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Article

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Plant-inspired polyaleuritate-nanocellulose composite photonic films

José A. Heredia-Guerrero^{1,2}, Cyan Williams³, Giulia Guidetti³, Pietro Cataldi^{1,4}, Luca Ceseracciu⁵, Doriana Debellis⁶, Athanassia Athanassiou¹, Susana Guzman-Puyol^{1,2}, Wadood Y. Hamad⁷ and Silvia Vignolini^{3*}*

¹ Smart Materials, Istituto Italiano di Tecnologia, Via Morego 30, Genova, 16163, Italy.

² IHSM La Mayora, Departamento de Biología Molecular y Bioquímica, Universidad de Málaga, 29071, Málaga, Spain.

³ Melville laboratory for Polymer synthesis, Department of Chemistry, Cambridge University, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

⁴ National Graphene Institute, University of Manchester, Booth Street East, Manchester M13 9PL, United Kingdom.

⁵ Materials Characterization Facility, Istituto Italiano di Tecnologia, Via Morego 30, Genova, 16163, Italy.

⁶ Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, Genova, 16163, Italy.

⁷ Transformation and Interfaces Group, FPInnovations, 2665 East Mall, Vancouver, BC, Canada V6T 1Z4

*Corresponding authors: jaheredia@uma.es, sv319@cam.ac.uk

Abstract

Plant epidermis is a complex composite material composed by the cuticle and the epidermal cells. In order to prevent dehydration the cuticle is a water barrier composed of an outer layer (proper cuticle) connected to the cell wall of the epidermal cells via a complex matrix often referred to as cutinised cell wall, that acts as compatibilizer for the water repellent cutin and the hydrophilic polysaccharides in the cell walls. Here, biomimetic plant epidermis-inspired films with selective reflection properties were prepared by formation of an aliphatic polyester coating on chiral nematic cellulose nanocrystal (CNC) films. Aleuritic acid, a polyhydroxylated fatty acid, was sprayed on CNC films and polymerized by hot-pressing. The micromorphology of the resultant samples was characterized by scanning electron microscopy (SEM). Polarised optical microscopy confirmed the CNCs helicoidal organization in the films, responsible for the reflection of circularly polarised light, before and after the hot-pressing. The chemical analysis by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) confirmed the polymerization of aleuritic acid into polyaleuritate with differences between filter paper and woodpulp substrates that were ascribed to water elimination during polycondensation. The characterization of the mechanical (Young's modulus and hardness from nanoindentation tests) and hydrodynamic (water uptake and water vapor transmission rate) properties indicated that this process enhances the robustness and waterproof behaviour of CNC films. These properties were comparable to those of commercial and biodegradable materials commonly used in packaging such as polyesters and cellulose derivatives, thus making these natural composite ideal for optically responsive packaging applications.

Keywords: cellulose nanocrystals, aleuritic acid, plant cuticle, biomimetic plant structures, structural colour.

1.- Introduction

The plant cuticle is a multifunctional biocomposite that covers and protects the outermost part of non-lignified epidermis of aerial organs such as leaves, fruits, petals, and stems^{1,2}. It consists mainly of cutin (a polyhydroxylated polyester made of condensed C16 and C18 fatty acids that acts as a polymer matrix), polysaccharides from the epidermal cell wall, and minor fractions of waxes and phenolic compounds³. Although the structure of the plant cuticle is currently under discussion⁴, the cuticular membrane is considered to be formed by an external cuticle proper (rich in cutin) and an underneath cuticular layer. The latter, often referred to as cutinized cell wall, is mainly composed of polysaccharides and acts as compatibilizer with the cell walls⁵, whose cellulose nanofibrils are the main components.

Plant cuticles have inspired many biomimetic systems and cutin, due to its barrier properties, has been exploited to fabricate free-standing films with applications in food packaging^{6–13}. Additionally, cutin and cutin-like monomers (*i.e.*, 9,10,16-trihydroxyhexadecanoic or aleuritic acid, a commercially available fatty acid extracted from shellac resin¹⁰) have been polymerized, blended, or grafted to several polysaccharides such as alginate¹⁴, pectin^{15,16}, or cellulose^[22,23,24] to fabricate films with improved mechanical properties. Similarly, the hierarchical structures found in the plant cell wall have been mimicked by using cellulose nanocrystals (CNCs)^{20,21}. Cellulose nanocrystals can be isolated from cellulose^{22,23} of woodpulp and cotton *via* acid hydrolysis^{24–27} to give charged, rigid rod-like particles with length up to 200 nm. When dispersed in water CNCs can self-assemble into a lyotropic liquid crystal chiral nematic phase²⁸, which, upon increase in concentration, evolves first in a kinetically arrested chiral gel and then dries in solid structurally coloured CNC films with helicoidal arrangement^{29–31}. The CNCs birefringence induces a periodic variation of the refractive index in the solid films which can interfere with visible light to selective reflect polarised light at specific wavelengths, thus generating a polarized photonic response³².

