

All Starch Nanocomposite Coating for Barrier Material

Déborah LeCorre, Alain Dufresne, Martine Rueff, Bertine Khelifi, Julien Bras

The International School of Paper, Print Media and Biomaterials (Pagora), Grenoble Institute of Technology, BP65, F-38402 Saint Martin d'Hères Cedex, France

Correspondence to: J. Bras (E-mail: julien.bras@pagora.grenoble-inp.fr)

ABSTRACT: Starch nanocrystals (SNC) are nanofillers of growing interest for barrier and mechanical improvement of bio-based polymers. However, their potential use as fillers for organic coating material of industrial packaging has never been investigated. In this study, SNC processability in coating is assessed and the final properties of coated papers are measured. Coating colors composed of plasticized starch show higher Brookfield viscosity when filled with SNC even with the addition of water but rod-coating is still possible. These diluted water-based coatings induce paper wetting and surface crackling issues during drying as proved by drying process analysis. However no gelatinization of the SNC is observed whichever the type of drying. SNC compensate some of the water induced loss of mechanical properties of the base paper and decrease the water vapor permeability (WVP) up to 40% compared with the base paper. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39826

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INTRODUCTION

Nowadays, most efficient materials used for food packaging are usually undegradable¹ and fuel based representing a serious environmental and sustainability problem. Despite an increasing number of studies,^{2–5} the use of bio-based materials has been limited due to their poor processing and performances such as brittleness, gas, and moisture barrier. Another area of study is the development of functional coatings⁶ using low amounts of fillers. Nanofillers (defined as material exhibiting at least one dimension smaller than 100 nm)⁷ have strong reinforcing effects due to their size. They have a high positive impact on mechanical properties of their ensuing nanocomposites and studies have also shown their positive impact on barrier properties.^{8,9} Hence a strategy for new barrier materials consists in combining bio and nanotechnologies.

An all-starch coating consisting of thermoplastic starch and starch nanocrystals (SNC) is a candidate for this application. Indeed, starch is a natural, renewable, biodegradable polymer produced by many plants as a source of stored energy. It is one of the most abundant biomass materials in nature. It is found in plant roots, stalks, crop seeds, and staple crops such as rice, corn, wheat, tapioca, and potato.¹ The predominant model for starch is a multi-scale structure in which the granule (2–100 μm) consists in alternating amorphous and semicrystalline growth rings (120–500 nm). The latest is made of amorphous

and crystalline lamellae (9 nm)¹⁰ containing two glucosidic macromolecules: amylopectin and amylose (0.1–1 nm).³ Amylopectin is usually assumed to be the framework of the crystalline region. SNC result from the disruption of the semicrystalline structure of starch granules by the hydrolysis of the amorphous part. They exhibit a platelet-like morphology comparable to that of some clays no matter the botanic origin of the native starch.¹¹

Recent studies have shown that SNC could be used as fillers in polymeric matrices to improve mechanical^{12,13} and barrier properties of biocomposites.^{14–17} Their use for industrial packaging is now being investigated. Giving their promising platelet morphology, SNC appear to be good candidates for reducing coatings' permeability to grease, oxygen and water vapor following similar approach than nonrenewable and nondegradable nanoclays.¹⁸ However, the processing of SNC presents several challenges. First, nanoparticles are known to modify the rheological behavior of formulations. Second, starch tends to gelatinize with increasing water content and temperature. Thus their processing in industrial coating conditions has never been investigated.

This study assesses for the first time SNC processability in coating, and the influence of the coating formulation and drying on the final properties of a coated paper for packaging. Starch-based coating colors composed of plasticized starch show higher

Table I. Formulation of Glycerol-Plasticized Starch Coating Filled with 0, 5, or 30 wt % Starch Nanocrystals (SNC)

Parts	Ref	SNC 5 wt %	SNC 30 wt %
Starch	100	100	100
Glycerol	20	20	20
SNC	–	6	51
Water	400	456	463

Brookfield viscosity when filled with SNC but rod-coating is still possible. This diluted water-based coating induces paper wetting and surface crackling issues during drying. However no gelatinization of SNC is observed. SNC compensate slightly the water induced loss of mechanical properties of the base paper and decrease water vapor permeability.

