Opportunities for Cellulose Nanomaterials in Packaging Films: A Review and Future Trends

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ABSTRACT: Performance requirements for packaging films may include barrier properties, transparency, flexibility, and tensile strength. Conventional packaging materials, such as plastic films and laminates, are typically made from petroleum-based polymers. Currently, there is a drive to develop sustainable packaging materials. These alternative materials must be able to be manufactured economically and on a commercial scale, exhibit barrier properties and transparency, and provide adequate mechanical performance. As a biobased, renewable material, cellulose nanomaterials (CNs) are ideally suited to be used in sustainable packaging applications. CNs include cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) and each can provide benefit to packaging films. Manufactured CNF films can be used as packaging films or laminates and have been shown to have good strength properties and good barrier properties, particularly at low humidity. Both CNCs and CNFs can be added to other polymers to improve strength and barrier properties. The flexibility of CNs to be used in a variety of ways in packaging applications has resulted in considerable attention and research activity. This article summarizes the current applicability for CNs in packaging films and discusses the future trends and opportunities for these materials.

KEYWORDS: Cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), cellulose nanomaterials, packaging, films, composites, mechanical properties, barrier properties, water vapor transmission rate, oxygen transmission rate, modification

1 INTRODUCTION

The U.S. plastic film industry has been forecast to grow to 15.4 billion pounds with a value estimated at $24.9 billion by 2018 [1]. This includes applications such as food packaging, medical packaging, and consumer goods such as trash bags. Of these applications, food packaging is expected to have the largest growth in market share over the next several years [1]. Packaging products that use films include blister packs, pouches, stand-up pouches, tray lidding film, and bagged materials used to protect such foods as fresh food, convenience food, dried food, processed chilled food, snack foods, baked goods, cheese, and meats. The key drivers of growth include the trend toward smaller packaging sizes as households get smaller and the population ages, the trend toward "on-the-go" lifestyles, growing requirements for brand enhancement and differentiation, and increasing awareness of environmental issues [2].

The majority of plastic packaging films are manufactured from petroleum-based polymers. Petroleum-based plastics are easy to process, low cost and have excellent barrier and mechanical properties. However, the use of non-biodegradable petroleum-based plastics may lead to increased landfill space, increased marine litter, and a dependence on foreign oil. As we look to use renewable resources to fulfill our material needs, there becomes a growing interest in replacing petroleum-based polymers with sustainable materials [3]. Sustainable packaging materials, those that are renewable, recyclable, or biodegradable, must be both environmentally acceptable and commercially viable [4]. Cellulose nanomaterials (CNs) have great potential for use in packaging applications which maintain product quality, increase product safety, and provide convenience in an environmentally friendly way.

2 CELLULOSE NANOMATERIALS

Cellulose is considered to be one of the most abundant biopolymers and therefore shows considerable promise as a raw material for packaging applications.

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Interest in cellulose nanomaterials (CNs) has grown tremendously in the past decade. The term CN encompasses a class of cellulosic particles having at least one dimension in the nanoscale. Compared with other nanoparticles they are considered low-cost, lightweight, environmentally friendly, and easy to recycle or compost. Wood, the most important industrial source of cellulose, is also the most common source of CNs. Typically bleached kraft pulp is the starting material for the conversion of wood into CNs. Other lignocellulosics, such as agricultural crops, including flax, hemp, and sisal, and agricultural byproducts, such as corn, pineapple, and coconuts, can also be used. Non-wood plants generally contain less lignin and therefore the process of conversion to CNs is less demanding [5].

As lignocellulosics are broken down into CNs, characteristics such as high surface area and nanoscale morphology contribute to properties such as low-density, high strength, transparency, barrier properties, and low thermal expansion, which make them ideally suited for packaging applications. Generally, there are two different types of CNs extracted from lignocellulosics that are applicable to packaging films: cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs), each of which exhibits different properties. The easiest way to distinguish between these two CNs is to consider their preparation. CNFs are extracted through a mechanical process while CNCs are extracted through a chemical process. CNFs have both amorphous and crystalline regions, while CNCs are highly crystalline. This review will focus on both CNFs and CNCs, as each have attributes suitable for packaging applications. A third type of CN, bacterial cellulose, is secreted from certain types of bacteria. It is not covered in this review.

The production of CNFs from cellulose fibers is primarily a mechanical process consisting of two steps, refining and homogenizing. The most common refiner, a disc refiner, consists of a rotating disc plate, a stationary disc plate, and housing. During disc refining a dilute fiber suspension is forced through a gap between the two discs which mechanically separates fiber bundles and fibrillates cell wall structures. Homogenization is a process used to distribute particles uniformly throughout a liquid. During CNF production, a dilute slurry of refined cellulose fibers is homogenized by pumping at high pressure and then subjecting the slurry to a large pressure drop. Homogenization is typically repeated a number of times. Other CNF production methods not discussed here include grinding and cryocrushing [6]. Because the mechanical conversion of cellulose fibers into CNFs is energy intensive, chemical or enzymatic pretreatments may be used to reduce the energy requirements [5, 6]. The source material, fibrillation techniques, and pretreatments contribute to the morphology of the CNFs. In the literature, CNFs may be referred to as cellulosic microfibrils, nanofibrillated cellulose, and microfibrillar cellulose. It is worth noting that the material referred to is sometimes a single microfibril (2–10 nm in diameter and several tens of microns long) or aggregates of microfibrils (20–60 nm in diameter and several micrometers long) [5].

