

Starch-cellulose nanofibril multilayer coated paper with enhanced oxygen and water vapor barrier for food packaging applications

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ABSTRACT

Developing green, sustainable, and high-performance cellulose-based paper materials to replace single-use plastic packaging is both promising and essential to meet consumer demands and industry targets for renewable packaging. Herein, a novel starch-cellulose nanofibril multilayer coated paper with excellent oxygen and improved water vapor barrier properties was developed. Starch was used as a base layer to fill the porous structure of the paper, thereby reducing the amount of functional TEMPO-mediated oxidized cellulose nanofibrils (TCNFs) required to achieve oxygen barrier properties. Moreover, reduced viscosity of TCNF-based coating dispersions contributed to lower surface roughness and improved coating uniformity, while surface tension showed no significant effect. As a result, the required TCNF coating weight was reduced from $9.4 \pm 0.9 \text{ g/m}^2$ to $3.1 \pm 0.4 \text{ g/m}^2$ while maintaining functionality when the starch layer coating weight ranged from 10.9 ± 1.2 – $26.8 \pm 1.9 \text{ g/m}^2$. Notably, incorporation of the starch layer enabled the composite system to maintain strong oxygen barrier performance under high humidity conditions. At 80% relative humidity (RH) and 23°C , oxygen transmission rates were reduced from 130.6 to 22.7–34.7 $\text{cm}^3 \text{ m}^{-2} \text{ day}^{-1}$, corresponding to a 73.4–82.6% reduction compared with TCNF-only coatings. Meanwhile, water vapor transmission rates were also reduced by 50.0–59.9%. This study provides a new, sustainable, and versatile approach for the large-scale production of fully bio-based, recyclable, and biodegradable paper materials that provide oxygen barrier properties meeting industry specific targets with low coating weights.

1. Introduction

Paper-based packaging derived from renewable cellulose is a promising alternative to plastic due to its environmental friendliness, renewability, scalability, and cost effectiveness (Chen et al., 2024a; Wang et al., 2025). However, its intrinsic porous structure results in poor barrier properties against oxygen and water vapor, limiting its applications in food preservation (Wang et al., 2025). To overcome this limitation, surface coating is widely used to provide functional barrier layers. Commercially available paper-based barrier coatings often rely on aluminum, or synthetic polymers such as ethylene vinyl alcohol (EVOH) and polyvinyl alcohol (PVOH) (Mujtaba et al., 2022). Although effective, these coatings are difficult to separate from the paper surface, complicating recycling and raising concerns regarding sustainability and environmental impact (Wang et al., 2025). As a result, increasing attention has been directed toward developing fully bio-based or

recyclable barrier coatings that allow paper repulping while maintaining adequate protection (Mujtaba et al., 2022; Guyer et al., 2025; Priyadarshi et al., 2025; Babaeipour et al., 2026; Cai et al., 2026).

Cellulose nanomaterials (CNMs), including cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs), have emerged as promising sustainable barrier materials due to their high crystallinity, outstanding mechanical strength, biodegradability, and excellent oxygen barrier performance under low humidity conditions (Cainglet et al., 2025; Las-Casas & Arantes, 2024; Sabo et al., 2024; Wang et al., 2018; Paudel et al., 2026). When applied as coatings on paper, CNM can achieve oxygen barrier properties comparable to aluminum foil, EVOH, and PVOH at low humidity while maintaining compostability and recyclability (Wang et al., 2018). However, their inherently hydrophilic nature leads to significant water uptake at high relative humidity (RH), disrupting the hydrogen-bonded network and causing a sharp deterioration in oxygen barrier performance. For example, Franke et al. (2024)

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reported that the oxygen permeability (OP) of TCNF coated paper increased from $6.2 \pm 2.5 \text{ cm}^3 \cdot \mu\text{m}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at 30% RH to $405 \pm 93 \text{ cm}^3 \cdot \mu\text{m}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$ at 70% RH. Moreover, simply increasing the thickness of pure CNF coatings or films is insufficient to provide adequate water vapor barrier performance, highlighting the need for material modification or multilayer designs (Cainglet et al., 2025). Addressing the humidity sensitivity of CNF-based materials is critical for their commercial application in food packaging.

Several strategies have been explored to mitigate the high humidity sensitivity of CNM films and coatings, including metal ion crosslinking (Chen et al., 2022; Ren et al., 2024), polymer blending (Venkatesan et al., 2024; Zheng et al., 2026), and lamination with non-polar polymer films (Yu et al., 2022; Chen et al., 2024a; Nan et al., 2026). Although these approaches can substantially improve oxygen and water vapor barrier properties, they have notable limitations. Metal ion crosslinking may complicate coating processes by altering suspension rheology, hindering uniform film formation, and often provides limited water vapor barrier performance under high humidity. Polymer blending can enhance mechanical strength and barrier properties; however, it may lead to phase separation, reduced interfacial compatibility, and compromised transparency, and the barrier improvement is often highly dependent on blend composition and environmental humidity (Zhang & Youngblood, 2025). Lamination with synthetic polymers offers improved barrier performance at high humidity but reintroduces non-renewable and non-biodegradable components, compromising the sustainability of bio-based systems (Fotie et al., 2020; Wang et al., 2020; Yu et al., 2022). Therefore, there is a clear need for fully bio-based, recyclable multilayer coating systems that maintain robust barrier performance under humid conditions.

An additional challenge in coating CNMs onto paper at industrial scale is the large amount of water present in CNF suspensions, which leads to high drying energy demand and reduced production efficiency. One effective strategy to mitigate this issue is to reduce CNF coating weight. However, due to the porous nature of paper, a minimum coating amount is required to form a continuous barrier layer. Incorporating a low-cost base layer that can fill the paper surface pores offers a promising solution by reducing the amount of CNF needed and, consequently, the water that must be removed during drying. Starch is an attractive candidate for this purpose due to its low cost, renewability, slightly better moisture resistance than CNMs, and favorable oxygen barrier properties. In addition, starch can be applied at much higher solid concentrations than CNF suspensions, substantially reducing drying requirements. Previous studies have shown that aldehyde groups in TCNF can form hemiacetal bonds with hydroxyl groups in starch, improving water stability and mechanical strength in composite membranes (Hamid et al., 2024; Soni et al., 2020). However, the oxygen barrier performance of starch–TCNF systems under high humidity conditions remains insufficiently explored.

This study aimed to develop a fully bio-based multilayer coating system using starch as a base layer and TCNF as a thin functional barrier layer. The hypothesis is that starch can fill paper porosity, improve coating uniformity, reduce TCNF usage, and enhance humidity resistance, thereby improving oxygen and water vapor barrier performance under humid conditions. The work investigated the influence of formulation parameters on coating quality and barrier properties, with the goal of producing recyclable, biodegradable paper materials suitable for thin-film food packaging. The proposed approach is compatible with existing industrial processes and supports circular economy objectives by valorizing agricultural and forestry resources.

2. Materials and methods

2.1. Materials

The TCNFs were produced at the Forest Products Laboratory in Madison, WI, US. The TCNFs (1.19% w.t) used in this study had a

carboxyl level of 1.47 mmol/g (dry basis) as determined by a modified TAPPI T237 method (Franke et al., 2024; Zuber et al., 2019). PENFORD® GUM 280 starch was obtained from Ingredion Inc. (Westchester, IL, USA). The paper substrate used for coating was a 50 g/m² basis weight machine glazed food wrapping paper provided by Pixelle Specialty Solutions LLC (WI, USA). The plasticizers examined included sodium carboxymethyl cellulose (CMC) with 90,000 g/mol average weight molecular weight (M_w), purchased from Sigma Aldrich, biobased polyvinyl alcohol (PVOH) with 24,000 g/mol average M_w derived from sugarcane provided by Bioplastics International, and triethyl citrate Citroflex™ 2 (TEC) manufactured by Aurorium.

2.2. Preparation of coating solution

A 15 wt% starch solution (400 g) was prepared by dissolving 60 g starch in 360 g DI water and heating at 85 °C for 1 h under stirring. Separately, 5 wt% PVOH and 5 wt% CMC solutions (400 g each) were prepared by dissolving 20 g polymer in 380 g DI water and heating at 95 °C for 2 h until fully dissolved. All solutions were stored at 4 °C.

Three TCNF-based coating solutions (400 g each) were prepared: (i) TCNF: 270 g TCNF suspension (1.19 wt%) with 130 g DI water; (ii) TCNF–10CMC: 270 g TCNF with 6.4 g CMC solution and 123.6 g DI water; and (iii) TCNF–20TEC–10PVOH: 270 g TCNF with 0.64 g TEC, 6.4 g PVOH solution, and 122.96 g DI water. All mixtures were stirred at 800 rpm for 30 min, degassed in a vacuum oven at 85 °C for 2–3 h, and maintained at 60 °C for application.

2.3. Paper coating

The 50 g/m² machine-glazed paper was coated on the glazed side using a compact tape-casting film coater (MSK-AFA-III, MTI Corporation, USA). Papers were cut to approximately 18 cm × 33 cm, taped to the vacuum plate, and held in place using vacuum (10–40 kPa) to minimize distortion during coating and drying. Coatings were applied using a 10 cm-wide doctor blade translated along the paper length, with blade gaps adjusted to control coating thickness. Gap settings ranged from 1 to 90, corresponding to 10–900 μm (10 μm per increment). Samples were named based on coating formulation and doctor blade gap (e.g., TCNF 90, TCNF–10CMC 90, TCNF–20TEC–10PVOH 20, 40, and 90, and Starch 1 and 15).

Multilayer-coated paper was fabricated by sequential coating. A starch layer was first applied and dried completely, followed by coating of the TCNF–20TEC–10PVOH formulation as the top layer. Based on the doctor blade gap settings (corresponding to coating weight) used for the starch layer and the TCNF–20TEC–10PVOH top layer, the multilayer samples were designated as Starch 1/TCNF–20TEC–10PVOH and Starch 15/TCNF–20TEC–10PVOH, respectively. In these formulations, 10CMC, 20TEC, and 10PVOH indicate 10% carboxymethyl cellulose, 20% triethyl citrate, and 10% polyvinyl alcohol relative to TCNF dry weight. The numbers 20, 40, and 90 represent the doctor blade gap settings for TCNF-based coatings, while 1 and 15 represent the gap settings for starch-based coatings. For simplicity, the sample names were abbreviated as TCNF10C, TCNF20T10P 20, 40, or 90, S1, S15, S1/TCNF20T10P 20, 40, or 90, and S15/TCNF20T10P 20, 40, or 90 (Table 1). After coating, samples were dried using forced air at 90 °C unless otherwise specified. Coating weights were determined gravimetrically by comparing the mass of coated and uncoated paper samples of fixed area (10 cm × 25 cm). In addition, cast films of each TCNF formulation and starch were prepared by drying dilute (<1 wt%) suspensions in polystyrene petri dishes at room temperature. These films, with thicknesses of 10–40 μm, were used for oxygen permeability testing to assess intrinsic material properties independent of the coating process.

2.4. Rheological properties analysis

Small-amplitude oscillatory shear and rotational shear tests of TCNF-

Table 1

More detailed information on sample abbreviations.

