

# Surfactant-Assisted Poly(lactic acid)/Cellulose Nanocrystal Bionanocomposite for Potential Application in Paper Coating

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**ABSTRACT:** The current article addresses a new strategy for the preparation of polylactic acid/cellulose nanocrystal (PLA/CNCs) nanobiocomposite films with improved structural morphology, mechanical and barrier properties for food packaging applications. The addition of hexadecyltrimethylammonium bromide (CTAB) and sodium lauryl sulfate (SLS) as cationic and anionic surfactants respectively, was found to play a crucial role in preventing re-aggregation of the CNCs during drying and improving the dispersion of CNCs in the PLA. The coated paper was characterized using mechanical tests, water vapor permeability (WVP), X-ray diffraction (XRD), scanning electron microscopy (SEM) and air permeability. The results showed that the paper coated with PLA containing 7.5% CNCs and 0.15% CTAB based on weight of PLA, gives the highest measured paper properties, where an increase in tensile strength (+133%), Young's modulus (+309%), tear index (+183%), burst (+60.8) and a decrease in air permeability (-92%) was obtained.

**KEYWORDS:** Cellulose nanocrystal, surfactant, paper coating, mechanical properties, air permeability, water vapor permeability

## 1 INTRODUCTION

Biobased composite has recently been employed for food packaging because it has various favorable properties such as biodegradability, renewability, recyclability, and mechanical flexibility [1]. However, the paper's composite surface is normally accompanied by some drawbacks like high porous structure, poor grease resistance and water vapor permeability. These drawbacks negatively affect the quality of the paper used in food preservation. Various strategies have recently begun to emerge for coating the paper sheet to enhance its prospects for food preservation [2]. Paper coating is a process where a coating film is applied onto the paper to impart certain qualities to the paper, including density, surface gloss, and smoothness, and in addition to protect paper surfaces

from moisture, grease and water. The coating materials widely used are thin laminated-plastic films or liquid polymeric coat. These materials are not biodegradable and therefore cause problems due to an increase in the percentage of nondegradeable packaging wastes. Biopolymers, such as chitosan [3], cellulose [4], and alginate [5], have recently emerged as sustainable and biocompatible alternatives to petroleum-based polymers in biomaterials. In order to be competitive with crude oil, these materials should have acceptable price and equally good performance as compared to the petroleum-based polymers. One of the most promising and interesting biopolymers is polylactic acid (PLA), which is thermoplastic, biodegradable, and biocompatible. It also possesses high strength and modulus and good processability and can compete with petroleum-based polymers on a cost-performance basis [6]. However, PLAs have a few drawbacks, such as brittleness, medium barrier properties, and low solvent resistance, which limit the demand for some end-use applications and need to be improved. PLA film performance can be improved

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via the incorporation of nanosized filler for increasing specific properties such as biodegradability, biocompatibility, stiffness, and density [7].

Cellulose nanocrystals (CNCs) obtained from acid hydrolysis of cellulose fibers have been realized as a new class of nanomaterials [8]. Compared to cellulose fibers, CNCs possess many advantages such as nanoscale dimension, high specific strength and modulus, high surface area, unique optical properties, etc. [9]. Recent trials have been carried out to incorporate the CNCs as promising reinforcement material as an efficient strategy to tailor new composite materials. For example, CNCs/polypropylene nanocomposite has been successfully designed as active packaging with the additional feature of microwave application [1].

The most important challenge for using CNCs as a reinforcing nanofiller is the low compatibility and poor interfacial adhesion arising from the hydrophilic nature of CNCs and the hydrophobic nature of the polymer matrix. In addition, the probability of strongly bonded CNCs nanoparticles increases due to the deficiency of adhesion force between the CNCs and polymeric material. Many studies had been conducted to tune the surface of CNCs as a filler during nanocomposite formation such as adsorption of macromolecules onto its surface or covalent bond formation between CNCs and polymer matrix. Solvent exchange process was found to improve the dispersion of CNCs in an appropriate organic medium and in the polymer matrix [10].