EXPERIMENTAL

Materials

Waxy maize (WM) starch (C \star Gel 04201, 98% amylopectin) and wheat (WS) starch (Cerestar PT 20002) used to prepare SNC were kindly provided by Cargill (Krefeld, Germany). Sulfuric acid (96–99%, Sigma Aldrich) was used after dilution at 3.16M with distilled water. A commercial acid-thinned hydroxypropylated starch (Cargill Krefeld, Germany) was used as matrix/coating medium and glycerol (99+%, Alfa Aesar, Johnson Matthey, Germany) as its plasticizer. Base paper was a 50 g m⁻² coated on one side and noncalendered (Gerbier, Ahlstrom Stenay, France).

Preparation of Starch Nanocrystals (SNC)

SNC from both starches were prepared separately as described elsewhere.^{11,19,20} Briefly, 147 g of native starch was mixed with 1L of previously prepared diluted sulfuric acid (3.16M). The suspension was kept under 100 rpm mechanical stirring at 40°C, using a silicon bath, for 5 days. The final suspensions were washed by successive centrifugation with distilled water until reaching neutral pH and redispersed using Ultra Turrax for 5 min at 13,000 rpm to break aggregates. The obtained suspensions were filtered on a filter tissue (40 μ m, ref. 03–41/31 Buisine, France). Sodium azide was added to the suspensions before storage at 4°C to avoid microbial growth.

SNC Characterization

SNC's morphology was characterized with a Zeiss Ultra 55 Field Emission Gun Scanning Electron Microscope (FEG-SEM). Their crystallinity was estimated by wide angle X-ray diffraction (XRD) with a PAN analytical X'Pert PRO MPD diffractometer equipped with a X'celerator detector. Differential scanning calorimetry (DSC) measurements were performed on a DSC Q100 (TA Instruments, NewCastle). Detailed results are described elsewhere.^{20,21}

Coating Color Preparation

The acid-thinned hydroxypropylated starch was gelatinized under mechanical stirring. The temperature of the solution was kept at 95°C for at least 30 min to completely gelatinize the starch granules. The opening of the flask was covered with an aluminum foil to avoid water evaporation. Starch was then cooled down to

60–65°C and the plasticizer was added to 20 parts per hundred (pph) of the starch. The starch-glycerol mixture was kept under stirring at 60°C for a minimum of 30 min. Then, the mixture was cooled down to 40°C. In the meantime the SNC suspension was placed in an ultrasound vessel for sonication (3 times 1 min to avoid over heating), then added to the starch-glycerol mixture and dispersed by stirring for 30 min at 40°C.

To assess the influence of SNC on the properties of plasticized starch coated paper, either 0, 5, or 30 wt % (based on dry content) of SNC was added to the plasticized starch coating color. Base coating color was made of acid-thinned hydroxypropylated starch heated at a concentration of 30 wt %, and glycerol 20 pph, so that formulations can be summarized as in Table I.

The viscosity of the three different formulations was assessed in triplicates using a Rheometer Rheolabs QC (Anton Paar, Austria) using a Couette geometry and a shear rate ramp from 0 to 1000 s⁻¹ at 20°C.

Coating and Drying Process

The coating suspensions were applied to the uncoated back side of the substrate using a semi-industrial rod coater (Endupap Universal Coating Machine, L&W BK, CTP, France). It combines a classic rod coater with an in-line infrared (IR) drying chamber with two lamps. With a metering bar number 5, under controlled pressure and a bar moving speed of 6.6 m min⁻¹, a dry coating thickness of \sim 15 μ m was obtained.

The applied coatings were dried under different conditions, including: (i) long wave IR drying system (referred to as “IR-3500W” where 3500W is the power of the lamp used for drying), (ii) a 50°C glazing plate to simulate a contact drying cylinder (referred to as “Contact-50°C”), and (iii) ambient air drying (referred as “Ambient Air –25°C”). All samples were touch-dry upon removal from the drying media and double coated. The monitoring of the substrate temperature was carried out with a Copper-Constantan thermocouple fixed onto the substrate by applying a resin adhesive spot and connected to a Picotechnology TC-08 data logger. The temperature was recorded every second by the host computer using to the logger data acquisition program. To calculate the power provided by the IR lamp 3500W to the paper, a copper plate sample painted with black paint (Crown 7191) on the exposed side was used as absorbing media and the following formula was used:

$$P(W.m^{-2}) = \frac{1}{\varepsilon} \left(m C_p \frac{dT}{dt} \right) \frac{1}{S} = \frac{\rho h C_p}{\varepsilon} \frac{dT}{dt} \quad (1)$$

where m is the copper plate mass (kg), ε is the emissivity of the black surface, C_p is the copper heat capacity (J kg⁻¹ K⁻¹), T is the temperature (K), t is the drying time (s), and S the surface area of the copper plate (m²), ρ the density of copper (kg m⁻³) and h the thickness of the plate (m).

