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SPRAYING CELLULOSE NANOFIBRILS FOR IMPROVEMENT OF TENSILE AND BARRIER PROPERTIES OF WRITING & PRINTING (W&P) PAPER

Seyedmohammad Mirmehdi,[1] Maria Luiza Cafalchio de Oliveira,[1] Paulo Ricardo Gherardi Hein ,[1] Marali Vilela Dias,[2] Claire Isabel Grígoli de Luca Sarantópoulos,[3] and Gustavo Henrique Denzin Tonoli[1]

[1]Departamento de Ciências Florestais, Universidade Federal de Lavras, Lavras, MG, Brazil
[2]Departamento de Ciência dos Alimentos, Universidade Federal de Lavras, Lavras, MG, Brazil
[3]Instituto de Tecnologia de Alimentos, Universidade Estadual de Campinas, São Paulo, SP, Brazil

An experimental spray coater was used to coat writing and printing (W&P) paper substrate with cellulose nanofibrils (CNFs) suspensions. The effects of spraying variables (i.e. concentration of suspension, spray pressure, distance and time of spray) on the coated sheets were analyzed in terms of the tensile strength, water vapor transmission rate (WVTR), and oxygen transmission rate (OTR). Basis weight and the thickness of coated layers in the different treatments were measured. In addition, image analysis of the microstructure examined the coating adhesion. The WVTR of the papers decreased, while tensile strength increased with one layer of CNF coating. The OTR was not changed with the CNF coating. The tensile strength and microstructure images of the coated papers indicate good adhesion between the CNF coating and the paper substrate when using the spray coater.

KEYWORDS. Cellulose nanofibers, spray coating, barrier properties, natural fiber, tensile strength

INTRODUCTION

Cellulose nanofibrils (CNFs), which are constituted by an abundant natural biopolymer formed by repeated connection of D-glucose molecules occurring in the cellular walls of vegetables fibers, have received heightened interest because they are renewable, nontoxic, biodegradable, stable, and inexpensive.[1–3]

Cellulose fibers can be processed to obtain nanostructures with different properties that rely on extraction method and on cellulose source. Recent studies reported the production of cellulose nanostructures from wood,[4–9] and some non-wood resources such as rice straw, hemp,[10] banana stem,[11] jute,[12] bagasse, bamboo,[13,14] areca nut husk,[15] sisal,[16] algae,[17] and bacteria.[18] Three types of cellulose nanostructures have been explored for commercial applications: cellulose nanofibrils (CNFs), cellulose nanocrystals (CNC), and bacterial nanocellulose (BC), which differ from each other by size, crystalline structure, source, and extraction process. CNF can be extracted by delamination of cellulosic material (wood or non-wood fibers) by mechanical pressure and/or after chemical or enzymatic treatment. Amorphous and crystalline regions constitute these structures, with an average diameter between 20 and 50 nm and several micrometers of length.[19] CNCs are crystalline structures that may be obtained by acid hydrolysis with average size of 5–70 nm diameter and 100–250 nm length. Lastly, BC is produced from low-molecular-weight sugars and alcohols by bacterial synthesis, in a bottom-up approach, with average size of 20–100 nm diameter.[20]

Address correspondence to Seyedmohammad Mirmehdi, Departamento de Ciências Florestais, Universidade Federal de Lavras, Cx P. 3037, 37200-000, Lavras, MG, Brazil. E-mail: mohamadmirmehdi@yahoo.com
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Several applications have been reported in literature for the use of CNF, such as improvement of paper properties,[21–23] in biomedical applications, nano-metal complexes,[24–26] hybrid materials,[27] electronics device industry, as reinforcement for polymeric matrices,[28–31] and in the packaging industry.[32] The use of nanoscale materials may be justified by the capacity to improve mechanical and barrier properties due to their high surface area. CNFs can form a large network structure, and, consequently, increase mechanical resistance and decrease water vapor and gas permeability of paper sheets. In this sense, CNFs may be used for development of cellulosic packaging, including wrapping materials and containers, primary and secondary packages, and flexible and rigid packaging products,[32] or as a coating layer to improve mechanical and/or barrier properties in paper packaging.[33,34,32,35]

