

Cellulose nanomaterials review: structure, properties and nanocomposites

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This *critical review* provides a processing-structure-property perspective on recent advances in cellulose nanoparticles and composites produced from them. It summarizes cellulose nanoparticles in terms of particle morphology, crystal structure, and properties. Also described are the self-assembly and rheological properties of cellulose nanoparticle suspensions. The methodology of composite processing and resulting properties are fully covered, with an emphasis on neat and high fraction cellulose composites. Additionally, advances in predictive modeling from molecular dynamic simulations of crystalline cellulose to the continuum modeling of composites made with such particles are reviewed (392 references).

Introduction

Consumers, industry, and government are increasingly demanding products made from renewable and sustainable

resources that are biodegradable, non-petroleum based, carbon neutral, and have low environmental, animal/human health and safety risks. Natural cellulose based materials (wood, hemp, cotton, linen, *etc.*) have been used by our society as engineering materials for thousands of years and their use continues today as verified by the enormity of the world wide industries in forest products, paper, textiles, *etc.* These first generation uses of cellulose took advantage of the hierarchical structure design within these materials. Natural materials develop functionality, flexibility and high mechanical strength/weight performance by exploiting hierarchical structure design that spans nanoscale to macroscopic dimensions (Fig. 1). However, the properties, functionality, durability and uniformity that will be required for the next generation of cellulose based products and their engineering applications

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cannot be achieved with traditional cellulosic materials. Put another way, traditional forest products have their place, but cannot meet the demands of modern society for high performance materials. Sustainability asks that human science and technology evolve and that we ask more from trees. Fortunately, there is a base fundamental reinforcement unit that is used to strengthen all subsequent structures within trees, plants, some marine creatures, and algae: cellulose nanoparticles. By extracting cellulose at the nanoscale, the majority of the defects associated with the hierarchical structure can be removed, and a new cellulose based “building block” is available for the next generation of cellulose based composites.

Cellulose nanoparticles (CNs) are ideal materials on which to base a new biopolymer composites industry. Crystalline cellulose has a greater axial elastic modulus than Kevlar and

its mechanical properties are within the range of other reinforcement materials (Table 1). CNs have high aspect ratio, low density (1.6 g cm^{-3}), and a reactive surface of –OH side groups that facilitates grafting chemical species to achieve different surface properties (surface functionalization). Surface functionalization allows the tailoring of particle surface chemistry to facilitate self-assembly, controlled dispersion within a wide range of matrix polymers, and control of both the particle–particle and particle–matrix bond strength. Some variety of CN composites produced to date can be, transparent, have tensile strengths greater than cast iron, and have very low coefficient of thermal expansion (CTE). Potential applications include but are not limited to barrier films, antimicrobial films, transparent films (Fig. 2a), flexible displays (Fig. 2b), reinforcing fillers for polymers, biomedical implants, pharmaceuticals, drug delivery, fibers and textiles, templates for electronic components, separation membranes, batteries, supercapacitors, electroactive polymers, and many others.

Over the past several decades there has been extensive research in cellulose, cellulose-based particles and cellulose-based composites. There have been several review articles and books^{1–3} describing various aspects of cellulose: cellulose structure,^{4–6} CN processing,^{7–10} bacterial cellulose,^{8,11–14} regenerated cellulose,^{12,15} chemical modification of cellulose surfaces,^{7,8,12,15–21} rheological behavior of cellulose suspensions,^{16,17,22} self-assembly of suspensions,^{5,22,23} interaction with water,¹⁹ CN composites,^{5,7–10,19,24–29} and patent literature.⁹ This current critical review builds off these earlier reviews and, where appropriate, specific topic areas adequately covered in previous reviews are summarized and referenced out to the corresponding review paper(s).

This critical review gives a processing-structure-property perspective to the CN and CN composites literature, which provides a method for the differentiation of several CN types (based on cellulose biosynthesis and extraction processes) and



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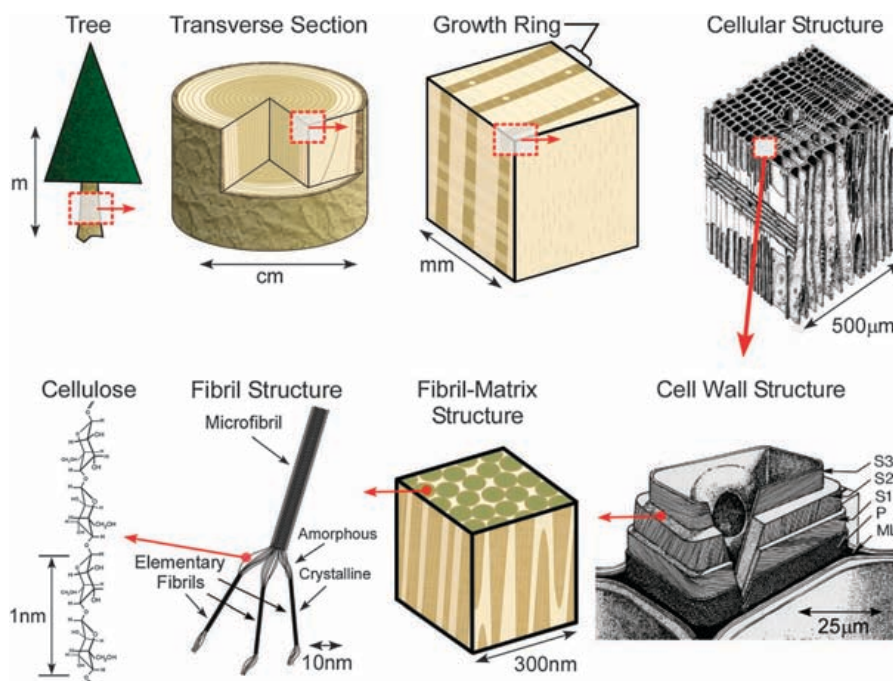


