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Overview of Cellulose Nanomaterials, Their Capabilities and Applications

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Cellulose nanomaterials (CNs) are a new class of cellulose particles with properties and functionalities distinct from molecular cellulose and wood pulp, and as a result, they are being developed for applications that were once thought impossible for cellulosic materials. Momentum is growing in CN research and development, and commercialization in this field is happening because of the unique combination of characteristics (e.g., high mechanical properties, sustainability, and large-scale production potential) and utility across a broad spectrum of material applications (e.g. as an additive, self-sustaining structures, and template structures) that CNs offer. Despite the challenges typical for materials development, CN and near-CN production is ramping up with pilot scale to industry demonstration trials, and the first commercial products are starting to hit the marketplace. This review provides a broad overview of CNs and their capabilities that are enabling new application areas for cellulose-based materials.

INTRODUCTION

Cellulose is the world's most abundant polymer, representing 1.5×10^{12} tons of the planet's total annual biomass production,[1] an almost inexhaustible source of raw material. Not surprisingly, then, cellulose-based products are prolific within our society, as demonstrated by the enormity of the world-wide industries in cellulose derivatives, paper/packaging, textiles, and forest products. Nevertheless, to meet the needs of modern society for high-performance materials while advancing sustainability and renewability, we must ask more from cellulose-based materials. And cellulose is responding. Over the past decade, advances in cellulose nanomaterials (CNs) have demonstrated cellulose-material utilization possibilities that were thought impossible. CNs fill a unique gap in the cellulose size spectrum previously used by industry (Fig. 1). Currently, industry is adept at using molecular cellulose for cellulose derivatives (e.g., cellulose acetate), pulp fiber (e.g., individual wood/plant fibers) for paper and packaging, and large particles from wood (e.g., saw dust, chips, flakes, veneer, lumber, and even tree stems) to create thousands of different engineered wood products. The "gap" that CNs fill lies between molecular cellulose and individual wood fibers (e.g., pulp). CNs can do things that neither molecular cellulose nor pulp can do. As such, CNs are a new class of cellulose-based "building blocks" that are inspiring advances in cellulose science, technology, and product development for the next generation of renewable/sustainable products.

CNs are nanosized particles with highly ordered bundles of cellulose chains aligned along the bundle axis, giving them new properties, as compared with pulp fibers and wood particles. CNs have high aspect ratios, high mechanical properties, low thermal expansion, low density, and surface-accessible hydroxyl groups that can readily be chemically modified to give additional functionalities.[2,3] When compared with inorganic nanoparticles (INPs), CN properties are not necessarily unique. Yet, some key drivers in the development of CN technology are its sustainability, biodegradability, low/minimal environment, health and safety risks (based on preliminary testing[4,5]), and processing at industrial scale with relatively low

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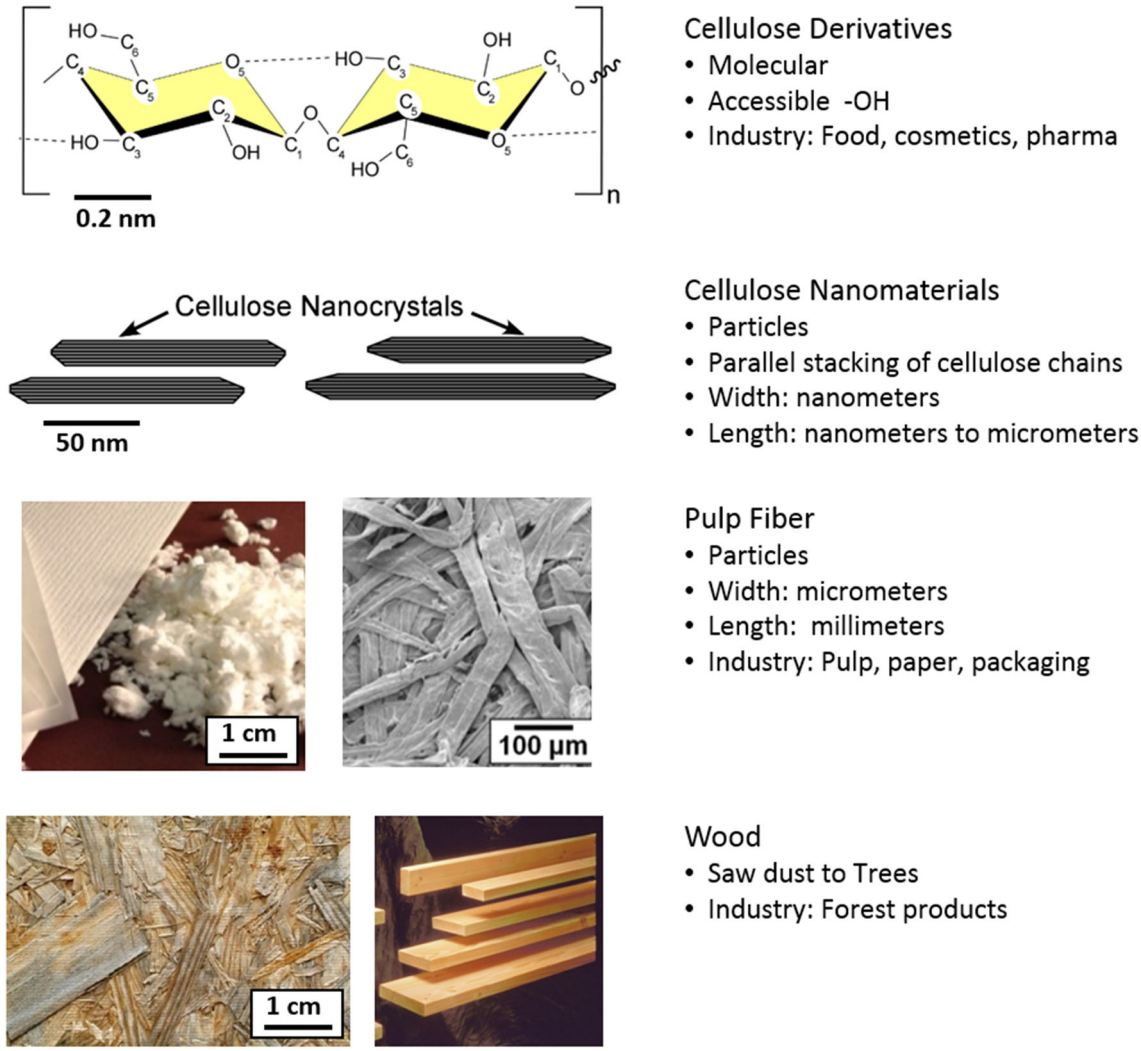

