforcement contribute to enhance all properties analyzed, except for corrugating medium test, only influenced by grammage, WVP and WVTR, that presented no tendency;
- Resistance to air passage, tensile index, stretch and MOE stand out for improvements being result only of the cellulose nanofibril reinforcement, with no influence from grammage;
- Reinforcement with cellulose nanofibrils enhanced paper barrier properties and mechanical resistance even with grammage reduction.

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REFERENCES

AFRA, E.; MOHAMMADNEJAD, S.; SARAEYAN, A. Cellulose nanofibrils as coating material and its effects on paper properties. **Progress in Organic Coatings**, v. 101, p. 455–460, 2016.

AFRA, E. et al. Comparative effect of mechanical beating and nanofibrillation of cellulose on paper properties made from bagasse and softwood pulps. **Carbohydrate Polymers**, v. 97, p. 725– 730, 2013.

ANDERSON, R. E. et al. Multifunctional single-walled carbon nanotube-cellulose composite paper. **Journal of Materials Chemistry**, v. 20, p. 2400–2407, 2010.

ASTM E96-00, Standard Test Methods for Water Vapor Transmission of Materials, ASTM International, West Conshohocken, PA, 2000.

BENÍTEZ, A. J. et al. Understanding toughness in bioinspired cellulose nanofibril/polymer nanocomposites. **Biomacromolecules**, v. 17, n. 7, p. 2417–2426, 2016.

BENÍTEZ, A. J.; WALTHER, A. Cellulose nanofibril nanopapers and bioinspired nanocomposites: a review to understand the mechanical property space. **Journal of Materials Chemistry A**, v. 5, p. 16003–16024, 2017A.

BENÍTEZ, A. J.; WALTHER, A. Counterion size and nature control structural and mechanical response in cellulose nanofibril nanopapers. **Biomacromolecules**, v. 18, n. 5, p. 1642–1653, 2017B.

BÖRJESSON, M.; WESTMAN, G. Crystalline Nanocellulose - Preparation, Modification, and Properties. In: POLETTO, M. **Cellulose - Fundamental Aspects and Current Trends**. London: InTech, 2015. Chapter 7, p. 159-191.

BRODIN, F. W.; GREGERSEN, O. W.; SYVERUD, K. Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material – A review. **Nordic Pulp & Paper Research Journal**, v. 29, n. 1, p. 156-166, 2014.

EICHHORN, S. et al. Review: current international research into cellulose nanofibres and nanocomposites, **Journal of Materials Science**, v. 45, n. 1, p. 1-33, 2010.

EL-SAMAHYA, M. A. et al. Synthesis of hybrid paper sheets with enhanced air barrier and antimicrobial properties for food packaging. **Carbohydrate Polymers**, v. 168, p. 212–219, 2017.

GUIMARÃES JÚNIOR, M. et al. High moisture strength of cassava starch/polyvinyl alcohol-compatible blends for the packaging and agricultural sectors. **Journal of Polymer Research,** v. 22, p. 192-209, 2015

MARSH, K.; BUGUSU, B. Food packaging - roles, materials, and environmental issues. **Journal of Food Science**, v. 72, p. 39–55, 2007.

MARTINS, N. C. T. et al. Electrostatic assembly of Ag nanoparticles onto nanofibrillated cellulose for antibacterial paper products. **Cellulose**, v. 19, p. 1425–1436, 2012.

MIRMEHDI, S. et al. Spraying cellulose nanofibrils for improvement of tensile and barrier properties of writing & printing (W&P) paper. **Journal of Wood Chemistry and Technology**, v. 38, p. 1-13, 2018.

OGIHARA, H. et al. Simple method for preparing superhydrophobic paper: spray-deposited hydrophobic silica nanoparticle coatings exhibit high water repellency and transparency. **Langmuir**, v. 28, p. 4605–4608, 2012.

SAMYN, P. et al. Review: nanoparticles and nanostructured materials in papermaking. **Journal of Materials Science**, v. 53, p. 146–184, 2018.

SEHAQUI, H. et al. Fast preparation procedure for large, flat cellulose and cellulose/inorganic nanopaper structures. **Biomacromolecules**, v. 11, n. 9, p. 2195–2198, 2010.

SHALLHORN, P.; GURNAGUL, N. A semi-empirical model of the tensile energy absorption of sack Kraft paper. **BioResources**, v. 5, n. 1, p. 455-476, 2010.

SCATOLINO, M. V. et al. Impact of nanofibrillation degree of eucalyptus and Amazonian hardwood sawdust on physical properties of cellulose nanofibril films. **Wood Science and Technology**, v. 51, n. 5, p. 1095-1115, 2017.

SIRÓ, I.; PLACKETT, D. Microfibrillated cellulose and new nanocomposite materials: a review. **Cellulose**, v. 17, p. 459–494, 2010.

TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY – TAPPI. T 205 sp-95. **Forming handsheets for physical tests of pulp.** Atlanta, 2006. 13 p.

