

Recent Developments in Cellulose Nanomaterial Composites

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Cellulose nanomaterials (CNMs) are a class of materials that have recently garnered attention in fields as varied as structural materials, biomaterials, rheology modifiers, construction, paper enhancement, and others. As the principal structural reinforcement of biomass giving wood its mechanical properties, CNM is strong and stiff, but also nontoxic, biodegradable, and sustainable with a very large (Gton yr^{-1}) source. Unfortunately, due to the relatively young nature of the field and inherent incompatibility of CNM with most man-made materials in use today, research has tended to be more basic-science oriented rather than commercially applicable, so there are few CNM-enabled products on the market today. Herein, efforts are presented for preparing and forming cellulose nanomaterial nanocomposites. The focus is on recent efforts attempting to mitigate common impediments to practical commercialization but is also placed in context with traditional efforts. The work is presented in terms of the progress made, and still to be made, on solving the most pressing challenges—getting properties that are competitive with currently used materials, removing organic solvent, solving the inherent incompatibility between CNM and polymers of interest, and incorporation into commonly used industrial processing techniques.

1. Introduction

Cellulose nanomaterials (CNMs) are a class of nanomaterials that, while not new, have been gaining popularity in composites (among other applications). Part of this is the world's focus on climate change and while CNM have high stiffness, strength, and thermal transport, they also happen to be biorenewable, natural, nontoxic, and sustainable—in short, “green.”^[1] However, the explosion of interest is also driven by recent commercial semi-industrial scale production capacity allowing bulk purchases at relatively low cost, in some cases rivaling

engineering polymer prices.^[2] This trifecta makes for a convergence that, as shown in **Figure 1**, creates conditions such that the amount of publications on cellulose nanocomposites has exploded. While there are many types of CNMs, each type has its own unique flavor. This combined with the fact that these are bioderived, so properties can be dependent upon source biomass leads to a seemingly endless array of very similar, but not quite the same materials with very different results.

Herein, we endeavor to make sense of this ever-expanding research literature. Importantly, while some older research will be presented for context and comparison, as this article is not a “review,” but a “progress report,” focus will be squarely on the most recent work that progresses the field. The most important themes will be presented, specifically discoveries, innovations, and pathways forward of industrial relevance. Afterall, if CNM are to ever have the impact that the field envi-

sions, such as in automotive, packaging, and coating applications, CNM and their composites must successfully transition to the marketplace where they can cost-effectively improve both performance and the environment. However, if the reader would like a more comprehensive report, there are many reviews on the subject.^[3–5]

2. Characteristics of Cellulose Nanomaterials

CNMs are cellulose-based particles that have at least one dimension at the nanosize scale (1–100 nm). CNMs can be produced from various cellulose source materials (e.g., trees, plants, tunicate, algae, bacteria, and biomass residual streams) and by different approaches, as summarized in the following review articles.^[1,6–13] Consequently, there are many varieties of CNMs, consisting of a wide spectrum of particle morphologies (e.g., shape, size, and aspect ratio) and surface characteristics (e.g., charge, chemistries, etc.). Additionally, the surface characteristics of CNMs can be subsequently modified by chemical modification as summarized in the following review papers.^[7,11,14–17] The implications for CNM composites is that the CNM morphology and surface characteristics strongly affect the processing (e.g., dispersion in solvents, rheology, flow),

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DOI: 10.1002/adma.202000718

structure (e.g., CNM dispersion in polymers, self-assembly, CNM-polymer interface, volume fractions, etc.), and the properties (e.g., mechanical, optical, thermal, etc.) of the resulting composite.^[18–22] Thus, when working with CNMs or when assessing the published literature, it is important to pay close attention to the CNM morphology and surface characteristics when comparing results between different studies. Likewise, when studies using similar CNMs are identified, it is good practice to use extreme caution so as not to overstate the relevance of comparisons. To help resolve some of the CNM characterization issues, the recent review by Foster et al., gives a practical guide of how to characterize relevant parameters of CNMs.^[23]

CNMs can be grouped into five general categories: cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), tunicate CNCs (t-CNCs), algal cellulose (AC), and bacterial cellulose (BC).^[1,23,24] As shown in **Figure 2**, these materials have distinct particle morphologies and thus would be expected to affect the processing and properties of any resulting nanocomposite differently.^[18,25,26] Since the majority of the CNM composite research involves CNCs and CNF materials, only CNC and CNFs will be described here. CNCs are produced by acid hydrolysis (typically sulfuric, hydrochloric, or phosphoric acids) which preferentially dissolves the disordered regions of the cellulose source material and leaves behind the crystalline regions. These nanosized particles have a spindle-like morphology (e.g., 50–500 nm in length and 5–20 nm width, aspect ratios usually less than 50, with tapered ends, and no branching), are rigid, highly crystalline, with minimal entanglement between particles (Figure 2a). CNCs have been produced from wood, plants, tunicates, algae, and bacterial cellulose source materials.^[1,8,10] t-CNC should be considered separately as they are longer (up to micrometers in length), have higher aspect ratios, and higher crystallinity (Figure 2d).^[1,8,24] In general, the cellulosic source for CNCs influences the dimensions, aspect ratio and crystallinity of the resulting nanoparticles, while the surface chemistry, charge, and particle aspect ratio are determined by the hydrolysis conditions. The CNC nomenclature has been inconsistent in the past, where such particles have also been referred to as cellulose nanowhiskers (CNW), needles, and nanocrystalline cellulose (NCC). Over the past few years there has been more consensus in the use of CNC, which is based on the International Standards Organization (ISO) nomenclature standard for CNMs.^[27] It should be noted that there is still considerable variation in particle morphology and surface characteristics within the CNC classifications based on the type of acid hydrolysis, and thus subcategorization has been used, typically by adding the acid identifier attached to the front of the CNC.

CNFs are produced by mechanical treatments where the mechanical shear tears the cellulose source material apart.^[12] The resulting nanosized particles have a fibril-like morphology (e.g., micrometers in length, nanometers in width, with aspect ratios usually greater than 50, and can have branching), are flexible, semicrystalline, and form entanglements between CNFs (e.g., network-like structures). CNFs have been produced from wood, plants, and algal cellulose source materials, and the resulting particle aspect ratio, width, degree of branching, surface chemistry and charge are determined by the pretreat-



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ments and mechanical shear process. The fibrillation process typically results in a complex mixture of particles where there is a wide spectrum in particle morphology, which is extremely difficult to systematically quantify.^[9,11,12] Approaches have been developed by Desmaisons et al. and Kangas et al., to give guidance on how to gain a more collective description of CNFs by using multiple characterization methods.^[28,29] CNFs can range from coarse (20–100 nm wide) extensively branched interconnected network structures (Figure 2c) to fine isolated fibrils that are ≈4–10 nm wide (Figure 2b), and most typically they lie

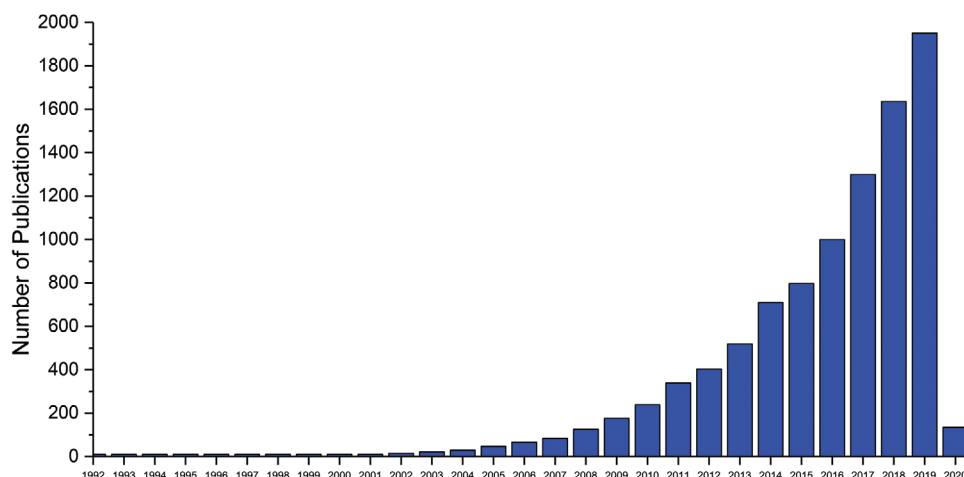


Figure 1. Publications listed in the Web of Science Core Collection by year based on a topical search on “cellulose nano* and *composite” on January 24, 2020. The asterisks represent a “wildcard” for the Boolean search engine capturing all words that contain the text associated with it.

somewhere in between. Here, CNF is used to generally refer to these particles, following the ISO naming standard,^[27] which is synonymous with the term nanofibrillated cellulose (NFC) that is also extensively used in the literature. To help distinguish between different CNF varieties, other subcategorization has been used in this review. Cellulose microfibrils (CMF) are used to describe the coarser materials that are typically produced only by mechanical refinement, these materials are also referred to in the literature as microfibrillated cellulose (MFC). Additionally, with the addition of chemical pretreatments thin fibrils can be produced, and the naming of the resulting particle typically has a chemical identifier attached to the front of the CNF. For example, one of the most prevalent chemical pretreatments, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation, the resulting particles are typically named TOCNF or TEMPO-CNF.

3. CNM Thermoset Nanocomposites

As crosslinked polymers, thermosets come in two flavors, glassy and rubbery. While both generally need enhanced strength, the critical factor in many systems is damage tolerance, or toughness, which is the weak spot of thermosets. Luckily, their sustainability, good properties, nontoxicity, and nanoscale makes CNM an ideal reinforcing phase of thermoset composites (TSCs). The barrier that must be overcome is the hydrophilic nature of CNM which is in direct contrast to the hydrophobic materials used in commercial TSCs. Hydrophobicity is an ideal state for maintaining stability and performance in a moisture laden world, and many TSCs are used in areas where moisture is present but cannot be allowed to affect performance. Thus, acceptance into applications requires CNM to be incorporated into, compatibilized with, or reacted with hydrophobic resins.