Due to the formation of sulphate ester groups, CNCs possess negative charges on their surface during sulphuric acid hydrolysis of cellulose fibers, which enhances their stability in aqueous solutions but restricts their dispersibility in most organic solvents. Heux *et al.* [11] have successfully modified the surface of CNCs via surfactants consisting of mono- and diesters of phosphoric acid bearing alkylphenol tails. It has been shown that surfactant-coated CNCs surfaces are effective in improving CNCs dispersion in organic solvents and polypropylene [11].

The most important challenge for preparation of PLA/CNCs solution is to improve with the dispersion of the CNCs, which have a strong hydrophilic nature in PLA. In this study, CTAB (cationic surfactant) and SLS (anionic surfactant) were used as a compatibilizer to incorporate cellulose nanocrystal with PLA. These surfactants are expected to improve the interface adhesion between the CNCs and PLA and consequently improve the performance of the nanocomposites for paper coating. Moreover, solvent exchange technique was adjusted to obtain never-dried CNCs with no strong hydrogen bonds between the nanoparticles to successfully disperse CNCs in PLA matrix.

## 2 MATERIALS AND METHODS

### 2.1 Materials and Chemicals

Poly(lactic acid) pellets, commercial grade 4042D, were purchased from NatureWorks LLC (Blair, NE, USA). This polymer was dried for at least 3 h at 50 °C before being used in the nanocomposite preparation. Analytical grade of hexadecyltrimethylammonium bromide (CTAB, Acros Organics) and sodium lauryl sulfate (SLS, Sigma-Aldrich) were used. Alpha cellulose isolated from rice husk bleached pulp was used as a source of cellulose nanocrystals (CNCs). Sulfuric acid for acid hydrolysis was obtained from Junsei Chemical Co., Ltd., and was diluted to 64 wt% prior to use. Chloroform and acetone were purchased from Sigma-Aldrich and used for the solvent exchange.

### 2.2 Preparation of Cellulose Nanocrystals

Cellulose nanocrystals were prepared from alpha cellulose isolated from rice husk using sulfuric acid hydrolysis according to the method described previously [12]. Briefly, 20 g of dry rice husk pulp was added to 200 mL of 64 wt% sulfuric acid preheated to 45 °C. The reaction was kept at 45 °C for 25 min and afterwards diluted to 10% of the original concentration in order to stop the reaction. The suspension was centrifuged at 6000 rpm for 15 min, washed with water and centrifuged. The remaining acid was washed for several days with dialysis until the pH of the surrounding water was neutral. The concentration, as determined by gravimetric analysis, was 1.3 wt%. The surface charge was determined by conductometric titration and was 0.6 mmol/g.

Aqueous dispersion of the CNCs was solvent exchanged by centrifugation/redispersion. First 200 ml of acetone was added to a centrifuge containing an aqueous suspension of CNCs (50 ml, 1.3% w/w). Then the mixture was stirred for 30 min and afterwards centrifuged at 7000 rpm for 15 min. The supernatant was removed and the residue of CNCs was redispersed in 100 mL of acetone. After three successive mixings with acetone followed by centrifugation, the CNCs residue was mixed with chloroform (50 ml) and mechanically stirred for 20 min, obtaining a stable suspension that was sonicated for 10 min. (Sonics Vibra-Cell VCX 750, Sonics & Materials, USA) [13]. Three different suspensions in chloroform from cellulose nanocrystals were prepared before drying. The nanocomposite used for paper coating was prepared according to the wt% shown in Table 1.

**Table 1** Composition of the prepared nanocomposite solutions used in this study.

Samples	PLA (wt%)	CNCs (wt%)	Surfactant (2 wt. % with respect to CNCs weight)
PLA0	100.0	---	---
PLA1	97.5	2.5	–
PLA2	95.0	5.0	–
PLA3	92.5	7.5	–
PLA4	90.0	10.0	–
PLA5	88.5	12.5	–
CTAB1	97.5	2.5	CTAB
CTAB2	95.0	5.0	CTAB
CTAB3	92.5	7.5	CTAB
CTAB4	90.0	10.0	CTAB
CTAB5	88.5	12.5	CTAB
SLS1	97.5	2.5	SLS
SLS2	95.0	5.0	SLS
SLS3	92.5	7.5	SLS
SLS4	90.0	10.0	SLS
SLS5	88.5	12.5	SLS