_____. T 220 sp-96. **Physical testing of pulp handsheets.** Atlanta, 1996.

_____. T403 om-97. **Bursting strength of paper**. Atlanta, 1997.

_____. T411 om-97. **Thickness (caliper) of paper, paperboard, and combined board**. Atlanta, 1997.

_____. T414 om-98. **Internal tearing resistance of paper (Elmendorf-type method).** Atlanta, 1998.

_____. T 494 om-96. **Tensile properties of paper and paperboard (using constant rate of elongation apparatus).** Atlanta, 1999.

_____. T 536 om-96. **Air resistance of paper (Gurley method).** Atlanta, 2006.

_____. T 809 om-93. **Flat crush of corrugating medium (CMT test).** Atlanta, 1993.

_____. T 822 om-93. **Ring crush of paperboard (rigid support method).** Atlanta, 2007.

TURBAK, A. F.; SNYDER, F. W.; SANDBERG, K. R. Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. **Journal of applied polymer science. Applied polymer symposium**, v. 37, p. 815–827, 1983.

ZHU, H. et al. Transparent paper: fabrications, properties, and device applications. **Energy & Environmental Science**, v. 7, p. 269–287, 2014.

ARTIGO 2 - NEAR INFRARED SPECTROSCOPY ESTIMATING PROPERTIES OF PACKAGING PAPERS REINFORCED WITH CELLULOSE NANOFIBRILS

Lidiane Costa Lima, Maria Lúcia Bianchi, Lívia Ribeiro Costa, Paulo Ricardo Gherardi Hein

Abstract: The aim of this study was to investigate near infrared spectroscopy capability to estimate nanofibrils content, physical and mechanical properties of packaging papers reinforced with cellulose nanofibrils. Paper sheets were prepared by mixing unbleached Eucalyptus fibers and cellulose nanofibrils from mechanical defibrillation, following the standardized steps: homogenizing, vacuum filtration, pressing and room temperature drying. Twelve treatments result from the combination of the final grammages 75, 85, 95 and 105 g/m² with the nanofibril concentrations of 1, 5 and 10wt%, with 7 sheets per treatment. Principal component analysis (PCA), partial least squares (PLS) and partial least squares discriminant analysis (PLS-DA) based on laboratorial and spectral information were utilized. At PCA there was no separation between specimens related to nanofibril content. PLS generated models for nanofibril content, tensile index, stretch and resistance to air passage with R^2cv range from 0.73 to 0.98, indicating that NIRS technique is suitable for predicting physical and mechanical properties of packaging papers and can detect cellulose nanofibril into the paper matrix. PLS-DA models correctly classify more than 98% of the samples according to nanofibril content.

Keywords: Nanocellulose. Nanopaper. Multivariate models. Mechanical resistance. NIRS.

1 INTRODUCTION

Cellulose is the most abundant biopolymer of the world, with characteristics and properties that allow its employment in several industries and products, such as paper, pharmaceutical, food, cosmetics, pesticides, fabric, among others. Its renewability and biodegradability keeps cellulose-based products matter in constant research and improvement, due to the crescent awareness of society about the necessity to preserve and protect the environment.

Considering that the world paper and paperboard production in 2016 was 409 millions of tons (FAO, 2018) and that paper quality control analysis are time consuming and expensive activities, with each property measured frequently requiring a specific instrument and sample

preparation (FARDIM; FERREIRA, DURÁN, 2005), the increasing search in the past years for alternatives to fast, reliable measurements at low cost is understandable.

Among methods of monitoring, the near infrared (NIR) spectroscopy emerged as a rapid-response analytical tool, with increasing acceptance from industries related to its applicability on the production line. The technique aims to examine a sample in order to acquire qualitative/quantitative information by means of the interaction of near infrared electromagnetic waves with the material constituents. Its fast, non-destructive, non-invasive, minimum sample preparation and nearly universal application, which includes any molecule containing C-H, N-H, S-H or O-H bonds (PASQUINI, 2003), explain the large number of studies in several areas that have been carried out over the years involving the technique.

According to Pasquini (2003), in a given wavelength range, some frequencies will not be absorbed while other will be partially or completely absorbed, forming a complex figure of intensity of absorption versus wavelength that constitutes the unique absorption spectra of a substance or sample. NIR spectra must be associated with strong information from traditional laboratory analysis and chemometric tools in order to calibrate, validate and extract information from data, allowing the prediction of properties, estimative of concentration of a substance in a sample, identification of different samples in a group by its differences or similarities, between other applications.

In terms of cellulose pulp, researches involving NIR spectroscopy began with the estimation of pulp kappa number (BIRKETT; GAMBINO, 1989), real-time estimation of effective alkali, lignin, and dissolved organic in the cooking liquor (YAN; KRISHNAGOPALAN, 2003), prediction of pulp yield and cellulose content (WRIGHT; BIRKETT; GAMBINO, 1990), determination of changes in chemical composition of pulp samples during Kraft pulping (WALLBACKS et al., 1991) and as a measuring method for the control of pulp composition and chemical additives on the paper machine (REITER et al., 1999).