Coating Materials	
TCNF	Tempo-oxidized CNF
TCNF/C	TCNF with 10% carboxymethyl cellulose
TCNF/TP	TCNF with 20% triethyl citrate and 10% polyvinyl alcohol
Paper Coatings	
S1, S15	Starch coating with a doctor blade gap setting of 1 or 15
S1/TCNF/TP 20, 40, or 90	Starch coating with a doctor blade gap setting of 1, followed by a TCNF20T10P coating at a doctor blade gap setting of 20, 40, or 90
S15/TCNF/TP 20, 40, or 90	Starch coating with a doctor blade gap setting of 15, followed by a TCNF20T10P coating at a doctor blade gap setting of 20, 40, or 90

based coating dispersions were performed using an MCR 302 rheometer (Anton Paar, Graz, Austria) with a 25 mm parallel-plate geometry at 25 and 60 °C. Evaporation was minimized using a hood and a customized roughened aluminum bottom plate (3 mm thick, 30 mm diameter aluminum disk), with the sample dish filled with water. Samples were equilibrated for 5–10 min before testing, and multiple gaps were evaluated; results shown used a 1 mm gap. Amplitude sweeps (0.1–10% strain, 1 Hz) determined the linear viscoelastic range. Sixty-minute time sweeps (0.5% strain, 1 Hz) confirmed stability against evaporation. Rotational shear time sweeps at 10 s⁻¹ showed that 15 min pre-shear was sufficient to fully disrupt TCNF structure, and this condition was used before collecting flow curves from 10 to 1000 s⁻¹.

2.5. Surface morphology and roughness characterization

Surface morphology was examined by SEM (Zeiss Evo 15 LS, 3–10 kV) on gold-coated surface and cryo-fractured cross-section samples mounted on aluminum stubs. Cross-sectional surfaces were prepared by cutting uncoated and coated paper after freezing with liquid nitrogen. Surface topography was further analyzed using a Keyence VK-X3000 confocal laser microscope with 10 × objective (Keyence, Osaka, Japan), where root mean square (RMS) roughness was measured over 1 mm sections with 16 repeated measurements per image following Guyer et al. (2025) with modification. Surface roughness values are reported as mean ± standard deviation (SD) based on 16 measurements collected from different locations on each sample. The relatively large SD observed for some samples reflects the inherent spatial heterogeneity of the coated surfaces rather than measurement artifacts. Nanoscale roughness was characterized by tapping-mode atomic force microscopy (AFM) (TT-2, AFM Workshop) over scan areas of 1 × 1, 5 × 5, and 15 × 15 μm², and roughness parameters were calculated using Gwyddion software based on established methods (Yaduraj & Kumari, 2016). The average roughness (Ra), root-mean-square roughness (Rq), and peak-to-peak roughness (Rt) values are reported as mean ± standard deviation (SD) based on 12 measurements collected from different locations on each sample. The relatively large SD observed for some samples reflects the inherent spatial heterogeneity of the coated surfaces rather than measurement artifacts.

2.6. Thermal degradation analysis

The thermal properties of the samples were analyzed using a Mettler-Toledo TGA/DSC3 + system (Mettler-Toledo, LLC, Columbus, OH, USA) at the temperature range of 30–600 °C with a heating rate of 10 °C min⁻¹. The tests were done in duplicate for each sample.

2.7. Water resistance analysis

The water resistance was evaluated using contact angle measurements by an optical tensiometer (TL100, Theta Lite, Biolin Scientific Oy, Finland). The contact angle change over time was recorded after a drop

of DI water was deposited onto the surface of paper-based samples.

2.8. OTR and WVTR testing

Oxygen transmission rates were measured using a MOCON OX 2/22 L (AMETEK MOCON, USA) in accordance with ASTM F1927–20 at 23 °C and controlled relative humidities, with matched humidity setpoints for test and carrier gas streams. Measurements were conducted using repeated 60 min test cycles with a 2% convergence criterion across the final three cycles to ensure equilibrium. Instrument re-zeroing was performed for 60 min at the start of each run and every eight test cycle thereafter. At least two replicates were tested for each sample type.

WVTR were measured on a MOCON Permatran 3/34 (AMETEK MOCON, USA) following ASTM F1249–20 at 23 °C and various relative humidities. Test was performed in 60-minute cycles with a convergence criterion of 3% across the last three test cycles at each humidity step to ensure sample equilibrium. An instrument re-zero was performed for 30 min at the beginning of each sample run and repeated every eight tests. Samples were masked using adhesive aluminum tape to reduce the test area of the samples. A minimum of two replicates of all sample types were tested. The error bars represent standard deviation (SD) obtained from independent replicate measurements.

2.9. Permeability of multi-layer structures

Theoretical values of oxygen transmission rate of a layered structure can be determined from oxygen permeabilities of individual layers based on the following equation:

$$TR_T = \frac{1}{\frac{L_A}{P_A} + \frac{L_B}{P_B} + \dots + \frac{L_N}{P_N}} \quad (1)$$

where TR_T is the total transmission rate and P_N is the permeability of a singular layer of a multi-layer structure with N layers denoted A, B, ..., N assuming homogeneity and uniform thickness (L_N) of each layer.

3. Results and discussion

3.1. Rheological properties and coating uniformity

3.1.1. Effect of TCNF concentration

The appearance of TCNF suspensions at different concentrations is shown in Fig. S1(A) in Supplementary Data. An inverted vial test revealed strong concentration-dependent rheological behavior. The 1 wt% TCNF suspension exhibited solid-like, gel behavior and did not flow upon inversion, whereas 0.8 wt% and 0.6 wt% suspensions flowed immediately, indicating a transition from solid-like to liquid-like behavior with decreasing concentration.

Rheological properties are critical for determining the quality of coated films, affecting factors such as uniformity, continuity, and thickness (Chen et al., 2024a). Dynamic shear rheology was used to evaluate the viscosity (η), storage modulus (G'), and loss modulus (G'') and their impact on coating performance. The viscosity changes of different concentrations of TCNF dispersions over time at different temperatures are presented in Fig. 1 (A). The viscosity increased with TCNF content, irrespective of temperature. Additionally, regardless of temperature, the viscosity initially decreased with time and then gradually stabilized. The 1 wt% TCNF suspension required approximately 30 min to reach a steady-state viscosity, whereas the 0.8 wt% and 0.6 wt % suspensions stabilized within 10 min and 6 min, respectively. This indicated a stronger fiber network at higher concentration. Increasing the temperature from 25 °C to 60 °C reduced the stabilized viscosities of the 1%, 0.8%, and 0.6% suspensions from 860.5 to 577.6, 438.0–282.7, and 224.6–146.4 mPa·s, respectively, indicating that elevated temperature effectively lowers suspension viscosity. Fig. 1 (B) illustrates the steady-state viscosity of TCNF suspensions as a function of shear rate at

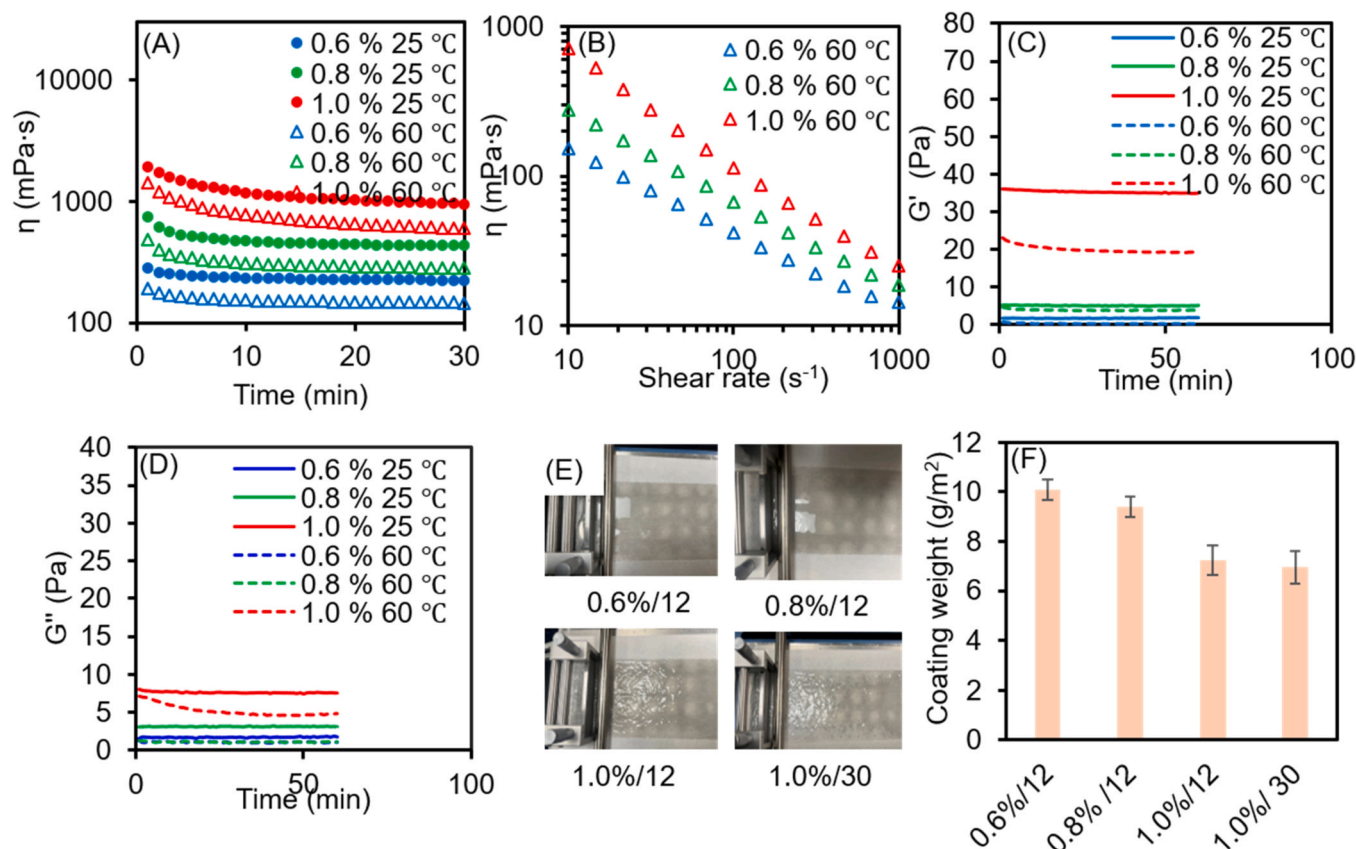


Fig. 1. Effects of TCNF concentration and temperature on rheological properties and coating uniformity. (A) Viscosity evolution over time. (B) Viscosity as a function of shear rate. (C) Shear storage modulus (G') over time. (D) Loss modulus (G'') over time. (E) Wet coating uniformity with TCNF concentration and coating speed (mm/s). (F) Resulting coating weight obtained with different plasticizers.

various concentrations. Again, an increase in viscosity with TCNF content was observed. At $10 s^{-1}$, viscosities for 1%, 0.8%, and 0.6% suspensions were 711.7, 323.9, and 152.4 mPa·s, respectively, decreasing to 25.3, 19.1, and 14.5 mPa·s at $1000 s^{-1}$. Therefore, the initial decrease in viscosity over time, combined with the reduction in viscosity at elevated high temperatures and higher shear rates, suggests that TCNF suspensions can flow easier under these conditions.