In contrast, extraction of CNCs from lignocellulosics is primarily a chemical process. Similar to the production of CNFs, the first step is removing the non-cellulose components from the source material. In the second step, CNCs are extracted by acid hydrolysis using either hydrochloric or sulfuric acid to obtain the crystalline components of the purified cellulose. During acid hydrolysis the amorphous regions, considered structural defects, are removed, leaving the crystalline regions intact [6]. The result is whisker-like particles. CNCs prepared by hydrochloric acid hydrolysis have no charge, while those prepared by sulfuric acid hydrolysis have negatively charged surfaces and are thus colloidally stable [7]. In the literature a variety of terms have been used to describe CNCs, including cellulosic nanocrystals, cellulose whiskers, nanowhiskers, and nanorods.

CNCs are stiff materials due to their highly crystalline nature, with aspect ratios (L/d) which can be more than 100. Manufacturing variables impact CNC dimension. For example, CNC length decreases with prolonged hydrolysis time [8]. Raw material source may also impact CNC dimension. In one study, CNCs from wood were reported to be 3–5 nm in width and 100–200 nm in length while those from *Valonia*, a sea plant, were reported to be 10–20 nm wide and 1000–2000 nm in length [9]. The strength of crystalline cellulose has been reported to be 7.5–7.7 GPa while the axial modulus has been reported as 110–220 GPa [10]. Due to their high stiffness and strength, small number of defects, high surface area, modifiable surface properties, and biodegradable nature, CNCs lend themselves to potential reinforcement in packaging films [11].

A common pretreatment of importance to both the production of CNFs and CNCs is TEMPO oxidation. During this pretreatment cellulose is treated with TEMPO (2,2,6,6,-tetramethylpiperidine-1-oxyl), which transforms cellulose hydroxyl groups to carboxyl moieties [9]. It promotes the nanofibrillation process, increases crystallinity, and increases dispersion in water of CNs [12]. Excellent summaries of production methods and reported morphological properties of both CNFs and CNCs can be found other review articles [12–14].

Typical CN production results in aqueous suspensions of CNs. However, commercial plastic film production is not a process that is tolerant of water.

Therefore CNs must be dried. Drying is also important from a materials handling consideration as water is expensive to transport and dry CNs are less expensive to transport. The drying method must be carefully considered, and meeting the challenge to dry CNs while maintaining the nanoparticle morphology and properties is important for commercial application in packaging films. Typically either freeze-drying or spray-drying are used for large quantities of CNs.

3 CELLULOSE NANOMATERIAL FILMS

Usually CNF films with low porosity are prepared from CNF suspensions by either casting or drying under vacuum, or filtration followed by drying. As water is removed, hydrogen bonding between CNFs and fiber entanglement results in stiff, strong, translucent films. Once the film is produced the CNFs are generally not redisbursable in water. CNF films have been referred to as nanopaper due to the analogous production methods with cellulosic-based paper [15]. A range of properties are shown in the literature and differences can arise from factors such as CNF raw materials, CNF production method, film preparation technique and testing conditions [6, 16–19]. For example, increasing the film thickness increased tensile strength and elongation (Table 1) [19]. Another study found that the elastic modulus of CNF films was higher for unbleached wood pulp compared with bleached wood pulp (Table 2) [18]. CNF films can also be the starting point for impregnation with polymers which further improve mechanical properties [20, 21].

Barrier properties important for food security and protection include water vapor permeability, measured as water vapor transmission rate (WVTR), and oxygen permeability, measured as oxygen transmission rate (OTR). The small pores of CNF films, the strong hydrogen bonding between nanoparticles, and high crystallinity within nanoparticles can all contribute to good barrier properties. Material source, morphology, and chemical composition impact barrier properties of CNF films.

The impact of types and chemical compositions of wood sources on WVTR were reported, and CNF films from hardwoods had lower WVTRs than CNF films from softwoods (Table 2) [22]. The inclusion of lignin also impacted the WVTR. The CNF films containing some lignin increased WVTR, possibly due to larger pores [22].

There have been attempts to improve the WVTR of CNF films through chemical modification. For example, acetylated CNF films showed a WVTR of 90 g/m^2/day compared with 234 g/m^2/day for unmodified CNF films [23]. In another method, coating CNF films with starch, beeswax, and paraffin using a dipping method decreased the WVTR from 220 g/m^2/day before treatment to 50 g/m^2/day after treatment [24]. The decrease was likely due to surface pore closure and filling of the pore network. Adding

Table 1 Influence of film thickness on mechanical properties of cellulose nanofibril (CNF) films prepared by freeze-drying CNFs manufactured from bleached spruce sulphite pulp (adapted from [19]).

