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Editor's Choice



Lignin Nanoparticles as an Interfacial Modulator in Tough and Multi-Resistant Cellulose–Polycaprolactone Nanocomposites Based on a Pickering Emulsions Strategy

Erfan Kimiaei, Muhammad Farooq, Rafael Grande, Kristoffer Meinander, and Monika Österberg*

Free-standing nanocellulosic films (nanopapers) emerge as attractive sustainable materials to replace traditional plastics. However, the moisture sensitivity of cellulose and its poor dispersion in hydrophobic polymers are challenges to its widespread application. Harnessing the inherent properties of cellulose, lignin, and polycaprolactone, a Pickering emulsion approach is proposed to produce multifunctional cellulose nanofibril (CNF) nanocomposite films. Aqueous CNF dispersion is combined with hydrophobic polycaprolactone (PCL) using colloidal lignin nanoparticles (CLPs) as the emulsion stabilizer. CNF-PCL nanocomposite films with over 134% increase in dry strength compared to nanocomposites without CLPs are fabricated. This interfacial engineering strategy results in a CNF-based nanocomposite with wet strength up to 87 MPa without any chemical modification or crosslinking agents. The mechanism behind the achieved excellent dry and wet strength and water resistance is investigated and it is suggested that it is due to the amphiphilic CLPs that are able to form non-covalent bonds with both cellulose and PCL, thus binding these together. Furthermore, the nanocomposite films' protection against UV and oxidation is significantly enhanced by increasing the CLPs content. Our proposed interfacial engineering strategy can be generically applied to other polymer systems and shows a great potential to pave the way toward replacing fossil-based plastics.

1. Introduction

Nanoscale building blocks from renewable natural resources are key to developing sustainable materials. At this new

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frontier of materials science, designing biobased solutions that compete with conventional fossil-based plastics is crucial. Cellulose nanofibrils (CNFs) are prominent contenders for high-performance applications due to their nanoscale dimensions,^[1] large surface area,^[2] and exceptional mechanical characteristics.^[3] The strength of CNF-based materials is a consequence of extensive hydrogen bonding between fibrils arising from the presence of surface hydroxyl groups. However, these hydroxyl groups efficiently bind water molecules, increasing moisture sensitivity and reducing wet strength.^[4] In addition, the hydrophilic nature of CNFs hinders their combination with hydrophobic polymers, which is an obstacle to developing CNF-reinforced polymer nanocomposites with high modulus and ductility due to the poor compatibility between CNF and polymer matrix.^[5] Several strategies, such as esterification,^[6] silylation,^[7] acetylation,^[8] urethanization,^[9] amidation,^[10] and polymer grafting,^[11] are frequently employed for the surface modification of CNFs to enhance the hydrophobicity. In recent

studies, engineering the interface of CNF and hydrophobic polymers by reactive compatibilizers such as amphiphilic block and random copolymers is shown as a versatile tool to improve the miscibility of CNF with polymer matrices in melt processing.^[12,13] However, hydrophobization strategies mostly target the surface hydroxyl groups, which curtail the hydrogen bonding pattern within the CNF network and lead to mechanically weaker material with poorer oxygen barrier properties than pure CNF nanopapers.^[14] Furthermore, these chemical modifications increase the environmental impact of the material production process and hamper CNF's natural biodegradability,^[15] a motivating factor for using CNF. Furthermore, to uplift the CNF status as an ultimate material platform for biomaterial design, the critical challenges associated with water interaction and its dispersion in hydrophobic media need to be addressed in a sustainable and scalable manner. To address these perplexing challenges, we suggest a natureinspired solution exploiting the inherent properties of CNF and another natural polymer, lignin. The conversion of crude





lignin into colloidal lignin nanoparticles (CLPs) overcomes the hurdles commonly posed by its complex structural heterogeneity. At the same time, the conversion enables dispersion in aqueous media. The size and charge of resulting nanoparticles can be tailored for specific needs because of their nano-scale morphology and well-defined surface characteristics, evident in research disseminated in the last few years.^[16] Among the demonstrated applications of CLPs, including nanocomposites,^[17] bio-adhesives,^[18] drug delivery,^[19] UV absorbents,^[20] hybrid nanoparticles,^[21] and antioxidant agents,^[22] their use as stabilizing agents for Pickering emulsions is of immense interest.^[23–27] Pickering emulsions are more stable than surfactant-stabilized emulsions because of the high energy required to remove solid particles from the oil/water interface.^[28]

Recently, Pickering emulsion has been used as a template for either polymerization or compatibilizing media to build polymeric composites reinforced with cellulose.^[29,30] For example, Lio et al.^[31] developed polymethylmethacrylate (PMMA)/CNF composites via drying the PMMA Pickering emulsion gel stabilized with CNF into the interconnected structure network. Fujisawa et al.^[32] produced polystyrene (PS) nanoparticle/CNF composites by encapsulating styrene monomers in a CNF-stabilized Pickering emulsion and subsequently polymerizing the styrene by heating before filtration and melt processing. In a unique report, Moreno et.^[33] used CLPs as the stabilizer for free radical polymerization of Pickering emulsion to produce PS and poly (butyl methacrylate) (PBMA) latex dispersion that was subsequently melted into the nanocomposite films. Nonetheless, to the best of our knowledge, there are yet no reports using CLPs and CNF together in the Pickering emulsion media prior to film making. Moreover, most of the developed nanocomposites are neither biobased nor biodegradable. We also noted that although they all report increase in strength related to the soft polymer, the developed nanocomposite films are still weaker than pure CNF nanopaper.^[34–36]

In this work, we demonstrate that the Pickering emulsion stabilized with lignin nanoparticles approach can provide a convenient platform to design nanocomposite systems incorporating hydrophobic polymer and hydrophilic CNF, overcoming the high interfacial tension between hydrophilic CNF and hydrophobic polymers with the aid of amphiphilic CLPs. This strategy allows the even dispersion of polycaprolactone (PCL) onto the CNF network inducing waterproof characteristics to the CNF-based nanocomposite films and enabling synergistic effects of PCL and CNF, resulting in composites with higher tensile strength and toughness than pure CNF nanopapers in both dry and wet conditions. To elucidate the mechanism of CLPs as the interfacial mediator between CNF and PCL, the surface and bulk structures of nanocomposite films were characterized. Furthermore, we show that the inclusion of CLPs induces additional functionality, such as UV shielding and antioxidant properties to the developed free-standing films, making them interesting for packaging applications. Overall, this study offers a facile route to design multifunctional cellulose-based nanocomposites using only biodegradable polymers and lignocellulosic nanoparticles by controlling the interfacial interactions.

2. Results and Discussion

2.1. Design and Fabrication

Our particular aim was to prepare tough, waterproof, and fully biobased composites with high dry and wet tensile strength. The main challenge was finding biobased components that exhibit all these properties. We chose CNF due to its high modulus and strength and PCL, a semi-crystalline hydrophobic polymer, for its excellent flexibility. Both components are biobased and biodegradable, but the question remained: how to combine them without chemically modifying or crosslinking them, thus hampering their biodegradability? To enable good compatibility between hydrophobic PCL and hydrophilic CNF, we needed a third component and a smart molecular design approach. Our pragmatic approach was to identify a natural component with surface properties enabling interactions with both PCL and CNF. PCL can form hydrogen bonds through its carbonyl group with the phenolic hydroxyl group of lignin.^[37,38] Therefore, we opted for CLPs as the emulsion stabilizer due to the presence of phenolic hydroxyl groups on their surface along with their excellent emulsion stabilization tendency and demonstrated favorable interactions with CNF.^[39] We speculated that the hydrogen-bonding ability of all components, in combination with the amphiphilic character of CLPs, would enable good compatibility between the components. We envisioned that this Pickering emulsion template can produce a supramolecular assembly of small PCL droplets stabilized by CLPs or cationic CLPs (c-CLPs) uniformly distributed within a CNF network (Figure 1a). To proceed, we first prepared a Pickering emulsion containing PCL (dissolved in toluene 10 wt% concentration) in an aqueous phase containing the CLPs or c-CLPs.