### 2.3 Preparation of PLA Coating Solutions

A PLA solution of 10% w/w was prepared by completely dissolving PLA in chloroform at 40 °C. The cellulose nanocrystal dispersion medium was changed from water to acetone and then to chloroform; thus, changing the solvent medium is one way to prevent the agglomeration of CNCs in nonaqueous solution to obtain PLA/CNCs solution. For each sample, CNCs was added to 2 g of PLA solution (10% in chloroform), with different ratios ranging from 2.5 to 10% with 2.5 intervals, and applied on the surface of paper using a 120 micron-coating applicator (a type of film applicator combining 4 gap sizes in one unit [30, 60, 90, and 120 μm]). The coated papers were dried in an oven at 85 °C for 30 min.

The CNCs was added to the PLA solution with and without anionic and cationic surfactants. Sample blend formulations and their concentrations are summarized in Table 1.

### 2.4 Characterization of Coated Reference Papers

The physical and mechanical properties of the reference and coated papers were determined by conditioning the paper sheets at 25 °C and 65% relative humidity for 24 h. After that, all paper properties were measured using standard methods of testing. Standard deviation for the measurements was calculated on the basis of 5 replicates for each sample.

#### 2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy for the CNCs was done on a FTIR spectrometer (Mattson 5000 FTIR) using KBr discs in the range of 4000–500 cm<sup>-1</sup>.

#### 2.4.2 Transmission Electron Microscopy (TEM)

Transmission electron microscope images of CNCs were taken with a JEOL JEM-2100 electron microscope at 100k× magnification, with an acceleration voltage of 120 kV.

#### 2.4.3 Scanning Electron Microscopy (SEM)

A scanning electron microscope (FEI Quanta 200 SEM, FEI Europe B.V., Netherlands) with an acceleration voltage of 20 kV was used to study the surface morphology of the reference and coated papers. The test samples were mounted on specimen stubs and examined by SEM at an accelerating voltage of 10 kV with a tilt angle of 45°.

#### 2.4.4 X-ray Diffraction (XRD)

The X-ray diffraction patterns were recorded using an X-ray diffractometer (PANalytical, Netherlands) at room temperature with a monochromatic Cu Kα radiation source ( $\lambda = 0.154$  nm) in step-scan mode with a 2θ angle ranging from 5° to 60° with a step of 0.04 and a scanning time of 5.0 min.

#### 2.4.5 Water Vapor Permeability (WVP)

Water vapor permeability of coated paper described in Table 1 was determined according to Tunc *et al.* [14]. Water vapor permeability was gravimetrically determined according to the ASTM E96-95 standard method [15]. Samples (discs 4 cm<sup>2</sup> in diameter) were conditioned at 25 °C and 60% RH (relative humidity) for 24 h and then hermetically sealed (with Teflon seals and silicone grease) in a glass permeation cell containing 3 g of anhydrous calcium chloride. The permeation cell was placed at 20 °C in desiccators containing

potassium sulfate, thus obtaining a RH of about 97%. The WVP was evaluated from the slope of the mass gain versus time curve as follows:

$$\text{WVP}(\text{g}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}) = \frac{\Delta m x}{A \Delta t \Delta p}$$

where  $\Delta m$  is the mass increase (in grams) of the  $\text{CaCl}_2$ ,  $x$  is the coated paper thickness (mm),  $\Delta t$  is the time of weight loss (s),  $A$  is the area of exposed paper ( $\text{mm}^2$ ) and  $\Delta p$  is the partial water vapor pressure difference across the samples corresponding to 0–97% RH, i.e., 1875 Pa.

#### 2.4.6 Air Permeability Measurements

Air permeability is a critical property of papers used in food packaging. Water vapor and  $\text{O}_2$  are critical compounds that can penetrate through the packaging materials and degrade food quality. The air permeability values of the paper sheets were measured using a Bendtsen smoothness and porosity tester made in Denmark (Andersson & Sorensen, Copenhagen). Air permeability was determined by measuring the rate of air flow under standard pressure between the paper surface and two concentric, annular metal rings applied to the paper. The air permeability of a paper web is a physical parameter that characterizes the degree of web resistance to air flow. The air permeability of coated papers is partially dependent on the uniformity and porosity of the coating layer [2].