Fig. 1 Schematic of the tree hierarchical structure.¹¹³ Reprinted with permission from ref. 113 © 2011 IOP Publishing Ltd.

Table 1 Properties of cellulose and several reinforcement materials

Material	$\rho/\text{g cm}^{-3}$	σ_f (GPa)	E_A (GPa)	E_T (GPa)	Reference
Kevlar-49 fiber	1.4	3.5	124–130	2.5	368, 369
Carbon fiber	1.8	1.5–5.5	150–500	—	369
Steel Wire	7.8	4.1	210	—	369
Clay Nanoplatelets	—	—	170	—	370
Carbon Nanotubes	—	11–63	270–950	0.8–30	371, 372
Boron nanowhiskers	—	2–8	250–360	—	373
Crystalline Cellulose	1.6	7.5–7.7	110–220	10–50	See Table 3

ρ = density, σ_f = tensile strength, E_A = elastic modulus in axial direction, E_T = elastic modulus in transverse direction.

CN composite types (based on processing). The role of CN particle and composites types on CN composite properties is reviewed, with particular focus on neat CN films and modified CN films. Additionally, a detailed review of the atomistic modeling of the crystalline cellulose structure and properties and the application of analytical models to predict CN composites properties provides an approach for probing the potential of CNs and CN composites.

1. Structure of cellulose

Cellulose is a linear chain of ringed glucose molecules and has a flat ribbon-like conformation. The repeat unit (Fig. 3) is comprised of two anhydroglucose rings ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$; $n = 10000$ to 15000 , where n is depended on the cellulose source material) linked together through an oxygen covalently bonded to C1 of one glucose ring and C4 of the adjoining ring (1 → 4 linkage) and so called the β 1–4 glucosidic bond.⁵ The intrachain hydrogen bonding between hydroxyl groups and oxygens of the adjoining ring molecules stabilizes the linkage and results in the linear configuration of the cellulose chain. During biosynthesis, van der Waals and intermolecular

hydrogen bonds between hydroxyl groups and oxygens of adjacent molecules promote parallel stacking of multiple cellulose chains forming elementary fibrils that further aggregate into larger microfibrils (5–50 nm in diameter and several microns in length). The intra- and inter-chain hydrogen bonding network makes cellulose a relatively stable polymer, and gives the cellulose fibrils high axial stiffness. These cellulose fibrils are the main reinforcement phase for trees, plants, some marine creatures (tunicates), algae, and bacteria (some bacteria secrete cellulose fibrils creating an external network structure). Within these cellulose fibrils there are regions where the cellulose chains are arranged in a highly ordered (crystalline) structure, and regions that are disordered (amorphous-like). The structure and distribution of these crystalline and amorphous domains within cellulose fibrils have yet to be rectified (Fig. 3b).⁶ However, it is these crystalline regions contained within the cellulose microfibrils that are extracted, resulting in cellulose nanocrystals (CNCs) (Fig. 3c).

1.1 Crystalline cellulose

There are several polymorphs of crystalline cellulose (I, II, III, IV). Each has been extensively studied.⁴ Cellulose I is the

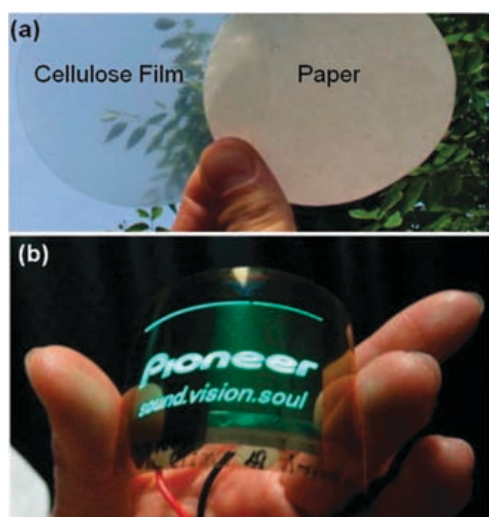


Fig. 2 Applications of cellulose nanoparticles. (a) Transparent paper for packaging,²⁸³ and (b) luminescence of an organic light-emitting diode deposited onto a flexible, low-CTE and optically transparent wood-cellulose nanocomposite.²⁹² Reprinted, (a) with permission from ref. 283 © 2009 WILEY-VCH, (b) from ref. 292 © 2009 with permission from Elsevier.