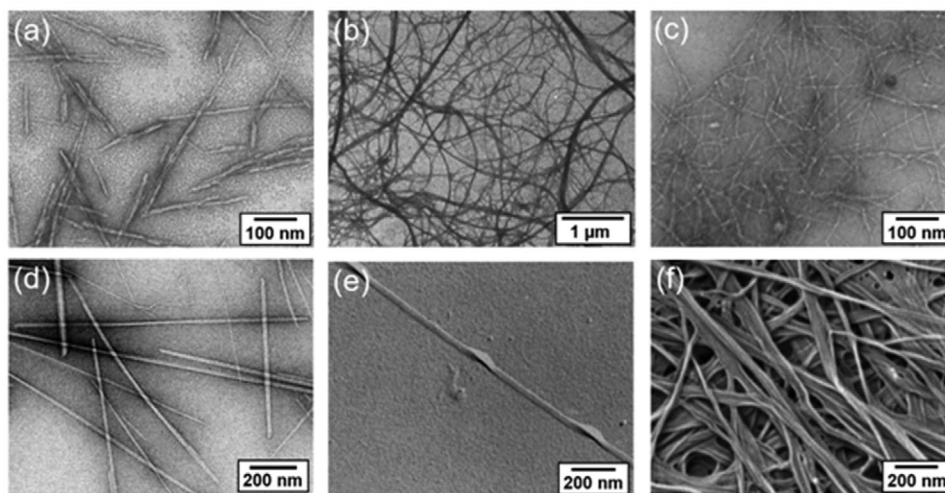


Figure 2. Electron microscopy images of several CNM types. a) Transmission electron microscopy (TEM) image of CNCs. Reproduced with permission.^[158] Copyright 2013, TAPPI Press. b) TEM image of CNF without fibrillation pretreatments. Reproduced with permission.^[159] Copyright 1997, John Wiley and Sons. c) TEM image of TOCNF with TEMPO fibrillation pretreatment. Reproduced with permission.^[158] Copyright 2013, TAPPI Press. d) TEM image of t-CNCs (image provided by and used with permission from Yu Ogawa, CERMAV). e) TEM of AC. Reproduced with permission.^[160] Copyright 1997, Springer Science+Business Media B.V. f) Scanning electron microscopy (SEM) image of BC. Reproduced with permission.^[161] Copyright 2007, American Chemical Society.

In this section we examine progress to date on CNM reinforced TSCs. In evaluating these CNM/TSC it has been shown that the degree of storage modulus reinforcement above T_g is a good indicator of the degree of dispersion.^[30] This will be noted if the data is provided. Overall, there are four general methods to incorporation of CNM into thermosets: solvent blending, CNM preform infiltration, direct solid CNM blending, and use of hydrophilic thermoset resin systems. However, use of surface modification to react the CNM directly with the thermoset is common and will be discussed. Generally speaking, solvent based methods lack industrial feasibility, so while it is by far the most common method, it will be only discussed in brief.

3.1. Thermoset CNM Composites via Solvent Blending

CNM/TSC have been fabricated by direct mixing with hydrophobic resins, usually with an organic solvent compatibilizer resulting in the co-suspension of the CNM and the resin or curing agent. This method is by far the most common method, but due to the difficulty of using high boiling solvents, and the VOCs involved, lacks long term feasibility. An early example is Tang and Weder dispersing cotton and tunicate derived CNCs into DMF and then blending them separately with epoxy and hardener also dissolved in DMF via shear and sonication. The composites exhibited significant gains in storage modulus especially above T_g .^[31] A similar method was also used to produce CNC/urethane and TOCNF/urethane TSC.^[32,33] Whereas the former had across-the-board tensile improvements, the latter showed that tensile modulus dropped while strength and elongation increased significantly with TOCNF concentration. Fukui et al. DMF blended TOCNF in hydrogenated acrylonitrile-butadiene rubber.^[34] The composites were stiffer with much improved tensile properties. The authors contend that these composites are in the form of fully dispersed TOCNF within the matrix where latex based approaches result in TOCNF segregated into domains around the polymer and therefore was less efficient.

Unfortunately, the solvents utilized such as DMF are difficult to remove due to their high boiling points, so groups have also explored moving toward easier to handle solvents. For example, Shibata and Nakai solvent exchanged CMF from water to an ethanol slurry.^[35] This was blended with a biobased epoxy and dried in vacuum and heat compression molded. Storage moduli changes were similar to those achieved with DMF with tensile stiffness and strength increasing at the expense of elongation. However, CMF are large fibers amenable to filtration based solvent exchange where CNC and CNF would require centrifugation. This approach was also applied to fabricate blends of CNF in a polycaprolactone-epoxy phase-separated system and CNC in epoxidized natural rubber.^[36,37]

3.2. Thermoset Composites via Infiltration of CNM Preform

More recently, groups have explored alternatives to solvent blending of CNM into thermosets. One alternative is to create a water-free 3D solid preform or loose assemblage of CNM that can be infused with a low viscosity resin. For example, CNM can

be filtered or pressed and dried to create cakes or “nanopapers” which can then be infiltrated with resin. As example, a CNF cake was produced by filtration and washing with acetone.^[38] This was infiltrated with an epoxy/amine resin dissolved in acetone. The advantage of the filtration process is the ability to attain concentrations of CNM up to 50 wt%. Hence, the composites exhibited significant increases in tensile modulus and strength at the expense of elongation with storage moduli having little to no change at T_g and above. Nair et al. modified this method further by using a CNF which contained residual lignin to produce an acetone soaked mat that was then soaked with epoxy/hardener diluted in acetone.^[39] Improvements in tensile modulus and strength were observed with only a slightly increased rate of water uptake indicating that the lignin was associated with the CNF hydrophilic surface preventing it from absorbing water.

Alternatively, solid preforms can be prepared by freeze-drying the CNM. In a solvent-free process, Aitomäki et al. placed freeze-dried (FD) CNF preforms in a vacuum bag and then used vacuum to assist in the infusion of a low-viscosity epoxy/hardener resin in a method similar to resin infiltration composites.^[40] Comparing the tensile properties of these composites versus that from CNF/resin blend dried from various solvents, and resin impregnated kraft paper showed the preform approach to be inferior to these alternatives due to a large number of entrapped voids. Likely, the incompatibility between unmodified CNF and hydrophobic epoxy/resin blend is the cause of these voids and vacuum was insufficient to force incompatible contact.

3.3. Thermoset Composites via Direct Solid CNM Blending

Processing methods can be used to impart energy into an incompatible system forcing the establishment of a kinetically trapped system. If thermoset cure takes place immediately afterward then such systems can be stable. Cao et al. blended t-CNC and epoxidized natural rubber in the aqueous state then coagulated the system and isolated a dried powder.^[41] The powder was blended with vulcanizing additives and then compounded in a two-roll mill. Morphological analysis revealed a uniform dispersion of small agglomerates of t-CNCs. Nonetheless the storage modulus below and above T_g , modulus, tensile strength and work of fracture were all increased as a function of t-CNC loading at the expense of strain to failure in a scalable process. Saba et al. evaluated the simpler approach of directly adding FD-CNF to an epoxy resin via high shear mixing.^[42] The resulting composites had improved tensile strength, modulus, and impact strength optimized at 0.75 wt% loading of FD-CNF. Overall, these efforts are recent and unexpectedly effective from simple processes and low concentrations.

3.4. Thermoset Composites via Hydrophilic Systems

Hydrophilic CNMs can be used directly in resin systems that are compatible/miscible with water or are dispersed in water such as in latexes. In both cases, water in the resin or latex must be removed prior to cure. As many of these systems are coatings, air drying is an acceptable process provided the wettability

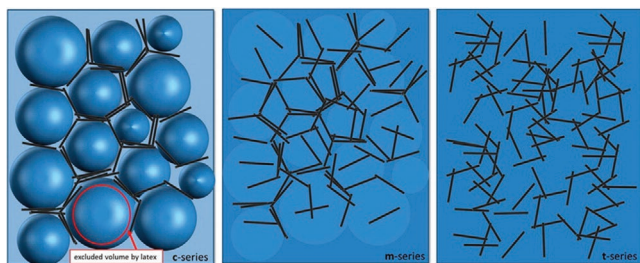


Figure 3. Illustrations of CN networks around latex (left), compacted (center), and compacted with some agglomerates (right). Reproduced with permission.^[30] Copyright 2014, American Chemical Society.

to the substrate is not disrupted. In the cases of water-soluble resins, CNM can be well dispersed and therefore the CNM can greatly enhance properties, but due to the hydrophilicity of the resins, typically the resins are not commercially viable. For example, Shibata and Nakai blended an aqueous dispersion of CMF with water-diluted bioepoxy and tannic acid and then freeze-dried and compression molded it to obtain composites.^[35] These composites exhibited improved stiffness with the most significant gains above T_g .

More commonly observed and more commercially applicable are the emulsified hydrophobic resins or latexes. Among latex/CNM composites, natural rubber (NR) has been perhaps the most widely studied. Substantial improvements in rubbery plateau modulus indicated CNM were well dispersed regardless of type although CMF composites tended to have superior modulus compared to CNCs at a greater expense to elongation. The effect of crosslinking was evaluated with CNM/NR latex composites with and without vulcanization where CNM and vulcanization were synergistic.^[19,43–46] The composites had improved stiffness with high storage modulus values above T_g indicating good dispersion. Looking at the storage modulus data there is a sharp increase in reinforcement between 2 and 5 wt% CNCs which is attributed to improved dispersion at higher loadings.