NIR spectrometry can also be suitable to detect changes in paper mechanical properties, once they are directly related to intra and intermolecular interactions present in the material (FARDIM; FERREIRA, DURÁN, 2005), which can contribute to the determination of cellulose nanofibrils in the matrix, once they interact with the matrix through hydrogen bonds.

The aim of this study was to investigate near infrared spectroscopy capability to estimate nanofibrils content, physical and mechanical properties of packaging papers reinforced with cellulose nanofibrils.

2 METODOLOGY

2.1 Nanofibrils production

Cellulose nanofibrils were obtained from bleached Kraft pulp of Eucalyptus (Klabin SA), through mechanical defibrillation. The pulp was soaked overnight in deionized water, disintegrated in a mechanical stirrer (Fisatom 722) and defibrillated in a Masuko Supermascoloider grinder (MKCA-2J, Masuko Sangyo Ltd.), with rotation of 1500 rpm, pulp concentration of 2% (w/v) and 30 cycles. Figure 1 presents the equipment used in this process.

2.2 Paper sheets formation

a) Matrix preparation: unbleached Kraft pulp from eucalyptus, provided by Klabin SA, was refined to a Schooper-Riegler degree of 21, aiming to dissociate the fibers but limiting the influence of refining on paper properties, so that the grammage and nanofibrils concentration were the real influences.

b) Paper preparation: The papers were produced at the Pulp and Paper Laboratory of the Universidade Federal de Viçosa, according to the standard T 205 sp-95 (TAPPI, 2006). The cellulose nanofibrils were sonicated for ten minutes, then mixed up with the refined unbleached cellulose pulp in a homogenizer, respecting the quantities establish in Table 1. The mixture was placed in a paper forming machine and underwent to a vacuum filtration process, forming the wet specimens, that were pressed in an electronic press and dried at room temperature. The resultant paper sheets presented area of 0,0201 m^2, compound 12 treatments and 7 paper sheets per treatment, totalizing 84 specimens with final grammages of 75, 85, 95 and 105 g/m^2 and nanofibril concentrations of 1, 5 and 10% in relation to the paper grammage (wt%).

Table 1 - Treatments code, grammage and nanofibril concentration.

Treatment	Unbleached pulp (g/m²)	Nanofibrils (g/m²)	Final grammage (g/m²)
75-1	74.25	0.75 (1%)	75
75-5	71.25	3.75 (5%)	75
75-10	67.50	7.50 (10%)	75
85-1	84.15	0.85 (1%)	85
85-5	80.75	4.25 (5%)	85
85-10	76.50	8.50 (10%)	85
95-1	94.05	0.95 (1%)	95
95-5	90.25	4.75 (5%)	95
95-10	85.50	9.50 (10%)	95
105-1	103.95	1.05 (1%)	105
105-5	99.75	5.25 (5%)	105
105-10	94.50	10.50 (10%)	105

Source: The authors (2019).

2.4 Paper laboratory analysis

The tests performed in the specimens were realized in a controlled room, with humidity of 50% and temperature of 23°C:

a) Resistance to air passage: this method measures the time it takes for 100 cm³ of air, with a pressure differential of approximately 3 kPa, to pass through the test specimen, along with any possible leakage of air across the surface. Gurley instrument, standard T 536 om-96 (TAPPI, 2006);

b) Tearing index: the test measure the work required for complete tearing the paper. Elmendorf pendulum, standard T 414 om-98 (TAPPI, 1998);

c) Bursting index: It consists of measuring the applied hydraulic pressure necessary to produce the material overflow. Müllen apparatus, standard T 403 om-97 (TAPPI, 1997);

d) Tensile index: the specimen is subjected to a uniformly increasing tensile stress until its rupture. The test also provide results of Stretch, Tenacity (TEA) and Modulus of elasticity (MOE). Dynamometer, standard T 494 om-96 (TAPPI, 1999);

e) Compressive strength: it is measured as the compression force applied to the specimen. Ring crush test (RCT) determines the compression resistance of paper containers, standard T 822 om-93 (TAPPI, 2007). Corrugating medium test (CMT) determines the compression resistance of corrugated boards, standard T 809 om-93 (TAPPI, 1993).

2.5 NIR spectra acquisition

The near infrared spectra were acquired using a Bruker spectrometer (model MPA, Bruker Optik GmbH, Ettlingen, Germany) in diffuse reflectance mode, based on a Fourier transform and equipped with an integrating sphere. Spectral analysis was performed within the 12500-3600 cm^{-1} range, at 8 cm^{-1} resolution (each spectrum consisted of 2307 absorption values). Each NIR spectrum was obtained with 32 scans, means were calculated and compared to the sintered gold standard used as background to obtain the absorption spectrum of the sample. Two NIR spectra were recorded for each paper specimen. The spectrometer was connected to a computer that stored the spectra data collected by means of the OPUS program, Version 7.5.

