

Highly Transparent Cross-Linked Cellulose Nanocrystal Coatings with High Gas Barrier and Enhanced Water Resistance for Sustainable Food Packaging

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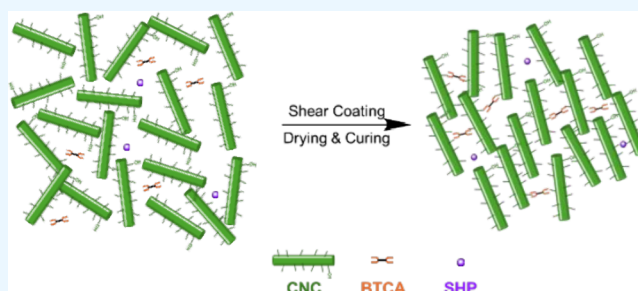
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ABSTRACT: Cellulose nanocrystals (CNCs), owing to their high crystallinity, thermal stability, and strong mechanical performance, serve as promising candidates for sustainable, high gas barrier packaging materials. However, their inherent moisture sensitivity and poor water resistance limit their practical applications. This study presents a strategy to overcome this limitation by constructing a network within CNC coating layers using 1,2,3,4-butanetetracarboxylic acid (BTCA) as a cross-linker and sodium hypophosphite (SHP) as a catalyst. The resulting cross-linked network had improved water resistance, enabling the coatings to maintain structural integrity during water immersion without redispersing. Furthermore, cross-linking concurrently enhanced oxygen and water vapor barrier properties, overcoming the common trade-off between the two. For the coating formulation with 30% cross-linker, the oxygen barrier performance was improved by nearly 2 orders of magnitude compared to plain polylactic acid (PLA), while the water vapor transmission rate was also significantly lowered by 63% under dry cup conditions. In addition, a substantial portion of the enhanced barrier properties were retained after water immersion, showing great potential for its application in real-world packaging scenarios where the films may be exposed to high humidity or wet environments. Importantly, the enhanced oxygen barrier performance was demonstrated in a guacamole storage test where the cross-linked CNC coatings effectively slowed oxidative browning. This work demonstrates a viable path for developing water-resistant, high barrier, and sustainable packaging materials.

KEYWORDS: Cellulose Nanocrystals, Gas Barrier Coating, Cross-Linking, BTCA, Water Resistance, Oxygen Permeability, Sustainable Packaging



1. INTRODUCTION

Cellulose, with a history of use spanning thousands of years, has regained research interest amid growing environmental concerns. Owing to its natural abundance, cellulose serves as a sustainable and biodegradable alternative to petroleum-based plastics.^{1,2} Modern research into cellulose has been focusing on cellulose nanoparticles (CNs), which exhibit outstanding mechanical, thermal, and gas barrier properties attributed to their unique molecular structure, high crystallinity, and specific particle morphology.^{1,3,4} A major research thrust involves the gas barrier performance of cellulose materials, a critical criterion for food packaging applications.⁵ The extensive amount of hydroxyl groups within cellulose facilitates inter- and intramolecular hydrogen bonding, promoting dense chain packing and high crystallinity. This structure creates highly tortuous pathways for gas permeation in CN assemblies and nanocomposites. Additionally, nonpolar gas molecules like oxygen exhibit low solubility within the polar cellulose matrix, further contributing to low gas permeability. Collectively, these properties underpin the high gas barrier performance. As a result, CNs have been extensively investigated as high gas

barrier materials in the format of coatings,⁶ free-standing films,^{7–10} and as fillers in polymer matrices.^{11–14}

Cellulose nanocrystals (CNCs), one of the main types of CNs, are rod-shaped nanoparticles characterized by a high aspect ratio, high crystallinity, and high mechanical strength, making them a promising candidate for high gas barrier packaging materials.^{1–3,15,16} However, the abundance of hydroxyl groups also renders cellulosic materials such as CNCs very hydrophilic and prone to significant moisture sorption. The moisture sorption isotherm of cellulose materials typically follows a sigmoid shape that can be categorized as a type II Brunauer–Emmett–Teller (BET) sorption isotherm.^{9,17,18} In a high relative humidity (RH) environment,

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water molecules act as plasticizers within the cellulose matrix, adsorbing onto CNC particle surfaces, interparticle voids, and also within CNC particles, increasing interparticle distance and enhancing the flexibility.^{8,18–20} Consequently, the gas barrier properties of cellulose materials show a drastic decrease in high RH environments.^{5,21} Moreover, upon direct contact with liquid water, cellulose materials may redisperse, creating easy pathways for gas permeation.

To address this limitation, various strategies have been explored.^{2,22} One of the common practices involves constructing multilayer structures to physically shield the cellulose layer from high humidity environments.^{10,22–26} However, conventional coating materials such as plastic and aluminum, commonly used in paper cups and milk cartons, can pose hazards during application and compromise the biodegradability of the packaging. Additionally, multilayer lamination can be susceptible to delamination.²³ Furthermore, disparities in the thermal expansion coefficient and elastic modulus between the cellulose layer and protective layers can lead to interfacial failure, compromising any gains in barrier properties.

Another widely adopted strategy involves chemical modifications to reduce the hydrophilicity of CN films, employing techniques such as esterification, silanization, and reacting with isocyanates, substituting hydroxyl groups with alkyl chains.^{2,8,14} Here, researchers often face a trade-off between moisture barrier and oxygen barrier performance.^{5,8,22} For example, Bras et al. investigated the effect of increasing the acyl chain length on the barrier properties of fully substituted cellulose esters. Their findings indicated that while longer acyl chains reduced the water vapor permeability, oxygen permeability increased concomitantly. The authors attributed this to the dual role of the fatty acid side chains, which act as a hydrophobic barrier but also as an internal plasticizer.⁸

Alternatively, cross-linking CNs has emerged as a focus of studies that is promising in reducing the moisture sensitivity while decreasing gas diffusion coefficients. A variety of cross-linking agents have been investigated for CNs.²⁷ Dialdehydes are among the most frequently used cross-linkers, with glutaraldehyde and glyoxal being widely adopted to enhance the wet strength of paper or impart antiwrinkle properties to cellulose-based fabrics.^{28–31} Despite their high reactivity and cost-effectiveness, dialdehydes raise concerns regarding cytotoxicity and environmental impact.³² Polyamide epichlorohydrin (PAE) represents another prevalent cross-linking agent for cellulose materials.^{33–36} Although PAE exhibits a better environmental profile compared to dialdehydes, its higher cost and potential impact on biodegradability and recyclability at excessive concentrations present a noticeable limitation.³⁷ In addition, CNCs are typically produced via sulfuric acid hydrolysis or oxidation; thus, the nanoparticles carry a negative surface charge. Our preliminary investigations suggest that the negatively charged CNCs interact with the cationic PAE via electrostatic forces, leading to particle agglomeration, which can compromise intended applications. There has been increasing research interest in boric acid (BA) in recent years for polysaccharides due to its cost-effectiveness, environmental sustainability, and biocompatibility. The cross-linking mechanism involves the stepwise formation of monodiol and didiol complexes between borate, the conjugate base of boric acid, and polysaccharide.³⁸ However, this reaction requires precise control over pH and temperature.³⁹ Polycarboxylic acids have been employed as cellulose cross-linkers for over five decades.^{27,40} The cross-linking proceeds

via a two-step mechanism: initial formation of anhydride intermediates within the polycarboxylic acids, followed by esterification with cellulose hydroxyl groups.^{41–44} This cross-linking typically necessitates high curing temperatures, but the addition of sodium hypophosphite (SHP) as a catalyst could effectively lower the required temperature.^{29,43} Among polycarboxylic acids, citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA) are predominantly used.^{42,45,46} BTCA, possessing an additional carboxyl group compared to CA, demonstrates enhanced cross-linking efficiency.^{40,47,48} Although considerable research has been devoted to cellulose cross-linking, the correlation between cross-linking density and the barrier properties of cross-linked CNC coatings remains insufficiently explored in the current literature.

In this study, CNC coatings were formulated with the cross-linker BTCA and the catalyst SHP at varying concentrations. The formulations were shear-coated onto polylactic acid (PLA) substrates, followed by oven curing at 100 °C for 30 min. Successful cross-linking was confirmed by Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and water resistance tests. The adhesion of the CNC coatings to the PLA substrate was evaluated using a cross-hatch test. The optical transparency and alignment of CNC were analyzed by UV–vis spectroscopy with optical polarizers. The water affinity of the coatings was assessed through water contact angle measurements and the equilibrium moisture content at different RH levels. Furthermore, the barrier performance of the composite materials was analyzed by investigating the water vapor transmission rate (WVTR) and oxygen permeability (OP) as a function of cross-linker concentration. The deterioration of performance after exposure to a wet environment was quantified by the change in barrier properties before and after water immersion. Finally, the practical efficiency of the coating was evaluated through a guacamole storage test, demonstrating its potential for real-world food packaging applications.