Figure 1. Fabrication of nanocomposite by Pickering emulsion approach. a) Schematic representation of the assembly of nanocomposite components. Top-view SEM image of b) a droplet containing PCL dissolved in toluene stabilized by CLPs and CNFs. c) Ambient dried nanocomposite film after filtration. d) Hot pressed dried nanocomposite film. The characterized nanocomposite film comprised 70% CNF and 30% PCL stabilized by CLPs.







Figure 2. The effect of CLPs and c-CLPs aqueous dispersion concentration on PCL emulsion stability, size of oil phase droplets (D), and uniformity (U). All experiments were performed 3 h after emulsion formation. a) Visual observation of emulsions stabilized by CLPs and c-CLPs. b) Inverse oil droplet diameter. c) Uniformity index. d,e) Optical micrographs of oil droplets as a function of concentration of CLPs and c-CLPs, respectively.

Subsequently, this emulsion was combined with an aqueous dispersion of CNF. The presence of CNFs further reduces the oil droplet size due to their fibrillar percolation network that increased the viscosity of the aqueous phase and provided steric hindrance against the coalescence of oil droplets.^[40] The CNFs were expected to accumulate at the oil-water interface interacting with the CLPs. Scanning electron microscopy (SEM) image of the obtained emulsion after the addition of CNF confirmed this hypothesis, showing that PCL droplets were entirely covered with both CLPs and CNF (Figure 1b). Then, semi-dried nanocomposite films were formed through pressurized filtration of the emulsions (Figure 1c). Afterward, hot pressing melted the PCL on the CNF without destroying the CNF fibrillar network, resulting in a uniform nanocomposite film (Figure 1d).

2.2. Stability of PCL Pickering Emulsion

As the first step toward even distribution of all components and good interfacial adhesion in the nanocomposite films, we evaluated the optimal concentration and surface charge of CLPs (Figure 2; Table S1, Supporting Information) to stabilize aqueous dispersions of PCL. The volume of the PCL dissolved in toluene was kept constant during the experiments, and the stability of the Pickering emulsions was determined 3 h after preparation to follow the limited coalescence process.^[41] Based on the visual appearance (Figure 2a), stable Pickering emulsion could be formed at concentrations of 1.5 and 2.0 wt% for c-CLPs and CLPs, respectively. Below these optimum concentrations, emulsions were unstable against creaming and phase separation, although a decrease in the phase-separated volume fraction can be observed as a function of CLPs concentration (Figure 2a). An increase in the concentration of c-CLPs and CLPs induced a steady decrease in oil droplet diameter (observed as an increase in inverse oil droplet diameter) and an increase in uniformity (Figure 2b,c). The uniformity index (U) leveled off at 1.5 wt% for CLPs and 1.0 wt% for c-CLPs. Further increasing the CLPs concentration to 2 wt% still decreased the emulsion droplet size. This observation is consistent with the fact that, at a higher concentration of emulsion stabilizer, more particles can adsorb at the oil-water interface, subsequently reducing the interfacial tension, which leads to smaller oil droplets with narrower size distribution.^[24,42] The microstructure of the oil droplets presented in Figure 2d,e shows that, for all the examined concentrations (0.2, 0.5, 1.0, 1.5, and 2.0 wt%), the oil droplets are spherical in geometry and display CLPs concentration-dependent droplet size. The emulsions stabilized by c-CLPs produced smaller oil droplets than CLPs, possibly due to favorable electrostatic and cation- π interactions at the oil/water interface.^[24] From a nanocomposite ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com ADVANCED MATERIALS INTERFACES www.advmatinterfaces.de

perspective, the smaller the PCL droplets, the better the dispersion of PCL within the CNF network and the more even the composition will be. As the uniformity leveled off at 2 wt% of lignin particles, we speculated that a redundant amount of CLPs might negatively affect composite strength.^[39,43,44] Thus, we selected 2 wt% concentrations for both CLPs and c-CLPs to prepare nanocomposite films using the Pickering emulsion method.

2.3. Characterization of Nanocomposite Films

To evaluate the potential application of nanocomposite films, we characterized them (**Table 1**) in terms of morphological, mechanical, structural, surface wetting properties, water uptake, UV and oxidation shielding, as well as thermal properties.

2.3.1. Mechanical Properties

To evaluate the nanocomposite films' ability to withstand stress in both dry and wet conditions, dry tensile testing at 50% RH and 23 °C and wet tensile testing after soaking the samples in water for 2 h were performed. The tensile behavior of the nanocomposites endorsed our hypothesis of the positive effect of the lignin nanoparticles. Nanocomposite films containing 10% or 30% PCL emulsion stabilized by either CLPs or c-CLPs exhibited an extraordinary combination of dry and wet tensile strengths with a significant improvement compared to neat CNF (**Figures 3**a–d and 4a; Figure S3 and Tables S2 and S3, Supporting Information). At these ratios, the dry tensile strength of the composites stabilized using unmodified CLPs (90C10E [–] and 70C30E [–]) were as high as 134 and 119 MPa,

Table 1. Sample acronyms and composition of pure CNF and nanocomposite films. The ratio between PCL and CLP was kept constant at 5:1, but the ratio between CNF and PCL emulsions stabilized by CLPs was systematically varied. The obtained film from pure CNF is referred CNF, and nanocomposite films containing PCL stabilized by lignin particles are denoted with its CNF weight fraction beside letter C, emulsion weight fraction beside letter E, and surface charge([–],[+]) of lignin nanoparticles to distinguish between CLPs and c-CLPS. Nanocomposites from CNF and PCL without CLPs are denoted similarly to the above but using the letter P for PCL content (no CLPs).

Sample code	CNF weight fraction [%]	PCL weight fraction [%]	CLPs/c-CLPs weight fraction [%]
CNF	100	_	—
90C10E [-]	90	8.33	1.66
70C30E [-]	70	25	5
50C50E [-]	50	41.66	8.33
30C70E [-]	30	58.33	11.66
90C10E [+]	90	8.33	1.66
70C30E [+]	70	25	5
90C10P	90	10	_
90C10P	70	30	_
90C10P	50	50	_
90C10P	30	70	_
PCL	_	100	_

and exhibiting around five and six times higher strain, respectively, than the neat CNF film. Adding higher amounts of PCL emulsion (50% or 70%) led to a decrease in strength. This may be due to either disruption of the CNF's hydrogen bonding network or the negative effect of too high a concentration of spherical and hard CLPs.^[45] On the other hand, at optimal CNF/PCL/CLP ratio, a synergetic effect of noncovalent interactions (van der Waals interactions, hydrogen bonding, and hydrophobic forces) led to good interfacial adhesion between fibrils and polymer, combined with restriction of fibril aggregation, resulting in excellent mechanical performance. Meanwhile, in the absence of CLPs or c-CLPs, the lack of interactions between the PCL and CNF and high interfacial tension between polymer and fibrils resulted in phase separation leading to poor dry and wet strength (Figures 3b and 4a; Figures S1 and S2 and Tables S2 and S3, Supporting Information). These observations support our hypothesis that the presence of lignin nanoparticles acts as an interface mediator between the PCL and CNF, promoting adhesion between the two phases, resulting in better mechanical properties.[46-48]

Afterward, the effect of the surface charge of the CLPs was evaluated. The dry tensile strength reached up to 174 MPa with 10% loading of PCL emulsion stabilized by c-CLPs with ≈7% strain, leading to the highest toughness among the studied nanocomposite films (Figures 3c and 4b; Table S2, Supporting Information). As 10% and 30% loading of PCL emulsion displayed the best mechanical performance, these two ratios were chosen for studying the effect of drying and further experiments. Nanocomposite films with 10% and 30% emulsion content were then dried in ambient drying conditions (50% RH, 5 kg load) for comparison. Ambient dried nanocomposite films exhibited marginally lower tensile strength than the hotpressed ones but with higher strain at the break, possibly due to the plasticizing effect of residual water.^[4,49] 90C10E [+] nanocomposite film dried in ambient conditions showed up to 8% strain at break with 160 MPa tensile strength (Figure S1, Supporting Information). Due to the plasticizing effect of water molecules,^[4] ambient dried nanocomposite films exhibited higher toughness than the hot-pressed ones (Table S2, Supporting Information).