Fig. 1. Various cellulose-based materials. Cellulose nanomaterials fills a "gap" between the molecular cellulose and the wood pulp, providing a new particle type to work with.

costs.[6] Thus, CNs can help satisfy consumer, industry, and government demands for products made from renewable and sustainable resources with low environmental impact and low environmental, animal/human health, and safety risks.

Over the past decade, there has been explosive growth in CN research and development (e.g., less than 20 articles in 2005 to more than 650 in 2015)* and patents.[7–9] Research in CN is covering an ever broadening scope of topics, including improved CN production technologies,[10–12] rheology,[13] surface functionalization,[2,3] characterization techniques,[14] composites processing,[15] self-assembly,[16] optical properties,[16] barrier properties,[17,18] predictive modeling,[19] life cycle analysis,[20] and environment-health-safety.[5] Research in and development of various application areas include additives to adhesives, cements, inks, drilling fluids, paper products, cosmetics, barrier/separation membranes,[7,17] antimicrobial films, transparent-flexible electronics,[21] biomedical,[4,22,23] continuous fibers and textiles, catalytic supports,[24] batteries, supercapacitors, food coatings,[25] and many more emerging applications.[6,26] There have been several review articles and books[27,28] describing various aspects of CN. Many are referenced in this review.

In 2015, CNs began to enter the marketplace with a near-CN product FiberLean™ produced by IMERYS[29] as a coating material for paper, NCC™ produced by Celluforce as an adhesive additive,[30] Signo307 with CN inks,[31] Nippon Paper Cellulose Nanofiber as an additive to disposable diapers,[32] and others. Additionally, several laboratory-scale efforts have progressed to pilot scale and industrial production/demonstration projects, as well as to full-scale commercialization.[6,33] In the fourth quarter of 2015, there were several CN pilot processing facilities (10–1000 ton/day) across Europe, North

Estimates were based off of a May 2016 Web of Science search, with a manuscript title search for Cellulose AND (nanofib OR nanowhisk* OR nanocrystal* OR microfib* OR nanomaterial*) OR Nanocellulose.

Table I. Particle morphology of various cellulose particle types

	Particle size			
Particle type	**Length (μm)**	**Width (nm)**	**Height (nm)**	**Crystallinity[a] (%)**
CNF[b]	>1	4–100	4–100	51–69
CNC[b]	0.05–0.5	3–20	3–20	54–88
t-CNC	0.1–4	~20	~8	85–100
AC				>80%
Valonia	>1	~20	~20	–
Micrasterias	>1	20–30	5	–
BC				
Acetobacter	>1	30–50	6–10	65–79
WF and PF	>2000	20–50 (μm)	20–50 (μm)	43–65
MCC	10–50	10–50 (μm)	10–50 (μm)	80–85

Adapted from Moon et al.[19] *CNF* cellulose nanofibers, *CNC* cellulose nanocrystals, *t-CNC* cellulose nanocrystals from tunicates, *AC* algae cellulose, *BC* bacterial cellulose, *WF* wood fiber, *PF* plant fiber, *MCC* microcrystalline cellulose.[a]Cellulose crystallinity estimated from various x-ray diffraction approaches.[b]Axial cross-section shape is considered to vary between circular and square-like.

America, and Japan,[33] and market forecasts suggest significant growth potential, with an estimate for the U.S. market of 6 million metric tons annually.[34] All of this demonstrates that CNs have moved beyond being a scientific curiosity.

This review gives a broad overview of CN capabilities and applications. The review describes CNs and their properties and summarizes how CNs are being used to create new interactions/structures that are enabling new application areas for cellulose-based materials.

CELLULOSE NANOMATERIALS

There are many different varieties of CNs, presenting a wide spectrum of shapes, sizes, and properties. In general, variations in CN arise from three general factors: (I) cellulose source, (II) the extraction/production method, and (III) surface chemistry.