2.6 Multivariate data analysis

The software The Unscrambler® (CAMO AS, Oslo, Norway, v. 9.7) was used for the data multivariate analysis. Principal component analysis (PCA) was realized in order to previously explore the data and to evaluate the dependence of the data by means of clusters. The analysis was calculated with the maximum number of eight principal components (PC). Multiplicative Scatter Correction was applied to

Partial least squares (PLS) were adjusted based on NIR spectra and laboratory determined nanofibril concentration, physical and mechanical properties, forming the calibration set. The calibration was validated by cross validation, with 6 segments and 14 samples per segment, chosen randomly.

The models were adjusted from original spectra, the number of PC selected for each model was the one that minimized the residual variance of the calibration and validation. The models were chosen based on statistics coefficient of determination of cross-validation (R^2cv) and root mean standard error of cross-validation (RMSEcv).

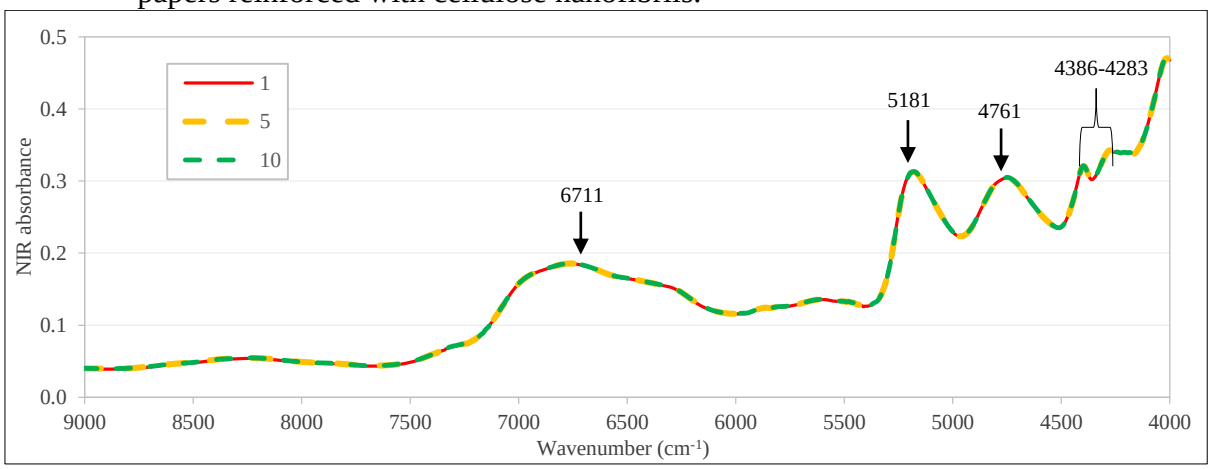
Partial least squares discriminant analysis (PLS-DA) was carried out to classify the nanofibril concentration by cross-validation. From this approach, the nanofibril concentration was considered as a categorical variable, not presenting continuous but discrete values. In this study, the samples were grouped into three different classes, 1, 5 and 10% nanofibril content. Then, the values 0 or 1 were assigned to all the samples in each class, and when the sample belonged to that category, the value 1 was assigned and when the sample did not belong to the

category, the value 0 was assigned, defining so to which group a sample belongs. Preliminary PLS models were performed to estimate continuous values in each of three categories.

3 RESULTS AND DISCUSSION

The mean spectrum of each nanofibril concentration can be observed in Figure 1. This figure demonstrates the homogeneity of the spectral profile, with no differentiated signals between nanofibril concentrations. Characteristic bands of lignocellulosic materials can be observed in the spectra: OH of alcohol (6711 cm^{-1}, 1490 nm), OH of water (5181cm^{-1}, 1930 nm) and OH of phenol (4761 cm^{-1}, 2100 nm), as observed by Fardin et al. (2005), C-H stretching and CH_2 deformation combination (4283-4386 cm^{-1}, 2280–2330 nm), as described by Workman Jr. and Weyer (2008).

Figure 1 - Mean NIR spectra for each nanofibril concentration (1, 5 and 10%) of packaging papers reinforced with cellulose nanofibrils.



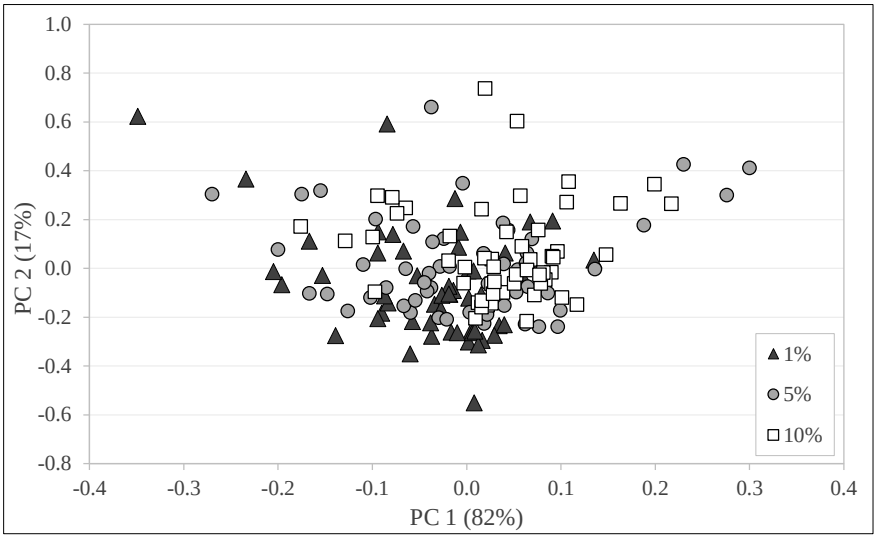
Source: The authors (2019).