Weight basis	Thickness	Density	Tensile modulus	Tensile strength	Elongation
(g/m^2)	**(μm)**	**(kg/m^3)**	**(GPa)**	**(MPa)**	**(%)**
17 ± 1	21 ± 1	811 ± 47	15.7 ± 1.3	104	5.3 ± 1.0
23 ± 1	23 ± 1	878 ± 24	16.7 ± 0.7	126	5.4 ± 1.5
30 ± 1	30 ± 1	974 ± 42	16.5 ± 0.2	136	8.0 ± 0.8
35 ± 3	33 ± 2	1069 ± 70	17.5 ± 1.0	154	8.6 ± 1.6

Table 2 Influence of pulp type on properties of cellulose nanofibril (CNF) films manufactured using casting-evaporation (adapted from [18, 22]).

Pulp type	Thickness	Density	Elastic modulus	WVTR	WVTR
	(μm)	**(kg/m^3)**	**(GPa)**	**(g*μm/(m^2*day))**	**(g/(m^2*day))**
Bleached softwood	35 ± 3	860 ± 74	6.67 ± 0.65	24,000	686
Bleached hardwood	33 ± 2	903 ± 44	6.31 ± 0.63	20,000	606
Unbleached hardwood	31 ± 1	972 ± 38	7.71 ± 0.45	22,000	710
Unbleached softwood-low lignin	38 ± 3	784 ± 58	8.72 ± 2.00	30,000	789
Unbleached softwood-high lignin	38 ± 2	792 ± 32	8.64 ± 0.40	46,000	1210
Thermo-mechanical pulp	58 ± 3	514 ± 25	5.13 ± 0.83	51,000	879

non-cellulosic materials can also decrease WVTR. For example, adding 25% clay to CNF films decreased WVTR from 299 g/m^2/day to 197 g/m^2/day, although this did somewhat negatively impact film transparency [25]. Compared with common barrier films, the WVTR of CNF films is much higher due to the hydrophilic nature of the CNFs (Table 2, Table 3).

Generally, CNF films exhibit oxygen transmission rates favorable for packaging films. The low porosity of CNF films results in oxygen diffusion rather than transport, and at a sufficient thickness the pores are not interconnected, which contributes to the impermeability [27]. The OTR of CNF films can be a function of treatment, production method, film thickness, and test conditions (Table 4). For example, OTR decreases as CNF film thickness increases and as relative humidity decreases [28]. Further reducing void volume through the addition of glycerol as a plasticizer decreases oxygen diffusivity [27]. However the permeability of oxygen through CNF films dramatically increases with relative humidity due to their hydrophilic nature [19, 21, 28]. In one study, the OTR of a CNF film increased from 0.0006 (cm^3*µm)/(m^2*day*kPa) to 0.85 (cm^3*µm)/(m^2*day*kPa) when the relative humidity increased from 0% to 50%. In this study the OTR remained low until approximately 70% relative humidity, at which point there was a sharp increase in OTR [28]. At 100% relative humidity the OTR of a CNF film was reported to be 8.13 (cm^3*µm)/(m^2*day*kPa) [21], which may no longer be reasonable for barrier packaging films.

Modifying CNFs or incorporating them into hydrophobic polymers has been speculated as a method to improve the barrier properties of CNFs at high humidity but has not been fully successful. In one effort, the OTRs of CNF-phenol formaldehyde composite films were reported (Table 5). Although adding phenol formaldehyde to CNF films resulted in improved water resistance at 35% relative humidity, there was no improvement in OTR at 100% relative humidity [21]. Adding non-cellulosic materials can also decrease OTR. For example, adding 25% clay to CNF films decreased OTR from 50 (cm^3*µm)/(m^2*day*kPa) to 3.0 (cm^3*µm)/(m^2*day*kPa). In this study the initial OTR was higher than reported elsewhere, and it was suggested that this was due to agglomeration of the fibrils which opened pathways for oxygen to permeate through the film [25]. In most cases, OTR for CNF films is comparable to or better than traditional packaging films (Table 3).

While most CN-based films have been produced using CNFs, films can also be produced using CNCs. A study which investigated the percolation threshold and modulus of CNC films produced from different source materials found that the stiffness of the film increased with the aspect ratio of the CNCs [29]. However, CNFs are typically more suitable for making films than CNCs because CNF films are generally

Table 3 Typical barrier properties of common plastic films (adapted from [26]).

Material	**Water Vapor Transmission Rate (WVTR)**	**Oxygen permeability**
	(g*µm/(m^2*day))	**(cm^3*µm/(m^2*day*kPa))**
Polyethylene terephthalate (PET)	472	18
High-density polyethylene (HDPE)	118	719
Low-density polyethylene (LDPE)	512	1943
Polypropylene (PP)	197	971
Polystyrene (PS)	3,346	1282
Cellophane	26,378	3
Cellulose acetate	9,843	521

Table 4 Reported oxygen permeability for select cellulose nanofibril (CNF) films (adapted from [28]).

Material	**Oxygen permeability**	**Film thickness**	**Test conditions**
	(cm^3*µm)/(m^2*day*kPa)	**(µm)**	
CNF (carboxymethylated)	0.009	2.54	0% RH
CNF (carboxymethylated)	0.0006	3.19	0% RH
CNF (carboxymethylated)	0.85	3.19	50% RH

Table 5 Impact of phenol formaldehyde (PF) on oxygen transmission rate of cellulose nanofibril (CNF) films (adapted from [21]).