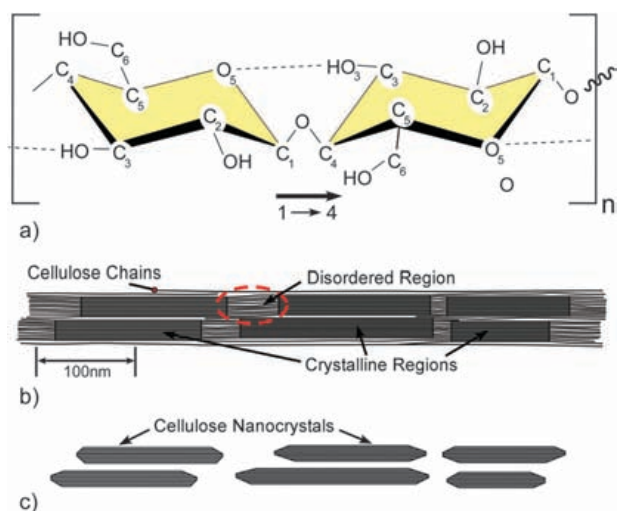


Fig. 3 Schematics of (a) single cellulose chain repeat unit, showing the directionality of the 1 → 4 linkage and intrachain hydrogen bonding (dotted line), (b) idealized cellulose microfibril showing one of the suggested configurations of the crystalline and amorphous regions, and (c) cellulose nanocrystals after acid hydrolysis dissolved the disordered regions.

crystalline cellulose that is naturally produced by a variety of organisms (trees, plants, tunicates, algae, and bacteria), it is sometimes referred to as “natural” cellulose. Its structure is thermodynamically metastable and can be converted to either cellulose II or III.⁴ To date cellulose II has been the most stable structure of technical relevance and can be produced by two processes: regeneration (solubilization and recrystallization) and mercerization (aqueous sodium hydroxide treatments).¹² Cellulose II has a monoclinic structure, and has been used to make cellophane (transparent films), Rayon and Tencel™

(synthetic textile fibers).¹² Cellulose III can be formed from Cellulose I or II through liquid ammonia treatments, and subsequent thermal treatments can then be used to form Cellulose IV. This review focuses on the Cellulose I structure, which is the crystal structure with the highest axial elastic modulus, E .³⁰

Cellulose I has two polymorphs, a triclinic structure ($I\alpha$) and a monoclinic structure ($I\beta$), which coexist in various proportions depending on the cellulose source.^{4–6} The $I\alpha$ structure is the dominate polymorph for most algae³¹ and bacteria,³² whereas $I\beta$ is the dominant polymorph for higher-plant cell wall cellulose and in tunicates.³³ The $I\alpha$ polymorph is metastable and can be converted to $I\beta$ by hydrothermal treatments ($\sim 260^\circ\text{C}$) in alkaline solution,^{31,34,35} and high-temperature treatments in organic solvents and helium gas.³⁶ Typically, $I\alpha$ -rich algal and bacterial cellulose have been used in these conversion studies, and the extent of $I\alpha$ to $I\beta$ conversion can be controlled by adjusting the treatment parameters. However, complete conversion to $I\beta$ is typically not achieved.^{31,35,36}

The $I\alpha$ and $I\beta$ crystal structures are shown in Fig. 4. Nishiyama and co-workers used synchrotron X-ray and neutron fiber diffraction and have provided the most accurate characterization of the $I\alpha$ and $I\beta$ lattice structures to date.^{37,38} The $I\alpha$ unit cell, space group P_1 , contains one cellulose chain, and the unit-cell parameters are $a = 0.672\text{ nm}$, $b = 0.596\text{ nm}$, $c = 1.040\text{ nm}$, $\alpha = 118.08^\circ$, $\beta = 114.80^\circ$, $\gamma = 80.375^\circ$.³⁸ The $I\beta$ unit cell, space group $P2_1$, contains two cellulose chains, and the unit-cell parameters are $a = 0.778\text{ nm}$, $b = 0.820\text{ nm}$, $c = 1.038\text{ nm}$, $\gamma = 96.5^\circ$.³⁷ Despite the differences between $I\alpha$ and $I\beta$ unit-cell parameters, the shifts in the cellulose chain arrangement are small when viewed along the chain axis (Fig. 4a). Three lattice planes with approximate d-spacings of 0.39 nm, 0.53 nm, and 0.61 nm are shared and correspond to $I\alpha$ lattice planes $(110)_t$, $(010)_t$, and $(100)_t$, and $I\beta$ lattice planes $(200)_m$, $(110)_m$, and $(1\bar{1}0)_m$, respectively. The subscripts t and m represent triclinic and monoclinic, respectively. The main difference between $I\alpha$ and $I\beta$ is the relative displacement of cellulose sheets (parallel stacking of cellulose chains in one plane) along the $(110)_t$ and $(200)_m$ planes (called “hydrogen-bonded” planes) in the chain axis direction (Fig. 4c and d). For $I\alpha$ there is a relative displacement of $c/4$ between each subsequent hydrogen-bonded plane, while for $I\beta$ the displacement alternates between $c/4$ and $-c/4$.^{38,39}