Moreover, we evaluated the wet strength of the nanocomposite films. Different approaches are utilized to develop cellulosic nanopapers with high wet strength, but they often involve complicated chemical modifications, toxic solvents, or solutions that sacrifice their mechanical properties in the dry state.^[50-52] Herein, we gained similar or even better results via a strategic choice of components and mixing strategy. The wet strength of nanocomposites stabilized by CLPs or c-CLPs was significantly higher than CNF nanopaper or nanocomposites without CLPs (Figure 4a-d; Figure S1 and Table S3, Supporting Information). 70C30E [+] nanocomposite film demonstrated a remarkable wet tensile strength of 87 MPa (Figure 4b; Table S3, Supporting Information). This value is significantly higher than the previously reported wet strength of CNF crosslinked with tannic acid, epoxies, or multivalent metal ions between 30 and 70 MPa, [53-55] despite the lack of formation of covalent bonds in our system. Although 90C10E [+] nanocomposite film displayed the highest average toughness of 10.5 MJ m⁻³ in the dry state, a higher fraction of the hydrophobic PCL was







Figure 3. Mechanical and morphological properties of neat CNF and nanocomposite films in dry condition. Stress-strain curves of dry tensile test of neat CNF and nanocomposite films containing a) PCL emulsion stabilized by unmodified CLPs. b) PCL and CNF mixed without CLPs or c-CLPs. c) PCL emulsion stabilized by CLPs and c-CLPs, and PCL and CNF without CLPs or c-CLPs. SEM image from cross-section view of fractured area e) 90C10E [-]. f) 90C10P. g) 30C70E [-]. h) 30C70P.

beneficial for wet strength; hence 70C30E [+] films performed the best in wet conditions. The extensive swelling of CNF nanopapers in aqueous media leads to overestimating the wet strength if the thickness in the dry state is used for calculations.^[56] To avoid this, we used the thickness of wet films when calculating strength. The ionic strength of the swelling medium also affects the extent of swelling: the higher the ionic strength, the lower the swelling. Thus, we used deionized







Figure 4. Mechanical and morphological properties of neat CNF and nanocomposite films in wet condition after 2 h of immersing in water. Stressstrain curves of wet tensile test of neat CNF and films containing a) mixture of PCL and CNF without CLPs and PCL emulsion stabilized by CLPs. b) mixture of PCL and CNF without CLPs or PCL emulsion stabilized by c-CLPs. c) PCL emulsion stabilized by CLPs or c-CLPs and without CLPs or c-CLPs. d) Toughness values of neat CNF and nanocomposite films in dry and wet states. SEM image from cross-section view of fractured samples after wet tensile test. e) Neat CNF. f) 30C70E [+].

water in this study to illustrate the resistance against swelling. There could be multiple reasons for the better performance of nanocomposites stabilized by cationic CLPs than unmodified CLPs. First, a smaller droplet size enables an even coverage of all fibrils with hydrophobic PCL protecting them from water. Second, as suggested by Benitez et al.,^[4] the positively charged c-CLPs can have attractive electrostatic interactions with the carboxylic groups in CNF. Third, the electrostatic attraction between amino groups on c-CLPs and carboxylic groups in CNF could also facilitate the locking of the CNF fibrillar network, subsequently hindering the film's swelling.^[57] A closer observation of the stress-strain curves for wet films suggests the absence of an elastic region, implying that the pure CNF and nanocomposite films directly enter the plastic region upon applying axial load. In nanocomposite films, the availability of hydroxyl groups on the CNF surface is significantly reduced. However, penetration of water molecules to available sites is inevitable in wet conditions. Water molecules act as lubricating agents; therefore, the applied stress directly caused fibril sliding relative to one another, jumping from the elastic to the plastic region. Water allows for easier elastic elongation, reducing Young's modulus. The highest average value of Young's modulus observed in the wet state was 2.4 GPa, and it was obtained for 70C30E [+] nanocomposite film. In comparison, the pure CNF has Young's modulus of only 0.7 GPa due to its hydrophilic nature. Surprisingly, the composites at 10% and 30% PCL loading without CLPs showed even lower modulus than the

pure CNF (Table S3, Supporting Information) due to the poor interactions between CNF and PCL. These findings clearly indicate that efficient interfacial interactions between CNF and the polymeric matrix are necessary to gain satisfactory nanocomposite properties in both dry and wet conditions. We anticipate that PCL covers the surface of fibers in the presence of CLPs or c-CLPs, causing a reduction in hydroxyl groups accessible to water on the CNF surface.

2.3.2. Morphological Properties

To explain the excellent mechanical properties and gain further understanding of the nanocomposite structure, we examined the nanocomposite films' morphology from both cross-section and top view using SEM, as displayed in Figure 3e–h; Figures S4–S6, Supporting Information. The fracture zone morphology of 90C10E [–], 70C30E [–], 50C50E [–], and 30C70E [–] nanocomposite films were similar to the reference CNF (Figure 3e–h; Figures S4–S6, Supporting Information), revealing a compact layered structure with no fiber pullout. This suggests good adhesion between all components. In comparison, clear phase separation and fiber/matrix debonding were observed for nanocomposite films without CLPs or c-CLPs; 90C10P, 70C30P, 50C50P, and 30C70P (Figure 3f,h; Figure S5, Supporting Information). For example, 30C70P nanocomposite film exhibits streaks of delaminated polymer separated from



the CNF, demonstrating a loosely packed structure (Figure 3h). We also compared the cross-section of 70C30E [+] nanocomposite film fractured in the wet state, which showed the best performance in the wet tensile test with neat CNF film in the same condition. Neat CNF nanopaper swelled significantly when immersed in water (discussed further in Section 2.3.5.) because water molecules could diffuse into the film, disrupting the hydrogen bonds between fibrils. This led to disruption of the layered film structure upon drying (Figure 4e). It is well known that the high tendency of CNF films to swell in the presence of water is one of the main reasons for the deterioration of their mechanical properties in wet conditions. Swelling of the network structure increases the porosity, thereby decreasing bonding between fibrils, ultimately leading to an overall decrease in elastic modulus.

Interestingly, the compact layered structure of the 70C30E [+] film is still observed even after immersion in water for 2 h (Figure 4f). The alkyl chain of polycaprolactone in our system is anticipated to reduce the water-accessibility of the hydroxyl groups of CNF. As a result, the disruption of hydrogen bonds by water molecules usually observed for CNF is restricted, achieving a good cohesion in the nanocomposites' structure.

2.3.3. Surface and Bulk Structural Properties

To further elucidate the mechanism behind the performance of CLPs as interfacial mediators, we analyzed the surface and bulk structural properties of nanocomposite films. The composition and molecular interactions between the constituents of nanocomposite films were confirmed using FTIR spectroscopy. The strongest band and their assignments for pure PCL, CNF, and CLPs are tabulated in Figure 5a. Upon the addition of PCL emulsion stabilized by CLPs into the CNF at different loadings, the most obvious change occurs in the carbonyl stretching mode of PCL around 1720 cm⁻¹. For 70C30E [-] film, the v(C=O) peak of pure PCL shifted to a higher wavenumber from 1720 to 1724 cm⁻¹ (Figure 5a,b). For 30C70E [–], the v(C=O) peak shifted from 1720 to 1723 cm⁻¹ and broadened. This indicates distinct interactions in the form of hydrogen bonding between PCL and the phenolic hydroxyl groups of CLPs and the hydroxyl groups of CNFs or dipolar interactions between carbonyl bonds.^[58-60] The systematic change in the carbonyl band intensity at different loadings also reflects the homogeneous distribution of polymer within the nanocomposite system.