2. EXPERIMENTAL SECTION

2.1. Materials

Cellulose nanocrystal (CNC) aqueous suspension, solid content of 10.6 wt % containing 1.1 wt % sulfur on dry CNC sodium form (Lot: 2023-FPL-CNC-233) was purchased from the University of Maine Process Development Center (Orono, ME, USA). 1,2,3,4-Butanetetracarboxylic acid (BTCA) (99%) and sodium hypophosphite (SHP) (≥99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Deionized (DI) water (18.2 MΩ·cm) was used for all experiments. Polylactic acid (PLA) film (thickness: 30 μm) was purchased from BI-AX International Inc. (Wingham, ON, Canada). Polypropylene (PP) film (thickness: 25 μm) was purchased from PH PERKHOMY Store (Tianjin, China). Polyethylene terephthalate (PET) film (thickness: 25 μm) was procured from McMaster-Carr (Part Number: 8567K12) (Elmhurst, IL, USA). Linear polarizers, 42% ± 2% single pass transmission at 400–700 nm (Model No.: AP42-004T), were purchased from American Polarizers Inc. (Reading, PA, USA). Dry oxygen compressed gas with 99.6% purity was purchased from Indiana Oxygen Co. (Lafayette, IN, USA). Guacamole paste (brand: Wholly) was purchased from a local grocery store.

2.2. CNC Coating Formulations

A 10 wt % CNC suspension was prepared by diluting the as-received 10.6 wt % CNC suspension with DI water. Separately, 10 wt % aqueous solutions of BTCA and SHP were prepared by dissolving each chemical in DI water. The BTCA and SHP solutions were then added to the CNC suspension in varying weight ratios relative to the

CNC suspension. The specific formulations are detailed in Table 1. All formulations were mixed via a FlackTek SpeedMixer (Landrum, SC, USA) at 2000 rpm for 8 min under ambient lab conditions.

Table 1. CNC Barrier Coating Formulations

Sample name	10 wt % CNC (parts)	10 wt % BTCA (parts)	10 wt % SHP (parts)
CNC-0%BS	10	0	0
CNC-10%BS	10	1	0.5
CNC-20%BS	10	2	1.0
CNC-30%BS	10	3	1.5

2.3. Coating Application

The coating procedure was adapted from previous literature methods.^{6,26,49,50} Briefly, the PLA substrate film was taped onto a 10" × 10" glass plate. The coating thickness was controlled using 130 μm thick masking tape (#2020, 3M, Saint Paul, MN, USA) as a spacer. Prior to coating, the PLA surface was activated via corona treatment (BD-20AC Laboratory Corona Treater, Electro-Technic Product, Chicago, IL, USA) for at least 3 min to enhance adhesion. The formulated CNC mixtures were then shear-coated onto the treated PLA substrates. The coated films were then dried and cured in an oven at 100 °C for 30 min. The final coating thickness was averaged to be 5 μm, measured by a micrometer (293-340, Mitutoyo, Japan). After curing, all samples were stored in file binders for subsequent characterization.

Due to inherent thickness variations in the PLA substrate film (nominal thickness: 30 μm) and the manual coating process, the exact thickness of both the substrate and the coating layer varies slightly across samples. A digital micrometer was used at multiple spots per sample. Cross-sectional SEM images of representative samples are provided in Figure S1 (Supporting Information) for a direct visualization of the typical coating thickness.

2.4. Post-Treatment Rinsing

To evaluate the efficacy of cross-linking and to quantify the barrier performance of the coating after being exposed to a wet environment, a rinsing step was performed on a subset of the samples. Un-cross-linked CNC coatings would readily redisperse and be washed away upon water contact, whereas successfully cross-linked CNC coatings would remain. This rinsing procedure involved immersing the films in copious amounts of DI water for 15 min, followed by overnight drying under ambient conditions. Preliminary characterizations by FTIR confirmed that this 15 min immersion was sufficient to remove residual water-soluble components. For the consistency of sample nomenclature, all the CNC coated samples before rinsing were assigned the suffix "br", and all the CNC coated samples after rinsing were assigned the suffix "ar".

2.5. Surface Morphology and Chemical Structure Characterization

The surface morphology of the coatings was examined using scanning electron microscopy (SEM, FEI Teneo VolumeScope, Thermo Fisher, Waltham, MA, USA) operating in the secondary electron imaging mode. SEM samples were coated with platinum for 90 s using a sputter coater (208HR, Cressington Scientific Instruments, Watford, UK). Images were acquired in high vacuum at an accelerating voltage of 2 kV and beam current of 13 pA, with a working distance of around 3 mm. In addition, the thickness of the CNC coating was verified via cross-sectional SEM. Cross-sectional images were acquired in high vacuum at an accelerating voltage of 5 kV and beam current of 50 pA, with a working distance of around 13 mm.

The chemical structure of the coatings was analyzed by Fourier-transform spectroscopy with attenuated total reflection (FTIR-ATR, Spectrum 100, PerkinElmer, Waltham, MA, USA) for each sample before and after the rinsing step. Spectra were collected in the range of 4000 to 600 cm⁻¹, with a resolution of 4 cm⁻¹ and data interval of 1

cm⁻¹. Each spectrum represents an average of 16 scans, and a minimum of three different spots were examined for each sample.

2.6. Thermal Stability

The thermal stability of CNC coatings was assessed by thermogravimetric analysis (TGA, Q50, TA Instruments). To isolate the thermal properties of the coatings from the PLA substrate, free-standing CNC films were prepared on glass plates following the same application and curing procedures as described in Section 2.3. After being cooled, the coatings were carefully peeled off of the glass substrate using a razor blade. Samples weighing 10–15 mg were then loaded into a platinum pan and heated from 30 to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere. An initial temperature equilibration at 30 °C was performed to establish equilibrium prior to the temperature ramp. TGA was performed on both unrinsed and rinsed coatings. Only one test was performed for each sample.

2.7. Coating Adhesion Cross-Hatch Test

Coating adhesion to the PLA substrate was evaluated using the cross-hatch test according to ASTM D3359 Method B. Two sets of parallel scratches, perpendicular to each other, were cut on coated PLA films with a 1 mm gap 11-teeth multiblade cutter (Paul N. Gardner Company, Columbia, MD, USA). Detached coating flakes were removed with a soft brush. A pressure-sensitive tape was then applied over the grid. After 90 s, the tape was quickly removed at 180°. The tested area was inspected between cross polarizers, and the adhesion level was categorized based on the area of peeled off coatings. Cross-hatch adhesion tests were performed on both unrinsed and rinsed samples. A minimum of three replicates were tested for each sample.

2.8. Optical Properties and Anisotropic Analysis

Optical transparency and CNC order parameters were measured using a UV–vis spectrometer (Cary 6000i UV–Vis–NIR, Agilent Technologies, Inc., Santa Clara, CA, USA). The transparency was measured across the visible light spectrum (380 to 750 nm) for uncoated and coated PLA films before and after rinsing. A minimum of three replicates were examined for each sample.

Hermans' order parameter (*S*) of the CNC coatings was determined in a similar procedure as described in previous literature.^{26,49–51} Due to the intrinsic birefringence of biaxially oriented PLA films, the order parameter was measured from coatings deposited on nonbirefringent glass slides. The dichroic ratio (*D*) was determined by

$$D = \frac{I_{\max}}{I_{\min}} = \frac{I_{45^\circ}}{I_{0^\circ \text{ or } 90^\circ}} \quad (1)$$

Here, *I*_{max} is the transmission light intensity when the sample was positioned 45° between the cross-polarizer films, whereas *I*_{min} is the transmission light intensity when the sample was positioned 0° or 90° between the cross-polarizer films.

The correction factor *g* is assumed to be 1, as the refractive index difference between the anisotropic cellulose film is low.⁴⁹ In this case, the true dichroic ratio *D*^{*} is assumed to be of the same value as *D*. Herman's order parameter is then determined by

$$S = \frac{D^* - 1}{D^* + 2} = \frac{D \times g - 1}{D \times g + 2} = \frac{D - 1}{D + 2} \quad (2)$$

2.9. Water Affinity Analysis

The static water contact angle analysis (WCA) was performed on coated samples before and after rinsing with a goniometer (Advance, Krüss, Hamburg, Germany) using the sessile drop method, following ASTM D5946. Briefly, a 3 μL DI water droplet was dispensed onto the surface using a 22-gauge syringe. The contact angle was monitored for 30 s, and the value at the 10 s mark was used for analysis. A minimum of five measurements were taken for each sample.