For both $I\alpha$ and $I\beta$ unit cells the cellulose chains are arranged in what is called the “parallel up” configuration.⁶ Since the cellulose repeat unit (Fig. 3a) has a different structure on either side of the 1–4 linkage, the directionality of the 1-to-4 linkage ($1 \rightarrow 4$ linkage) along the length of the cellulose chain affects how neighboring chains interact with each other. The term “parallel” is used when all the cellulose chains are arranged such that the $1 \rightarrow 4$ link points in the same direction. In contrast “antiparallel” describes alternating stacking of the cellulose chains in the $1 \rightarrow 4$ link directionality between different hydrogen bonding planes (Fig. 4a). The direction of the cellulose chain $1 \rightarrow 4$ link with respect to the c -axis of the unit cell is also defined because this alters the interaction between neighboring hydrogen bonding planes (Fig. 4a). This happens because differences in configuration resulting from

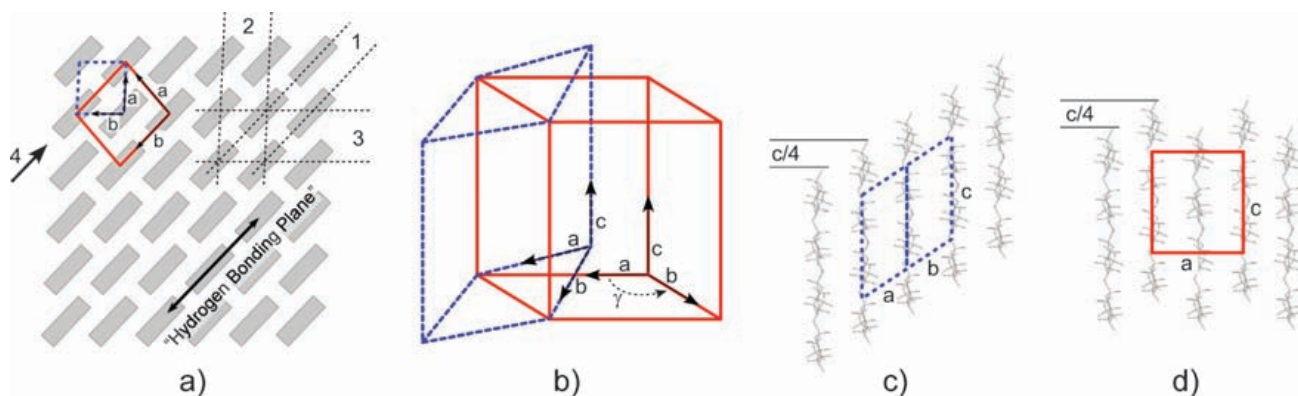


Fig. 4 Schematic of the unit cells for cellulose I α (triclinic, dashed line) and I β (monoclinic, solid line). (a) projection along the chain direction with the I α and I β unit cells superimposed on the cellulose I crystal lattice (adapted from Imai *et al.*¹⁰⁹), showing the parallelogram shape of both unit cells when looking down the *c*-axis. In this orientation both unit cells have nearly identical molecular arrangements, sharing the three major lattice planes, labeled 1, 2, and 3, with the corresponding *d*-spacings of 0.39, 0.53, and 0.61. The corresponding lattice planes for 1, 2, and 3, are (110)_{*r*}, (010)_{*r*}, and (100)_{*r*} for I α and (200)_{*m*}, (110)_{*m*}, and (1 $\bar{1}$ 0)_{*m*} for I β . (b–d) View along the direction labeled 4 (*i.e.* [1 $\bar{1}$ 0]_{*r*} for I α , and [010]_{*m*} for I β), (b) relative configuration of I α with respect to I β unit cell (adapted from Sugiyama *et al.*³⁹) and the displacement of the hydrogen bonding sheets for (c) I α of +*c*/4, and for (d) I β alternating +*c*/4 and –*c*/4.

the anisotropic crystal structure (monoclinic and triclinic), in particular the parallelogram shape in the unit cell *a*–*b* plane (Fig. 4a), combined with the anisotropic structure of the cellulose chain. The “up” configuration corresponds to the 1 $\rightarrow$ 4 link direction pointing in the positive *c*-axis direction of the unit cell, while the “down” configuration the 1 $\rightarrow$ 4 link direction pointing in the negative *c*-axis direction. Note that most of the literature uses a different convention, in which “up” *versus* “down” are defined in terms of the relative location of the O5 and C5 atoms (see Fig. 3a) along the positive *c*-axis of the unit cell. In the “up” configuration, the position of O5 is greater than that of C5, while in the “down” configuration the position of O5 is less than that of C5.^{4,40,41} Both I α and I β have the “parallel up” configuration, thus all cellulose chains are arranged such that the 1 $\rightarrow$ 4 link points in the same direction (Fig. 4c, d and 5) and that direction is in the positive *c*-axis direction of their respective crystalline unit cell.