Here, a thin layer of polyaleuritate is deposited on the cellulose nanocrystals photonic films by spray coating of aleuritic acid and subsequent polymerization via hot-pressing. We demonstrate that the coating covers the CNC photonic films maintaining their photonic properties, inducing a lower interaction with water and significantly improving

their mechanical properties, similarly to cutinized cell wall layer. Moreover, the prepared plant-inspired composites combine photonic response with mechanical and hydrodynamic properties comparable to those of other commercial biodegradable packaging materials, allowing the production of fully natural composites ideal for optically responsive packaging applications.

2.- Experimental part

2.1.-Materials

Aleuritic acid (9,10,16-trihydroxyhexadecanoic acid, 98% purity by NaOH titration) was purchased from TCI Europe. Mater-Bi (a commercial blend of PCL with thermoplastic starch) was obtained from commercial biodegradable market bags. Polycaprolactone (PCL), ethyl cellulose (EC), carboxymethyl cellulose (CMC), cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose, chloroform, potassium hydroxide, and methanol were purchased from Sigma-Aldrich. Filter paper Grade 1 was purchased from Whatman and sulfuric acid 99% from Fisher Scientific. Chemicals were used as received without additional purification.

2.2.- Preparation of CNC suspension

Two different type of CNC were used. The filter paper (FP) cellulose nanocrystal (CNC) suspension was prepared from acid hydrolysis²⁵ of Whatman Grade 1 cellulose filter paper (60 g) with sulfuric acid (64 wt.% 840 mL) at 60 °C for 30 min, followed by quenching with deionized water and ice. The CNCs were then centrifuged at 20000g for 30 min (Sorvall Lynx 6000 Thermo Scientific) for 3 times: at each step the supernatant was discarded and the pellet re-dispersed in MilliQ (MQ) water for the next centrifugation step. The CNC suspension was then dialyzed against MQ water until the conductivity of the dialysis water was comparable to the conductivity of the MQ water. Finally, the CNC suspension was filtered with 8.0 µm and 0.8 µm nitrocellulose filters (Sigma Aldrich), tip-sonicated (1900 J/g, Fisher Ultrasonic disintegrator), heat treated (6 h at 60 °C) and diluted with MQ water to the desired concentration. The filter paper CNCs were (190 ± 103) nm in length and (17 ± 10) nm in height with a sulphate content of 245 mmol S/kg. The woodpulp (WP) CNC suspension was instead provided by CelluForce. The woodpulp CNCs were (100 ± 70) nm in length and (3.8 ± 2) nm in

height with $[-OSO_3^-] = 243 \text{ mmol/Kg}$ as measured by titration against NaOH. Both the CNCs size and sulphate content were in agreement with previously reported values^{33,34}.

2.3.- Preparation of CNC films

Films with FP and WP CNCs were prepared by pouring respectively 2 and 3 mL of 2 wt.% filter paper and woodpulp suspensions in polystyrene Petri dishes (3.5 cm, ref. 430688, Corning) and letting them dry at ambient conditions. The dry films were detached from the substrate and neutralized to increase their thermal stability to be able to retain their optical properties during the hot-pressing treatment: each film was immersed in 30 wt.% potassium hydroxide solution for 24 h, then rinsed with Milli-Q water and subsequently dried.

2.4.- Preparation of CNC-polyaleuritate films

Aleuritic acid (100 mg/mL) was dissolved in chloroform:methanol (1:1, v:v). The solution was then sprayed (18 cm, 2.2 bar) on only one side of the CNC films using a Paasche air brusher (VL siphon feed, 0.73 mm nozzle). After drying, films were hot-pressed (160 bar, 30 min) at 200°C using a Specac-Atlas Power Presses T8 press. Other conditions were also tried. However, longer reaction times and higher temperatures induced the degradation of cellulose substrates, resulting in brittle and burned samples.