The moisture sorption behavior of CNC coatings was investigated by using dynamic vapor sorption (DVS, Intrinsic, Surface Measurement Systems Ltd., London, UK). This analysis provides insight into

the water sorption capability and the interaction between water molecules and the cellulose matrix, which is crucial for understanding gas barrier performance.^{9,19,52,53} Free-standing coatings (around 15 mg) prepared on glass slides, as detailed in Section 2.6, were used. Among the various models used to fit the moisture sorption isotherm, the Guggenheim–Anderson–de Boer (GAB) model, an extension of BET theory, is typically used for its accurate fit with experimental data across broad humidity ranges and also for demonstrating good connections between the model parameters and the underlying physical sorption mechanisms. Consequently, the GAB model is used in this study to analyze the moisture sorption behavior of CNC coatings at varying cross-linking densities.

$$C = C_m \times \frac{C_G \times K \times a_w}{(1 - K \times a_w) \times (1 - K \times a_w + C_G \times K \times a_w)} \quad (3)$$

$$a_w = \frac{p}{p_0} \quad (4)$$

Here, C is the amount of water molecules sorbed, and C_m is the monolayer gas adsorption capacity. C_G is the Guggenheim constant that is related to the heat of adsorption. K is the constant related to multilayer adsorption. a_w is the water activity. p is the equilibrium vapor pressure within materials, and p_0 is the saturated vapor pressure of pure water at the same temperature.

An isotherm (25 °C) method was developed with controlled RH environments based on trial studies to ensure equilibrium moisture sorption at each RH. The RH was increased from 0% to 90% RH in 10% increments, corresponding to a_w from 0.1 to 0.9. The total gas flow rate was set to 200 sccm, and the sample mass was recorded every minute.

2.10. Water Vapor Barrier Properties

The water vapor barrier properties of the coated films were determined by WVTR following ASTM D1653-13 using permeation cups (Gardco Inc., Columbia, MD, USA). Both dry (0% RH inside) and wet (100% RH inside) cup methods were employed, with the CNC coated side facing the chamber environment (50% RH). The dry cup condition was achieved using a desiccant, while the wet cup condition was established with DI water. Both dry and wet WVTR tests were conducted at 23 °C. The schematic of the test setup is provided in the Supporting Information (Figure S2). The WVTR was calculated using the following equation:

$$\text{WVTR} = \frac{\Delta m}{A \times t} \quad (5)$$

Here, Δm (g) is the weight change of the perm cup assembly. A (m²) is the exposed area of the films toward the RH gradient, which is 1×10^{-3} m², specified by the perm cup manufacturer. t (day) is the time gap between each measurement. A minimum of three replicates were tested for each sample.

2.11. Oxygen Barrier Properties

Oxygen permeability (OP) was measured using a custom-built gas permeability setup.^{26,51} The sample film was cut into a circular shape with a diameter of 2.5 cm and placed in a high-pressure film holder (XX4502500, Millipore Sigma, Burlington, MA, USA), with the coated side facing the high-pressure upstream. The upstream portion was connected to an oxygen gas cylinder and a pressure sensor (GS4200-USB0100AM, SUCOESI, St. Louis, MO, USA), while the downstream portion was connected to a constant-volume cylinder and a vacuum pressure sensor (627E, MKS, Andover, MA, USA). All measurements were conducted at room temperature.

The leak rate was determined by evacuating the entire system and measuring the rate of pressure rise. The oxygen permeation rate was measured by supplying the upstream with oxygen at approximately 250 cmHg and measuring the rate of pressure rise. The rate of pressure increase was determined from the linear region of the pressure–time curve. The oxygen permeability was calculated by

$$\text{OP} = \frac{Vl}{\text{PART}} \left[\left(\frac{dP}{dt} \right)_{\text{perm}} - \left(\frac{dP}{dt} \right)_{\text{leak}} \right] \quad (6)$$

Here, V (cm³) is the total downstream volume, which was measured to be 85 cm³. This value was in accordance with the sum of the available volume and cavities provided by the manufacturer of all of the downstream components. l (cm) is the film thickness, which was measured using a micrometer, with the average value taken as the final thickness. P (cmHg) is the absolute pressure in upstream. A (cm²) is the permeation area, which is specified by the manufacturer as 3 cm². R is the gas constant, which is 0.278 cmHg·cm³/[cm³(STP)·K]. T (K) is the absolute temperature, which was recorded and averaged for each test. $(dP/dt)_{\text{perm}}$ and $(dP/dt)_{\text{leak}}$ (cmHg/s) are the pressure increase rate during the permeation and leak stage, respectively. The subtracted value was the permeation rate of the testing film.

The oxygen permeability of the CNC coating was then calculated using

$$\text{OP}_{\text{coating}} = \frac{l_{\text{coating}}}{\frac{l_{\text{total}}}{\text{OP}_{\text{total}}} - \frac{l_{\text{substrate}}}{\text{OP}_{\text{substrate}}}} \quad (7)$$

2.12. Food Storage Test: Guacamole Oxidation

The practical oxygen barrier performance was evaluated by a guacamole storage test. Untreated commercial food packaging films, polypropylene (PP) and polyethylene terephthalate (PET) of similar thicknesses, were used as comparison groups. Films of PP, PET, PLA, and coated PLA films (PLA-CNC-0%BS-br, PLA-CNC-10%BS-br, PLA-CNC-20%BS-br, and PLA-CNC-30%BS-br) were cut into 8" × 4" sheets and sealed into 3" × 3" pouches by an impulse heat sealer (Model: PFS-300, Jinhong Plastics, China). Grade 4–5 was used for PP, PLA, and coated PLA sealing, while grade 6–7 was used for PET sealing. Each sealing was performed for 3 s. For the coated PLA films, the CNC coatings were on the outside of the pouches (i.e., not in direct contact with the guacamole paste). All of the sample films were used without sterilization. Each pouch was filled with approximately 50 g of guacamole paste (brand: Wholly). The guacamole was transferred from the original commercial sealed container to a pastry piping bag and then quickly piped into the sample pouches. The total time of material transfer to final pouch sealing was less than 10 min. Prior to the final sealing, air was expelled from the pouches to minimize initial oxidation. All sealed pouches were stored in an ambient environment (~23 °C, ~30% RH). A sketch of pouch preparation is provided in Figure S3. Only one pouch was prepared for each sample.

The extent of guacamole oxidation was quantified by monitoring its surface color change over time using a colorimeter (model: WR-10QC, FRU Inc., Guangdong, China) in the CIE $L^*a^*b^*$ color space. Color measurements were taken at 5 different spots for each pouch every 12 h. The average values were used for calculation. The color change was evaluated by calculating the total color difference (ΔE) using

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (8)$$

Here, ΔL^* represents the change in lightness. Δa^* represents the change in the red–green axis. Δb^* represents the change in the blue–yellow axis.

In addition, the mass of each pouch was measured every 12 h to monitor the moisture loss.

2.13. Statistical Analysis

All data were statistically analyzed using one- and two-way analysis of variance (ANOVA) at 95% confidence intervals.