Indeed, cellulose is one of the most important material in the packaging industry. About 40% of the total packaging materials are based on cellulose.[34] Actually, paper and paperboard are the mainly renewable materials widely used for packaging, despite the fast growing and scaling up of new biopolymer materials under research. Nevertheless, paper and paperboards use is restricted for packaging, given their poor barrier properties, due to their large porosity and permeability.[36] Therefore, much effort has been applied to improve mechanical and barrier properties of cellulose packaging materials.[33,37,34,32,35] Thin coating layers are powerful tools for enhancing many properties of food and beverage packaging materials.[37] The thickness of such layers normally ranges from tenths of nanometers to few micrometers. Thickness of conventional petroleum-based plastic films can be reduced through a thin layer of functional and high-performing bio-based material. Cellulose nanofibers have also been investigated as a functional layer on various substrates.[34]

The spray coating is an convenient way to apply the cellulose nanofibers, presenting some advantages compared to other techniques: (i) the coating is carried out contactless, and a contour coat can be applied to uneven surfaces; (ii) substrate topography does not influence coating weight; (iii) tear-sensitive web materials can be coated with a spray; (iv) low coating weights are achievable at high velocities and (v) a dense film can be achieved with a decreased amount of liquid, reducing costs and improving quality.[38] Few research works were found about the use of spraying CNF on paper or its efficiency for improving mechanical and barrier properties. Then, in the present study, kraft writing and printing (W&P) papers were spray coated with CNF suspensions to decrease the oxygen transmission rate and the water vapor transmission rate, and to increase tensile strength. Spraying parameters (concentration, pressure, distance and time of spray) were investigated for optimizing the use of CNFs for improving mechanical and barrier properties of W&P paper.

MATERIALS AND METHODS

Materials

The paper substrate used in this research was commercial writing & printing (W&P) paper (Suzano Papel e Celulose, Brazil), made of 100% cellulose of *Eucalyptus* with a nominal basis weight of 75 g/m² and a nominal thickness of 95.5 µm.

Cellulose nanofibrils (CNFs) were obtained from commercial *Eucalyptus* bleached kraft pulp (Jacareí/SP, Brazil), composed of approximately 99 wt.% holocellulose (cellulose + hemicelluloses). The cellulose fraction was composed of ~92.2 wt.% α-cellulose, 6.9 wt.% β-cellulose and 0.9 wt.% γ-cellulose, according to a TAPPI T 203 cm-99[39] standard.

Obtaining the Cellulose Nanofibrils (CNFs)

The starting eucalyptus pulp was soaked overnight in deionized water and disintegrated in a lab mechanical stirrer (Fisatom, model 722). Then, the pulp was defibrillated in a SuperMasscolloider (Model: MKCA6-2J, Masuko Sangyo Co., Ltd., Japan) at 1,500 rpm, using a pulp suspension with solid consistency of 1% (w/w) and 30 passages through the

defibrillator, following suggestions of previous works.[7,40,13,14,41]

Morphological Characterization of Fibers and Nanofibrils (CNFs)

A Leica DM4000B compound light optical microscope (OM) was used for the initial investigation of the morphology of the starting pulp fibers, and after defibrillation. Suspensions were stained with a drop of ethanol-safranin solution (0.5% v/v) in order to increase the contrast between phases. The obtained CNFs were viewed with a transmission electron microscope (TEM) FEI Tecnai 12 operated at 120 kV. A drop of the suspension was deposited on a 400-mesh copper grid coated with formvar/carbon, and dried before viewing with TEM. The average diameter of the micro/nanofibrils was determined by digital image analyses (Image J 1.48v, National Institutes of Health, USA). A minimum of 500 measurements was collected for data analysis.

Experimental Setup for Spray Coating

CNF/water suspensions were sprayed onto paper substrates using a laboratory-assembled spray coater (see Figure 1). There are seven controllable variables in this kind of spraying that are of fundamental importance: (i) concentration of suspension; (ii) spray pressure; (iii) spray distance; (iv) time of spraying; (v) nozzle type; (vi) drops size; and (vii) drop impact. Since spray nozzles are designed to perform under many different spraying conditions, more than one nozzle may meet the requirements for a given application. Surfaces may be sprayed with any pattern shape. Results are fairly predictable, depending on the type of spray pattern specified. If the surface is immovable, which it is in the present case, the preferred nozzle is usually some type of full cone nozzle (Figure 1), since its pattern will cover a larger area than the other types.[42] The variables and parameters evaluated in the present work are presented in Table 1 and were defined based on previous exploratory tests. Spray impact and drops size were not evaluated here.