Figure 2 presents the principal component analysis (PCA), performed to verify a possible agglomeration of specimens with the same nanofibril content. With the principal components 1 and 2 (PC 1 and PC 2) from the PCA of untreated data it was possible to explain, respectively, 82 and 17% of the data variability, explaining 99% of the variance, although the PCA had not displayed a clear separation between papers reinforced with 1, 5 and 10% of cellulose nanofibrils.

The first derivative was then applied aiming the separation of the data, but the values of PC 1 and PC 2 decreased to 77 and 11%, respectively, with no formation of clusters among specimens, demonstrating that it was not possible to separate papers through the NIRS

technique from the specimens set and experimental procedure used in this study. This difficulty can be associated to the unequal amount of nanofibril in each treatment (TABLE 1), once the percentages are associated with the paper grammage and the real value added to the paper increases for each grammage, even in the same nanofibril concentrations.

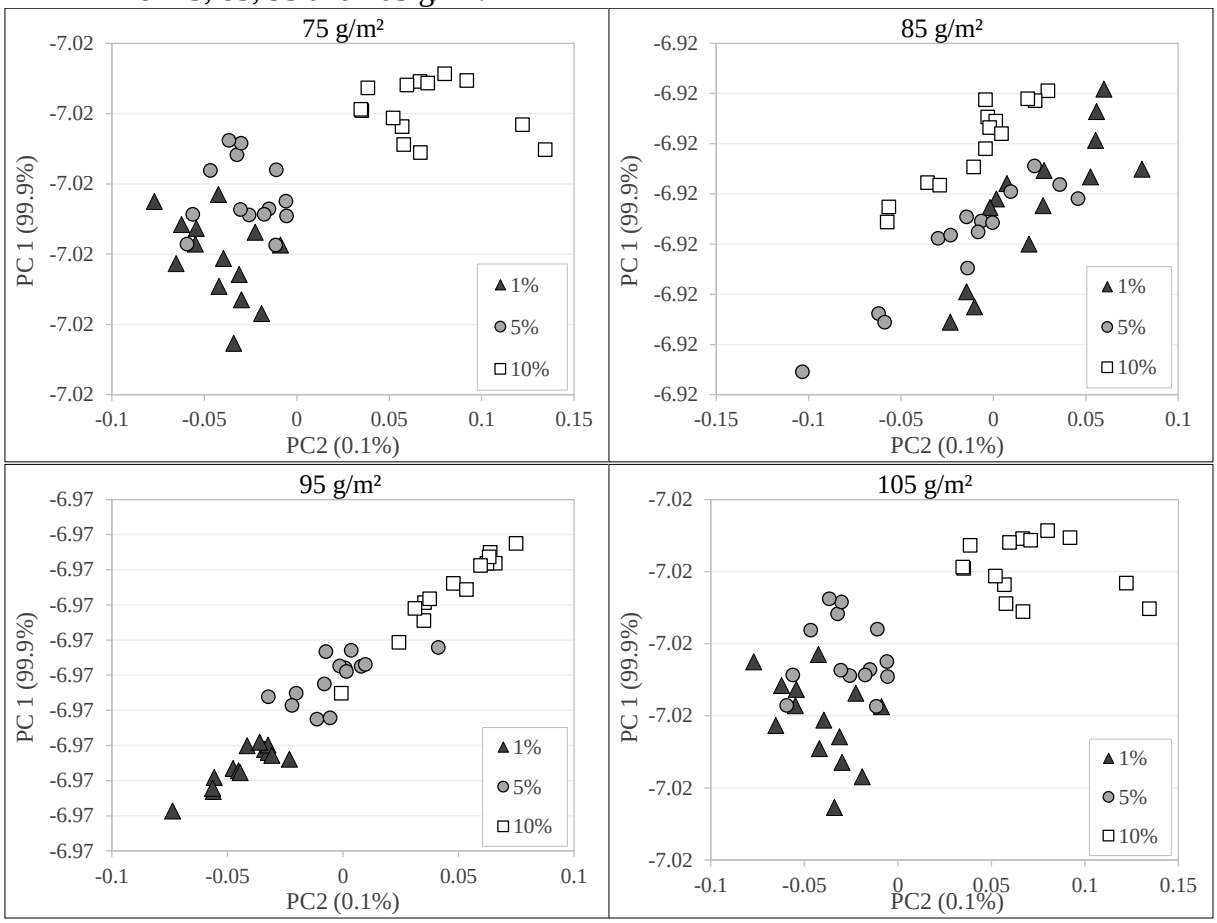
Figure 2 - Scores of a PCA applied to untreated NIR spectra recorded from packaging papers reinforced with cellulose nanofibrils.