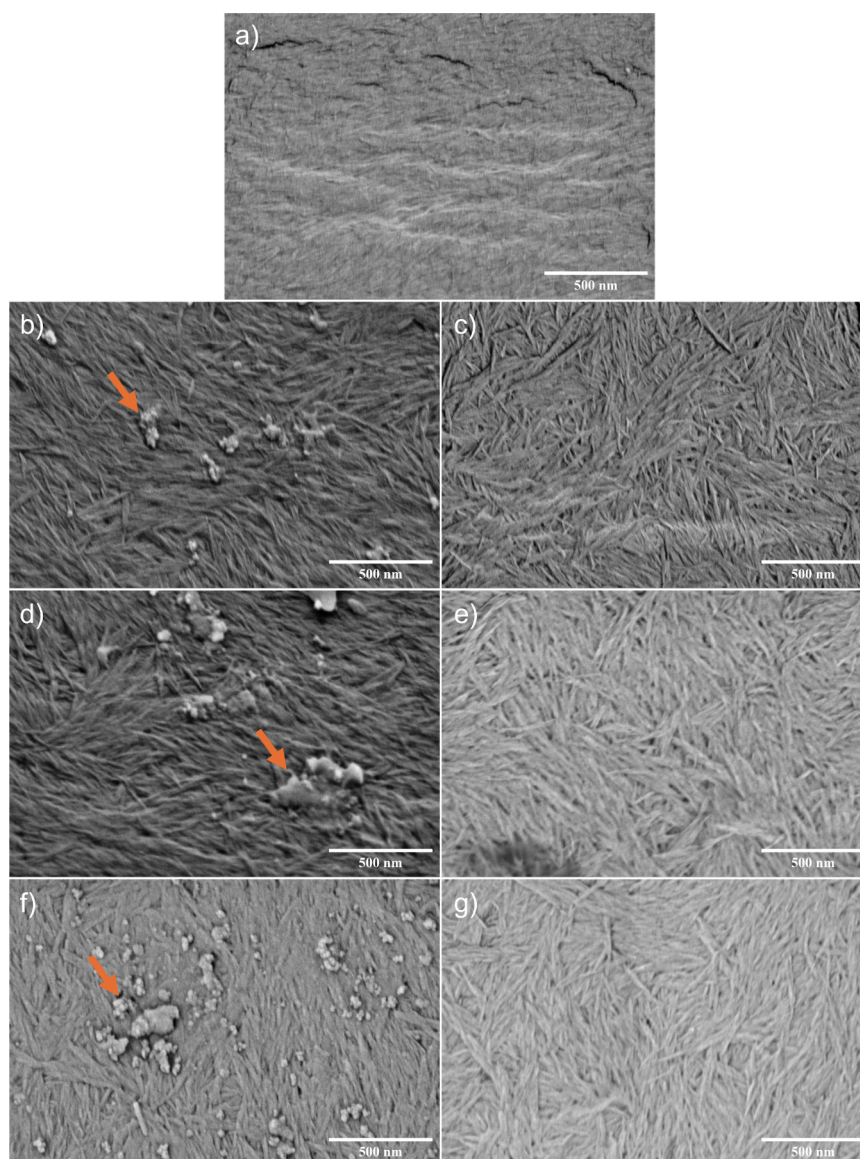


Figure 1. SEM images of PLA-CNC-0%BS-br (a), PLA-CNC-10%BS-br (b), PLA-CNC-10%BS-ar (c), PLA-CNC-20%BS-br (d), PLA-CNC-20%BS-ar (e), PLA-CNC-30%BS-br (f), and PLA-CNC-30%BS-ar (g). The “particulate structures” (arrows) on film surfaces are removed after rinsing.

3. RESULT AND DISCUSSION

3.1. Surface Morphology and Chemical Structure Characterization

Figure 1 presents the surface morphology of CNC coated PLA films before and after rinsing as imaged by SEM. Notably, there were particulate structures distinct from the rod-like CNC particle morphology observed on the surface of all cross-linked samples prior to rinsing (Figure 1b,d,f). Those particulates were believed to be unreacted BTCA/SHP crystals, as the density of these particles increased with higher BTCA/SHP concentration. Overall, the unrinsed coatings presented a dense structure where the CNC network was consolidated by the BTCA/SHP. Expectedly, after the rinsing process, the particulates were removed, showing only the assembly of cross-linked CNC nanoparticles (Figure 1c,e,g).

Additionally, among the SEM images, no distinct long-range alignment of the CNC particles was evident. We believe there are several possible reasons. First, the high magnification and narrow field of view in SEM imaging capture the surface

features of a very small area, which may not be representative of macroscopic order. More importantly, after the shear force is removed, CNC particles have a high tendency to relax from the aligned state. This increase in entropy is more significant for surface CNCs, as they possess greater rotational freedom. This surface relaxation does not contradict the bulk alignment achieved during the coating process, as confirmed by polarized optical microscopy in Section 3.4, where a high degree of in-plane CNC alignment was successfully achieved at the macroscopic scale.

FTIR spectroscopy was employed to verify the successful application of the coating and to characterize the cross-linking reaction between CNC and BTCA. The proposed chemical reactions between CNC and BTCA/SHP are provided in Figure S4. Figure 2 shows the FTIR spectra of PLA films coated with CNC at varied concentrations of BTCA/SHP. The spectrum of the plain CNC coating exhibits characteristic cellulose bands at 3335, 2900, and 1645 cm^{-1} , which can be attributed to the stretching vibration of O–H, the stretching vibration of C–H, and the bending vibration of O–H from

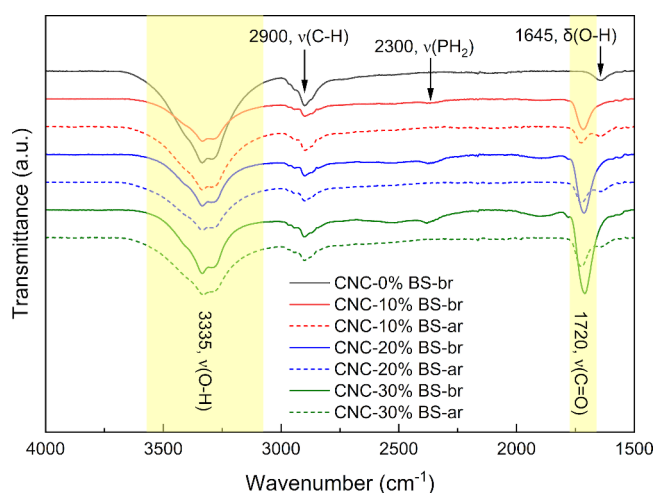


Figure 2. FTIR spectra of the CNC coating layers before and after rinsing.

chemically sorbed water, respectively.^{54,55} A new band at 1720 cm^{-1} emerged with the addition of BTCA, corresponding to the stretching vibration of $\text{C}=\text{O}$.

In the unrinsed samples, the intensity of the $\nu(\text{C}=\text{O})$ increased concomitantly with the BTCA concentration. In addition, the $\nu(\text{O}-\text{H})$ displayed a decrease compared to the un-cross-linked CNC coating. There was no linear trend observed for the decrease in $\nu(\text{O}-\text{H})$ with the increase of cross-linker concentration. This could be explained by the catalyst SHP itself contributing to the absorption band at around 3335 cm^{-1} , which was confirmed in a reference spectrum (Figure S5).

FTIR spectroscopy was also conducted on the rinsed coatings. The removal of unreacted BTCA and SHP was confirmed by the complete disappearance of the symmetric and asymmetric stretch vibration of the PH_2 group at around 2300 cm^{-1} .⁵⁶ The band intensity at 1720 cm^{-1} for $\nu(\text{C}=\text{O})$ displayed an obvious reduction after rinsing, indicating the relatively low cross-linking efficiency for the CNC-BTCA/SHP system under the current cross-linking conditions (100 °C for 30 min). The efficiency was expected to improve with a higher cross-linking temperature, but due to the limitations of the PLA substrate, the highest temperature in this study was limited to 100 °C. Nevertheless, the band at 1720 cm^{-1} displayed an increasing trend with the initial BTCA/SHP concentration, indicating the successful cross-linking of CNC by BTCA/SHP.

3.2. Thermal Stability

The thermal stability of unrinsed CNC coatings was evaluated by TGA, with the resulting curves and their derivatives (DTG) presented in Figure S6. The plain CNC coating exhibited an onset degradation temperature of 254.9 °C and a DTG maximum at 262.1 °C. These values are consistent with those reported for CNC-Na, where pyrolysis in an inert environment is attributed to the formation of free radicals that ultimately lead to charring.⁵⁷

A notable improvement in thermal stability was observed upon cross-linking with BTCA/SHP. The cross-linked coatings demonstrated an increase of approximately 30 °C in both the onset degradation temperature and the DTG maximum compared to the plain CNC. Specifically, the onset degradation temperatures for the 10%, 20%, and 30% BTCA/SHP samples

were 286.1, 276.9, and 281.1 °C with corresponding DTG maxima at 300.0, 292.6, and 297.6 °C, respectively. This improvement can be attributed to the formation of ester linkages, which consume the readily available hydroxyl groups on the CNC surface and thereby suppress the pathway for free radical generation during the initial stage of thermal decomposition. No clear trend was observed between the cross-linker concentration and the measured thermal stability parameters.

The thermal stability of the cross-linked coatings decreased after rinsing, with onset degradation temperatures observed at approximately 200 °C for all formulations. Additionally, two major DTG maxima were observed, the first one at around 195 °C and the second one at around 235 °C. This decrease in thermal stability is likely attributed to the residual water absorbed into the cross-linked network during immersion. Water molecules can form hydrogen bonding with the CNC matrix and thus are not readily removable during ambient drying. The residual water molecules would act as plasticizers, lowering the thermal decomposition temperature. The exact underlying mechanism is worth further investigation.

3.3. Cross-Hatch Adhesion Test

The adhesion of the CNC coatings to the PLA substrate was evaluated using the cross-hatch test. According to the test standard ASTM D3359, the adhesion test results are classified into six categories, ranging from 5B (0% removal) to 0B (>65% removal). The results for both unrinsed and rinsed samples are summarized in Table S1.

Before rinsing, all of the coatings exhibited relatively good adhesion. CNC coatings without cross-linker and with 10% cross-linker were classified as 3B, corresponding to 5%–15% coating removal. In comparison, CNC coatings with 20% or 30% cross-linker showed improved adhesion, classified as 4B, achieving less than 5% coating removal. After water immersion, a decrease in adhesion was observed for all cross-linked samples. The 10% BTCA/SHP coating dropped to 1B, corresponding to 35%–65% removal, while the 20% and 30% BTCA/SHP cross-linked coatings dropped to 2B, corresponding to 15%–35% removal. The un-cross-linked coating redispersed in water and was completely detached during rinsing.

