

Review

Multifunctional polymer composite coatings and adhesives by incorporating cellulose nanomaterials

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SUMMARY

Regardless of their applications, polymers are still considered mechanically weak and functionally insufficient for certain demanding coating and adhesive uses. To address those issues, nanomaterials have been extensively studied as reinforcing fillers, which have been proven to effectively promote the performance of polymer coatings/adhesives. However, conventional nanofillers are expensive and non-biodegradable. Meanwhile, cellulose nanomaterials (CNMs), a class of nanomaterials produced from biomass feedstocks, can circumvent the drawbacks of conventional nanofillers. This review paper first focuses on the multi-functionalities CNMs bring to polymer coatings, including mechanical reinforcement (wear resistance and hardness enhancement), gas barrier, flame resistance, corrosion resistance, self-healing (controlled-release), optical regulation, self-cleaning/antifouling, and antimicrobial characteristics. Then we discuss the benefits of CNM addition to polymer adhesives, such as mechanical enhancement, curing promotion, volatile organic compound (VOC) suppression, and electrical conductivity. Finally, we provide insights into future research efforts with CNMs. The goal of this paper is to promote the pilot-scale study and commercial use of CNMs as multifunctional additives in green and sustainable polymer composite coating and adhesive formulations.

INTRODUCTION

Polymeric coatings are often used to protect substrates from chemical, physical, and biochemical degradation. Numerous base polymers are used for coating formulations, including both thermoplastics (waxes, elastomers, ethylene vinyl alcohol copolymer, etc.) and thermosets (phenolic resins, acrylics, epoxies, etc.).¹ Among them, polyurethanes (PUs), epoxies, acrylic resins, and polyesters are the most intensively investigated for nanocomposite coating innovations.^{2–5} Polymeric adhesives can be classified into two major groups: natural (starch, lignin, animal glue, protein, natural rubber, etc.) and synthetic (acrylics, epoxies, silicones, etc.).⁶ The most studied base polymers for nanocomposite adhesive applications are epoxies, PUs, acrylics, and silicones.⁶ These base polymers are popularly adopted because of their excellent processability, chemical resistance, strong adhesion, and reasonable cost.³ Despite their extensive applications, the properties of the base coating polymers may not be sufficient for durable service. For example, epoxies can have poor

PROGRESS AND POTENTIAL

From early-stage natural ingredients to modern synthetic formulations, polymeric coatings and adhesives have been playing indispensable roles throughout human history. The modern synthetic polymeric coatings and adhesives are criticized for the lack of renewable components in their formulations, negative environmental impact, and sometimes insufficient protection to their substrates. Cellulose nanomaterials (CNMs) are an interesting class of nanomaterials, derived from biomass. The large surface area, superior mechanical properties, and biodegradable nature of CNMs make them highly suitable for various applications, including biomedical implants, food packaging, polymer composites, sensors, and wastewater treatment. Among them, the polymer composite applications have been intensively investigated. Developing nanocomposite coatings and adhesives can potentially address the drawbacks of existing formulations. Here we reviewed the progress of multi-functionalizing polymeric coatings and adhesives through CNM incorporation.

crack resistance, low abrasion/wear resistance, and low barrier to moisture and gases. These issues can be additive by allowing water, oxygen, ionic species, and/or biological agents to attack the protected surface and start degradation via various mechanisms.³ Meanwhile, the structural applications of polymer adhesives require the polymers to possess high stiffness and strength achieved through increasing crosslinking density, which unfortunately can cause undesirable brittleness.⁷ Structural adhesives should be toughened without deteriorating their stiffness and strength.

One way to enhance the performance of coating/adhesive base polymers is through nanofiller incorporation. Nanofillers have been formulated to bring multi-functionality to the base polymers, enhancing their mechanical performance (crack resistance, wear resistance, etc.) and making them^{3,8} corrosion resistant,⁴ antifouling,⁹ and antibacterial.¹⁰ Numerous nanofillers have been investigated for polymer nanocomposite applications, including nanoclays, carbon nanotubes, metal or metal-oxide nanoparticles, ceramic nanoparticles, and cellulose nanomaterials (CNMs).^{2–4} Compared with other nanomaterials, CNMs can be equally effective in enhancing polymer matrices while also having considerable environmental benefits, including being renewable, biodegradable, nontoxic, and less energy intensive during production.¹¹ For example, 5 wt % nanosilica addition to an epoxy coating reduced its mass loss during an abrasion test by 30%.¹² Similarly, the abrasion mass loss of a CNM-reinforced acrylic composite coating (10 wt % fiber content) was also ~30% lower than the base polymer.¹³

CNMs are predominately produced from woody biomass with some more unusual variants derived from bacteria and tunicates. CNMs are classified according to their morphology and origin, with a large volume produced from plants, typically wood fibers (Figure 1A). Refined wood fibers such as microcrystalline cellulose (MCC) are another source for generating CNMs (Figure 1B). Both mechanical fibrillation and acid hydrolysis can be applied to isolate CNMs from their raw materials. Mechanical fibrillation generates CNMs with a hierarchical branched architecture spanning orders of magnitude in both length and width from micron-long fibers to nanometer-wide fibrils.¹⁴ These nanomaterials are typically referred to as cellulose nanofibril (CNF), although cellulose microfibril (CMF) and microfibrillated cellulose (MFC) are sometimes used in the literature (Figure 1C).¹¹ CNF can contain cellulose, hemicellulose, and lignin components depending on the various pretreatments applied to the starting material. The flexible hemicellulose segments of CNF enable it to bend and entangle to form an intense network structure. Chemical treatments can be applied before mechanical fibrillation, which produces CNF with different morphology.¹⁵ For example, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was used to oxidize cellulose fibers. With sonication, homogeneous CNF was produced and named TEMPO-oxidized CNF (TOCN), as displayed in Figure 1D.¹⁶ The dimensions of TOCN are 4–10 nm in width and a few microns in length.¹⁷ The TEMPO treatment can significantly increase the surface charge of CNF, depending on treatment conditions. Acid hydrolysis produces rod-like CNMs with a smaller aspect ratio (5–20 nm wide, 50–350 nm long).¹⁷ Such nanomaterials are called cellulose nanocrystals (CNCs) or cellulose nanowhiskers (CNWs) (Figure 1E).¹⁸ Attributable to the strong acid-catalyzed hydrolysis of the amorphous cellulose regions, CNCs are much shorter and more crystalline than CNFs, with higher surface charge, depending on hydrolysis conditions. Besides being produced from plants via mechanical/chemical means, animals/bacteria are also sources of CNMs. Tunicates can be acid hydrolyzed to generate tunicate-CNCs (t-CNCs) with a higher aspect ratio (~20 nm wide and 100–4,000 nm) than plant-derived CNCs (Figure 1F). Algae is another good source for producing CNMs (Figure 1G). Certain bacteria can secrete

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<https://doi.org/10.1016/j.matt.2022.11.024>

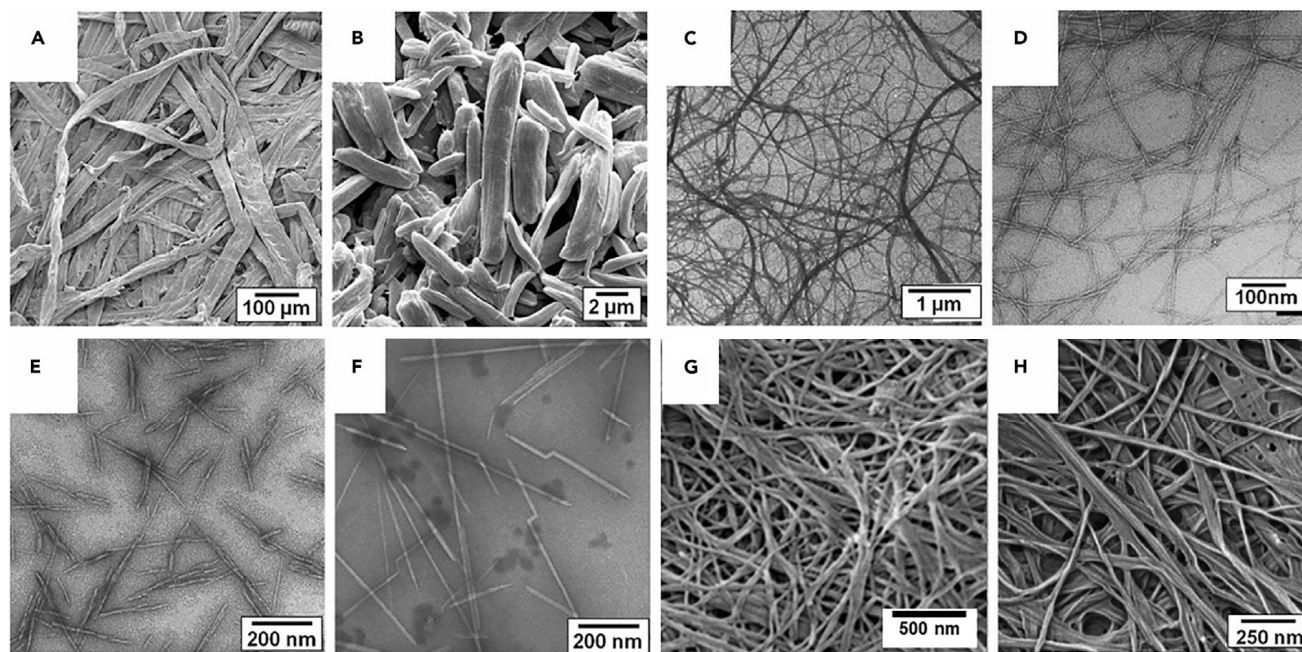


Figure 1. Various types of CNMs and their origins

(A–H) Scanning electron microscopy (SEM) graphs of wood fiber (WF) (A), microcrystalline cellulose (MCC) (B), transmission electron microscopy (TEM) images of cellulose microfibril (CMF) (C), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibrils (TOCN) (D), cellulose nanocrystals (CNCs) from wood (E), CNCs from tunicate (F), algae cellulose particles (G), and SEM image of bacterial cellulose (BC) (H). (A, B, E, and F) Reprinted from Moon et al.¹⁸ with permission from the Royal Society of Chemistry. (C) Reprinted from Dufresne et al.¹⁹ by permission from John Wiley & Sons. (D) Reprinted with permission from Saito et al.,¹⁶ copyright (2007) American Chemical Society. (G) Reprinted from Mihranyan.²⁰ (H) Reprinted with permission from Ifuku et al.,²¹ copyright (2007) American Chemical Society.

bacterial cellulose (BC) whose diameter is at the nanoscale (Figure 1H). BC's aspect ratio and morphology depend on the specific bacteria and culturing conditions.¹⁸ Thus, these different physical and chemical structures are important to understand as they can profoundly affect composite properties.

Multiple methods were investigated for processing CNM-reinforced polymer composites, including solvent casting, melt extrusion, layer-by-layer dip coating, fiber partial dissolution, spraying, spinning, and resin impregnation.^{22,23} Schemes of such processes are shown in Figure 2. Readers can refer to Oksman et al.²² for a detailed description on each process. Thermoplastic composites are often produced by extrusion, while resin impregnation is the common method to process thermoset composites. The most challenging issue in producing high-performance CNM-reinforced polymer composites is how to achieve nanoscale dispersion of fibers in a polymer matrix, especially in thermoplastics whose melt viscosity is adversely high.²³ Once CNM-reinforced polymer composites are well prepared, the next step is to identify proper methods to apply them to a substrate. A few techniques were utilized to apply coating materials to their substrates; for instance, rod coating, slot die coating, extrusion coating, roll coating, screen coating, flexography, ink-jet printing, and plasma/chemical/electro-deposition.¹ Partially overlapping with coating methods, the application methods of polymer adhesives depend on their forms, typically including brushing, flowing, spraying, roll coating, knife coating, silk screening, oil can and squeeze bottle, dip coating, and extrusion.⁶

With adequate reviews available for polymer nanocomposite coatings/adhesives containing non-cellulosic nanoparticles,^{4,5,8,9,25} reviews of the coating/adhesive

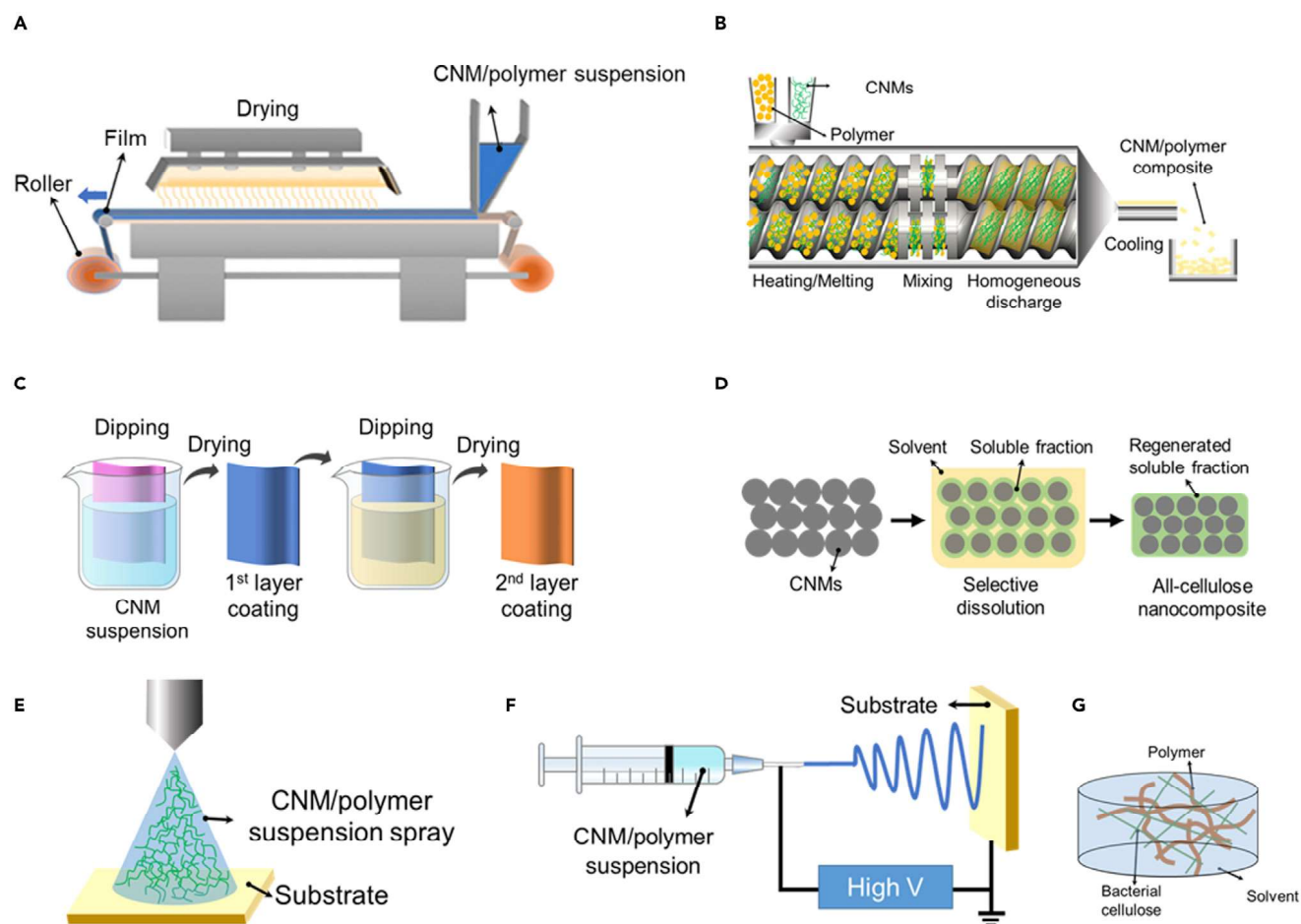


Figure 2. Processing methods of cellulose nanomaterial (CNM)-reinforced polymer composites

(A) solvent casting
(B) melt extrusion
(C) layer-by-layer dip coating
(D) partial dissolution to produce all cellulose nanocomposites
(E) spray coating
(F) spinning
(G) resin impregnation. Reprinted from Silva et al.²⁴

applications of CNM-reinforced polymer composites are limited.^{26,27} A few relevant review papers are available. However, they either focus on using CNMs alone^{28,29} or only covered the topics of this review as a subsection.^{30,31} In the past 5–10 years, there have been increasing research activities centered on the coating/adhesive applications of CNM-reinforced polymer composites. The CNM incorporation provided interesting multi-functionalities to base polymers. From our assessment, a review paper will be necessary and beneficial. The objectives of this review are to (1) selectively summarize those research activities focusing on utilizing CNMs to impart multi-functionalities to polymer coatings/adhesives, mainly in the past 5–10 years, and (2) to analyze research outcomes and provide insights on future research needs. The common ground between the coating and adhesive applications of CNM-reinforced polymer composites regarding their material preparation and application methods justifies the combination of those two areas in one review paper.