### 3 RESULTS AND DISCUSSION

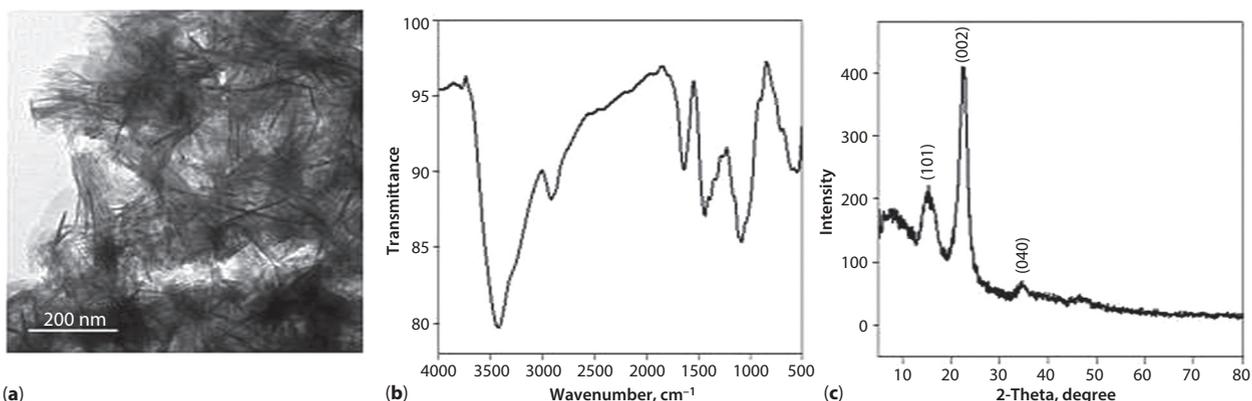
#### 3.1 Isolation and Characterization of CNCs

It has been reported that controlled acid hydrolysis could cleave amorphous regions in the cellulosic fibers and

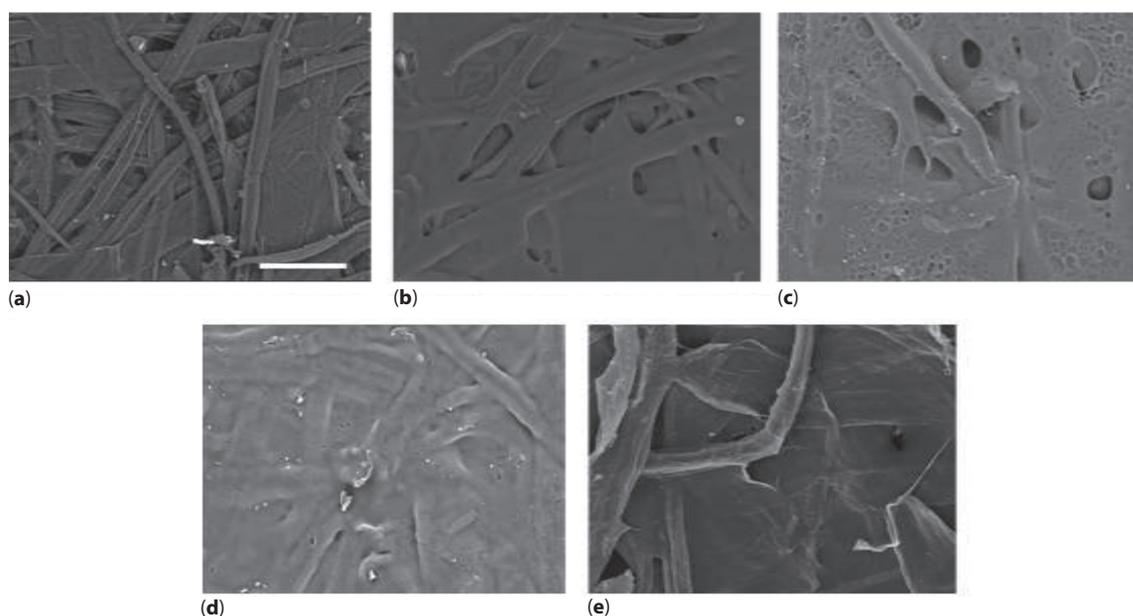
consequently reduce their size from micron to nanometer scale [16]. The internal structure of the prepared CNCs extracted from rice husk via acid hydrolysis was examined by TEM, as shown in Figure 1a. It is clear that CNCs appear as a rod-like structure with some agglomerated network. This agglomeration can be interpreted as being due to the strong hydrogen bond and high surface area of CNCs extracted from rice husk. The width of isolated nanocrystals was in the range of 5–7 nm while the length was in the range of 79–150 nm. These results agree with other studies reported elsewhere [17, 18]. The chemical structure of CNCs was characterized using FTIR spectroscopy, as shown in Figure 2b. The broad band at  $3428\text{ cm}^{-1}$  and peak at  $2924\text{ cm}^{-1}$  correspond to the O-H stretching and C-H stretching vibration modes, respectively [4]. Moreover, the peak at  $1638\text{ cm}^{-1}$  is attributed to the presence of adsorbed water molecules on the CNCs' surface; peaks at  $1200\text{--}1000\text{ cm}^{-1}$  to the stretching vibration of C-O for the glycosidic bonds and C-O of primary and secondary hydroxyl groups; and a peak at  $850\text{ m}^{-1}$  to out-of-plane deformational vibration of O-H groups [19]. Furthermore, the FTIR results indicate the disappearance of the characteristic peaks of hemicelluloses and lignin which are present in the raw rice husk. Figure 1c shows the X-ray diffraction pattern of CNCs. The XRD pattern shows the known diffraction peaks of cellulose I with crystalline peaks at about  $2\theta = 15.4, 22.3$  and  $34.6^\circ$ . These peaks correspond to the (101), (002), and (040) crystallographic planes of typical cellulose I structure, respectively [20]. The calculated crystallinity index of the nanocrystals reached 85%, which may be attributed to the hydrolysis of the amorphous region in the neat cellulose fibers.