Source: The authors (2019).

PCA data treated with Multiplicative Scatter Correction were used in each grammage separately (FIGURE 3), to avoid the problem described above. It was observed the formation of clusters for the grammage 75 g/m² just for the 10% nanofibril content, with no separation among 1 and 5% concentrations. The same behavior was observed for the grammage 105 g/m². The grammage 95 g/m² presented separation for all three nanofibril contents, and no cluster formation was observed for grammage 85 g/m², demonstrating that not only the differences in the real content of nanofibrils with the same percentage represents an obstacle for the NIR technique to accurately identify and separate samples.

Figure 3 - Scores of PCAs applied to NIR spectra treated with Multiplicative Scatter Correction, recorded from packaging papers reinforced with cellulose nanofibrils with grammage of 75, 85, 95 and 105 g/m².



Source - The authors (2019).

Table 2 - Calibration and validation of PLS models to estimate nanofibril content, grammage, physical and mechanical properties of papers reinforced with cellulose nanofibrils.

Property	PCs	R²c	RMSEc	R²cv	RMSEcv
Nanofibril content	8	0.98	0.01	0.98	0.01
Tensile index (TI)	8	0.93	1.90	0.91	2.27
Stretch (ST)	7	0.80	0.18	0.74	0.21
Resistance to air passage (RAP)	6	0.79	6.55	0.73	7.52
Bursting index (BI)	8	0.75	24.46	0.65	28.74
Tensile energy absorption (TEA)	7	0.70	12.72	0.62	14.76
Modulus of elasticity (MOE)	5	0.68	0.19	0.60	0.22
Grammage	8	0.68	6.35	0.59	7.18
Tearing index (TR)	7	0.63	100.97	0.29	139.81
Corrugating medium test (CMT)	8	0.55	16.42	0.17	22.27
Ring crush test (RCT)	8	0.53	0.10	0.15	0.13

R²c - coefficient of determination for calibration; RMSEc - mean square error for calibration; R²cv - coefficient of determination for cross validation; RMSEcv - mean square error for cross validation.
Source: The authors (2019).

According to Costa et al. (2018), the root mean standard error (RMSE) measures the efficiency of the calibration model to predict the property of interest in unknown samples, then only the models that yielded the lowest RMSEcv were selected and presented in Table 2.

According to the data presented, the calibration for nanofibril content had the highest R^2cv, demonstrating that NIRS technique can be used to detect the presence of cellulose nanofibrils on the paper matrix. The same behavior could be inferred for tensile index, stretch and resistance to air passage, which presented satisfactory R^2cv and low RMSEcv.

We like to highlight that in previous work with the same material (LIMA et al., 2019) the three properties mentioned before statistically presented differences between treatments only related to nanofibril content, with no contribution from grammage, while the other properties results showed contribution of both variables. Once nanofibril content had great prediction capacity and grammage had poorer, it is possible to infer that the better R^2cv of TI, ST and RAP compared to TR, BI, TEA, RCT and CMT is correlated to the strong relationship of the first three with nanofibril content, while the others are also influenced by grammage, with inferior NIR spectroscopy prediction capacity.

Fardim, Ferreira and Durán (2005) analyzed hand-sheets produced from pulps refined to different levels by means of NIR spectroscopy and found models with very good ability to predict TR, TI, BI, MOE and ST, with RMSEcv ranging from 0.13 to 3.64% and the performance maintaining itself when a new set of samples were analyzed. The authors supported the applicability of NIRS technique in-line.

Samistraro et al. (2009) studied Kraft papers with grammages between 115 and 440 g/m² by means of NIR spectroscopy and found R^2cv from 0.87 to 0.94 and RMSEv from 1.5 to 8.2% for the mechanical properties TI, BI, TR and RCT. Although the TI found in this study be as good as the one found by Samistraro et al., the superiority in the NIR prediction of the other properties can be associated with the larger range of grammages studied by the authors, that may have provided more variability to construct a robust calibration.