Other thermoset systems have also been explored using emulsion methods. Girouard et al. explored this via fabrication of CNC reinforced WB epoxy composites via low shear mixing methods.^[47] Either all three components (epoxy, amine, and CNC) were combined at once or premixing of the epoxy latex and aqueous CNCs was carried out prior to water soluble amine addition. All cured films were transparent yet examination under crossed polarized optical microscopy revealed that the all-at-once addition contained numerous CNC-rich domains whereas the two-step mixing has fewer CNC-rich domains and are significantly more diffuse. Mechanical properties of the films were similar indicating that less agglomeration does not necessarily equate to a stronger reinforcing phase.

Unfortunately, in latex systems such as these, the hydrophilic CNM stays in the water phase and does not fully incorporate into the thermoset to form a well-dispersed nanocomposite. Overall, it has been unclear if this impacts performance.^[30] TEM imaging found CNCs dispersed around latex particles as opposed to a compacted and agglomerated state for the molded and acetone solvo-gel approaches, respectively, depictions of which are shown in **Figure 3**.

The largest issue with water-based hydrophilic systems is that the hydrophilic nature of CNM can potentially affect moisture uptake characteristic of resins, many of which suffer from this issue anyways, at least in the case of latex systems. Sanches et al. found that a rise in humidity from 30 to 60% RH halved the tensile strength of CNF/PU latex composites.^[48] This is surprising as 30–60% RH is a typical indoor-outdoor variation. Nonetheless, the composites had tensile strengths ranging from 50 to 300% higher than the urethane matrix at both humidity levels. The matrix had a greater drop in tensile strength at 60% RH than the CN composites. Others have shown that well-dispersed CNC/SBR composites have lower maximum water uptake with higher absorption rates than the matrix.^[30]

3.5. Surface Modification of CNM in Thermoset Composites

While both thermoset and thermoplastic systems make use of surface modification to increase compatibility, unlike thermoplastic composites, TSCs can have large changes in properties due to surface chemistry of the CNM as they can be modified for chemical incorporation/crosslinking into the thermoset matrix (m-CNM). Due to the large surface areas of CNM, these chemically reactive particles can induce large changes in free volume, crosslink density, and T_g in a similar vein to nanosilica. Due to the large industrial usage of silanes, one of the most common means of surface functionalization is silanization, for example, with amino or glycidol groups to better incorporate with epoxy.^[49,50] Commonly, amino silane modified CNM is effective at improving stiffness above T_g . For example, Yue et al. amino functionalized CNCs with amino-silane, and cured with epoxidized diphenolic acid and curing agent.^[51] Optical microscopy revealed the m-CNC composites to be well dispersed where the unmodified CNC composites had a multitude of CNC-rich domains.

Beyond silane modification there is a broad array of synthetic approaches applicable to convert hydroxyl groups and transform CNM compatibility and reactivity. Rosilo et al. utilized esterification with undecenoyl chloride to provide a vulcanizable double bond.^[52] The resultant reactive CNCs were blended with poly(butadiene rubber) (PBR) dissolved in THF and vulcanized with a dithiolalkane and UV initiation. In this way the CNCs were connected to the PBR via thiol-ene click chemistry. Loading levels of the m-CNCs ranged from 0 to 80 wt% such that the morphology transitioned to one dominated by m-CNCs intercalated with PBR. The tensile moduli at such high loadings of m-CNC was two orders of magnitude higher than PBR with a one order improvement in tensile strength, although ductility dropped from ~80% to ~10% at these high loadings. Chen et al. used Huisgen click chemistry to connect alkynyl anhydride functionalized CNCs with alkynyl-functionalized hydroxy terminated polybutadiene via a glycidyl azide functionalized polymer.^[53] Low loading levels of the m-CNC increased crosslink density while those higher than 1 wt% decreased it due to their physical interference between polymeric coreactants. Tensile strength and modulus improved with m-CNC loadings up to 2 wt% where it leveled off and the elongation to break decreased. Trovatti et al. employed Diels–Alder (DA) chemistry to create crosslinked

rubber that is thermoreversible such that recycling would be facilitated.^[54] The reversible rubber was accomplished by functionalizing polyisoprene with furan and then reversibly crosslinking this with bismaleimide. CNCs were also reversibly crosslinked into this matrix by functionalizing it with amino maleimide. Polyurethane TSCs can make use of an asymmetric isocyanate, isophorone diisocyanate in this case, to selectively react primary or secondary isocyanate groups with CNM hydroxyls via amine or tin catalysts, respectively.^[55] Consequently, this selectively leaves the unreacted isocyanate group free for further chemistry. Composites fabricated with tin catalyzed functionalization were reacted with a triol to create crosslinked urethane films with enhanced tensile strength and elongation.

4. CNM Thermoplastic Nanocomposites

Unlike thermosets, thermoplastics generally have good toughness, but a major goal is to increase stiffness and strength to take advantage of the ease of processing and low density over materials such as metals in the automotive and aerospace industries and will be emphasized in the following section.^[56] However, CNM can also impart enhanced barrier performance,^[57] thermal conductivity,^[58] improve crystallization rates,^[59–61] and is a useful rheology modifier.^[62] Moreover, addition of these materials can nucleate new crystal structures or change the deformation mechanism.^[63] Regardless of processing method, incompatibility (engineering polymers are nonpolar), is a key issue in creating CNM nanocomposites. The formation of agglomerates can act as defects and weak interfacial interaction between the CNM and polymer will negatively impact properties—whether that is mechanical, thermal, optical, or otherwise.

CNM nanocomposites have been prepared and investigated for a wide variety of thermoplastics including: poly(vinyl alcohol) (PVA),^[64–69] poly(lactic acid) (PLA),^[70–76] thermoplastic starch,^[77] poly(vinyl acetate) (PVAc),^[78] cellulose acetate,^[79,80] thermoplastic polyurethane,^[81] polypropylene (PP),^[56] polyethylene (PE),^[82,83] polyacrylonitrile (PAN),^[84] poly(acrylonitrile-styrene-butadiene) (ABS),^[85] polyamide 11,^[63,86] and polyamide 12,^[87,88] although this list should not be viewed as exhaustive. Early in the investigation of CNM/thermoplastic composites, solution-processed nanocomposites dominated as water-soluble polymers like PVA could be easily prepared and tested.^[64–67,89] While solution methods preserve nanocellulose dispersion, many of these processes draw criticism for not being industrially or economically viable due to lack of scalability, use of organic solvents (i.e., VOCs), being time intensive (days), or can only be used for a limited selection of polymers. Whereas melt processing of thermoplastics like extrusion are commonplace in industry, these methods have only recently become the focus of efforts for creating thermoplastic CNM nanocomposites. Some of the primary challenges faced in melt-preparation are agglomeration issues due to drying of nanocelluloses and thermal stability. The focus of this section will be more heavily on the nonsolution-based methods, as they have more industrial feasibility, although solution-based methods will be described briefly for completeness.

4.1. Solution-Prepared Thermoplastic Composites

Due to the ease of fabrication and generally low equipment investment, nanocomposites prepared by solution methods are among the most prolific, especially in the early development of these nanocomposites. Due to the abundance of research in this area, a concise rather than exhaustive summary of recent research in solution-prepared nanocomposites will be provided in this section. In its simplest form, mutual solvents that can dissolve the polymer and disperse the CNMs are used to create a solution that is then cast to make a film or extruded such as in the fiber-spinning processes discussed later. Furthermore, solution-cast films can be used as a precursor to melt-forming methods like compression molding or melt-spinning.^[63,81] Preparation methods relying on solutions are usually presumed to have the best dispersion as often never-dried CNMs are employed while drying can result in irreversible hydrogen bonding and thus permanent agglomeration.

Water-solubility and intrinsic chemical compatibility have made PVA the go-to thermoplastic matrix material for solution-processed thermoplastic CNM nanocomposites. The presence of hydroxyl groups in PVA enables strong interaction between CNM and the polymer, which is ideal for stress transfer across the interface. Consequently, PVA nanocomposites demonstrate improvement in mechanical performance, such as increased stiffness and strength in nanocomposite fibers like those of Shrestha et al.^[64] or Uddin et al.^[65] Studies like these have served to establish general expectations as far as aspect ratio, nanoparticle concentration, and nanoparticle orientation are concerned as due to the anisotropy of CNM, orientation along the fiber or tensile axis is typically targeted to maximize the mechanical properties. Although other material properties, such as the thermal conductivity, of CNC/PVA films demonstrate a strong directional dependence as well.^[58] Chowdhury et al. created PVA/CNC nanocomposites with thermal conductivities as high as $3.5 \text{ W m}^{-1} \text{ K}^{-1}$, which is substantially higher than most polymers (e.g., polyimides $\approx 0.9 \text{ W m}^{-1} \text{ K}^{-1}$ and aluminum filled HDPE is $0.7\text{--}1.25 \text{ W m}^{-1} \text{ K}^{-1}$).^[58] Thermal conductivity was very sensitive to the alignment of the nanoparticles, which was achieved from the shearing of the polymer solution (**Figure 4**).^[58] Moreover, Chowdhury et al. also demonstrated that barrier properties such as water vapor transport rate (WVTR) of PVA/CNC nanocomposites was less than either neat PVA or CNC due to low free volume in the aligned nanocomposite.^[57]

Native CNM, which exhibit two distinct solubility spheres in Hansen solubility space, do not have many solvents in common with engineering polymers, although considerable effort has been put into changing the surface chemistry to tune the compatibility of CNM with various solvents.^[90,91] The primary solvents used in nonwater-soluble polymer systems are dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetone. Although by chemically modifying CNM, these nanoparticles can be exchanged into a wide variety of solvents and is commonly done to improve chemical compatibility of the reinforcement and polymer.^[14,90,91] Using these solvents and/or surface modification, CNM has been incorporated into many nonpolar polymers and, similar to the water-soluble thermoplastics, improved mechanical and thermal properties. While

