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EVALUATION OF POLY(VINYL ALCOHOL) ADDITION EFFECT ON NANOFIBRILLATED CELLULOSE FILMS CHARACTERISTICS.

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HIGHLIGHTS

Biodegradable polymers from renewable sources attract a lot of attention, due to the increase in environmental awareness and the problem of depletion of fossil sources.

Polymer matrix nanocellulose reinforcements provide greater added value and superior performance in extensive applications to new materials.

Innovative and promising results are obtained in the conversion of lignocellulosic materials into new products used in engineering.

ABSTRACT

In this study, based on the mechanical shear treatment, the cellulosic pulp was fibrillated in nanofibrils dispersed in aqueous suspension. Nanofibrillated Cellulose (NFC) matrix - Polyvinyl Alcohol (PVA) nanocomposite films were prepared by casting from NFC/PVA suspension mixtures. The thermal and mechanical properties of the obtained films were evaluated. Low levels (2, 5 and 10 wt%) of PVA were used as an additive in a nanofibrillated cellulose (NFC) matrix. The predominant use of NFC, with superior properties due to its purity, with an efficient and environmentally friendly method, has allowed the production of NFC-based biodegradable materials with enhanced properties for high-level applications. The addition of PVA to the NFC matrix produced positive results, as it causes little aesthetic interference, without changes in surface brightness. After the addition of PVA the films showed a great gain in mechanical strength, increasing by 24% in Young's modulus with the addition of 10% PVA. Even after addition, the samples' chemical composition remains unchanged and the mixture shows a decrease in the film surface hydrophilicity when compared to pure NFC. Composite material thermal analysis indicates that thermal degradation temperatures remain unchanged after the addition of PVA. Although PVA is not very temperature resistant, in the proportions used, NFC thermal resistance is preserved.

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INTRODUCTION

A large number of living organisms can naturally produce high-performance extracellular structural biocomposites consisting of a fibrous reinforced matrix with biopolymers, for example, cellulosic fiber, a major component of hemp, wheat straw, rice straw, bagasse, wood. In particular, lignocellulosic materials in general, are considered unlimited and renewable resources for the production of functional biocomposites (XIAO et al., 2016, LINDSTROM et al., 2015).

Considerable interest is currently directed to the micro or nanofibrils of cellulose and its composites, due to its low-cost properties, biocompatibility, bioactivity, low toxicity, biodegradability, and oxygen barrier (SPOLJARIC et al., 2014; ABDUL KALIL et al., 2012). These particularities give them many potential applications, such as the controlled release of substances of interest, tissue engineering, food packaging, and reinforcement in materials (LU et al., 2017; XU et al., 2015; KISONEN et al., 2015; LENDLEIN; SISSON, 2011).

Ways to extract nanofibrillated cellulose (NFC) from different sources are the subject of some research, such as a combination of chemical and mechanical treatments. Jonooobi et al. (2009) nanofibrils isolated from unbleached and bleached kenaf pulp. The obtained nanofibrils presented greater crystallinity and thermal stability in relation to crude kenaf. Among the reported studies of cellulose nanofibril-reinforced composites from chemo-mechanical pulp, they have received increasing interest as prepared with reinforced phenolic resin (NAKAGAITO; YANO 2008), acrylic resin (YANO et al., 2005) and polylactic acid compounds (FRONE et al., 2013). The composites exhibited higher tensile strength and modulus of elasticity than pure polypropylene. Nanocomposite films with NFC addition to polyvinyl alcohol (PVA) in order to produce films with higher mechanical strength and potential for use were prepared. In the researchers' report, the study offered an efficient and environmentally friendly method of manufacturing green NFC-based biodegradable materials with enhanced properties for high-level applications (NGUYEN; LIU 2013). The NFC was well dispersed in the medium showed good reinforcing effects on the PVA matrix, for example, the tensile stress and modulus have been increased, were increased by 63% when nanocrystalline cellulose was added to PVA (KABOORANI, et al., 2012). In the case of low NFC content (less than 5% by weight), the results were expressive, indicating a good increase in mechanical resistance.

Research from PVA/NFC hydrogels with a controlled and highly connected porous structure using poly (ethylene glycol) (PEG) with three different molecular weights, such as the physical porogen during crosslinking, reveals that the swelling properties were quite high, improved due to the presence of porous structure (XU et al., 2015). After adding the NFC to the PEG-modified hydrogels, a highly porous and interconnected matrix was formed with increased swelling and thermal properties. Hydrogels are shown promising for application in controlled release and other functional engineering fields.