Cellulose Sources

CNs have been extracted/produced from a wide variety of cellulose sources (trees, plants, tunicate, algae, bacteria), and they have been produced from recycled paper products and other biomass residual streams (e.g., carrot pulp and coconut husks) as summarized in the following review papers.[10–12,19] The influence of cellulose source on CN arises from the cellulose biosynthesis process, which is highly specific to the cellulose-producing organism. During biosynthesis, individual cellulose molecules assembled into ordered bundles, elementary fibrils, or nanofibrils that subsequently end up as CN. Because the biosynthesis processes of trees and plants are similar, the CNs extracted from them are similar, with some subtle differences.[11] In contrast, there are large differences in the biosynthesis processes comparing plant versus tunicate versus algae versus bacteria, and thus, the resulting CNs extracted from them are considerably different in terms of particle aspect ratio, length, width, cross-section morphology, and crystal structure, as summarized by Moon et al.[19] and Table I.

For large-scale CN production at lower costs, tree- and plant-based cellulose sources are preferred because the pulp/paper, packaging, pharmaceutical, and textile industries have the necessary infrastructure. Although CNs from bacteria typically have much lower production rates and higher production costs, these particles may be practical for specialized applications in the medical area.[35] In contrast, CNs from tunicate and algae are expensive to collect and extract and are used as idealized particles for research purposes.

Isolation of Cellulose Nanomaterials

There are several approaches for the extraction of CN as summarized in recent reviews.[10,12,36–39] Continued research and development has focused on optimizing processes to lower costs and to increase yields, consistency, and quality. Processes are multistep and tailored for the specific cellulose source. Generally extraction consists of pretreatment step(s) followed by refinement step(s). Pretreatments typically purify and homogenize the starting material so that it reacts more consistently in subsequent treatments. Afterward, additional chemical or enzymatic treatments are performed to facilitate the controlled fragmentation of the cellulose source material during the refinement step(s). There are two main refinement approaches to fragment cellulose source materials into nanosized particles: mechanical shear and acid hydrolysis. Refinement by mechanical treatments use high shear to tear the cellulose source material apart.[12] The resulting particles are called cellulose nanofibrils (CNFs), and they have fiber/fibril morphologies with high flexibility and aspect ratios (~10–100).

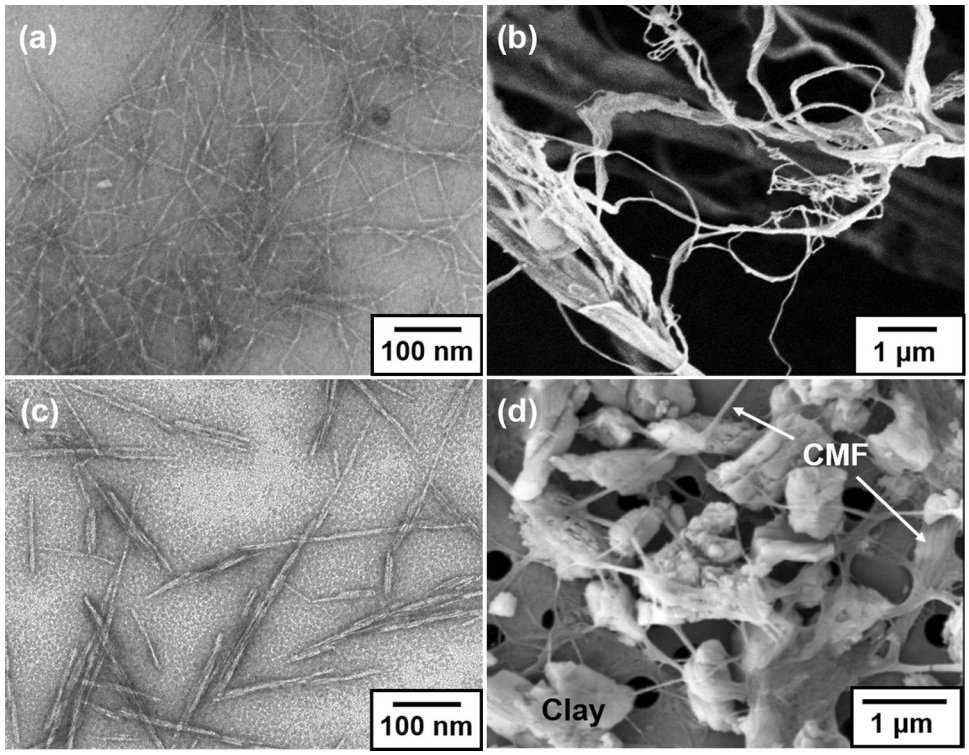

Fig. 2. Micrographs showing various CN types. (a) CNFs produced using pretreatments produced from a CNF pilot plant located at FPL.[42] (b) CNFs produced without pretreatments produced from a CMF pilot plant located at the Process Development Center at UMaine.[43] (c) CNCs produced from a CNC pilot plat located at FPL.[44] (d) FiberLean™.[29]

Current technology, with pretreatments, produces CNFs with diameters around 4–10 nm. Without pretreatment, the resulting fibrils are much coarser, typically 20–100 nm in diameter, and have been generally referred to as cellulose microfibers (CMFs).[19] Nevertheless, the current International Standards Organization (ISO) nomenclature standard for cellulose nanomaterials has grouped CNFs and CMFs together.[40] In contrast, refinement by acid hydrolysis (typically sulfuric acid) preferentially dissolves the disordered regions of the cellulose source material, and the resulting particles are called cellulose nanocrystals (CNCs).[10] CNCs are stiff, with spindle-like morphologies and aspect ratios of ~5–30, where the surface chemistry, charge, and aspect ratio are determined by the hydrolysis conditions.[41]