#### 3.2 PLA/CNCs Nanocomposite as a Paper Coating Material

Extracted CNCs were used to reinforce PLA to form the nanocomposite which will be applied as a paper



**Figure 1** TEM (a), FTIR (b) and XRD (c) of CNCs prepared from rice husk.



**Figure 2** Representative SEM images of (a) reference paper, (b) PLA0, (c) PLA3, (d) CTAB3 and (e) SLS3 (scale bar 50 micrometer).

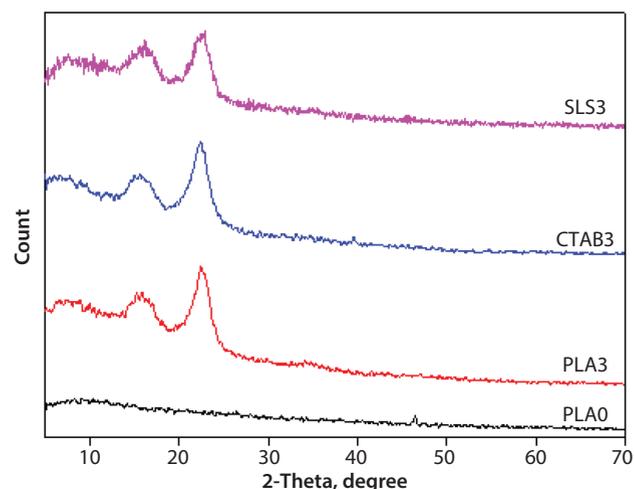
coating material. The effect of the addition of CTAB and SLS on the performance of coated papers were studied.

### 3.2.1 SEM

Figure 2 displays representative images for the morphology of the surfaces of the reference paper and papers coated with nanocomposite with and without surfactants. Reference paper (Figure 2a) shows a typical morphology of the normal papers, which is a fiber network with free pores. However, these free pores become relatively smooth after treating with PLA (Figure 2b). Adding CNCs also shows smooth surface compared with reference paper, but with agglomerated regions. The CNCs dispersion was highly improved after adding surfactants as seen in Figure 2d,e. Adding surfactants prevents the agglomeration of CNCs and consequently improves the paper smoothness. The cationic surfactant (CTAB) showed much more homogeneous cross sections dispersed in the PLA compared to anionic surfactant.