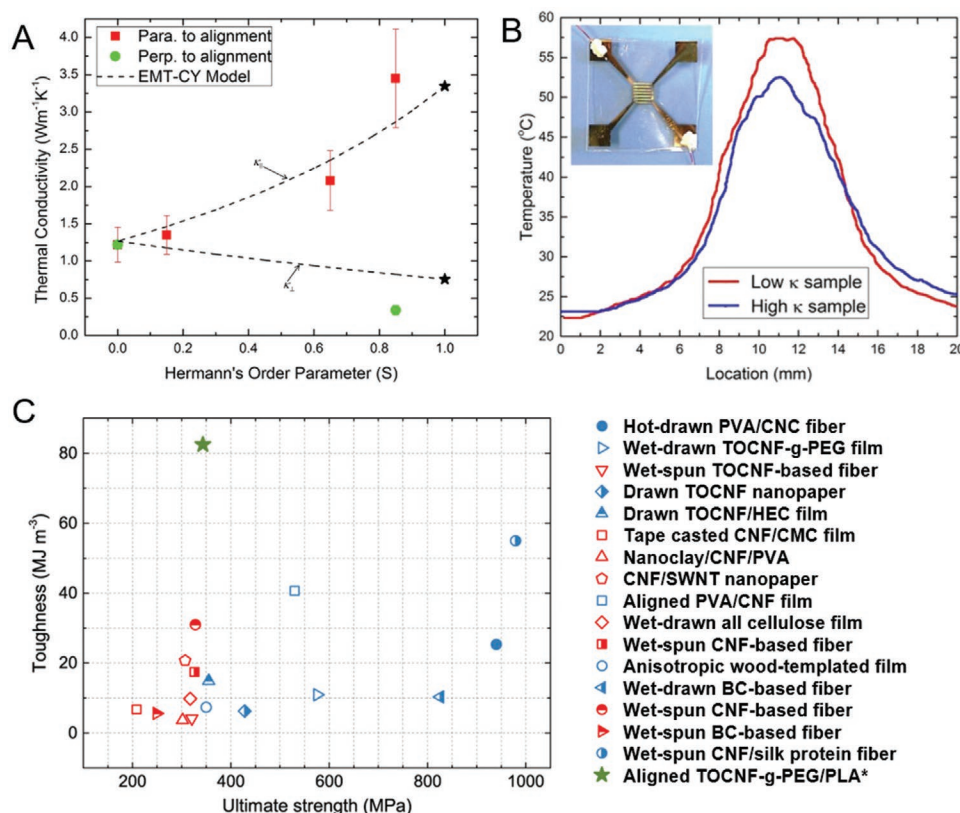


Figure 4. A) Thermal conductivity (κ) measurements made parallel (para) and perpendicular (perp) to CNC alignment direction in PVA/CNC films demonstrating directional dependence of thermal conductivity and B) the temperature difference between a low κ (PVA) sample and a high κ (90 wt% CNC–10 wt% PVA) nanocomposite. A,B) Reproduced with permission.^[58] Copyright 2019, Elsevier. C) Toughness versus ultimate strength of very small (0.1 wt%) amounts of PEG-modified TOCNF in PLA as compared to other pure and polymer (hydroxyethylcellulose (HEC) and carboxymethylcellulose (CMC)) nanocomposite materials such as single wall carbon nanotube (SWNT), nanoclay, and CNM demonstrating the effectiveness of small concentrations of nanoparticles after alignment. Original work in ref. [94] is denoted by * in the figure legend. Adapted with permission.^[94] Copyright 2020, American Chemical Society.

such processing is not generally industrially feasible, there are a few areas where solvent-based processing is still practiced and where CNM has been investigated and are relevant and recent. For example, PAN precursor fiber accounts for 98% of the production of carbon fiber and is primarily wet-spun using copious amounts of solvent.^[92] Jiang et al. explored the effects of different aspect ratios and sources of CNM at 0.1 wt% in gel-spun PAN. They discovered that, while only small differences were observed in strength (up to 19%) and stiffness (up to 27%) of the precursor fiber, that large differences resulted in the carbon fiber due to large differences in aspect ratio and CNM crystallinity; CNCs (low aspect ratio) strength improved by 4–87% while CNFs (large aspect ratio) improved by up to 172%.^[84] Furthermore, these improvements were accompanied by a decrease in the extent of cyclization at low temperature in creating carbon fiber, a process essential to stabilizing the fiber during conversion.

4.2. Melt-Prepared Nanocellulose/Thermoplastic Composites

Melt-preparation methods are attractive as many polymers (polyamides, polyesters, and polyolefins) are conventionally

processed this way. Unfortunately, many CNMs start to degrade (200–250 $^{\circ}\text{C}$) within the processing temperature zones of many polymers.^[56,81,86] Yellowing and eventual browning of the material occurs when exposed to relevant processing temperatures.^[56,86,88,93] Functionalization or derivation from other acids can improve thermal stability; for instance hydrolyzation by phosphoric acid rather than sulfuric acid results in a more thermally stable nanoparticle.^[93] Another barrier to melt-processing is incompatibility of the hydrophilic CNM with many hydrophobic polymers. Thus, functionalization is also common to prevent agglomeration and improve compatibility, such as the grafting of poly(ethylene glycol) (PEG) to the surface as in Figure 4.^[94]

Continuous and masterbatch methods are common strategies for melt-processing of these nanocomposites. In continuous processes, all constituents are mixed simultaneously while a masterbatch is a highly concentrated mixture prepared first and then diluted in additional materials in secondary mixing steps; the latter is also common in processes where combined solution and melt-forming techniques are used. Many melt processes for preparing thermoplastic nanocomposites utilize twin-screw compounding and extrusion since good distributive and dispersive mixing can be achieved without additional steps.^[71,77,95] CNM have been added as freeze-dried powders,

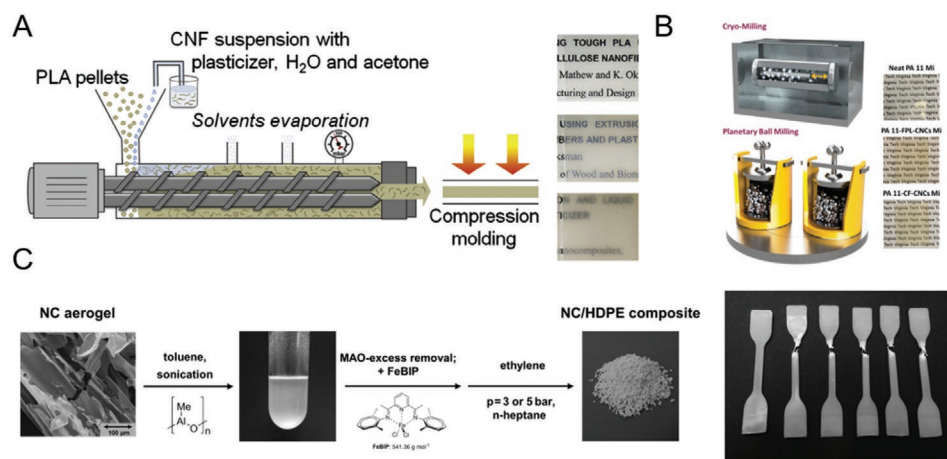


Figure 5. Examples of preparation methods and nanocomposites produced with to demonstrate dispersion, transparency, and color change. A) Schematic of twin-screw, liquid-assisted melt-compounding and extrusion process for PLA. Reproduced with permission.^[95] Copyright 2014, Elsevier. B) Images of two-step milling (cryomilling followed by ball milling) to produce polyamide 11 nanocomposites. Reproduced with permission.^[86] Copyright 2019, Elsevier. C) Process schematic for production of HDPE nanocomposites using CNC aerogels as supports for the catalyst in situ polymerization of PE. Powders used to injection mold nanocomposite films. Reproduced with permission.^[83] Copyright 2017, Wiley-VCH.

liquid slurry, and solid or liquid mixtures like a polymer blend. Inherent incompatibility is sometimes solved by using a compatibilizer. These materials can be dispersant, plasticizers, or other polymers that are either compounded prior to the addition of the CNM or act as a carrier material.

Direct liquid injection or liquid assisted melt-compounding is a method for preparing thermoplastic nanocomposites where a liquid is injected into the polymer melt (Figure 5). However, specialized extruders with vents to enable the evaporation of solvents during the process are needed, otherwise, the residual solvent can cause air entrapment, plasticization, and related issues.^[95,96] Likewise, water injection into polycondensation polymers like PLA can be problematic as it can cause loss of molecular weight and thus, properties. Several manifestations of liquid compounding have been observed in the literature for liquid feeding of CNM/water slurry,^[75,96] feeding a CNM/additive/solvent slurry mixture,^[95,97] and feeding of a solvent-free liquid additive/CNM mixture.^[71] These processes can be run as a masterbatch or continuous and typically demonstrate good dispersion.^[71,95]

PLA is one of the largest commercially available and utilized renewable polymers and, as such, PLA/CNM nanocomposite processing continues to be an active area of research. Common methods for producing these nanocomposites are to use continuous liquid feeding processes as described above as well as masterbatch processes, where the masterbatch can be prepared by solution or melt methods, and then melt-compounded with virgin material.^[62,71,78,95] Several studies have demonstrated recently the effectiveness of even very small concentrations of CNM. Geng et al. (Figure 4) and Clarkson et al. demonstrated that ultralow/very small quantities of CNM could be effective in the reinforcement of PLA, especially when aligned along the tensile direction.^[71,94] Furthermore, Singh et al. and Clarkson et al. demonstrated the effectiveness of CNM, even at very small concentrations, as heterogeneous nucleation agents in plasticized PLA.^[59,60] Melt rheology is a critical component in forming and CNM has also been demonstrated

to be an effective rheology modifier for PLA. For instance, film blowing of PLA is challenging as the melt viscosity is low and melt strength is weak such that a stable film cannot be easily formed. Gupta et al. used a lignin-modified CNC to increase the melt viscosity and melt strength such that film blowing of PLA at only 0.3 wt% lignin-modified CNC was possible.^[62]