	Oxygen Transmission Rate (OTR)	**Film thickness**	**Test conditions**
	(cm^3/(m^{2}*day))	**(μm)**	
CNF (TEMPO-oxidized)	0.00165 ± 0.00010	61	35% RH
CNF (TEMPO-oxidized)	13.5 ± 3.6	61	100% RH
CNF-10% PF (TEMPO-oxidized)	0.000223 ± 0.00020	61	35% RH
CNF-10 % PF (TEMPO-oxidized)	19.5 ± 1.4	61	100% RH

less brittle than CNC films. Additionally, CNF films were also recently found to act as better oxygen vapor barriers than neat CNC films despite similarities in water permeability [30]. This suggests that the entanglements of the long flexible nanoparticles and lower porosity of the CNF films compared with CNC films result in barrier domains and increased tortuosity of the diffusion pathway. CNF films are also more thermally stable than CNC films [31]. One area where CNC films can provide benefit is as coatings on other polymeric films. One study reported the OTR of PLA to be 18.65 (cm^3*μm)/(m^2*day*kPa). Coating the PLA with CNCs resulted in tremendous improvements in OTR, decreasing it to 0.029 (cm^3*μm)/(m^2*day*kPa) [32].

4 CELLULOSE NANOMATERIAL COMPOSITE FILMS

Cellulosic fibers have been added as fillers or reinforcing agents in polymer-based composites for many years. Recently, CNs have attracted significant interest as a component of composite plastic packaging films. At low loading levels, CNs may provide improvements in mechanical properties and barrier properties while maintaining film transparency. At first glance, combining the benefits of CNs with the benefits of traditional plastic packaging films based on polymeric materials seems like a straightforward approach. The strength of the composite films depends upon the properties of the matrix, the properties of the CN, the CN-matrix compatibility, and the dispersion of the CN in the matrix [33]. It is expected that nanocomposite packaging materials will provide barrier properties, high mechanical strength, thermal stability, chemical stability, recyclability, biodegradability, dimensional stability, heat resistance, and transparency [34].

Solvent casting, which involves dispersion of CNs and a polymer in a solvent (typically aqueous) is straightforward and can yield good dispersion and significant mechanical reinforcement of the polymer while maintaining film transparency [35,36]. Although extensively researched and a good way to understand how CNs perform in matrices, solvent casting is not a common technology in the commercial production of packaging films and it is unlikely solvent-cast films will result in commercial packaging films. In order to be commercially feasible CN composites will likely be melt-processed [37]. This includes film manufacturing on traditional processing equipment such as cast-film extrusion and blown-film extrusion. Because these techniques typically have little tolerance for water, CNs may have to be dried. As CNs are dried, they form strong hydrogen bonds and can be difficult to redisburse. Therefore the main challenge of melt-processing CN composites includes feeding the nanomaterials and obtaining well-dispersed and distributed nanocrystals [38].

Interactions between the hydrophilic CNs and a hydrophilic matrix usually result in satisfactory interfacial properties [39]. However, the polymeric matrix for packaging applications will usually be hydrophobic. Compatibility between the polar cellulosic nanomaterial and nonpolar matrix provides a critical role in composite film properties. Poor compatibility can lead to low moisture resistance, poor barrier properties, poor dispersion due to hydrogen bonding, and poor mechanical properties, all of which can be undesirable in packaging applications. Nevertheless, efforts are underway to combine the two materials in order to obtain novel packaging films with enhanced properties, including attempts to modify CNs to improve properties. Most modifications impart a hydrophobic character to the CN to improve compatibility with nonpolar polymers. Common modifications include using a surfactant, acetylation, esterification, silylation, or polymer grafting [37].

4.1 Matrices

The processing temperature of CNs is limited to about 200 °C, which limits the polymeric matrices that they can be incorporated into [33]. Petroleum-based, nonbiodegradable polymers, such as polyethylene (PE) and polypropylene (PP), are the most common commodity plastics used for packaging films, and are non-biodegradable. They are inexpensive, widely available, and easy to process, and have been investigated as potential matrices for CNs. Polycaprolactone (PCL) is a petroleum-based biodegradable polymer that has also been investigated as a potential matrix for use with CNs.

There is a movement toward replacing petroleum-based polymers currently used in packaging films with polymers derived from renewable resources. However, compared with petroleum-based polymers many of these biobased polymers are more expensive, more brittle, and have poor barrier properties. Awareness is also increasing regarding the environmental impact of packaging waste. Therefore there is an increased demand for biodegradable packaging. Biobased polymers include polylactic acid (PLA), polyhydroxyalkanoates (PHAs), Bio-PE and Bio-PP and starch-based plastics.

Due to its attractive mechanical properties and relatively low cost, PLA derived from renewable resources is the most widely available commercial biopolymer [40]. The melting temperature of PLA can vary between 180 °C and 230 °C [41], which makes it appropriate for processing with CNs. It is of interest for use in packaging applications due to its good transparency, high modulus, reasonable strength, thermal plasticity, excellent aroma and flavor barrier capacity, good heat sealability, processability, and degradation in biological environments [42]. The crystallinity of PLA can vary depending upon the monomers used during synthesis, and the final polymer may be highly crystalline, semicrystalline, or completely amorphous. The mechanical properties of crystalline PLA surpass those of amorphous PLA. In packaging applications, commercial use of PLA has been limited as it is more expensive, more brittle, and more difficult to process than traditional petroleum-based polymers [43]. PLA also has lower impact resistance, lower thermal stability, and the same or lower barrier properties than many petroleum-derived polymers [34, 42]. These disadvantages may be overcome with the inclusion of CNs.