1.2 Hydrogen bonding

Understanding the hydrogen bonding within the I α and I β structures is important as it governs the stability and properties of these polymorphs. The characterization of hydrogen bonding networks has been problematic, but a consensus as to their structure is emerging.^{6,38,42} With the hydroxyl groups being equatorial to the cellulose ring plane, the intra- and inter-chain hydrogen bonding is most prevalent within the (110)_{*r*} and (200)_{*m*} planes, and thus the name “hydrogen-bonded” plane. Two coexisting hydrogen bonding networks (network A and B) have been proposed, which are described in detail elsewhere,⁴² and are schematically shown in Fig. 5. The intrachain hydrogen bonding is dominated by the strong O3–H $\cdots$ O5 bond, this bond configuration is the most agreed upon in literature. There is less consensus in the literature on the other intrachain bonding configurations, which are much more difficult to characterize, as they are linked with inter-chain bonding within the (110)_{*r*} and (200)_{*m*} planes,⁴² and possibly linked with bonding outside of these planes. It is

this intrachain hydrogen bonding within I α and I β that is responsible for the high axial chain stiffness.^{43,44} The intraplane hydrogen bonding for I β is distributed over a region of better bonding geometry than I α , and has a higher percentage (~70–80%) of network A hydrogen bonding configuration. The inter-chain hydrogen bonding within the other planes (010)_{*r*}, (100)_{*r*}, and (110)_{*m*}, and (1 $\bar{1}$ 0)_{*m*} is substantially lower and attractive van der Waals forces are believed to dominate the cohesion between cellulose chains.^{38,45} Within these planes the number of the weak inter-chain hydrogen bonds in I β is believed to be greater than in the I α polymorph and has been suggested to contribute to the higher stability of I β , as compared to I α .³⁸ Likewise, it has been suggested that these weak hydrogen bonds are of weaker strength in I α than in I β , and because of this, the hydrogen bonds in I α thermally degrade at lower temperatures,³⁴ contributing to the lower I α stability.

2. Structure of cellulose nanoparticles

Cellulose can be extracted from a broad range of plants and animals, and there is a wide range of cellulose particle types that are being studied for myriad commercial applications. The diversity of cellulose particle types results from two main factors: (i) the biosynthesis of the crystalline cellulose microfibrils, which is dependent on cellulose source material, and (ii) the extraction process of the cellulose particles from the cellulose microfibrils, which includes any pre-treatments, disintegration or deconstruction processes. Note that additional particle functionality can be obtained through subsequent surface modification (*e.g.*, TEMPO regioselective oxidation, sulfonation, carboxylation, acetylation, silane treatments, polymer grafting, surfactant and polyelectrolyte adsorption) which is described in detail in section 4. This section focuses on describing the variety of cellulose source materials, cellulose microfibril biosynthesis, particle extraction methods, and defining a general classification of cellulose particle types based on the morphology and crystalline structure of these

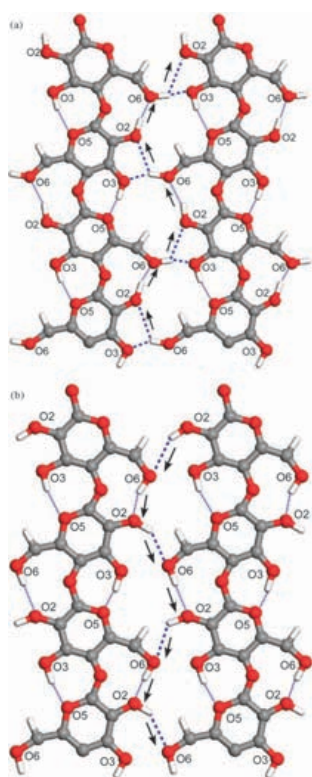


Fig. 5 Schematics of two suggested hydrogen bonding cooperative networks (a) A, and (b) B, within the hydrogen-bonded plane, (110)_h and (200)_m. Thin dotted lines highlight the intrachain hydrogen bonding, while the thick dotted line shows the inter-chain hydrogen bonding. Arrows show the donor–acceptor–donor directions, adapted from Nishiyama *et al.*⁴²

different particle types. For a detailed listing of research studies using a particular source material for extraction of cellulose particles, the reader is referred to the review by Hubbe *et al.*⁷

2.1 Cellulose source materials

2.1.1 Wood. Wood as a cellulose source material has many advantages. Most significantly, it is abundant. In addition, an existing infrastructure is in place for harvesting, processing and handling, *i.e.*, the pulp and paper, packaging and pharmaceutical industries. In general, extraction of CNs starts with “purified” wood, *i.e.* wood with most of the lignin, hemicellulose and impurities removed. Typical materials are bleached Kraft pulp and dissolving pulp (used for the production of regenerated cellulose products such as Rayon).