The reduction in adhesion can be attributed to the variance in the water swelling between the two layers. During water immersion, the CNC coating layer absorbs more water and expands to a greater extent than the PLA substrate. Upon drying, the absorbed water evaporates with the coating contraction. This volume change could induce mechanical stress at the interface, thus adversely affecting the adhesion. The better retention of adhesion in the coatings with 20% and 30% cross-linker compared to the un-cross-linked and 10% BTCA/SHP cross-linked coatings suggests that higher cross-linking density helps mitigate this effect by restricting the extent of swelling. Nevertheless, this observation highlights an area for future optimization.

3.4. Optical Transparency and Anisotropic Analysis

The optical transparency of packaging films is a critical property, particularly for food packaging, where product visibility is desired. UV–vis spectroscopy serves as a common approach for evaluating the transparency of films in terms of the percentage of light transmittance across a wavelength range. The light transmittance in the visible light spectrum is provided in Figure S7. The light transmittance values of

Table 2. Visible Light Transmittance of Coated Films at 600 nm and Order Parameters of CNC Coatings before and after Rinsing (Average Based on Three Samples)

$T_{600\text{ nm}}$ (%)	PLA	PLA-CNC-0%BS	PLA-CNC-10%BS	PLA-CNC-20%BS	PLA-CNC-30%BS
Before rinsing	91.7 ± 0.5	90.9 ± 1.0	89.2 ± 0.8	88.2 ± 0.4	87.7 ± 0.2
After rinsing	-	-	88.7 ± 0.5	86.8 ± 0.1	86.3 ± 0.4
Order parameter (S)		CNC-0%BS	CNC-10%BS	CNC-20%BS	CNC-30%BS
Before rinsing		0.90 ± 0.01	0.89 ± 0.04	0.85 ± 0.02	0.77 ± 0.06
After rinsing		-	0.92 ± 0.01	0.82 ± 0.03	0.78 ± 0.04

uncoated and coated PLA films before rinsing at 600 nm are summarized in Table 2. The uncoated PLA film exhibited a high transmittance of 91.71% at 600 nm. The application of a plain CNC coating resulted in a less than 1% reduction in transmittance. In addition, a slight decrease in transmittance was observed for CNC coatings with an increasing amount of cross-linker, which could be attributed to the scattering of unreacted salts, as shown in SEM images. Despite this trend, all coated films displayed high optical clarity, with transmittance exceeding 87% at 600 nm. Pictures of the CNC coated PLA films are available in Figure S8.

After rinsing, the optical transparency of the cross-linked coatings was largely retained. The transmittance at 600 nm for rinsed samples was 88.7%, 86.8%, and 86.3%, respectively, showing a less than 2% reduction compared to their unrinsed counterparts. This suggests that the cross-linked coatings maintained high optical transmittance after water exposure.

The shear-induced alignment of the birefringent CNC nanoparticles was quantitatively analyzed by measuring Herman's order parameter (S) between cross-polarized conditions.^{49–51} The images of CNC coated glass substrates between crossed polarizers are displayed in Figure S9. The un-cross-linked CNC coating (CNC-0%BS) lost its birefringence and appeared dark after rinsing, confirming its redispersion in water. In contrast, all cross-linked coatings retained strong birefringence post rinsing, providing visual evidence of their water-resistant cross-linked network.

The order parameters of CNC coatings on glass substrates are listed in Table 2. Overall, the high S values (≥ 0.77) confirm that the shear-coating process was effective in aligning the CNC nanoparticles. A slight decrease in order parameter was observed with increasing cross-linker and catalyst concentration. This is likely due to the increased suspension viscosity imparted by the multivalent BTCA and SHP molecules. No significant difference in order parameters was observed for CNC coatings post rinsing, supporting our previous statement that the cross-linked structure maintains its integrity and alignment upon water exposure.

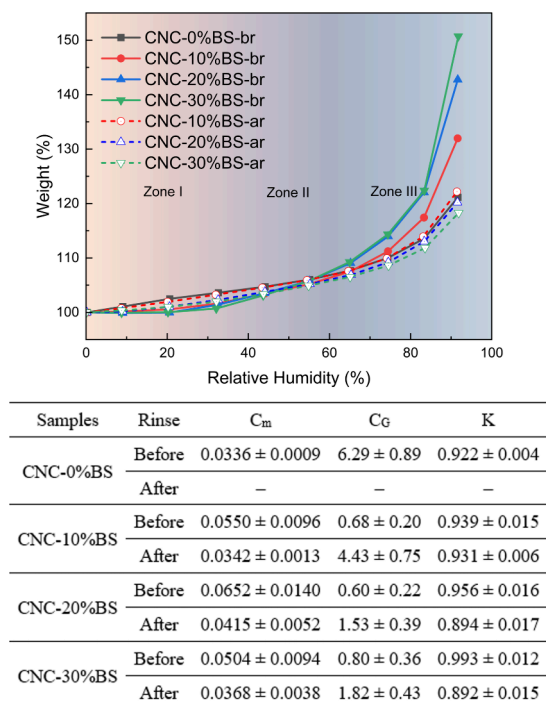
3.5. Water Affinity Analysis

Static water contact angle (WCA) measurements were conducted to evaluate the hydrophilicity of the coatings. The results are summarized in Figure S10. All coated samples exhibited relatively low WCAs, consistent with the hydrophilic nature of CNC. Before rinsing, the WCA decreased with increasing cross-linker concentration, which is attributed to the introduction of highly hydrophilic BTCA and SHP molecules. A notable increase in WCA was observed for all cross-linked coatings after the rinsing step, confirming the effective removal of these water-soluble components. The WCA of the rinsed un-cross-linked coating approaches that of the bare PLA substrate, which aligns with the complete removal of the un-

cross-linked coating as previously indicated by its loss in birefringence.

Cellulose materials typically display a sigmoid-shaped moisture sorption isotherm and can be categorized into three zones of water activity, each dominated by different sorption mechanisms.^{9,19,58} At low water activity (Zone I), water vapor sorption occurs primarily via the Langmuir mode onto readily accessible hydrophilic sites, such as surface hydroxyl groups and microvoids within the cellulose structure. In the intermediate range (Zone II), water molecules penetrate the amorphous regions of the cellulose, leading to a linear increase in sorption governed by Henry's law. At high RH (Zone III), the mechanism is characterized by water clustering where multilayer sorbed water molecules increase the interchain distance, allowing further water molecule sorption. The moisture sorption isotherm curves for CNC coatings are shown in Figure 3. The corresponding mass change over time profiles are provided in Figure S11.

The un-cross-linked CNC coating exhibited the characteristic sigmoid-shaped sorption isotherm curve typical of cellulose. In contrast, the cross-linked CNC coatings before rinsing showed reduced moisture sorption below 50% RH but increased sorption above 60% RH. The lower sorption at lower RH can be attributed to the esterification of readily accessible

**Figure 3.** Equilibrated moisture content of CNC coating layers with fitted sorption parameters C_m , C_G , and K of the GAB model with varied cross-linker concentration before and after water rinsing.

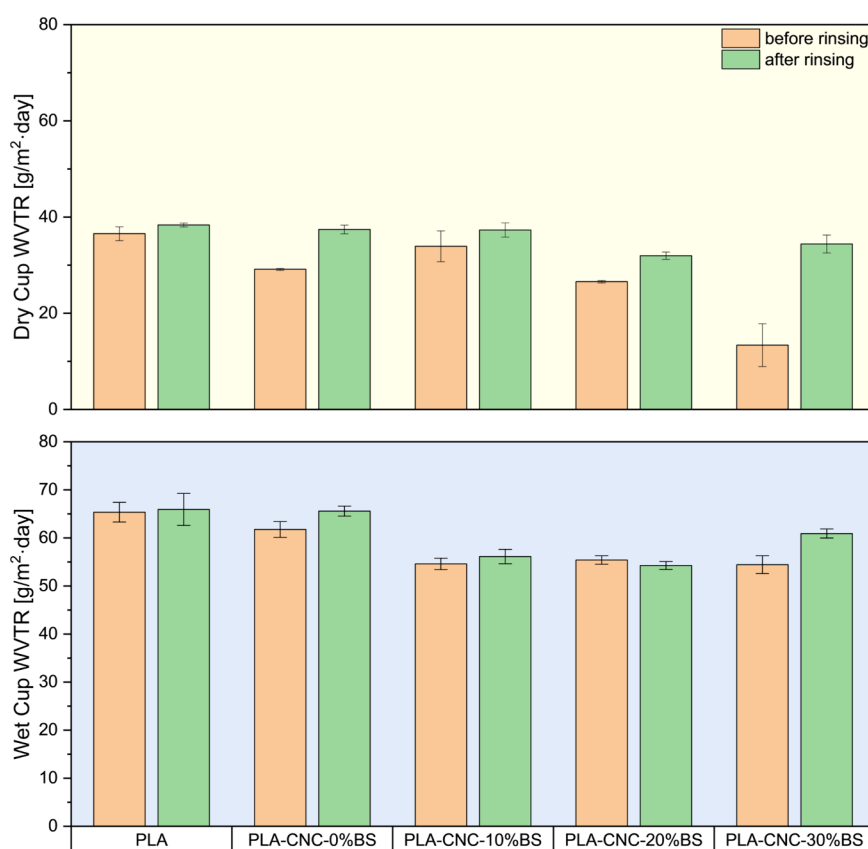


Figure 4. Dry cup (top) and wet cup (bottom) WVTR of CNC coated PLA films before and after rinsing.

surface hydroxyl groups on CNC surfaces during cross-linking reaction. The subsequent increase at high RH, however, is likely driven by the inherent hydrophilicity of the unreacted BTCA and SHP, which introduce new and highly hydrophilic functional groups into the matrix as the uptake scales with cross-linker content.