We also performed XPS measurements to complement the FTIR data. The XPS spectra displays the surface chemical composition of the nanocomposite films with a penetration depth of not more than 10 nm. This technique can reveal if the PCL is evenly distributed on the surface of films. All nanocomposite films exhibited a relative surface content of carbon between 62% for the CNF and 78% for pure PCL. The O/C steadily decreased as the emulsion concentration in the nanocomposite films increased, correlating with a higher amount of PCL and lignin (Table S4, Supporting Information).^[61] Figure 5c shows C 1s high resolution spectra fitted with four Gaussian components correlating to the respective type of carbon atoms.^[62] The (O–C=O) is possibly the best indicator of the PCL content at the surface of the nanocomposite films. The ester functional



group appears to increase linearly with increasing PCL content (Figure 5d; Table S5, Supporting Information). This indicates that both PCL and CNF are homogeneously distributed in the surface layers of the nanocomposite films. Otherwise, if PCL was segregated at the top-most layers of the samples, the signal from the PCL components would most likely saturate toward higher values or at least show a logarithmic rather than linear increase.

2.3.4. Mechanism Behind the Lignin Nanoparticles as the Interfacial Mediator

The prerequisite for fabrication of nanocomposite by Pickering emulsion strategy is restraint transition of emulsion droplets into nanostructured composite films. Despite the recent research efforts,^[29,31,32,35,36] even very stable emulsion did not turn into the uniform and robust nanocomposite films, most likely due to the poor interfacial bonding between hydrophobic polymer matrix and hydrophilic CNF, which adversely affects the mechanical properties. In the present work, we utilized the amphiphilic characteristic of lignin nanoparticles and their active surface sites to assist the interfacial bonding between CNF and PCL to efficiently transfer the stress by the soft PCL to fibers at the interface. The possible mechanisms behind the performance of lignin nanoparticles as an interfacial modulator are listed below.

The first prerequisite for a good composite is the stable Pickering emulsion with very small droplets formed due to the synergistic stabilizing effect of both CLPs/c-CLPs and CNF, which promotes the even distribution of PCL in the CNF network. However, good affinity between the components in the dry composite is also needed. One factor promoting this is the ability of CLPs to form noncovalent interactions such as hydrogen bonding with both PCL and CNF (Figure 5e). The observed chemical shifting for the carbonyl bonds in the FTIR analysis (Figure 5b) corroborates the hydrogen bonding between phenolic groups in CLPs with carbonyl groups in PCL with respect to CLPs and CNF interactions. We have previously shown that CLPs slightly disrupt the interfibrillar hydrogen bonding in CNF. However, at optimized amounts, this is compensated by the CLPs' capability to form hydrogen bonds with CNF.^[39] We furthermore suggest that the lignin nanoparticles are softened during hot pressing enabling them to fill the voids between the fibrils,^[43]increasing the bonded area, which is crucial for achieving an interconnected layered microstructure in nanocomposites.^[63] Due to this softening and partial melting of the CLPs, the lignin molecules can also assemble on the CNF surface with more hydrophobic molecules in contact with the hydrophobic PCL, thus tailoring the polarity of CNF. This mechanism is similar to the role of residual lignin on the cellulose fibrils in enhancing the compatibility of CNF with hydrophobic polymers.^[64,65]

2.3.5. Water Resistance and Water Uptake

To assess the potential suitability of obtained nanocomposites in packaging applications, we also evaluated their water www.advancedsciencenews.com

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Figure 5. FT-IR and XPS analysis: a) The position and assignments of strongest bands in PCL, CNF, and CLPs. b) The carbonyl bond region in 1770–1660 cm⁻¹ in FT-IR spectra. c) XPS analysis of high resolution C1s spectra, according to standard chemical shifts, with peak positions at 284.8 eV (C-C), 286.5 eV (C-O), 287.8 eV (C=O), and 288.9 eV (O-C=O). d) Relative surface concentration of carbon with three bonds to oxygen (O-C=O) in neat CNF and nanocomposite films based on XPS data plotted as a function of emulsion content (PCL + CLPs). e) Schematic illustration of possible interactions between nanocomposite's components.

resistance and protection against UV and oxidation. First, inspired by the excellent wet strength of the three-component nanocomposite films, we explored the nanocomposites' wetting properties using dynamic water contact angle (WCA) measurements. As expected, the CNF film exhibited the lowest WCA. The WCA was significantly increased as we increased the relative amount of PCL emulsion stabilized by CLPs. The advancing WCA was 76° for 90C10E [-] and above 95° for both 50C50E [-] and 30C70E [-] nanocomposite films (Figure 6a,b). Comparing advancing and receding WCAs, we observed that

the majority of nanocomposite films showed low hysteresis, with less than 10° difference between advancing and receding WCA (Figure S6, Supporting Information), which is further evidence of good homogeneity of the nanocomposites films.^[66-68] As the small droplets used in WCA measurements evaporate upon longer exposure, adopting a method by Forsman et al.^[69], we qualitatively assessed the long term water-resistance of nanocomposite films by following the absorption or spreading of a water droplet as a function of time. The water was quickly absorbed into the neat CNF film within a few minutes, while







Figure 6. Water resistance, water uptake, UV and oxidation shielding, and thermal properties of neat CNF, neat PCL, and nanocomposite films. a) Dynamic WCA measured by increasing the water volume (5–20 μ L and then decreasing to 5 μ L) at 60s exposure for each value. b) Photos of the water droplet profile on top of nanocomposite films at 60 s acquired during WCA measurements. c) Water droplets on the CNF and nanocomposite films immediately, 60 min, and 120 min after placing, showing possible absorption or spreading. d) Water uptake of CNF and nanocomposite films after 2 h of immersing in deionized water. e) UV–vis light transmittance spectra of neat CNF and nanocomposite films. f) Antioxidant activity of neat CNF and nanocomposite films. Curve fit: $y = a-b \times c^x$, where a = 60.3312, b = 58.3157, and c = 0.9522. g) Endothermic process in the DSC thermogram of PCL and nanocomposite films.

the droplet stayed on the surface of the nanocomposite films for over 2 h (Figure 6c). These results suggest that the long alkyl chains of polycaprolactone induce hydrophobicity to the nanocomposite films, which is in agreement with XPS results showing a higher amount of nonpolar C–C carbon and a lower amount of polar C–O carbon at the surface upon increasing the PCL content.

We then assessed the water uptake capacity of nanocomposite films as the minimal water penetration into the films suggests that the PCL may also diminish the water uptake of CNF. As expected, the CNF showed a high level of water uptake, close to 132.5%, associated with the abundance of accessible OH-groups on its surface.^[70] The water uptake was inversely proportional to the PCL content of the nanocomposite film (Figure 6d). Indeed, increasing the PCL content abruptly decreased the water-uptake capacity of nanocomposite films to only 7% for the 30C70E [-] nanocomposite film. Intriguingly, we observed that the nanocomposite films without CLPs exhibited higher water uptake, although these include even slightly more PCL. The difference between the water uptake capacity of nanocomposite films with and without CLPs increases linearly with the PCL content (Figure 6d). These results confirm our previous hypothesis that CLPs are needed to acquire a strong affinity between PCL and CNF, where PCL, in the presence of CLPs, can cover the cellulose nanofibrils and act as an efficient barrier for water binding. In the absence of CLPs, water molecules can still access the CNF due to poor binding between PCL and CNF. With the WCA and wet tensile strength, our Pickering emulsion stabilized by CLPs implemented an innovative strategy to design materials with excellent mechanical properties in both dry and wet conditions.