The incorporation of NFC into biodegradable polymer matrix has been explored as an important strategy to obtain nanocomposites with environmentally correct performance (QIU; NETRAVALI 2012; HABIBI et al., 2010; EICHHORN et al., 2010); for example, NFC-reinforced polylactic acid nanocomposites have also shown improved mechanical properties (FRONE et al., 2013; JONOObI et al., 2010). Although extensive work has been done to prepare biodegradable polymeric materials reinforced with nanofibrillated cellulose (EICHHORN et al., 2010), poor mechanical performance remains a fundamental problem that restricts its applications.

Due to the highly ordered molecules in the NFC, high resistance, high specific modulus, and good dielectric performance are evidenced by some researchers (LU et al., 2017, SIRÓ; PLACKETT, 2010, TARRÉS et al., 2016, XU et al. 2015). Generally, NFC has impressive mechanical properties, especially wood-based nanocellulose. The literature reports that the tensile forces of NFC films consisting of randomly oriented NFCs known as nanopapers were 210 MPa and 213 MPa respectively (LI et al., 2013, WU et al. 2012).

Polyvinyl alcohol is the most popular water-soluble, semi-crystalline, non-toxic, transparent and biocompatible synthetic as well as biodegradable synthetic polymer produced in the world. The degree of solubility and biodegradability, as well as other physical properties, can be controlled by varying the molecular weight and degree of polyvinyl acetate hydrolysis. PVA is used in a wide spectrum of applications, for example in engineered fabrics, filtration materials, membranes, protective clothing, enzymatic immobilization and controlled release of drugs, etc. However, the low mechanical strength and integrity of PVA require the use of reinforcing agents, for example, carbon nanotubes (JEONG et al., 2007; WONG et al., 2009), cellulose nanofibrils and chitin whiskers.

This study was based on the mechanical shear treatment of cellulosic pulp, that was defibrillated in nanofibrils and dispersed in an aqueous suspension. NFC/PVA nanocomposite films were prepared by the casting method. NFC films containing different PVA concentrations (2%, 5%, 10%, w/w, dry basis) were form. The film's thermal and mechanical properties were evaluated. PVA was a minority component, having been used as an additive in a nanofibrillated cellulose matrix (NFC), proposing the predominant use of NFC with properties superior to its pure ones, through an efficient and environmentally friendly method of producing NFC-based biodegradable materials with enhanced properties for high-level applications. The main objective of this work was to evaluate the effect of PVA addition on NFC films, evaluating their compositions, physical and physical-mechanical and thermal properties.

MATERIALS AND METHODS

Materials

Commercial bleached eucalyptus "Kraft" pulp supplied by Company Klabin S/A, Monte Alegre, Brazil was used and Poly (vinyl alcohol) with a hydrolysis degree between 90% and 95% was donated by Atias Química, São Paulo, Brazil.

Methods

Preparation of Cellulose Nanofibrils

The cellulosic material was treated mechanically by fibrillation in a Super Masscolloider Masuko Sangyo mill (MKCA6-3; Masuko Sangyo Co., Japan.). The samples of cellulosic material were suspended in distilled water at the concentration of 1% (w/w) based on dry mass (IWAMOTO et al., 2008).

The distance between the disks (approximately 0.1 mm) was adjusted according to the literature (NAKAGAITO; YANO 2005; STELTE; SANADI 2009). In addition to adjusting distances, the fibrillator mill also allows frequency control that can be up to 3000 rpm. In this study, a frequency of 1500 rpm, as used in Silva et al., (2019).

The material obtained after 10 passes, was called nanofibrillated cellulose (NFC), and was used in the film preparation. The material was diluted to a concentration of 0.5% to be mixed with PVA.

Preparation of films by Casting

The casting technique is based on the sample suspension spreading on a substrate (polystyrene plate). After the solvent evaporation, the film was formed. The

film thickness was controlled by adjusting the sample concentration in the suspension. This technique was adopted in this work because it is simple and easy to reproduce.