The samples were labelled according to the CNCs source and the thermal treatment. FP and WP refer to the CNC films fabricated, from filter paper and woodpulp, respectively, while FPA and WPA to CNC films from filter paper and woodpulp, respectively, with a polyaleuritate top coating. A graphical presentation of the composite films' preparation is shown in Figure 1.

Figure 1. Schematic representation of the plant cuticle-like film preparation. The helicoidal CNC films were first spray-coated with a layer of aleuritic acid and then hot-pressed to induce the polymerisation of the coating to polyaleuritate, thus forming a bilayer composite.

2.5.- Preparation of reference materials

Water uptake, water vapor transmission rate, and indentation properties of CNC and CNC-polyaleuritate films were compared to those of several free-standing films of the following reference materials with different physical properties and used at large scale in many industrial processes: PCL, EC, CA, CAP, Mater-bi, amorphous cellulose, and carboxymethyl cellulose (CMC). Films (200-300 μm thickness) were prepared by drop casting 15 mg/mL solutions of these polymers in different solvents (chloroform for Mater-bi, PCL, CAP, and CA, water for CMC, trifluoroacetic acid for cellulose, and ethyl acetate for EC) in glass Petri dishes and letting them drying under an aspirated hood for 72 h.

2.6.- Scanning Electron Microscopy (SEM)

SEM imaging was carried out using a JEOL JSM 7500FA (Jeol, Tokyo, Japan) equipped with a cold field-emission gun (FEG), operating at 15 kV acceleration voltage. Samples were coated with a 10 nm thick film of gold. Imaging was performed with a secondary electrons detector to analyse the morphology of the samples.

2.7.- Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy

Infrared spectra were obtained with an ATR accessory (MIRacle ATR, PIKE Technologies) coupled to a FTIR spectrometer (Equinox 70 FT-IR, Bruker). All spectra were recorded in the range 3800 - 600 cm^{-1} with a resolution of 4 cm^{-1} , accumulating 128 scans. To assess the homogeneity of chemical composition, ATR-FTIR spectra were recorded three times in different areas for each sample.

2.8.- Optical characterization

Optical characterization was performed on a customized Zeiss Axio microscope³⁵ using a Halogen lamp (Zeiss HAL100) as a light source with Koehler illumination. The light reflected off the samples was collected from the objective (50x, T Plan SLWD, Nikon), then directed through a quarter wave plate and a polarizing filter, specifically oriented to let either left- or right-circularly-polarized light pass before being split between a CCD camera (Thorlabs DCC3240C) and an optical fibre (200 μm , Avantes) mounted in confocal configuration and connected to a spectrometer (AvaSpec-HS2048, Avantes).

The reflectance spectra were normalized to the reflection of a silver mirror in the left-circularly-polarized channel.

2.9.- Nanoindentation

The mechanical properties of CNC and CNC-polyaleuritrate films were characterized by nanoindentation with a CSM UHNT ultrananoindenter. Tests were performed with a Berkovich tip, under a maximum load of 500 μN . Additional tests were performed at lower load, namely 300 μN , in order to exclude the influence of the substrate on the measurements (data not reported). For all measurements, the maximum penetration was lower than 1/10 of the upper coating thickness. The load was applied and removed at 1 mN/min loading rate and it was kept constant at maximum load for 30 s, to allow for saturation of the creep response of the materials. At least 10 measurements were performed for each material. From the unloading portion of the curves, Young's modulus E and hardness H were calculated following the Oliver & Pharr method³⁶, assuming a Poisson coefficient $\nu = 0.30$.

2.10.- Water uptake, water contact angle, and barrier properties

Water uptake measurements were carried out as follows: dry samples were weighed (~30 mg) and, then, placed in a chamber at 100% relative humidity (RH). Samples were kept in the chambers until no change in sample weight was measured. The amount of adsorbed water was calculated as the difference with the initial dry weight.

Static water contact angle measurements were performed by using the sessile drop method using a DataPhysics OCAH 200 contact angle goniometer equipped with a CCD camera and image processing software operating under laboratory conditions (temperature 22-25 °C and relative humidity 50-60%). For the characterization, 3 μL droplets volume MilliQ water were used. Up to 10 contact angle measurements were carried out on every sample at random locations and their average values are reported.