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2.3.6. UV and Oxidation Shielding Properties

The UV-shielding potential of nanocomposite films, an important property for packaging applications to preserve food, was further evaluated. The UV portion of sunlight can accelerate the oxidation of lipids via initiating the formation of free radicals, leading to changes in the color, taste, and nutritional properties of packaged food products.^[71-73] Increasing CLPs content in the nanocomposite films resulted in higher suppression of UV transmittance (Figure 6e). The addition of merely 10% PCL emulsion stabilized by CLPs demonstrated strong UV absorption in UV-A (315-400 nm) region and complete absorption for the UV-B (280-315 nm) region (Figure 6e). Furthermore, nanocomposite films at higher CLP content could absorb almost all UV light in UV-A and UV-B regions. It is worth highlighting that the nanocomposite films' UV-blocking performance was independent of the type of lignin nanoparticles, where nanocomposite films containing c-CLPs exhibited similar performance compared with nanocomposite films containing CLPs (Figure S7, Supporting Information), correlating with a previous finding by Farooq et al.^[39]. We achieved excellent protection against UV light for nanocomposites, thanks to the abundance of UV-absorbing chromophore groups in lignin's structures, including aromatic phenolic groups, ketones, and various quinoid units, making lignin a natural sun blocker.^[74,75] The optical transmittance of the nanocomposite films decreased, as expected, with increasing the CLP content, turning the color of nanocomposite films brown due to more lignin particles in the nanocomposite composition (Figure S8, Supporting Information). However, only a slight reduction in the transmittance of visible light was observed in the 90C10E [-] nanocomposite film, whereas the UV shielding behavior was impressively increased, suggesting that these films are suitable contenders where transparent, but UV-shielding films are needed, for example, in solar cells.

Apart from UV shielding, all nanocomposite films revealed promising antioxidant activity compared with the pure CNF, owing to the free radical scavenging ability of phenolic groups in lignin.^[76–78] The presence of lignin in nanocomposite films can stimulate the neutralization of 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS*+) solution with radical quenching activity through a hydrogen donation mechanism. The antioxidant activity of nanocomposite films correlated with the lignin content similar to their UV-shielding performance, where increasing lignin content translated into the higher antioxidant activity of nanocomposites (Figure 6f). The antioxidant activity of all nanocomposite films was dramatically increased in the first 60 min and then reached a plateau due to the depletion of the ABTS⁺⁺ radical solution. The addition of 10% emulsion prompted a 60% increase in antioxidant activity compared with the pure CNF film, with almost zero antioxidant activity. In 70C30E [-], 50C50E [-], and 30C70E [-] nanocomposite films, the antioxidant activity reached ≈90% after 3 h, showing great promise for lipid autoxidation inhibition in food packaging applications. Nanocomposite films containing c-CLPs instead of CLP showed similar antioxidant activity (Figure S7, Supporting Information), regardless of their differences in size and charge. The more lignin in nanocomposite films, the higher their antioxidant activity.



2.3.7. Thermal Properties

The composition and possible interactions between the components of a nanocomposite system can largely affect their thermal properties. DSC analysis was performed to estimate the thermal properties of neat PCL and nanocomposite films (Figure 6g; Figure S8, Supporting Information). Adding CNF and CLPs to the nanocomposites did not remarkably change the melting point (T_m) compared with pure PCL. However, the crystallization temperature (T_c) was slightly decreased from 33.46 °C to 30.16 °C for 90C10E [-] and 70C30E [-] nanocomposite films, respectively (Table S6, Supporting Information), indicating a marginal change in the crystallization kinetics of nanocomposite films. Nonetheless, the melting enthalpy of nanocomposite films was broadened upon increasing the PCL content (Figure 6 g; Table S6, Supporting Information). Melting enthalpies of 0.48 and 27.3 J.g⁻¹ were observed for 90C10E [-] and 30C70E [-] nanocomposite films, respectively, indicating an increase in crystallinity degree associated with more semi-crystalline PCL in the nanocomposites. More details about thermal data are provided in Table S6, Supporting Information. These results suggest that the inclusion of CNF and CLPs into the PCL does not significantly affect the thermal properties of PCL. The absence of such an effect is crucial and promising for processing as additives and property enhancers may influence the melting temperature, limiting the processing and service temperature of the nanocomposites.

3. Conclusion

In this work, we showed a facile and sustainable route to develop CNF-reinforced biopolymer nanocomposites by engineering the CNF and polymeric matrix interface using CLPs. The CLPs in combination with CNF, enabled the production of stable Pickering emulsions of PCL with small droplet sizes. Hence, nanocomposites with an even distribution of components were achieved. The nanocomposite films exhibited unprecedented mechanical properties in both dry and wet states due to the favorable interfacial interaction between CLPs and PCL and between CLPs and CNF. Furthermore, the addition of PCL and CLPs restricted the accessibility of surface hydroxyl groups of CNFs, conferring the nanocomposite films with remarkable water resistance and diminished swelling. UV-shielding and antioxidant activity were the other favorable attributes of this rational nanocomposite design. Overall, these findings open new pathways for introducing multifunctional and water-resistant CNF-based nanocomposites without compromising the material's biodegradability. These are critical parameters for the packaging industry and many other applications. Our approach accomplishes the following: harnessing the inherent properties of all three components, achieving excellent mechanical robustness via interfacial engineering through hydrogen bonding and other non-covalent interactions, and avoiding chemical modification or crosslinking. Future development should include a techno-economic analysis and a lifecycle assessment of a developed biocomposite to evaluate its potential for scaling up and commercialization.

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4. Experimental Section

Materials: Softwood Kraft lignin (BioPiva 100) isolated by the LignoBoost technology at Domtar's Plymouth plant (NC, USA) was used in this work. Detailed chemical characterization of this lignin can be found in Sipponen et al.'s work.^[79] Cellulose nanofibrils (CNFs) were prepared following the procedure described by Österberg et al.,[80] where never-dried bleached hardwood Kraft pulp fibers were washed into sodium form to control the counterions and ionic strength without any chemical pretreatment before subjecting to mechanical disintegration. In the next step, the pulp was fibrillated by using an M-110P microfluidizer (Microfluidics, Newton, Massachusetts, USA) by a single pass through a series of 400 and 200 μ m chambers, followed by six passes through a series of 400 and 100 μm chambers at 2000 bar operating pressure. The CNF suspension was acquired at 2.3 wt% solid content, and it was stored at +4 °C until use. Polycaprolactone (PCL) ($M_n = 80000$) was purchased from Sigma-Aldrich, and it was used as it was received. Toluene and acetone were obtained from VWR chemical with purity ≥99.5. All purchased chemicals and solvents were used without further purification.

Preparation of Colloidal Lignin Particles: Colloidal lignin particles (CLPs) were prepared following the authors' previously reported method.^[39] Briefly, dry softwood kraft lignin (10 g) was dissolved in a mixture of acetone/water (1000 gram) 3:1 (v/v) by stirring for 3 h at room temperature, followed by filtrating using a glass microfiber filter (Whatman GF/F, pore size 0.7 μ m) to remove the remaining undissolved solids. The filtered solution was quickly transferred into vigorously stirred deionized water (2000 mL) to produce CLPs. Afterward, acetone was evaporated under reduced pressure at 40 °C by rotavapor. The obtained CLPs dispersion was filtered by VWR qualitative filter paper, 415 (particle retention 12–15 μ m), and the final concentration was adjusted to 2 wt%. The final mass yield of produced CLPs was 87%.