Post rinsing, the removal of unbound BTCA and SHP resulted in a large decrease in equilibrium moisture content (EMC) at RH above 60% compared to unrinsed samples. All cross-linked CNC coatings after rinsing showed similar curves and water uptakes at 90% RH regardless of cross-linker amount that were also similar to those of the un-cross-linked control. It was expected that the cross-linking process reduces the moisture sorption capacity by consuming readily accessible hydrophilic hydroxyl groups and by introducing a three-dimensional network that restricts the water uptake and swelling of the cellulose matrix. However, the differences between rinsed and un-cross-linked films are generally small, which could be a consequence of a relatively low cross-linking density or the fact that the newly introduced residual hydrophilic carboxyl acid groups from partially reacted BTCA outweigh the reduction in hydroxyl groups.

The GAB model provided a good fit for the experimental moisture sorption curve, and the fitted data are summarized in Figure 3. The fitted moisture sorption curves for un-cross-linked and cross-linked CNC coatings before and after rinsing are provided in Figure S12. The collected data corroborate the interpretations above and are consistent with previously reported data for cellulose materials.^{9,19} C_m , related to the monolayer gas adsorption capacity, initially increased with the addition of BTCA/SHP, reflecting the introduction of new

sorption sites from the cross-linker system, and then decreased after rinsing as these components were removed, leaving a less hygroscopic network. Conversely, the Guggenheim constant C_G , related to the heat of sorption, initially decreased with the introduction of cross-linkers, suggesting a lower energy barrier for water molecules binding to the CNC matrix. The decrease was restored post rinsing. The multilayer sorption constant K showed minimal variation, indicating that the fundamental mechanism of multilayer water formation remains largely unaffected by cross-linking.

3.6. Water Vapor Barrier Properties

The water vapor transmission rate (WVTR) is a critical parameter for food packaging, as it directly influences product shelf life. Suitable packaging materials should help prevent the dehydration of fresh foods and moisture uptake for dry goods. Therefore, this study evaluated both dry and wet conditions for the CNC coated PLA films.

The dry cup and wet cup WVTR values of the CNC coatings, with and without cross-linking, before and after water rinsing, are shown in Figure 4. Under dry cup conditions, all CNC coated films displayed improved moisture barrier performance compared with the plain PLA film (36.5 g/m²·day). The most significant improvement was observed for the CNC-30%BS coating, which achieved 13.4 g/m²·day. For cross-linked coatings, the dry cup WVTR decreased with increasing cross-linker concentration, except for the CNC-10% BS coating, which achieved a higher WVTR than the un-cross-linked CNC coating. This nonmonotonic behavior can be explained by the competing effects of introducing BTCA/SHP. While the introduction of BTCA/SHP increases tortuosity and restricts polymer chain mobility, thereby hindering water vapor

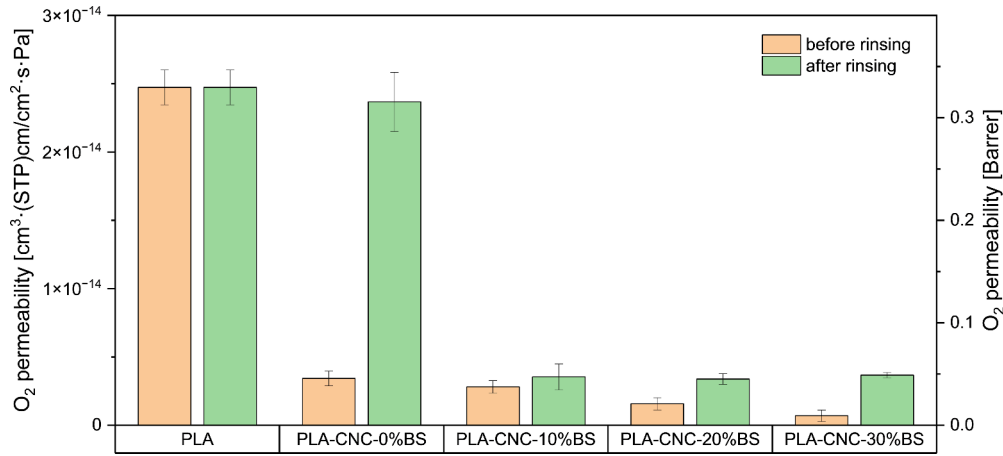


Figure 5. Oxygen permeability of CNC coated PLA films before and after rinsing.

Table 3. Oxygen Permeability of CNC Coating Layer (Decoupled from PLA Substrate per Eq 7) before and after Rinsing

Samples	Rinse	Oxygen permeability		Reference
		($\times 10^{-16}$) $\text{cm}^3(\text{STP})\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{Pa}$	($\times 10^{-3}$) barrier	
CNC-0%BS	Before	4.89 $\pm$ 0.88	6.52 $\pm$ 1.18	This work
	After	-	-	
CNC-10%BS	Before	3.91 $\pm$ 0.70	5.21 $\pm$ 0.93	
	After	5.11 $\pm$ 1.56	6.81 $\pm$ 2.08	
CNC-20%BS	Before	2.09 $\pm$ 0.64	2.79 $\pm$ 0.85	
	After	4.81 $\pm$ 0.64	6.42 $\pm$ 0.85	
CNC-30%BS	Before	0.90 $\pm$ 0.55	1.21 $\pm$ 0.73	
	After	5.27 $\pm$ 0.32	7.03 $\pm$ 0.43	
PLA	-	247 $\pm$ 12.7	330 $\pm$ 17	5,61,62
PP	-	~675	~898	
PET	-	~12.8	~17	

diffusion, the highly hydrophilic of BTCA and SHP molecules can promote water sorption and permeation. After rinsing, the barrier property provided by un-cross-linked CNC coating was eliminated, with WVTR approaching that of plain PLA. The WVTR of the cross-linked CNC samples also saw increases post rinsing.

In the wet cup WVTR test, the water vapor barrier performance showed a less pronounced but still significant improvement. The cross-linked groups consistently outperformed both the plain PLA film (65.3 g/m²·day) and the un-cross-linked CNC coating (61.8 g/m²·day), with CNC-10% BS, CNC-20%BS, and CNC-30%BS coated samples showing 54.6, 55.4, and 60.0 g/m²·day, respectively. A similar coating removal was shown for the un-cross-linked CNC coatings in wet cup WVTR.

3.7. Oxygen Barrier Properties

Lipid oxidation, another major cause of food deterioration, underscores the importance of high oxygen barrier performance in packaging materials.^{5,59,60} CNC films have been reported to exhibit great oxygen barrier properties under dry conditions.^{6,26,50,51} In this study, we evaluated the oxygen permeability (OP) of CNC coated PLA films to assess their efficiency.

As shown in Figure 5, the unmodified CNC coating reduced the OP of the PLA substrate by over 86%, decreasing it from 2.47×10^{-14} to 3.43×10^{-15} cm³(STP)·cm/cm²·s·Pa (corresponding to 3.30×10^{-1} and 4.57×10^{-2} barrer, respectively). Cross-linking further enhanced this barrier

property in a concentration-dependent manner. The OP values for PLA films coated with CNC-10%BS, CNC-20%BS, and CNC-30%BS were 2.81×10^{-15} , 1.57×10^{-15} , and 6.99×10^{-16} cm³(STP)·cm/cm²·s·Pa, respectively (corresponding to 3.75×10^{-2} , 2.09×10^{-2} , and 9.32×10^{-3} barrer, respectively). The most cross-linked formulation (CNC-30% BS) achieved an OP that was nearly 2 orders of magnitude lower than that of the uncoated PLA film. This enhancement aligns with the WVTR results and is attributed to the increasing cross-linker density, which creates a more tortuous diffusion pathway and restricts polymer chain mobility.

