THERMAL STABILITY AND UV RESISTANCE OF NANOCELLULOSE/TANNIN HYBRID FILMS

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Nanofibrillated cellulose can be used as a robust scaffold filled with tannin particles. Such reinforcement may confer particular chemical features needed for the production of hybrid films used as active packaging. Based on this hypothesis, powdered tannin particles were incorporated into nanocellulose-based films at two different weight fractions. The chemical, thermal and mechanical properties of these films were determined. Also, their resistance to UV exposure was evaluated in terms of colorimetric and mechanical characteristics. Neither chemical nor thermal noticeable adverse effects could be ascribed to the tannin insertion. On the other hand, the insertion of 1 wt% tannin induced an increase of 60% in tensile strength, although this effect was not retained after UV exposure. Meanwhile, the film that incorporated 3 wt% tannin appeared to present stable mechanical properties after UV exposure. This mechanical stability over UV exposure was not obtained with the inclusion of 1 wt% tannin content. The hybrid nanofilms acquired brown shades, which were not retained when the films were exposed to UV radiation.

Keywords: active packaging, UV exposure, eco-friendly films, nanocellulosic fibers, tannin

INTRODUCTION

Countless products must be packaged to retain their own features over time and, in most cases, polymers from non-renewable sources are used for this purpose. In recent years, there is a growing generation of packaging wastes owing to socio-economic changes, such as growing incomes, urbanization dynamics, as well as changes in both lifestyle and consumption patterns. Furthermore, a growing number of small packages have been produced, especially in Europe.[1]

According to the European Environment Agency,[2] many ecosystems are threatened by the pollution caused by the massive production and discarding of packaging and, in order to protect them, environmental laws must be enforced to avoid improper extraction of natural resources, and the use of harmful and toxic substances. Packaging technologies also play an important social role, since unsuitable packages may allow unexpected biotic and abiotic stresses in foods, pharmaceuticals, and cosmetics, which consequently leads to deleterious oxidative reactions in the living beings that consume these products.[3]

The production of eco-friendly packages should be encouraged as an alternative to mitigate these social and environmental impacts. Future trends indicate that the frontier of knowledge in this field is moving towards the preparation of active packages based on sustainable resources.[4] For instance, films based on cellulosic materials have been investigated.[3] Nanofibrillated cellulose (NFC) are micrometer-long entangled fibrils with 3-50 nm in diameter,[5] in which a d-glucopyranose-based flat ribbon-like structure is linked through hydrogen bonds, forming crystalline regions interspersed by amorphous paracrystalline ones.[6] The NFC ally low density, low toxicity, high biodegradability, and high biocompatibility, as well as high levels of mechanical strength, surface area, chemical inertness, and barrier properties.[7,8] NFC are generally produced by disintegrating commercial cellulose pulp, using high-pressure homogenization, microfluidization, ball milling, ultrasonication, grinding, cryocrushing, or combined methods, preserving the length of the native cellulosic fibrils.

Besides, there are some other lignocellulosic materials that can be incorporated as fillers in active films. Beyond coming from a renewable source, the filler must confer some particular characteristic to the sustainable film, increasing its range of applications. Very recently, bio-based films based on carboxymethylcellulose, chitosan, and oleic acid were incorporated with zinc oxide (ZnO) particles and proved to be efficient to prolong the shelf-life of sliced wheat bread.[9] Yu and coworkers[10] studied soy protein-based films incorporated with cellulose nanocrystals and a certain pine needle extract. These two fillers synergistically helped to increase tensile properties, antioxidant ability, and water vapor barrier capacity. Besides that, these authors reported that phenolic compounds from the pine needle extract presented strong antioxidant activities. Salah and coworkers[11] evaluated the effect of HPMC and HPMC/CNC in enhancing the water absorption of the pure chitosan membrane. The authors reported that their results demonstrated the possibility to prepare modified chitosan films, with enhanced water resistance, biodegradability, antimicrobial activity, high mechanical properties and no oxygen permeability, entirely from renewable and non-toxic feedstock. Besides, the modification process using HPMC and HPMC/CNC reduced the water absorption of the pure chitosan membrane from 70% to 22%, and to 9-11% by weight, respectively. Thus, HPMC/CNC reduced the water absorption of the composite film even more than HPMC alone. The prepared composite films showed homogenous morphology, high mechanical properties, and enhanced antibacterial activity. Leite and coworkers[12] synthesized CNCs and incorporated them in gelatin films to enhance their physical properties for antimicrobial CNC-packaging. The authors reported that CNCs were successfully functionalized with rosin and used as bactericidal nanofiller in gelatin for achieving multifunctional packaging. In particular, the r-CNCs consistently improved the optical, and water vapor barrier properties of gelatin films, as compared to conventional CNCs. The mechanical strength of the gelatin matrix was increased and could be tuned by varying the r-CNCs content. De Oliveira and coworkers[13] isolated cellulose nanocrystals from rice and oat husks for the utilization of this material in the preparation of absorbent aerogels for food packaging. The authors reported that the cellulose nanocrystals and the aerogels presented varying structural, morphological, and crystallinity properties, depending on the source of the cellulose. The aerogel with rice cellulose nanocrystals showed the highest water absorption capacity (402.8%). The use of rice and oat husks, which are considered agroindustrial waste, for the production of cellulose nanocrystals for application in aerogels has the potential to be applied in many industrial areas, including as aerogel absorbers of water in food packaging.