Preparation of Cationic Lignin: Cationic lignin was prepared from the same lignin batch as previously used to prepare CLPs. The synthesis procedure described by Farooq et al. was followed with slight modification.^[39] In brief, a dry basis of kraft lignin (6 g) was added in aqueous 0.2 M NaOH with glycidyltrimethylammonium chloride (GTMAC) (2.4 g) at 70 °C for 1 h. The pH of the mixture was adjusted to 7 and the resultant suspension was purified by dialysis in a Spectra/ Por 1 tubing with a molecular weight cut-off (MWCO) of 7 kDa against deionized water.

Preparation of Cationic Colloidal Lignin Particles: Cationic colloidal lignin particles (c-CLPs) were produced by gradually adding CLPs dispersion into vigorously stirred aqueous cationic lignin solution (the dry weight ratio between cationic lignin to CLPs was 200 mg.g⁻¹).

Particle Size and ζ -Potential Analysis of CLPs and C-CLPs: Particle size and ζ -potential of CLPs and c-CLPs were determined using dynamic light scattering a Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd, United Kingdom). Dynamic light scattering describes the hydrodynamic radius of the particles in the colloidal suspensions. Disposable cell and dip cell probe were used to measure the particle size and zeta potential, respectively. Physical characteristics of obtained CLPs, including the hydrodynamic diameters (D_h) and zeta potential, are tabulated in Table S1, Supporting Information.

Preparation of PCL Emulsions: The PCL emulsion was formed by mixing PCL dissolved in toluene (10 wt%) as the oil phase with aqueous dispersion of CLPs or c-CLPs as the water phase and stabilizer using a T18 basic IKA homogenizer. The volume fraction of the oil and water phase and the ratio between PCL and CLPs were constant at 0.5 and 5:1, respectively.

Microstructure of Emulsion: The microstructure of the emulsion was studied by an optical microscope, Leica Zeiss (DM750), equipped with Leica imaging software to capture the images of oil droplets in emulsions at room temperature. ImageJ software was used to analyze the recorded images.^[81]

Droplet Diameter and Uniformity of Emulsions: The mean droplet diameter was measured based on volume data (d_{43} , De Brouckere Mean Diameter) using static light scattering (Mastersizer 2000, Malvern, UK).



The refractive indices of dispersed and continuous phase used in the calculation were 1.49 and 1.33, respectively. To further assess the stability of emulsions, reciprocal Sauter mean diameter $(D_{32} = \sum n_i d_i^3 / \sum n_i d_i^2)$ and uniformity index (Equation (1)) were calculated. All measurements were performed 3 h after the emulsion preparation following the limited coalescence phenomena.^[41] Mean values of 30 measurements for each sample were used to analyze and represent the data.

Uniformity =
$$\sum X_i | d(\nu, 0.5) - d_i | / d(\nu, 0.5)_i$$
 (1)

Where $d(\nu, 0.5)$ is the median diameter in the volume-based distribution, d_i is the diameter in class i, and X_i is the corresponding volume fraction in %.

Film Preparation by Pickering Emulsion Template: Pure CNF film was prepared as the reference, according to the given procedure by Österberg et al., with slight modification.^[80] CNF dispersion was diluted with deionized water to 0.6 wt% solid content and then stirred for 2 h before filtration. Nanocomposite films derived from the Pickering emulsion template were produced by adding PCL emulsion stabilized by CLPs to the CNF dispersion. Briefly, the mixture was homogenized in Ultraturrax T18 basic IKA homogenizer and subsequently transferred into the container for pressurized filtration. Then, the dispersion was filtrated at 1.5–2 bar pressure for 1 h over a 10 μ m pore size open mesh Sefar Nitex polyamine monofilament fabric, placed on the top of a VWR grade 415 filter paper. The obtained wet films were ambiently dried (48 h at 23 °C and 50% relative humidity) and then subjected to a hot press machine (Fred S. Carver Inc.) (75 °C, 4000 Psi for 1.5 h). For comparison, a few samples were placed under a 5 kg load instead of using a hot press machine (referred to with AM abbreviation).

Characterization of Films: The mechanical properties of obtained films were evaluated in both dry and wet conditions. Dry and wet tensile testing was performed using the universal testing machine (Instron 4204, USA) subjected to a 100 N load cell in 50% RH and 23 °C. Samples were cut into rectangular film specimens (5 cm in length and 5 mm in width), and their thickness at the edges and in the center was measured using a Lorentzen & Wettre (L&W) micrometer. The average of three measured thicknesses for each specimen was used for the tensile analysis. Young's modulus was calculated from the slope of the initial linear part of the stress-strain curve, and toughness was determined from the area under the stress-strain curve up to the fracture point. The presented results were achieved as mean value \pm one standard deviation of five samples. To measure the tensile properties, dry films were conditioned at 50% RH and 23 °C 48 h before the experiment. Wet tensile testing was performed by fully immersing films in deionized water for 2 h. Before tensile testing, the thickness of the films was measured again, and the measurement was immediately performed.

The microstructure of nanocomposite films was observed by SEM (Zeiss Sigma VP, Germany, and Hitachi S-4800, Japan) equipped under vacuum and at the accelerated voltage of 2–3 kV. Before using the SEM, all films (pure CNF and nanocomposites) were mounted on the metal stub with double-sided carbon tape. Sputter coating was performed using a Leica EM ACE600 sputter coater, depositing a thin layer of \approx 4 nm using the gold–palladium alloy.

The XPS analysis was performed with a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer using a monochromate Al_{Kat} X-ray source (1486.7 eV) run at 100 W. Pass energy of 80 eV and a step size of 1.0 eV were used for the survey spectra, while pass energy of 20 eV and a step size of 0.1 eV were used for the high-resolution spectra. Photoelectrons were collected at a 90° take-off angle under ultra-high vacuum conditions, with a base pressure typically below 1 × 10⁻⁹ Torr. The diameter of the beam spot from the X-ray was 1 mm, and the analysis area for these measurements was 300 × 700 µm.

Wetting properties of the films were carried out through both static and dynamic WCA measurement using a Theta flex optical tensiometer (Biolin Scientific, Addlife-Sweden). Static WCA measurement was conducted by dropping 5 μ L deionized water onto the film's surfaces, and the images were recorded for 60 s at a rate of one frame per second. Advancing and receding WCAs were



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measured by increasing the water volume from 5 to 20 μL in the 60 s period and then decreasing to 5 μL . The hysteresis, which defines surface heterogeneity, was calculated according to the advancing and receding contact angle difference. At least ten experiments were repeated from different regions of each film, and the average values were reported as the mean value. The contact angle was automatically calculated from the shape of the droplets using the full Young–Laplace equation.

The water uptake of films was evaluated by measuring the weight of films before and after immersing in 20 mL of deionized water for 1 h. The weight of wet samples was calculated after gently blotting the excess water on the surface of the films with soft tissue. The percentage of water uptake (*WU*) ratio was calculated using Equation (2).

$$WU\% = (W_2 - W_1) / W_1 \times 100$$
 (2)

Where W_2 is the weight after dipping in water and W_1 is the weight of the dried sample.

The UV-shielding performance of nanocomposite films was analyzed following the procedure described earlier.^[82,83] The transmittance of the films in the wavelength ranging from 200 to 800 nm using a UV–vis spectrophotometer was recorded by Shimadzu UV-2550.

The antioxidant activity analysis was performed following Erel et al.'s procedure^[84] with slight modifications. In brief, a freshly 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid (ABTS⁺⁺) radical solution was produced by reacting ABTS with sodium persulfate in the dark and room temperature (RT) conditions for 16 h. Afterward, the prepared solution was diluted (1:60) until reaching an absorbance of 0.8 at 734 nm in RT. Rectangular specimens of films weighing 3–5 mg were immersed in 2 mL of ABTS⁺⁺ solution, subsequently agitating with an orbital shaker vortex, and placing on a Stuart tube rotator SB2. Reduction in the absorbance of ABTS⁺⁺ radical solution at 734 was selected as a reference, and the antioxidant radical scavenger activity was analyzed by monitoring the absorbance of the ABTS⁺⁺ radical solution at different times. The results were reported as the average value of triplicate measurement for each sample.