NFC films containing different PVA concentrations (2%, 5%, 10%, w/w, dry basis) were form. The films were dried with the aid of an air circulation oven at a temperature of 35°C. The films' morphological, chemical, physical and mechanical characteristics were evaluated in order to verify the interference of PVA in the NFC properties. All specimens were prepared with a length of 13 cm, a width of 1.5 cm and an area of 20 cm², according to ASTM D882 (2018) standard.

Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was performed in a Bruker spectrometer, model Tensor 37, the films were used directly on the support, with measurements taken between 4000 cm⁻¹ to 400 cm⁻¹, using the transmission mode, with an accumulation of 64 scans and nominal resolution of 4 cm⁻¹. The spectra were treated, with the OPUS Spectroscopy Software (Bruker, Germany), to remove environmental interference (H₂O and CO₂) and also for baseline adjustment.

Mechanical Analysis

The mechanical analysis is able to provide information about the system viscoelastic behavior, dismembering the module into two components: elastic and viscous contribution. This technique aims at correlating the macroscopic properties, such as the mechanical properties, with molecular relaxations, conformational changes, and the microscopic deformations, generated from molecular rearrangements. The tensile tests were performed on an Emic DL2000 universal test machine (Instron, USA), Trd Cell 20, with a speed of 12.5 mm·min⁻¹, following the ASTM D882 (2018) standard. From each material six specimens with dimensions of 13 cm length, 1.5 cm wide and 20 cm² area were evaluated.

The traction index (TI) was calculated by the ratio between the tensile strength (TS), expressed in kilonewtons per meter and the test piece weight (W), in grams per square meter (g·m⁻²). The tensile index is given in newtons meter per gram (N·m·g⁻¹). This procedure followed the recommendations of the ABTCP Standard P7: 1994 - "Determination of traction properties - Constant charge speed method". The Traction Index calculation was done according to Equation 01, where: TI = Traction Index (N·m·g⁻¹); TS = tensile strength (kN·m⁻¹); W = Weight (g·m⁻²)

$$TI = \frac{TS}{W} \cdot 10^3 \quad [1]$$

Wettability

The wettability of films surface was analyzed using the apparent contact angle (AC) technique on a Krüss DSA25 goniometer (Krüss GmbH, Germany) by the sessile drop method. The tests were performed by depositing five drops of 5.0 μL deionized water on the film surface. The assay was performed in triplicate for each film sample. AC was measured at 5 s and 30 s after drop deposition on the sample surface using the Laplace-Young algorithm.

Thermal Analysis (TGA/DTA)

It was used a thermostatic Setaram Setsys Evolution TGA-DTA/DSC 1500 (Setaram, France), where the crucible used is Alumina. For the analysis, only the crucible, in the same conditions of analysis, is burn to generate the blank. After crucible calcination to the blank, the sample is placed and the analysis conditions were: constant temperature at 30°C for 10 min (stabilization), heating from 30°C to 650°C at a rate of 10°C·min⁻¹ (thermoanalysis) and cooling from 650°C to 30°C at a rate of 30°C·min⁻¹ (finalization). The mass loss data (thermogram) are acquired in the thermoanalysis step, all at an Argon flux of 20mL·min⁻¹.

Visible Spectrometry - Brightness and Color

To examine the films' brightness, they were analyzed for light reflectance in the 400 nm to 750 nm range. The films were cut and taken for reading, by reflectance, on a Konica Minolta CM-5 spectrophotometer (Konica Minolta, Japan). According to the equipment manual, this instrument uses a Xenon lamp, the geometry di: 8°/of: 8° according to CIE standard No. 15, (diffuse illumination, 8° viewing angle) and offers automatic SCI (specular component included, total reflectance) and SCE (specular exclusion, reflectance) automatic switching.

RESULTS AND DISCUSSION

Infrared Spectroscopy with Fourier Transform – FTIR

According to the evaluation of FTIR spectra, performed on 0.5% NFC films containing PVA, small changes in the material composition were observed, because the addition of PVA is at low concentrations in relation to the NFC material mass and hence the additive presence may not be detected by the technique.

The observed bands are characteristic to cellulose (Figure 1): the intense and broadband, in the region of 3500

cm⁻¹ to 3400 cm⁻¹, corresponds to the absorption of OH groups; the signal near 2900 cm⁻¹ represents the symmetrical stretches of C-H bonds, originating from the H-C-OH (C-2 and C-3 carbon) and CH₂ OH (C-6 carbon) glucosidic units presents on cellulose chain; the band in the region of 1640 cm⁻¹ can be attributed to the presence of conjugated carbonyls, probably due to the oxidation of carbohydrates during the bleaching process (Silva et al., 2019).