Tannin, which is a natural substance present in all vegetables, is a promising alternative filler for films. However, only certain natural matrices rich in tannins are economically feasible as sources of tannic chemicals. For instance, the bark of some trees has a large amount of tannins, which are mostly used in the leather industry due to their antioxidant activities. Nevertheless, recent studies have addressed the use of tannin for producing active packages. For instance, Wang and Wang[14] developed a bio-based packaging film based on soybean by-products incorporated with a valonea tannin, which conferred increases in physical and antioxidant properties. This improvement was explained by certain chemical interactions, including hydrogen bonds, which were developed between hydroxyl groups from the tannin and amide carbonyls from the peptide backbone of the protein. Olejar and coworkers[15] studied antioxidant films produced with ethylcellulose incorporated with tannin from grape berry flesh and concluded that even low filler contents (up to 60 wt%) yielded efficient films for active packaging. More recently, Missio and coworkers[3] produced thin NFC/tannin-based films using tannin particles from *Acacia mearnsii* wood bark in a weight ratio of 5:1 and reported increases in thermal, mechanical, and hygroscopic properties ascribed to the tannin insertion.

According to Huang and coworkers,[16] as an organic UV blocker for protecting packaging films, tannin particles can transform UV light into thermal energy through the photoelectric effect of functional groups, including benzophenone, benzotriazole, and hindered amine. The incorporation of tannin into NFC-based films to play anti-oxidative and UV-absorbing roles was already studied by Li and coworkers.[17] They used quebracho wood-based tannin and reported that an adjusted filler weight fraction may yield significant increases in thermal stability, tensile strength, as well as antioxidant and UV-shielding abilities. They also indicated that their biohybrid films can potentially be exploited in sustainable applications, such as biocomposites and packaging materials. Nevertheless, these applications were not yet ascertained for tannin extracted from black wattle wood bark, which is a known promising tannin source in Brazil. The present study aimed to produce NFC-based films incorporated with two different weight fractions of 1 wt% and 3 wt% of powdered tannin extracted from black wattle wood bark.

EXPERIMENTAL

NFC-based hydrogels

NFC was prepared following the procedure described by Kumode and coworkers.[18] For this, an aqueous suspension of commercial cellulose pulp, with a concentration of 2 wt%, was passed through a Super Masscoloider mill (Masuko Sangyo brand) at 1500 rpm until a homogeneous cellulose hydrogel was obtained (Fig. 1B). Tannin was obtained from *Acacia mearnsii* bark using the SETA® industrial process. For this, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,20-azobis(2-amidinopropane) dihydrochloride (AAPH), and sodium fluorescein were purchased from Sigma-Aldrich. Monobasic and dibasic potassium phosphate were purchased from Vetec. Ultrapure MiliQ water (18.2 MU cm, Millipore Corp., Bedford, MA) was used for evaluating the antioxidant activity of tannin particles. All the procedures were performed according to Missio and coworkers.[4]

The morphological features of the tannin-filled NFC dispersions were investigated with a transmission electron microscope (TEM) using Jeol equipment, model JEM-1200 EXII. For this, the dispersions were diluted to 0.1% w/v, dispersed in an ultrasonic bath for 30 min, and then poured on a copper TEM sample grid.[4]

NFC-based films

The tannin powder and NFC were manually mixed for 5 min at a tannin/NFC weight ratio of 1 and 3, as proposed by Olejar and coworkers.[12] After that, 50 mL of distilled water and 1.4 g of the NFC mixture were also added to NFC/tannin solution, which was kept for an extra 5 min under manual mixing. Afterward, this solution was poured on a Whatman® filtration system, comprised of a nylon membrane (diameter ¼ 47 mm; porosity ¼ 0.22 mm) connected to a vacuum pump. An areal density of 30 g/m^2 was targeted and films with 35 mm in diameter were immediately air-dried for 4 h, removed from the membrane, and stored in a climate chamber at 20 ºC and 65% RH (Fig. 1C).