Thermal analysis of the nanocomposites was studied by differential scanning calorimetry (DSC) performed on a TA-Instruments model MT-DSC Q2000 (USA) equipped with an intercooler system supported by nitrogen atmosphere. Before measurement, an empty aluminum pan was placed in the equipment as the reference, and another pan containing samples weighted \approx 5 g was used for the analysis. Two heating–cooling cycles in the range of –70 °C to 140 °C with a flow rate of 10 °C min⁻¹ were performed. The first cycle was used to remove the thermal history, and the second cycle was operated to determine the crystallization temperature (T_c), melting temperature (T_m), crystallization enthalpy (ΔH_c), and melting enthalpy (ΔH_m) of the samples. The heat of fusion was calculated by integrating the melting peaks, and the crystallinity degree was determined by (Equation (3)).

$$\chi(\%) = (100 - \varphi)\Delta H_{\rm m} / \Delta H_{\rm m}^{\circ} \tag{3}$$

Where φ is the weight fraction of CNF and CLPs or c-CLPs in the nanocomposites, $\Delta H_{\rm m}$ is the melting enthalpy, and $\Delta H_{\rm m}$ is the heat of fusion for 100% crystalline PCL considering 135.31 j.g^{-1.[85]}

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

cellulosic nanocomposite, interfacial compatibilizer, lignin nanoparticles, Pickering emulsion, wet strength

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- [1] K. De France, Z. Zeng, T. Wu, G. Nyström, Adv. Mater. 2021, 33, 2000657.
- [2] M. E. Lamm, K. Li, J. Qian, L. Wang, N. Lavoine, R. Newman, D. J. Gardner, T. Li, L. Hu, A. J. Ragauskas, H. Tekinalp, V. Kunc, S. Ozcan, *Adv. Mater.* **2021**, *33*, 2005538.
- [3] H. Tu, M. Zhu, B. Duan, L. Zhang, Adv. Mater. 2021, 33, 2000682.
- [4] A. J. Benítez, J. Torres-Rendon, M. Poutanen, A. Walther, Biomacromolecules 2013, 14, 4497.
- [5] X. Yang, S. K. Biswas, J. Han, S. Tanpichai, M. C. Li, C. Chen, S. Zhu, A. K. Das, H. Yano, *Adv. Mater.* **2021**, *33*, 2002264.
- [6] A. Quellmalz, A. Mihranyan, ACS Biomater. Sci. Eng. 2015, 1, 271.
- [7] C. Goussé, H. Chanzy, M. L. Cerrada, E. Fleury, Polymer 2004, 45, 1569.
- [8] S. Deng, R. Huang, M. Zhou, F. Chen, Q. Fu, Carbohydr. Polym. 2016, 154, 129.
- [9] G. Siqueira, J. Bras, A. Dufresne, Langmuir 2010, 26, 402.
- [10] N. Follain, M. F. Marais, S. Montanari, M. R. Vignon, *Polymer* 2010, 51, 5332.
- [11] K. Littunen, U. Hippi, L. S. Johansson, M. Österberg, T. Tammelin, J. Laine, J. Seppälä, *Carbohydr. Polym.* 2011, *84*, 1039.
- [12] K. Sakakibara, H. Yano, Y. Tsujii, ACS Appl. Mater. Interfaces 2016, 8, 24893.
- [13] T. Kaldéus, A. Träger, L. A. Berglund, E. Malmström, G. Lo Re, ACS Nano 2019, 13, 6409.
- [14] L. S. Johansson, T. Tammelin, J. M. Campbell, H. Setälä, M. Österberg, Soft Matter 2011, 7, 10917.
- [15] B. P. Frank, C. Smith, E. R. Caudill, R. S. Lankone, K. Carlin, S. Benware, J. A. Pedersen, D. H. Fairbrother, *Environ. Sci. Technol.* 2021, 55, 10744.
- [16] M. Österberg, M. H. Sipponen, B. D. Mattos, O. J. Rojas, Green Chem. 2020, 22, 2712.

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- [17] E. Lizundia, M. H. Sipponen, L. G. Greca, M. Balakshin, B. L. Tardy, [50] W. Yang, H. Bian,
- O. J. Rojas, D. Puglia, Green Chem. **2021**, 23, 6698.
- [18] M. L. Mattinen, G. Riviere, A. Henn, R. W. N. Nugroho, T. Leskinen, O. Nivala, J. J. Valle-Delgado, M. A. Kostiainen, M. Österberg, *Nanomaterials* **2018**, *8*, 1001.
- [19] L. Siddiqui, J. Bag, Seetha, D. M., A. Leekha, H. Mishra, M. Mishra, A. K. Verma, P. K. Mishra, A. Ekielski, Z. Iqbal, S. Talegaonkar, *Int. J. Biol. Macromol.* **2020**, *152*, 786.
- [20] B. Wang, D. Sun, H. M. Wang, T. Q. Yuan, R. C. Sun, ACS Sustainable Chem. Eng. 2019, 7, 2658.
- [21] T. Zou, M. H. Sipponen, A. Henn, M. Österberg, ACS Nano 2021, 15, 4811.
- [22] X. Zhang, M. Yang, Q. Yuan, G. Cheng, ACS Sustainable Chem. Eng. 2019, 7, 17166.
- [23] L. Bai, L. G. Greca, W. Xiang, J. Lehtonen, S. Huan, R. W. N. Nugroho, B. L. Tardy, O. J. Rojas, *Langmuir* **2019**, *35*, 571.
- [24] M. H. Sipponen, M. Smyth, T. Leskinen, L. S. Johansson, M. Österberg, Green Chem. 2017, 19, 5831.
- [25] X. Li, J. Shen, B. Wang, X. Feng, Z. Mao, X. Sui, ACS Sustainable Chem. Eng. 2021, 9, 5470.
- [26] L. E. Low, K. C. Teh, S. P. Siva, I. M. L. Chew, W. W. Mwangi, C. L. Chew, B. H. Goh, E. S. Chan, B. T. Tey, *Environ. Nanotechnol.*, *Monit. Manage.* **2021**, *15*, 100398.
- [27] K. S. Silmore, C. Gupta, N. R. Washburn, J. Colloid Interface Sci. 2016, 466, 91.
- [28] D. G. Ortiz, C. Pochat-Bohatier, J. Cambedouzou, M. Bechelany, P. Miele, *Engineering* **2020**, *6*, 468.
- [29] A. Chakrabarty, Y. Teramoto, ACS Sustainable Chem. Eng. 2020, 8, 4623.
- [30] F. Wang, Y. Zhang, X. Li, B. Wang, X. Feng, H. Xu, Z. Mao, X. Sui, *Carbohydr. Polym.* 2020, 234, 115934.
- [31] X. Liu, X. Qi, Y. Guan, Y. He, S. Li, H. Liu, L. Zhou, C. Wei, C. Yu, Y. Chen, *Carbohydr. Polym.* **2019**, *224*, 115202.
- [32] S. Fujisawa, E. Togawa, K. Kuroda, Biomacromolecules 2017, 18, 266.
- [33] A. Moreno, M. Morsali, J. Liu, M. H. Sipponen, *Green Chem.* **2021**, *23*, 3001.
- [34] Y. Jiang, Y. Zhang, L. Ding, J. A. De La Cruz, B. Wang, X. Feng, Z. Chen, Z. Mao, X. Sui, *Carbohydr. Polym.* **2019**, *223*, 115079.
- [35] S. Tanpichai, S. K. Biswas, S. Witayakran, H. Yano, Composites, Part A 2020, 132, 105811.
- [36] D. W. Kim, J. Shin, S. Q. Choi, Carbohydr. Polym. 2020, 247, 116762.
- [37] S. W. Kuo, C. F. Huang, F. C. Chang, J. Polym. Sci., Part B: Polym. Phys. 2001, 39, 1348.
- [38] R. Pucciariello, M. D'Auria, V. Villani, G. Giammarino, G. Gorrasi, G. Shulga, J. Polym. Environ. 2010, 18, 326.
- [39] M. Farooq, T. Zou, G. Riviere, M. H. Sipponen, M. Österberg, Biomacromolecules 2019, 20, 693.
- [40] G. Bahsi Kaya, Y. Kim, K. Callahan, S. Kundu, Carbohydr. Polym. 2022, 276, 118745.
- [41] S. Arditty, C. P. Whitby, B. P. Binks, V. Schmitt, F. Leal-Calderon, Eur. Phys. J. E: Soft Matter Biol. Phys. 2003, 11, 273.
- [42] Z. Hu, S. Ballinger, R. Pelton, E. D. Cranston, J. Colloid Interface Sci. 2015, 439, 139.
- [43] E. Rojo, M. S. Peresin, W. W. Sampson, I. C. Hoeger, J. Vartiainen, J. Laine, O. J. Rojas, *Green Chem.* **2015**, *17*, 1853.
- [44] Y. Liu, ACS Sustainable Chem. Eng. 2018, 6, 5524.
- [45] T. Zou, N. Nonappa, M. Khavani, M. Vuorte, P. Penttilä, A. Zitting, J. J. Valle-Delgado, A. M. Elert, D. Silbernagl, M. Balakshin, M. Sammalkorpi, M. Österberg, J. Phys. Chem. B 2021, 125, 12315.
- [46] P. Fratzl, I. Burgert, H. S. Gupta, Phys. Chem. Chem. Phys. 2004, 6, 5575.
- [47] D. Kai, W. Ren, L. Tian, P. L. Chee, Y. Liu, S. Ramakrishna, X. J. Loh, ACS Sustainable Chem. Eng. 2016, 4, 5268.
- [48] P. Samyn, ACS Appl. Mater. Interfaces 2020, 12, 28819.
- [49] Y. Z. Hou, Q. F. Guan, J. Xia, Z. C. Ling, Z. Z. He, Z. M. Han, H. Bin Yang, P. Gu, Y. B. Zhu, S. H. Yu, H. A. Wu, ACS Nano 2021, 15, 1310.