Polyhydroxyalkanoates (PHAs) are a family of biopolyesters which are totally synthesized by microorganisms. Polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-cohydroxyvalerate) (PHBV) are the most well known and studied of these polymers. PHAs have a very narrow processing window and can experience rapid reduction in molecular weight during processing [41]. These polymers are not widely available commercially, but efforts are underway to improve performance and commercialize the manufacturing process.

Recently, there have been efforts to synthesize typical petroleum-based polymers from renewable resources. Bio-PE and Bio-PP have both been synthesized using feedstocks such as starchy crops, sugar crops, and other lignocellulosics [41]. The properties of these materials are similar to petroleum-based PE and PP.

Starch-based polymers are polysaccharides, and can be difficult to process. Under normal circumstances the softening temperature is higher than the degradation temperature. However, the use of plasticizers and the correct processing temperatures can result in a thermoplastic-like material [41]. Thermoplastic starch (TPS) has low mechanical properties and poor barrier properties, which could be improved for packaging applications by incorporating CNs [44].

4.2 Composite Films Containing Cellulose Nanofibers (CNFs)

There has been a limited amount of work incorporating CNFs into petroleum-based matrices. In one early effort, incorporating 5% CNFs into PP and PE did not significantly increase mechanical properties. This was due to poor dispersion [45].

The most common matrix evaluated for use with CNFs appropriate for packaging films is PLA. One advantage of adding CNFs to PLA is that they act as nucleating agents and alter the crystallization of PLA [46]. In one study, the addition of 10% CNFs as nucleating agents for PLA reduced by half the annealing time needed to crystalize the neat PLA without changing mechanical properties [47]. In some cases, partially crystallized PLA-CNF composites can replace fully crystallized PLA [48]. However, other nucleating agents, such as phenylphosphonic acid zinc, have been more effective at accelerating crystallization of PLA than CNFs [48].

Improvements in mechanical properties have been reported after adding CNFs to PLA using solvent evaporation. In one study PLA and CNFs were premixed using an organic solvent, kneaded to attain uniform dispersion, and films were hot-pressed. The addition of 5% CNFs increased Young's modulus and tensile strength of PLA by 26% and 17%, respectively. Increasing the CNF content to 10% resulted in an increase in Young's modulus and tensile strength of PLA by 38% and 33%, respectively [49]. In another study, PLA was suspended as microparticles in water and blended with CNF, then the water was removed via membrane filtration and compression molded. Increases in modulus and strength of up to 58% and 210%, respectively, were obtained for 32% CNF composites [50]. The brittleness of PLA may be improved with toughening agents. Unfortunately this can also decrease the tensile properties. One study demonstrated that the use of biobased toughening agents resulted in a loss in tensile properties, but the addition of CNFs could recover the tensile properties [51]. Although the production methods are not feasible for manufacturing packaging films, the studies confirm that CNFs can reinforce PLA.

There are fewer studies that looked at the properties of PLA-CNF composites manufactured using melt-processing techniques which have had mixed results. One study used twin-screw extrusion to disperse CNFs into PLA. Dyeing the fiber allowed for assessment of fiber distribution by laser confocal microscopy. Images showed uniform dispersion [52]. In another, polyethylene glycol (PEG) was used as a processing aid to improve dispersion (Table 6) [53]. Unfortunately, mechanical properties did not improve with the addition of CNFs and PEG, highlighting the difficulty in melt-processing these composites. Preparing PLA-CNF composites in a two-step process consisting of a solvent cast master batch preparation followed by extrusion and injection molding showed better dispersion [54]. In another effort, liquid glycerol triacetate (GTA) was added as a plasticizer to PLA and CNF during extrusion. The CNFs were added at 1%. The plasticizer addition was helpful in elongation at break, which increased from 2% to 31% [55].

Modification of CNFs has largely been aimed at improving compatibility with nonpolar matrices. Coating fibers with styrene maleic anhydride or ethylene-acrylic acid improved their ability to interact with both PLA and PHB matrices [45]. In another effort, CNFs were grafted with poly(epsilon-aprolatone) in order to make it more compatible with PCL [56]. CNFs modified with N-octodecyl isocyanate as a grafting agent were used to reinforce PCL. Addition of 3% modified CNFs increased tensile modulus and strength by 60% and 145%, respectively, compared with neat PCL. Modification also resulted in a better dispersion of the CNFs [57].

Table 6 Tensile properties of polylactic acid (PLA) composites containing cellulose nanofibrils (CNFs) and polyethylene glycol (PEG) (adapted from [53]).