For 0.6% and 0.8% of TCNF, both G' (Fig. 1C) and G'' (Fig. 1D) remained stable throughout the measurement periods and temperatures, indicating time and temperature-independent viscoelastic behavior. In contrast, both the storage modulus (G') and loss modulus (G'') of the 1% TCNF coating dispersion showed an initial decrease followed by stabilization after 30 min. After stabilization, the 1 wt% TCNF suspension exhibited pronounced viscoelastic solid behavior, with storage modulus (G') values of 36.1 Pa at 25 °C and 23.2 Pa at 60 °C, both of which were substantially higher than the corresponding loss modulus (G'') values of 8.0 Pa and 7.0 Pa, respectively. The resulting $\tan \delta$ values (0.22 at 25 °C and 0.26 at 60 °C) were well below 1, further confirming dominant elastic behavior. In contrast, the 0.8 wt% suspension displayed much lower G' values (5.3 Pa at 25 °C and 4.6 Pa at 60 °C) and higher $\tan \delta$ values (0.58 and 0.61, respectively), indicating behavior between solid-like and liquid-like. The 0.6 wt% suspension showed even lower G' values (1.6 Pa at 25 °C and 0.8 Pa at 60 °C) and $\tan \delta$ values of 1.03 and 1.54, characteristic of fully liquid-like behavior under both temperatures. The increase in $\tan \delta$ with temperature demonstrates that warming the suspension enhances its fluidity by weakening its elastic network. Although increasing the temperature from 25 °C to 60 °C reduced the G' of the 1 wt% suspension, it still retained solid-like characteristics. This strong viscoelastic solid response in the 1 wt% formulation suggests limited flowability, which may lead to practical

challenges in coating applications such as poor coating continuity and reduced coating weight.

These rheological results are consistent with visual observations of the wet coating surface. The 1% TCNF film at 60 °C exhibited a non-uniform, irregular appearance (Fig. 1E, bottom images). Furthermore, as the TCNF concentration increased from 0.6% to 1%, the coating weight decreased from $10.1 \pm 0.4 g/m^2$ to $7.2 \pm 0.2 g/m^2$ (Fig. 1F), further confirming the detrimental impact of high viscosity and rigidity on film deposition. In contrast, the lower G' and G'' values of the 0.8% and 0.6% suspensions facilitated better flow behavior, which in turn supported more uniform coating layers. Therefore, based on the rheological performance and wet coating quality, we selected 0.8% TCNF as the optimal concentration and 60 °C for subsequent coating experiments.

3.1.2. Effect of plasticizers

One key limitation of CNM barrier coatings is poor durability due to brittleness, which can cause cracking and reduced gas barrier performance (Franke et al., 2024). Plasticizers and water-soluble polymers are commonly added to improve flexibility (Franke et al., 2024; Roy et al., 2022). However, these additives also alter the rheological behavior of the coating solution, which in turn impact coating uniformity. To date, limited research has explored how such additives influence both rheology and coating performance. This section investigates the effects of plasticizers and water-soluble polymers on the rheological properties of TCNF-based coating solutions and their implications for coating uniformity.

Based on our previous work, a TCNF-based formulation containing 20 wt% TEC and 10 wt% PVOH (TCNF/TP, relative to dry TCNF) showed improved durability. CMC was also selected due to its reported

ability to improve CNF dispersion (Mazhari et al., 2017; Youngblood et al., 2022). Accordingly, pure TCNF, TCNF/C and TCNF/TP formulations were evaluated at 0.8%. All suspensions flowed immediately at room temperature upon bottle inversion (Fig. S1(B) in Supplementary Data). Viscosity initially decreased over time (Fig. 2 (A)), reaching steady state after approximately 10 min for TCNF and TCNF/C, whereas about 15 min for TCNF/TP, indicating a more robust internal network in the latter. The viscosity change over shear rate was presented in Fig. 2 (B). When the shear rate increased from 10 to 1000 s^{-1} , the viscosities of pure TCNF, TCNF/C, and TCNF/TP reduced from 278.5, 240.2, and 555.2 mPa·s to 18.1, 17.1 and 21.2 mPa·s, respectively, indicating pronounced shear-thinning behavior. Moreover, adding 10% CMC reduced the viscosity, consistent with previous reports that the negatively charged carboxymethyl groups of CMC induce electrostatic repulsion with TCNF, thereby lowering suspension viscosity (Mazhari et al., 2017). In contrast, the combination of 20% TEC and 10% PVOH significantly increased the viscosity. This is likely because the additional PVOH produced more interactions between the hydroxyl groups characteristic of both TCNFs and PVOH. PVOH does not have a negative surface charge and therefore does not produce the electrostatic effect that CMC does. The storage modulus (G') (Fig. 2(C)) and loss modulus (G'') (Fig. 2(D)) increased after adding 20TEC–10PVOH. Specifically, the G' and G'' of TCNF were 3.9 and 2.5 Pa, while the G' and G'' of the TCNF/TP formulation increased to 14.9 and 4.2 Pa, respectively. However, the G' value of TCNF10C increased to 7.6 Pa, while the G'' value remained unchanged compared with that of TCNF (2.5 Pa), indicating enhanced elastic behavior without affecting viscous dissipation. The increase in G' for TCNF/C is attributed to physical bridging and hydrogen bonding between CMC chains and TCNF fibrils, which strengthens the elastic network, while the low CMC content does not alter viscous dissipation, resulting in an unchanged G'' . At this low

concentration (10%), CMC remains highly solvated and mobile in water and does not form a separate viscous phase. The $\tan \delta$ of TCNF, TCNF/C, and TCNF/TP were 0.61, 0.27, 0.28, respectively. Despite these notable differences in rheological behavior, the coating weights of all three formulations showed no significant variation. This suggests that at a TCNF concentration of 0.8 wt%, the rheological modifications induced by these additives do not substantially affect the coating mass or uniformity under the tested conditions.

In addition, surface tension measurements were conducted for the TCNF dispersions with different plasticizer combinations. The results showed that the addition of 20% TEC and 10% PVOH reduced the surface tension from 71.2 to 64.8 mN/m (Fig. 2 (E)). TEC is known to have a surfactant effect in water. However, this change in surface tension did not appear to influence the rheological properties or coating weights (Fig. 2 (F)). This may be due to the chemical similarity between the TCNF-based coating material and the cellulose-based paper substrate, which minimizes surface tension-driven spreading effects. In contrast, surface tension may play a more critical role in coating coverage when applying CNM-based coatings onto non-cellulosic hydrophobic (e.g., plastic) substrates (Kim et al., 2024).

3.2. Morphology properties

The surface topography of paper plays a critical role in determining its environmental interactions and fundamental properties, such as tribology, absorption, optical behavior, adhesion, wettability, and biocompatibility (Samyn et al., 2016). Fig. 3 (A) shows uncoated paper with a rough, porous surface, where the vestiges of individual cellulose pulp fibers are clearly visible. In contrast, Fig. 3 (B–E) depict the morphologies of paper coated with TCNF and various plasticizers. These coated samples display smoother surface regions, as the porous structure

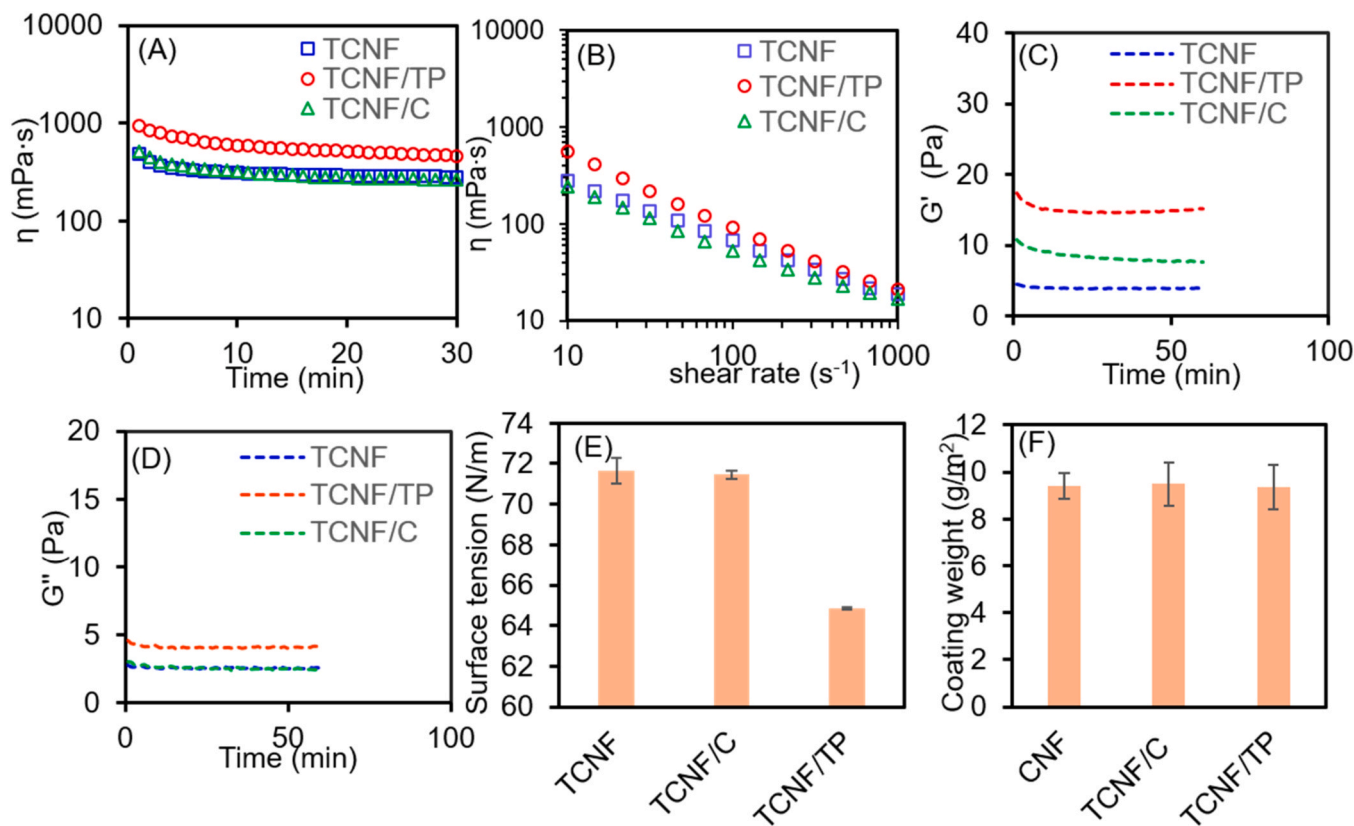


Fig. 2. Effect of plasticizer on rheological properties and coating uniformity. (A) Viscosity evolution over time. (B) Viscosity as a function of shear rate. (C) Shear storage modulus (G') over time. (D) Loss modulus (G'') over time. (E) Surface tension of TCNF dispersions containing different plasticizers. (F) Resulting coating weight obtained with different plasticizers.