The bands centered around 1430 cm⁻¹ and 1370 cm⁻¹ are due to the C-H angular carbon chain deformation; absorptions in the region 1330 cm⁻¹ and 1320 cm⁻¹ correspond to the angular OH vibrations of primary and secondary alcohols; the bands located in the regions 1165 cm⁻¹ and 1110 cm⁻¹ are due to the asymmetric axial deformations of C-O-C, the bands between 1050 cm⁻¹ and 1030 cm⁻¹ correspond to the axial deformations of C-O in primary and secondary alcohols; and finally the deformation at 896 cm⁻¹ is attributed to the anomeric carbon (C-1) of anhydroglucose.

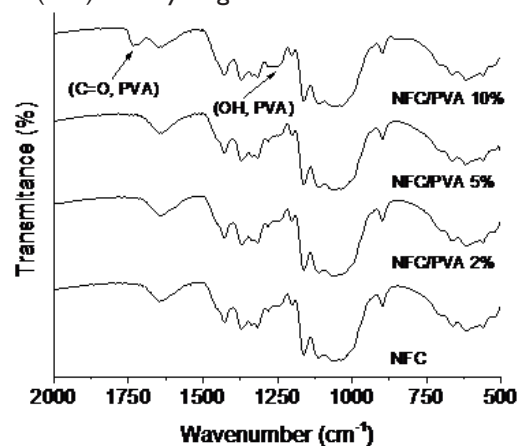


FIGURE 1 FTIR spectra for NFC samples with and without PVA addition.

The spectroscopic profile is similar to that NFC except for two small signals that appeared in the sample containing 10% of PVA in its composition (1716 cm⁻¹ due to the carbonyl present in the PVA and the other in 1258 cm⁻¹ of PVA OH bonds), showing that the other concentrations were not detected by the analytical method.

Physical and Mechanical Properties

The films were evaluated for some of their physical characteristics and the results are shown in Table 01.

NFC and PVA films showed a thickness reduction is about 10% in relation to the pure NFC, due PVA action on the stiffness reduction with this improving the material conformation. According to the presented results, it is possible to verify that the measured parameters show that the preparation process was efficient for all generated films, independent of its composition.

TABLE 1 Films' Physical and Mechanical Properties containing NFC and NFC_PVA.

Sample	Thickness (mm)	Mass (g)	Weight (g·cm ⁻²)	TI (Nm·g ⁻¹)	D (g·cm ⁻³)	YM (MPa)
NFC	0.022c	0.020a	10.26a	54.0a	370	88.8b
NFC_PVA2	0.020b	0.022b	11.28b	69.2d	436	85.5a
NFC_PVA5	0.018a	0.022b	11.28b	66.7b	538	99.1c
NFC_PVA10	0.018a	0.023c	11.79c	67.4c	567	110.1d

TI = Traction Index (Nm·g⁻¹), D = Density (g·cm⁻³), YM = Young's Modulus (MPa). Different letters next to the values indicate significant differences between the samples, for Tukey at 95% confidence.

From physical/mechanical test results, it was possible to calculate the tensile index of the produced films and, thus, to compare these values with already published data. It can be observed that addition of PVA has an influence on the traction index (TI) of formed film when compared to the film composed only by NFC. The tensile index (TI) for the NFC pure film was 57.09 Nm·g⁻¹. From the addition of 2%, 5% and 10% PVA (based on the dry weight of NFC), the composite films TI values increased to 72.66 Nm·g⁻¹; 72.07 Nm·g⁻¹ and 70.75 Nm·g⁻¹, respectively. Even the addition of small amounts of PVA causes an approximately 26% increase in film IT and all three formulations (2%, 5% and 10%).

Intermolecular forces between NFC and PVA increase the composite films tensile strength as these forces maintain the fibril's tensile strength intact (LU et al., 2008, LI et al., 2014). In addition, hydrogen bonds significantly strengthen the interface by interfering positively with composite material mechanical properties (LI et al., 2014).