For $m = 0.045$ kg, $\varepsilon = 0.95$, $C_p = 395$ J kg⁻¹ K⁻¹ and $S = 5 \times 5$ cm², the slope $dT/dt = 0.232$ K s⁻¹, the power provided by IR-3500W is $P = 1800$ W m⁻².

Coated Paper Characterization

Coated papers were characterized in terms of coating thickness, pin holes, morphology, FTIR spectroscopy and water vapor

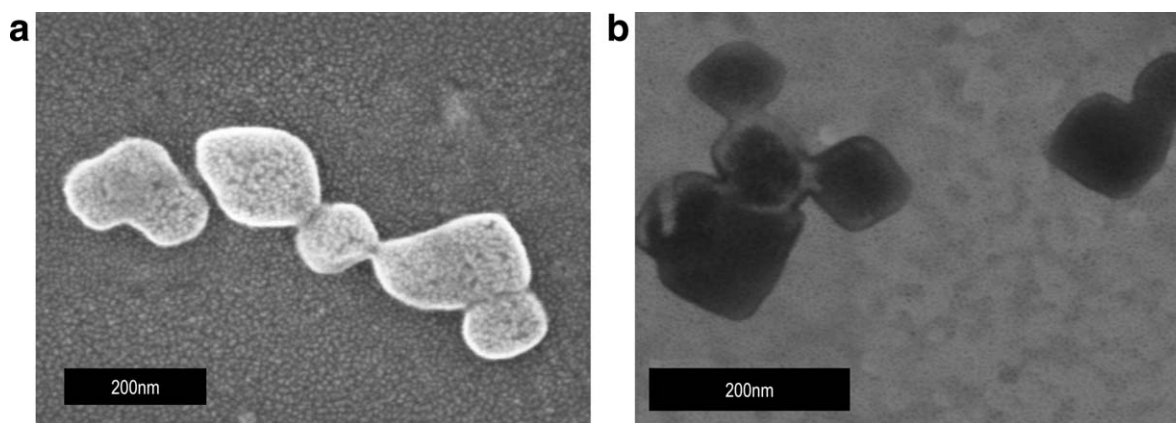


Figure 1. Field emission gun scanning electron micrographs of SNC from (a) waxy maize starch (WM SNC) and (b) wheat starch (WS SNC).

permeability. Thickness was measured using an Adamel & Lhomargy (MI20, Ivry, France).

Pin holes detection was performed using colored oil. Samples of 100x40 mm² were taped on a cardboard sheet and the oil uniformly applied onto the sample. After 1 min, the excess oil was removed with paper tissue and the surface checked for colored dots, indicating pinholes.

Coatings surface and cross-section were analyzed with an environmental scanning electron microscope (ESEM) on a Quanta 200 FEI device by depositing samples onto a carbon tape. FTIR analysis was performed with a Mattson 5000 spectrometer, equipped with a high refractive index ZnSe crystal. Attenuated total reflectance (ATR) sampling technique was performed on paper, as samples were too opaque and thick for standard transmission method, to evidence possible molecular change in the coating.

The static water vapor permeability (WVP) was measured according to the cup method (ASTM Standards, 1995).²² Circular coated paper samples (60 cm²) were placed to hermetically cover with an o-ring an aluminum cup containing 5 g of desiccant (anhydrous CaCl₂). The whole device was weighted and placed in humidity and temperature controlled chamber (23°C, 50%RH). The cups were weighted at regular interval of time until reaching equilibrium. All the tests were performed in triplicate at atmospheric pressure (1atm) and WVP was reported as the average of these three values as:

$$WVP(g.m^{-1}.s^{-1}.Pa^{-1}) = \frac{\Delta m.e}{A.\Delta t.\Delta P} \quad (2)$$

where Δm is the mass increase (g) of the CaCl₂ sample, A is the area of the paper sample, Δt is the exposure time in the chamber, e the thickness of the sample and ΔP the partial water vapor pressure difference across the film specimen corresponding to 0–50%RH, i.e. 1426 Pa.