	Tensile strength	Tensile modulus	Elongation
	(MPa)	(GPa)	(%)
PLA	58 ± 6	2.0 ± 0.2	4.2 ± 0.6
PLA + 5% CNF	58 ± 5	2.6 ± 0.1	2.8 ± 0.5
PLA + 5% PEG	51 ± 3	2.1 ± 0.6	Na
PLA + 5% PEG + 5% CNF	59 ± 2	2.3 ± 0.1	3.3 ± 0.2

The CNFs can also be used as a reinforcement in TPS, and the dispersion of the CNFs into TPS was investigated using a torque rheometer [58]. CNF gels were combined with starch powder using continuous twin-screw extrusion to improve the mechanical properties and moisture sensitivity of TPS while retaining translucency [59, 60].The addition of CNFs to starch can also improve barrier properties. In one effort the addition of CNFs to starch decreased the WVTR of films from 2.66 (g*mm)/(kPa*h*m^2) to 1.67 (g*mm)/(kPa*h*m^2) [61]. The addition of CNF in TPS can also reduce the fungal degradation rate [62].

In a hybrid processing technique, PHBV powder dispersed in water was mixed with an aqueous suspension of CNFs and freeze-dried. The resulting composite was then used as a master batch for melt processing. Adding 5% CNFs increased the tensile modulus of the PHBV by 55% and tensile strength by 9% [63].

4.3 Composite Films Containing Cellulose Nanocrystals (CNCs)

The dispersion of CNCs into nonpolar matrices is challenging owing to high surface energy, large specific surface area, and hydrophilic nature, resulting in a tendency to aggregate.

There has been an investigation of CNCs as a reinforcing agent for petroleum-based packaging films. Incorporating 2% to 15% CNCs into a PP matrix using twin-screw extrusion did not improve tensile strength of the neat PP, however flexural strength slightly improved and crystallinity increased [64]. Using a coupling agent did little to further enhance mechanical properties or crystallinity [64]. The lack of improvement in mechanical properties was likely due to poor dispersion; therefore others have investigated alternative melt-blending techniques to improve dispersion. In one effort, the dispersion of 1% to 10% CNCs into a PP matrix was improved when the composites were melt-blended two times before injection molding [65]. Better dispersion of CNCs in PP and PE was found using solid-state shear pulverization (Table 7) [66]. This technique exposes polymers to larger shear and compressive forces than found during typical melt-processing [66]. Modification of CNCs by grafting with organic aliphatic acid chains with different lengths in an esterification reaction resulted in a more homogeneous mixture when incorporated into PE when sufficiently long chains were grafted [67]. Raman spectroscopy was successfully used to determine the dispersion of CNCs in PP composites extruded filaments [68]. This could be a useful technique in studying dispersion in polymer films.

Table 7 Tensile properties of polyethylene (PE) and polypropylene (PP) composites containing cellulose nanocrystals (CNCs) produced using solid-state shear pulverization (adapted from [66]).

	Young's modulus	Yield strength	Elongation at break
	(GPa)	(MPa)	(%)
PE	0.16 ± 0.01	10 ± 1	510 ± 30
PE – 3% CNC	0.22 ± 0.01	11 ± 1	490 ± 30
PE – 7% CNC	0.25 ± 0.01	12 ± 1	500 ± 40
PE – 10% CNC	0.27 ± 0.01	13 ± 1	460 ± 30
PP	1.20 ± 0.02	36 ± 1	700 ± 40
PP – 3% CNC	1.68 ± 0.05	39 ± 1	15 ± 2
PP – 7% CNC	1.73 ± 0.06	39 ± 1	13 ± 2
PP – 10% CNC	1.83 ± 0.07	38 ± 1	12 ± 3

Table 8 Effect of cellulose nanocrystal (CNC) loading level on tensile properties of polylactic acid (PLA)-CNC composites (adapted from [69]).

	Tensile modulus	Tensile strength	Elongation at Break
	(GPa)	(MPa)	(%)
PLA	1.886 ± 0.009	58.2 ± 0.3	6.0 ± 1.3
PLA + 1 wt% CNC	1.197 ± 0.004	30.4 ± 0.2	6.9 ± 0.3
PLA + 2 wt% CNC	0.990 ± 0.175	26.8 ± 0.8	7.6 ± 2.0
PLA + 3 wt% CNC	1.070 ± 0.362	36.5 ± 7.0	12.6 ± 3.8
PLA + 5 wt% CNC	1.225 ± 0.208	37.2 ± 3.3	8.20 ± 0.7

It has been shown that CNCs also increase PLA crystallinity [69]. Similar to composite films containing CNFs, in order for CNCs to be used as reinforcing agents in packaging applications they must be dried and then incorporated into polymer matrices. Poor compatibility can negatively impact mechanical properties. PLA-CNC composites were manufactured via solvent casting at 0%, 1%, 3%, and 5% CNCs. The void volumes of the films were 1.2%, 8.7%, 11.2%, and 13.9% respectively. The addition of CNCs decreased modulus and strength, which suggests poor compatibility (Table 8) [69]. Adding CNCs also results in increased water sorption due to the hydrophilic nature of the CNCs. When solvent-cast PLA-CNC films were exposed to water at various temperatures, water uptake of the film increased with both increasing CNC content and temperature [70].