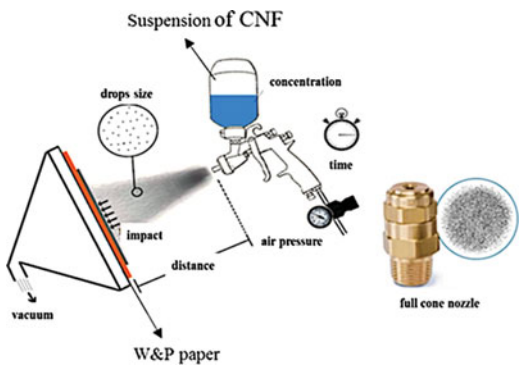

FIGURE 1. Scheme of the experimental procedure used for spray coating on the writing & printing paper with cellulose nanofibrils (CNFs) suspension.

TABLE 1. Variables and parameters of the spray coating tested in this study

Concentration of CNF suspension (%)	Spray pressure (bar)	Spray distance (cm)	Time of spraying (s)
1.4	4	15	20
1.7	5	30	30

Basis weight and thickness of the papers were measured for each treatment before spraying the CNF. The results of spray coating are in Table 1. No CNF suspension appears to have been lost during the spraying process. Vacuum dewatering was applied to obtain consistent removal of the water from the coated papers before oven drying. The coated papers were oven dried for 1 h at 103°C without pressing, in order to preserve the superficial profile of the coating deposition. After drying, the coated papers were pressed (1 bar). Each treatment was performed in three replicates. Control specimens of W&P paper were submitted to the same spraying and drying procedures, however, using deionized water instead of CNF suspension. All samples were conditioned and tested at 23°C and 50% relative humidity (RH) prior to characterizations.

Thickness and Basis Weight of the Papers

Paper thickness was measured at five positions on each sample, using a Regmed micrometer (model ESP/SA-10, Brazil) according to the

standard method ASTM D645-97.[43] The basis weight or grammage of the papers was determined using an electronic analytical balance (JKI, model JK-EAB-2204N, China), according to the standard method ASTM D646-96.[44] The thickness and basis weight of the papers were measured before and after spray coating with the CNF suspension.

Tensile Strength of the Papers

Tensile strength was determined on a tensile strength tester, Stable Microsystems (model TATX2i, England) according to ASTM D828-97.[45] All paper specimens were cut in the machine direction. The standard dimension of the specimens required for performing this test is 25.4 ± 0.5 mm wide and around 254 mm length. The distance between the grip clamping zones was 180 ± 5 mm with the rate of dislocation of 25.4 mm/min.

Water Vapor Transmission Rate (WVTR) of the Papers

The water vapor transmission rate (WVTR) measurements were performed according to the desiccant method of ASTM E96 / E96M-16,[46] at 25°C and 50% RH. Results are the average of three measurements per sample. The changes of mass were monitored every day until constant mass was attained.

Oxygen Transmission Rate (OTR) of the Papers

The oxygen barrier properties were tested by measuring the OTR of samples according to the ASTM D3985-05[47] standard, using an OX-Tran oxygen permeability testing system, model 2/20 (Mocon, Inc., USA). At a selected temperature and humidity (23°C and 1% RH), the coated papers were sealed between a chamber containing oxygen and a chamber without oxygen. A coulometric sensor measures the oxygen that was transmitted through the material. The commonly used unit is $cm^3\ m^{-2}\ 24\ h^{-1}$. The coated face of the specimens was positioned in contact with the permeant gas (100% O_2) into the chamber system. The readings were corrected to 1 atm partial pressure gradient of permeant gas. The permeation area of the samples was 5 cm^2 and they were conditioned at 23°C for 72 h in a desiccator with silica gel.

Scanning Electron Microscopy (SEM) of the Papers

Surface and cross section of the papers were assessed by scanning electron microscopy (SEM) using a Zeiss LEO EVO 40 XVP (Germany) with secondary electron (SE) detector and accelerating voltage of 20 kV. Samples were gold coated with a sputter coating technique.