Tensile tests were carried out with a RSA3 (TA Instrument, USA) equipment fitted with a 100N load cell. Measurements were performed, in triplicate, at room temperature (~25°C), with a cross head speed of 0.6 mm min⁻¹ for the first 250 s, then 1.5 mm min⁻¹ up to 2000 s, and finally 3 mm min⁻¹ up

to the break. The samples dimensions were 10x10 mm² and results were averaged on four replicates.

RESULTS AND DISCUSSION

SNC Characterization

Two different starches were used to prepare the SNC to be used in coating color: waxy maize starch (WM) and wheat starch (WS). Previous studies report the influence of starch type on the morphology¹¹ and final properties²¹ of SNC. Briefly, both native WM and WS are A-type crystallinity starches that render A-type crystallinity SNC. WM is more crystalline than WS and the same is observed for their SNC counterparts.¹¹ Contrary to native starch, no significance influence of starch type was observed on final thermal properties of SNC.²¹ Hence WM and WS SNC were selected for this work based on their square-like morphology (shown in Figure 1) and crystalline-type, expecting better barrier properties. Such morphology is close to that of nanoclays which are known to be an efficient barrier material.²³ Also, in its native state A-type crystalline packing is described as more densely packed than B-type.²⁴

SNC and Coating Process

The viscosity of SNC suspensions is presented in Figure 2. As expected the addition of SNC to the coating color induced an increase in viscosity even though coating color is diluted due to SNC being obtained as a suspension as detailed in experimental section. Nevertheless coating was possible as viscosity was rather close to 1000 mPa s at room temperature, especially at high shear rate. For most common paper coating technologies maximum viscosity is generally considered to be 2000 mPa s. Also, SNC-filled coating color still exhibited a shear thinning behavior.

After the first SNC-starch coating trials, the coatings' integrity were tested (with the oil test described in experimental section). Papers dried under ambient air and contact did not show any pin holes. However, although infra-red (IR) drying was the *a priori* preferred drying method because it is expected to dry rapidly the top layer of the coating, leaving intact the SNC, papers dried with IR- 3500 W for 1 to 10 s exhibited most defects. SEM micrographs, presented in Figure 3, confirmed

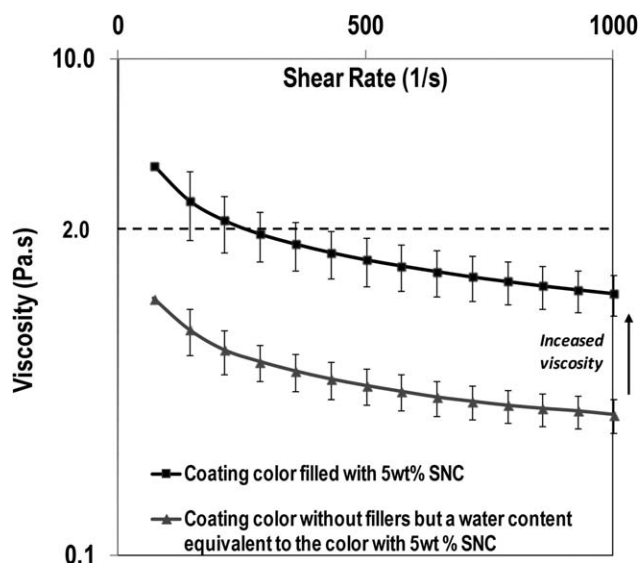


Figure 2. Viscosity of glycerol-plasticized-starch with: (\blacktriangle) water (equivalent to the amount of water added when SNC are in suspension), (\times) with 5% NM SNC in suspension.

that IR-dried papers showed cracks and blisters at the surface and air bubbles in the cross-section. It is obvious that such defects will affect barrier properties and gas permeation. This is why, it was important to understand the impact of the drying technique.

First, tests were conducted to assess if SNC could be the cause of the pin-holes. Indeed, they could (i) unexpectedly gelatinize, or (ii) bring too much water for the coating color to be dried. Hence the same coating was performed without SNC. Similar

pin holes were obtained. SNC were therefore excluded as a cause of pin-holes defects due to gelatinization (i).