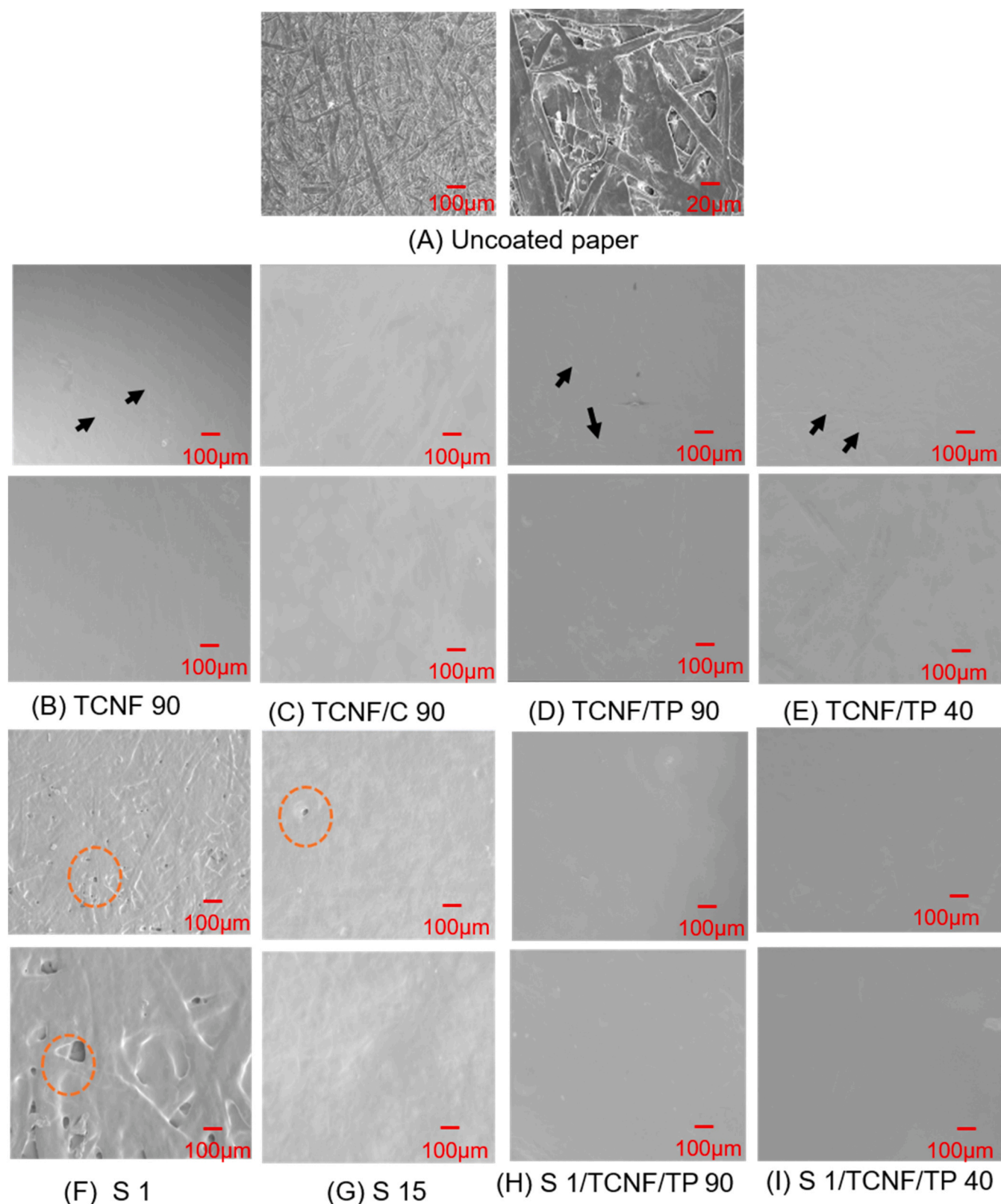


Fig. 3. SEM images of paper surfaces for the uncoated sample (A), samples coated with various formulations of TCNF (B–E), samples coated with starch (F, G) and starch followed by TCNF20T10P (H, I).

and larger pulp fibers are mostly concealed beneath the much finer TCNF or TCNF and starch network. However, some thicker cellulose fibers still form noticeable bulges (marked with black arrows), especially in the TCNF/TP 40 sample. Here, the coating weight decreased from 9.4

$\pm 0.9 \text{ g/m}^2$ to $3.4 \pm 1.8 \text{ g/m}^2$ when reducing the doctor blade setting from 90 to 40 (Table 2), which allowed more of the underlying fiber bulges to protrude. A starch base layer was examined to determine if

Table 2

Coating thickness, total coating weight, TCNF portion of coating weight, OTR and WVTR of coated paper.

Samples	Thickness (μm)	Coating weight (g/m^2)	TCNF coating weight in multilayer (g/m^2)	OTR ($\text{cm}^3/(\text{m}^2 \cdot \text{day})$)			WVTR ($\text{g}/(\text{m}^2 \cdot \text{day})$)		
				RH 20%	RH 50%	RH 80%	RH 20%	RH 50%	RH 80%
Uncoated paper	56.0 ± 0.4	/	/	Failed	Failed	Failed	251.4	660.5	1092.9
TCNF 90	60.0 ± 1.6	8.6 ± 0.6	8.6 ± 0.6	0.2	2.3	252.5	± 8.1	± 22.9	± 39.6
				± 0.0	± 0.1	± 21.2	54.6	453.8	1406.3
TCNF/C 90	62.6 ± 2.3	9.5 ± 0.9	9.5 ± 0.9	0.2	2.2	109.9	± 5.0	± 62.4	± 221.8
				± 0.0	± 0.0	± 4.5	60.7	375.9	1129.2
TCNF/TP 90	63.0 ± 1.9	9.4 ± 0.9	9.4 ± 0.9	1.2	2.6	130.6	± 10.7	± 12.2	± 47.7
				± 1.3	± 0.8	± 14.6	29.96	248.3	939.9 ± 33.6
TCNF/TP 90	62.0 ± 2.1	3.4 ± 1.8	3.4 ± 1.8	Failed	Failed	Failed	± 4.9	± 23.2	/
S1	62.0 ± 1.8	10.9 ± 1.2	/	Failed	Failed	Failed	/	/	/
				Failed	Failed	Failed	56.5	323.7	1038.5
							± 2.7	± 14.9	± 40.9
S 15	71.4 ± 2.5	26.8 ± 1.9	/	Failed	Failed	Failed	32.4	196.1	791.3 ± 48.9
							± 0.5	± 7.9	
S1/TCNF/TP 20	65.6 ± 1.3	11.4 ± 1.1	1.1 ± 0.5	0.7	2.8	43.8 ± 2.9	40.9	270.6	943.1
				± 0.0	± 0.1		± 1.8	± 43.1	± 187.3
S1/TCNF/TP 40	62.5 ± 2.1	13.8 ± 0.6	3.1 ± 0.4	0.3	1.2	34.7 ± 1.8	23.2	158.4	685.4 ± 51.7
				± 0.0	± 0.1		± 2.4	± 7.8	
S1/TCNF/TP 90	64.8 ± 2.7	18.1 ± 0.9	7.2 ± 1.9	0.4	1.2	34.4 ± 0.8	16.9	122.9	807.8 ± 69.3
				± 0.0	± 0.1		± 5.5	± 33.2	
S15/TCNF/TP 20	72.7 ± 1.2	28.5 ± 2.2	1.3 ± 0.8	0.3	1.3	22.3 ± 0.5	20.9	145.5	608.6 ± 10.5
				± 0.0	± 0.0		± 2.1	± 5.5	
S15/TCNF/TP 40	73.80 ± 2.9	32.0 ± 1.1	6.0 ± 1.5	0.2	1.3	22.7 ± 0.7	34.4	133.7	654.9 ± 16.8
				± 0.0	± 0.1		± 3.9	± 7.3	
S15/TCNF/TP 90	74.8 ± 3.0	35.4 ± 3.4	8.8 ± 1.8	0.2	0.9	20.9 ± 3.1	15.8	106.6	563.3 ± 4.4
				± 0.0	± 0.1		± 0.2	± 1.6	

filling the porosity of the paper with a low-cost starch would allow for lower coating weights of the TCNF to form a better oxygen barrier. The papers coated with different amounts of starch are shown in Fig. 3 (F) and (G). Compared with Starch 1, Starch 15 coated paper exhibited nearly complete coverage of surface pores due to an increase in the coating weight from $10.9 \pm 1.2 \text{ g}/\text{m}^2$ to $26.8 \pm 1.9 \text{ g}/\text{m}^2$. Furthermore, the surface of the starch–TCNF multilayer coated paper appeared smoother, with fewer protruding underlying pulp cellulose fibers. Even with the low coating weights of each material, e.g., the $10.9 \pm 1.2 \text{ g}/\text{m}^2$ of starch base and $3.1 \pm 0.4 \text{ g}/\text{m}^2$ of TCNF, the underlying paper fibers are not apparent in the surface images (Fig. 3 (H) and (I)).

Cross-sectional micrographs of uncoated and coated paper are shown in Fig. 4. Compared with uncoated paper (Fig. 4A), coated samples (Fig. 4B–I) exhibit a dense surface film covering the porous cellulose fiber network, while the internal paper structure remains unchanged, indicating limited coating penetration into the gaps between cellulose fibers. This is attributed to rapid film formation during drying. No interfacial gaps were observed between starch and TCNF layers, suggesting strong interlayer adhesion through hemiacetal crosslinks between the hydroxyl moieties of starch and the aldehyde moieties of TCNF, as well as hydrogen bonding between hydroxyl groups on both (Soni et al., 2021). The starch base layer effectively sealed surface pores, facilitating the formation of a continuous TCNF layer at lower coating weights while maintaining gas barrier performance. Further details are discussed in the gas barrier 3.6.

Topographical height maps from confocal laser scanning microscopy show how well the coating covers the roughness of the paper below (Fig. S2) in Supplementary Data. Fiber agglomeration, either of TCNF alone or in combination with plasticizers (TEC) or water-soluble polymers (e.g., starch, CMC, or PVOH)—can be observed as surface protrusions or the formation of specific patterns. These features likely result from self-organization tendencies between TCNF fibrils and other components such as CMC, PVOH, or TEC (Fig. S2 (A–L)). AFM was conducted to further investigate the surface topography (Fig. S3) in Supplementary Data. On the uncoated paper (Fig. S3 (A)), long and thick cellulose fibers were clearly visible, whereas the TCNF-coated paper exhibited short, thin fibrils typical of nanocellulose (Fig. S3 (B–D)) (Yaduraj & Kumari, 2016). Notably, the TCNF/TP coated paper displayed distinct surface protrusions, possibly caused by non-uniform

coating applications. This irregularity is attributed to the high viscosity and solid-like nature of the TCNF/TP solution. In contrast, the TCNF/C coated paper surface appeared much smoother, which can be explained by the lower viscosity and more liquid-like rheological behavior of the coating solution. Additionally, some aggregation protrusions were found from the S1/TCNF/TP 20 coated paper surface, while other starch single layer or starch/TCNF/TP coated paper surfaces are more uniform and homogeneous (Fig. S3 (E–L)).

Surface quality is commonly qualified by surface roughness, which plays a significant role in determining gas barrier performance. Surface roughness increases with the expansion of the sampling area at both microscale (Fig. 5 (A and B)) and nanoscale (Fig. 5 (C–H)). At the microscale, the surface roughness of uncoated paper increased from $3.04 \pm 0.7 \mu\text{m}$ at a sampling area of $100 \times 100 \mu\text{m}^2$ to $3.98 \pm 1.0 \mu\text{m}$ at $500 \times 500 \mu\text{m}^2$. In comparison, all coated papers showed reduced roughness, attributed to the coverage of coarse cellulose fibers by nanoscale TCNF fibrils and/or starch. For example, the S1/TCNF/TP 20 coated paper exhibited surface roughness values of $2.9 \pm 0.6 \mu\text{m}$ ($100 \times 100 \mu\text{m}^2$) and $1.8 \pm 0.7 \mu\text{m}$ ($500 \times 500 \mu\text{m}^2$), which although the highest among the coated samples, were still lower than those of uncoated paper. The nanoscale roughness data followed a similar trend over different scanning areas 1×1 , 5×5 , and $15 \times 15 \mu\text{m}^2$. For uncoated paper, the average roughness (Ra), root-mean-square roughness (Rq), and peak-to-peak roughness (Rt) in the $1 \times 1 \mu\text{m}^2$ area were 59.0 ± 49.1 , 70.3 ± 53.6 , and $249.5 \pm 152.4 \text{ nm}$, respectively. These values increased to 517.9 ± 506.7 , 582.5 ± 539.6 , and $1917.4 \pm 1156.0 \text{ nm}$, respectively, in the $15 \times 15 \mu\text{m}^2$ area. In contrast, the S1/TCNF/TP 20 coated paper showed significantly reduced roughness at all scales. In the $1 \times 1 \mu\text{m}^2$ area, Ra, Rq, and Rt were 43.0 ± 22.5 , 50.4 ± 26.4 , and $191.0 \pm 88.2 \text{ nm}$, respectively, increasing to 308.3 ± 181.9 , 366.9 ± 209.2 , and $1328.9 \pm 608.1 \text{ nm}$ in the $15 \times 15 \mu\text{m}^2$ area. These results collectively demonstrate that coating significantly smooths the paper surface at both micro- and nanoscales, which is expected to contribute to improved barrier properties.