CNM-FUNCTIONALIZED POLYMER COATINGS

Barrier-related performances

While CNMs are promising replacements for petroleum-based polymers in barrier applications as a single component, CNM-reinforced polymer composite coatings also garner considerable attention. In general, the barrier properties of a polymer coating are controlled by the diffusivity of molecules through the coating. The incorporation of highly crystalline CNMs with high aspect ratios in composites reduces the penetration of molecules by creating a more tortuous path (Figure 3A),³² thus improving the barrier properties of the reinforced packaging materials. Therefore, a dense, nonporous film or coating containing CNMs can be used for barrier application. Despite their morphological differences, CNCs and CNF showed similar barrier performance, attributed to the similar tortuous paths created by them in a matrix.³³

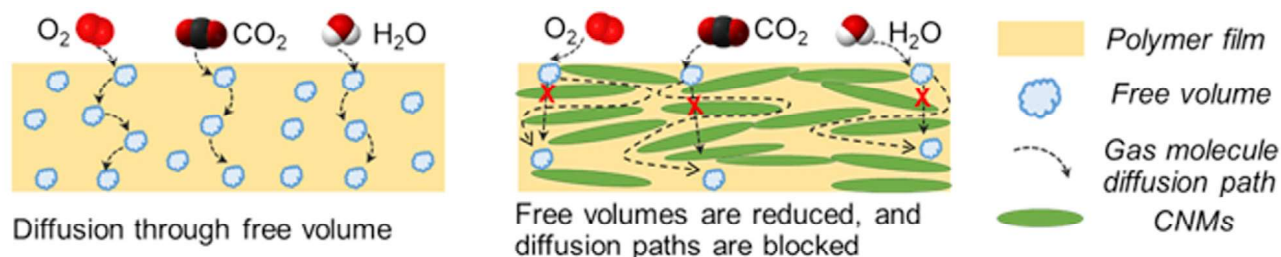
Gas-barrier property

Various CNM-reinforced polymer composite formulations have been developed to coat different substrates for gas-barrier applications.^{34–36} Because of the hydrophilic nature of the CNMs, hydrophilic polymers have principally been studied as matrices owing to a better dispersion of CNMs in the final composite.^{34,36} For instance, a CNF/polyvinyl alcohol (PVA) coating has been shown to improve a polypropylene (PP) film's oxygen barrier and CO₂ barrier performances by 96% and 90%, respectively, compared with a neat PP substrate.³⁴ The synergistic effect of the aligned CNCs and a lower free volume (PVA occupied the free volume of the interfacial space) was the basis of such improvements. The coating demonstrated excellent barrier performance compared with high barrier ethylene vinyl alcohol copolymer (EVOH) films. In another study, a CNC-reinforced UV-curable acrylic coating reduced the water vapor transmission rate (WVTR) and water vapor permeability (WVP) of the virgin polymer because of the tortuous path created by CNCs.³⁷ An emerging barrier application of CNC/polymer composites is protective coatings for fruit preservation.^{38–40} For instance, CNCs were added to chitosan coating to reduce oxygen and moisture transmission.³⁸ It was reported that, with less O₂, ethylene production was greatly reduced, attributable to an altered internal gas atmosphere. Therefore, the ripening and quality deterioration (browning, reduced firmness, weight/water loss, etc.) of pears was delayed.

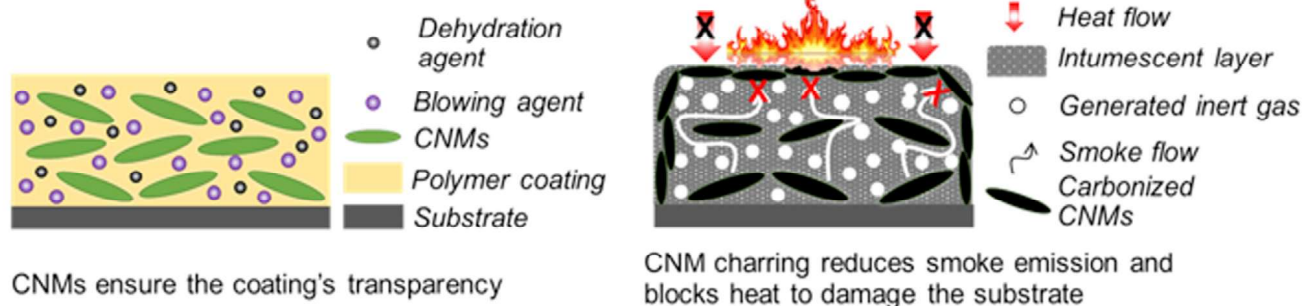
Thermal/flame resistance

Thermal stability is among the most important topics for polymer coating research, especially for automotive and aerospace applications where high-temperature conditions often exist.⁴¹ CNMs possess a unique degree of thermal and flame retardancy as a result of their nanoscale morphology.⁴² Several authors explored the effects of CNM inclusion on the thermal stability and flame retardancy of polymer coatings.^{41,43–46} Generally, the improved thermal stability of CNM addition is ascribed to the formation of hydrogen bonding between CNMs and certain polymers, such as PVA.⁴¹ In one example, CNC-reinforced photocurable acrylic resins exhibited better thermal stability than that of an MCC-reinforced one, at a lower fiber content.⁴⁴ Similarly, the onset degradation temperature of a CNC/acrylic (5 wt % CNCs) composite coating was seen to increase from 400°C to 412°C with the addition of CNCs. The addition of CNF to polymer composite coatings has also been shown to improve their flame retardancy. Pan et al.⁴⁶ modified CNF with melamine, phytic acid, and polyethylenimine (PEI) via layer-by-layer coatings. Heat release rate (HRR) and total heat release (THR) were measured using a microscale combustion calorimeter. The layer-by-layer structure was effective in improving PVA's thermal stability and flame retardancy, which was attributed to the formation of an intumescent system by adsorbed chemicals, as shown in Figure 3B. CNF acted as the carbon source, phytic acid as the acid source, and a combination of melamine and PEI acted as blowing agents.

A Coating for gas barrier



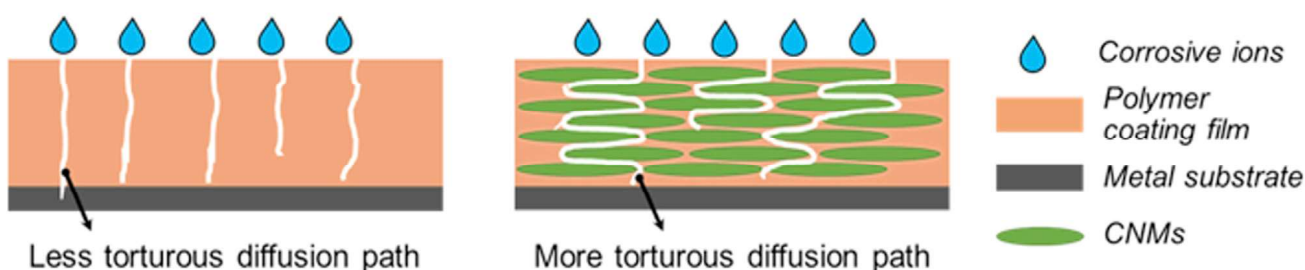
B Flame retardant coating



CNMs ensure the coating's transparency

CNM charring reduces smoke emission and blocks heat to damage the substrate

C Anticorrosive coating



D Coating for slow release

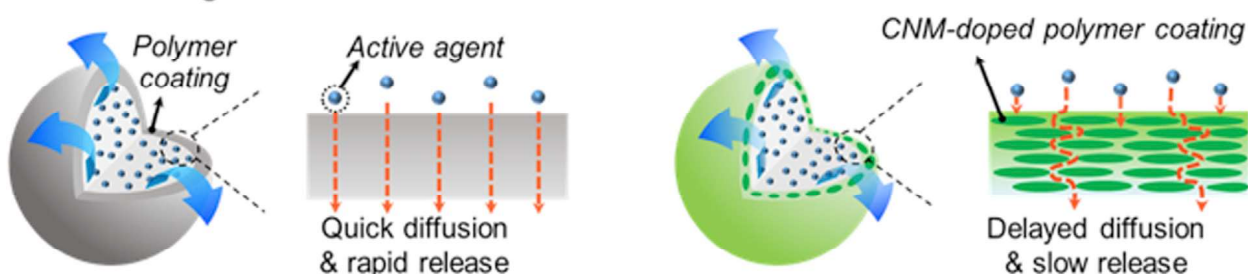


Figure 3. Coatings incorporating CNMs for multiple purposes

(A) Scheme of improved gas-barrier performance of CNM/polymer composite coatings as a result of the free volume filled by CNMs and new tortuous paths.

(B) Scheme of an intumescent flame-retardant polymer composite coating where CNMs act as the carbon source and produce tortuous paths.

(C) Protection mechanism of a polymer-coated metal surface with CNMs producing tortuous paths.

(D) A polymer microcapsule with CNMs in the shell to impede the diffusion of released chemicals.

Corrosion resistance

Corrosion is a naturally occurring metal deterioration process that happens because of the physicochemical interactions between metals and their surrounding environment. The annual economic loss associated with metal corrosion is estimated to be

US\$2.5 trillion worldwide.⁴⁷ Applying organic coatings such as epoxies, urethanes, and acrylates to metal surfaces is the most effective and widely used method in metal protection. Polymer coatings usually serve as a physical barrier that provides passive protection to metal surfaces by impeding the access of corrosive species such as O₂, H₂O, and aggressive anions to the metal surface. The common mechanisms used in corrosion-resistant CNM-reinforced polymer coatings on metals are retarding the penetration/diffusion of corrosive-substances, facilitating the templated-synthesis of anti-corrosive agents, and controlling the release of anti-corrosive agents.

Polymer coatings usually contain free volume and micro-voids that greatly influence barrier performance.⁴⁸ Adding nanoparticles or nano-crosslinkers is recognized as a simple and effective method for enhancing the polymer coatings' properties.⁴⁹ CNMs have been used for reinforcing anti-corrosive polymer coatings because of their high surface area, excellent mechanical properties, and surface functionality, which play an important role in its anti-corrosion mechanisms. A CNF/graphene oxide/zinc oxide (ZnO) nanocomposite was prepared for waterborne polyester coating reinforcement, where CNF served as a template for the nucleation of ZnO nanorods.⁵⁰ In comparison with the neat coating, the reinforced coating exhibited better tensile strength, impact resistance, adhesion resistance, and corrosion resistance. The improved corrosion resistance can be partially attributed to the barrier property of CNF, as shown in Figure 3C. Anema et al. prepared CNC-reinforced anti-corrosive epoxy coatings by the direct addition of dried CNCs into epoxy resin, with mechanical stirring and sonication employed during CNC addition to ensure a good dispersion of CNCs in the coating polymer.⁵¹ The reinforced epoxy coating with 1 wt % of CNCs exhibited superior corrosion resistance with a maintained high impedance modulus at 0.1 Hz ($|Z|_{0.1}$) of $10^9 \Omega \text{ cm}^2$ even after 30 days of immersion in 3.5 wt % NaCl solution, which is three orders higher than that of the neat epoxy coating. The enhanced corrosion resistance was mainly attributed to a decrease in coating porosity through coating pore filling by CNCs. Interestingly, increasing the CNC loading from 1 to 2 wt % decreased the corrosion resistance of the epoxy coatings because the aggregation of CNCs induced structural defects.

Although direct incorporation of dried CNMs into coating chemicals is simple, it is challenging to fully disperse the dried CNM aggregates because the majority of the coating chemicals have high viscosity and low polarity. This issue can be resolved by surface modification of CNMs to reduce their polarity and increase their compatibility with coating chemicals. Alternatively, solvent-assisted dispersion is a good laboratory-scale method for dispersing CNMs into coating matrices for anti-corrosive applications. For instance, dimethylformamide has been used to disperse CNCs in PU coatings because of its compatibility with both CNCs and PU coating chemicals.⁵² CNCs served as a nano-barrier in the film that significantly enhanced the corrosive resistance of PU coating.

Slow release

The barrier properties of CNM-reinforced composites make them effective at controlling the slow release of chemicals. One example of this is how a coating matrix can slow the release of fertilizers by reducing their contact with water. Fertilizer formulations containing poly(3-hydroxybutyrate) (PHB), thermoplastic starch (TPS), CNF, and potassium nitrate, were developed and evaluated.⁵³ PHB is a biodegradable and environmentally friendly polymer. Starch, another biodegradable polymer, was blended with PHB to lower the material cost and improve processability.⁵³ Because of the physical interactions between CNF and potassium nitrate fertilizers, CNF was believed to assist the dispersion of fertilizers in the matrices. Fertilizers

were encapsulated with CNF by spray drying and the dried mixtures were melt compounded with PHB and TPS. The results showed that CNF encapsulation reduced the K^+ release rate from 24.3%/10 min to 19.2%/10 min in the matrix of PHB/TPS. In another study, chitosan, fertilizers, and CNF were blended and formed into particles by spray drying.⁵⁴ A chitosan-only coating delayed the fertilizers' initial release rate by 2 h through ionic interaction, while a chitosan/CNF coating with 10 wt % CNF delayed it by 5 h. When present, CNF appears to act as a barrier layer, further slowing down the release rate of the fertilizers.

Besides fertilizers, He et al. investigated the slow release of antibacterial agents through a CNC-polymer coating for food packaging application.⁵⁵ To reduce the toxicity of accumulated silver nanoparticles (AgNPs) in the human body and maintain their antibacterial activity, AgNPs were immobilized onto the CNC surfaces in an aqueous suspension, with sodium citrate as a green reductant. The resulting AgNPs@CNCs were incorporated into carboxymethyl cellulose (CMC) solutions to form composite coatings for dip coating paper packaging. The CMC/AgNPs@CNCs coating extended the shelf life of paper packaged strawberry up to 7 days, while uncoated paper package did not reach that duration. Yoo incorporated CNCs in poly(urea-urethane) shell structures to create sustained-release microcapsules.⁵⁶ The CNCs were modified with lactic acid oligomers and fatty acids to assist their dispersion in the polymeric shell. CNCs prolonged the release of dyes by extending their diffusion paths through the shell, as shown in Figure 3D. For instance, the complete release time of 2-ethyl-1-hexanol was improved from 4 to 10 h when 7.5 wt % CNCs were introduced to the polymeric shell.

Mechanical performance

This section of the review covers the improvements in the mechanical properties of polymer coatings reinforced with CNMs, which are summarized in Table 1.

Strength/strain/modulus of elasticity

A full scope of studies investigating the strength/strain/modulus of elasticity properties of CNM-reinforced polymer composite coatings are summarized in Table 1. CNMs can readily reinforce hydrophilic polymers or polymers formed via emulsion polymerization with water as the processing/dispersion aid, where a small amount of CNMs was reported to improve the polymer mechanical performance.^{64,68,70,71,80} Generally, rod-like CNCs or TOCN can be more easily dispersed in low-viscous matrices than CNF. CNF forms intensive entangled networks, making them difficult to disperse. For instance, Cheng et al. reinforced water-based polyurethane (WPU) with 0.1–5 wt % TOCN.⁷⁶ The tensile strength and Young's modulus values of neat WPU were 4.7 and 8.59 MPa, respectively, which were increased to 11 and 440 MPa, respectively, in the coating containing 5 wt % TOCN. However, the elongation at break decreased from 629% (neat WPU coating) to 50% (5 wt % TOCN reinforced WPU coating). The increase of WPU's mechanical properties were attributed to the strong interfacial adhesion between WPU and TOCN via hydrogen bonding and the formation of entangled TOCN network in the polymer matrix (Figure 4).