RESULTS AND DISCUSSION

Morphology of Fibers and Nanofibrils (CNFs)

Figures 2a and b show light microscopy images of the eucalyptus pulp fibers before and after grinding defibrillation, respectively. The fiber cell wall is constituted of nanofibrils in a multi-layered structure connected by hydrogen bonds. The shearing forces generated by the grinding stones, which individualize the nanofibrils, break down these hydrogen bonds.[3] The average values of length and diameter of the eucalyptus raw fiber were around 0.7 ± 0.3 mm and 17 ± 4 µm, respectively, which are in the same range as found by Belini et al.[48] and Brisola and Demarco.[49] Figure 2c shows a typical TEM image of the obtained nanofibrils. Figure 3 depicts the diameter distribution of nanofibrils determined by measurements using TEM images. Almost 55% of the nanofibril diameters were lower than 40 nm. The average nanofibril diameter in the suspension was 50 ± 40 nm, similar to those obtained by other authors using various methods such as sonication,[50] mechanical defibrillation,[7] mechanical defibrillation after anaerobic pretreatment,[41] and microfluidizer homogenization.[51]

LM images (Figure 2b) show fiber fragments that were not completely deconstructed. Zuluaga et al.[52] reported that the existence of residual hemicelluloses and lignin in the pulp could prejudice the mechanical defibrillation

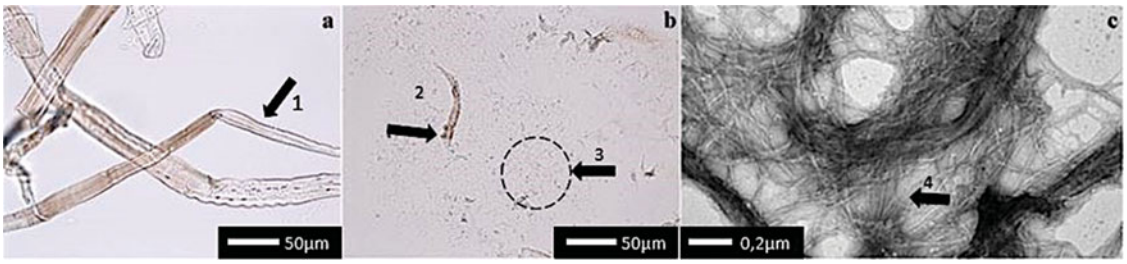

FIGURE 2. (a) and (b) Typical light microscopy (LM) images of the fibers before and after defibrillation, respectively; (c) typical transmission electron microscopy (TEM) micrograph of the cellulose nanofibrils (CNF) derived from the defibrillation process. Note the intact fiber cell wall (arrow 1), disruption of the fiber cell wall (arrow 2), fibrillation of the fiber due to mechanical shearing (arrow 3), the individualized nanofibrils after defibrillation (arrow 4).

process. Furthermore, the wetting and drying step applied to the pulp before defibrillation may cause strong hydrogen bonds between the amorphous domains of cellulose fibrils,[53] which can prejudice the defibrillation process.

Sheet Thickness and Basis Weight

Figure 4 presents the average and standard deviation values of thickness and basis weight of the applied CNF layers. The thickness (Figure 4a) and basis weight (Figure 4b) of the CNF layers were directly correlated, and were in the range between 5.8 ± 0.1 µm to 11.0 ± 0.1 µm and 3.7 ± 0.1 to 9.9 ± 0.1 g/m^2, respectively. Figure 4 shows that the higher thickness and basis weight (9.9 ± 0.1 g/m^2) occurred using 1.4% concentration, 5 bar pressure, 15 cm distance, and 30 s of application. The lower thickness and basis weight (3.7 ± 0.1 g/m^2) was reached using 1.7% concentration, 4 bar pressure, 30 cm distance, and time of 20 s. The lower values of thickness and basis weight for papers with higher CNF concentration (1.7%) may be associated with the higher viscosity of this suspension, which lead to a lower volume of CNF to be sprayed in the same nozzle configuration. The CNF suspension presents a pseudoplastic behavior, being viscous under natural conditions and less viscous when agitated. Even at low solid levels (<2%), the fluid behavior is non-Newtonian, presenting high viscosities.[54] In addition, increasing air spray pressure from 4 to 5 bars increased the output suspension. The spray distance of 15 cm led to higher load of CNF on the paper than 30 cm, probably due to the higher spread of CNF to the air, causing lower effective deposition of CNF on paper surface.