The rinsing process validated the structural integrity of the cross-linked network. The un-cross-linked CNC coating was completely removed, as evidenced by its OP reverting to that of plain PLA. In contrast, all cross-linked coatings retained significant barrier function after rinsing, with OP values remaining approximately 1 order of magnitude lower than that of the PLA substrate.

The intrinsic OP of the decoupled CNC coating layers is summarized in Table 3. Prior to rinsing, the coating exhibited outstanding barrier properties, with OP values ranging from 4.89×10^{-16} to 0.90×10^{-16} cm³(STP)·cm/cm²·s·Pa (corresponding to 6.52×10^{-3} and 1.21×10^{-3} barrer, respectively). These values surpass the OP of conventional packaging plastics such as polypropylene (PP) ($\sim 6.75 \times 10^{-14}$ cm³(STP)·cm/cm²·s·Pa, ~ 0.9 barrer) and are competitive with that of polyethylene terephthalate (PET) ($\sim 1.28 \times 10^{-15}$ cm³(STP)·cm/cm²·s·Pa, ~ 0.017 barrer), highlighting the

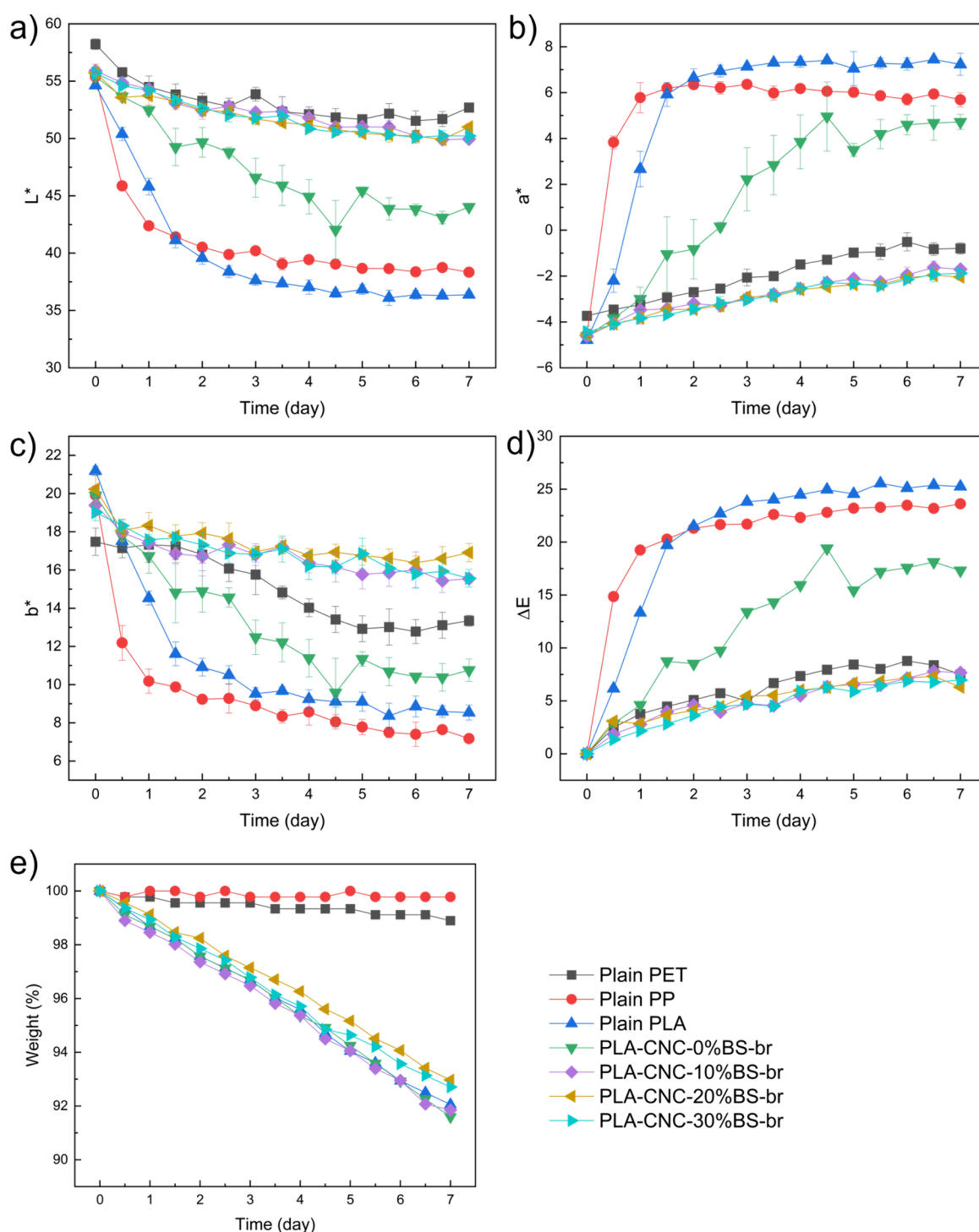


Figure 6. Color parameters and weight change of guacamole paste during storage: (a) L^* (lightness), (b) a^* (red–green), (c) b^* (yellow–blue), (d) ΔE (total color difference), and (e) weight change.

potential of cross-linked CNC as a high-performance barrier material.^{5,61,62}

After rinsing, a noticeable increase in intrinsic OP was observed for all cross-linked coatings, especially for CNC-30% BS. This increase could be attributed to the subtle microstructure changes within the coating during the immersion and drying process, such as the formation of nanovoids or microcracks. A more detailed investigation into the exact nature of the molecule requires future characterization. Importantly, the rinsed CNC-30%BS coating still maintained

an oxygen permeability significantly lower than that of the neat PLA film.

Construction of multilayer structures is a commonly adopted approach for high barrier packaging films, where a CNC layer typically serves as the core barrier layer shielded by the outer protection layers.⁶³ Zhang et al. reported that introducing a CNC/polyvinyl alcohol (PVA) layer reduced the OP of PLA films from 2.40×10^{-14} to 3.0×10^{-16} cm³(STP)·cm/cm²·s·Pa.²⁶ However, as the protective layers typically possess high oxygen permeability, the overall OP is lowered,

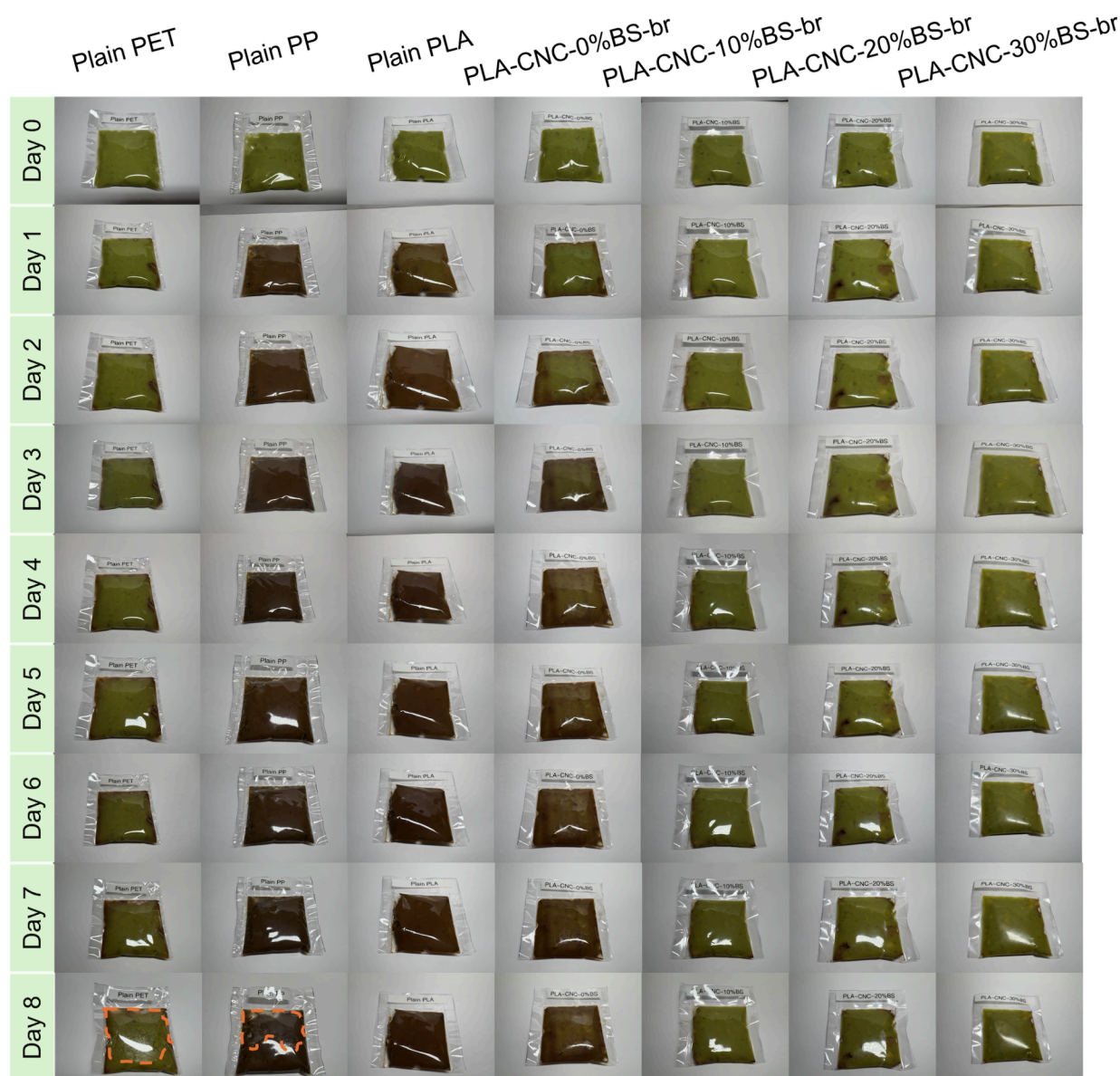


Figure 7. Pictures of guacamole paste sealed in various packaging material pouches from day 0 to day 8. Pouches were stored in an ambient environment. Inflation for PET and PP pouches is circled with orange dashed lines.