Types of Cellulose Nanoparticles

There are many varieties of CNs, and to facilitate comparisons, CNs are typically grouped into five categories: CNFs, CNCs, tunicate CNCs (t-CNCs), algal cellulose (AC), and bacterial cellulose (BC) (Table I). A more detailed description is given in Moon et al.[19] CNFs and CNCs are considered to be in different categories because of vastly different particle morphologies resulting from the isolation methods (Fig. 2), where CNFs are flexible and more like entangled network-forming fibers (e.g., spaghetti), while CNCs are considered to be stiff rods (e.g., rice). In contrast, the t-CNC particles are much larger than CNCs from plants/trees, while algal and BC are more fibril-like (with BC being more ribbon-like) with minimal branching. Because of these differences in particle morphology (and crystal structure), they are typically listed separately from CNFs. Note that these categories preclude the role of surface chemistry. Different surface chemistries are categorized as subcategories to the major CN types. As examples of the size ranges involved, pulp fibers, which are traditionally used in the paper/packaging industries, wood fiber (WF) and plant fiber (PF) are typically millimeter-long particles while microcrystalline cellulose (MCC) used in pharmaceutical and food industries is composed of micron-sized particles. In contrast, CNs have at least two dimensions at the nano-length scale (< 100 nm). Some examples of commercially produced CNs are NCC by Celluforce,[45] BioPlus™ by API,[46] FiloCell by Kruger,[47] and BGB-Ultra by Bluegoose,[48] and the near-CN microfibrillated product FiberLean™ produced by IMERYS.[29]

Surface Chemistry

The surface chemistry of CNs is critically important in determining how the particles interact with their environment, controlling their dispersion in

solvents or polymers, rheology, self-assembly and agglomeration, and CN–CN and CN-polymer interfacial bond strength. Chemical modification routes primarily target the accessible hydroxyl groups (-OH) on CN surfaces, and the challenge in some cases is doing the modification without dissolving or altering the CN. A wide variety of chemistries have been explored and summarized in recent reviews.[3,18,49] Research and development continues on new modification routes, in particular for reactions that target cellulose carbons, as opposed to only the –OH groups. A large array of surface modifications by covalent (e.g., sulfonation, oxidation, esterification, amidation, carbamation, etherification, nucleophilic substitution, silylation, urethanization/carbanylation, and click-chemistry) and noncovalent (e.g., adsorption, surfactants, and electrostatic) methods are reported. Examples of some applications for surface-modified CNs are improved processing and performance of CN-matrix composites, adjusting hydrophilic-hydrophobic balance, fluorescent labeling for imaging,[50] polymer grafting, nanoparticles for catalyst,[24] and templated structures.[3]

Properties

Cellulose nanomaterials have a unique combination of properties: high mechanical properties (Table II), low thermal expansion, thermal stability to ~200–250°C, relatively low density (1.6 g/cm^3) compared with inorganics and metals, birefringence,[51] high optical transparency,[52] and biodegradability,[53]

One common trait among all CN types is the parallel stacking of cellulose chains along the particle length. This high order of stacking is the result of extensive intra- and inter-chain hydrogen bonding, making organized cellulose an exceptionally stable polymer, which gives the CNs high mechanical properties along the length of the particle (i.e., fiber axial direction). This ordered stacking of cellulose molecules also results in very high anisotropy; i.e., the properties transverse to the cellulose chain are very different, and usually lower, than the properties in the direction of the chain.[54]

Environmental Health and Safety

Preliminary work on toxicity of as-produced CNs without surface modification have shown low-to-minimal adverse health effects from oral (i.e., ingestion) or dermal (i.e., contact with skin) studies. Nevertheless, pulmonary (i.e., respiratory) and cytotoxicity (i.e., effects of CNs on cell viability) studies have yielded conflicting results.[5,20,58] The toxicity of various CNs is an area of active study, both with and without specific surface functionalization, as well as studies to develop best approaches for monitoring workplace safety.[14] Life cycle analyses (LCAs) have been used to assess environmental impact and for adapting manufacturing process to achieve best practices for mass production.[20,59,60] Results show that CNs exhibit prominent environmental advantages over the other nanomaterials, such as carbon nanotubes.[60]

CAPABILITIES WITH CELLULOSE NANOMATERIALS

The high surface-area-to-volume ratio of CNs allows them to exert a large effect on their local surroundings, while acting as a stiff phase in suspensions and composites. This differentiation allows CNs to do things that neither molecular cellulose nor wood/plant pulp materials can do. A few general examples are described as follows.