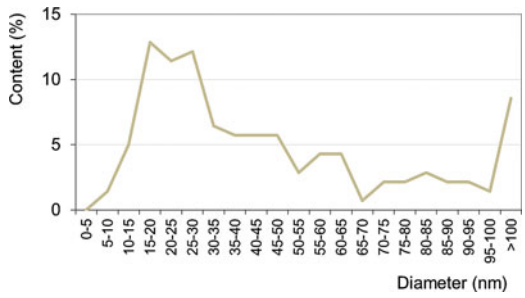

FIGURE 3. Diameter distribution histogram of the cellulose nanofibrils (CNFs) LM images (Figure 2b) show fiber fragments that were where not completely deconstructed. Zuluaga et al.[52] reported that the existence of residual hemicelluloses and lignin in the pulp could prejudice mechanical defibrillation process. Furthermore, the wetting and drying process applied to the pulp before defibrillation cause strong hydrogen bonds between the amorphous domains of cellulose fibril,[53] that can prejudiced the defibrillation process.

Tensile Strength of the Paper Specimens

Figure 5 shows the average and standard deviation values of tensile strength obtained from the paper specimens. Tensile strength increased for all coated papers when compared to control specimens (without CNF coating). Tensile strength was directly related to basis weight and paper thickness. Figure 6 shows the changes of tensile strength of the paper as a function of the basis weight and thickness of the deposited CNF layer. Coated papers with higher basis weight and thickness presented higher strength. In the best

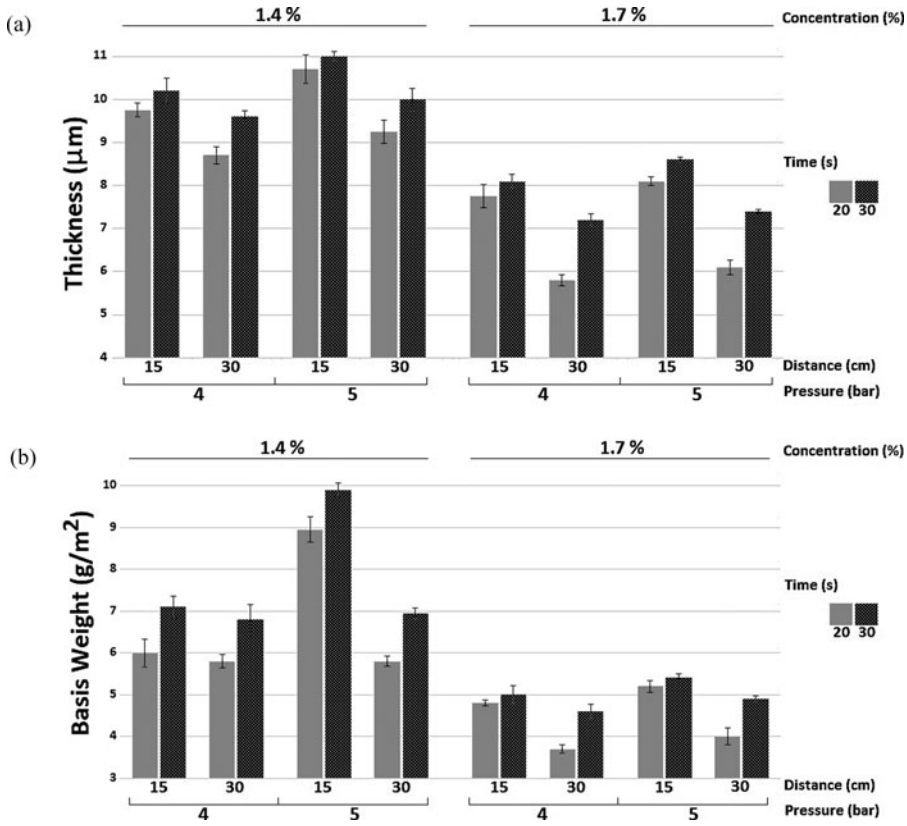

FIGURE 4. Average and standard deviation values of: (a) thickness; and (b) basis weight of the coated papers as a function of CNFs concentration (1.4 and 1.7%), air pressure (4 and 5 bar), and distance of application (15 and 30 cm) and time of spraying (20 and 30 s).

condition, tensile strength increased about 18% in relation to control paper. These values agree with the measurements of Rodionova et al.,[55] which investigated the impact of thickness and basis weight on tensile strength of layered films prepared by bar coating. Beneventi et al.[33] also observed that mechanical properties linearly increased with the increase of the CNF basis weight in different paper substrates by the spray coating method. They