with the PLA-CNC/PVA-PLA trilayer achieving 3.3×10^{-16} $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$. Similarly, Le Gars et al. observed an OP reduction from 1.80×10^{-14} to 1×10^{-15} $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$ when comparing plain PLA to a PLA-CNC-PLA trilayer structure (unit conversion applied).⁶⁴

In addition to multilayer structures, Le Gars et al. also investigated the effect of hydrophobization by blending rosin, a hydrophobic nature compound, into the CNC coating layer. With the addition of rosin, the OP was increased to 9×10^{-15} $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$.⁶⁴ This increase is attributed to the adsorption of rosin interfering with hydrogen bonding within the cellulose matrix, increasing interparticle spacing and creating a more porous structure. Bras et al. adopted another hydrophobization practice using fully substituted cellulose esters with hydrophobic acyl groups.⁶⁵ They were able to observe a higher water contact angle and lower water vapor permeability with increasing acyl chain length. However, the OP increased from 2.77×10^{-13} to 1.51×10^{-12} $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$ (unit conversion applied) with an acyl chain

increase from C8 to C18. This increase was attributed to the hydrophobic substituent groups acting as internal plasticizers, increasing the free volume between cellulose chains.

In contrast to hydrophobization, chemical cross-linking can reduce moisture sensitivity without sacrificing the dense network required for gas barrier performance. Nuruddin et al. reported cross-linked CNC with citric acid on a PP substrate, observing an improvement in OP of about 1.2 orders of magnitude (from 3.18×10^{-14} to 1.84×10^{-15} $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$), while the CNC coating without CA showed a 1.1 orders of magnitude improvement (2.62×10^{-15} $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$) compared to the PP substrate.⁶ This level of improvement is comparable to that observed in our work.

3.8. Food Storage Test: Guacamole Oxidation

The practical efficacy of CNC coatings was evaluated through a guacamole storage test. Guacamole, an avocado-based dish, is highly susceptible to enzymatic browning through polyphenol

oxidase and melanin formation when exposed to oxygen, which greatly affects its taste, texture, and nutrition.⁶⁶ Typical industrial practices involve incorporating acids into the ingredients to lower the pH and slow the browning process. In addition, the industry uses high oxygen barrier packaging materials to hinder oxygen exposure. In this study, the extent of oxidation was used to evaluate the oxygen barrier performance of each packaging material. Furthermore, weight loss served as an indicator of the water vapor barrier performance of the packaging materials. A previous work showed that due to the relatively high WVTR of CNC coated PLA, high water fruits such as apples were not the best application space; hence, a low water fruit such as an avocado-based material was selected for this evaluation.²⁶

The color evaluation (L^* , a^* , b^* , and ΔE) and weight loss of the guacamole over time are summarized in Figure 6. The L^* value denotes the lightness on a scale from 0 (black) to 100 (white). The a^* and b^* values are on a scale from -128 to 127 , where positive a^* values signify red and negative values signify green. Similarly, positive b^* values signify yellow, and negative b^* values signify blue. The Lab scale was chosen (as opposed to RGB) because it better represents how people perceive color and, therefore, would match visual observation better. Photographs of each pouch were taken throughout test and are provided in Figure 7.

As anticipated, both PP and uncoated PLA films exhibited the most significant color change. This is attributed to their low oxygen barrier properties. Initially, the PP package showed the most rapid color change, consistent with its highest oxygen permeability among the test films. However, after approximately 1.5 days, the sample in the plain PLA package surpassed PP in the degree of browning. This shift is attributed to the water vapor barrier performance difference between the two materials. The higher water vapor barrier performance of PP slowed the browning of guacamole, and thus, PP displayed a slower color change compared to the plain PLA beyond the initial stage. Application of the un-cross-linked CNC coating to PLA substantially delayed oxidation. Most notably, the cross-linked CNC coatings demonstrated superior performance, effectively inhibiting browning, showing a better performance than the commercial PET package.

In addition, in the airtight packages, the guacamole primarily underwent an anaerobic biodegradation. This process typically consists of a hydrolysis stage and acidogenesis stage. During hydrolysis, fats are broken down into fatty acids and glycerol, proteins are broken down into peptides and amino acids, and carbohydrates are broken down into shorter-chain sugars. This stage is observable as a change in texture where the guacamole paste becomes loose and watery. During acidogenesis, the products from the previous stage are consumed by fermentative bacteria and converted into smaller organic chemicals such as organic acids, ketones, alcohols, carbon dioxide, and hydrogen.⁶⁷ This gas generation is the direct cause of pouch inflation. This stage is characterized by gas generation and further liquefaction. Both stages are highly dependent on water content, as the enzyme activity requires high water activity. In packages with low water vapor permeability, such as PP and PET, the moisture was entrapped, maintaining a high water content that facilitated these degradation processes, resulting in visible pouch inflation. In contrast, for the cross-linked CNC coated packages studied here, moisture was able to evaporate, albeit slowly. This led to a reduction in the water content, which slowed the spoilage of guacamole. This suggests

that for certain applications, a degree of moisture permeability could be beneficial in delaying spoilage and reducing food waste. The resulting inflation of the PP and PET pouches, in contrast to the noninflated test groups, is visible in Figure 7.

4. CONCLUSION

In this study, we successfully developed water-resistant cellulose nanocrystal (CNC) coatings with tunable gas barrier properties by cross-linking with 1,2,3,4-butanetetracarboxylic acid (BTCA) and sodium hypophosphite (SHP). The shear-coating process produced highly transparent coatings ($\geq 87\%$ transmittance at 600 nm) with strong in-plane alignment.

Multiple lines of evidence, including the complete loss of birefringence, water contact angle, and barrier performance after water exposure, confirmed that un-cross-linked coatings readily redispersed in water, whereas cross-linked coatings maintained their structural integrity. The cross-linked network not only improved resistance to redispersion but concurrently enhanced both water vapor and oxygen barrier properties. Our approach overcomes the classic trade-off in packaging materials, where improving the barrier property of polar molecules like water vapor often compromises the barrier performance of nonpolar molecules like oxygen, by establishing a densely cross-linked network that both increases the tortuosity of the diffusion pathway for gas and limits the polymer chain mobility.

The cross-linked formulations reduced the oxygen permeability by orders of magnitude and substantially lowered the water vapor transmission rate. Critically, these enhanced barrier properties were largely retained after water rinsing, demonstrating the structural integrity essential for practical applications. The oxygen permeability of the CNC coating layer is highly competitive when compared to conventional petroleum-based plastics. In addition, this high barrier performance was vividly demonstrated through a guacamole storage test, where the cross-linked CNC coating significantly inhibited food oxidation, showing a better browning inhibition performance than PET.

Overall, this work demonstrates a promising strategy for creating sustainable, high barrier packaging coatings. Future efforts will focus on improving the mechanical flexibility of free-standing cross-linked CNC films while maintaining the high gas barrier performance to further advance the development of practical biobased packaging materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.6c00129>.

Cross-sectional SEM images; scheme of WVTR test; sketch of pouch preparation procedure; scheme of CNC-BTCA/SHP chemical reactions; FTIR spectra of BTCA and SHP; TGA data of CNC coatings; cross-hatch adhesion results of coated films; transmittance of coated films; photographs of coated films; photographs of coated glass slides under crossed polarizers; water contact angles of coated films; moisture sorption profiles of CNC coatings; and GAB fitting curves of CNC coatings (PDF)

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Author Contributions

Y.W. and J.P.Y. both designed the experiments. Y.W. conducted the experiment, collected and analyzed the data, and drafted the manuscript. All authors commented on the manuscript, read, and approved the final manuscript.

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Notes

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