Rheology Modifiers

Rheology is a fundamental part of working with CNs as they are produced as aqueous suspensions, are incorporated into various solvents and polymers in the manufacturing of composites, and are used as rheology modifier additives (e.g. in adhesives, cosmetics, drilling fluids, paints). As a result of this the rheology of CNs in various solvents and polymer mixtures has been widely studied.[13,61] The rheology behavior can be complex but shows a great ability to tailor shear thinning behavior as compared with molecular cellulose or pulp. This decrease in the viscosity with increasing shear rate, similar to other INPs with high aspect ratios,[62] is useful in applications like paints, where during application, flow is

Table II. Properties of various cellulose particles

Material	E_A (GPa)	E_T (GPa)	σ_f (GPa)	ε_f (%)	CTE_A (ppm/K)	Tc_A (W/mK)
Experimental						
CN	57–180	2.7–70	1.6–6.4	–	–	–
WF and PF	5–45	–	0.3–0.8	1.3–23	–	–
MCC	21–29	–	–	–	–	–
Modeling						
Cellulose Iβ[a]	110–206	5–98	5.4–7.7	5.1–6.7	2–6	5.7

Adapted from Moon et al.,[19] E_A elastic modulus in axial direction, E_T elastic modulus in transverse direction. σ_f tensile strength (tensile testing), ε_f strain to failure (tensile testing), CTE_A coefficient of thermal expansion in axial direction. Tc_A thermal conductivity[a]Model Cellulose IB data collected from Refs. 54–57, 107 and 108.

wanted so the paint can wet and coat the surface; then once applied, the paints regain their high viscosity and flow stops (e.g., no dripping). The reduction in viscosity at higher shear rates for CN-suspensions is a result of alignment of the CN fibers in the direction of shear, thereby greatly reducing their interaction volumes. Several variables have been shown to influence the shear thinning rheology behavior: solvent and CN-solvent interaction, polymer system, temperature, and CN morphology, size distribution, surface charge, chemistry, and concentration. Although both CNFs and CNCs are shear thinning, there are differences in behavior as reported in Ref. 63; in general, the longer CNF particles alter the rheology at much lower solids loadings as compared with CNCs.

Reinforcement of Polymers

The development of CN-reinforced matrix composites exploits CN high mechanical properties, high surface-area-to-volume ratio, and high particle aspect ratio. Much of the work to date has been extensively reviewed.[10,11,15,18,19,38,39,64,65] For nanoparticle-matrix composites, achieving dispersion of the nanoparticle reinforcement phase is key to maximizing their effectiveness at altering the matrix polymer properties. This has been one challenge for CNs as they are naturally hydrophilic while most industrially relevant polymers are hydrophobic, resulting in a high propensity for agglomeration. In general, CNFs are more difficult to disperse than CNCs. Significant progress has been made in obtaining a good CN dispersion in a variety of polymers (e.g., thermosets, thermoplastics, bio-based, hydrophobic, and hydrophilic) using various surface functionalization strategies in conjunction with composite possessing methods (solution casting, melt-compounding, partial dissolution, fiber spinning). As a result, CN additions have been shown to dramatically alter the thermomechanical and dynamic mechanical properties of many matrix polymers. The extent to which CNs can alter polymer materials depends on CN (I) dispersion, (II) alignment, (III) surface chemistry, (IV) interfacial properties, (V) particle morphology, (VI) percolation (interconnected network structure), and (VII) the matrix polymer. Expanding the property space of polymer materials is of great industrial interest, particularly for plant-based polymer matrices where CN additions maintain the renewable/biodegradable properties.

Network Structures

CNs in suspension can self-assemble into interconnected networks, the arrangement of which is dependent on CN type, morphology, surface chemistry, suspension characteristics, shear state, and solvent properties.[16] By controlled removal of the solvent, the resulting monolithic solid has a CN interconnected-network structure reminiscent of the structure in the starting suspension. The rate and method of solvent removal (e.g., solution casting and freeze drying) also influences the final CN network structure. These CN-network structures can have much different properties compared with what can be produced with molecular cellulose or pulp, and they can be broadly grouped into four categories: (I) interconnected fiber network structures, (II) dense aligned fiber structures, (III) chiral nematic structures, and (IV) aerogels. Interconnected fiber networks are typically produced from air drying during solution casting. The density of the fiber packing is dependent on drying rates, and by applying mechanical shear, it is possible to produce a dense network of highly aligned CNs in the shear direction.[66] In general, CNFs more readily form a network structure and are more extensive/entangled than what are produced by CNCs; a hint of this can be seen when comparing Fig. 2a and c. Unique to CNCs, the spindle-like particles self-assemble into chiral nematic structures (e.g., helix of stacked pseudo-planes of CNCs with their long axes parallel to the plane of the layers).[16] Aerogels are considered separately here because the drying process (e.g., freeze drying and super critical drying) produces CN-networks with extremely low densities (10^{-4}–10^{-2} g/cm^3), high surface areas (100–600 cm^2/g), and high porosity.[67–71] Additionally, it is possible to produce hierarchical pore structures with freeze drying, where the CN-network results in the nanoscale pores between the CN fibrils, while ice crystals leave micron-sized pores.[71]

Optical Properties

The nanodimensional diameters of CNs result in lower light scattering compared with the micron-to-millimeter size of pulp fibers, making good transmittance and low-haze CN-composites possible.[16,19] Several factors have been shown to influence the optical transmittance, including CN particle size, volume fraction, alignment, dispersion, the wavelength of light, index of refraction difference between CN and the matrix, volume fraction of voids, film thickness, and film surface roughness. One optical property that is unique for CNCs comes about from the liquid crystalline nature of CNC suspensions, which allows CNCs to self-assemble into nematic and chiral nematic structures. These highly ordered structures persist in the final composite, resulting in interesting optical phenomena.[16,72,73] When the nematic structure is preserved, the highly aligned CNCs result in transparent composites. And when the chiral nematic structures are preserved, an iridescent/pearlescent optical behavior is observed.[16] By tailoring the CNC suspension and composite processing properties, it is possible to control the color of the dried film.