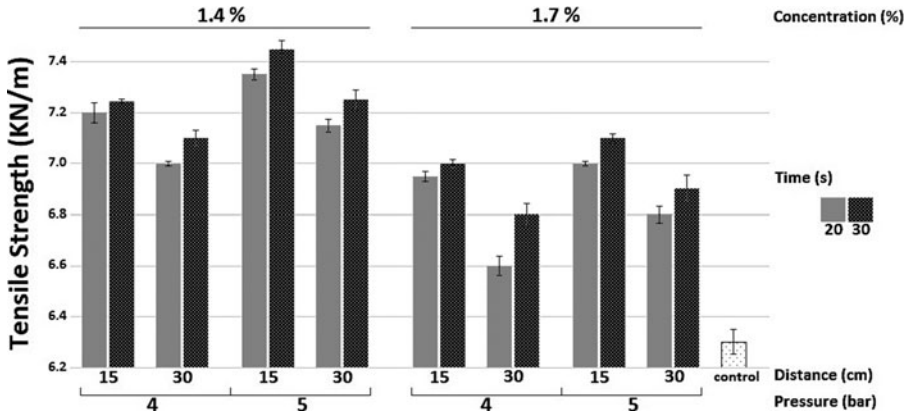

FIGURE 5. Average and standard deviation values of tensile strength of the coated papers as a function of CNFs concentration (1.4 and 1.7%), air pressure (4 and 5 bar), distance of application (15 and 30 cm) and time of spraying (20 and 30 s).

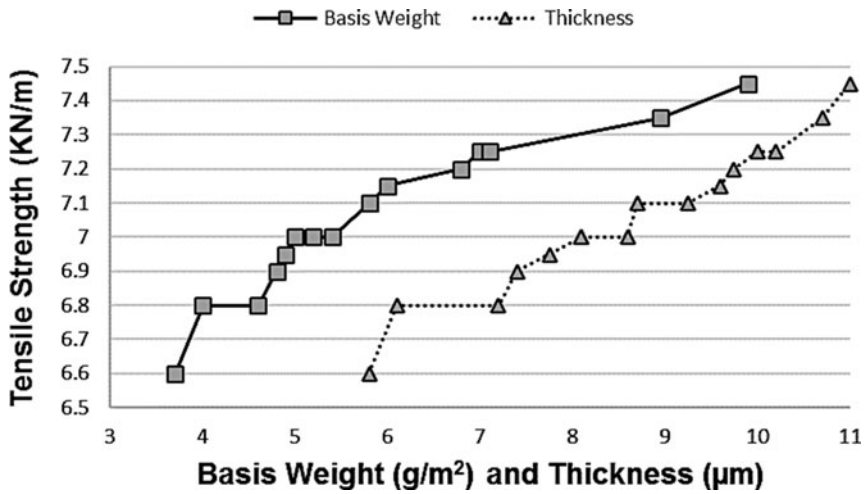

FIGURE 6. Tensile strength of coated papers as function of basis weight and thickness of the CNFs layer.

associated this fact with the good interface between CNF and paper and CNF's characteristics such as inter- and intra-bonding, high aspect ratio and capacity to form dense networks. Other authors[56,57] reported the improvement of mechanical properties with CNF addition in different composites.

Water Vapor Transmission Rate (WVTR)

Generally, water vapor transport in paper occurs under diffusion mechanisms through inter-fiber void space, Fick diffusion, Knudsen diffusion, surface diffusion, bulk solid diffusion within fibers, and capillary transport. However, the dominant transport mechanism in paper is the diffusion through inter-fiber void space.[58] Water vapor transmission rate (WVTR) is depicted in Figure 7. CNF coating decreased WVTR of the specimens in relation to control paper. In the best condition, WVTR of paper (~28.5 g m^{-2} 24 h^{-1}) decreased around 16% using 11 µm of CNF layer (~24 g m^{-2} 24 h^{-1}). Cellulose is a hydrophilic polymer with high water absorption capacity; however, when disintegrated to nanoscale particles, it forms a very closed net of nanofibrils, which creates a tortoise path for water molecules and increases the resistance to their diffusion. Thus, the CNF coating on paper sheets can provide improvement to barrier properties.