2.1.2 Plant. Like wood, plants are an attractive cellulose source primarily because they are abundant and there is a preexisting infrastructure in the textile industries for harvesting, retting/pulping (*i.e.* to treat and isolate micron sized cellulose particles), and product processing. In general, plants can be “purified” similarly to wood. A wide variety of plant materials have been studied for the extraction of CNs,⁷ including cotton,^{46,47} ramie,⁴⁸ sisal,^{49,50} flax,⁵¹ wheat straw,^{52–54} potato tubers,⁵⁵ sugar beet pulp,^{56–58} soybean stock,^{53,59} banana rachis,⁶⁰ *etc.*

2.1.3 Tunicate. Tunicates are the only animals known to produce cellulose microfibrils. Tunicates are a family of sea animals that have a mantle consisting of cellulose microfibrils embedded in a protein matrix. It is this thick leathery mantle in their mature phase that is used as a source of cellulose microfibrils. Most research has used a class of Tunicates that are commonly known as “sea squirts” (*Ascidacea*), marine invertebrate filter feeders. Note that there are over 2300 species of *Ascidacea* and because of this cellulose microfibril researchers often use different species. The cellulose microfibril structure and properties are expected to be comparable between species, but there may be small differences in the cellulose microfibril formation process which may be reflected in the resulting microfibril structure.⁶¹ Some of the most frequently studied species have been: *Halocynthia roretzi*,⁴⁶ *Halocynthia papillosa*,^{62,63} and *Metandrocarpa uedai*.⁶⁴

2.1.4 Algae. Several species of algae (green, gray, red, yellow-green, *etc.*) produce cellulose microfibrils within the cell wall. There are considerable differences in cellulose microfibril structure between the various algae species caused by differences in the biosynthesis process. Most cellulose microfibril researchers have used various species of green algae. Some of the most frequently studied species have been: *Micrasterias denticulata*,^{65,66} *Micrasterias rotata*,⁶⁵ *Valonia*,^{67–70} *Caldophora*,⁷⁰ and *Boergesenia*.⁷⁰ The similar cellulose microfibril biosynthesis for most green algae will result in a similar microfibril structure.⁷¹

2.1.5 Bacterial. The most studied species of bacteria that produces cellulose is generally called *Gluconacetobacter xylinus* (reclassified from *Acetobacter xylinum*).¹¹ Under special culturing conditions the bacteria secrete cellulose microfibrils, producing a thick gel composed of cellulose microfibrils and ~97% water, called pellicle, on the surface of the liquid medium.^{14,72} The reason why the bacteria generate cellulose is unclear, but it has been suggested that it is necessary for their survival, such as to guard against ultraviolet light, or to act as a barrier to fungi, yeasts and other organisms. The advantage of bacterial derived cellulose microfibrils is that it is possible to adjust culturing conditions to alter the microfibril formation and crystallization.^{32,73}

2.2 Cellulose microfibril biosynthesis

Understanding cellulose microfibril biosynthesis leads to insights into what particle types and shapes can or cannot be extracted from a given cellulose source. Cellulose microfibril biosynthesis is a multistep process that is highly specific to the organism producing the cellulose. Variations in this process dictate the morphology, aspect ratio, crystallinity, and crystal structure ($1\alpha/1\beta$ ratio) of the resulting microfibril. These properties are reflected in the final nanocellulosic product obtained. Detailed descriptions of cellulose biosynthesis can be found in Brown,⁷¹ and Brown and Saxena.⁷⁴

In general, cellulose is extruded from terminal enzyme complexes (TC) located in the cell wall. The configuration of the TCs dictates the resulting microfibril architecture.⁷¹ TCs are made up of many identical subunits, each containing multiple catalytic sites from which a single cellulose chain is