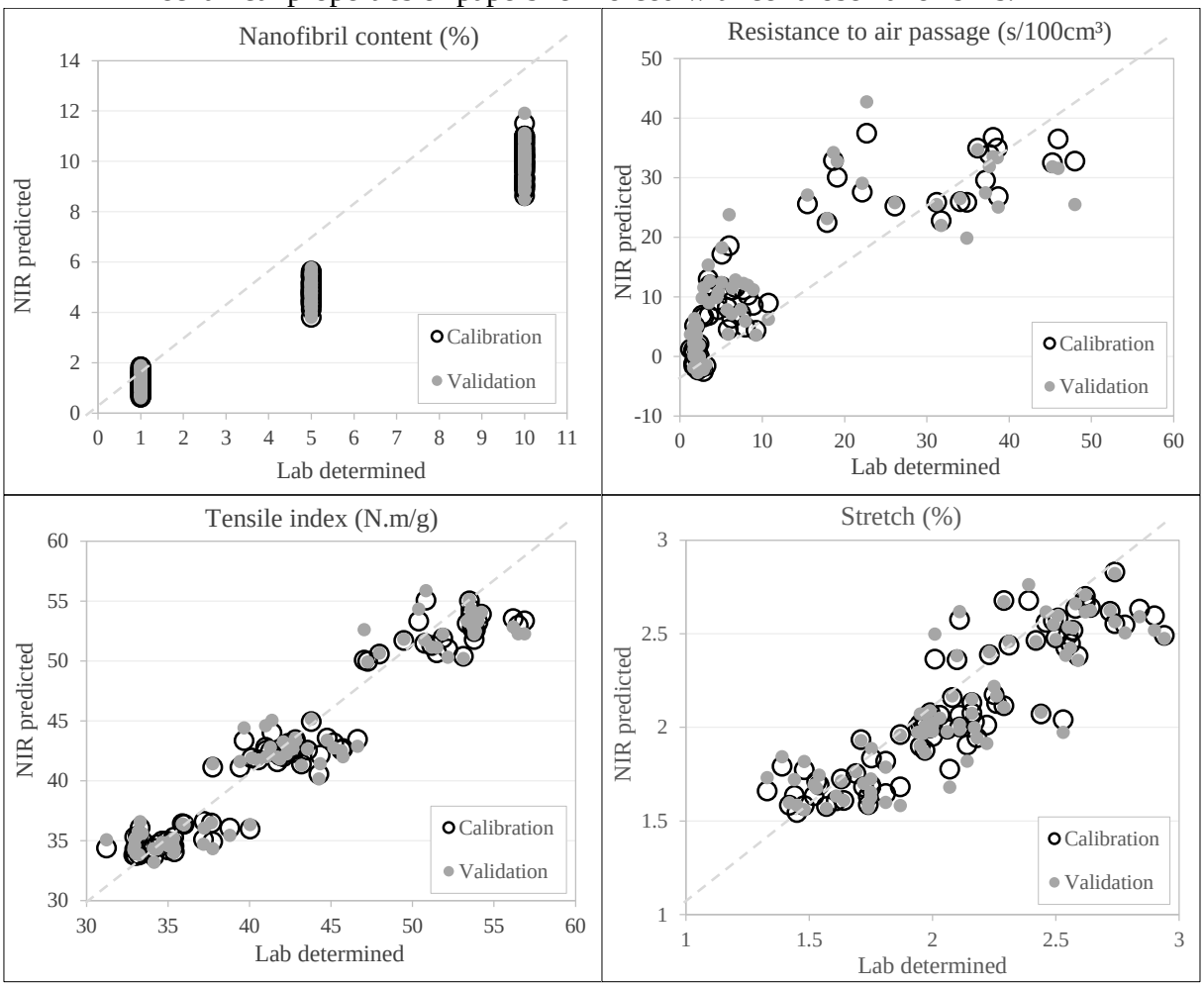
Tyson et al. (2012) studied mechanical properties of unbeaten bleached hand-sheets with grammage equal to 60 g/m² collected direct from the production line. The authors found R^2cv for tensile index of 0.51, resistance to air passage of almost 0.40 and stretch lower than 0.10, all calibrations considered poor. The authors justified that the calibration models were constructed from data with little variability, reflection of the reality of a commercial pulping operation, where the pulping process is tightly regulated and the variability of the final product is minimized.

Viana et al. (2015) analyzed cellulosic nanostructured films and found an R^2cv for bursting index of 0.93 and for tensile index of 0.83, confirming the NIRS technique ability to predict properties of nanocomposites.

TR, RCT and CMT presented the poorer R^2cv, no literature data was found to compare NIR calibration for CMT. Grammage, TEA and MOE presented regular values of R^2cv, no literature research analyzing grammage and TEA by NIRS was found.

Figure 4 shows the plots of measured versus predicted values for the calibrations with grater R^2cv. The strong association between the nanofibril content, resistance to air passage, tensile index and modulus of elasticity determined in laboratory and that predicted by the NIR model, indicate the possibility of using the NIRS technique to estimate nanofibril content, physical and mechanical properties of unknown papers.

Figure 4 - Lab determined versus NIR Spectroscopy predicted values to estimate physical and mechanical properties of papers reinforced with cellulose nanofibrils.



Source - The authors (2019).

Once the nanofibril concentration was considered a categorical variable, presenting discrete values, the PLS-DA is considered a more suitable classification analysis then the PLS.