The surface energetics of many CNM varieties are often incompatible with those of the polymer matrices used in composite production. Such incompatibility results in insufficient dispersion of CNMs in the polymer, which leads to ineffective reinforcement. CNF-reinforced (0.5–10 wt %) epoxy nanocomposites from sugarcane bagasse were investigated.⁷⁷ The tensile strength and Young's modulus were found to be 23.7 ± 1.8 MPa and 1.27 ± 0.86 GPa for neat epoxy, respectively. The tensile properties of the CNF-epoxy nanocomposites were seen to increase up to 3 wt %

Table 1. Mechanical properties of polymer composite coatings reinforced with CNMs

Polymer matrix ^a	CNM type/source ^b	Modification ^c	Processing methods	Mechanical property change percentage			Reference
				Strength/strain/modulus of elasticity ^d	Wear resistance	Hardness	
Acrylic (butyl acrylate, BA-methyl methacrylate, MMA copolymer)	CNCs, 6 wt %, FD powder/NA	IEM	solution casting	strength: ↑100% strain at break: ↓31%	–	↑53%	Dogan-Guner et al. ⁵⁷
Acrylic (acrylic oligomers, methacrylate, and acrylate monomers)	CNCs, 1 wt %, FD powder/NA	HDTMA	UV curable	reduced modulus: ↑95%	–	↑200%	Kaboorani et al. ⁴¹
Acrylic	CNCs, 3 wt %, FD powder/NA	HDTMA	UV curable	strength: ↑32% strain at break: ↓13% MOE: ↑36%	↑93%	↑18%	Kaboorani et al. ⁵⁸
Polyurethane-acrylate	CNCs, (22.5 wt % CNC-IBOA suspension), FD powder/NA	AOI	UV curable	↑20%	–	↑ from 2B to HB ^o	Lee et al., 2021 ⁵⁹
Furan resin	CNCs, 20 wt %, FD powder/NA	No modification	dip coating	E _c : ↓9% E' glass: ↓13%	–	–	Asaro et al. ⁶⁰
Polyurethane-acrylate	CNCs, 2 wt %, powder/NA	HDTMA, TMA, C ₃ H ₅ ClO	UV curable	–	abrasion: ↑37% scratch: ↑27%	no significant difference	Vardanyan et al. ⁶¹
Non-polar polymer (acrylate AESO)	CNCs, 2 wt %, FD powder/NA	HDTMA, acryloyl chloride	UV curable	strength: ↑36% strain at break: ↓25%–141% MOE: ↑54%	–	↑ from F to 6H ^o	Auclair et al. ⁶²
Cationic starch	CNCs, 5 wt %, suspension/cotton	no modification	bar coating	tensile index: ↑20%	–	–	Vaezi et al. ⁶³
Polyaniline	CNCs, 4 wt %, suspension/NA	no modification	rod coating	tensile index: ↑14.6% folding strength: ↑30.7%	–	–	Huang et al. ⁶⁴
PVA	CNCs, 6 wt %, FD powder/cotton	polydopamine (coated)	free-standing films	strength: ↑75.8% Young's modulus: ↑69.2% elongation at break: ↑58.1%	–	–	Liu et al. ⁶⁵
PVA	CNCs, 6–12 wt %, powder/NA	lignin (coated)	spray coating	–	abrasion cycles: ↓ from 5 to 1	–	Huang et al. ⁶⁶
Polyurethane	CNCs, 65 wt %, suspension/NSBK	no modification	brush coating	–	–	↑3H ^o shore D: ↑81	Chowdhury et al. ⁶⁷
Polyurethane-acrylate	CNCs, 1 wt %, suspension/Ramie	no modification	free-standing films	strength: ↑20%–95% Young's modulus: ↑16.6%–27.7%	–	–	Furtak-Wrona et al. ⁶⁸
Bio-polyester methacrylate	CNCs, 2.5–7.5 wt %, powder/NA	no modification	UV curable	strength: ↓13% elongation at break: ↓10% bending strength: ↑33% bending modulus: ↑79%	–	shore D: ↑21.3% ↑ from 4H to 5H ^o	Tian et al. ⁶⁹
Polyvinyl alcohol	CNCs, 10 wt %, gel/NSBK	no modification	solvent casting, bar coating	Young's modulus: ↑76%	–	–	Niinivaara et al. ⁷⁰
Acrylic/polyester	CNF, 20 wt %, suspension/Poplar	γ-aminopropyltriethoxysilane	free-standing films	Young's modulus: ↑600% breakpoint elongation: ↓30%	mass loss: ↓35%	↑ from 2H to 4H ^o	Tan et al. ¹³

(Continued on next page)

Table 1. Continued

Polymer matrix ^a	CNM type/source ^b	Modification ^c	Processing methods	Mechanical property change percentage			Reference
				Strength/strain/modulus of elasticity ^d	Wear resistance	Hardness	
Latex	CNCs/NA, CNF/NSBK, 2 wt %, FD powder	no modification	twin roll coater	storage modulus: ↑33–67% loss modulus: ↓12.5%–↑50%	–	–	Hutton-Prager et al. ⁷¹
Acrylic	CNCs/NSBK, CNF/NSBK, 0.5–2 wt %, FD powder	acetylation	free-standing films	strength: ↓17%–↑34% elastic modulus: ↓31%–↑105%	–	–	Kluge et al. ⁷²
Acrylic, alkyd, polyurethane/acrylic, polymer dispersion (ethylene, methacrylic ester, and vinyl acetate)	CNF, 2.5 wt %, suspension/beech pulp	no modification	bar coating	storage modulus: ↑15–20%	–	–	Künniger et al. ⁷³
Acrylic	CNF (lignin), 2 wt %, suspension/spruce and sugar maple	no modification	brush coating	–	abrasion: ↑40%	↑ from 2H to 5H ^e	Huang et al. ⁷⁴
Linseed oil	CNF, 1 wt %, suspension/NSBK	acetic anhydride, (2-dodecen-1-yl) succinic anhydride	spray coating	–	↑	–	Veigel et al. ⁷⁵
Polyurethane	CNF, 5 wt %, suspension/dissolving pulp	TEMPO oxidized	metering rod coating	strength: ↑134% Young's modulus: ↑5,000% elongation at break: ↓92%	–	↑ from B to 4H ^e	Cheng et al. ⁷⁶
Epoxy	CNF, 3 wt %, suspension/SCB	NaOCl ₂	free-standing films	strength: ↑35% Young's modulus: ↑12% elongation at break: ↓23%	scratch: ↑	–	Wongjaiyen et al. ⁷⁷
Epoxy (diglycidyl ether of diphenolate ethyl ester)	BC, 30 v.%, membrane-FD/ <i>Gluconacetobacter xylinus</i>	trimethylsilyl chloride	hot press	strength: ↑36% Young's modulus: ↑700% elongation at break: ↓600%	–	–	Yue et al. ⁷⁸
Polyvinyl alcohol	BC (as matrix), 5 wt % (AgNP/BC) slurry/ <i>G. xylinus</i>	no modification	reduction, UV	strength: ↓56% elongation at break: ↑4,000%	–	–	Wang et al. ⁷⁹
Polyvinyl alcohol/starch	BC, 2 wt %, suspension/ <i>G. xylinus</i>	no modification	solvent casting	strength: ↑95% Young's modulus: ↑110% elongation at break: ↓80%	–	–	Chiulan et al. ⁸⁰

^aBA, butyl acrylate; MMA, methyl methacrylate; AESO, acrylate epoxidized soybean oil.

^bFD, freeze-dried; CNC, cellulose nanocrystal; CNF, cellulose nanofiber; BC, bacterial cellulose; IBOA, isobornyl acrylate; AgNP, silver nanoparticle; NSBK, northern softwood bleached kraft pulp; SCB, sugarcane bagasse.

^cIEM, isocyanatoethyl methacrylate; HDTMA, hexadecyltrimethylammonium bromide; AOI, 2-isocyanatoethyl acrylate; TMA, tetramethylammonium bromide.

^dMOE, modulus of elasticity.

^ePencil hardness.

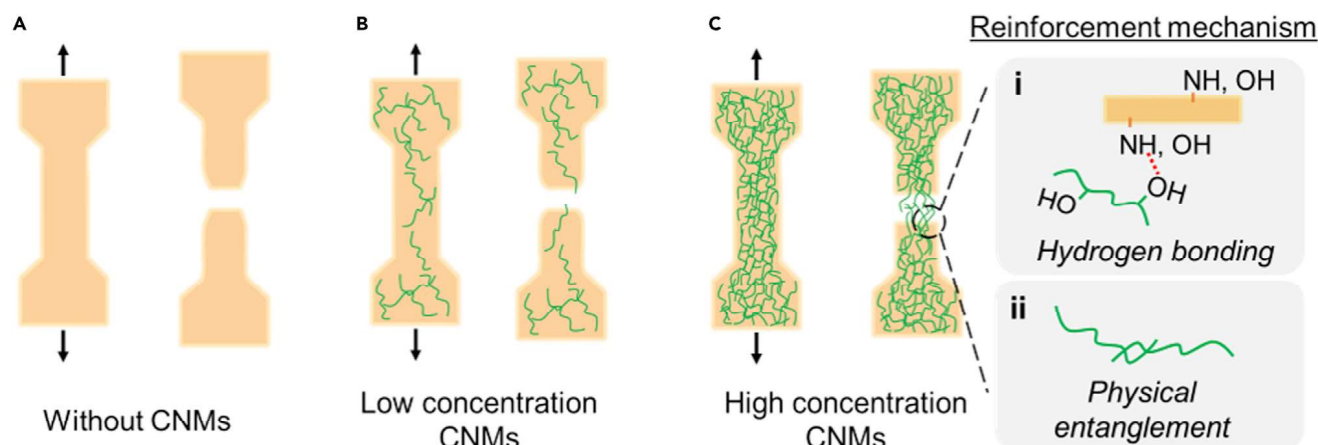


Figure 4. CNM reinforcement of polymers under tension

(A–C) Schematic illustrating the tension failure of polymers without (A) and with (B and C) CNM reinforcement, as well as the CNM-reinforcement mechanisms.

CNF and then decrease for higher CNF loadings (≥ 5 wt %). Surface modifications are often applied to improve the fiber/polymer interfacial interaction, aimed at enhancing the fiber reinforcing ability.^{13,41,59,62,65,72} Grafted-CNCs (gmCNCs) modified with isocyanatoethyl methacrylate (IEM) (a bifunctional molecule carrying isocyanate and vinyl groups) increased the tensile strength of pure acrylic films from 6.9 ± 1.0 MPa to 13.8 ± 1.2 MPa, while no significant difference was observed for unmodified CNCs.⁵⁷ The strain at break value of the pure polymer film decreased from 80% to 42% and 31%, respectively, with the addition of CNCs and gmCNCs. The decreased strain value was attributable to the fact that polymer grafting increased the compatibility between CNCs and the acrylic matrix, resulting in more intensive restraints from the fibers on polymer motion.

Besides CNM dispersion and interfacial compatibility, another factor to be considered is the interference of CNMs on resin curing. In a study on developing a more environmentally friendly alternative to traditional phenolic coatings used in protecting aluminum, 10 wt % and 20 wt % CNC-filled furan resins were investigated.⁶⁰ Apparent modulus of elasticity (E_c) decreased from 14.9 GPa for neat furan resin to 13.5 GPa for nanocomposite containing 20 wt % CNCs. The storage modulus (E'_{glass}) values in the glassy region for the neat furan resin and nanocomposite (20 wt % CNCs) were measured to be 4.40 and 3.82 GPa, respectively. E'_{glass} was shown to decrease with the addition of CNCs, in line with the E_c trend. The degraded modulus values were attributed to CNC's adverse effect on the resin's polymerization, which inhibited the furan matrix crosslinking.

Wear resistance (scratch and abrasion)

The wear resistance of CNM-reinforced polymer composite coatings was investigated in a number of studies, where positive effects of CNM addition were often reported, as shown in Table 1.^{13,58,74,77} Wear resistance, an important property for coatings, is a measure of surface resistance to abrasion. Compared with pure polymer coatings, the abrasion depth became shallower for CNM-reinforced polymer composite coatings because a higher force was needed to disintegrate reinforced composites.^{13,77} A good dispersion of CNMs in the polymer matrix is highly effective in reinforcing polymers because of interactions between nano-sized elements forming a permeated network connected by hydrogen bonds. Scratch testing measures both the internal cohesion of the coating layer and its adhesion to the substrate.

During the scratch test, the cohesive properties of the coating are evaluated. Since the cellulose reinforcement improves the cohesive properties of the coating layer, the coated surfaces have higher scratch resistance.⁸¹ Vardanyan et al. investigated UV-curable water-based coatings for wood substrates with three different modifications on CNCs (hexadecyltrimethylammonium bromide [HDTMA]; tetramethylammonium bromide [TMA]; Acryloyl or acryloyl chloride, C_3H_3ClO).⁶¹ The abrasion and scratch resistance of the samples with 2 wt % CNCs in the polyurethane-acrylate (PUA) matrix was 30%–40% higher than the unmodified-CNC/nanocomposites. It was noticed that varnishes containing CNC-HDTMA and CNC-Acryloyl were more enhanced, which was attributable to better dispersion of HDTMA and Acryloyl.

Hardness

CNMs increased the hardness of the nanocomposite coatings, as shown in Table 1, attributed to the intrinsic high hardness of CNMs and strong/intensive interfacial interaction between CNMs and polymer matrices brought by the sufficient dispersion of nanofibers.^{41,57} In one study, the hardness of nanocomposite films was investigated to understand the performance of CNCs in an acrylic matrix.⁵⁷ The indentation hardness of the pure acrylic film increased from 36.1 ± 6 MPa to 55.3 ± 5 MPa with gmCNCs, while no difference was observed for unmodified CNCs. In a study by Kaboorani et al., while the hardness value of nanocomposite containing 3 wt % CNCs was higher than base polymer, it was lower than 1 wt % CNC/acrylic nanocomposite, attributable to poor dispersion of CNCs.⁴¹

Optical properties

Because of their nanoscale diameter, CNMs can suppress light scattering when they are densely packed, leading to transparent materials.⁸² The high optical transparency of composite coatings can be achieved if CNMs are mixed with hydrophilic polymers (Figure 5A).^{34,36} In hydrophobic polymer matrices, CNMs tend to entangle and agglomerate because of a high surface energy.¹³ The insufficient dispersion of CNMs significantly decreases the optical transparency of the composite coatings. From this perspective, CNF tends to impair the transparency of polymers, attributable to the difficulty of its dispersion. Some processing techniques, such as chemical modification or emulsion fabrication, have been exploited to obtain better optical performance of composite coatings.^{13,83} For instance, γ -aminopropyltriethoxysilane (0.16 wt %) was used to modify and assist dispersing CNF in suspensions.¹³ The modified CNF was subsequently incorporated into waterborne acrylic resin/polyester polymer blend coatings and could retain around 90% transparency of the acrylic film.

Above a critical concentration, CNC suspensions form a chiral nematic phase by self-assembly, and this structure can be preserved in solid films.^{86–88} When the helical pitch is on the order of the visible light wavelengths (around 400–700 nm), CNC films display iridescence.⁸⁹ Polymer coatings can also exhibit iridescent colors if doped by an appropriate amount of CNCs, with tunable colors dependent on CNC loading. The ratio between CNCs and polymer has an influence on the pitch length, which determines the CNC-film color. For example, CNC/polyethylene glycol (PEG) mixtures were coated on a polyacrylonitrile-butadiene-styrene (ABS) substrate.⁸⁴ The reflective color of the coatings gradually turned from blue to red with increasing PEG content, attributed to increased pitch lengths (Figure 5B). However, the color faded away at high PEG loading (50%) because of the loss of the ordered structure of CNCs. The colors of CNC-composite coatings are process dependent. Fast evaporation leads to the formation of colorless and transparent coatings as CNC films are trapped in an isotropic arrangement, while iridescence can be created

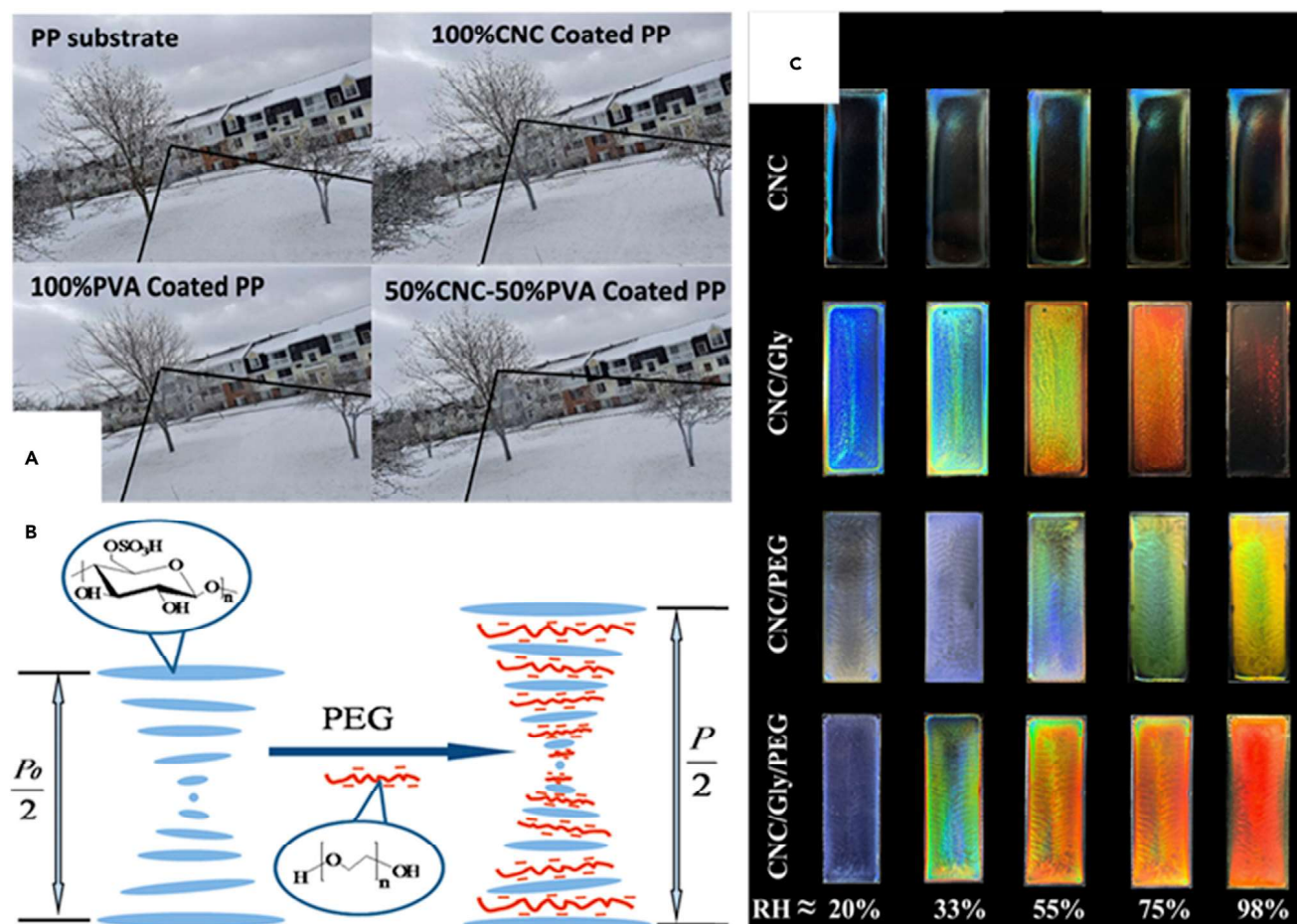


Figure 5. Optical properties of CNC-reinforced polymer coatings

(A) Transparent CNC/PVA-coated PP films (A), reprinted from Nuruddin et al.,³⁴ copyright (2021) American Chemical Society.

(B) Scheme of the half cholesteric pitch changed with polyethylene glycol (PEG) doping, reprinted from Gu et al.,⁸⁴ copyright (2016) American Chemical Society.