To test the effect of the dilution of the coating color upon the addition of SNC (ii) the drying mechanisms were studied in detail. This was also important for checking that SNC will not gelatinize during processing and lose their crystalline structure and morphology (which are valuable for barrier applications).

Influence of Drying

Possible explanations for the pin-hole defects induced by IR-drying could be the followings: (i) molecular changes in the coating, (ii) evaporation of the plasticizer, and/or (iii) intense vaporization of the water contained in the coating color at the surface of the coating.

A simple comparison of FTIR analysis (not shown) of coated paper dried with IR-3500W, Contact-50°C and Ambient air-25°C revealed no significant differences, setting aside hypothesis (i).

Glycerol has a boiling point around 290°C; therefore it is unlikely that its evaporation can cause blisters or cracks. Although the drying temperature was assessed, such high temperature could not be achieved without deterioration of the paper and starch matrix. This is not the case, eliminating hypothesis (ii).

Last hypothesis (iii) was postulated from known drying rate differences between IR-drying and contact drying. Indeed IR drying is a very efficient non contact irradiation drying process which allows fast drying when containing molecules which can absorb IR radiation. In our case, the IR used was long waved, that is, usually between 3 μm and 1000 μm . It was selected

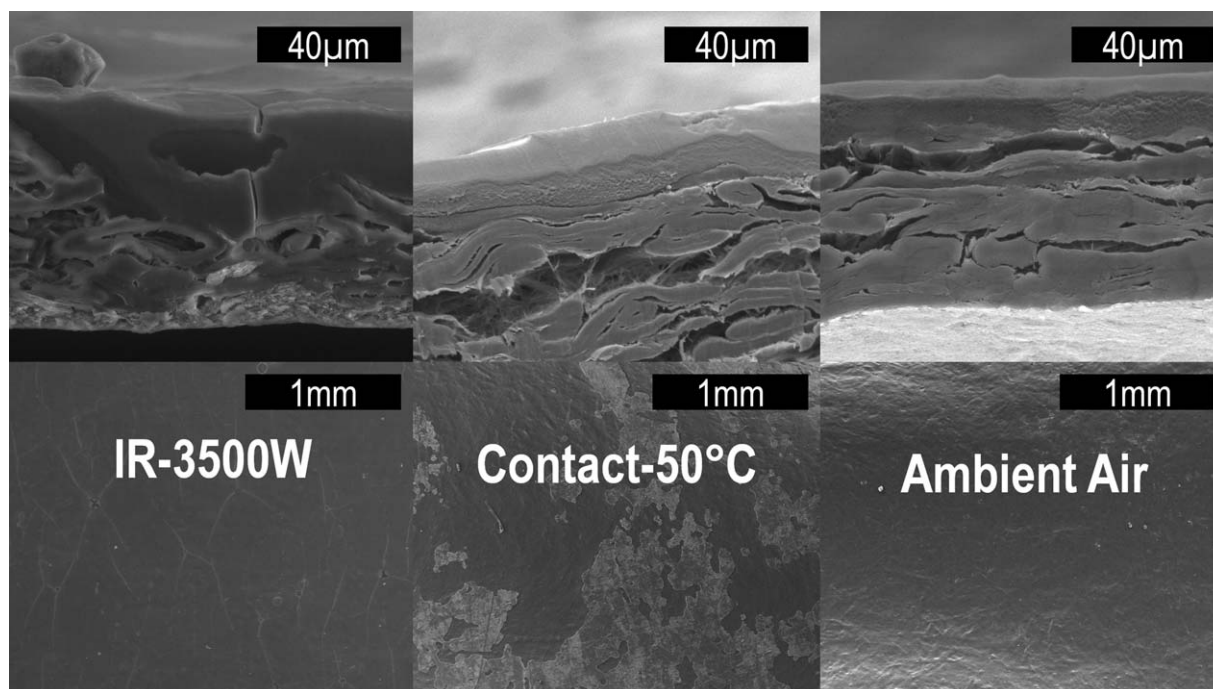


Figure 3. Scanning electron micrographs of cross-section and surface of glycerol-plasticized starch coated papers dried with (a) IR-2500W, (b) Contact-50°C and (c) Ambient Air.