Polyamides are used extensively in the automotive industry and there is interest in reinforcing these materials with nanofillers, but compared to PLA or PVA, few studies investigate polyamide/CNM nanocomposites. A potential hurdle is that the processing temperatures of polyamides, like nylon 6 which melts between 210 and 220 °C, are within the temperature range that many CNMs will begin to thermally degrade. Moreover, the melt viscosity of polyamides like nylon 6 or 6/6 is high due to strong interchain hydrogen bonding. However, Zhu et al. investigated the properties of melt-spun nylon 6/CNF nanocomposites using a masterbatch method where spray-dried CNFs were compounded in a corotating twin screw extruder and then diluted with additional nylon 6 to obtain concentrations up to 10 wt%.^[98] Despite significant CNF loading, only a modest improvement of 40–50 cN/text in filament tenacity (specific strength used for textiles) was observed while the elongation at break went from ≈150% to ≈75%. However, moisture adsorption for CNF/nylon 6 composites did improve which, as these materials could be used in textiles, could be desirable. Other polyamides, nylon 11 and nylon 12, have also been melt processed and they are generally easier to process due to lower melting temperatures. For example, nylon 12 has been prepared with freeze-dried sulfuric acid CNC and phosphoric acid CNC.^[87,88]

Extremely nonpolar systems are challenging for CNM as the poor chemical compatibility with the matrix will typically result in poor particle/matrix interaction as well as the agglomeration of CNM. Palange et al. chemically modified CMF using a water-based, facile method to first attach tannic acid (TA) to the surface and then an alkyl amine, hexylamine, to create a less hydrophilic nanoparticle surface.^[99] The

nanoparticles were melt-mixed with PP–PE copolymers using a twin-screw extrusion system; up to 20 wt% modified MFC was added. Despite chemical modification, materials showed evidence of agglomerates, with a typical aggregate length of $\approx 100\ \mu\text{m}$. The Young's modulus increased approximately linearly with increasing concentration of nanofiller and maxed at $\approx 1.5\ \text{GPa}$.

4.3. Alternative Methods for Nanocellulose/Thermoplastic Composites

Alternative preparation methods are exactly that—not solution and not melt-mixed. These can generally be broken into two styles: solid state mixing as with milling and in situ polymerization of the thermoplastic around the dispersed CNM. Much more has been done with the latter as emulsion and interfacial polymerizations are well known processes, whereas solid state incorporation is somewhat new for polymer composites.

4.3.1. Milling and Pulverizing

Milling/pulverizing is commonly used in ceramics processing to homogenize and disperse powders and has recently been proposed as a method to create nanocomposites. As this is a relatively new technique for nanocomposite fabrication overall, it is no surprise that there are only a few instances the authors could find in literature of its use for CNM nanocomposite fabrication.^[100] However, now that this method has been successfully utilized and reported, it is expected that many more will occur as this method negates many of the issues of CNM nanocomposite processing as it is solventless (or just water), can be done in bulk, provides reasonable dispersion, can achieve high CNM concentrations, and can be low temperature to limit CNM degradation. Venkatraman et al. used a combination of cryomilling and planetary milling as a low-temperature process to combine polyamide 11 and freeze-dried CNCs (Figure 5).^[86] The method resulted in visually clear nanocomposites, which, compared to the compounded material were less yellow and exhibited superior mechanical properties for both phosphoric acid CNC and sulfuric acid CNC.^[86]

4.3.2. In Situ Polymerization

One of the newer areas for the creation of thermoplastic/CNM nanocomposites is in situ polymerization of a thermoplastic monomer with dispersed CNM. In situ polymerization techniques are used industrially in processes such as resin transfer molding for the creation of continuously reinforced composites. In situ polymerization of PE using CNM aerogels as catalyst supports present a promising method for incorporating CNM in nonpolar polymers. The hydroxyls on the CNM aerogel serve as sites to coordinate the catalyst and, after polymerization, the aerogel acts a mechanical reinforcement in the thermoplastic. Hees et al. created a CNF aerogel, impregnated with methylaluminoxane (MAO), as the support to immobilize iron catalysts for the in situ polymerization of ethylene (Figure 5C).^[83] Injection

molding of the nanocomposite powders produced samples with highly competitive mechanical properties compared to the silica support and commercial comparisons; at 3 wt% CNF, Young's elastic modulus was 1.6 GPa and the tensile strength was 54 MPa compared to 0.93 GPa and 27 MPa for a commercially available HDPE.^[83] Another recent study by Hendren et al. attached a metallocene dibromide catalyst to a CNC aerogel to be used as a support. The melt pressed films produced with these materials were slightly yellow, but transparent and AFM revealed a well-dispersed structure with modulus and strength of 1.6 GPa and 29 MPa, respectively.^[82] However, both in situ preparation methods for PE resulted in a decrease in the elongation at break compared to controls and comparison groups.

Water-soluble polymers have been used previously to disperse CNCs into less hydrophilic polymers. Geng et al. took this idea a step further to polymerize PVAc in an in situ emulsion polymerization reaction around CNCs.^[78,101] Their first study examined a method for in situ polymerization of PVAc/CNC which saw improved dispersion compared to nanocomposites formed by mechanical mixing and improved toughness as compared to the controls.^[101] Their second investigation examined using this in situ PVAc/CNC nanocomposite in PLA so that the PVAc could act as a compatibilizer.^[78] The PLA/PVAc/CNC blends demonstrated improved mechanical performance in strength (23%) and toughness (153%) for only 0.1 wt% CNC in the nanocomposite.^[78]

Lastly, interfacial polymerization of polyamides with CNM in the water phase was recently investigated by Reid et al.^[102] They created a CNM/polyamide nanocomposite in a process akin to the “nylon rope” trick, a common classroom science demonstration where the oil phase contains the acid chloride monomer and the water phase contains a water-miscible amine monomer. Their research added CNCs to the water phase of the interfacial polymerization reaction and they created films, fibers, and spherical particles. While they did not explicitly investigate any properties of the polyamide nanocomposites, the preparation method has potential as a low-temperature method for preparing polyamide nanocomposites as interfacial polymerizations are practiced industrially.

5. Discrete CNM Macrophase Composites

Due to the CNM incompatibilities with hydrophobic polymers, a variety of groups have taken a different track in using pure or very high concentration CNM macrophases as a reinforcement with a polymer matrix to hold the structure together rather than as dispersed nanoparticles. We term these here as “discrete macrophase composites” (DMC). Fabrication of these materials allows separation of the processing of the CNM phase from the subsequent polymer resin processing, which removes the impediments of compatibility mismatch (hydrophilic vs hydrophobic) and deleterious issues with high CNM loadings in polymer (rheology, embrittlement, and dispersion). Thus, while this area has little reported work compared to thermoset and thermoplastic CNM nanocomposites, it is expected that discrete phase composites will expand rapidly in the future as bulk fabrication of pure CNM phases (extrusion, R2R) enables sufficient scale production of pure and high phase CNM materials.

5.1. Layered/laminar Structures

By far the most research on discrete CNM DMC are in layered structures. Generally, there have been two methods to produce these laminar structures: sequential coating or “Layer-by-layer” (LbL) approaches and more the traditional composites “lay-up” method. Lay-up processes have been extensively used in the commercial composite industry to produce composites. The method involves a matrix material reinforced with mechanically strong layers or fibers that are laid on top of each other and consolidated all at once by pressing, vacuum bagging, autoclaving, etc. In comparison to LbL methods, lay-up methods greatly speed composite fabrication as the buildup of the structure layer by layer is time consuming.^[103]

5.1.1. Lay-Up Method

Recently, CNMs have been introduced in laminated materials using the lay-up approach. The idea takes advantage of the self-assembly capabilities of CNF as well as their mechanical strength, flexibility, and low thermal expansion, to produce mechanically enhanced layered structures. For example, Mautner et al. fabricated laminate structures where two-component epoxy was impregnated between CNF nanopapers and cured. The final structure of the laminates was constituted by two layers of CNM (80 vol% structure) and epoxy (20 vol%) as the middle layer. The sandwich-like structure showed increased thermal stability and better mechanical performance.^[104] Later, Kurita et al. inserted three different CNF layers (neat CNF, an epoxy coated CNF sheet and a mixed solution of CNF and epoxy resin) between glass-fiber-reinforced plastics (GFRPs). Results showed a substantial increase in the flexural properties for the epoxy films with low additions of CNF.^[105] Similarly, but with TOCNF, Liu et al. laminated wood flakes (WFs) with TOCNF films using a phenol-formaldehyde (PF) resin and increased strength and modulus 200% and 300%, respectively. The increased mechanical properties were attributed to a combined effect of the presence of CNF and the phenol-formaldehyde crosslinking.^[106] Moving up in size scale, Forti and co-workers laminated up to 60 TOCNF films together with a clear epoxy to create thick (>1 mm), highly transparent laminates with enhanced strength and toughness. It was found that the weaker adhesion than the cohesion of the TOCNF led to crack deflection at the interface and was well explained by laminate theory.^[107]

Whereas some researchers have used dry CNF films to produce sandwich-like structures, others, have found ways to remove drying steps, eliminating a big roadblock in the continuous production of CNF materials and finding uses of CNM in aqueous suspensions. The final structures are later consolidated into low weight and high strength materials. An excellent example is found in a nanolaminate produced by University of Maine (Figure 6). The material consists of a lay-up structure composed of sheets of paper bonded together using CNF and Polycup (a crosslinker) with a subsequent heated press step to set and dry the material. Tensile modulus and strength were similar to glass reinforced polypropylene.^[108] In more recent work, El Awad Azrak et al. achieved pure CNF materials with