WVTR was negatively correlated to the thickness and basis weight of the CNF layer

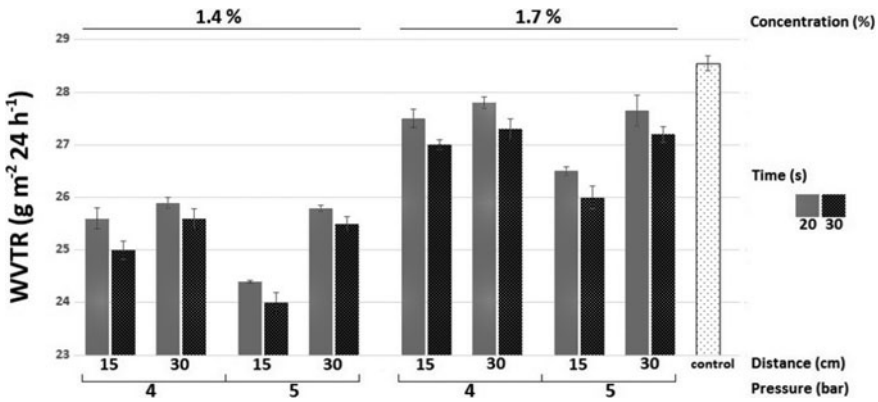

FIGURE 7. Average and standard deviation values of water vapor transmission rate (WVTR) of coated papers as a function of CNF concentration (1.4 and 1.7%), air pressure (4 and 5 bar), distance of application (15 and 30 cm) and time of spraying (20 and 30 s).

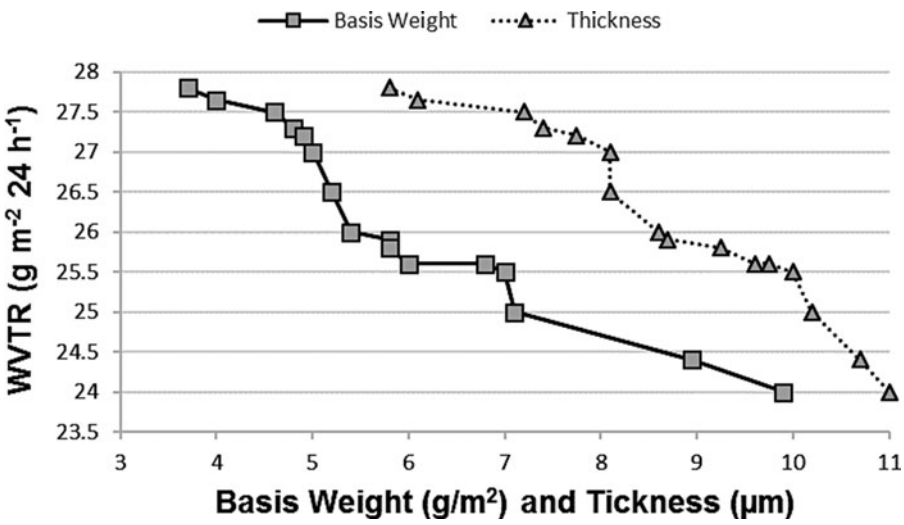

FIGURE 8. Average water vapor transmission rate (WVTR) values of coated papers as function of basis weight and thickness of the CNF layers.

(Figure 8). Higher values of WVTR were found to lower values of thickness and basis weight of the CNF coatings. It implies that CNF layer is acting as water vapor barrier. Hult et al.[36] showed that this technique could be an effective way to extend the application of paper-based materials in the food packaging area, and to avoid the use of petroleum-derived products. Reduction of WVTR was also observed in previous studies.[59–61,58]

Oxygen Transmission Rate (OTR)

Actually, OTR values of coated papers produced here were too high (OTR > 155,000 cm^3 m^{-2} 24 h^{-1}), which did not permit an evaluation. The obtained results are typical for cellulose papers,[62] because paper is not an efficient barrier for oxygen. CNF coating applied here with spray deposition did not permit reaching the barrier properties achieved by Syverud and Stenius[63] with 30 µm–thick CNF film. When the OTR of a 25 µm–thick film is less than 10 cm^3 m^{-2} 24 h^{-1} (at 25°C, 50% RH), it is considered a high oxygen barrier.[64,65] The barrier properties provided by the CNF layers were not efficient as expected, probably because of the incomplete blocking of the surface pores of the papers and heterogeneities from the application. Increasing the basis weight of the CNF layer would probably improve the barrier properties. The Van der Waals diameter of an O_2 molecule is 0.29 nm[36]; therefore, the mat of CNF must be able to form a dense layer with nanopores lower than those diameters in order to brake the passage of oxygen molecules. Thomas et al.[66] measured OTR on corn zein–coated paper and found poor oxygen barrier properties.