The films were exposed to UV radiation in a closed black box at a vertical distance of 100 mm from a UV-C lamp and were kept under this condition for 720 h. The films were evaluated for chemical features via Attenuated total reflectance/Fourier transform infrared spectroscopy (ATR/FTIR), using Perkin-Elmer equipment.

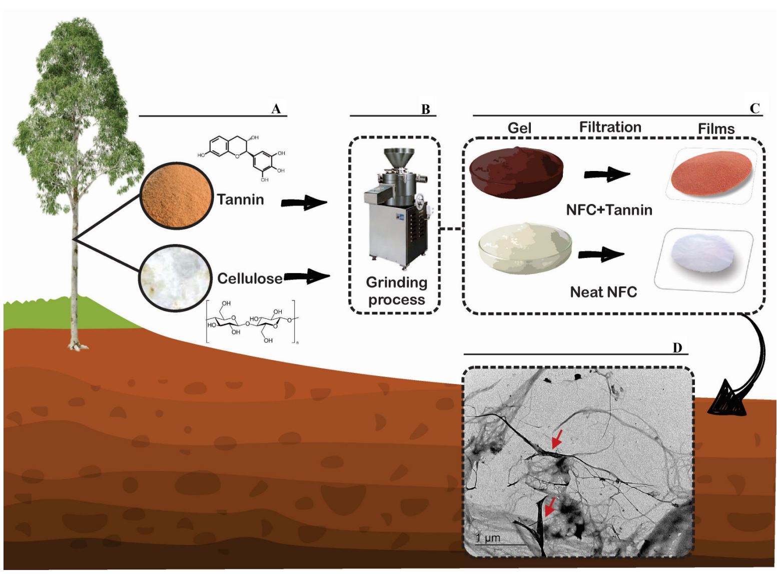

Figure 1: Scheme of the preparation of tannin/nanocellulosic films, including raw materials (A), grinding process (B), nanocellulosic hydrogels and films (C), as well as a TEM image for the tannin/NFC hydrogel (D)

Their thermal degradation was evaluated using a SetSys thermogravimetric analyzer in the 30-600 ºC temperature range, which was conducted at a constant heating rate of 15 ºC.min^{-1} under an argon flow rate of 20 mL min^{-1}. Tensile properties were measured in films with the dimensions of 50 × 5 × 0.2 mm³ at a velocity of 0.2 mm.s^{-1} using a universal testing machine (Instron brand), equipped with a paper tensile test apparatus, following DIN EN31 (DIN, 1993). Colorimetric parameters were measured following the CIELab method. Two readings were performed on 10 samples per group using a Konica Minolta CR-400 colorimeter adjusted for a 10° observation angle and a D65 light source.

Statistical analysis

The homogeneity of variances and data normality were verified using Levene and Shapiro-Wilk tests, respectively. Regarding the ANOVA tests, whenever the null hypothesis was rejected, Fisher tests were used to compare the means. All statistical analyses were developed at a significance level of 5%.

RESULTS AND DISCUSSION

The FTIR spectra (Fig. 2) of all films showed a major band at 3370 cm^{-1}, which is ascribed to absorbed moisture. The bands at 1030, 1110, 1160, and 2910 cm^{-1} represent C–O stretching, C–H stretching, C–O stretching, and ring asymmetric C–H stretching, respectively.[19,20] There were no different prominent bands when comparing the films, which indicates that the incorporated tannin did not induce any chemical reaction. This fact corroborates the findings of Missio *et al.*,[4] who studied NFC-based films incorporated with 1 wt% of powdered tannin. However, these authors affirmed that the tannin can interact with the nanocellulose by secondary bonds, like Van der Waals forces, short-range dipole-dipole (through quadrupole), or even multiple hydrogen bonds. Perhaps, this occurred for the hybrid film incorporated with 1 wt% of tannin, since its band at 3370 cm^{-1} was broader than those of the other films. The morphological effect of this interaction can be seen in Figure 1D, in which the TEM image of the hydrogel shows that most NFC is coated with tannin particles (highlighted by red arrows).