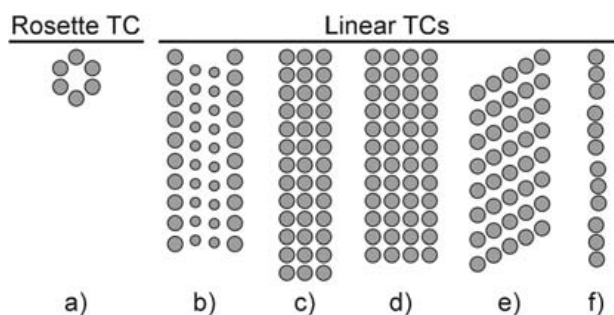


Fig. 6 Schematics of rosette and linear TCs (adapted from Brown *et al.*⁷¹), for (a) wood, plants (6 chains/subunit), green algae (*Micrasterias*), (b) Tunicate (*Metandrocarpa uedai*) (unknown number of chains/subunit) (adapted from Kimura *et al.*⁶⁴), (c) green algae (*Valonia*) (10–12 chains/subunit), (d) red algae (*Erythrocladia*) (4 chains/subunit), (e) yellow-green algae (*Vaucheria*) (1 chains/subunit), and (f) bacterial (*Acetobacter*) (16 chains/subunit). Each dark circle represents a single subunit.

polymerized. The first stage of cellulose crystallization involves the self-assembly of the cellulose chains within a given TC subunit producing a “minisheet” of ordered cellulose chains, the geometry of which is dependent on the number and arrangement of the catalytic sites and can be either an isolated single chain, a single layer of parallel stacking, or multiple layers of parallel stacking. Within each TC, the subunits are arranged in two general configurations, linear or rosette (Fig. 6). The second stage of cellulose crystallization is the self-assembly of these cellulose “minisheets”. The configuration of the subunits within the TC combined with the geometry of cellulose minisheet, both of which vary between organisms, dictates the aggregation process, and thus the resulting cellulose fibril structure. The final stage involves the assembly of cellulose fibrils into either micro or macrofibrils, depending on the organism. For trees and plants, the TC is believed to be organized into six-membered rosettes (Fig. 6a) with each subunit producing a linear sheet of 6 cellulose chains. From a single TC the resulting cellulose elementary fibril has 36 cellulose chains, a square cross-section 3–5 nm in size and contains both crystalline and amorphous regions. These elementary fibrils further self-assemble into a larger microfibrillar structure (Fig. 7). The influence of the biosynthesis structure on the resulting extracted CNs is best shown by wood and plant cellulose sources, in which the microfibrillar structures are constituted of the microfibril (MFC) particles (Fig. 7c and d), the elementary fibrils are constituted of the nanofibrillated (NFC) particles (Fig. 7b), and the small crystalline regions are constituted of the CNCs (Fig. 3c and 7d).

Various linear TC configurations are present in tunicate,^{61,64} algal⁷¹ and bacterial^{71,75} microfibril biosynthesis. The TCs for tunicates are unique in that they are composed of two differently sized subunits. Beyond this very little is known about the biosynthesis process. It has been proposed that (110) cellulose minisheets stack with an offset to form a parallelogram cross-section.⁶² The resulting microfibrils are ribbon-like, having a ~20 nm by 8 nm cross-section, high crystallinity, and a high fraction of I β crystal structure. The TCs for green algae (*Valonia*) consists of three rows of subunits and each subunit produces 10–20 cellulose chains that arrange in a

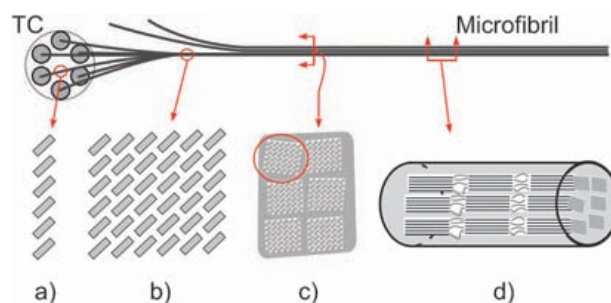


Fig. 7 Schematic of the different levels of the formation of a wood microfibril (a) minisheet cross-section believed to form from a single subunit, in which van der Waals forces hold the cellulose chains together. Each grey box represents a cellulose chain looking down the chain-axis. (b) elementary fibril cross-section, the assembly of 6 minisheets into a cellulose crystal I lattice of ~3–5 nm dimensions. The consolidation of multiple elementary fibrils forms a microfibril, (c) microfibril cross-section composed of 6 elementary fibrils (modified Frey-Wysling model),³⁹² (d) microfibril lateral section showing the series configuration of crystalline and amorphous regions.⁶

linear cellulose “minisheet” that subsequently stacks to produce the microfibril. Typically the *Valonia* microfibrils consists of ~1000 cellulose chains, have a square cross-section (~20 nm by 20 nm), have a high crystallinity, and a high fraction of I α crystal structure. Variations have been observed in related green algae, *e.g.* in *Boergesenia*, which is hypothesized to contain fewer catalytic sites and a longer TC region, the resulting microfibrils produced are rectangular in cross-section and are thinner than *Valonia* microfibrils.⁷¹ For bacterial cellulose, typically, the TC consists of a single row of subunits (grouped in triplets) and each subunit produces at least 16 cellulose chains that arrange in a mini-crystal (elementary fibril). For each triplet subunit the three elementary fibrils stack to produce a ribbon like microfibril, and additional stacking of triplet subunits produces microfibrils of larger widths, but the thickness remains the same. Typically the *Acetobacter* microfibrils have a rectangular cross-section (6–10 nm by 30–50 nm), have a high crystallinity, and a high fraction of I α crystal structure.