The water vapor transmission rate (WVTR) of films was determined at 25 °C and under 100 % relative humidity gradient (ΔRH %) according to the ASTM E96 standard method. 400 μL of deionized water (which generates 100 % RH inside permeation cell) was placed in each test permeation cell with a 7 mm inner diameter and a 10 mm inner depth. Films were cut into circles and mounted on the top of the permeation cells. The permeation cells were placed in a desiccator with anhydrous silica gel used as a

desiccant agent (~0 % RH.) The water transferred through the film was determined from the weight change of the permeation cell every hour during the first 8 h using an electronic balance (0.0001 g accuracy). The weight loss of the permeation cells was plotted as a function of time. The slope of each line was calculated by linear fitting. Then, WVTR was determined as follows³⁷:

$$WVTR (g/(m^2 \cdot day)) = \frac{Slope}{Area\ of\ the\ film} \quad (1)$$

3.- Results and discussion

3.1.- Optical characterization

Photonic CNC films with chiral nematic architecture³⁸⁻⁴¹ selectively reflecting left circularly polarised light were prepared with CNCs from two sources (woodpulp and filter paper) as the thermal stability of CNCs varies with their source^{20,39}. Figure 2 shows the optical analysis of the cellulose nanocrystal films before and after the application of the polyaleuritate coating for filter paper (FP), Figures 2A,C, and for woodpulp (WP), Figures 2B,D. As expected, the pure CNC films displayed a strong reflection signal in the left polarization channel (LCP) while no reflection peak in the right channel (RCP). This optical response confirms the left-handed helicoidal assembly of the CNCs in the films. After the treatment, both FPA and WPA showed a small red shift in the optical response, indicating that the CNCs chiral nematic structure was retained and the coating probably partially intercalated in it inducing an increase in the CNCs helicoidal pitch and therefore in wavelength of the reflected light.

Figure 2. **A** and **B** Polarized optical microscopy images for left and right circular polarization and photographs, of CNC films produced from woodpulp (WP) and filter paper (FP) before and after the addition of the polyaleuritate coating by spray and hot-pressing (WPA, FPA). **C** and **D** corresponding reflectance spectra for both polarizations, before and after the addition of polyaleuritate coating by spray and hot pressing.

3.2.- Morphological characterization

To further confirm the retain of the helicoidal structure, SEM imaging was performed to CNC films before and after the spray of aleuritic acid and hot-pressing, as shown in Figure 3. As expected, both FP and WP CNC films showed the typical pseudo-layered helicoidal structure^{40–42} given by the cellulose nanocrystals chiral assembly which is retained in solid films. After the spray-coating, both FP (thickness between 39 and 44 μm) and WP (thickness between 89 and 99 μm) morphology was comparable to the one of the pure CNC films with an additional top coating with a thickness between 2.9 and 3.7 μm . This external layer, made of polyaleuritate, only partially impregnated the cellulose substrate, most likely because of the compactness and lack of pores of the cellulose films. Both layers showed a good adhesion, despite the well-defined interface, as no delamination was observed during any step of sample handling. Presumably, free hydroxyl groups in polyaleuritate structure can interact by H-bonds with OH groups of the CNC substrate, resulting in such good adhesion between both components.

Figure 3. A, B, C, D, cross-section SEM images of FP, FPA, WP, and WPA, respectively. The typical CNC helicoidal arrangement is observed for all samples. No delamination between the polyaleuritate layer and the CNC films could be observed by SEM imaging. Scale bars: 2 μm .

3.3.- Chemical and hydrodynamic characterization

ATR-FTIR spectra of CNC and CNC-polyaleuritate films are shown in Figure 4A. As expected, infrared spectra of FP and WP were very similar. The main absorptions were associated with the typical vibrations of cellulose: OH stretching mode at 3308 cm^{-1} , CH stretching mode at 2890 cm^{-1} , adsorbed water at 1647 cm^{-1} , asymmetric C-C stretching mode at 1157 cm^{-1} , and C-O stretching mode at 991 cm^{-1} ¹⁸. In the case of FPA and WPA films, additional bands related to the formation of polyaleuritate (*i.e.*, an aliphatic, polyhydroxylated, and cross-linked polyester) were observed: OH stretching mode at 3337 cm^{-1} , asymmetric and symmetric CH_2 stretching modes at 2928 and 2851 cm^{-1} , respectively, C=O stretching mode of free and H-bond interacting ester groups at 1730 and 1713 cm^{-1} , respectively, CH_2 scissoring mode at 1466 cm^{-1} , and CH_2 rocking mode at 721 cm^{-1} ^{12,17,43}. Usually, the degree of polymerization of this type of thermoset polymers and natural cutins is qualitatively characterized by the esterification index. It is defined as the relationship between the methylene groups, the most repeated structural unit in the polyaleuritate matrix that results unaffected by the polymerization process, and the ester functional group, the bond that links aleuritic acid monomers after