According to some authors, in works with NFC-enhanced PVA films, the stress modulus increase can be influenced by the stiffness increase and fragility of films when NFC is added (LEE et al., 2009, VISAKH et al., 2012, LI et al., 2014). For some authors, increasing the amount of NFC in the PVA base causes an increase in the composite stiffness, in addition, the strong interaction between the cellulose nanofibrils and the PVA chains acts to restrict chain movements and, therefore they block their ability to flow, reducing their ductility (VISAKH et al., 2012).

Since in the literature no information was found of NFC films with addition of PVA as an adjuvant, it can be said that in this work the addition of PVA to NFC caused the generated film to be less rigid and with this, there is an improvement in the property of tensile strength.

The results of Young's modulus vary according to the material strength, being higher when PVA is added, showing variation in mechanical strength by -4%, + 11.6% and + 24% for NFC with the addition of 2%, 5% and 10% PVA, respectively.

Thermogravimetric Analysis

Thermogravimetry indicates greater or lesser thermal resistance of one material relative to another. According to thermogravimetric analysis, the addition of

PVA to NFC does not cause large changes in its maximum degradation temperature. In Figure 02 the results of thermogravimetry are presented for the samples.

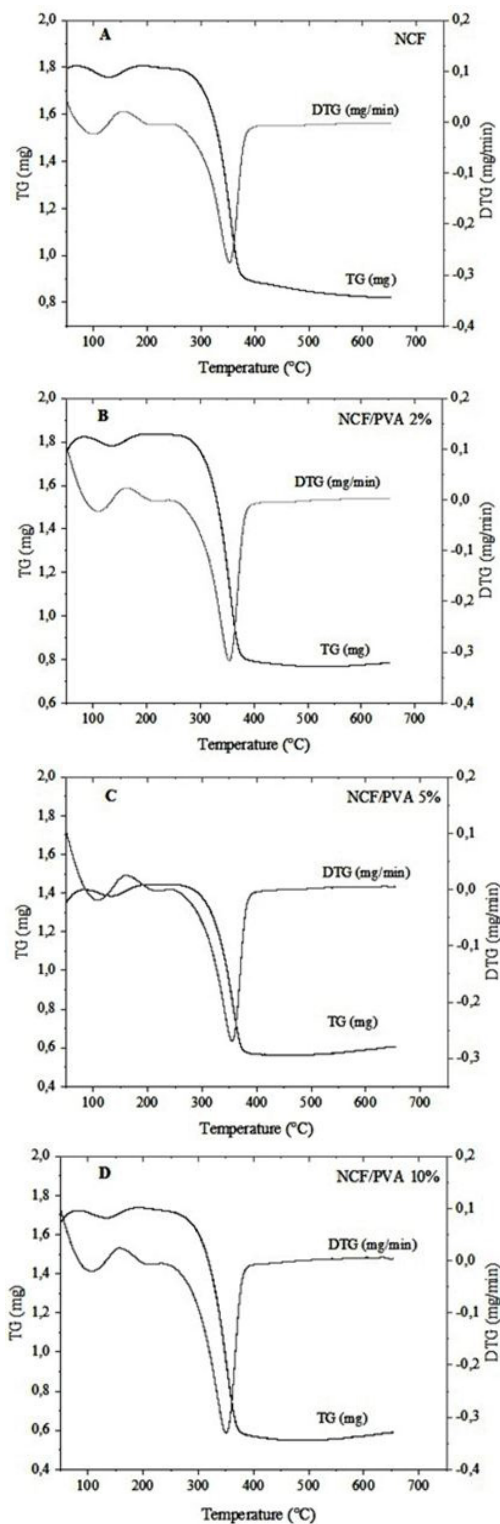


FIGURE 2 Thermograms for samples containing NFC and NFC / PVA (A) NFC, (B) NFC/PVA2%, (C) NFC/PVA5% and (D) NFC/PVA10%.

The thermogravimetric analysis demonstrates that the addition of PVA does not significantly alter the temperature of maximum degradation, but it increases the loss of mass. This behavior is due to the PVA being an organic compound which is consequently degraded together with the NFC.

It is observed that the thermogravimetric profile is not altered with the addition of PVA and the maximum degradation temperature was with an average of $352 \pm 2^\circ\text{C}$.