However, although SEM and confocal laser scanning microscopy images suggested a visually smoother and more continuous surface morphology after multilayer coating, the roughness differences among the various coated formulations were not statistically significant. This may be because SEM mainly reflects localized surface morphology and

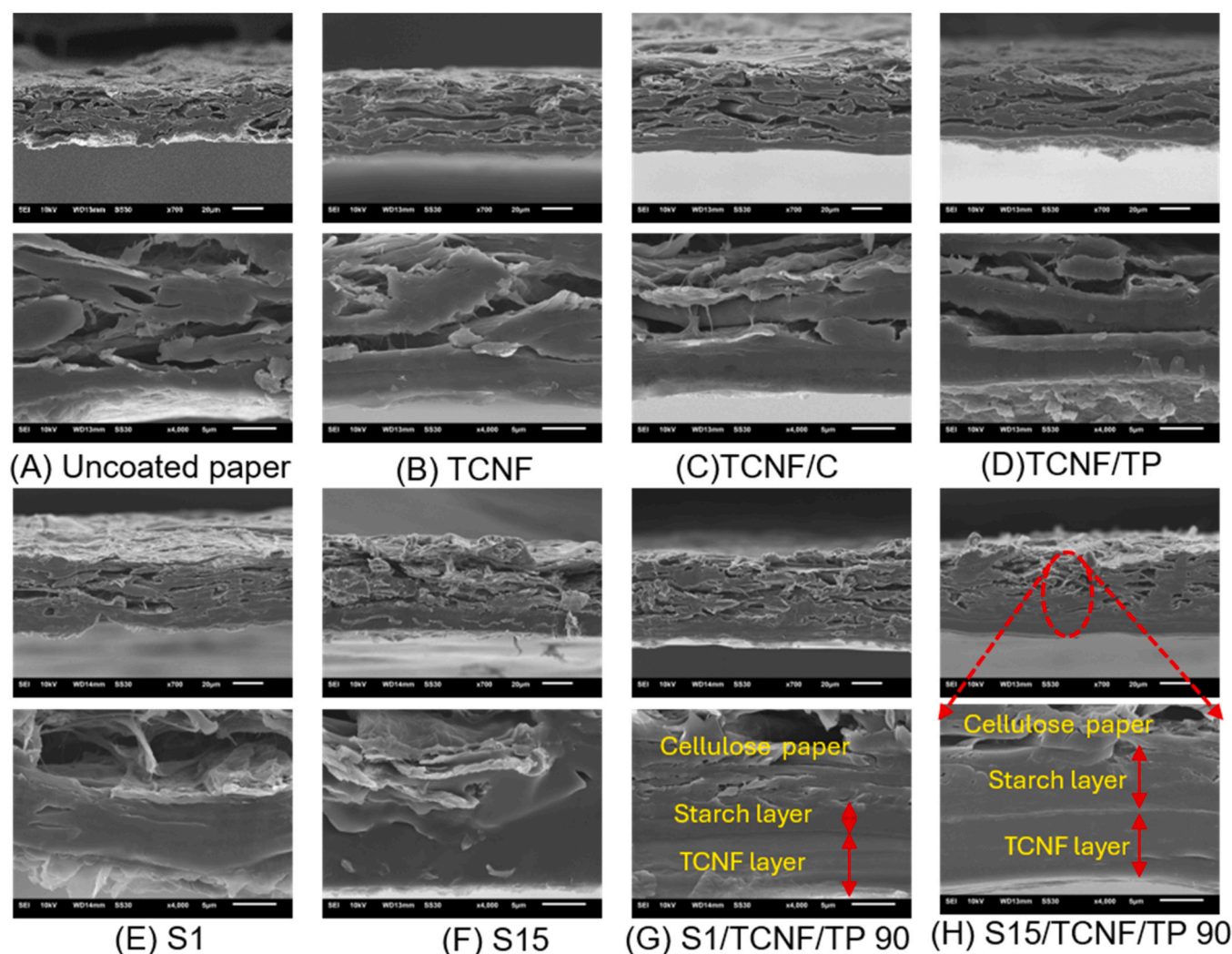


Fig. 4. SEM images of the cross-section of paper surfaces for the uncoated sample (A), samples coated with various formulations of TCNF (B–D), samples coated with starch (E, F) and starch followed by TCNF/TP (G, H). The magnification factors were 200x for samples in the first and third rows and 4,000x for those in the second and fourth rows.

pore coverage, whereas roughness measurements are more sensitive to microscale height variations and coating nonuniformity over larger scanned areas.

3.3. Thermal stability

Thermal stability and decomposition behavior of uncoated and coated paper was evaluated by thermogravimetric analysis (TGA) under nitrogen, using onset degradation temperature (T_o) and peak degradation temperature (T_p) to assess decomposition behavior (Zhao et al., 2021). The uncoated paper exhibited the highest thermal stability, with T_o and T_p values of 319.0 °C and 343.2 °C, respectively (Fig. S4 (A) in Supplementary Data and Table 3), attributed to the highly crystalline structure of native cellulose fibrils (Amara et al., 2024; Kim et al., 2021). The TCNF-coated paper showed greater thermal stability than the starch-coated paper, with a higher T_o (310.7 °C compared to 303.9 °C), indicating greater thermal resistance of TCNF than starch. For the Starch-TCNF multilayer coated paper, the T_o and T_{p2} decreased with decrease of TCNF coating weight or an increase of the starch coating weight. (Fig. S4 (B) in Supplementary Data). This reduction in thermal stability may be attributed to the higher mass of thermally unstable material introduced by the thicker starch coatings, which increases the proportion of low-stability components. In multilayer coatings,

interfacial interactions, such as hydrogen bonding or trapped moisture, can alter the thermal degradation pathways. These interfaces may create disordered regions that degrade earlier than uniform, single-layer coatings. Additionally, thick or multilayer coatings can disrupt the inherent crystalline structure of the base paper or TCNF layer, further reducing thermal stability.

3.4. Water resistance

The initial water contact angle (WCA) was measured to evaluate the hydrophilic properties of the uncoated and coated paper. As shown in Fig. 6 (A), all samples exhibited WCAs below 90°, confirming their hydrophilic nature. Further, the water contact angle over time was measured to evaluate the water resistance of coated papers (Fig. 6 (B) and (C)). This measurement essentially quantifies how fast water will soak into a sample. The uncoated paper exhibited the highest initial WCA ($77.6 \pm 12.4^\circ$), likely due to residual surface treatments applied during manufacturing to enhance smoothness, gloss, and resistance to smudging, scratching, and moisture. However, the WCA of uncoated paper rapidly decreased to 0° before 3 min, reflecting the porous and hydrophilic nature of the cellulose matrix. In contrast, all coated papers showed lower initial WCA values (less than 55.1°), due to the hydrophilic hydroxyl groups in starch and TEMPO-oxidized cellulose

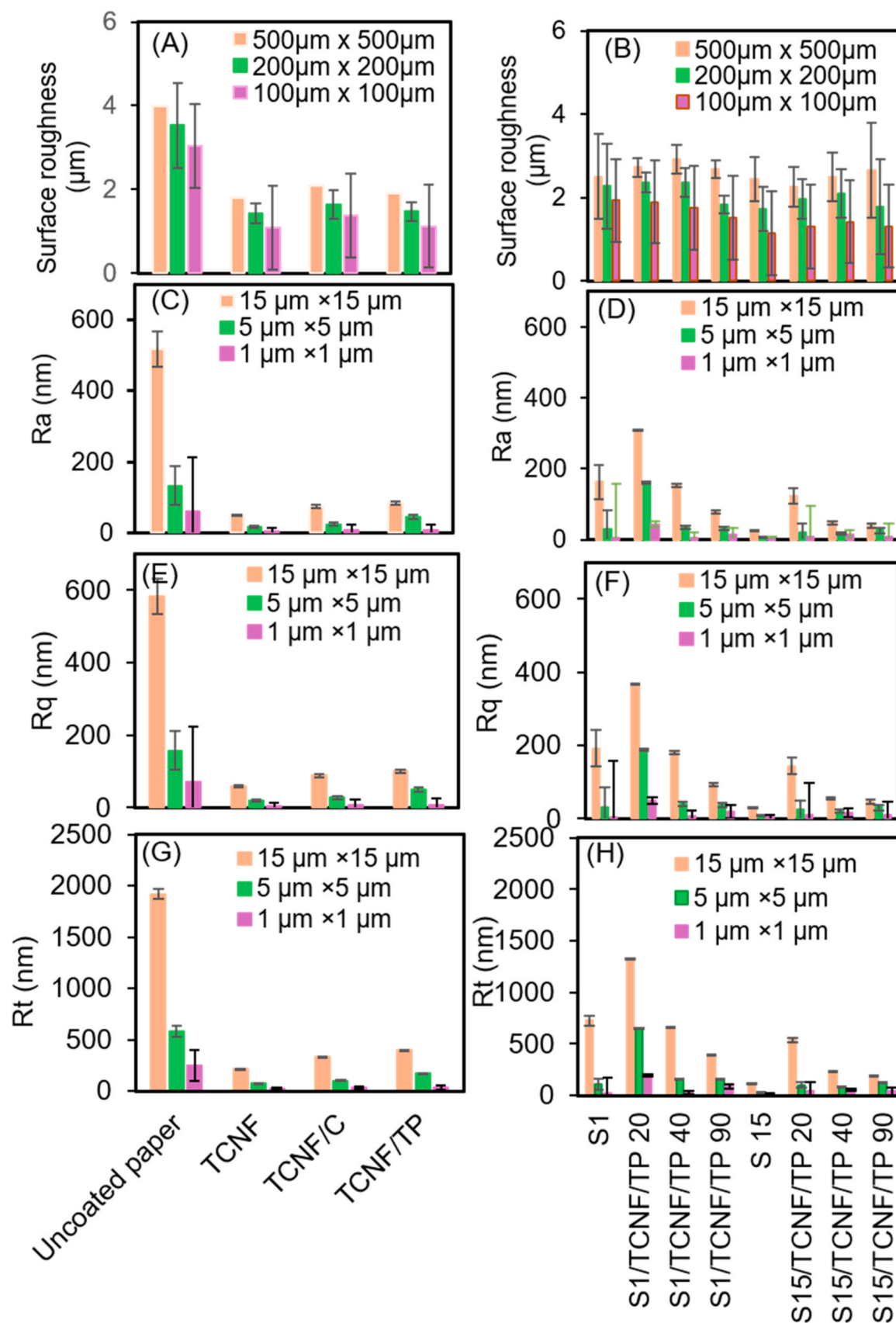


Fig. 5. Quantitative surface roughness analysis of uncoated paper and paper coated with TCNF, starch, and starch-TCNF composites. (A and B) Microscale roughness data obtained by confocal laser scanning microscopy in sampling area of $L \times L = 500 \times 500\mu\text{m}^2$, $200 \times 200\mu\text{m}^2$, $100 \times 100\mu\text{m}^2$. (C-H) Nanoscale roughness parameters determined by atomic force microscopy (AFM), including average roughness (Ra) (C-D), root-mean-square roughness (Rq) (E-F), and peak-to-peak roughness (Rt) (G-H) in sample area of $L \times L = 1 \times 1\mu\text{m}^2$, $5 \times 5\mu\text{m}^2$, and $15 \times 15\mu\text{m}^2$. Error bars represent standard deviations.