(C) Iridescences of CNC, CNC/glycerol (Gly), CNC/PEG, and CNC/glycerol/PEG nanocomposite membranes with changing relative humidity, reprinted from Babaei-Ghazvini and Acharya.⁸⁵

when the coatings are dried under milder conditions, leading to long-range CNC arrangement.⁶⁷ The polymers usually locate between chiral nematic layers, which increases the moisture sorption and water capacity of composites. Accordingly, the color of coatings changed from blue to red with an increase in relative humidity (RH), attributable to increased pitch length (Figure 5C).⁸⁵ The color of CNC/PVA-glutaraldehyde coatings also changed from red to yellow or blue by increasing the NaCl solution concentration from 0.5 or 1 mM.⁹⁰

Self-healing (controlled release)

Controlled release refers to the situations where encapsulated chemicals (e.g., drugs, proteins, fertilizers, nutrients, and other biologically active agents) are released because of external stimulation (temperature, pH, humidity, light, etc.).⁹¹ One application of controlled release is self-healing. A few studies focused on the controlled-release behavior of CNF-reinforced polymer composite coatings for metal surfaces.^{92–95} Few studies were published with other types of CNMs, possibly because of the formation of a unique fibril network by CNF, which is considered as beneficial for self-healing metal coatings because of their encapsulating ability and

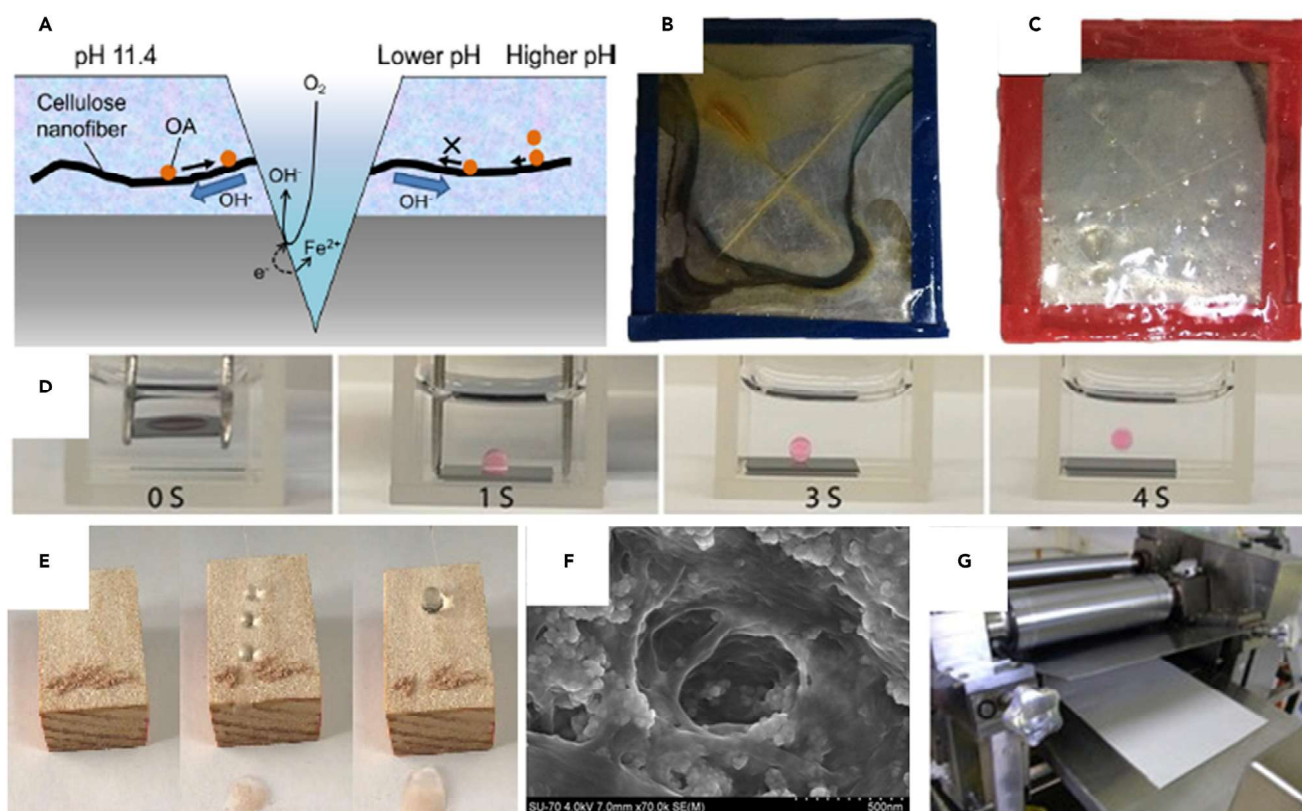


Figure 6. Self-healing, self-cleaning, and antimicrobial properties of CNF-reinforced polymer coatings

(A) A scheme of pH-controlled self-healing coating enabled by CNF and OA, reprinted from Yabuki et al.,⁹² copyright 2016 with permission from Elsevier.

(B and C) Photographs of an epoxy coating (B) and an epoxy coating containing CNF loaded with epoxy monomers and curing agents (C) after 2 weeks of immersion in 10 wt % NaCl solution, reprinted from Vijayan et al.,⁹⁵ copyright 2017 with permission from Elsevier.

(D) An anionic surface coated by CNF fouled by Sudan-red-stained canola oil (30 μ L) in air and cleaned by water immersion, reprinted from Huang and Wang⁹⁸ by permission of John Wiley & Sons.

(E) Self-cleaning of a CNF/polydimethylsiloxane (PDMS)-coated wood surface, reprinted from Huang et al.¹⁰⁰

(F and G) SEM micrograph of CNF and ZnO nanoparticle antimicrobial composite coating (F), and coating paper with antibacterial CNF/ZnO/starch nanocomposite (G), reprinted from Martins et al.,¹⁰⁴ copyright 2013 with permission from Elsevier.

sustained release of corrosion inhibitors. Nawaz et al. loaded dodecylamine (DOC; a corrosion inhibitor) and polyethyleneimine (PEI; a self-healing agent) to cellulose microfibril (CMF).⁹⁴ When scratched, DOC and PEI were released and formed a protective film layer over damaged steel adsorptions. As a result, the electrochemical impedance value for the CMF/DOC/PEI/epoxy coatings was higher than that of the CMF/epoxy coatings, which indicated a more healed surface in the former case. To further control the release of corrosion inhibitors, Yabuki et al. investigated coating systems containing CNF, oleic acid (OA; a corrosion inhibitor), and epoxy whose pH was adjusted to 11.4.⁹² OA was found to be released from CNF when the surrounding pH value was below 8 or above 12. When steel corrodes by anodic reaction, hydroxyl ions are produced at the steel surface, attributable to cathodic reaction, which increased the pH of the system beyond 12, thus triggering the release of OA. A scheme depicting such a pH-controlled self-healing mechanism is shown in Figure 6A. One way to achieve self-healing of a two-component coating is to controlled-release polymeric monomers and curing agents to the scratched sites.⁹⁵ Both epoxy monomers and amine curing agents were immobilized onto CNF surface by simple agitation mixing and centrifugal washing. Chemical-loaded CNF was

added into epoxy resins to form composite coatings on carbon steel. Upon coating damage and water intrusion, CNF deformed and released loaded chemicals onto the damaged areas. Released epoxy monomers and curing agents then reacted to form a new coating to heal the scratch, as shown in [Figures 6B and 6C](#).

Self-cleaning/antifouling

Self-cleaning coatings are broadly classified into two major categories: (1) hydrophilic and (2) hydrophobic. In a hydrophilic coating, water is made to spread as a sheet over the surface, which can wash away dirt and other impurities while preventing hydrophobic compounds from adsorbing. In a hydrophobic coating, the water droplets slide and roll over the surfaces, thereby cleaning them. A major limitation of hydrophilic self-cleaning coatings is that its exposure to air causes an inward orientation of the surface polar groups to minimize surface energy. Once this occurs, reconstructing the surface is quite difficult.⁹⁶ Circumventing this requires techniques such as immediate submersion in aqueous media; photochemical reaction; or use of complex, non-scalable chemistries such as zwitterionic groups.⁹⁷ Surface-modified CNMs could provide a significant advantage for self-cleaning membranes. Huang and Wang demonstrated a carboxylate surface-modified CNF monolayer as a hydrophilic coating for a polymer substrate.⁹⁸ They found both wet and dry CNF-coated steel meshes were able to successfully filter various oils from water (canola oil, engine oil, pentanol, and butanol), with the behavior accelerating after adding salt to the water phase ([Figure 6D](#)). In the end, the authors indicated this work could be applied to help with cleanup after oceanic oil spills by providing a more effective oil-from-water separation technology.

Another group demonstrated the utility of superhydrophobic, self-cleaning, anti-abrasive coatings made from lignin-coated CNCs, PVA, water, and 1H,1H,2H,2H-perfluorooctyltrichlorosilane with and without organic solvent.^{98,99} In this case, the CNCs were used as a surface-roughening agent to help with adhesion and a superhydrophobic coating was sprayed on using chemical vapor deposition (CVD). The coatings were able to achieve water contact angles (WCAs) of 157°–158°, which, in parallel with the micro-nano roughness formed by stacking of CNC particles, enabled spheres of water to form and roll easily off the surface, carrying dust and other contaminants with them. Another reference from this same group aimed to develop a one-pot superhydrophobic coating.¹⁰⁰ They utilized 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FOTS)-modified CNF in PDMS mixtures as a superhydrophobic coating for wood deposited by a one-step spray method. With this technique they were able to achieve WCA of 158°, enabling self-cleaning characteristics ([Figure 6E](#)).

Many applications for membranes are limited by fouling, or attachment of undesirable particles, in wastewater processing applications. The benefit of CNMs in this application is its low cost, high hydrophilicity, and its high stiffness, which can reduce attraction between foulants (especially proteins in the waste water) and enable membrane cleaning through water action.¹⁰¹ In a recent study, Lotfikatouli et al. demonstrated the utility of a thin-film nanofibrous composite-CNF-coated membrane to filter domestic wastewater compared with state-of-the-art coatings.¹⁰¹ The authors identified that the flux of water through the membrane was higher in CNF-modified membranes, but their function did decrease significantly over 60 min (by 56%–59% depending on the cycle). Using contact angle analysis, they were able to identify a significantly higher hydrophilicity in CNF-modified membranes compared with conventional, but their hydrophobicity slightly increased during the 60-min operation time. By measuring total organic carbon,

total proteins, and total carbohydrates in filtered water, they were able to identify that CNF-modified membranes had a significantly higher filtration performance for both carbon and protein but a reduced total carbohydrate rejection rate, which they indicated may be more attributable to the size of polysaccharides than the membrane surface itself. In either case, a significant advantage to CNF-modified membranes was their ability to be cleaned by washing rather than chemical cleaning, although air scouring worked well for both membranes.

Antimicrobial

Accumulation of unwanted growth of microorganisms on the surface of a substance can detrimentally affect its performance and longevity. Nanoparticles with antimicrobial properties were studied, where their antimicrobial performance can be reduced with insufficient particle dispersion.¹⁰² CNMs, with a large surface area, can act as a deposition template for those nanoparticles to prevent their severe agglomeration.¹⁰² One study looked at how silver nanoparticle-decorated CNF could function as antimicrobial agents in a hyperbranched epoxy systems.¹⁰³ Silver-modified CNF was surface modified using triethyleamine and added to an epoxy system in varying amounts between 1 and 3 wt %. A significant reduction in both *Staphylococcus aureus* and *Candida albicans* strains was observed in the 3 wt % systems, with active, sustained release of 0.08% silver nanoparticles over 7 days. Another group utilized a waterborne epoxy impregnated with CNCs and between 0 and 10 wt % silver nanoparticles as an antimicrobial coating for wood.¹⁰² The maximum antibacterial performance toward *Escherichia coli* was observed at 5 wt % silver, with further loading reducing antibacterial performance. Another group utilized CNF and ZnO nanoparticles through electrostatic assembly in an aqueous medium, using polyelectrolytes as macromolecular linkers for an antimicrobial paper coating for health care and food applications (Figure 6F).¹⁰⁴ The addition of CNF and ZnO to the starch paper coatings (Figure 6G) was found to be strongly antibacterial toward both gram-positive and -negative bacteria, attributed to the generation of reactive oxidative species during light exposure.

CNM-ENHANCED POLYMER ADHESIVES

Mechanical enhancement

Two goals of incorporating CNMs into adhesive systems are (1) to improve mechanical properties via the inclusion of strong and stiff reinforcements, which possess the ability to form percolated networks at proper loadings; and (2) to decrease the environmental impact of the materials via the incorporation of bio-derived and biodegradable materials. In an attempt to explore the literature with these nuances in mind, the type of CNMs used in each study is denoted in the first column of Table 2, along with the adhesive matrix employed, the dimensions of the CNMs, and the mechanical improvements reported in the references.

CNCs are an appealing option as reinforcements for adhesives attributable to the colloidal stability imparted by the surface sulfate esters attached in their production, the high inherent crystallinity in the materials, and the high aspect ratio of the nanocrystals (Figure 7A). Two general schemes exist to use CNCs in adhesive systems: physical incorporation into the preformed polymeric materials used as the matrix or chemical incorporation into the adhesive system during the curing process, relying on their compatible surface chemistry to crosslink them into the thermoset network.¹⁰⁷ The first approach has seen success in pressure-sensitive adhesive systems where physical incorporation of CNCs increases peel strength¹⁰⁹ and in systems such as polyvinyl acetate, where CNC addition improved bonded wood joints, most likely by the formation of a percolated nanocrystal network, which transfers

Table 2. Mechanical improvements of CNM-reinforced adhesive systems

CNM type/source ^a	Dimension ^b	Modification ^c	Matrix ^d	Improvements ^e	Reference
CNCs/NA	L = 269 nm W = 40.1 nm	–	P(nBA-co-2EHA)	13% tack, 176% peel	Karimi Shamsabadi et al. ¹⁰⁹
CNCs /Alfa fibers	L = 250 nm W = 10 nm	–	PVA	195% shear	Mabrouk et al. ¹⁰⁶
CNCs/NSBK	–	aminopropyltriethoxysilane	UF	29.3% MOR, 38.2% MOE	Khanjanzadeh et al. ¹¹⁰
CNCs/NSBK	L = 50–200 nm W = 5–20 nm	–	UF	28.8% MOR 30% MOE	Mesquita et al. ¹¹¹
CNCs/cotton	L = 291 ± 23.7 nm W = 12.7 ± 1.2 nm	–	glycerol-based copolymers	150% shear	Figueiredo et al. ¹¹²
CNCs/cotton	L = 10–100 μm W = 2–20 μm	–	DGEBA epoxy	125% shear, 378% shear toughness	Pruksawan et al. ¹¹³
CNCs/MxG	L = 270 nm W = 4.3 nm	3-mercaptopropionic acid	disulfide network	122% shear	Cudjoe et al. ¹¹⁴
TOCN/NA	L = 200–600 nm W = 3–8 nm	alkoxy silane cardanol and dopamine hydrochloride coated	soy protein	131% shear	Wang et al., 2019 ¹¹⁵
TOCN/NA	–	3-aminophenylboronic acid	soy protein + hyperbranched PE	31% tensile, 172% toughness	Li et al. ¹¹⁶
TOCN/NA	L = ~1 μm W = ~5 nm	–	soybean meal adhesive	130% shear	Li et al. ¹¹⁷
CNF/BUP	L = 1,030 ± 334 nm W = 20 ± 14 nm	–	zein, gluten	240% shear, 133% MOR	Oh et al. ¹¹⁸
CNF/hemp	–	–	rubber toughened DGEBA epoxy	34% shear, 59% impact	Padinjakkara et al. ¹¹⁹
CNF/NA	L = 400–600 μm W = 10–50 nm	–	pine tannins	13% IB, 4% MOR	Cui et al. ¹²⁰
CNF/rice straw	W = 20–50 nm	–	UF	33% MOR, 32% MOE	Moslemi et al. ¹²¹
LCNF/western red cedar	–	–	pMDI	109% shear	Chen et al. ¹⁰⁷
CNF/cypress, TOCN/spruce	W = 10–30 nm	glycidyltrimethylammonium chloride	P(2-EHA-co-MMA)	123% shear	Yang et al. ¹²²
CNF/NA	L = 0.5–2.5 μm W = 50 ± 15 nm	–	P(HEMA-co-DMA)	44% shear	Tang et al. ¹⁰⁵

^aCNCs, cellulose nanocrystals; CNF, cellulose nanofibril; TOCN, TEMPO-oxidized CNF; BC, bacterial cellulose; LCNF, lignin containing CNF. NSBK, northern softwood bleached kraft pulp; MxG, *Miscanthus x giganteus*; BUP, bleached eucalyptus pulp.

^bLength and width measurements for CNMs used as written by the authors of the relevant publications with a dash indicating that no value was reported.

^cChemical treatments to the CNMs used in the study; a dash indicates the material was used as received with no additional treatment.

^dPolymer matrix employed as the adhesive; P(nBA-co-2EHA), poly(n-butyl acrylate co 2-ethyl hexyl acrylate); UF, urea-formaldehyde; DGEBA, diglycidyl ether of bisphenol A; pMDI, polymeric methyl diphenyl diisocyanate; P(2-EHA-co-MMA), poly(2-ethyl hexyl acrylate co methyl methacrylate); P(HEMA-co-DMA), poly(hydroxy ethyl methacrylate co dopamine methacrylamide).

^eMechanical improvements reported by authors. IB, internal bond; MOR, modulus of rupture; MOE, modulus of elasticity; shear, lap shear testing; tensile, maximum tensile strength.