Templated CN Structures

CNs with their high surface area and surface reactivity have been used as templates for chemical synthesis and deposition of INP.[13,14] Templating

with CNs has primarily focused on two areas: (I) isolated INP deposition and (II) coatings on CN structures. For isolated INP deposition, various metallic (e.g., Ag, Au, Cu, Ni, Pd, Pt, Ru, or Se) or ceramic (e.g., CdS, CuO, Fe_3O_4, PbS, TiO_2, or ZnS) nanoparticles have been deposited on either individual CNs, CN network structures, or CNC chiral nematic structures. The optimization of INP coverage has focused on controlling the INP surface density, maximizing INP surface area, and minimizing agglomeration or coalescing of INP. The new capabilities CNs provide are an alternative method for the synthesis of INP, minimization of INP agglomeration/coalescence, and production of ultra-fine INP distributions.

For coatings, the focus has been complete coverage of the CN particles, or CN self-assembled network structures, typically with silica-based or titania-based materials, and creating a near-perfect patterning at the tens of nanometer length scale.[3] The CN-network can then be subsequently burned out (or carbonized), producing free-standing hollow (or carbonized) core hierarchical structures (nanometers up to millimeters) patterned by the CN-network. The unique capabilities that CNs bring is an alternative approach for producing these structures. New application possibilities with CN template structures are in the areas of biosensors, catalysis, photovoltaics, drug delivery, filters, antimicrobial applications, and others.

Barrier

Because of the tight packing of cellulose chains within CNs and the ability to produce dense percolated CN-networks, CN-network structures and CN-polymer composites have attracted interest as barrier films[17–19] with uses in filtration[74] and packaging applications. For filtration, the porosity in CN-networks can remove ultra-fine particulates[74] and with corresponding surface chemistry can be used to screen chemicals.[75] In general, the extensive CNF network structures have been better suited for filtration applications than CNCs. In CN-polymer composites, improved barrier properties result from the increased tortuosity provided by the nanoparticles. The barrier properties of CN structures and composites have been shown to depend on CN (I) particle morphology, (II) surface chemistry, (III) dispersion, (IV) alignment, (V) volume fraction, (VI) interfacial properties, and (VII) the matrix polymer. To date, most of the work has focused on oxygen permeability and water vapor transmission (WVT).[17–19] CNs have been shown to lower oxygen permeability in most polymer systems. In contrast, for WVT, CN influence is dependent on the hydrophobicity of the polymer matrix material. Hydrophilic polymers like starch show lower WVT with CN additions, whereas in hydrophobic polymers, CN additions increase WVT.[18]

POTENTIAL APPLICATION AREAS

The recent availability of large volumes of CN materials for research and pilot studies has spurred significant growth in research and development in many application areas. A partial list is given here.

Additive to Adhesives

CNs have been examined as adhesive additives, primarily examining their impact on wood adhesives for panel products. An example is the combination of CMFs, CNFs, and CNCs with urea formaldehyde (UF) adhesives for use in laminated veneer lumber, particle board, oriented strand board, and fiber board.[76–79] Common findings from this research include significantly increased viscosity that limited the loading levels of the fibrils, enhancements in mechanical performance, and sometimes, reductions in formaldehyde emissions.

Additive to Paper-Based Products

With their high mechanical and barrier properties, ability to form nanoscale entanglements, and bonding affinity to cellulose surfaces (e.g., wood pulp fibers), CNs are an excellent choice for incorporation into paper-based products.[80–82] CNFs are easy to incorporate into the paper manufacturing processes, and they can be blended with additives (e.g., clays) for additional functionality where the CNFs act as carriers and/or binders. Two strategies for incorporating CNFs into paper-based materials have been (I) surface coatings and (II) bulk additions. As a surface coating, CNFs fill voids between pulp fibers (Fig. 3), resulting in enhanced strength, improved barrier properties (e.g., air, gas, water vapor, grease, and oils), increased surface smoothness, higher opacity, higher coating hold-out, and improved printing. Roll-to-roll possessing is one method being explored in scaling up the application of CNF coatings on paper.[83] Alternatively, CNFs can be incorporated into the bulk of the paper, either by direct addition to the pulp or by embedding layers of CNFs in a laminated paper sheet. Bulk additions of CNFs have been shown to alter mechanical properties, paper density, air permeability, and optical properties (e.g., brightness and opacity).[80] The extent to which CNFs alter performance depends on the CNF characteristics (e.g., morphology, size distribution, and surface charge), pulp type, additive formulations, and the paper manufacturing process.[80]

Despite the challenges of introducing a new additive and the resulting process changes, industry is moving forward with using CNF and near-CNF to unlock new performance opportunities. FiberLean™,[29] a cellulose microfibrillated fiber/mineral commercial product, which bonds better to paper surfaces and has less mineral loss as compared with current coatings. Additionally, Nippon Paper has