Table 3
Thermal properties of neat films and composite films (°C).

Paper samples	T ₀	T _{p1}	T _{p2}
Control	319.4	/	343.2
TCNF	310.7	293.2	341.9
TCNF/C	310.6	293.2	341.9
TCNF/TP	310.6	293.2	341.9
S1	303.9	293.2	341.8
S1/TCNF/TP 20	300.8	293.2	339.7
S1/TCNF/TP 40	296.6	293.2	335.3
S1/TCNF/TP 90	286.7	293.2	332.9
S15	277.9	293.2	337.1
S15/TCNF/TP 20	275.1	293.2	334.3
S15/TCNF/TP 40	271.7	293.2	332.6
S15/TCNF/TP 90	267.7	293.2	330.5

nanofibrils (TCNF) (Fig. 6 (B)). TCNF, TCNF/C, and TCNF/TP-coated papers required about 15 min to reach 0°, attributed to the dense network formed by TCNF. The WCA stability of starch-coated paper depended on starch content (Fig. 6 (C)). Starch 1 (coating weight $10.95 \pm 1.21 \text{ g/m}^2$) coated paper had an initial WCA of 52.7° and took less than 20 min to drop to 0°, while starch 15 (coating weight $26.78 \pm 1.97 \text{ g/m}^2$) obtained initial WCA of 52.9° and reduced to 0° after around 30 min (Table 2). Notably, the starch-TCNF multilayer coated paper exhibited the highest water resistance, with WCA persisting for 30–40 min before reaching 0°. This improvement is partly due to increased coating thickness but primarily attributed to the formation of

dense structure via hemiacetal crosslinks between the hydroxyl groups in starch and aldehyde groups in TCNF, as reported by previous research (Hamid et al., 2024; Soni et al., 2020, 2021).

3.5. Gas barrier properties

To reduce packaging costs while maximizing barrier performance, optimizing the thickness of base and functional layers is also essential. In this study, both oxygen and water vapor barrier properties of paper coated with varying amounts of starch and TCNF were investigated (Table 2 and Fig. 6 (D) and (E)). The oxygen barrier test failed (over-range on the oxygen permeation equipment) for uncoated paper and samples TCNF 40 (coating weight: $6.0 \pm 1.5 \text{ g/m}^2$), S1 ($10.9 \pm 1.2 \text{ g/m}^2$), and S15 ($26.8 \pm 1.9 \text{ g/m}^2$). This means the coating amounts are insufficient to fully fill the porous structure of the paper or cracks formed due to poor coating durability. The lack of continuous film is shown in SEM images presented in the previous section (Fig. 3). This suggests that when TCNF is used without a base layer on a machine glazed paper, a coating weight on the order of 10 g/m^2 (doctor blade setting of 90) is required to form a continuous film. For all tested samples, the OTR were all less than $1.1 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ at 20% RH and less than $2.8 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ at 50% RH. This means that in 20% RH, these coated papers can serve as effective oxygen barrier packaging for some of the highest oxygen requirement foods, such as instant coffee (Wang et al., 2018). At 50% RH, the coated papers can serve as packaging for other types of oxygen sensitive foods such as peanuts, modified atmosphere meat, and

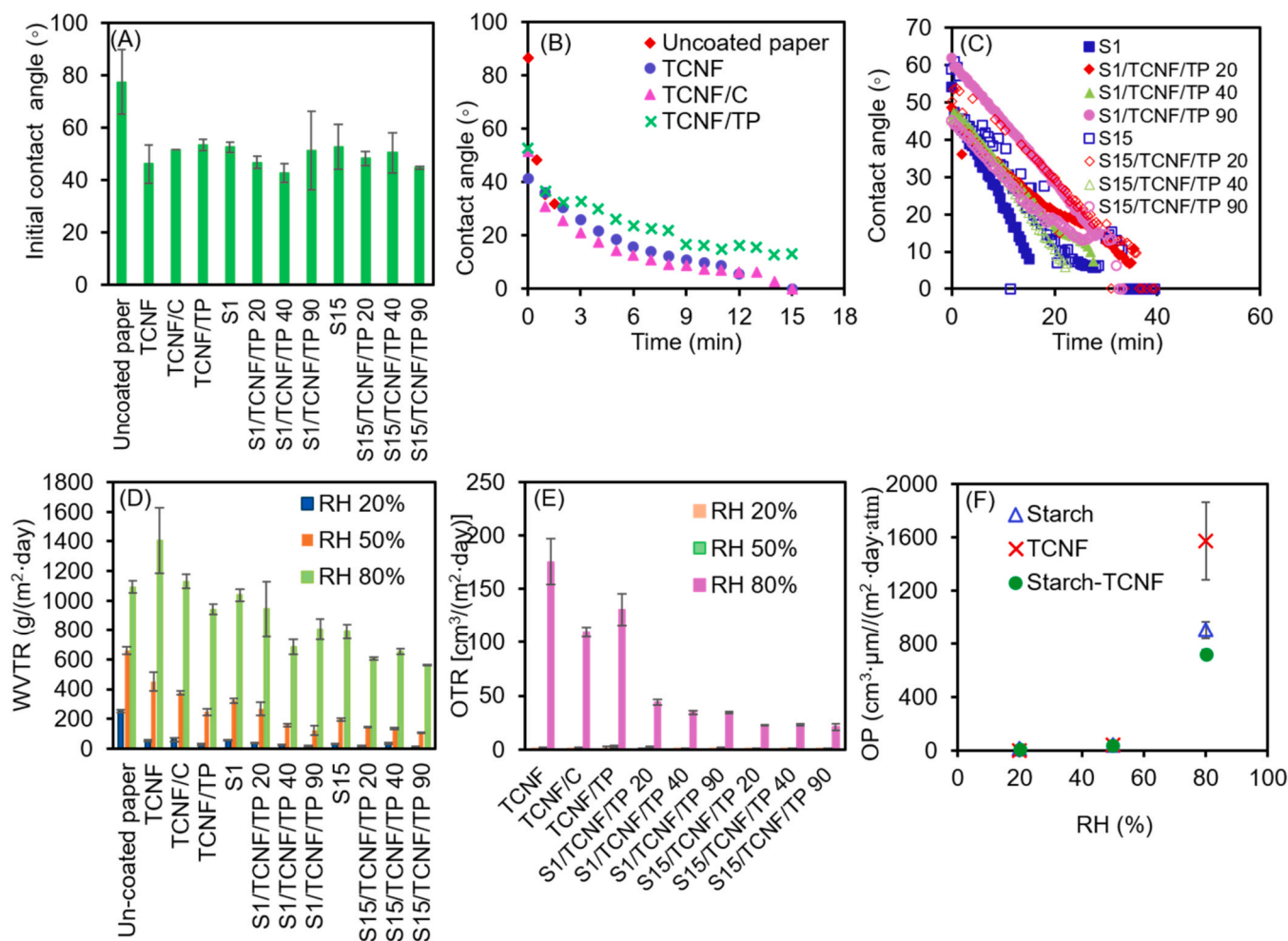


Fig. 6. Initial water contact angle of uncoated and coated papers (A), water resistance of TCNF-coated paper over time (B), and water resistance of starch-TCNF multilayer-coated paper over time (C). The WVTR (D), OTR (E) of TCNF coated paper and starch-TCNF multilayer coated paper, respectively. (F) OP of casting films at varying humidities.

cheese (Wang et al., 2018). It is well known that CNMs lose their oxygen barrier performance at high humidity. Therefore, more discussion in this study will focus on OTR and WVTR at 80% RH. The OTR up to $252.5 \pm 21.2 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ at 80% RH for TCNF 90 single layer coated paper. This is an order of magnitude above any of the food packaging requirements. The OTR values of TCNF/C and TCNF/TP coated papers at 80% RH decreased to 109.9 ± 4.5 and $130.6 \pm 14.6 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$, respectively—both lower than TCNF alone. For WVTR, TCNF/TP exhibited substantially lower values 29.9 ± 4.9 , 248.3 ± 23.2 , and $939.9 \pm 33.6 \text{ g}/(\text{m}^2 \cdot \text{day})$ at 20%, 50%, and 80% RH, respectively compared to the TCNF-coated paper (54.6 ± 5.0 , 453.8 ± 62.4 , and $1406.3 \pm 221.8 \text{ g}/(\text{m}^2 \cdot \text{day})$). These reductions were more pronounced than those observed for TCNF/C (60.7 ± 10.7 , 375.9 ± 12.2 and $1129.2 \pm 47.7 \text{ g}/(\text{m}^2 \cdot \text{day})$). These results indicate that the incorporation of 20% TEC–10% PVOH improved both oxygen and water vapor barrier performance. PVOH is likely to fill the free volume between fibrils through its dense hydrogen-bonded network and high cohesive energy density, thereby increasing the resistance to oxygen diffusion and permeation (Schiessl et al., 2022). TEC is known to be more hydrophobic than hydrophilic, which may reduce the composite material's affinity for water. The TEC and PVOH additions were also shown to increase the durability of the TCNF layer in prior work (Franke et al., 2024). Therefore, the TCNF/TP formulation was selected for multi-layer coatings with starch.

For the starch–TCNF multilayer coated paper, both OTR and WVTR at 80% RH decreased with increasing coating thickness or coating weight of the starch and TCNF-based layers. Specifically, the OTR and WVTR of S1/TCNF/TP 20 coated paper were $43.8 \pm 2.9 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ and $943.1 \pm 187.3 \text{ g}/(\text{m}^2 \cdot \text{day})$, respectively. To improve properties, first the coating thickness of the starch layer and TCNF layer were increased independently. Increasing the thickness of only the TCNF layer decreased OTR and WVTR to $34.40 \pm 0.83 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ and $685.4 \pm 51.7 \text{ g}/(\text{m}^2 \cdot \text{day})$, respectively (S1/TCNF/TP 90). However, the barrier properties were improved further by only increasing the starch base layer (S15/TCNF/TP 20), with OTR and WVTR at $22.3 \pm 0.5 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ and $608.6 \pm 10.5 \text{ g}/(\text{m}^2 \cdot \text{day})$, respectively. Increasing both the starch base layer and the amount of the TCNF (S15/TCNF/TP 40 and S15/TCNF/TP 90) resulted in OTR values, the OTR values of S15/TCNF/TP 40 and S15/TCNF/TP 90 remained similar to the thick starch base layer with the thin TCNF layer (S15/TCNF/TP 20) at high humidity. All of the samples with the thick starch base layer had OTRs on the order of $20 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$, which is much lower than what is typically observed with CNM coatings of this thickness, and near the useful range of oxygen transmission requirements for food packaging ($15 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$). These results are important because they demonstrate that good barrier properties can be obtained with very thin CNF coating if the pores are filled with starch, a much less expensive coating.

The key to understanding the oxygen barrier performance of the multilayer system at different humidities is to understand the oxygen barrier performance of each material (casted films) at varying humidities (Fig. 6 (F)). The TCNF performs better than the starch (permeability a factor of 6 lower) at the low humidity. This is as expected due to the higher crystallinity of the TCNF material preventing oxygen movement through the material. However, at the 80% RH condition the starch has a 40% lower permeability than the TCNF based material. Both materials will swell in the presence of water, which reduces their ability to prevent oxygen transmission. However, it appears that TCNF has a higher affinity for water, swelling more than the starch at elevated humidity. This is due to the highly hydrophilic nature of the carboxylate groups on the TCNF surface.