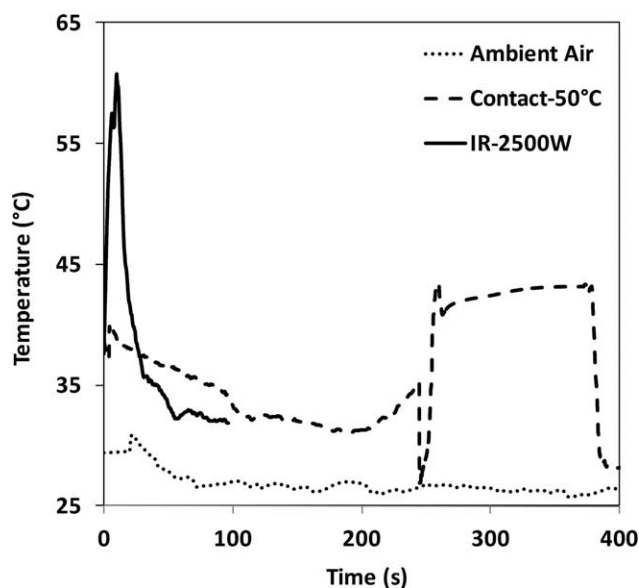


Figure 4. Temperature kinetics of glycerol-plasticized-starch coated papers dried with (...) Ambient Air, (- - -) with Contact-50°C, and (-) with IR-2500W.

because study²⁵ has shown that, considering the spectral characteristic of water films with thickness up to 10 μm , the spectral absorption range from 2 to 7 μm is best suited for heating water.²⁵ Temperature records such as that illustrated in Figure 4 explain some of the phenomena taking place.

When the sample is exposed to the IR radiation, a small part of the incident energy is reflected (less than 14% considering the optical properties of water in the infrared region^{26,27}) and the remaining part is absorbed in the sample. A small temperature gradient whose value depends on the water content of the coating layer and the thermal properties of the substrate develops in the sample thickness. Evaporation of water takes place at the free surface. The important temperature increase rate observed is due to the high energy applied and the good absorption by the material. At any time, the temperature attained results from the energy balance between radiation absorption, water evaporation and warm up of the sample. These results also show that the sample must be removed before the film is totally dry in order to avoid overheating and burning.

In the case of contact drying, the physical phenomena taking place are different. Heat is conducted from the side in contact with the metallic plate to the surface. The water evaporated from the surface has to diffuse through the felt that covers the sample. The temperature gradient within the sample is lower than with IR since a lower power density is required to maintain the dryer plate at a constant temperature. Therefore drying is more homogeneous. The temperature drop at the beginning of the drying is due to the plate temperature control and the warm up at the end of the experiment shows that the sample is dry.

Finally, for ambient air drying, drying temperature is much lower and the drying rate is very slow. Drying is homogeneous if water does not migrate inside the substrate.

The difference in drying mechanism of IR combine to the high water content of coating colors could explain the crackling/blistering. To assess (a) the temperature at which the paper is brought up during drying and (b) if SNC will gelatinize or not depending on the process, the drying kinetics of the papers for the different drying techniques has been investigated using a thermocouple (see Experimental).

Figure 4 confirms that IR-3500W drying temperature strongly exceeds that of contact drying which creates coating defects. In contrast, contact drying temperature never exceeds 45°C (Figure 4). As reported in a previous study,²¹ whatever the starch source, SNC can be processed in a water-based media without gelatinizing at temperatures below 90°C. Therefore, for the rest of the study coatings were prepared using SNC dried with Contact-50°C.

SNC-Plasticized Starch Coated Paper Properties

Water Vapor Permeability (WVP). Resistance to WVP is an essential requirement in applications such as packaging. Despite the high moisture sorption of pure polysaccharides, it has been reported that the use of starch nanocrystals can reduce WVP thanks to their platelet-like morphology, induced crystallinity and tortuosity.^{28,29} The WVP of starch-SNC coated papers are reported in Figure 5. Slight differences between coated papers can be evidenced. Improvement of WVP by adding SNC has already been reported for nanocomposites films with SNC contents below 3 wt %¹⁷ or higher than 30 wt %.³⁰ This can be explained by the fact that at very low content, SNC can effectively disperse into the matrix. At higher contents, the amount of crystalline particles is sufficiently high to lower the permeability. The present study reveals that as for nanocomposite, the addition of SNC to the coating color renders coated papers with lower WVP than glycerol-plasticized starch-coated one. At 5 wt %, it seems that there are already enough SNC to decrease water vapor permeability. For WM the addition of 30% SNC does not significantly reduce further the WVP. Whereas, coating