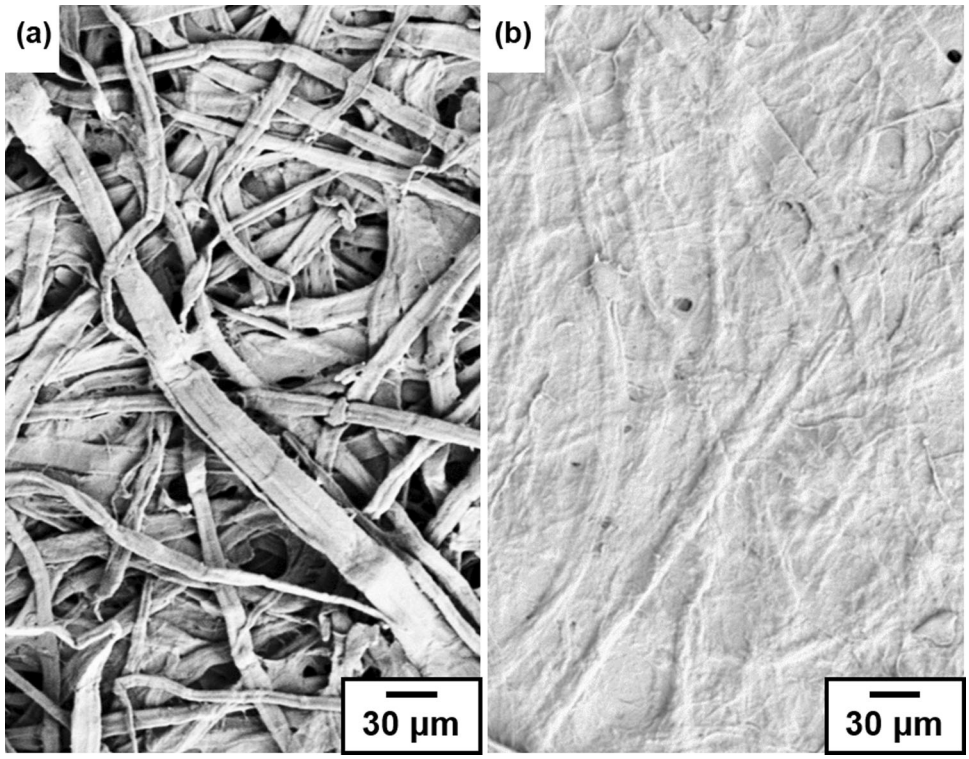

Fig. 3. Scanning electron images of CMF coatings on paper surfaces showing how CMFs fill voids between pulp fibers, to create smoother, denser surfaces. (a) Uncoated paper, (b) with CMF coating 1 g/m^2 with CMFs produced from a CMF pilot plant located at the Process Development Center at UMaine.[43]

publicly announced that it is developing disposable diapers that incorporate CNFs for improved odor absorbance.[32]

Additive to Drilling Fluids

The safety, sustainability, and strong shear thinning properties of CNs makes them a natural additive to drilling fluids in oil and gas drilling operations. Interestingly, CNC additions have shown self-assembled structures that give stronger shear-thinning properties and additional functionality to the drilling fluid. CNC additions to bentonite/water-based drilling fluids have demonstrated that strong surface interactions and high particle mobility allowed CNCs to form "core–shell" structures around bentonite particles, which subsequently gave the drilling fluid enhanced rheological properties (e.g., stronger shear-thinning), higher temperature stability, and less fluid loss.[84] This mechanism provides a new capability to tailor the functionality and performance of drilling fluids, potentially reducing the volume of additives. No commercial products are yet on the market, but there is a growing patent literature.[85]

Additive to Cement-Based Materials

In the broad area of cement-based materials, cellulose derivatives and natural fibers (wood/plant pulp fibers) have shown potential to advance both performance and sustainability.[86–88] CNs may also be pertinent in the development of new admixtures and reinforcement materials. Research has focused on CNs as a strength enhancer for various cementitious materials. Although fiber-reinforced cement composite mechanical improvements have been attributed to the fiber bridging mechanism[89] in which the millimeter length particles span across the crack and apply resistance to crack opening, the applicability of this mechanism with CNs may be limited as the particles may not be long enough to extend across cracks and restrict their opening. Despite this, small CN additions (0.2–7 wt.%) to cementitious materials have been shown to increase mechanical properties (e.g., stiffness and strength),[90–92] which was attributed to CNs altering the hydration reactions, affecting how the cement cures. Cao et al.[91] proposed that CNCs preferentially self-assemble in a loose network structure around the surface of the cement particles, providing (I) steric stabilization allowing for better particle mixing, and (II) a fast water transport path outside the hydration product shell during the hydration reaction, allowing for more reactions to take place. This mechanism may give a new capability for optimizing the hydration reaction kinetics and thereby achieve higher strength cementitious materials. Additionally, CN additions were also shown to alter rheology (e.g., yield stress for material flow) and to decrease set times of cement pastes, properties of interest in various cement

applications. Applications could include CNs being added to concrete, mortar, dental glass, roof tiles, bone cement, etc.

Food Coatings

CN applications in food span the range of possibility from reinforcement of plastic film for packaging, to the use of pure CNF in film form, to food additives for stabilization of food (e.g., ice cream), to functional food ingredients, typically as a fat replacement/reducer.[93] One new use for CNs is their incorporation in food coatings applied directly to the surface of fruit (Trademarked as "Innofresh").[94] Recent publications show advantages in the preharvest treatment of cherries to prevent rain cracking,[95] extension of shelf-life of pome fruits and bananas (unpublished data, Yanyun Zhao, Oregon State University), and the preservation of anthocyanin containing fruits such as blueberries, which allows the fruit to be preserved (e.g., canned) while retaining the nutritional benefits and color of the anthocyanins in the fruit (Fig. 4).[96] We can expect to see the use of CNs, and especially CNFs, due to its history and growing documentation of low toxicity (see the section on EHS), to increase in food applications in the future.