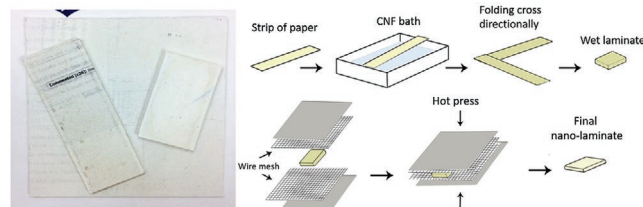


Figure 6. Bio-nanocomposite laminate structure produced by a cross-laminating layup method (left). The procedure involves dipping strips of paper on a CNF bath, cross folding in a wire mesh, and pressing to produce a thick dense laminate (right). Adapted with permission.^[108] Copyright 2016, Scrivener Publishing LLC.

millimeter-scale thicknesses by stacking wet CNF sheets (up to 24 layers) and hot pressing to dry the material. The specific strength was comparable to 2024 aluminum.^[109]

5.1.2. Layer-by-Layer Approach

In the CNM field, researchers have utilized methods developed for LbL of polyelectrolytes, where oppositely charged polymers are alternately adsorbed to a substrate substituting the negatively charged polyelectrolytes with CNM, producing very organized multilayer films.^[110] An excellent representation of this method is by Aulin et al. who used an aqueous charge-stabilized dispersion of CMF stabilized by either positive or negative charges (using a quaternary amine for positive charges, or carboxymethylation for negative) to produce cationic/anionic CMF films.^[111] Later, a 50-layer sandwich-like structure of CNF with a cationic polyethyleneimine (PEI) was deposited on a flexible poly(lactic acid) (PLA) substrate which was transparent and with barrier properties comparable with those of poly(vinyl alcohol) and ethylene vinyl alcohol films.^[112] However, this LbL style generally lacks industrial practicality for applications other than coatings due to the long times required and thin layers.

Other strategies can produce multilayer films without relying on the strong chemical interaction of the components involved where they are instead flow coated or sprayed in a sequential fashion. These procedures are fit for applications where thickness control is not needed, but an enhancement in mechanical or barrier properties is desired (CNMs have been known to provide excellent barrier properties against grease and oxygen). A great example is found in the work of Aulin and Ström.^[113] In this work, paperboard was coated with multiple layers of CNM with subsequent deposition of renewable alkyd resin providing a moisture sealant layer, showing that cost-effective multilayer films can be achieved with barrier properties high enough to be considered in packaging applications.^[113] Likewise, Koppolu CNM-coated paperboard followed by a thin film of poly(lactic acid) (PLA), reducing oxygen and water transmissions.^[114] In a recent work, Kim et al. took advantage of LbL assembly to design a highly flexible, visible light and radio frequency transparent coating on a poly(ethylene terephthalate) PET film by blending negatively charged CNF with positively charged chitin nanowhiskers.^[115] Furthermore, Laufer et al. achieved a 30-layer LbL of positively

charged chitosan and anionic montmorillonite which exhibited reduced oxygen permeability. The coating was applied to flexible polyurethane foams, prohibiting melting of the foam when it was exposed to direct flame.^[116]

Thermoplastics have also been thrown in the mix; Vähä-Nissi et al. sandwiched CNM as a barrier layer with HDPE and LDPE films. While oxygen and grease barrier for dry food applications was promising, performance degraded when irradiated for sterilization purposes.^[117] Nevertheless, the advantages of using environmentally friendly materials are still substantial, especially when many of the commercially available barrier packaging options are not recyclable, while Vartiainen et al. has demonstrated the mechanical recyclability of LDPE films coated with CNF.^[118]

5.2. Particle Reinforced Composites

Particle reinforced composites (PRC) are typically composed of low aspect ratio hard/strong phase in a soft phase, such as silica and carbon in rubber for tires. Macroparticles of CNM are similar to aggregates and would thus likely not be better than other, cheaper materials. As such no work has been found loading CNM macroparticles into composites. However, there is still work being done in CNM particulate composites which typically take advantage of the adhesive nature of CNM to bind other macrophases together or use a second phase to tune the properties of the CNM matrix, and sometimes even use nanoadditives—a nanocomposite with CNM as the matrix.

5.2.1. CNM as a Binder

While at first glance it may seem counterintuitive to “flip” the structure where other materials reinforce a continuous matrix phase of CNM, it is reasonable when considering that particle reinforced composites can take advantage of the adhesive capabilities of CNF due to the large surface area and that a highly hydroxylated structure leads to good adhesion. For example, Kojima et al. used CNF as an adhesive for wood flour, producing composites of 3 mm of thickness where mechanical properties were optimized at a 20 wt% fiber content.^[119] Later, the University of Maine used CNF as a wood binder in conjunction with some mineral additives to produce a resin free particleboard (a commercial wood composite panel, where urea-formaldehyde is usually used as a binder) that met industrial performance standards, making this product more sustainable in the long run and safer (due to no formaldehyde off-gassing).

5.2.2. Functional Additives to CNM

Most applications where CNM is used as a matrix in PRC is where the intent is to enhance the properties of the CNM with the particle additive. In this vein, work by Malho et al. introduced graphene into CNF to prepare aligned assemblies of multilayered graphene and CNF by a simple filtration process. The obtained films had excellent mechanical properties where 1.25 wt% graphene displayed Young's modulus of 16.9 GPa,

an ultimate strength of 351 MPa, strain to failure of 12% and a work of failure of 22.3 MJ m⁻³.^[120] Wu et al. added clays such as montmorillonite (MTM) and saponite (SPN) to TOCNF producing transparent and flexible films with good oxygen barrier properties with moduli of 18 GPa, tensile strength of 509 MPa and a work to failure of 25 MJ m⁻³.^[121,122] The mechanical performance increase was explained by the presence of hydrogen bonds and ionic bonds formed at the interfaces between the MTM and TOCNF. Likewise, Liimateinen et al. and Liu et al. also fabricated flexible films by integrating CNF with platelets like talc and aminoclays, respectively.^[123,124] While the addition of particles has proven to introduce a significant increase in mechanical performance, it can also generate an enhancement of thermal properties. A good example is found in the work done by Carosio et al. where it was shown that the inclusion of aligned clay platelets in a CNF matrix generates a film with thermal shielding properties. When the films were exposed to a temperature of 900 °C, they showed a temperature drop of 300 °C on the unexposed side.^[125]

6. Forming, Shaping, and Fabrication of CNM Nanocomposites

Due to the isolation processes used and the inherent gel forming behavior at low solids concentrations, dilute (0.05–5 wt% solids) waterborne fabrication techniques like solution/solvent casting have been the most common and earliest methods used to process CNM nanocomposites.^[1] Solvent casting has been used extensively in laboratory settings to easily produce self-standing neat (i.e., pure or nearly pure CNM) films and nanocomposites of CNMs.^[126] Though suitable for preliminary research purposes to see what is possible, casting requires very long drying periods (e.g., several days) to prepare relevantly sized areas and thicknesses without cracking or curling, and outputs only a limited number of samples (i.e., it is batch based). Recently, research efforts regarding the fabrication of CNM nanocomposites has shifted from semiautomatic and batch processes such as casting and spin-coating to more continuous and industrially viable methods like roll-to-roll (R2R) and fiber spinning.^[127] As shown in **Figure 7**, these continuous methods can be loosely classified into three groups: 1) those which fabricate CNM nanocomposites into 1D structures (fibers), 2) those which fabricate CNM nanocomposites into 2D structures (e.g., films and coatings), and 3) those that process CNM nanocomposites into 3D bulk structures (e.g., extrusion, compression molding, and 3D printing).

6.1. Films and Coatings (Continuous Casting, Spraying, and R2R)

Recently, methods like continuous casting have allowed for the continuous formation of CNM films. In continuous casting, CNM slurries in a reservoir are shaped by a doctor blade and simultaneously deposited on a moving web which then passes through a set of drying ovens. This process is very similar to the “forming” and “drying” sections of a typical papermaking machine (e.g., Fourdrinier machine). These systems can have the substrate move from a wound “roll” through the casting