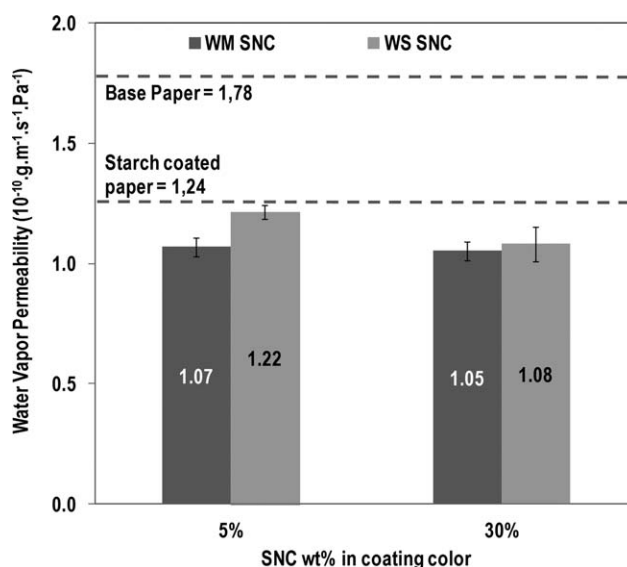


Figure 5. Water vapor permeability of papers coated with diluted coating color: WM SNC and WS SNC at 5 wt % and 30 wt %.

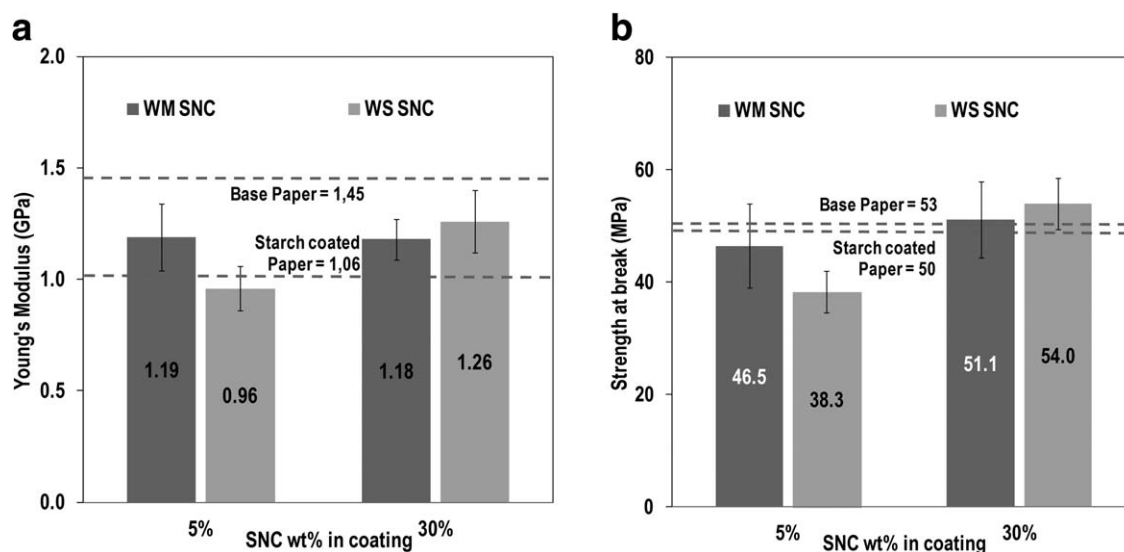


Figure 6. Mechanical properties of papers coated with diluted coating color containing WM SNC and WS SNC at 5 wt % and 30 wt %: (a) Young's modulus and (b) strength at break.

of 5% WS SNC has significantly higher WVP than WM and an increase in WS SNC content leads to a further decrease in WVP.