### 3.2.2 X-ray Diffraction

The crystallite structure was studied by X-ray diffraction to determine the effect of addition of CNCs and surfactants to PLA solution. Figure 3 shows the diffractogram of PLA0, PLA3, CTAB3 and SLS3. A broad peak at around  $10^\circ 2\theta$  shows the amorphous portion of the PLA. The other samples exhibit atypical CNCs peak at around  $14^\circ 2\theta$  and  $22^\circ 2\theta$ , which can be attributed to



**Figure 3** XRD of PLA0, PLA3, CTAB3 and SLS3 samples.

the addition of cellulose nanocrystals. The calculated crystallinity index percent was 67, 69, and 68 for PLA3, CTAB3 and SLS3 respectively. In conclusion, the crystallinity of reinforced PLA series used for paper coating was increased after addition of CNCs due to the higher crystallinity index, which was 85%. On the other hand, the crystallinity of CTAB and SLS series did not significantly change compared with PLA series.

### 3.2.3 Mechanical Properties of Coated Paper

The mechanical properties, including tensile strength, burst factor, tearing resistance and modulus of

elasticity for paper sheets, were prepared as described in Table 1. The results were calculated and displayed in Table 2. Tensile strength of the paper sheets coated with PLA (PLA0) was increased by about 33% compared to the reference paper sheet. Moreover, the incorporation of CNCs with different ratios (PLA1 to PLA5) resulted in further increase in tensile strength of paper sheets by about 5–14% as compared to PLA0 sample. These results show that increasing the content of CNCs was accompanied by a slight increase in tensile strength of coated paper sheets. The mechanical properties results showed an enhancement with increasing the content of CNCs from 2.5 to 7.5% and then tended to level off with further increase of CNCs. The addition of 2% of surfactants (CTAB and SLS) significantly affected the tensile strength, as observed in Table 2. The maximum value was observed at 7.5% CNCs solutions and recorded 56% and 11% for CTAB3 and SLS3 respectively. It is clear that the addition of cationic surfactant favored the dispersion and had better interfacial compatibility of CNCs and PLA compared to anionic surfactant. Also, Young's modulus of reference paper sheets and the coated paper prepared samples as described in Table 1 followed a similar trend, as can be observed in Table 2. It is obvious that the increasing content of CNCs in composite layer showed an increase in Young's modulus from 18 to 106% by increasing the CNCs content from 2.5 to 7.5%,

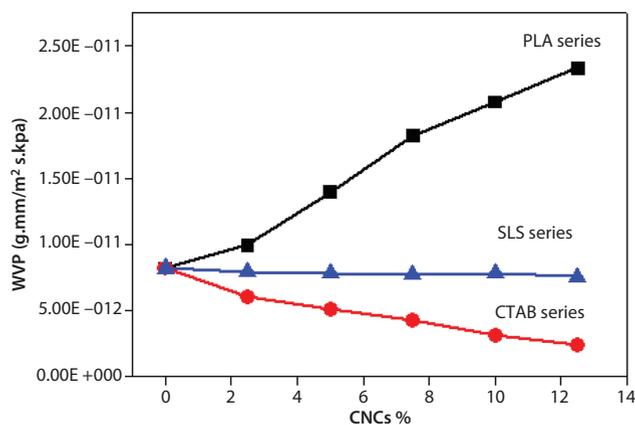
respectively, as compared to PLA0 sample. Moreover, the addition of surfactants was accompanied by an increase in Young's modulus to 164% and 152% for the samples labeled with CTAB3 and SLS3 respectively. Also, the results show that addition of CNCs to PLA resulted in an increase in the tear burst strength up to nanocrystals loading of 7.5%. The increase in tear and burst strength ranged from 18% to 28% and 5% to 16% upon using 2.5% to 7.5% of CNCs, respectively, while the increase in tear and burst strength reached 105% and 48% upon using 2% CTAB surfactant with 7.5% CNCs.