To understand the transmission through the layered paper coated system, a standard multilayer diffusion resistance model for the starch layer and TCNF layer in series was examined (Eq. 1). This model treats oxygen transmission rate (OTR) as a series resistance of individual layers based on their thickness and permeability. The example of coated paper consisting of S 1/TCNF/TP 40 was used for this analysis because the

combination of the coating weights and barrier performance are closest to target values for paper manufactures. At these coating conditions, the coating weight of the starch was $13.8 \text{ g}/\text{m}^2$ (Table 2), which translates to an idealized film thickness of $9 \mu\text{m}$ assuming a density of starch of $1.5 \text{ g}/\text{cm}^3$ (Table 4). The coating weight of the TCNF based suspension was $3.1 \text{ g}/\text{m}^2$, which translates to a film thickness of $2 \mu\text{m}$ when assuming a density of the TCNF film of $1.6 \text{ g}/\text{cm}^3$. The idealized thickness and the measured intrinsic oxygen permeability can be used to estimate the resistance (R) to oxygen permeation of each individual layer at different humidities by dividing thickness by permeability. In the low humidity condition, the much thinner TCNF film has a larger resistance to oxygen transmission than the starch, likely due to the higher crystallinity. However, in the high humidity condition (80% RH), the more hydrophilic TCNF saw a greater reduction in its oxygen barrier performance and the starch became the larger resistance, e.g., the driver of barrier performance of the system at this elevated humidity. Ideally the barrier properties of both materials would retain more of their intrinsic properties at this high humidity, which could potentially be achieved by chemical modification. The resistance model illustrates how different layered materials with properties varying across humidities can potentially be used to provide greater barrier performance at a larger range of humidities, as replacing some of the TCNF with the low-cost starch reduces the overall oxygen transmission at higher humidities while still allowing the TCNF to provide enhanced performance at low humidities.

Using the resistance of the two layers in series for the S1/TCNF/TP 40, the model predicts oxygen transmission rates of $0.6 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ and $89 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ for 20% RH and 80% RH, respectively. These can be compared to the average measured values for that condition of $0.27 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ and $34.7 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ for 20% and 80% RH, respectively. The modeled value is in the same order of magnitude as the measured but approximately a factor of three greater. This could be due to the fact the model assumes flat even layers when in reality the layers are coated onto paper fibers. The starch base coating partially encapsulates some of the paper fibers at the surface of the paper which may incorporate the fibers into the barrier properties. Oxygen can flow around paper fibers when just a porous mesh, but when starch encapsulates the fiber would extend the thickness of the solid mass oxygen has to permeate through.

A theoretical composite OTR of $106.8 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ was calculated based on the measured permeabilities and thicknesses of the starch and TCNF layers. In comparison, the experimentally measured OTR of the S1 / TCNF/TP 40 film was only $34.7 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$, indicating that additional oxygen blocking mechanisms must be present beyond mere layer stacking. Additionally, there is the potential for hemiacetal cross linking between oxidized TCNF and starch. The TCNF component carries surface aldehyde groups (via TEMPO oxidation). These aldehydes can form hemiacetal bonds with starch hydroxyls, effectively creating a partially cross-linked network at the interface that resists swelling and reduces moisture pressure. Such hemiacetal cross linking has been shown to improve the wet strength and barrier properties of TCNF starch films in previous studies (Hamid et al., 2024; Soni et al., 2020; Soni et al., 2021). This chemical linkage enhances structural stability and limits oxygen diffusion even at 80% RH conditions.

3.6. Gas barrier properties of this study compared to those of other studies at high humidity

The fully bio-based starch–TCNF multilayer coated paper exhibited excellent oxygen barrier performance across all humidity conditions, particularly at high relative humidity (80%). Its performance was comparable to the latest reported strategies. Wang et al. (2020) laminated a CNC film with polypropylene (PP) using a polyurethane (PU) adhesive layer to create a flexible multilayer film. This approach reduced the OTR of the CNC film from 126 to $6.1 \text{ cm}^3/(\text{m}^2 \cdot \text{day})$ and the WVTR from 516 to $1.0 \text{ g}/(\text{m}^2 \cdot \text{day})$ at 80% RH. Similarly, Yu et al. (2022)

Table 4

Resistance model parameters for the example of the S1/TCNF/TP 40 coated paper.

Materials	Density (g/cm ³)	L [μm]	P (20% RH) [cm ³ ·μm/(m ² ·day·atm)]	R(L/P) 20%RH [m ² ·day·atm / cm ³]	P (80% RH) [cm ³ ·μm/(m ² ·day·atm)]	R(L/P) 80%RH [m ² ·day·atm / cm ³]
Starch	1.5	9	12.2	0.738	903	0.010
TCNF	1.6	2	2.2	0.909	1574	0.001

prepared a multilayer film by first coating CNC onto PET film, followed by a top layer of short chitin nanowhiskers (ShNW)/chitosan (CS) suspension, achieving an OTR of 24.9 cm³/(m²·day) at 80% RH. While these methods significantly improved barrier properties under high humidity, they relied on non-renewable and non-biodegradable substrates such as PET and PP (Fotie et al., 2020; Wang et al., 2020; Yu et al., 2022). Additionally, cellulose nanocrystal (CNC) films crosslinked with Fe³⁺ ions showed an OTR reduction from 90 to 40–41 cm³/(m²·day) at 85% relative humidity (RH), while the WVTR reduced from 557 to 500 g m⁻²·day⁻¹ (Chen et al., 2022). However, metal ion crosslinking is not well-suited for coating processes, as the addition of metal salts alters the rheological properties of the CNM suspension, making it difficult to achieve uniform coatings. Additionally, the WVTR still needs to be reduced in the future for some water sensitive food or medicine packaging. Recent studies have explored organic–inorganic multilayer coating strategies to improve the gas barrier performance of paper-based packaging materials under humid conditions. For example, a multilayer paper-based composite film incorporating polyvinyl alcohol/polyacrylate organic layers and functionalized SiO₂@polydopamine nanoparticles as the inorganic barrier layer achieved excellent barrier performance, with the OTR reduced from over 50,000 cm³/(m²·day) for pristine paper to 0.31 cm³/(m²·day) at 23 °C and 50% RH for multilayer paper and the WVTR reduced from 1830.45–4.11 g/(m²·24 h) at 38 °C and 90% RH (Chen et al., 2024b). However, the system relied on synthetic polymers, inorganic nanoparticles, and silane crosslinking agents, which may reduce overall biodegradability and complicate recycling or repulping processes. More recent studies have continued to explore multilayer coating strategies for improving the barrier performance of paper-based packaging materials under humid conditions. Multilayer composite paper-based materials were prepared by successively coating calcium chloride-treated Kraft paper with modified sodium alginate (M-SA), acrylic emulsion (AE), and polyvinyl butyral (PVB) reduced the WVTR from 220.12 ± 7.12 g/(m²·24 h) for uncoated paper to 16.02 ± 0.45 g/(m²·24 h) at 38 °C and 90% RH, demonstrating that multilayer architectures are effective for improving moisture barrier properties (Ning et al., 2026). However, such systems still partially rely on synthetic polymer components, including acrylic emulsions and PVB layers. Therefore, our starch-anchored TCNF approach provides an effective strategy for maintaining oxygen and water vapor barrier performance at 80% RH while substantially reducing the required TCNF coating weight. This reduction in TCNF usage may improve the commercial feasibility and scalability of biodegradable CNM-coated paper packaging materials.

Industry-relevant benchmarks for high-barrier packaging materials require simultaneously maintaining an oxygen transmission rate (OTR) of ≤ 15.5 cm³/(m²·day) and a water vapor transmission rate (WVTR) of ≤ 10 g/m²·day across varying temperature and humidity conditions (PolyPrint, 2026). While the developed starch/TCNF/TP multilayer coatings substantially improved both oxygen and moisture barrier performance compared with uncoated paper, achieving OTR values between 0.2–0.7 cm³/(m²·day) at low humidity (20% RH), 0.9–2.8 cm³/(m²·day) at moderate humidity (50% RH), and 20.9–43.8 cm³/(m²·day) at high humidity (80% RH), as well as WVTR values between 15.8–40.9 g/m²·day at 20% RH, 106.6–270.6 g/m²·day at 50% RH, and 563.3–943.1 g/m²·day at 80% RH, the results demonstrate the effectiveness of the multilayer coating strategy in simultaneously enhancing oxygen and moisture barrier properties over a broad

humidity range. The coatings met the industry-relevant OTR benchmark at low and moderate humidity conditions and approached the target under high-humidity conditions. However, further improvements in water vapor barrier performance, particularly under elevated humidity conditions, are still required to fully satisfy the stringent requirements for industrial high-barrier packaging applications.

4. Conclusions

This study presents an effective approach to developing high-performance, sustainable paper coatings by using starch as a base layer beneath TCNF-based formulations. The addition of a plasticizer and increased processing temperature was employed to optimize the rheological properties of the TCNF coating solutions, enabling the formation of a uniform, thin TCNF coating layer. The starch pre-layer effectively filled the pinholes in the porous paper substrate, significantly reducing the required amount of costly TCNF coating. This strategy not only improves economic viability but also enhances oxygen and water vapor barrier performance, particularly under high humidity conditions (80% RH), as starch retains more of its inherent properties. As a result, the TCNF coating weight was reduced from 9.4 ± 0.9 g/m² to 3.1 ± 0.4 g/m², while maintaining functionality, with the starch base layer applied at 10.9 ± 1.2–26.78 ± 1.97 g/m². Notably, the inclusion of starch led to a 50% reduction in water vapor transmission rate (WVTR) and a 74.5–83.0% reduction in oxygen transmission rate (OTR) at 80% RH and 23 °C. This study provides further insight into development of biodegradable paper coatings with improved barrier properties under humid conditions, a major challenge in fiber-based packaging. These findings offer strong potential for replacing plastic films in food and pharmaceutical packaging applications where high humidity resistance is critical.

CRedit authorship contribution statement

Yufei Nan: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Daniel J. Franke:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Nicole M. Stark:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Laurent M. Matuana:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Cody A. Schilling:** Writing – review & editing, Formal analysis. **Ronald C. Sabo:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

ChatGPT was used only to improve the English language of the text after the draft was completed.

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Declaration of Competing Interest

The authors declare no conflict of interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.fpsl.2026.101815](https://doi.org/10.1016/j.fpsl.2026.101815).

Data availability

Data will be made available on request.