Cellulose nanomaterials (CNMs) continuous fabrication techniques

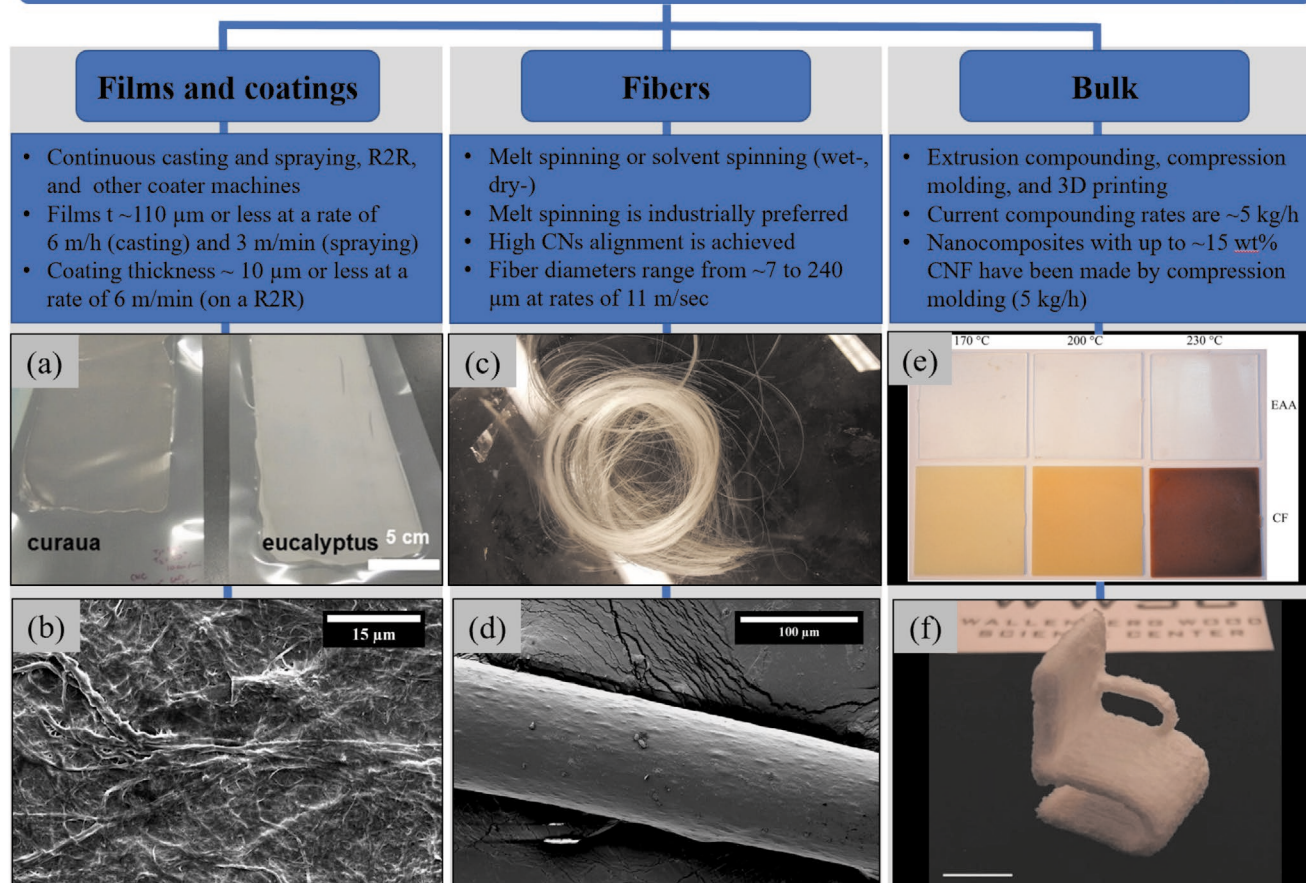


Figure 7. Cellulose nanomaterials continuous fabrication/forming techniques. a) Continuously cast CNC films. Reproduced with permission.^[129] Copyright 2018, Elsevier. b) SEM image of a solution-cast CNF film. c) Melt spun CNF/PLA nanocomposite fiber bundle (total 1.25 wt% CNF content) and d) SEM image. b–d) Reproduced with permission.^[71] Copyright 2019, American Chemical Society. e) Injection-molded CNF-reinforced ethylene–acrylic acid (EAA) nanocomposite plates processed at three different temperatures and compared against an unreinforced EAA matrix (dimensions of plates = $64 \times 64 \times 1.5 \text{ mm}$). Reproduced with permission.^[162] Copyright 2019, Society of Plastics Engineers, published by John Wiley and Sons. f) Freeze-dried 3D-printed CNF hydrogel chair; the scale bar corresponds to 10 mm. Reproduced with permission.^[151] Copyright 2016, Wiley-VCH.

and drying stages to a winder to reroll the material in the so-called “roll-to-roll” (R2R) process. The substrate can then be changed if a coated system is desired or the film can be delaminated if a self-standing film is desired.

Claro et al. used continuous casting to fabricate both CNC and CNF neat self-standing films at a rate of 10 cm min^{-1} or 6 m h^{-1} on a PET substrate.^[128,129] The dry film thickness produced for CNF was $87 \pm 5 \mu\text{m}$ while for CNC it was $100 \pm 7 \mu\text{m}$. Signs of nanofiber alignment toward the machine direction were present due to the imparted shear at the doctor blade and hence improved the mechanical properties for both CNC and CNF films along the machine direction (MD). Otoni et al. also continuously cast CNF nanocomposite made out of carrot waste as the base stock material (33 wt%), hydroxypropyl methylcellulose (14 wt%) and CNF fibers (53 wt%) as a reinforcing phase.^[130] Films were produced at a rate of 6 m h^{-1} on a PET substrate. Yet, during drying these biocomposite films experienced the formation of water vapor bubbles within the composite structure leading to reduced mechanical properties

when compared to solution-cast films. Both of these continuous casting efforts were performed on a pilot scale coater machine.

Coatings are similar to the free-standing films, except with a reduced dry thickness (rarely more than $10 \mu\text{m}$ thick) that prevent them from being delaminated. These are typically meant to improve some property of the substrate, such as provide a barrier to diffusion (e.g., O_2 and water vapor). Hence, coatings are primarily wet-deposited, dried, and remain permanently attached to a carrying substrate. In contrast to continuous film fabrication, a greater number of researchers have recently studied fabrication techniques for neat and nanocomposite CNM coatings.^[57,114,131–133] Chowdhury et al. continuously coated pure CNC solution onto a corona treated PET substrate using a R2R coater system.^[131] Importantly, the use of a micro-gravure allowed for the alignment of the CNC coating due to the imparted shear on the solution and improved the barrier properties of the coating. PVA was then added as a rheology modifier which improved alignment and barrier properties.^[57] Koppolu et al. and Kumar et al. showed that slurries of pure

CNC, CNC–sorbitol, CNF–carboxymethylcellulose (CMC), and pure CNF can also be coated onto paperboard using R2R and a slot die both expanding the substrate selection and the deposition style.^[114,132,133]

R2R can also be combined with continuous spraying, rather than traditional gravure or slot die coating to form CNM films. Beneventi et al. sprayed a CNF slurry at 2 wt% on a moving porous nylon substrate/fabric. Defect free (i.e., no pinholes/excessive agglomeration) CNF films with a thickness of 10 μm to 82 μm were produced at web speeds of 0.5–3 m min^{-1} .^[134] Yet, in their study the wet sprayed slurry was not dried in line and several semiautomatic processes were used (vacuum filtration, pressing, and vacuum drying) for final consolidation.

6.2. Fibers (Spinning)

Early research into fiber spinning with CNM was primarily focused on electrospinning due to the low capital costs, ease of use, and laboratory nature of the process. However, more industrially applicable fiber-spinning methods have recently been possible using common solvent spinning and melt spinning techniques. Solvent spinning techniques include wet-, dry-, and dry-jet wet-spinning to form fibers by extruding CNM mixture or “dope” through a small orifice.^[135] Collectively, for all solvent spinning techniques a solvent is present in the dope and must be removed or exchanged to achieve fiber formation/consolidation. On the other hand, dopes intended for melt spinning do not contain any solvents yet need to be melt processable and thus require a polymer matrix. Industrially, melt spinning is preferred due to the lower cost. Both CNF and CNC have been widely formed into neat or nanocomposite (e.g., with PLA, PVA, PAN, and PEO) fibers.^[66,71,79,136–140] In the most recent studies, undrawn CNM spun fiber diameters ranged from 7 to 240 μm and had a length of up to 10 m in a continuous process (extrusion or fiber line, not syringe), indicating industrially relevant sizes and processes.

Generally, the addition of CNMs greatly improved the mechanical properties in both ultimate strength and stiffness (increases >30% are typical). Some of the fastest neat CNF fiber production rates are in the range of 11 m s^{-1} which is much faster than CNM self-standing film or coating production (6 m min^{-1}), although not yet industrial speed.^[139] In contrast to film and coating fabrication, in spinning, CNM alignment toward the fiber direction or MD is readily achieved and is caused by the hydrodynamic shear inside the spinneret.^[79] Fiber alignment can be further enhanced by drawing (i.e., increasing the ratio of winding speed to extrusion speed) as is practiced in industry, which can greatly increase strength and stiffness.^[66,71] Overall, most of the spinning processes have been utilizing solvent-based fiber spinning due the difficulties in melt compatibilization of CNM and polymer. All main spinning styles have been utilized to great effect. Water-based dopes allows materials such as PVA to be dry-spun with the water evaporated to consolidate the fiber.^[141] However, nonwater soluble polymer CNM composite fibers, such as with cellulose acetate and PLA, can also be dry-spun from organic solvents, although the large amounts of VOCs produced make these dry-spinning methods industrially impractical.^[140] For polymers needing organic

solvents, wet-spinning and gel-spinning where a solvent-borne CNM/polymer dope is coagulated in a bath can also be performed, as has been performed with PVA and PAN fibers.^[66,142] In the latter case, the addition of CNM has led to improvements in carbon fiber production.^[143,144] Melt-spinning of fiber has been limited by the lack of CNM compatibility with thermoplastic polymers leading to few extrusion methods for the same. However, recently, melt-spinning of polymer with CNM has been accomplished.^[71,75,145] Still some common challenges dealing with the fabrication of nanocomposite CNM fibers is aggregation and thermal decomposition of the CNMs in nanocomposites both of which reduce the properties and processability of the fibers.^[95,146]

6.3. Bulk Forming (Extrusion, Injection Molding, and 3D Printing)

In this report, bulk forming of CNMs is defined as the formation of 3D structural parts/shapes where all dimensions have a larger size intended for application. More so than even the previously discussed methods, research efforts toward bulk fabrication for CNM composites are very scarce but include a combination of extrusion/compounding with compression molding, and more recently 3D printing. Some of the biggest challenges for bulk processing include the significant hydraulic capacity/drainage needed for dewatering CNM, a greater driving force for CNM to aggregate due to the higher concentrations, and the excessive shrinkage brought by water removal.