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3 thermal curing^{44–46}. This parameter is calculated as the ratio between the relative
4 intensities of the C=O stretching vibration of the free ester ($\sim 1730\text{ cm}^{-1}$) and the
5 asymmetric vibration of the methylene ($\sim 2928\text{ cm}^{-1}$). The esterification indices of FPA
6 and WPA were 0.82 and 0.70, respectively, indicating that the reaction progressed
7 slightly better on the surface of filter paper substrates. This could be related to a better
8 water removal during the polycondensation, since H_2O molecules can shift the reaction
9 equilibrium towards the hydrolysis.
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16 Figures 4B,C show the water uptake and the water vapor transmission rate (WVTR) of
17 the samples in comparison with common biodegradable materials such as
18 polycaprolactone (PCL), ethyl cellulose (EC), cellulose acetate (CA), cellulose acetate
19 propionate (CAP), Mater-Bi (a commercial blend of PCL with thermoplastic starch),
20 amorphous cellulose, and carboxymethyl cellulose (CMC). Water uptakes decreased
21 from ~ 45 and $\sim 46\%$ for FP and WP, respectively, to ~ 30 and $\sim 29\%$ for FPA and WPA,
22 respectively, despite the coating was performed only on one side of the film.
23 Interestingly, these values for FPA and WPA are close to those of other polysaccharide-
24 polyester mixture such as Mater-Bi. Water barrier properties were characterized by
25 calculating the WVTR of the samples. WVTR of FP and WP, ~ 4315 and $\sim 4015\text{ g m}^{-2}\text{ d}^{-1}$,
26 respectively, were typical of water permeable films. These values were significantly
27 reduced to ~ 1625 and $\sim 1340\text{ g m}^{-2}\text{ d}^{-1}$ for FPA and WPA, respectively, that correspond
28 to a decrease of ~ 62 and $\sim 67\%$, respectively. After the addition of the coating, the
29 samples exhibited a WVTR close to CAP and lower than CA, indicating that the
30 covering with polyaleuritate is, at least, as effective as the chemical modification of
31 cellulose by esterification. On the other hand, the water contact angle (W-CA) of the
32 films was also measured. FP and WP were water absorbing and their W-CAs could not
33 be measured, while the W-CAs of FPA and WPA measured on the coated side were $(75 \pm 1)^\circ$
34 and $(76 \pm 1)^\circ$, respectively. This value is typical of hydrophilic materials and close
35 to those published for free-standing films of polyaleuritate⁴⁷. Most likely, the presence
36 of free hydroxyl groups from aleuritate repetitive units is the responsible of such
37 hydrophilicity.
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Figure 4. A, ATR-FTIR spectra of FP, WP, FPA, and WPA samples. Main assignments for cellulose (blue) and polyaleuritate (orange) are included. B, C, water uptake and WVTR values for FP and WP (black) as well as FPA and WPA (red) in comparison with common cellulose derivatives and polyesters (gray).

3.4.- Mechanical characterization

Indentation tests were carried out to characterize the mechanical properties of the cellulose films with and without the coating, as reported in Figure 5. Figure 5A displays the typical indentation load-penetration curves of the samples, showing the characteristic behaviour of polymeric materials with relatively large viscous penetration during the dwell time at maximum load. FP and WP exhibited very similar curves with penetrations of ~ 295 nm. The CNC-side of FPA films showed the lowest penetration (~ 255 nm), while the CNC-side of WPA films presented an intermediate behaviour (~ 276 nm) between those and the cellulose nanocrystal films from filter paper and woodpulp. Polyaleuritate sides of FPA and WPA films displayed the deepest penetrations, most probably because of a more ductile mechanical behaviour of the polyaleuritate in comparison to the cellulose substrates, with values of ~ 363 and ~ 428 nm, respectively. From these curves, the Young's modulus and hardness were