According to Guo and coworkers,[21] phenols from tannin moieties present high H-bonding capacity and may strongly bond to hydrophilic substrates. For instance, when using gallic acid as a model molecule,[22] multiple H-bonding and quadrupolar interactions can take place between tannin and hydrophilic surfaces. Besides, the electrostatic potential mapping of the macromolecular state of tannin at equilibrium conformation (represented here as a typical linear polymerization of prorobinetinidin) shows a decisively positive structure, with some isolated negative areas. Beyond H-bonding and quadrupolar interactions, electrostatic forces can also occur between tannin and negatively charged cellulosic surfaces.[4] Nevertheless, none of these NFC/tannin interactions were captured by the infrared spectra shown in Figure 2.

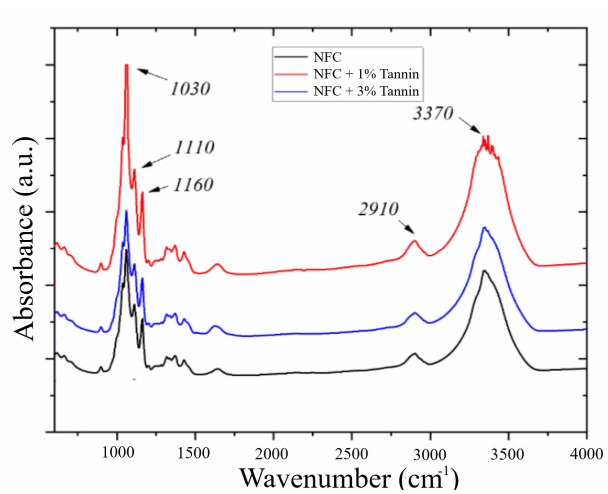

Figure 2: Infrared spectra for the NFC-based films

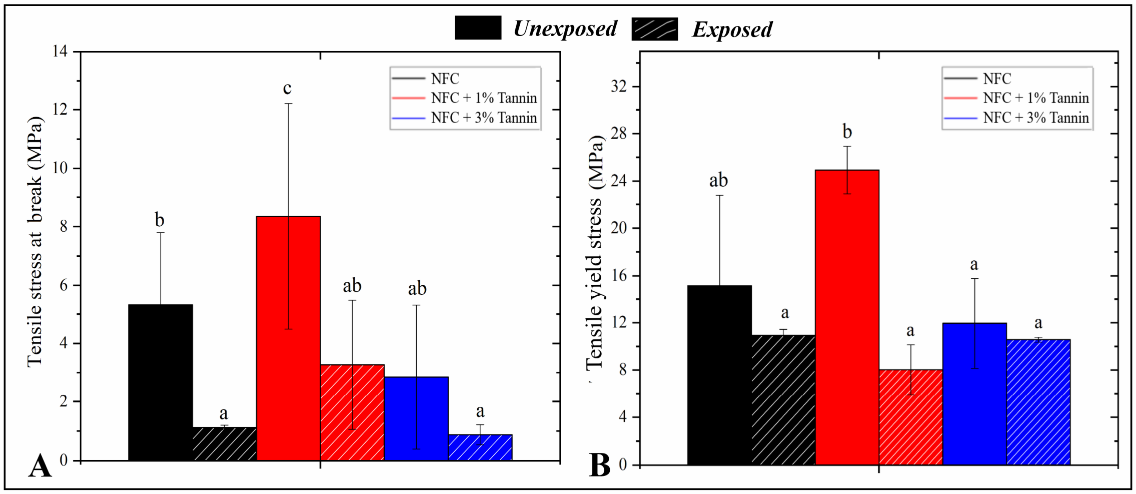

Figure 3: Tensile stress at break (A) and tensile yield stress (B) results for the NFC-based films