### 3.2.4 Water Vapor Permeability

Water vapor permeability (WVP) is one of the most important functions of food packaging to decrease the moisture between the food and the surrounding atmosphere; the WVP of the packaging material should be as low as possible [21]. Figure 4 shows WVP of the PLA, CTAB and SLS series of coated paper. Initially, the effect of CNCs concentration (0, 2.5, 5, 7.5, 10, and 12.5%) based on PLA on WVP after 24 h is shown in Figure 4. It is clear that WVP increased from  $8.19 \times 10^{-12}$  to  $2.33 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ kPa}^{-1}$  with increasing CNCs content from 2.5% to 12% respectively. This is attributed to the hydrophilicity of CNCs and the incompatibility of PLA/CNCs blend. A significant decrease in

**Table 2** Mechanical properties of reference paper, PLA series, CTAB series, SIS series and air permeability of coated paper.

Samples	Tensile strength (MPa)	Young's modulus (MPa)	Tear index (mN.m <sup>2</sup> /g)	Burst index (KPa.m <sup>2</sup> /g)	Air permeability (ml/min)
Reference paper	30.00 ± 2.11	1.10 ± 1.21	4.57	0.07	955.00
PLA0	40.43 ± 2.32	1.70 ± 1.42	6.30	0.08	780.00
PLA1	42.35 ± 1.71	2.00 ± 1.54	7.44	0.08	550.00
PLA2	43.54 ± 2.27	3.20 ± 1.20	7.61	0.08	525.00
PLA3	45.65 ± 3.23	3.50 ± 1.63	8.11	0.09	480.00
PLA4	42.78 ± 2.36	3.10 ± 1.32	7.34	0.08	400.00
PLA5	41.78 ± 2.41	2.70 ± 1.11	6.76	0.06	350.00
CTAB1	52.40 ± 1.47	2.50 ± 1.14	10.00	0.08	240.00
CTAB2	56.14 ± 1.31	4.10 ± 1.73	10.96	0.09	200.00
CTAB3	70.12 ± 2.49	4.50 ± 1.31	12.97	0.11	70.00
CTAB4	66.56 ± 2.10	4.20 ± 1.28	12.27	0.09	40.00
CTAB5	64.18 ± 2.10	3.50 ± 0.91	12.60	0.07	15.00
SLS1	46.40 ± 4.1	2.50 ± 1.20	7.00	0.08	300.00
SLS2	47.14 ± 4.2	3.50 ± 1.60	8.43	0.08	270.00
SLS3	50.12 ± 1.3	4.30 ± 1.30	9.27	0.10	150.00
SLS4	49.56 ± 1.4	4.70 ± 1.70	10.67	0.07	144.00
SLS5	48.18 ± 3.1	2.50 ± 0.70	11.60	0.07	90.00



**Figure 4** Water vapor permeability of the PLA, CTAB and SLS series of coated paper.

WVP was obtained upon addition of 2% CTAB with increasing CNCs percent. The results indicated that 2% CTAB decreased the WVP of PLA coated paper by 71% with 12.5% CNCs, which is due to the increased compatibility between CNCs and PLA. On the other hand, a slight decrease in WVP was obtained upon addition of 2% SLS with increasing CNCs content.

### 3.2.5 Air Permeability

The air permeability of reference paper (RP), PLA-coated paper and PLA/CNCs-coated paper with and without surfactant are listed in Table 2. The obtained results show that air permeability of papers coated with neat PLA was 18% lower than the reference paper. The air permeability of papers coated with PLA/CNCs improved significantly upon adding 2% surfactant into the coating solution, which is about 98% lower than the reference paper sheet. This is due to the compact coating structure filling the cracks and creating a tight and flat, smooth surface with less air permeability than reference paper.

## 4 CONCLUSION

The current article showed that cellulose nanocrystal was successfully prepared from rice husk as a promising reinforcement material for PLA matrix. The performance of the PLA/CNCs nanocomposite was highly improved with the addition of cationic (CTAB) and anionic (SLS) surfactants to act as a new category of coating material in packaging applications. The addition of surfactant was accompanied by higher tensile strength, good water permeability, and air permeability. Addition of CTAB during preparation of PLA/CNCs solutions inhibits the agglomerations of CNCs and leads to homogenous structural morphology of

coating solution. The bionanocomposites from PLA/CNCs in the presence of cationic surfactant are a promising coating for paper sheets in food packaging.

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