Very little work has been reported on the extrusion and molding of CNM and its composites, yet this method represents one of the most industrially scalable and promising techniques as the infrastructure and machines for processing of commodity polymers by these methods are already employed (e.g., extrusion, blow molding, injection molding, ram extrusion, and others).^[147] Hietala et al. was able to use a corotating twin screw extruder to compound thermoplastic starch plasticized with sorbitol and CNF.^[77] The compounded material was compression molded into translucent sheets with a thickness of ≈ 0.3 mm. Promisingly, aggregation was observed only for sheets with a CNF loading of 15 wt% and above. Oksman et al. and Herrera et al. utilized a corotating twin screw extruder to compound PLA with CNC and CNF, respectively.^[95,96] The compounded mixtures had final CNM contents of 5 and 1.3 wt%, respectively, and were compression molded into sheets. In a similar manner, rather than compression molding, Jonoobi et al. compounded CNF with PLA for injection molding.^[148]

Rather than molding, extrusion can be utilized to form material into thick 2D structures. We discuss it here, as unlike R2R and other coating methods, bulk sheet extrusion allows sheet thicknesses to approach those found in classical polymer extrusion, which is on the order of mm to cm. Unfortunately, due to the extreme rheological changes that high contents of CNM induce in polymers, and the poor cohesion of pure CNM, little work has been done on bulk extrusion of CNM and its composites. However, Dhar et al. utilized a twin screw extruder with a square sheet die to continuously process transparent self-standing PLA grafted CNC films.^[149] The processed films had CNC loadings of up to 2 wt% and a final width of up to 18.5 cm.

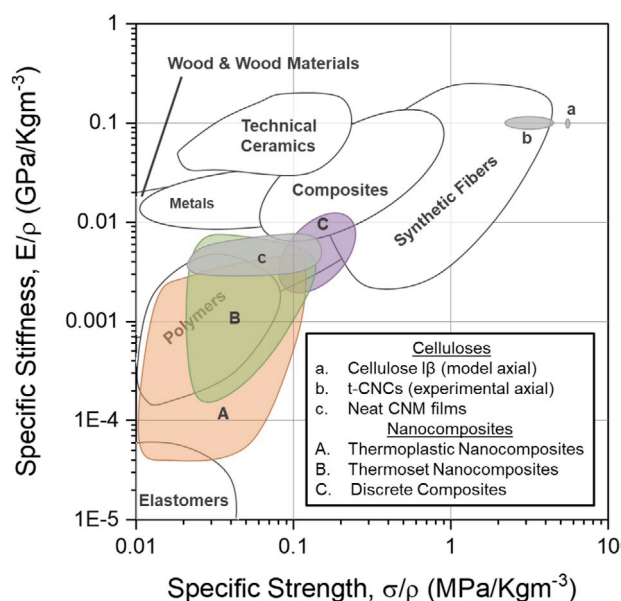


Figure 8. Ashby plot of specific stiffness versus specific strength for the CNM composites presented in this progress report compared to pure cellulose materials and common classes of materials. Cellulose I β is based on idealized model predictions for the axial modulus and strength at failure.^[1] CNC properties are given as those of the axial direction and represent the upper limit.^[163]

Sadly, the processing rates and film thicknesses were not stated in the report, however, the PLA/CNC films had improved barrier properties against oxygen (up to 65%) and water (up to 50%).

Extrusion-based 3D printing has also been used for bulk fabrication of CNM and its composites. Principally, this method is used to fabricate biomaterials including CNM inks/mixtures; a recent review summarizes the most current research efforts in the field.^[150] The biggest challenge associated with this fabrication technique is how to dry the printed ink and still retain the produced shape (i.e., reduce anisotropic shrinkage and collapse of the structure). In the research done by Håkansson et al., a CNF/water hydrogel at 2 wt% solids loading was printed and dried in a controlled manner by freeze drying or air drying.^[151] The printed parts (cube, chair, and chains) have dimensions greater than 10 mm and retained their shapes after drying. Siqueira et al. showed that CNC containing (up to 40 wt% CNC in HEMA/PUA matrix) and pure CNC inks are also 3D printable. Similar to CNF, the alignment of CNCs lead to structural anisotropies.^[152]

7. Outlook

Before predictions of the future are made, it is prudent to see where we are and how far we have come. Afterall, how can we know where we are going, if we don't know where we've been? To this, it is instructive to see how CNM composite mechanical properties stack up against more commonly used materials. **Figure 8** shows an “Ashby plot” of specific stiffness versus specific strength with the presented CNM composite classes compared against pure cellulose materials, and classes of commonly encountered materials. At first glance, it may be

discouraging as, when compared against previous plots such as these, such as in Moon et al., the nanocomposite (thermoset and thermoplastic) properties seem to have hardly increased in the past decade.^[1] However, when you consider that those reviews have typically used solvent based lab-scale methods, whereas here, the industrially feasible systems are presented, it becomes clear that much progress has been made. The prior plots should be seen as what was currently (then) “possible,” whereas here we are showing what is currently “practical.” The second important feature here is that, though discrete CNM composites have barely been studied, they have already surpassed the nanocomposites by a large amount, and have even surpassed pure CNM neat films, which has normally been considered the upper limit for properties. Lastly, and most importantly, these practical and industrially feasible CNM materials are now starting to compete in properties with highly engineered synthetic systems such as composites and synthetic fibers. Consider that results lately have shown that CNM composites have similar specific strength to aircraft aluminum.^[109]

Moving forward, while much work has been accomplished in cellulose nanocomposites, much still needs to be done to fully realize their potential in the marketplace. In addition to supply issues with regards to the CNM themselves, such as larger scale production to handle potential applications, better quality control/more consistent product, moving from batch to continuous production, and lower cost, the nanocomposite fabrication processes themselves also have research needs.

In the polymer matrix nanocomposite area, (thermoset and thermoplastic), much progress has been made beyond the traditional research on utilizing water-soluble polymers, which have limited industrial utility in composites, to using high boiling water miscible solvents such as DMF and DMSO as a compatibilizer, which is not industrially feasible. Recently, progress has been made on direct addition of CNM either to polymer melts or monomer mixtures. Unfortunately, many of these methods still utilize organic solvents to help disperse the CNM into the resin, either thermoset monomer or polymer melt. However, use of organic solvent in production will simply not be industrially feasible at scale due to environmental and worker safety regulations. Alternatively, many groups use solid CNM, typically freeze-dried or spray-dried. While much recent success with a modest amount of redispersal of CNM in water has been attained, use of dry-form CNM in hydrophobic polymer resins typically do not attain dispersion. Many groups have also attempted the use of surface modification of the CNM, with a small modicum of benefit, but not to a degree where the extra cost could be justified industrially. Likewise, dispersants such as surfactants have been used, but the dispersants, while effective at dispersing the CNM, typically compromise the properties of the nanocomposite, so little is gained. Add to all of this the remaining major challenges of compatibility mismatch (CNM matrix) leading to poor properties, and thermal degradation of many CNM types at processing temperatures which can compromise properties and/or aesthetics (i.e., turn a plastic brown), and it is tough to see the light at the end of the tunnel. Luckily, recent progress has made significant headway at alleviating these issues. Low cost, water-based modification methods have recently been reported to help with

compatibility in nonpolar media,^[153–155] melt-compounding by direct liquid feeding into melt polymers of water-based CNM slurries or CNM blended into compatible additives which allows compounding and extrusion of dispersed CNM nanocomposites have been reported,^[60,95] kinetic mixing into polymers,^[86] exchange of functional groups away from sulfate half-ester to prevent browning^[93] are all recent advancements that are exciting individually, but taken together really move the field forward toward commercialization of CNM nanocomposite products.

Work in discrete composites is the newest area, and therefore much less has been reported. While it is nascent, the limited research has shown that forming such things as laminate composites is a valid pathway that can ameliorate the aforementioned issues regarding matrix compatibility, excess water carried in the CNM, poor interfacial adhesion, embrittlement, etc., by fabricating a nearly pure CNM phase with excellent properties separately and then incorporating into a composite. It is expected that research into laminate systems will continue to expand as it takes advantage of classical paper making techniques. However, now that pure CNM macrofibers have been spun and also shown to have excellent properties due to induced alignment, it is likely that woven composites of CNM macrofibers will also be explored.

The fabrication of CNM nanocomposites into form has just begun to turn from laboratory batch-based approaches such as solvent/solution casting to more industrially viable continuous processes like continuous casting and spraying, R2R, and melt processing (spinning, extrusion, and compression molding). However, holding back this necessary research path is the large amounts of CNM and large forms which magnifies problems like aggregation and either have long drying times or are dried so fast, deformation of the CNM structure occurs. Even with the relatively high speeds compared to lab methods of these initial studies, these production rates of CNM films, coatings, fibers, and bulk structures are still quite slow when compared to common industrial papermaking or coating (greater than 1000 m min⁻¹^[156] for typical paper making vs 6 m min⁻¹^[131] for CNF coatings and 10 cm min⁻¹^[128,129] for CNF films) or single screw polymer extrusion lines (40 kg h⁻¹ at 122 rpm by Fang et al.^[157] vs 5 kg h⁻¹^[96] at 200 rpm for PLA/CNC compounding). While this is true, the current CNM fabrication efforts are still in the early development stages and have only employed pilot scale laboratory coaters and extrusion lines which are much smaller than their industrial counterparts, so it is expected that fabrication rates will further increase in the future. Still, a major oversight of these efforts is that final forming into complex shapes using methods such as injection molding has largely been unexplored.

As future CNM nanocomposite fabrication and forming grows into a more established field, it is likely that processes will become even more industrially viable. Still, it is likely that their entry into the marketplace will come in low risk areas that use and understand cellulose macrofibers—industrial papermaking and polymer melt processes utilizing pulp already. The confidence gained in these areas will then pave the way for CNM nanocomposite development in other areas. These efforts will ultimately reduce the consumption of oil-derived commodity polymers in the future.

Acknowledgements

The authors thank the US Endowment and the Public-Private Partnership for Nanotechnology for funding this research (Grant 109217) and the National Science Foundation Scalable Nanomanufacturing program (CMMI-1449358).

Note: When first published online, ref. 84 and 144 were the same. In order to address the duplicate reference, ref. 144 was changed for issue publication.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cellulose nanocrystals, cellulose nanofibrils, cellulose nanomaterials, industrial processing, nanocomposites

Received: January 31, 2020

Revised: February 26, 2020

Published online: July 21, 2020

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