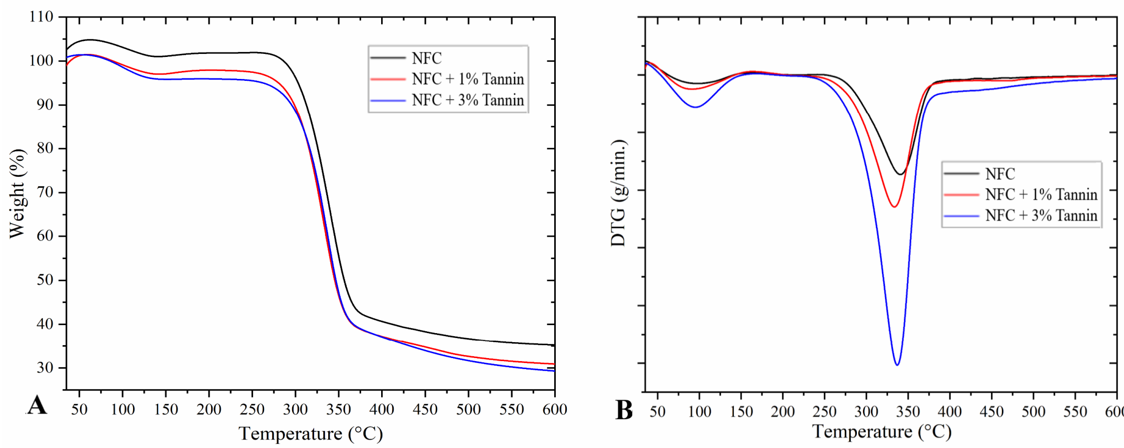

Figure 4: Thermogravimetric curves (A) and their derivative ones (B) for the NFC-based films

The hybrid film with 1 wt% of tannin showed a higher tensile strength, if compared to the neat NFC-based film, although this advantage was not retained after the UV exposure (Fig. 3). In this case, there was an initial increase of about 60%, which can be ascribed to the afore-mentioned secondary interactions indicated by infrared spectroscopy.[15] The film that incorporated 3 wt% presented similar tensile properties if compared to the neat film. According to Olejar and coworkers,[15] when incorporated at a certain weight fraction (around 3 wt%), the tannin can play a plasticizer role, which may impair its action as a real reinforcement.

Compared to the other films, the insertion of 3 wt% of tannin seems to have yielded a hybrid tannin film with more stable tensile properties. This increased UV resistance ascribed to the tannin insertion is similar to the findings reported in the literature.[15,23] For Noshirvani and coworkers,[9] the UV-shielding conferred by tannins can be attributed to their high quantum energy, which is particularly relevant in the context of light-catalyzed reactions.

There were decreases in the thermal stability of the films owing to the insertion of the tannic substances (Fig. 4). This can be ascribed to the smaller thermal degradation of tannin, compared to the NFC.[4] The cellulose itself is a linear homopolysaccharide composed of glucose units interconnected by β-1,4-glycosidic bonds, which results in very long linear and unbranched chains of d-glucopyranose conformed in a flat ribbon-like structure.[6] Its chains are tightly packed in crystalline microfibrils with a degree of polymerization,[24] which explains its remarkable thermal stability. Nevertheless, the similar shape of all the thermograms also confirms that there are very small differences when comparing the chemical structures of the studied films.

Compared to the neat film, the insertion of tannin yielded darker (>L*) films (Fig. 5). This filler also conferred reddish (>a*) and yellowish (>b*) shades. This overall color pattern was retained after the UV exposure and the aging only intensified these color changes. However, compared to the neat NFC film, the colors acquired by the hybrid films underwent higher changes ascribed to the UV radiation, which was probably due to the absorbed UV onto the tannin surface, as discussed above. The color changes took place up to approximately 500 h, and, after that, there was a general stabilization of the color levels. This plateau confirms that the exposure time was suitable to evaluate the studied films.