The summary of PLS-DA classifications for nanofibril content, including the number of correct and incorrect classifications and the correct classification percentage is displayed in Table 3, for cross-validation. The results showed that only two samples were misclassified, in the 5 and 10% categories, resulting in an incorrect classification of 1.8% for both categories. Costa, Trugilho and Hein (2018) used PLS-DA to classify charcoals by final temperature of carbonization, with one mistake in just one of the four categories, resulting in correct classifications of 97.8 to 100%. Belini et al. (2011) used PLS-DA to classify the percentage of sugarcane bagasse in MDF panels, with a 94% of the samples classified correctly by cross-validation. The results prove that the analysis can be successfully used to classify variables with discrete values.

Table 3 - Classification of 84 packaging paper specimens according to nanofibril content using PLS-DA models by cross-validation.

Nanofibrils	Nanofibrils estimated by NIR			Correct classification	
	1%	5%	10%	No.	%
1%	56			56	100
5%		55	1	55	98.2
10%		1	55	55	98.2

Source - the authors (2019).

Many studies were developed using NIR spectroscopy to control pulping process and, however the number of studies in the paper properties field is less numerous, the results found in the literature point to a secure applicability of the technique to in-line control of paper and paperboard production.

4 CONCLUSION

- The results found in this study show that near infrared spectroscopy has potential to predict physical and mechanical properties of papers;
- NIRS technique was capable to predict the nanofibril content on paper matrix with R^2cv of 0.98, although the PCA was not able to separate samples based on the nanofibril content;
- A property dependence with nanofibril content can help to improve its NIR prediction;

- PLS-DA models correctly classify more than 98% of the samples according to nanofibril content;
- With the intense research and raising development of less expensive and faster methods to produce cellulose nanostructures, the application of this material will increase and NIRS is capable to predict its in-line concentration.

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REFERENCES

BELINI, U. L. et al. Near infrared spectroscopy for estimating sugarcane bagasse content in medium density fiberboard. **BioResources**, v. 6, p. 1816–1829, 2011.

BIRKETT, M. D.; GAMBINO, M. J. T. Estimation of pulp kappa number with near-infrared spectroscopy. **TAPPI Journal**, v. 72, p. 193–197, 1989.

COSTA, E. V. S. et al. Influence of spectral acquisition technique and wood anisotropy on the statistics of predictive near infrared–based models for wood density. **Journal of Near Infrared Spectroscopy**, v. 26, n. 2, p. 106-116, 2018.

COSTA, L. R.; TRUGILHO, P. F.; HEIN, P. R. G. Evaluation and classification of eucalypt charcoal quality by near infrared spectroscopy. **Biomass and Bioenergy**, v. 112, p. 85–92, 2018.

FARDIM, P.; FERREIRA, M. M. C.; DURÁN, N. Determination of mechanical and optical properties of eucalyptus Kraft pulp by NIR spectrometry and multivariate calibration. **Journal of Wood Chemistry and Technology**, v. 25, p. 267–279, 2005.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS - FAO. **FAO Yearbook of Forest Products 2016**. Rome, 2018. 243 p.

LIMA, L. C. et al. Influence of cellulose nanofibrils on packaging papers resistance. In: LIMA, L. C. **Evaluation of packaging papers reinforced with cellulose nanofibrils by near infrared spectroscopy.** Lavras: 2019. Tese - Universidade Federal de Lavras, p. 37-50.

MARKLUND, A. et al. Prediction of strength parameters for softwood Kraft pulps. Multivariate data analysis based on orthogonal signal correction and near infrared spectroscopy. **Nordic Pulp & Paper Research Journal**, v. 14, p. 140–148, 1999.

PASQUINI, C. Near infrared spectroscopy: fundamentals, practical aspects and analytical applications. **Journal of the Brazilian Chemical Society**, v. 14, n. 2, p. 198-219, 2003.

REITER, C. et al. Characterization of pulp and chemical additives with the help of FT-NIR technique. **Papier**, v. 53, p. V20–V24, 1999.

SAMISTRARO, G. et al. Previsão das propriedades físicas do papel Kraft por espectroscopia no infravermelho próximo (NIR) e regressão por mínimos quadrados parciais (PLS). **Química Nova**, v. 32, n. 6, p. 1422-1425, 2009.

TYSON, J. A. et al. Development of near infrared calibrations for physical and mechanical properties of eucalypt pulps of mill-line origin. **Journal of Near Infrared Spectroscopy**, v. 20, p. 287–294, 2012.

WALLBACKS, L. et al. Multivariate characterization of pulp using solid-state 13C NMR, FTIR, and NIR. **TAPPI Journal**, v. 74, p. 201–206, 1991.

WORKMAN JR., J.; WEYER, L. **Practical guide to interpretive near-infrared spectroscopy**. Boca Raton, CRC Press, Taylor & Francis Group, 2008. 332 p.

WRIGHT, J. A.; BIRKETT, M. D.; GAMBINO, M. J. T. Prediction of pulp yield and cellulose content from wood samples using near-infrared reflectance spectroscopy. **TAPPI Journal**, v. 73, p. 164–166, 1990.

YAN, D. B.; KRISHNAGOPALAN, G. A. Dynamic modelling of carbohydrate degradation in Kraft pulping of softwood. **Appita Journal**, v. 56, p. 391–396, 2003.