There are limited studies where CNCs are melt-processed with PLA. In an early study, PLA-CNC composites were manufactured in a vented extrusion system where the CNCs were fed wet. A processing aid was used in liquid form to facilitate dispersion of CNCs in PLA. This method improved thermal degradation but no improvement in properties were noted compared with neat PLA, and it was suggested that this was due to the processing aids used and high processing temperatures [71]. This method did show promise, however, and in subsequent efforts processing temperatures and cooling rates were controlled. In this effort, an addition of 1% CNCs to plasticized PLA increased the yield strength by over 300%, improved the modulus, and maintained film transparency [38]. In another effort, PLA and CNCs were combined using twin-screw extrusion. In this case, the CNCs were well dispersed but SEM images revealed poor adhesion [72]. In an attempt to improve processability polyvinyl alcohol (PVOH) was used as a processing aid. It was either dry-mixed with PLA prior to extrusion or pumped as suspension with CNCs directly into the extruder. The results showed poor mechanical properties due to a phase separation between a continuous PLA phase and a discontinuous PVOH phase [73]. A two-step process consisting of melt-compounding CNCs with PLA using direct liquid feeding followed by melt fiber spinning and compression molding can minimize CNC agglomerate size [74]. CNCs were successfully added to a plasticized PLA-PHB blend in a microextruder, which improved thermal stability [75].

The high surface-to-volume ratios of CNCs and hydroxyl groups on their surface make many types of functionalization in order to improve compatibility with the matrix possible, including polymer grafting, modification with silanes, modification with surfactants, and esterification. During modification, there is a challenge in preserving the original morphology and maintaining the integrity of CNCs [76]. Modification by grafting l-lactic acid oligomers onto CNCs has been investigated as a method to improve compatibility with PLA [77]. CNCs modified with N-octodecyl isocyanate as a grafting agent were used to reinforce PCL. Addition of 3% modified CNC increased tensile modulus and strength by 15% or 45% respectively compared with neat PCL. Although the mechanical properties improved over neat PCL, compared with CNF-based composites the improvements in CNC-based composites were not as great. This was possibly due to the entanglements of CNF compared with the rod-like CNCs [57]. In another effort, CNCs were modified with silanes, which was found to increase dispersion in PLA, resulting in increased crystallinity and mechanical properties [43]. Modification of CNCs with a surfactant has been shown to improve mechanical performance of PLA-CNC composites [39]. In another effort, PLA-CNC films were produced using solvent casting. Modifying CNCs with a surfactant was shown to improve dispersion in the composite [78]. In addition, surfactant-modified CNCs not only improve compatibility with PLA, but the resulting composites maintain optical transparency and exhibit some plasticization [79].

The pathway through barrier films can be increased by increasing the polymer crystallinity, adding nanofillers, or forming multilayers [42]. Increasing the pathway tortuosity will improve barrier properties. Therefore, CNCs can increase barrier properties of films by both increasing crystallinity and by increasing the pathway for diffusion of gases. One study that reported barrier properties of PLA-CNC films prepared via solvent casting showed a reduction in water permeability and oxygen permeability compared with neat PLA (Table 9) [69]. In another study of solvent-cast films, adding 1% CNC to PLA resulted in a 9% decrease in OTR and 5% CNC resulted in a 43% decrease in OTR [80]. Adding CNCs to PLA-PHB blends improved OTR, and further improvements were observed when CNCs were modified with an acid phosphate ester of ethoxylated nonylphenol [75].

Limited studies of the degradability of PLA-CNC composites have been reported. The degradation of PLA starts with diffusion of water into the materials which results in chain scissions and molecular weight reduction. Microorganisms such as fungi and bacteria then metabolize macromolecules as organic matter. In one study, CNCs were modified using a surfactant and incorporated into PLA at a loading of 1–3%. The disintegrability of the solvent-cast PLA-CNC composites was monitored. Between 3 and 14 days, composites containing CNCs had a lower degree of disintegrability compared with neat PLA. However, after 14 days of testing, all samples reached a similar degree of disintegrability (90%) [81]. In another study of PLA-CNC composite films prepared via solvent casting, CNCs in PLA matrix had a clear delaying effect on the hydrolytic degradation of PLA [84]. It was suggested that the highly crystalline CNCs inhibited water absorption in the PLA-CNC composites [82]. These studies suggest it may be possible to use CNCs to control biodegradability and prolong the lifetime of PLA without ultimately impacting biodegradability.

5 SAFETY

Transparent films for packaging applications may be considered for food packaging, so concern regarding safety to human health needs to be considered. Exposure can take three main routes, dermal contact, inhalation, and ingestion [83]. Ingestion of nanoparticles in food packaging can occur if nanoparticles in films or nanosensors migrate inadvertently into the product they are protecting, or if active nanoparticles or bioactive nanoparticles are intended for migration into a product that is to be consumed. Although there is some concern, there is no concrete evidence that the public is at risk from the use of nanomaterials in food-related products [84]. Macroscopic wood fibers have generally been considered safe for food packaging applications. However, the unique properties of CNs compared with macroscopic cellulose, including the ability to be transported through dermal exposure, make it impossible to predict risk based solely on risk associated with macroscopic cellulose [85]. Initial research into the toxicity of CNs in various organisms has indicated that these materials do not exhibit any cytotoxicity, thus showing promise for use in food applications [86–89]. Although more work in this area is needed, these studies indicate little to no toxicity of cellulosic nanomaterials with LC50 (lethal concentration, 50%) levels orders of magnitude higher than conceivable worst-case exposure levels. However, gaps in knowledge about the toxicity of CNs in packaging remain one of the biggest safety challenges.