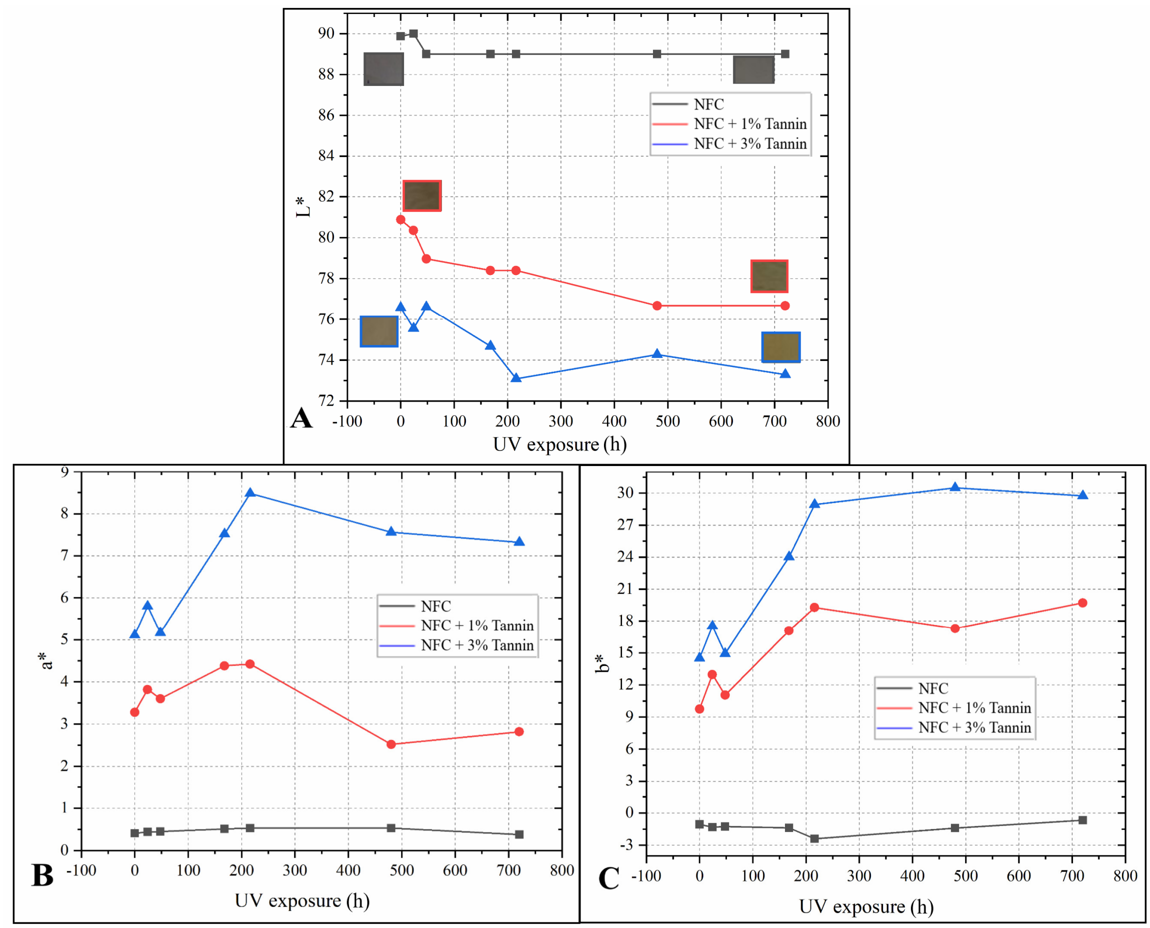

Figure 5: Brightness (A), green-red coordinate (B), and blue-yellow coordinate (C) for the NFC-based films

Similar results were reported in the literature. For instance, Olejar and coworkers[15] produced ethylcellulose-based films reinforced by grape tannin particles and reported decreases in brightness (<L*) ascribed to the insertion of tannin, which indicates that the hybrid films acquired the dark shades found for tannin substances. Besides, increases in reddish (>a*) and yellowish (>b*) shades were found for hybrid films, which again confirmed that the hybrid films resembled the incorporated filler.

CONCLUSION

In this study, NFC/tannin films were successfully produced using black wattle wood bark-based tannin. Compared to the neat film, the film that incorporated 1 wt% of tannin presented a higher tensile strength, although this advantage was not retained after 720 h under UV radiation. Also, compared to the neat NFC-based film, the mechanical properties of the film that incorporated 3 wt% of tannin were relatively stable to UV aging, which can be ascribed to the known ability of the tannin backbone of absorbing electromagnetic waves from the UV spectrum. The tannin insertion decreased the thermal stability of the NFC-based films, although all hybrid films presented similar thermal degradation profiles, compared to the neat one. The neat NFC-based film presented a white color, whereas the hybrid films resembled the tannin particles in terms of color pattern. These color changes induced by the tannin insertion may be valuable from an aesthetical standpoint. Overall, these findings indicate that the tannin from black wattle wood bark can be a valuable chemical, which may help socially depressed people, who exploit this vegetable matrix in underdeveloped countries.

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