calculated, Figure 5B. After the fabrication process, both parameters increased for the CNC sides of FPA and WPA. In fact, Young's moduli increased from ~5615 and ~6130 MPa for FP and WP films, respectively, to ~8050 and ~8645 MPa for CNC sides of FPA and WPA films, respectively (*i.e.*, an increase of ~30% in both cases). On the other hand, hardness values ranged between ~322 and ~318 MPa for FP and WP films, respectively, to ~406 and ~351 MPa for CNC sides of FPA and WPA films, respectively (*i.e.*, an increase of ~21 and ~10%, respectively). Such an increase in robustness can be related to a lower presence of water. In general, water acts as a plasticizer of cellulose materials^{48–50} and, hence, a lower water content, due to the presence of polyaleuritate, can induce a higher rigidity of the polysaccharide. In the case of the polyaleuritate sides of FPA and WPA films, the values of *H* and *E* were typical of less rigid polymers. Thus, the Young's moduli of polyaleuritate sides of FPA and WPA films were ~2284 and ~1767 MPa, respectively, while the hardness values were ~226 and ~157 MPa, respectively. The higher values of the polyaleuritate sides of FPA films can be attributed to a higher degree of polymerization, as confirmed by ATR-FTIR spectroscopy. Considering absolute values, when compared to conventional biodegradable materials such as Mater-Bi, PCL, EC, CMC, CA, and amorphous cellulose, polyaleuritate sides of FPA and WPA films showed values close to commercial cellulose derivatives, while the CNC sides exhibited the best mechanical performances, even surpassing those of the original cellulose substrates which is reported to vary between 1.5–5.8 GPa^{51–53}.

Figure 5. **A**, typical load-depth indentation curves for FP, WP, and the CNC and polyaleuritate sides of FPA and WPA. **B**, Hardness versus Young's modulus plot with the values of FP and WP (black) as well as the CNC (red) and polyaleuritate (green) sides of FPA and WPA in comparison to common cellulose derivatives and polyesters (gray).

4.- Conclusions

In this work, we developed a straightforward method to increase the robustness and reduce the interaction with water of photonic CNC films from filter paper and woodpulp. The deposition of aleuritic acid on self-assembled CNC films by spray coating and its polymerization into polyaleuritate by hot-pressing allowed the formation of a biomimetic plant epidermis-inspired bilayer structure. The CNC layer accounted for the optical response while the aliphatic polyester coating regulated the water interaction of the composite material. The optical properties of the films were practically not affected by the presence of the polyaleuritate top coating, as confirmed by polarized optical microscopy. ATR-FTIR revealed that the degree of polymerization of

polyaleuritrate was higher when CNC films from filter paper were used, most probably because of an easier water removal. On the other hand, the presence of polyaleuritrate reduced considerably the water uptake and permeability of the CNC films, showing that the coating acts as an effective polymer barrier. In addition, mechanical performances such as Young's modulus and hardness were analysed. Thus, in the case of the CNC side of the composites, these parameters increased after the treatment due to the lower water content, while the polyaleuritrate side was ductile. However, the addition of other substances (polysaccharides such as hemicelluloses and pectin, waxes, and phenolics) that can be found in the plant epidermis should be investigated in further studies in order to improve the physical properties. In conclusion, we demonstrate that CNC photonic films are compatible with hot-pressing and the obtained properties of the composite are comparable with the one of other conventional biodegradable materials, making our system suitable for functional packaging applications.

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Figure 1. Schematic representation of the plant cuticle-like film preparation. The helicoidal CNC films were first spray-coated with a layer of aleuritic acid and then hot-pressed to induce the polymerisation of the coating to polyaleuritate, thus forming a bilayer composite.

Figure 2. A and B Polarized optical microscopy images for left and right circular polarization and photographs, of CNC films produced from woodpulp (WP) and filter paper (FP) before and after the addition of the polyaleuritrate coating by spray and hot-pressing (WPA, FPA). C and D corresponding reflectance spectra for both polarizations, before and after the addition of polyaleuritrate coating by spray and hot pressing.

Figure 3. A, B, C, D, cross-section SEM images of FP, FPA, WP, and WPA, respectively. The typical CNC helicoidal arrangement is observed for all samples. No delamination between the polyaleuritate layer and the CNC films could be observed by SEM imaging. Scale bars: 2 μm .

Figure 4. A, ATR-FTIR spectra of FP, WP, FPA, and WPA samples. Main assignments for cellulose (blue) and polyaleuritate (orange) are included. B, C, water uptake and WVTR values for FP and WP (black) as well as FPA and WPA (red) in comparison with common cellulose derivatives and polyesters (gray).

Figure 5. A, typical load-depth indentation curves for FP, WP, and the CNC and polyaleuritate sides of FPA and WPA. B, Hardness versus Young's modulus plot with the values of FP and WP (black) as well as the CNC (red) and polyaleuritate (green) sides of FPA and WPA in comparison to common cellulose derivatives and polyesters (gray).

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