- [50] W. Yang, H. Bian, L. Jiao, W. Wu, Y. Deng, H. Dai, RSC Adv. 2017, 7, 31567.
- [51] H. Sehaqui, T. Zimmermann, P. Tingaut, Cellulose 2014, 21, 367.
- [52] M. Wu, P. Sukyai, D. Lv, F. Zhang, P. Wang, C. Liu, B. Li, *Chem. Eng. J.* 2020, 392, 123673.
- [53] K. Kriechbaum, L. Bergström, Biomacromolecules 2020, 21, 1720.
- [54] M. Shimizu, T. Saito, A. Isogai, J. Membr. Sci. 2016, 500, 1.
- [55] F. Ansari, E. L. Lindh, I. Furo, M. K. G. Johansson, L. A. Berglund, *Compos. Sci. Technol.* **2016**, *134*, 175.
- [56] A. Walther, F. Lossada, T. Benselfelt, K. Kriechbaum, L. Berglund, O. Ikkala, T. Saito, L. Wågberg, L. Bergström, *Biomacromolecules* 2020, 21, 2536.
- [57] T. Benselfelt, M. Nordenström, S. B. Lindström, L. Wågberg, Adv. Mater. Interfaces 2019, 6, 1900333.
- [58] S. Laurichesse, L. Avérous, Polymer 2013, 54, 3882.
- [59] Y. Xu, C. Wang, N. M. Stark, Z. Cai, F. Chu, Carbohydr. Polym. 2012, 88, 422.
- [60] R. Xiong, N. Hameed, Q. Guo, Carbohydr. Polym. 2012, 90, 575.
- [61] L. S. Johansson, J. M. Campbell, K. Koljonen, P. Stenius, Appl. Surf. Sci. 1999, 144–145, 92.
- [62] L. S. Johansson, Microchim. Acta 2002, 138-139, 217.
- [63] M. Jawaid, S. Boufi, H. P. S. Abdul Khalil, Cellulose-Reinforced Nanofibre Composites: Production, Properties and Applications, Elsevier Science, Amsterdam, the Netherlands 2017.
- [64] W. Gindl-Altmutter, M. Obersriebnig, S. Veigel, F. Liebner, ChemSusChem 2015, 8, 87.
- [65] S. S. Nair, H. Chen, Y. Peng, Y. Huang, N. Yan, ACS Sustainable Chem. Eng. 2018, 6, 10058.
- [66] M. E. Diaz, J. Fuentes, R. L. Cerro, M. D. Savage, J. Colloid Interface Sci. 2010, 343, 574.
- [67] L. Gao, T. J. McCarthy, Langmuir 2007, 23, 3762.
- [68] A. Kozbial, C. Trouba, H. Liu, L. Li, Langmuir 2017, 33, 959.
- [69] N. Forsman, L. S. Johansson, H. Koivula, M. Tuure, P. Kääriäinen, M. Österberg, Carbohydr. Polym. 2020, 227, 115363.
- [70] S. Väisänen, R. Pönni, A. Hämäläinen, T. Vuorinen, Cellulose 2018, 25, 6923.
- [71] C. Vilela, M. Kurek, Z. Hayouka, B. Röcker, S. Yildirim, M. D. C. Antunes, J. Nilsen-Nygaard, M. K. Pettersen, C. S. R. Freire, *Trends Food Sci. Technol.* 2018, 80, 212.
- [72] F. Tian, E. A. Decker, J. M. Goddard, Food Funct. 2013, 4, 669.
- [73] T. Koutchma, V. Popović, V. Ros-Polski, A. Popielarz, Compr. Rev. Food Sci. Food Saf. 2016, 15, 844.
- [74] Y. Qian, X. Qiu, S. Zhu, Green Chem. 2015, 17, 320.
- [75] M. H. Tran, D.-P. Phan, E. Y. Lee, Green Chem. 2021, 23, 4633.
- [76] W. Yang, J. S. Owczarek, E. Fortunati, M. Kozanecki, A. Mazzaglia, G. M. Balestra, J. M. Kenny, L. Torre, D. Puglia, *Ind. Crops Prod.* 2016, 94, 800.
- [77] D. Piccinino, E. Capecchi, E. Tomaino, S. Gabellone, V. Gigli, D. Avitabile, R. Saladino, Antioxidants 2021, 10, 274.
- [78] L. Xiao, W. Liu, J. Huang, H. Lou, X. Qiu, Ind. Eng. Chem. Res. 2021, 60, 790.
- [79] M. H. Sipponen, M. Farooq, J. Koivisto, A. Pellis, J. Seitsonen, M. Österberg, Nat. Commun. 2018, 9, 2300.
- [80] M. Österberg, J. Vartiainen, J. Lucenius, U. Hippi, J. Seppälä, R. Serimaa, J. Laine, ACS Appl. Mater. Interfaces 2013, 5, 4640.
- [81] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J. Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, A. Cardona, *Nat. Methods* **2012**, *9*, 676.
- [82] H. Sadeghifar, R. Venditti, J. Jur, R. E. Gorga, J. J. Pawlak, ACS Sustainable Chem. Eng. 2017, 5, 625.
- [83] Q. Xing, P. Buono, D. Ruch, P. Dubois, L. Wu, W. J. Wang, ACS Sustainable Chem. Eng. 2019, 7, 4147.
- [84] O. Erel, Clin. Biochem. 2004, 37, 277.
- [85] D. C. Hyun, RSC Adv. 2015, 5, 76321.