Wettability

The surface interaction of composite films with polar liquids, which characterizes their degree of hydrophobicity, was evaluated by determining the apparent surface contact angle with water (Figure 3). The values found indicated a significant decrease in apparent contact angle values, due to the incorporation of PVA in the NFC matrix. In addition, a significant reduction in apparent contact angle values as a function of exposure time was observed, which characterizes the presence of absorption and/or dispersion on the material surface. This decrease in the angle values occurs due to the addition of large amounts of polar groups from the PVA to the NFC, causing an increase in the material hydrophilicity.

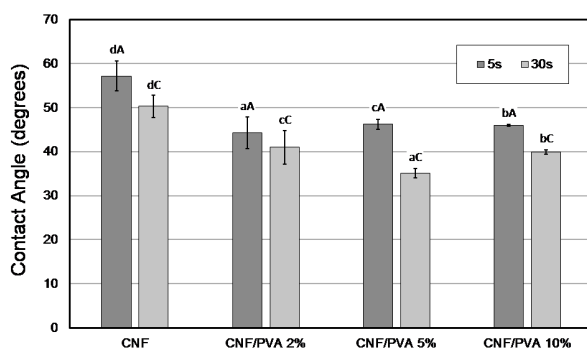


FIGURE 3 Contact angle values for NFC and NFC/PVA films. Different letters next to the values indicate significant differences in the values for Tukey to 95% confidence. Lowercase letters indicate the differences between the samples and upper case letters indicate the differences between the exposure times of the drop with the material.

Variations in surface roughness can cause pockets of air between the surface and the drop of water, altering the degree of hydrophobicity. The surface roughness has the effect of making the contact angle greater because the liquid tends not to penetrate the irregularities and pores generated in the solid and therefore, it can be considered as resting on a flat surface that is effectively part solid and part air. As there is virtually no adhesion between the liquid and the trapped air, the angle will increase. Surface roughness is a possible cause of contact angle hysteresis (SHAW, 1992).

In this case, the NFC/PVA composite films have a higher surface roughness and higher surface roughness than the NFC/PVA films (LEE et al., 2009; VISAKH et al., 2012; LI et al., 2014). It can also be observed that the higher amount of NFC in the films shows its greater resistance to water due to the existence of inter-component hydrogen bonds. The NFC/PVA interactions are mainly responsible for the variation in the angles of contact between the water and the film material. The hydrogen bonds between the NFC matrix and the PVA can decrease the hydrogen bonding points for water molecules (KISONEN et al., 2015).

Brightness

The evaluation of color and brightness of a film is an important aesthetic parameter of quality to evaluate its potential industrial application since consumers usually associated aspects such as packaging brightness and color, with the product quality it packs (KISONEN et al., 2015). The parameter L^* represents measures of luminosity. The higher the value the lighter the material and, consequently, the darker the value of L^* . Table 02 shows the average values for films' Brightness and Luminosity (L^*).

TABLE 2 Luminosity (L^*) and Brightness values for the films containing NFC and NFC/PVA.

Sample	L^*	Brightness
NFC	99.35d	96.19d
NFC_PVA 2	99.05c	95.02a
NFC_PVA 5	99.03b	95.32c
NFC_PVA 10	98.96a	95.08b

Different letters next to the values indicate significant differences in the Tukey values at 95% confidence.

As can be observed, the parameter L^* is little affected by the addition of PVA in the proportions used in this work. This result shows that the films, regardless of their composition, present values close to luminosities, with a variation of less than 0.5% in the values. This behavior demonstrates that in this respect there would not be much difficulty in its application.

As for surface gloss, the addition of PVA also did not show much change and almost had no influence on the surface brightness, with differences of only 1% for the three added concentrations. These results show that the addition of PVA at the concentrations used here does not alter the brightness and surface brightness properties, which would not affect an application where these properties are of great importance.

CONCLUSIONS

The addition of PVA to NFC produces positive results as it causes an approximately 26% increase in the IT film (mechanical properties) in the three formulations (2%, 5% and 10%) without affecting the formed film

aesthetics. Its addition to NFC is so low that it shows no interference in the chemical composition of composite films from NFC, nor does it influence the film surface gloss. After the addition of PVA, the thermal degradation temperatures were not changed, demonstrating that the NFC has its thermal resistance preserved. However, PVA acts to decrease the film surface hydrophilicity compared to pure NFC films, improving their hydrophobicity. Films formed by this blending model can be used in many applications, besides being more mechanically resistant and more hydrophobic, they still have preserved characteristics such as aesthetics, transparency and the resistance to thermal degradation from NFC.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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