In order for commercialization, application of nanotechnology in packaging films must also be accepted

Table 9 Effect of cellulose nanocrystal (CNC) content on water vapor and oxygen permeabilities of polylactic acid (PLA)-CNC composites (adapted from [69]).

	Water vapor permeability	**Reduction in water vapor permeability**	**Oxygen permeability**	**Reduction in oxygen permeability**
	(kg*m/(s*m^2*Pa))	**(%)**	**(m^3*m/(s*m^2*Pa))**	**(%)**
PLA	2.303 ± 0.065 e^{-14}		1.37 ± 0.006 e^{-17}	
PLA + 1 wt% CNC	0.819 ± 0.160 e^{-14}	54	0.23 ± 0.02 e^{-17}	83
PLA + 2 wt% CNC	0.505 ± 0.053 e^{-14}	78	0.14 ± 0.005 e^{-17}	90
PLA + 3 wt% CNC	0.422 ± 0.147 e^{-14}	82	0.15 ± 0.013 e^{-17}	90
PLA + 5 wt% CNC	0.439 ± 0.123 e^{-14}	81	0.16 ± 0.005 e^{-17}	88

by the consumer [83]. Migration tests with simulants to determine the total amount of nonvolatile substances that might migrate were below the overall migration limits indicated in current legislation in both nonpolar and polar simulants [80]. It is likely that some packaging films will be accepted more easily by the public than others. For example, packaging films containing CNs that do not migrate into the product may be more acceptable to the public than packaging films containing CNs meant to migrate into the product. To improve safety and public perception, gaps in knowledge need to be filled, including development of tools that can detect and characterize CNs in food, establishment of dose metrics, and identification of products currently on the market where CNs are used in food packaging [90].

6 TRENDS

One trend of food packaging films is the development of bioactive packaging, and there have been efforts to produce bioactive packaging films containing CNs. Bioctive packaging used with foods or pharmaceuticals includes packaging that functions beyond passive containment of the product. For example, bioactive packaging may control oxidation of the product, prevent the formation of off-flavors and undesirable textures of food, and provide antimicrobial properties. Packaging that incorporates bioactive agents which are released from the packaging film into the food surface in a controlled way is one application being investigated [3]. In this case, the migration into the food by the bioactive agent is purposeful and intended [83]. Bioactive packaging also includes packaging where the bioactive agents do not migrate, but provide antimicrobial and antifungal activities on the packaging surface [3]. For example, chitosan has been found to be nontoxic, biodegradable, and has antimicrobial and antifungal activities [3]. This could be incorporated into CNF films. Another approach could be to incorporate active compounds into the packaging films or encapsulation of the active compounds into a polymeric matrix [91]. In one effort, antimicrobial PLA-CNC films containing oregano essential oil were prepared by solvent casting. Addition of oregano oil did not affect the water vapor permeability, but had a plasticizing effect. The PLA-CNC composite containing oregano oil also revealed a strong antimicrobial potential, suggesting oregano oil shows promise as a bioactive packaging material to preserve fresh food products against foodborne pathogens [92]. In another approach, titanium dioxide nanoparticles and CNCs were incorporated into wheat gluten films. In this case, the titanium dioxide nanoparticles contributed to antimicrobial activity while the CNCs decreased water vapor transmission [93]. In an effort to manufacture packaging that provided protection against fatty food, three films were studied, including PLA, PLA and an antioxidant package, and PLA, CNF, and an antioxidant package. The study demonstrated that the release rate of the antioxidant was slower in the presence of CNFs, which would potentially increase the oxidative stability of fatty foods [94].

Another packaging trend is the development of smart or intelligent packaging. Smart or intelligent packaging includes the ability to track and trace packages through their lifetime through printed sensors on the package to monitor package conditions. Food manufacturers can use smart packaging to track individual packages of perishable goods to ensure quality upon arrival, provide real-time status of food freshness, eliminate inaccurate expiration dates, detect spoilage-related changes, pathogens, and chemical contaminants [95]. These nanosensors could reduce the time for pathogen detection from days to hours or minutes [44]. Opportunities for CNs include flexible electronics printed on CNF films.

Multilayer films, films consisting of one or more dissimilar layer, are common for packaging products. Individual layers may include gas barrier properties, anti-fog properties, super hydrophobicity, antimicrobial surfaces, or bioactive delivery [12]. Trends include the development of a multilayer structure where one or more layer contains active compounds through film co-extrusion, layer-by-layer assembly, and deposition of CNs onto polymer substrates. One interesting idea is to coat polymeric films with CNCs. In one case, when PLA was coated with CNCs there was a reported 700-fold decrease in oxygen permeability [32]. It has been suggested that coating polymers such as PET and PP with CNCs results in excellent transparency, anti-fog properties, and a 99% decrease in oxygen permeability [12]. There could also be potential to orient CNCs in a layer to provide superior mechanical properties. This has been demonstrated with polyvinyl alcohol in a solvent-cast film with good results [96].

As CNs make inroads into packaging applications, it is expected new modifications will be developed to allow for improved compatibility and higher barrier properties. There may be an emphasis on environmentally friendly modifications and an increased understanding of the mechanism of reactions occurring at the CN-plastic matrix interface [4]. There will also be a continued interest in the use of biopolymers and advances in processing technologies that will meet the challenge of producing CNs at an industrial scale.

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