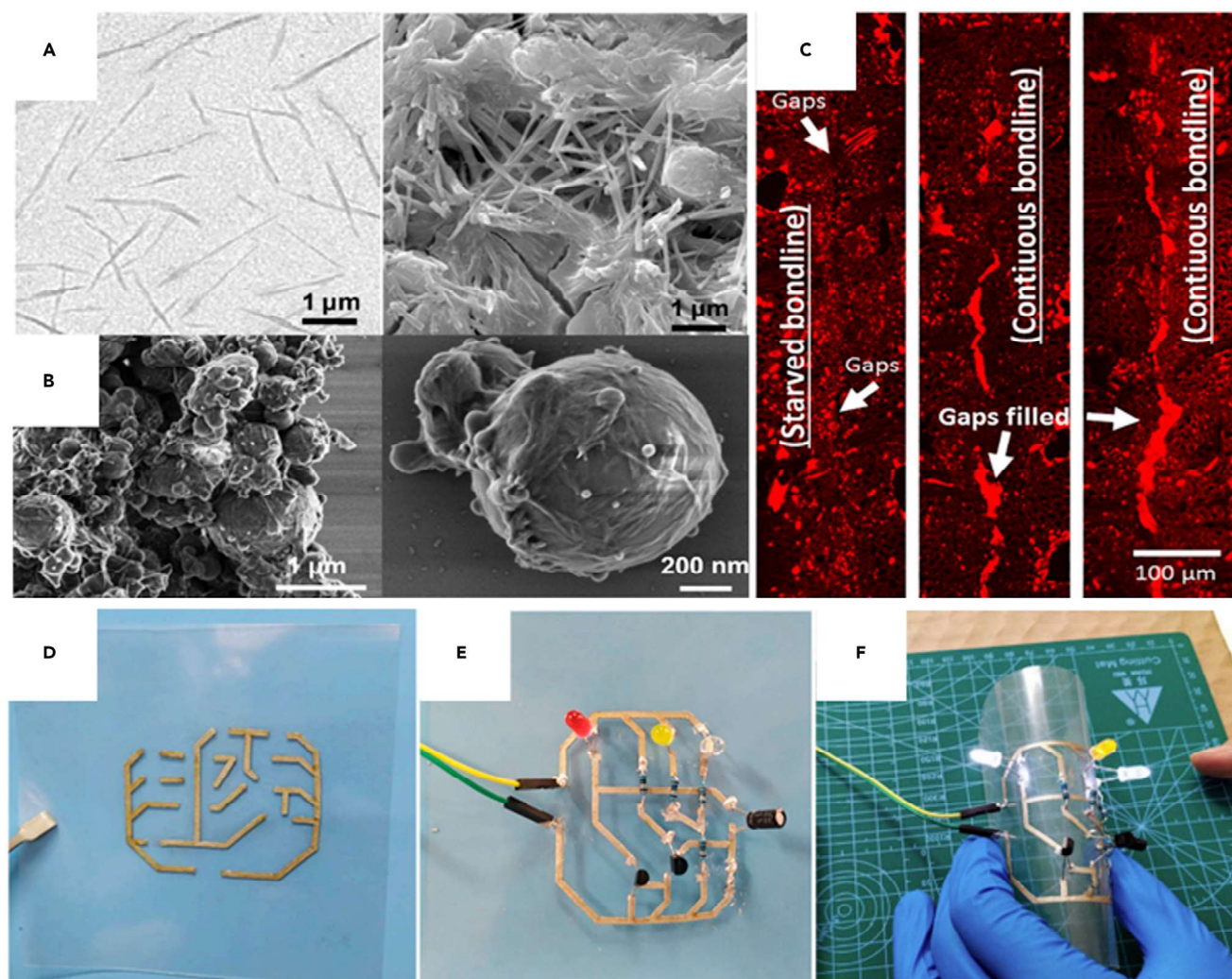


Figure 7. Applications of CNMs in polymer adhesives

(A) Native cellulose nanofibrils (left) used to reinforce a poly(hydroxyethyl methacrylate-co-dopamine methacrylamide) adhesive (right) for applications in steel bonding; reprinted from Tang et al.,¹⁰⁵ copyright (2022) American Chemical Society.

(B) CNCs stabilizing the surface of polyvinyl acetate emulsions used as waterborne adhesives for wood joints, reprinted from Mabrouk et al.,¹⁰⁶ copyright 2020 with permission from Elsevier.

(C) Confocal fluorescent scanning laser microscopy images of polymeric methyl diphenyl diisocyanate (pMDI)-bonded wood joints neat (left), with solvent-exchanged LCNF (middle), and with freeze-dried LCNF (right) showing better gap-filling properties for the more viscous composite adhesives, reprinted from Chen et al.,¹⁰⁷ copyright 2019 with permission from Elsevier.

(D–F) Printed circuit with a 1-mm line width from electrically conductive adhesives containing polyaniline, CNCs, Ag, and polyurethane (D); a printed circuit with lights indicating electrical conductivity using polyaniline/CNC/Ag/PU adhesive (E); a flashing light-emitting diode (LED) device working under the bending mode, printed with electrically conductive polyaniline/CNC/Ag/PU adhesive (F). Reprinted from Cao et al.¹⁰⁸

load to the reinforcement. Improvement was maximized when CNCs were used as the stabilizers in the emulsion polymerization of the PVA adhesive system instead of simply being added to a preformed polymer, most likely attributable to improved dispersion in the final adhesive joint, easily visualized in Figure 7B, by surface coating the particles with CNCs.¹⁰⁶ Aside from increases in adhesive strength, the incorporation of CNCs into PVA systems often leads to improvements in joint creep and stiffness, two parameters of importance for structural applications, attributable to the high modulus of elasticity of the nanocrystals increasing the overall stiffness of the composite.

The approach of chemically incorporating the CNCs into thermosetting adhesives is more widely used in the literature and has been successful with urea-formaldehyde for particle board formation^{110,111} and in epoxies derived from diglycidyl ether of bisphenol A (DGEBA) with amine curing agents.¹¹³ Cudjoe et al. took this incorporation method further by functionalizing CNCs with thiols and using them to form disulfide bonds with an oligomeric polythioether to produce an adhesive with almost double the lap shear strength of commercial adhesives. The dynamic nature of the disulfide bonds crosslinking the system allowed the fractured network to be reformed by heating, resulting in a material that could be rebonded at least three times while maintaining its adhesive performance.¹¹⁴

While CNCs have demonstrated their potential for adhesive applications, CNF has the advantages of an inherent network because of their branching nature, decreased material loss during production, and a potentially lower cost when employing mechanical refinement of feedstock. A large body of the work involving CNF in adhesive systems aims toward entirely sustainable alternatives to traditional petroleum-based solutions.¹²³ As such, studies incorporate CNF, usually as TOCN, into protein mixtures composed of gluten,¹¹⁸ tannins,^{120,124} and soy protein extract.^{115,117} These bio-based systems are an important step toward sustainable adhesives, and the incorporation of CNF did have a dramatic reinforcing effect on the protein matrices, often doubling and tripling the lap shear strength of these protein adhesives. The hypothesized mechanism of reinforcement in these systems is that the CNF is dynamically crosslinked by the various surface interactions present between fibril and protein, leading to a stronger network. This hypothesis is supported by the additional improvements in adhesive strength seen when a chemical crosslinker is added to the protein/CNF mixture.¹¹⁸ Oh et al. demonstrate the viability of these systems by showing a 133% improvement in the modulus of rupture (MOR) of plywood made with their 2 wt % CNF gluten-based adhesive compared with boards made using traditional methylene diphenyl isocyanate (MDI).¹¹⁸ Similarly, Zidanes et al. noted that they achieved 55% of the lap shear strength of a resorcinol-formaldehyde joint using a 5 wt % CNF/tannin adhesive, which was a marked improvement over a purely tannin-based adhesive that failed to bond the joint and delaminated after pressing.¹²⁴ Clearly these systems are reaching the point where they can compete with traditional structural adhesives, aided by the reinforcing nature of CNF networks.

Traditional adhesives systems have also been reinforced with CNF, with some notable examples being the improvement of MDI with lignin containing CNF (LCNF),¹⁰⁷ rubber toughened epoxy with freeze-dried CNF,¹¹⁹ and urea-formaldehyde with various types of CNF.^{121,125} In all of these cases, the available hydroxyl groups on the surface of the fibrils were likely crosslinking the reinforcement into the matrix, leading to mechanical improvements, although other factors, such as better bond line filling attributable to changes to the rheological properties of the adhesives as seen in [Figure 7C](#), play a role as well. Finally, interesting work was also done on copolymer emulsion systems where CNF acted as both a stabilizer and a reinforcing agent upon film formation,^{105,122} demonstrating improved adhesion to multiple substrates including steel, aluminum, wood, and to a lesser extent glass.

Wet shear strength

The wet shear strength of adhesives is critical for prolonged use, especially if the adhesives are expected to maintain their adhesion performance with high moisture contents. CNMs are hydrophilic; as such, they will enhance the hydrophilicity of polymer matrices once incorporated. An example of this can be seen in a study that

showed the thickness swelling rate of wood particleboards bonded with a tannin-based resin reinforced with CNF slightly increased compared with a control without CNF.¹²⁰ However, if interactions occur between CNMs and a polymer matrix, it may enhance water resistance of the matrix. Adhesives consisting of polyvinyl acetate (PVAc; base polymer), PVA (PVOH; emulsifier/stabilizer), dibutyl phthalate (coalescing promoter), and TOCN improved the wet shear strength of the adhesive.¹²⁶ Such an improvement was ascribed to the preferential hydrogen bonding among TOCN and PVOH, leading to reduced mobility of polymer chains, as shown by increased storage modulus and glass transition temperature. However, the effect of the adding CNMs to adhesives is not monotonic. For the reinforcement of lignin-based phenol-formaldehyde adhesive with CNCs, the wet shear strength of the bonds increased with increasing CNC content in the range between 0 and 0.25 wt % and then decreased in the range of 0.25 wt % to 1.5 wt %.¹²⁷ The same tendency also occurred for a CNC-reinforced phenol-formaldehyde resin-bonded plywood.¹²⁸ The wet shear strengths reached the maximum with the addition of 3 wt % CNCs and then decreased with higher loadings. At 3 wt % CNC loading, the wet shear strength values increased approximately 19% and 16% in comparison with reference samples tested after soaking and boiling, respectively. It was explained that the added cellulosic particles significantly improved the fracture toughness of the adhesives, leading to the increased wet shear strength at lower loadings. The deterioration of fracture toughness at high loading levels was ascribed to the agglomeration of CNCs. Moreover, the positive effect of adding CNMs can be material-type dependent. For instance, adding CNF to cottonseed protein isolate adhesives improved the wet shear strength of glued wood, but adding CNCs did not.¹²⁹

The wet strength of CNM-reinforced adhesives can be improved by functionalizing the CNM's surface. An adhesive formulated with soy protein isolate (SPI) and hydrophobized TOCN achieved a wet shear strength up to 1.27 MPa, which was 189% and 95% higher than that of the neat SPI, and the adhesive prepared with pristine TOCN, respectively.¹¹⁵ Another study showed that the wet bonding strength of plywood bonded with an adhesive comprising hydrophobized CNCs and SPI was 1.1 MPa, registering an increment of 600%, compared with the pristine SPI adhesive.¹³⁰ The incorporation of 2 wt % silylated CNCs into a urea-formaldehyde resin decreased the thickness swelling rate and water absorption rate of the medium density board after 24 h water soaking by 13.5% and 6.5%, respectively, compared with the one bonded with the neat resin.¹¹⁰

Thermal-property enhancement

The addition of CNM reinforcements has been shown to improve the thermal properties of WPU adhesives, which has been a highly studied base adhesive polymer.¹³¹ Larraza et al. investigated the effect of carboxylation degree on WPU/CNF composites.¹³² CNF with three different degrees of carboxylation was prepared via sequential periodate-chloride oxidation. It was found that the thermal degradation of both the neat polymer and the CNM-reinforced polymer composites occurred in two steps: thermal degradation of the hard segment consisting of urethane and urea groups, followed by the thermal degradation of the soft segment mainly formed by the polyol. The WPU/untreated-CNF composite with 5 wt % fiber loading exhibited a higher maximum degradation temperature ($T_{\max}$) of 390°C compared with a $T_{\max}$ of 330°C for neat WPU. WPU/carboxylated-CNF composite with 5 wt % reinforcement also showed a higher $T_{\max}$ of 360°C, which is higher than that for neat WPU but lower than that of WPU/untreated CNF. The improvement was attributed to the interactions between the CNF and the WPU, resulting in more

stable urethane groups and more confined structures that enhance the thermal stability of the material.

Besides water-based polyurethanes, other waterborne adhesives were also explored to understand the benefits of incorporating CNMs. Rigg-Aguilar et al. used CMFs from pineapple stems to reinforce urea-formaldehyde (UF) wood adhesives.¹³³ The addition of 0.5 wt % CMF increased the $T_{\max}$ of UF adhesives from 257°C to 262°C. An increase in the CMF content to 1.0 wt % further increased $T_{\max}$ to 270°C. The authors attributed the improvement in the maximum thermal degradation temperature to the formation of a rigid network that restricted molecular mobility and retarded decomposition. Li et al. studied the thermal stability of modified-soybean-meal (MSM)-based adhesives reinforced by ethylene glycol glycidyl ether and modified CNCs.¹³⁴ The modified CNCs were prepared by reacting with a silane coupling agent. Silane crosslinking increased the thermal stability of the resultant adhesive due to the formation of chemical bonds. The epoxy groups on the surface of modified-CNCs reacted with the soybean-meal protein molecules, which formed a more stable structure/crosslinking structure. The addition of unmodified CNCs did not affect the thermal stability of the MSM/CNC composite.

Other functions

CNMs are capable of providing other functionalities to adhesives, including curing promotion, electrical-conductivity enhancement, and VOC suppression.

Curing promotion

Epoxyes are commonly used in structural adhesive formulations because of their low shrinkage and high strength.¹³⁵ However, an appropriate curing rate, governed by the curing temperature and time, is a major challenge in epoxy adhesive formulation.¹³⁶ Faster curing decreases clamping time and increases production throughput, therefore reducing production cost. Patel et al. successfully engineered a bio-based, fast-curing epoxy adhesive.¹³⁵ The curing rate increased with increasing CNC concentration (from 0.5 to 1.5 wt %). This increase is probably attributable to the reaction of surface hydroxyls on the CNCs with unreacted epoxy, accelerated the epoxy curing.

Electrical conductivity

One major challenge of current flexible and electrically conductive adhesives is that they typically have limited conductivity and therefore need a large amount of metal fillers.¹⁰⁸ The metal fraction can contribute to an increased production cost of the adhesive. For traditional Ag-containing electrically conductive adhesives, the conductivity was largely improved by incorporating high-aspect-ratio conductive materials (e.g., carbon nanotubes). To save cost, Cao et al. synthesized polyaniline@cellulose nanowhiskers (PANI@CNCs), which were then added to Ag-containing adhesives to form thermoplastic polyurethane (TPU)/Ag/PANI@CNC composites.¹⁰⁸ CNCs provided 1D templates that promoted the growth of PANI on CNC surfaces to connect neighboring nanotubes. These formed high aspect-ratio (10–15) nanotubes, which, together with Ag flakes, constituted effective electrically conductive networks, which improved adhesive conductivity. Figures 7D–7F show the application of the electrically conductive adhesives in printed circuits. The TPU/Ag/PANI@CNC electrically conductive composite adhesive is a promising material for printed flexible electronics. Silver nanoparticles are widely used for conductive fillers because of their high electrical and catalytic performance. However, silver nanoparticles are costly and less stable.¹³⁷ The core-shell structure (polymer as core and metal as shell) exhibits both superior ductility and conductivity. In one study,

Wang et al. fabricated a hollow core-shell conductive nanoparticles using CNCs for conductive adhesives.¹³⁷ CNCs have nanoscale rod-like structure and can be used as a template to prepare core-shell structure where CNCs can be removed to produce a hollow core. The prepared CNC-templated Ag/dopamine (DA) nanoparticles exhibited excellent conductivity, with an electrical resistivity of only 0.2 mΩ cm.

VOC suppression

Another functional benefit CNMs can offer in polymer adhesives is the suppression of VOCs. Minimizing the release of VOCs, especially for indoor applications, is crucial for human health. Wood-based composites, such as medium-density fiberboard (MDF) are commonly used in indoor applications, and UF is commonly used as an adhesive in these applications, where formaldehyde emission from these composites can significantly decrease indoor air quality and even cause cancer. Adding CNMs into these polymeric adhesives can not only improve their mechanical performance but can also help reduce the VOC emission. Suppression of VOCs with the addition of nanomaterials can be attributed to multiple factors such as absorption of VOCs on these materials, their barrier properties, shielding effect, and the reaction between the surface groups on these nanomaterials and the active groups in UF.¹³⁸

Khanjanzadeh et al. studied the effect of addition of surface functionalized CNCs on formaldehyde release in UF adhesives used in MDF.¹¹⁰ The 3-aminopropyltriethoxysilane (APTES) was used to modify CNC surfaces, where the amine groups of APTES might have further suppressed formaldehyde release by reacting with it to form methylol groups.¹³⁹ A 17% lower formaldehyde emission was reported with 2 wt % CNC addition compared with use of only neat UF.¹¹⁰ Ayrlmis et al. studied the impact of addition of CMF into different grades of UF VOC emission.¹⁴⁰ Laminated veneer lumber (LVL) produced using three different UF resins with different formaldehyde emission levels were tested at three different temperatures (25°C, 35°C, and 45°C). The highest VOC release was found to be in the form of toluene, followed by xylene, benzene, and ethyl-benzene. While a significant decrease in VOC release was observed at 25°C and 35°C. The addition of CMF did not affect the VOC release at 45°C, showing the importance of end-use conditions. With the addition of 40 wt % CMF, the total VOCs decreased from 94.9 to 43.4 μg/m³ for one UF grade, while the drop was from 89.5 to 68.3 μg/m³ and 122.7 to 88.5 μg/m³ for the other two UF grades at 25°C. In a different approach, instead of directly adding CNF into UF resin, Wibowo et al. *in situ* modified the UF resin itself with the presence of CNF for plywood applications.¹⁴¹ CNF was dissolved in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) and mixed with UF resin during alkaline reaction. Addition of CNF during resin modification resulted in significant (up to 42%) decrease in formaldehyde emission in plywood.