References

- Amara, C., Razzak, A., Khiari, R., Dufresne, A., & Khwaldia, K. (2024). Sustainable production of cellulose nanofibers and nanopaper sheets from olive pomace waste through mechanical defibrillation. *Biomass Conversion and Biorefinery*, 15, 16619–16631. <https://doi.org/10.1007/s13399-024-06296-5>
- Babaeipour, S., Solin, K., Virkkala, T., Nousiainen, P., Österberg, M., & Bras, J. (2026). Biobased barrier dispersion coating from solvent shifting of functionalized lignin inside cellulose nanofibers aqueous suspensions. *Food Packaging and Shelf Life*, 53, Article 101698. <https://doi.org/10.1016/j.fpsl.2026.101698>
- Cai, L., Yang, J., Wang, Y., Hu, F., Liang, B., Qiu, W., Song, S., & Yu, L. (2026). Quaternary ammonium chitosan-based film reinforced with antibacterial Pickering emulsion synergistically stabilised by shellac nanoparticles and ε-polylysine for fruit preservation. *Food Packaging and Shelf Life*, 53, Article 101699. <https://doi.org/10.1016/j.fpsl.2026.101699>
- Cainglet, H. E., Black, J. R., Udugoda, H., Nasiri, N., Diaz-Arenas, G. L., Garnier, G., Batchelor, W., & Tanner, J. (2025). Can pure cellulose nanofibril films replace polyolefins as water vapor barriers in packaging? *Journal of Colloid and Interface Science*, 678, 547–555. <https://doi.org/10.1016/j.jcis.2024.09.060>
- Chen, C., Sun, W., Wang, L., Tajvidi, M., Wang, J., & Gardner, D. J. (2022). Transparent multifunctional cellulose nanocrystal films prepared using trivalent metal ion exchange for food packaging. *ACS Sustainable Chemistry & Engineering*, 10(29), 9419–9430. <https://doi.org/10.1021/acssuschemeng.2c01805>
- Chen, C., Wang, L., Es-haghi, S. S., Tajvidi, M., Wang, J., & Gardner, D. J. (2024a). Biodegradable and recyclable bio-based laminated films of poly (lactic acid) and cellulose nanocrystals for food barrier packaging. *Food Packaging and Shelf Life*, 42, Article 101244. <https://doi.org/10.1016/j.fpsl.2024.101244>
- Chen, X., Xiao, B., Yang, Y., Jiang, Y., Song, X., Chen, F., Wang, W., Wu, J., & Meng, Y. (2024b). A novel paper-based composite film with enhanced oxygen and water vapor barrier properties. *Progress in Organic Coatings*, 186, Article 108042. <https://doi.org/10.1016/j.porgcoat.2023.108042>
- Fotie, G., Gazzotti, S., Ortenzi, M. A., & Piergiovanni, L. (2020). Implementation of high gas barrier laminated films based on cellulose nanocrystals for food flexible packaging. *Applied Sciences*, 10(9), 3201. <https://doi.org/10.3390/app10093201>
- Franke, D. J., Sabo, R. C., & Schilling, C. A. (2024). Durability of cellulose nanofibril films examined via residual drying stress measurement. *Cellulose*, 31, 10845–10859. <https://doi.org/10.1007/s10570-024-06245-5>
- Guyer, K., Machold, M., Tang, X., Bechle, N. J., Zhu, J. Y., Bujanovic, B. M., Plaza, N. Z., Kitin, P., Turner, K. T., & Considine, J. M. (2025). Microfibrillated cellulose coatings for biodegradable electronics. *Nordic Pulp & Paper Research Journal*, 40(2), 317–331. <https://doi.org/10.1515/npprj-2024-0086>
- Hamid, I. D. H. A., Soni, R., Hsu, Y.-I., & Uyama, H. (2024). TEMPO-oxidized cellulose nanofiber reinforced starch film with pH-responsive weakening and rapid marine-degradability. *Polymer Degradation and Stability*, 219, Article 110618. <https://doi.org/10.1016/j.polymdegradstab.2023.110618>
- Kim, H.-J., Roy, S., & Rhim, J.-W. (2021). Effects of various types of cellulose nanofibers on the physical properties of the CNF-based films. *Journal of Environmental Chemical Engineering*, 9(5), Article 106043. <https://doi.org/10.1016/j.jece.2021.106043>
- Kim, T., Kim, B. J., Bonacchini, G. E., Ostrovsky-Snider, N. A., & Omenetto, F. G. (2024). Silk fibroin as a surfactant for water-based nanofabrication. *Nature Nanotechnology*, 19(10), 1514–1520. <https://doi.org/10.1038/s41565-024-01720-3>
- Las-Casas, B., & Arantes, V. (2024). From production to performance: Tailoring moisture and oxygen barrier of cellulose nanomaterials for sustainable applications—A review. *Carbohydrate Polymers*, 334, Article 122012. <https://doi.org/10.1016/j.carbpol.2024.122012>
- Mazhari Mousavi, S. M., Afra, E., Tajvidi, M., Bousfield, D., & Dehghani-Firouzabadi, M. (2017). Cellulose nanofiber/carboxymethyl cellulose blends as an efficient coating to improve the structure and barrier properties of paperboard. *Cellulose*, 24, 3001–3014. <https://doi.org/10.1007/s10570-017-1299-5>
- Mujtaba, M., Lippinen, J., Ojanen, M., Puttonen, S., & Vaittinen, H. (2022). Trends and challenges in the development of bio-based barrier coating materials for paper/cardboard food packaging; a review. *Science of The Total Environment*, 851, Article 158328. <https://doi.org/10.1016/j.scitotenv.2022.158328>
- Nan, Y., Franke, D. J., Schilling, C. A., Sabo, R. C., Stark, N. M., & Matuana, L. M. (2026). Functional multilayer films with nanocellulose core and plastic outer layers for high-performance oxygen and water vapor barrier food packaging. *Trends in Food Science & Technology*, 173, Article 105750. <https://doi.org/10.1016/j.tifs.2026.105750>
- Ning, Y., He, Y., Wang, C., Wei, Y., Dong, R., Chen, F., Bi, H., & Chen, G. (2026). Cellulose-based coated paper with high water vapor barrier properties through multi-scale structural synergy for sustainable packaging. *International Journal of Biological Macromolecules*, Article 150118. <https://doi.org/10.1016/j.ijbiomac.2026.150118>
- Paudel, S., Regmi, S., & Janaswamy, S. (2026). Cellulose-based packaging from agricultural residues: Extraction technologies, functional performance, emerging applications and future prospects. *Packaging Technology and Science*, 39(6), 811–828. <https://doi.org/10.1002/pts.70065>
- PolyPrint. (2026). Understanding film properties: Flexographic OTR and WVTR values. <https://www.polyprint.com/understanding-film-properties/flexographic-otr> (accessed June 2, 2026).
- Priyadarshi, R., Khan, A., & Rhim, J. W. (2025). Carrageenan-based washable coatings integrated with sulfur quantum dots for extending banana shelf life. *Food Packaging and Shelf Life*, 47, Article 101425. <https://doi.org/10.1016/j.fpsl.2024.101425>
- Ren, Y., Fan, X., Cao, L., & Chen, Y. (2024). Water-resistant and barrier properties of poly (vinyl alcohol)/nanocellulose films enhanced by metal ion crosslinking. *International Journal of Biological Macromolecules*, 277, Article 134245. <https://doi.org/10.1016/j.ijbiomac.2024.134245>
- Roy, S., Ghosh, B. D., Goh, K. L., Muthoka, R. M., & Kim, J. (2022). Modulation of interfacial interactions toward strong and tough cellulose nanofiber-based transparent thin films with antifogging feature. *Carbohydrate Polymers*, 278, Article 118974. <https://doi.org/10.1016/j.carbpol.2022.118974>
- Sabo, R., Schilling, C., Clemons, C., Franke, D., Gribbins, N. R., Landry, M., Hoxie, K., & Kitin, P. (2024). Grease, oxygen, and air barrier properties of cellulose-coated copy paper. *Polysaccharides*, 5(4), 783–806. <https://doi.org/10.3390/polysaccharides5040049>
- Samyn, P., Van Erps, J., & Thienpont, H. (2016). Relation between optical non-contact profilometry and AFM roughness parameters on coated papers with oil-filled nanoparticles. *Measurement*, 82, 75–93. <https://doi.org/10.1016/j.measurement.2015.12.035>
- Schiessl, S., Kucukpinar, E., Cros, S., Miesbauer, O., Langowski, H. C., & Eisner, P. (2022). Nanocomposite coatings based on polyvinyl alcohol and montmorillonite for high-barrier food packaging. *Frontiers in Nutrition*, 9, Article 790157. <https://doi.org/10.3389/fnut.2022.790157>
- Soni, R., Asoh, T.-A., Hsu, Y.-I., Shimamura, M., & Uyama, H. (2020). Effect of starch retrogradation on wet strength and durability of cellulose nanofiber reinforced starch film. *Polymer Degradation and Stability*, 177, Article 109165. <https://doi.org/10.1016/j.polymdegradstab.2020.109165>
- Soni, R., Hsu, Y.-I., Asoh, T.-A., & Uyama, H. (2021). Synergistic effect of hemiacetal crosslinking and crystallinity on wet strength of cellulose nanofiber-reinforced starch films. *Food Hydrocolloids*, 120, Article 106956. <https://doi.org/10.1016/j.foodhyd.2021.106956>
- Venkatesan, R., Sivaprakash, P., Kim, I., Tawfeek, A. M., & Kim, S.-C. (2024). Green synthesis of carbon nanoparticle-reinforced nanocomposites with gallic acid as a crosslinking agent on poly (butylene adipate-co-terephthalate): Preparation, characterization, and performances. *Industrial Crops and Products*, 209, Article 117949. <https://doi.org/10.1016/j.indcrop.2023.117949>
- Wang, H., Mai, Y.-A., Qiu, W., Liu, W., Yang, D., Fang, Z., & Qiu, X. (2025). Water-, oil-, and stain-resistant lignin-based degradable waterborne polyurethane for paper packaging coating. *ACS Sustainable Chemistry & Engineering*, 13(3), 1292–1303. <https://doi.org/10.1021/acssuschemeng.4c08269>
- Wang, J., Gardner, D. J., Stark, N. M., Bousfield, D. W., Tajvidi, M., & Cai, Z. (2018). Moisture and oxygen barrier properties of cellulose nanomaterial-based films. *ACS Sustainable Chemistry & Engineering*, 6(1), 49–70. <https://doi.org/10.1021/acssuschemeng.7b03523>
- Wang, L., Chen, C., Wang, J., Gardner, D. J., & Tajvidi, M. (2020). Cellulose nanofibrils versus cellulose nanocrystals: Comparison of performance in flexible multilayer films for packaging applications. *Food Packaging and Shelf Life*, 23, Article 100464. <https://doi.org/10.1016/j.fpsl.2020.100464>
- Yaduraj, S., & Kumari, U. (2016). Measurement of thickness and roughness using gwyddion. In *2016 3rd International Conference on Advanced Computing and Communication Systems (ICACCS)*, 1 pp. 1–5. IEEE.
- Youngblood, J. P., Azrak, S. M. E. A., Moon, R. J., & Schueneman, G. T. (2022). Composition of cellulose nanocrystals and carboxymethyl cellulose. *Google Patents*.
- Yu, Z., Ji, Y., & Meredith, J. C. (2022). Multilayer chitin–chitosan–cellulose barrier coatings on poly (ethylene terephthalate). *ACS Applied Polymer Materials*, 4(10), 7182–7190. <https://doi.org/10.1021/acscapm.2c01059>
- Zhao, Y., Troedsson, C., Bouquet, J.-M., Thompson, E. M., Zheng, B., & Wang, M. (2021). Mechanically reinforced, flexible, hydrophobic and UV impermeable starch-cellulose nanofibers (CNF)-lignin composites with good barrier and thermal properties. *Polymers*, 13(24), 4346. <https://doi.org/10.3390/polym13244346>

- Zhang, J., & Youngblood, J. P. (2025). Cellulose nanofibril-based hybrid coatings with enhanced moisture barrier properties. *Materials Advances*, 6(9), 2833–2844. <https://doi.org/10.1039/D4MA01276C>
- Zheng, C., Lyu, G., Janaswamy, S., Yang, G., Guo, Z., & Ji, X. (2026). High-strength, high-barrier active packaging films from lignin-compatible cellulose and beeswax. *Food Packaging and Shelf Life*, 55, Article 101739. <https://doi.org/10.1016/j.fpsl.2026.101739>
- Zuber, S. A., Rusli, A., & Ismail, H. (2019). Effectiveness of triacetin and triethyl citrate as plasticizer in polyvinyl alcohol. *Materials Today: Proceedings*, 17, 560–567. <https://doi.org/10.1016/j.matpr.2019.06.335>