Microstructure of the Coated Papers

Figure 9 presents typical SEM images of the surface and cross section of the papers. The network of CNF is denser than that of the W&P paper, as a consequence of the great connection between nanofibrils formed by hydrogen bonding. It plays a considerable role in increasing tensile strength and decreasing WVTR in coated papers and in the CNF layer.

Typical SEM micrographs demonstrated that the CNF layer reduced the porosity of the coated paper surface (Figure 9b) in relation to control (Figure 9a). This dense nanostructured layer (Figures 9c and 9d) formed by the nanofibrils resulted in the improvement of the WVTR properties as depicted previously (Figure 8). This modification of the microstructure of the pore network drove down the WVTR by reducing pore size and increased the mechanical properties.

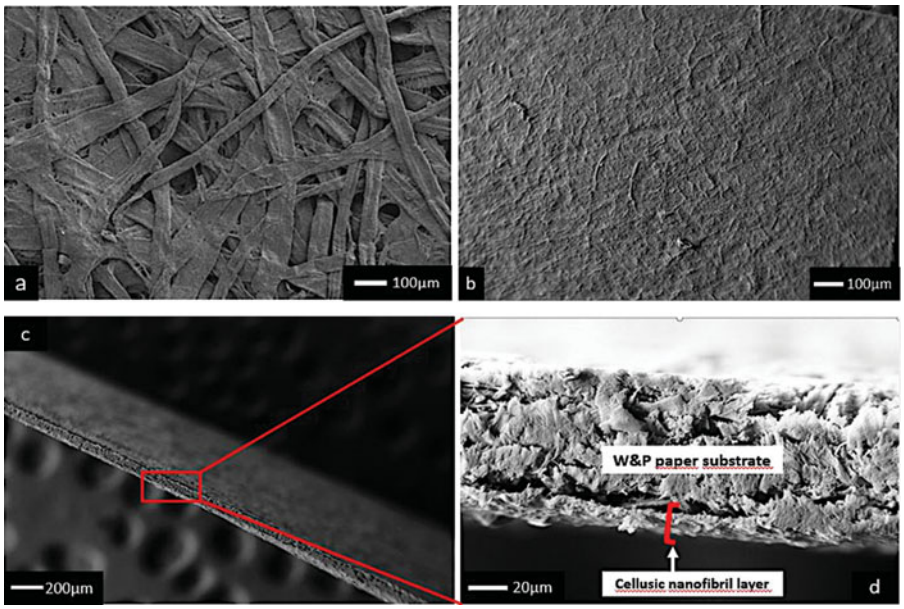

FIGURE 9. Typical scanning electron microscopy (SEM) images of the coated paper with 11 µm-thick layer of cellulose nanofibrils (CNF): (a) surface of the control (uncoated) paper; b) surface of the spray-coated paper with CNF; c) cross section of the coated paper.

CONCLUSIONS

Cellulose nanofibrils (CNF) were successfully obtained from eucalyptus kraft pulp by mechanical defibrillation, presenting an average diameter of 50 ± 40 nm, with around 55% of the nanofibrils with a diameter lower than 40 nm. The greater the CNF content, the higher the thickness and basis weight of the applied CNF layer and, consequently, of the coated papers, which interferes with their strength and barrier properties. The best condition for CNF application (1.4% CNF concentration, air spray pressure of 5 bar, spraying distance of 15 cm and 30 s of spraying application) resulted in a CNF layer with 11 µm thickness and basis weight of 9.9 g/m^2, leading to an 18% increase of tensile strength and a 16% decrease of WVTR in comparison to control paper (with no coating). The present work contributes with information about the use of spray coating for application of CNF on surface-coated papers. Further development of this approach could improve the performance of the papers and contribute to the development of new and engineered cellulose-based materials for paper-based packaging applications.

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ORCID

Paulo Ricardo Gherardi Hein
http://orcid.org/0000-0002-9152-6803

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