CONCLUSIONS AND FUTURE WORK

In this paper, we summarized the multi-functionalities that CNMs can bring to polymer coatings and adhesives. Those interesting benefits of CNM addition make it an appealing additive for coating and adhesive applications. The conclusions and future work are as follows.

CNM-based composite coatings can provide low gas permeability, especially oxygen permeability. However, attributable to the high hygroscopic nature of the CNMs, the WVTR of the CNM-containing coating is still challenging. One promising strategy is to use the surface-modified CNMs, such as hydrophobic modification, to

reduce the hygroscopicity of the CNMs and to achieve higher WVTR. The gas-barrier properties of CNMs are also critical for its anti-corrosive metal-coating applications. Because of their high polarity, CNMs could be good candidates for reinforcing waterborne anti-corrosive coatings. For hydrophobic solvent-borne coating materials, dispersion of CNMs in coating chemicals is the key to preparing effective anti-corrosive coatings, which will rely on greener and more efficient methods.

The addition of CNMs improved the thermal stability and flame retardancy of polymeric coatings. Such improvements were attributed to the strong fiber/polymer interfacial interaction and the carbonization effect of CNMs. Similarly, the addition of CNMs improved the thermal stability of different waterborne adhesive systems. The CNM-reinforced adhesive systems were found to have a higher maximum thermal degradation temperature attributable to the formation of a rigid network that restricted molecular movement and slowed down the progression of thermal degradation. For future work, more effective chemical modifications of CNMs would lead to higher improvements in thermal/flame properties of polymeric coatings/adhesives.

The mechanical properties of polymer coatings are improved with CNMs. In general, tensile, hardness, and modulus values of polymer coatings increased with CNM addition, while elongation at break decreased. This improvement depends on the size, shape, and degree of dispersion of the CNMs. CNMs have also been shown to improve the mechanical properties of both traditional and bio-renewable adhesives. Primarily, these improvements come in the form of increased adhesive strength, although select studies have improved adhesive toughness and re-bondability. There is room for improvement, however, particularly in incorporating more cost-efficient mechanically refined CNF into both bio-based and petroleum-derived adhesive systems. Moreover, adding CNMs into adhesives can improve their water resistance by increasing the wet shear strength once there is strong fiber/polymer interactions (e.g., hydrogen bond). In cases of limited interactions, modifying CNM surface to make it compatible with adhesive polymer matrices was proved to be effective in enhancing wet shear strength and reduce water swelling. Future work can explore greener routes of surface modifications and understand their roles in the resulting composite adhesive's water resistance.

CNM-reinforced polymer composites have proved to be effective in chemical-release regulation. The slow-release behavior of CNM-reinforced polymer composites originates from the physical barrier function of CNMs, attributable to their 3D net-working morphology. Besides, the controlled-release behavior of CNM composites relies on intelligent design, which enables the loaded chemicals being released in a controlled manner under external stimuli. In most cases, formulations were prepared in aqueous suspension. The investigated forms of slow/controlled-release systems were films and powders. Future research should expand the slow/controlled-release behavior of CNM-reinforced polymer composites into other application areas, such as pharmaceutical, diagnostic, marine, cosmetic, personal care, and food industries.

Polymeric composite coatings reinforced with CNMs showed high optical transparency if fiber dispersion and fiber/polymer interfacial compatibility issues could be addressed properly by surface modification. Otherwise, the composite coatings will lose their transparency, attributable to intensive light scattering caused by agglomerated fibers. In addition, the intrinsic iridescence behavior of CNCs and their polymer composites is an interesting optical property that can be tuned by

composite compositions, processing parameters, ionic strengths, RH, etc. The iridescence of CNCs endows their polymer composite coatings with multifunctional applications in sensors, photonic inks, actuators, etc. To further enhance the optical performance of CNM-reinforced polymer composite coatings, more effort should be spent on green and highly efficient surface modifications to improve fiber/polymer interfacial compatibility and fiber dispersion, design and/or fabrication of multi-response structural color films, and scalable production methods addressing the slow dewatering/drying of CNM suspension.

The highly hydrophilic surface of CNF, for example, is highly beneficial for self-cleaning, antifouling, and antimicrobial coatings, as identified above. In addition, the rigid chemical structure of CNF prevents inward orientation of the surface polar groups after exposure to air and hydrophobic media. This results in significantly improved performance. Utilizing these innate chemical performance criteria for CNF is a useful technique for enhancing performance of coatings while simultaneously increasing sustainability. CNF can also be easily surface modified using a variety of techniques to achieve coatings with different performance criteria, including antimicrobial, as identified above. Further applications and surface modification techniques will need to be explored to better understand such novel opportunities.

CNMs have been investigated and utilized to provide other functions to adhesives, including curing acceleration, electrical conductivity improvement, and VOC suppression. The epoxy's curing rate can be promoted via adding CNCs because of the presence of hydroxyl and carboxyl groups along the CNC surface. The use of CNMs can tune the structure of the composite's conductive network, therefore largely improving the conductivity. CNMs, modified or unmodified, can suppress VOC emission by either physisorption or chemisorption. There are several challenges that need to be addressed for the CNMs to be more widely used for functionalized adhesives, including the high raw-material cost.

ACKNOWLEDGMENTS

Authors from Oak Ridge National Laboratory (ORNL) are supported by the US Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, and Bioenergy Technologies Office, under contract DEAC05-00OR22725 with UT-Battelle LLC. Authors from University of Maine are grateful for the funding support from UT-Battelle LLC with the DOE under contract DEAC05-00OR22725 (subcontract # 4000174848). The authors thank Dr. Mahesh Parit for his contribution to paper structure formation, literature search, and management. Dr. Xuefeng Zhang acknowledges the support from Forest and Wildlife Research Center, Mississippi State University.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. L.W., conceptualization, writing – original draft, review and editing, visualization; P.V.K., C.C., K.L., S.B., H.T., J.W., M.O.S., E.A., writing – original draft, review and editing; N.O., writing – original draft; X.Z., writing – original draft, review and editing, visualization; M.K., writing – original draft; W.M.G., M.T., and E.W., writing – review and editing; S.O., conceptualization, writing – review and editing; D.J.G., conceptualization, writing –review & editing, supervision, funding acquisition.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

- Tracton, A.A. (2005). *Coatings Technology Handbook* (CRC Press).
- Zafar, F., Ghosal, A., Sharmin, E., Chaturvedi, R., and Nishat, N. (2019). A review on cleaner production of polymeric and nanocomposite coatings based on waterborne polyurethane dispersions from seed oils. *Prog. Org. Coat.* 131, 259–275. <https://doi.org/10.1016/j.porgcoat.2019.02.014>.
- Muralishwara, K., Kini, U.A., and Sharma, S. (2019). Epoxy-clay nanocomposite coatings: a review on synthesis and characterization. *Mater. Res. Express* 6, 082007. <https://doi.org/10.1088/2053-1591/ab1e15>.
- Radhamani, A.V., Lau, H.C., and Ramakrishna, S. (2020). Nanocomposite coatings on steel for enhancing the corrosion resistance: a review. *J. Compos. Mater.* 54, 681–701. <https://doi.org/10.1177/0021998319857807>.
- Kausar, A. (2020). High performance epoxy/polyester-based nanocomposite coatings for multipurpose applications: a review. *J. Plastic Film Sheeting* 36, 391–408. <https://doi.org/10.1177/8756087920910481>.
- Ebneshajad, S., and Landrock, A.H. (2014). *Adhesives Technology Handbook* (William Andrew).
- Kenig, S., Dodiuk, H., Otorogust, G., and Gomid, S. (2019). Nanocomposite polymer adhesives: a critical review. *Rev. Adhes. Adhes.* 7, 93–168. <https://doi.org/10.7569/RAA.2019.097306>.
- Bobby, S., and Samad, M.A. (2017). Enhancement of tribological performance of epoxy bulk composites and composite coatings using micro/nano fillers: a review. *Polym. Adv. Technol.* 28, 633–644. <https://doi.org/10.1002/pat.3961>.
- Selim, M.S., El-Safty, S.A., Shenashen, M.A., Higazy, S.A., and Elmarakbi, A. (2020). Progress in biomimetic leverages for marine antifouling using nanocomposite coatings. *J. Mater. Chem. B* 8, 3701–3732. <https://doi.org/10.1039/c9tb02119a>.
- Guo, L., Yuan, W., Lu, Z., and Li, C.M. (2013). Polymer/nanosilver composite coatings for antibacterial applications. *Colloids Surf. A Physicochem. Eng. Asp.* 439, 69–83. <https://doi.org/10.1016/j.colsurfa.2012.12.029>.
- Wang, L., Li, K., Copenhaver, K., MacKay, S., Lamm, M.E., Zhao, X., Dixon, B., Wang, J., Han, Y., Neivandt, D., et al. (2021). Review on nonconventional fibrillation methods of producing cellulose nanofibrils and their applications. *Biomacromolecules* 22, 4037–4059. <https://doi.org/10.1021/acs.biomac.1c00640>.
- Bautista, Y., Gonzalez, J., Gilabert, J., Ibañez, M., and Sanz, V. (2011). Correlation between the wear resistance, and the scratch resistance, for nanocomposite coatings. *Prog. Org. Coat.* 70, 178–185. <https://doi.org/10.1016/j.porgcoat.2010.09.022>.
- Tan, Y., Liu, Y., Chen, W., Liu, Y., Wang, Q., Li, J., and Yu, H. (2016). Homogeneous dispersion of cellulose nanofibers in waterborne acrylic coatings with improved properties and unreduced transparency. *ACS Sustain. Chem. Eng.* 4, 3766–3772. <https://doi.org/10.1021/acssuschemeng.6b00415>.
- Kelly, P.V., Gardner, D.J., and Gramlich, W.M. (2021). Optimizing lignocellulosic nanofibril dimensions and morphology by mechanical refining for enhanced adhesion. *Carbohydr. Polym.* 273, 118566.
- Copenhaver, K., Li, K., Wang, L., Lamm, M., Zhao, X., Korey, M., Neivandt, D., Dixon, B., Sultana, S., Kelly, P., et al. (2022). Pretreatment of lignocellulosic feedstocks for cellulose nanofibril production. *Cellulose* 29, 4835–4876.
- Saito, T., Kimura, S., Nishiyama, Y., and Isogai, A. (2007). Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* 8, 2485–2491. <https://doi.org/10.1021/bm0703970>.
- Foster, E.J., Moon, R.J., Agarwal, U.P., Bortner, M.J., Bras, J., Camarero-Espinosa, S., Chan, K.J., Clift, M.J.D., Cranston, E.D., Eichhorn, S.J., et al. (2018). Current characterization methods for cellulose nanomaterials. *Chem. Soc. Rev.* 47, 2609–2679. <https://doi.org/10.1039/c6cs00895j>.
- Moon, R.J., Martini, A., Nairn, J., Simonsen, J., and Youngblood, J. (2011). Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem. Soc. Rev.* 40, 3941–3994. <https://doi.org/10.1039/c0cs00108b>.
- Dufresne, A., Cavaillé, J.Y., and Vignon, M.R. (1997). Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. *J. Appl. Polym. Sci.* 64, 1185–1194. [https://doi.org/10.1002/\(SICI\)1097-4628\(19970509\)64:6<1185::AID-APP19>3.0.CO;2-V](https://doi.org/10.1002/(SICI)1097-4628(19970509)64:6<1185::AID-APP19>3.0.CO;2-V).
- Mihriyanyan, A. (2011). Cellulose from cladophorales green algae: from environmental problem to high-tech composite materials. *J. Appl. Polym. Sci.* 119, 2449–2460.
- Ifuku, S., Nogi, M., Abe, K., Handa, K., Nakatsubo, F., and Yano, H. (2007). Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: dependence on acetyl-group DS. *Biomacromolecules* 8, 1973–1978. <https://doi.org/10.1021/bm070113b>.
- Oksman, K., Aitomäki, Y., Mathew, A.P., Siqueira, G., Zhou, Q., Butylina, S., Tanpichai, S., Zhou, X., and Hooshmand, S. (2016). Review of the recent developments in cellulose nanocomposite processing. *Compos. Appl. Sci. Manuf.* 83, 2–18. <https://doi.org/10.1016/j.compositesa.2015.10.041>.
- Wang, L., Gardner, D.J., Wang, J., Yang, Y., Tekinalp, H.L., Tajvidi, M., Li, K., Zhao, X., Neivandt, D.J., Han, Y., et al. (2020). Towards the scale-up production of cellulose nanocomposites using melt processing: a critical review on structure-processing-property relationships. *Compos. B Eng.* 201, 108297. <https://doi.org/10.1016/j.compositesb.2020.108297>.
- Silva, F.A.G.S., Dourado, F., Gama, M., and Poças, F. (2020). Nanocellulose bio-based composites for food packaging. *Nanomaterials* 10, 2041. <https://doi.org/10.3390/nano10102041>.
- Bahramnia, H., Mohammadian Semnani, H., Habibolahzadeh, A., and Abdoos, H. (2020). Epoxy/polyurethane nanocomposite coatings for anti-erosion/wear applications: a review. *J. Compos. Mater.* 54, 3189–3203. <https://doi.org/10.1177/0021998320908299>.
- Mhd Haniffa, M.A.C., Ching, Y.C., Abdullah, L.C., Poh, S.C., and Chuah, C.H. (2016). Review of bionanocomposite coating films and their applications. *Polymers (Basel)* 8, 246. <https://doi.org/10.3390/polym8070246>.
- Lengowski, E.C., Bonfatti Júnior, E.A., Kumode, M.M.N., Carneiro, M.E., and Satyanarayana, K.G. (2019). Nanocellulose-reinforced adhesives for wood-based panels. In *Sustainable Polymer Composites and Nanocomposites* (Springer), pp. 1001–1025.
- Brodin, F.W., Gregersen, Ø.W., and Syverud, K. (2014). Cellulose nanofibrils: challenges and possibilities as a paper additive or coating material – a review. *Nord. Pulp Paper Res. J.* 29, 156–166. <https://doi.org/10.3183/npprj-2014-29-01-p156-166>.
- Tayeb, A., Amini, E., Ghasemi, S., and Tajvidi, M. (2018). Cellulose nanomaterials—binding properties and applications: a review. *Molecules* 23, 2684. <https://doi.org/10.3390/molecules23102684>.
- Kedzior, S.A., Gabriel, V.A., Dubé, M.A., and Cranston, E.D. (2021). Nanocellulose in emulsions and heterogeneous water-based polymer systems: a review. *Adv. Mater.* 33, 2002404. <https://doi.org/10.1002/adma.202002404>.
- Hubbe, M.A., Ferrer, A., Tyagi, P., Yin, Y., Salas, C., Pal, L., and Rojas, O.J. (2017). J. Nanocellulose in thin films, coatings, and plies for packaging applications: a review. *Bioresources* 12, 2143–2233.
- Ferrer, A., Pal, L., and Hubbe, M. (2017). Nanocellulose in packaging: advances in barrier layer technologies. *Ind. Crops Prod.* 95, 574–582. <https://doi.org/10.1016/j.indcrop.2016.11.012>.
- Wang, L., Chen, C., Wang, J., Gardner, D.J., and Tajvidi, M. (2020). Cellulose nanofibrils versus cellulose nanocrystals: comparison of performance in flexible multilayer films for packaging applications. *Food Packag. Shelf Life* 23, 100464.