These observations can be explained as follow. Our previous study showed that WS SNC and WM SNC had roughly the same percolation threshold (at about 20%).¹¹ However, on the one hand, WS SNC are significantly less crystalline than WM SNC,¹¹ and on the other hand, WS SNC are "squarer" than WM SNC. Hence, the differences in WVP reduction for 5% SNC could be related to differences in crystallinity. At 30% SNC, coatings exhibit comparable results because they both contain a percolated network.

Overall decreases of WVP of up to 41% compared to base paper and by 15% compared with starch-coated paper can be obtained. It seems more economical to use highly crystalline SNC (i.e., WM) to reduce WVP as a lesser amount is required.

Tensile Tests. As observed in Figure 6 and Table II, glycerol-plasticized starch coating is detrimental to the Young's modulus of the base paper. This is most likely due to the wetting of the paper during the coating process which weakens the bonds of the fiber mat. Additionally, as one side of the paper is already coated and therefore more closed than the other side, there are drying-

induced tensions in the paper. However, it seems that the addition of SNC to the coating color can compensate some of the loss in stiffness of the papers. Similar impact is observed for the stress at break. Indeed, it has been reported^{14,30–34} that SNC are good fillers for the reinforcement of a bio-based matrix.

Interestingly, comparison of mechanical properties of papers coated with WM SNC and WS SNC correlate well with results in WVP. Young's modulus and strength at break of 5% WM SNC coated papers are higher than 5% WS SNC-coated ones. However, at 30% SNC, Young's moduli and strengths at break are comparable. The greater properties of 5% WM SNC-filled coated paper can be attributed to greater crystallinity which increases the stiffness of the samples. At 30% SNC, the compensation in mechanical properties is attributed to the formation of a SNC network inside the SNC-starch nanocomposite coating deposited onto the surface of the paper. Unfortunately, TEM evidence of such network cannot be obtained for our material due to similarity in chemical composition and crystallinity of the filler and the matrix.

This work shows that SNC are promising fillers for organic barrier coating. It is expected that the use of more crystalline or

Table II. Coating Thickness, WVP, and Mechanical Properties of Papers Coated with WS and WM SNC Compared to Base Paper and Reference Paper (Glycerol-Plasticized Starch Coating)

Load	Sample	Coating Thickness (μm)	WVP _{coating} (10^{-10} g/m.s.Pa)	WVP _{coated paper} (10^{-10} g/m.s.Pa)	Relative WVP Reduction	Young's Modulus (GPa)	Strength (MPa)	Elongation at break (%)
0%	Base paper	0 ± 0.6	–	1.78 ± 0.01	0%	1.45 ± 0.08	53.0 ± 3.5	4.59 ± 0.47
	S + G	34.6 ± 3.0	0.53 ± 0.00	1.24 ± 0.04	30%	1.06 ± 0.02	49.6 ± 5.2	5.90 ± 0.43
5%	S + G + WS SNC	39.7 ± 1.3	0.57 ± 0.01	1.22 ± 0.03	31%	0.96 ± 0.01	38.3 ± 3.7	5.38 ± 0.39
	S + G + WM SNC	29.8 ± 2.4	0.42 ± 0.02	1.07 ± 0.04	40%	1.19 ± 0.15	46.5 ± 7.5	5.28 ± 0.43
30%	S + G + WS SNC	24.9 ± 2.7	0.38 ± 0.03	1.08 ± 0.07	39%	1.26 ± 0.14	54.0 ± 4.6	6.06 ± 0.29
	S + G + WM SNC	19.0 ± 1.7	0.31 ± 0.01	1.05 ± 0.04	41%	1.18 ± 0.09	51.1 ± 6.8	5.68 ± 0.56

S, starch; G, glycerol; W, water.

better filtered SNC suspensions^{11,19} would further decrease the WVP and compensate the moisture induced loss of mechanical properties.

CONCLUSIONS

Starch nanocrystals (SNC) have been introduced in a starch-based coating and the properties of the ensuing coating color and final coated paper were investigated. Coating colors containing SNC showed higher viscosity but were still processable. It was shown that SNC can resist studied drying processes without melting. Crackling/blistering issues have been observed with IR drying and were due to the intense drying of highly diluted coating color. SNC addition to the coating color decreased WVP and compensated some of the loss of mechanical properties due to the use of the water-based coating. Limits of using water diluted SNC suspension were evidenced. It was further concluded that highly crystalline SNC are promising bio-nanofillers for improving barrier properties of bio-based coated papers.

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