Transparent-Flexible Electronics

Transparent-flexible CN composite substrates are being developed for a variety of electronic devices/applications, including thin film transistors, organic-light emitting diodes, photovoltaic devices, printed foldable antennas, and resistive touch screens and sensors.[21] The CN properties of transparency, high mechanical properties, thermal stability to ~250°C, and low coefficient of thermal expansion (CTE) are all important to transparent-flexible substrates. The electronic devices are very thin multilayer structures with fine details; thus, substrates must have ultra-smooth surfaces to avoid device electrical shorts or leakage, as well as good "printability" (i.e., easily wet by the printing "ink" but maintaining good edge retention). Typical device fabrication processes are sputter coating, inkjet printing.[97] thermal evaporation, and spin coating. Most of the work to date has been done at the laboratory scale and has been focused on proof of concept. Nevertheless, this is now transitioning to pilot- and large-scale fabrication runs and techniques,[98] such as roll-to-roll and screen printing. CN advantages have also led to an additional focus on device sustainability and recyclability.[99,100]

Catalysis Support Structures

CN network structures are being developed as a support material for a wide range of catalytic reactions, such as reductions, oxidation, coupling reactions, electro-catalysis, and photo-catalysis.[24] The unique aspect of CNs is a combination of three factors: their nanoscale dimensions and, therefore, large surface area; their ability to self-assemble into porous network structures; and their reactive surface, which facilitates the deposition of a fine dispersion of INP on the CN network structure. This allows the development of tailored CN-INP network composites that have an extremely large catalyst surface area, which is critical for commercially viable catalytic reactions. Most work to date has been at the laboratory scale, but expectations are high for commercial development.

Fig. 4. Blueberries coated by Innofresh™ (treatment) vs uncoated (control) in light syrup (18 degrees Baume) at ambient condition (e.g., 20 ± 2 °C) after 1 week.

Biomedical Applications

With their biocompatibility, biodegradability, and low cytotoxicity,[4] CNs are being studied for a wide array of medical applications, such as drug delivery, tissue repair-healing-replacement, and medical implants.[4,101–103] In the area of tissue repair-healing-replacement, most work has centered on BC hydrogels because of their collagen-like, hierarchical, three-dimensional nanofiber network structure that can be controlled directly during biosynthesis. For tissue repair and healing (e.g., skin and bone), BC-based hydrogels provide a nontoxic, biocompatible platform for the growth of cells, which can then more readily activate and accelerate tissue repair and regeneration. Commercial products, XCell®, and Dermafill™[104] are BC hydrogel bandages that gently conform to the skin, allowing active fluid management, pain-free dressing changes, a barrier to bacteria, and show better and faster healing effects and less inflammatory response as compared with conventional bandages.[101] For replacement tissues (e.g., blood vessel, ligament, meniscus, cartilage, and heart valves), work has centered around BC hydrogel tubes for potential use as vascular grafts.[35,105,106] Clinical trials in rats, pigs, and sheep for up to 1 year have indicated the BC tubes remain stable. Nevertheless, no commercial products are on the market yet. For medical implants, biocompatible CN-composites are being developed to minimize the stiffness mismatch between the device and the surrounding tissue, subsequently lowering inflammatory responses.[106] One example is cortical implants, in which CN-based stimuli responsive

composites are being developed that are stiff to facilitate installation and undergo in situ softening by absorption of body water, a mechanism driven by CN-matrix and CN–CN interfaces.[102] Clinical trials are ongoing.

GRAND CHALLENGES

One of the fundamental challenges of working with any biomaterial, including CNs, is its susceptibility to water. Understanding the fundamental relationship of cellulose in its many forms with water is a complex and fascinating subject, mastery of which still eludes the scientific community. A second grand challenge is metrology.[14,107–109] Although advances have been made in recent years, precisely determining the size distribution of a CNC dispersion or the length distribution of CNF remains challenging. We now have several producers, but no producer's product is the same as another. Many companies are reluctant to use a product when it must be sole sourced. The development of CN-metrology is a challenge that, when overcome, will speed the adoption of CNs in the marketplace. A final grand challenge is finding a path to facilitate commercialization. Strategic, holistic, interdisciplinary (and well-funded) research programs focused on specific applications and with significant input from the product manufacturer are needed to facilitate the commercialization process. Often research has been funded and carried out in an attempt to solve some particular problem, but the solution developed was not commercially relevant. Although researchers do advance knowledge with their work, working with insufficient communication with the marketplace and product value chain is not efficient in terms of facilitating the revolutionary and transformative shifts that are commercially attainable with CNs. Finding ways to educate scientists about the needs of the marketplace is a grand challenge for all scientific disciplines but especially CN at this early stage of commercial development. For example, many lab-scale, proof-of-concept composite materials have been made with solvent casting. Except in certain specific cases, this technique is not appropriate for industrial-scale processes. Additionally, rushing to find the "killer app" contains a potential trap of not doing it right the first time and slowing the commercialization process.

We envision a nanocellulose revolution that will change the way people live, work, and play. In the future, it will hold an important niche in the more sustainable world most of humanity is wanting and creating at this point in history. The future is bright, but it will require hard and careful work to manifest the many benefits nature has bestowed on us in that most enigmatic of natural polymers, cellulose.

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