34. Nuruddin, M., Chowdhury, R.A., Szeto, R., Howarter, J.A., Erk, K.A., Szczepanski, C.R., and Youngblood, J.P. (2021). Structure–property relationship of cellulose nanocrystal–polyvinyl alcohol thin films for high barrier coating applications. *ACS Appl. Mater. Interfaces* 13, 12472–12482. <https://doi.org/10.1021/acsami.0c21525>.
35. Mølgaard, S.L., Henriksson, M., Cárdenas, M., and Svagan, A.J. (2014). Cellulose-nanofiber/polygalacturonic acid coatings with high oxygen barrier and targeted release properties. *Carbohydr. Polym.* 114, 179–182. <https://doi.org/10.1016/j.carbpol.2014.08.011>.
36. Chowdhury, R.A., Clarkson, C., Apalangya, V.A., Islam, S.M.N., and Youngblood, J.P. (2018). Roll-to-Roll fabrication of cellulose nanocrystal-poly(vinyl alcohol) composite coatings with controlled anisotropy. *Cellulose* 25, 6547–6560. <https://doi.org/10.1007/s10570-018-2019-5>.
37. Kaboorani, A., Auclair, N., Riedl, B., and Landry, V. (2016). Physical and morphological properties of UV-cured cellulose nanocrystal (CNC) based nanocomposite coatings for wood furniture. *Prog. Org. Coat.* 93, 17–22. <https://doi.org/10.1016/j.porgcoat.2015.12.009>.
38. Deng, Z., Jung, J., Simonsen, J., Wang, Y., and Zhao, Y. (2017). Cellulose nanocrystal reinforced chitosan coatings for improving the storability of postharvest pears under both ambient and cold storages. *J. Food Sci.* 82, 453–462. <https://doi.org/10.1111/1750-3841.13601>.
39. Deng, Z., Jung, J., Simonsen, J., and Zhao, Y. (2017). Cellulose nanomaterials emulsion coatings for controlling physiological activity, modifying surface morphology, and enhancing storability of postharvest bananas (*musa acuminata*). *Food Chem.* 232, 359–368. <https://doi.org/10.1016/j.foodchem.2017.04.028>.
40. Deng, Z., Jung, J., Simonsen, J., and Zhao, Y. (2018). Cellulose nanocrystals pickering emulsion incorporated chitosan coatings for improving storability of postharvest bartlett pears (*pyrus communis*) during long-term cold storage. *Food Hydrocoll.* 84, 229–237. <https://doi.org/10.1016/j.foodhyd.2018.06.012>.
41. Kaboorani, A., Auclair, N., Riedl, B., Hosseinaei, O., and Wang, S. (2017). Cellulose nanocrystal (CNC)-Based nanocomposites for UV curable high-solid coating systems. *J. Coat. Technol. Res.* 14, 1137–1145. <https://doi.org/10.1007/s11998-017-9929-2>.
42. Gan, P.G., Sam, S.T., Abdullah, M.F.b., and Omar, M.F. (2020). Thermal properties of nanocellulose-reinforced composites: a review. *J. Appl. Polym. Sci.* 137, 48544. <https://doi.org/10.1002/app.48544>.
43. Yoo, Y. (2017). *Synthesis and Characterization of Hydrophobized Cellulose Nanocrystal Enhanced Sustainable Polymer Composites via Capsule and Coat Processing* (Purdue University).
44. Cataldi, A., Esposito Corcione, C., Frigione, M., and Pegoretti, A. (2017). Photocurable resin/nanocellulose composite coatings for wood protection. *Prog. Org. Coat.* 106, 128–136. <https://doi.org/10.1016/j.porgcoat.2017.01.019>.
45. Ghanadpour, M., Carosio, F., Ruda, M.C., and Wågberg, L. (2018). Tuning the nanoscale properties of phosphorylated cellulose nanofibril-based thin films to achieve highly fire-protecting coatings for flammable solid materials. *ACS Appl. Mater. Interfaces* 10, 32543–32555. <https://doi.org/10.1021/acsami.8b10309>.
46. Pan, Y., Liu, L., Song, L., Hu, Y., Jiang, S., and Zhao, H. (2019). Reinforcement of layer-by-layer self-assembly coating modified cellulose nanofibers to reduce the flammability of polyvinyl alcohol. *Cellulose* 26, 3183–3192. <https://doi.org/10.1007/s10570-019-02298-z>.
47. Wang, X., Zhang, X., Caldona, E.B., Leng, W., Street, J., Wang, G., and Zhang, Z. (2021). Anticorrosive epoxy coatings containing ultrafine bamboo char and zinc particles. *J. Environ. Chem. Eng.* 9, 105707. <https://doi.org/10.1016/J.JECE.2021.105707>.
48. Shafaamri, A., Cheng, C.H., Wonnice Ma, I.A., Baig, S.B., Kasi, R., Subramaniam, R., and Balakrishnan, V. (2020). Effects of TiO₂ nanoparticles on the overall performance and corrosion protection ability of neat epoxy and PDMS modified epoxy coating systems. *Front. Mater.* 6, 336. <https://doi.org/10.3389/FMATS.2019.00336/BIBTEX>.
49. Cui, G., Bi, Z., Zhang, R., Liu, J., Yu, X., and Li, Z. (2019). A comprehensive review on graphene-based anti-corrosive coatings. *Chem. Eng. J.* 373, 104–121. <https://doi.org/10.1016/J.CEJ.2019.05.034>.
50. Dutta, G.K., and Karak, N. (2022). Bio-based waterborne polyester/cellulose nanofiber-reduced graphene oxide–zinc oxide nanocomposite: an approach towards sustainable mechanically robust anticorrosive coating. *Cellulose* 29, 1679–1703. <https://doi.org/10.1007/S10570-021-04414-4/SCHEMES/3>.
51. Aema, I., Ma, W., Shafaamri, A., Kasi, R., Zaini, F.N., Balakrishnan, V., Subramaniam, R., and Arof, A.K. (2017). Anticorrosion properties of epoxy/nanocellulose nanocomposite coating. *Bioresources* 12, 2912–2929.
52. Abd El-Fattah, M., Hasan, A.M.A., Keshawy, M., El Saeed, A.M., and Aboelenien, O.M. (2018). Nanocrystalline cellulose as an eco-friendly reinforcing additive to polyurethane coating for augmented anticorrosive behavior. *Carbohydr. Polym.* 183, 311–318. <https://doi.org/10.1016/J.CARBOL.2017.12.084>.
53. França, D., Angelo, L.M., Souza, C.F., and Faez, R. (2021). Biobased poly(3-hydroxybutyrate)/starch/cellulose nanofibrils for nutrients coatings. *ACS Appl. Polym. Mater.* 3, 3227–3237. <https://doi.org/10.1021/acsapm.1c00418>.
54. Messa, L.L., and Faez, R. (2020). Spray-dried chitosan/nanocellulose microparticles: synergistic effects for the sustained release of NPK fertilizer. *Cellulose* 27, 10077–10093. <https://doi.org/10.1007/s10570-020-03482-2>.
55. He, Y., Li, H., Fei, X., and Peng, L. (2021). Carboxymethyl cellulose/cellulose nanocrystals immobilized silver nanoparticles as an effective coating to improve barrier and antibacterial properties of paper for food packaging applications. *Carbohydr. Polym.* 252, 117156. <https://doi.org/10.1016/j.carbpol.2020.117156>.
56. Yoo, Y., Martinez, C., and Youngblood, J.P. (2017). Sustained dye release using poly(urea-urethane)/cellulose nanocrystal composite microcapsules. *Langmuir* 33, 1521–1532. <https://doi.org/10.1021/acs.langmuir.6b04628>.
57. Dogan-Guner, E.M., Schueneman, G.T., Shofner, M.L., and Meredith, J.C. (2021). Acryloyl-modified cellulose nanocrystals: effects of substitution on crystallinity and copolymerization with acrylic monomers. *Cellulose* 28, 10875–10889. <https://doi.org/10.1007/s10570-021-04219-5>.
58. Kaboorani, A., Auclair, N., Riedl, B., and Landry, V. (2017). Mechanical properties of UV-cured cellulose nanocrystal (CNC) nanocomposite coating for wood furniture. *Prog. Org. Coat.* 104, 91–96. <https://doi.org/10.1016/j.porgcoat.2016.11.031>.
59. Lee, S., Gavande, V., Kim, G., Kim, B., Jin, Y., Bae, S., Chun, J.H., and Lee, W.-K. (2021). Coating properties of UV-curable PUA nanocomposites with modified cellulose nanocrystals. *Mol. Cryst. Liq. Cryst.* 1–8. <https://doi.org/10.1080/15421406.2021.1946984>.
60. Asaro, L., Seoane, I.T., Fasce, L.A., Cyras, V.P., and Manfredi, L.B. (2019). Development of low environmental impact protective coatings based on a furan resin and cellulose nanocrystals. *Prog. Org. Coat.* 133, 229–236. <https://doi.org/10.1016/j.porgcoat.2019.04.035>.
61. Vardanyan, V., Poaty, B., Chauve, G., Landry, V., Galstian, T., and Riedl, B. (2014). Mechanical properties of UV-waterborne varnishes reinforced by cellulose nanocrystals. *J. Coat. Technol. Res.* 11, 841–852. <https://doi.org/10.1007/s11998-014-9598-3>.
62. Auclair, N., Kaboorani, A., Riedl, B., Landry, V., Hosseinaei, O., and Wang, S. (2018). Influence of modified cellulose nanocrystals (CNC) on performance of bionanocomposite coatings. *Prog. Org. Coat.* 123, 27–34. <https://doi.org/10.1016/j.porgcoat.2018.05.027>.
63. Vaezi, K., Asadpour, G., and Sharifi, S.H. (2019). Effect of coating with novel bio nanocomposites of cationic starch/cellulose nanocrystals on the fundamental properties of the packaging paper. *Polym. Test.* 80, 106080. <https://doi.org/10.1016/j.polymertesting.2019.106080>.
64. Huang, M., Tang, Y., Wang, X., Zhu, P., Chen, T., and Zhou, Y. (2021). Preparation of polyaniline/cellulose nanocrystal composite and its application in surface coating of cellulosic paper. *Prog. Org. Coat.* 159, 106452. <https://doi.org/10.1016/j.porgcoat.2021.106452>.
65. Liu, S., Chen, Y., Liu, C., Gan, L., Ma, X., and Huang, J. (2019). Polydopamine-coated cellulose nanocrystals as an active ingredient

- in poly (vinyl alcohol) films towards intensifying packaging application potential. *Cellulose* 26, 9599–9612. <https://doi.org/10.1007/s10570-019-02749-7>.
66. Huang, J., Lyu, S., Fu, F., Wu, Y., and Wang, S. (2017). Green preparation of a cellulose nanocrystals/polyvinyl alcohol composite superhydrophobic coating. *RSC Adv.* 7, 20152–20159. <https://doi.org/10.1039/C6RA27663F>.
 67. Chowdhury, R.A., Clarkson, C.M., Shrestha, S., El Awad Azrak, S.M., Mavlan, M., and Youngblood, J.P. (2020). High-performance waterborne polyurethane coating based on a blocked isocyanate with cellulose nanocrystals (CNC) as the polyol. *ACS Appl. Polym. Mater.* 2, 385–393. <https://doi.org/10.1021/acsapm.9b00849>.
 68. Furtak-Wrona, K., Kozik-Ostrówka, P., Jadwiszczak, K., Maigret, J.E., Aguié-Béghin, V., and Coqueret, X. (2018). Polyurethane acrylate networks including cellulose nanocrystals: a comparison between UV and EB-curing. *Radiat. Phys. Chem.* 142, 94–99. <https://doi.org/10.1016/j.radphyschem.2017.04.013>.
 69. Tian, Y., Gao, Y., Pan, X., Liu, Q., Wang, J., Jin, M., and Li, J. (2021). Renewable UV-curable polyester methacrylate/cellulose nanocrystals composite resin for wood waterproof coating. *Nanotechnology* 32, 275703. <https://doi.org/10.1088/1361-6528/abf20d>.
 70. Niinivaara, E., Desmaisons, J., Dufresne, A., Bras, J., and Cranston, E.D. (2021). Thick polyvinyl alcohol films reinforced with cellulose nanocrystals for coating applications. *ACS Appl. Nano Mater.* 4, 8015–8025. <https://doi.org/10.1021/acsanm.1c01244>.
 71. Hutton-Prager, B., Ureña-Benavides, E., Parajuli, S., and Adenekan, K. (2022). Investigation of cellulose nanocrystals (CNC) and cellulose nanofibers (CNF) as thermal barrier and strengthening agents in pigment-based paper coatings. *J. Coat. Technol. Res.* 19, 337–346. <https://doi.org/10.1007/s11998-021-00538-1>.
 72. Kluge, M., Veigel, S., Pinkl, S., Henniges, U., Zollfrank, C., Rössler, A., and Gindl-Altmutter, W. (2017). Nanocellulosic fillers for waterborne wood coatings: reinforcement effect on free-standing coating films. *Wood Sci. Technol.* 51, 601–613. <https://doi.org/10.1007/s00226-017-0892-y>.
 73. Künniger, T., Grüneberger, F., Fischer, B., and Walder, C. (2017). Nanofibrillated cellulose in wood coatings: viscoelastic properties of free composite films. *J. Mater. Sci.* 52, 10237–10249. <https://doi.org/10.1007/s10853-017-1193-4>.
 74. Huang, Y., Feng, Q., Ye, C., Nair, S.S., and Yan, N. (2020). Incorporation of ligno-cellulose nanofibrils and bark extractives in water-based coatings for improved wood protection. *Prog. Org. Coat.* 138, 105210. <https://doi.org/10.1016/j.porgcoat.2019.105210>.
 75. Veigel, S., Lems, E.-M., Grüll, G., Hansmann, C., Rosenau, T., Zimmermann, T., and Gindl-Altmutter, W. (2017). Simple green route to performance improvement of fully bio-based linseed oil coating using nanofibrillated cellulose. *Polymers (Basel)* 9, 425. <https://doi.org/10.3390/polym9090425>.
 76. Cheng, D., Wen, Y., An, X., Zhu, X., and Ni, Y. (2016). TEMPO-oxidized cellulose nanofibers (TOCNs) as a green reinforcement for waterborne polyurethane coating (WPU) on wood. *Carbohydr. Polym.* 151, 326–334. <https://doi.org/10.1016/j.carbpol.2016.05.083>.
 77. Wongjaiyen, T., Brostow, W., and Chonkaew, W. (2018). Tensile properties and wear resistance of epoxy nanocomposites reinforced with cellulose nanofibers. *Polym. Bull.* 75, 2039–2051. <https://doi.org/10.1007/s00289-017-2142-8>.
 78. Yue, L., Liu, F., Mekala, S., Patel, A., Gross, R.A., and Manas-Zloczower, I. (2019). High performance biobased epoxy nanocomposite reinforced with a bacterial cellulose nanofiber network. *ACS Sustain. Chem. Eng.* 7, 5986–5992. <https://doi.org/10.1021/acssuschemeng.8b06073>.
 79. Wang, W., Yu, Z., Alsammarraie, F.K., Kong, F., Lin, M., and Mustapha, A. (2020). Properties and antimicrobial activity of polyvinyl alcohol-modified bacterial nanocellulose packaging films incorporated with silver nanoparticles. *Food Hydrocoll.* 100, 105411. <https://doi.org/10.1016/j.foodhyd.2019.105411>.
 80. Chiulan, I., Frone, A.N., Panaitescu, D.M., Nicolae, C.A., and Trusca, R. (2018). Surface properties, thermal, and mechanical characteristics of poly (vinyl alcohol)–starch-bacterial cellulose composite films. *J. Appl. Polym. Sci.* 135, 45800. <https://doi.org/10.1002/app.45800>.
 81. Veigel, S., Grüll, G., Pinkl, S., Obersiebzig, M., Müller, U., and Gindl-Altmutter, W. (2014). Improving the mechanical resistance of waterborne wood coatings by adding cellulose nanofibers. *React. Funct. Polym.* 85, 214–220. <https://doi.org/10.1016/j.reactfunctpolym.2014.07.020>.
 82. Nogi, M., Iwamoto, S., Nakagaito, A.N., and Yano, H. (2009). Optically transparent nanofiber paper. *Adv. Mater.* 21, 1595–1598.
 83. Fujisawa, S., Togawa, E., and Kuroda, K. (2017). Facile route to transparent, strong, and thermally stable nanocellulose/polymer nanocomposites from an aqueous pickering emulsion. *Biomacromolecules* 18, 266–271. <https://doi.org/10.1021/acs.biomac.6b01615>.
 84. Gu, M., Jiang, C., Liu, D., Prempeh, N., and Smalyukh, I.I. (2016). Cellulose nanocrystal/poly(ethylene glycol) composite as an iridescent coating on polymer substrates: structure-color and interface adhesion. *ACS Appl. Mater. Interfaces* 8, 32565–32573. <https://doi.org/10.1021/acsami.6b12044>.
 85. Babaei-Ghazvini, A., and Acharya, B. (2021). Humidity-responsive photonic films and coatings based on tuned cellulose nanocrystals/glycerol/polyethylene glycol. *Polymers* 13, 3695. <https://doi.org/10.3390/polym13213695>.
 86. Tran, A., Hamad, W.Y., and MacLachlan, M.J. (2018). Fabrication of cellulose nanocrystal films through differential evaporation for patterned coatings. *ACS Appl. Nano Mater.* 1, 3098–3104. <https://doi.org/10.1021/acsnm.8b00947>.
 87. Xu, C., Huang, C., and Huang, H. (2021). Recent advances in structural color display of cellulose nanocrystal materials. *Appl. Mater. Today* 22, 100912. <https://doi.org/10.1016/j.apmt.2020.100912>.
 88. De France, K., Zeng, Z., Wu, T., and Nyström, G. (2021). Functional materials from nanocellulose: utilizing structure–property relationships in bottom-up fabrication. *Adv. Mater.* 33, 2000657. <https://doi.org/10.1002/adma.202000657>.
 89. Tran, A., Boott, C.E., and MacLachlan, M.J. (2020). Understanding the self-assembly of cellulose nanocrystals—toward chiral photonic materials. *Adv. Mater.* 32, e1905876. <https://doi.org/10.1002/adma.201905876>.
 90. Zhang, F., Ge, W., Wang, C., Zheng, X., Wang, D., Zhang, X., Wang, X., Xue, X., and Qing, G. (2021). Highly strong and solvent-resistant cellulose nanocrystal photonic films for optical coatings. *ACS Appl. Mater. Interfaces* 13, 17118–17128. <https://doi.org/10.1021/acsmi.1c02753>.
 91. Huynh, C.T., and Lee, D.S. (2015). Controlled Release - Encyclopedia of Polymeric Nanomaterials, S. Kobayashi and K. Müllen, eds. (Springer Berlin Heidelberg), pp. 439–449. https://doi.org/10.1007/978-3-642-29648-2_314.
 92. Yabuki, A., Shiraiwa, T., and Fathona, I.W. (2016). PH-controlled self-healing polymer coatings with cellulose nanofibers providing an effective release of corrosion inhibitor. *Corros. Sci.* 103, 117–123. <https://doi.org/10.1016/j.corsci.2015.11.015>.
 93. Yabuki, A., Kanagaki, M., Nishikawa, C., Lee, J.H., and Fathona, I.W. (2021). Effective release of corrosion inhibitor by cellulose nanofibers and zeolite particles in self-healing coatings for corrosion protection. *Prog. Org. Coat.* 154, 106194. <https://doi.org/10.1016/j.porgcoat.2021.106194>.
 94. Nawaz, M., Habib, S., Khan, A., Shakoar, R.A., and Kahraman, R. (2020). Cellulose microfibrils (CMFs) as a smart carrier for autonomous self-healing in epoxy coatings. *New J. Chem.* 44, 5702–5710. <https://doi.org/10.1039/c9nj06436b>.
 95. Vijayan P, P., Tanvir, A., El-Gawady, Y.H., and Al-Maadeed, M. (2017). Cellulose nanofibers to assist the release of healing agents in epoxy coatings. *Prog. Org. Coat.* 112, 127–132. <https://doi.org/10.1016/j.porgcoat.2017.07.008>.
 96. Lee, S.H., and Ruckenstein, E. (1987). Surface restructuring of polymers. *J. Colloid Interface Sci.* 120, 529–536. [https://doi.org/10.1016/0021-9797\(87\)90380-8](https://doi.org/10.1016/0021-9797(87)90380-8).
 97. He, K., Duan, H., Chen, G.Y., Liu, X., Yang, W., and Wang, D. (2015). Cleaning of oil fouling with water enabled by zwitterionic polyelectrolyte coatings: overcoming the imperative challenge of oil–water separation membranes. *ACS Nano* 9, 9188–9198. <https://doi.org/10.1021/acsnano.5b03791>.
 98. Huang, S., and Wang, D. (2017). Simple nanocellulose coating for self-cleaning upon

- water action: molecular design of stable surface hydrophilicity. *Angew. Chem. Int. Ed. Engl.* 129, 9181–9185. <https://doi.org/10.1002/ange.201703913>.
99. Huang, J., Lyu, S., Fu, F., Chang, H., and Wang, S. (2016). Preparation of superhydrophobic coating with excellent abrasion resistance and durability using nanofibrillated cellulose. *RSC Adv.* 6, 106194–106200. <https://doi.org/10.1039/C6RA23447J>.
100. Huang, J., Cai, P., Li, M., Wu, Q., Li, Q., and Wang, S. (2020). Preparation of CNF/PDMS superhydrophobic coatings with good abrasion resistance using a one-step spray method. *Materials (Basel)* 13, 5380. <https://doi.org/10.3390/ma13235380>.
101. Lotfikatouli, S., Hadi, P., Yang, M., Walker, H.W., Hsiao, B.S., Gobler, C., Reichel, M., and Mao, X. (2021). Enhanced anti-fouling performance in membrane bioreactors using a novel cellulose nanofiber-coated membrane. *Sep. Purif. Technol.* 275, 119145. <https://doi.org/10.1016/j.seppur.2021.119145>.
102. Cheng, L., Ren, S., and Lu, X. (2020). Application of eco-friendly waterborne polyurethane composite coating incorporated with nano cellulose crystalline and silver nano particles on wood antibacterial board. *Polymers* 12, 407. <https://doi.org/10.3390/polym12020407>.
103. Gogoi, B., Barua, S., Sarmah, J.K., and Karak, N. (2018). In situ synthesis of a microbial fouling resistant, nanofibrillar cellulose-hyperbranched epoxy composite for advanced coating applications. *Prog. Org. Coat.* 124, 224–231. <https://doi.org/10.1016/j.porgcoat.2018.04.025>.
104. Martins, N.C., Freire, C.S., Neto, C.P., Silvestre, A.J., Causio, J., Baldi, G., Sadocco, P., and Trindade, T. (2013). Antibacterial paper based on composite coatings of nanofibrillated cellulose and ZnO. *Colloids Surf. A Physicochem. Eng. Asp.* 417, 111–119. <https://doi.org/10.1016/j.colsurfa.2012.10.042>.
105. Tang, Z., Zhang, M., Xiao, H., Liu, K., Li, X., Du, B., Huang, L., Chen, L., and Wu, H. (2022). A green catechol-containing cellulose nanofibrils-cross-linked adhesive. *ACS Biomater. Sci. Eng.* 8, 1096–1102. <https://doi.org/10.1021/acsbomaterials.1c01494>.
106. Mabrouk, A.B., Dufresne, A., and Boufi, S. (2020). Cellulose nanocrystal as ecofriendly stabilizer for emulsion polymerization and its application for waterborne adhesive. *Carbohydr. Polym.* 229, 115504. <https://doi.org/10.1016/j.carbpol.2019.115504>.
107. Chen, H., Nair, S.S., Chauhan, P., and Yan, N. (2019). Lignin containing cellulose nanofibril application in PMDI wood adhesives for drastically improved gap-filling properties with robust bondline interfaces. *Chem. Eng. J.* 360, 393–401. <https://doi.org/10.1016/j.cej.2018.11.222>.
108. Cao, G., Gao, X., Wang, L., Cui, H., Lu, J., Meng, Y., Xue, W., Cheng, C., Tian, Y., and Tian, Y. (2019). Easily synthesized polyaniline@cellulose nanowhiskers better tune network structures in Ag-based adhesives: examining the improvements in conductivity, stability, and flexibility. *Nanomaterials* 9, 1542. <https://doi.org/10.3390/nano9111542>.
109. Karimi Shamsabadi, M., and Moghbeli, M.R. (2017). Cellulose nanocrystals (CNCs) reinforced acrylic pressure-sensitive adhesives (PSAs) prepared via miniemulsion polymerization. *Int. J. Adhes. Adhes.* 78, 155–166. <https://doi.org/10.1016/j.ijadhadh.2017.06.024>.
110. Khanjanzadeh, H., Behrooz, R., Bahramifar, N., Pinkl, S., and Gindl-Altmutter, W. (2019). Application of surface chemical functionalized cellulose nanocrystals to improve the performance of UF adhesives used in wood based composites-MDF type. *Carbohydr. Polym.* 206, 11–20. <https://doi.org/10.1016/j.carbpol.2018.10.115>.
111. Mesquita, R.G.d.A., Mendes, L.M., Sanadi, A.R., de Sena Neto, A.R., Claro, P.I.C., Corrêa, A.C., and Marconcini, J.M. (2018). Urea formaldehyde and cellulose nanocrystals adhesive: studies applied to sugarcane bagasse particleboards. *J. Polym. Environ.* 26, 3040–3050. <https://doi.org/10.1007/s10924-018-1189-4>.
112. Figueiredo, L.R., Nepomuceno, N.C., Melo, J.D., and Medeiros, E.S. (2021). Glycerol-based polymer adhesives reinforced with cellulose nanocrystals. *Int. J. Adhes. Adhes.* 110, 102935. <https://doi.org/10.1016/j.ijadhadh.2021.102935>.
113. Pruksawan, S., Samitsu, S., Fujii, Y., Torikai, N., and Naito, M. (2020). Toughening effect of rodlike cellulose nanocrystals in epoxy adhesives. *ACS Appl. Polym. Mater.* 2, 1234–1243. <https://doi.org/10.1021/acscapm.9b01102>.
114. Cudjoe, E., Herbert, K.M., and Rowan, S.J. (2018). Strong, rebondable, dynamic cross-linked cellulose nanocrystal polymer nanocomposite adhesives. *ACS Appl. Mater. Interfaces* 10, 30723–30731. <https://doi.org/10.1021/acscami.8b10520>.
115. Wang, Z., Zhao, S., Zhang, W., Qi, C., Zhang, S., and Li, J. (2019). Bio-inspired cellulose nanofiber-reinforced soy protein resin adhesives with dopamine-induced codeposition of “water-resistant” interphases. *Appl. Surf. Sci.* 478, 441–450. <https://doi.org/10.1016/j.apsusc.2019.01.154>.
116. Li, K., Jin, S., Wei, Y., Li, X., Li, J., Shi, S.Q., and Li, J. (2021). Bioinspired hyperbranched protein adhesive based on boronic acid-functionalized cellulose nanofibril and water-soluble polyester. *Compos. B Eng.* 219, 108943. <https://doi.org/10.1016/j.compositesb.2021.108943>.
117. Li, K., Jin, S., Li, X., Li, J., Shi, S.Q., and Li, J. (2021). Bioinspired interface engineering of soybean meal-based adhesive incorporated with biomineralized cellulose nanofibrils and a functional aminoclay. *Chem. Eng. J.* 421, 129820. <https://doi.org/10.1016/j.cej.2021.129820>.
118. Oh, M., Ma, Q., Simsek, S., Bajwa, D., and Jiang, L. (2019). Comparative study of zein- and gluten-based wood adhesives containing cellulose nanofibers and crosslinking agent for improved bond strength. *Int. J. Adhes. Adhes.* 92, 44–57. <https://doi.org/10.1016/j.ijadhadh.2019.04.004>.
119. Padinjakkara, A., Scarinzi, G., Santagata, G., Malinconico, M., Razal, J.M., Thomas, S., and Salim, N.V. (2020). Enhancement of adhesive strength of epoxy/carboxyl-terminated poly(butadiene-Co-acrylonitrile) nanocomposites using waste hemp fiber-derived cellulose nanofibers. *Ind. Eng. Chem. Res.* 59, 10904–10913. <https://doi.org/10.1021/acs.iecr.0c01053>.
120. Cui, J., Lu, X., Zhou, X., Chrusciel, L., Deng, Y., Zhou, H., Zhu, S., and Brosse, N. (2015). Enhancement of mechanical strength of particleboard using environmentally friendly pine (pinus pinaster L.) tannin adhesives with cellulose nanofibers. *Ann. For. Sci.* 72, 27–32. <https://doi.org/10.1007/s13595-014-0392-2>.
121. Moslemi, A., Zolfaghariloo koohi, M., Behzad, T., and Pizzi, A. (2020). Addition of cellulose nanofibers extracted from rice straw to urea formaldehyde resin; effect on the adhesive characteristics and medium density fiberboard properties. *Int. J. Adhes. Adhes.* 99, 102582. <https://doi.org/10.1016/j.ijadhadh.2020.102582>.
122. Yang, X., Yang, S., and Wang, L. (2022). Cellulose or chitin nanofibril-stabilized latex for medical adhesion via tailoring colloidal interactions. *Carbohydr. Polym.* 278, 118916. <https://doi.org/10.1016/j.carbpol.2021.118916>.
123. Tajvidi, M., Gardner, D.J., and Bousfield, D.W. (2016). Cellulose nanomaterials as binders: laminate and particulate systems. *J. Renew. Mater.* 4, 365–376. <https://doi.org/10.7569/JRM.2016.634103>.
124. Zidanes, U.L., Dias, M.C., Lorenço, M.S., Da Silva Araujo, E., Ferreira E Silva, M.J., Sousa, T.B., Ferreira, S.R., Ugucioni, J.C., Denzin Tonoli, G.H., Bianchi, M.L., and Mori, F.A. (2021). Preparation and characterization of tannin-based adhesives reinforced with cellulose nanofibrils for wood bonding. *Holzforschung* 75, 159–167. <https://doi.org/10.1515/hf-2020-0033>.
125. Heon Kwon, J., Lee, S.-H., Ayrilmis, N., and Hyung Han, T. (2015). Tensile shear strength of wood bonded with urea-formaldehyde with different amounts of microfibrillated cellulose. *Int. J. Adhes. Adhes.* 60, 88–91. <https://doi.org/10.1016/j.ijadhadh.2015.04.002>.
126. Chaabouni, O., and Boufi, S. (2017). Cellulose nanofibrils/polyvinyl acetate nanocomposite adhesives with improved mechanical properties. *Carbohydr. Polym.* 156, 64–70. <https://doi.org/10.1016/j.carbpol.2016.09.016>.
127. Zhang, B.F., Wang, J., Liu, Z.W., Zhao, Y.L., Li, D.D., Huang, T.Q., Gu, H., and Song, J.N. (2015). Reinforcement of lignin-based phenol-formaldehyde adhesive with nano-crystalline cellulose (NCC): curing behavior and bonding property of plywood. *World Neurosurg.* 83, 567–573. <http://creativecommons.org/licenses/by/4.0/>.
128. Kawalerczyk, J., Dziurka, D., Mirski, R., Siuda, J., and Szentner, K. (2020). The effect of nanocellulose addition to phenol-formaldehyde adhesive in water-resistant

- plywood manufacturing. *Bioresources* 15, 5388–5401.
129. Cheng, H.N., Kilgore, K., Ford, C., Fortier, C., Dowd, M.K., and He, Z. (2019). Cottonseed protein-based wood adhesive reinforced with nanocellulose. *J. Adhes. Sci. Technol.* 33, 1357–1368. <https://doi.org/10.1080/01694243.2019.1596650>.
130. Zeng, Y., Yang, W., Xu, P., and Ma, P. (2022). A water-resistance soy protein-based adhesive for various substrates application by incorporating tailor-made hydrophobic nanocrystalline cellulose. *Compos. Commun.* 32, 101151. <https://doi.org/10.1016/j.coco.2022.101151>.
131. Jiang, L., Ren, Z., Zhao, W., Liu, W., Liu, H., and Zhu, C. (2018). Synthesis and structure/properties characterizations of four polyurethane model hard segments. *R. Soc. Open Sci.* 5, 180536. <https://doi.org/10.1098/rsos.180536>.
132. Larraza, I., Vadillo, J., Santamaria-Echart, A., Tejado, A., Azpeitia, M., Vesga, E., Orue, A., Saralegi, A., Arbelaz, A., and Eceiza, A. (2020). The effect of the carboxylation degree on cellulose nanofibers and waterborne polyurethane/cellulose nanofiber nanocomposites properties. *Polym. Degrad. Stab.* 173, 109084. <https://doi.org/10.1016/j.polymdegradstab.2020.109084>.
133. Rigg-Aguilar, P., Moya, R., Oporto-Velásquez, G.S., Vega-Baudrit, J., Starbird, R., Puente-Urbina, A., Méndez, D., Potosme, L.D., and Esquivel, M. (2020). Micro- and nanofibrillated cellulose (MNFC) from pineapple (ananas comosus) stems and their application on polyvinyl acetate (PVAc) and urea-formaldehyde (UF) wood adhesives. *J. Nanomater.* 2020, 1–12. <https://doi.org/10.1155/2020/1393160>.
134. Li, X., Chen, M., Zhang, J., Gao, Q., Zhang, S., and Li, J. (2017). Physico-chemical properties of soybean meal-based adhesives reinforced by ethylene glycol diglycidyl ether and modified nanocrystalline cellulose. *Polymers* 9, E463. <https://doi.org/10.3390/polym9090463>.
135. Patel, A., Mekala, S., Kravchenko, O.G., Yilmaz, T., Yuan, D., Yue, L., Gross, R.A., and Manas-Zloczower, I. (2019). Design and formulation of a completely biobased epoxy structural adhesive. *ACS Sustain. Chem. Eng.* 7, 16382–16391. <https://doi.org/10.1021/acssuschemeng.9b03489>.
136. Zhao, X., Li, K., Wang, Y., Tekinalp, H., Larsen, G., Rasmussen, D., Ginder, R.S., Wang, L., Gardner, D.J., Tajvidi, M., et al. (2020). High-strength polylactic acid (PLA) biocomposites reinforced by epoxy-modified pine fibers. *ACS Sustain. Chem. Eng.* 8, 13236–13247. <https://doi.org/10.1021/acssuschemeng.0c03463>.
137. Wang, H., Pang, H., Wei, D., Li, T., Yong, Q., Huang, J., and Liao, B. (2018). Fabrication of hollow core-shell conductive nanoparticles based on nanocrystalline cellulose for conductive adhesive. *J. Mater. Sci. Mater. Electron.* 29, 9829–9839. <https://doi.org/10.1007/s10854-018-9023-2>.
138. Candan, Z., and Akbulut, T. (2014). Nano-engineered plywood panels: performance properties. *Compos. B Eng.* 64, 155–161. <https://doi.org/10.1016/j.compositesb.2014.04.021>.
139. Resetco, C., Frank, D., Dikić, T., Claessens, S., Verbrugge, T., and Du Prez, F.E. (2016). Thiolactone-based polymers for formaldehyde scavenging coatings. *Eur. Polym. J.* 82, 166–174. <https://doi.org/10.1016/j.eurpolymj.2016.07.008>.
140. Ayirlmis, N., Lee, Y.-K., Kwon, J.H., Han, T.-H., and Kim, H.-J. (2016). Formaldehyde emission and VOCs from LVLs produced with three grades of urea-formaldehyde resin modified with nanocellulose. *Build. Environ.* 97, 82–87. <https://doi.org/10.1016/j.buildenv.2015.12.009>.
141. Wibowo, E.S., Lubis, M.A.R., and Park, B.-D. (2021). In-situ modification of low molar ratio urea-formaldehyde resins with cellulose nanofibrils for plywood. *J. Adhes. Sci. Technol.* 35, 2452–2465. <https://doi.org/10.1080/01694243.2021.1890370>.