2.3 Isolation of cellulose particles

The isolation of cellulose particles from cellulose source materials occurs in two stages. The first stage is a purification and homogenization pretreatment of the source material so that it reacts more consistently in subsequent treatments. The particular pretreatment is dependent on the cellulose source material and to a lesser degree on the desired morphology of the starting cellulose particle for the second stage treatments. The pretreatments for wood and plants involve the complete or partial removal of matrix materials (hemicellulose, lignin, *etc.*) and the isolation of individual complete fibers (WF, PF). For tunicate the pretreatment involves the isolation of the mantle from the animal and the isolation of individual cellulose fibrils with the removal of the protein matrix. Pretreatments for algal cellulose sources typically involve culturing methods, and then purifying steps for removal of algal wall matrix material. Bacterial cellulose pretreatments focus on culturing methods for cellulose microfibrillar growth

and then washing to remove the bacteria and other media. Detailed descriptions of several of these pretreatments are available within the respective references for the following source materials, wood,⁷ plant,^{53,76} tunicate,^{77,78} algae,^{66,77} and bacteria.^{11,72,77,79}

The second stage involves the separation of these “purified” cellulose materials into their microfibrillar and/or crystalline components. There are several approaches to isolating cellulose particles and these have been previously reviewed.^{7–10,17} The three basic separation approaches are mechanical treatment,^{7,9,17,80} acid hydrolysis,^{7,9,16,17} and enzymatic hydrolysis.^{7,9} These approaches can be used separately, though in practice to obtain the desired particle morphology several of these methods are used in sequence or in combination. This review will briefly describe the two most common approaches for isolating cellulose particles, mechanical treatment and acid hydrolysis.

2.3.1 Mechanical. Mechanical processes, such as high-pressure homogenizers,^{54,57,80} grinders/refiners,⁸¹ cryocrushing,^{53,57,82} high intensity ultrasonic treatments,^{83,84} and microfluidization have been used to extract cellulose fibrils from WF, PF, MCC, tunicate, algae, and bacterial source materials. In general these processes produce high shear that causes transverse cleavage along the longitudinal axis of the cellulose microfibrillar structure, resulting in the extraction of long cellulose fibrils, termed microfibrillated cellulose (MFC). The concept of MFC was introduced by Turbak *et al.*⁸⁵ and Herrick *et al.*⁸⁶ who first prepared nanosized cellulose fibrils from softwood pulps. Typically, cellulose materials are run through the mechanical treatment several times (*i.e.*, number of passes). After each pass, the particles are generally smaller, more uniform in diameter, but have increased mechanical damage to the crystalline cellulose (*i.e.* have lower percent crystallinity⁸¹). A filtration step is included to remove the larger unfibrillated and partially fibrillated fractions. In addition, these mechanical processes can be followed by chemical treatments to either remove amorphous material or chemically functionalize the particle surface.

To facilitate the separation of cellulose microfibrils into thinner NFCs (Fig. 8), three preprocessing steps can be

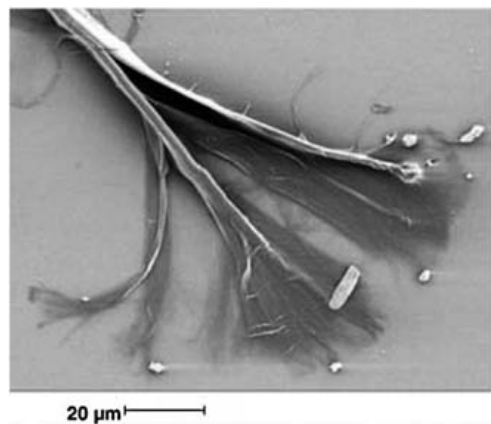


Fig. 8 Cellulose fiber disintegration into microfibrils with TEMPO-mediated oxidation.⁸³ Reprinted with kind permission from ref. 83 © 2009 Springer Science + Business Media B.V.

applied that effectively weaken the interfibrillar hydrogen bonds: the use of never dried source materials,⁸⁷ partial removal of matrix material,^{87–89} and chemical treatment.^{47,83,90,91} For wood and plant cellulose sources, the spaces between microfibril bundles collapse upon drying. When dried, hydrogen bonds are formed between the fibrils making it difficult to separate agglomerates. Reswelling (or rehydration) of dried starting materials does not displace all the hydrogen bonds between fibrils and so does not produce the same “weakening” effect.⁸⁷ Likewise, if the removal of the matrix material in the purification stage was incomplete (*e.g.*, hemicelluloses only partially removed), the matrix material can inhibit the coalescence of the microfibril bundles during drying and facilitate the subsequent fibrillation of the material.⁸⁷ Also, imparting a charge to the fibril surface of never dried materials increase the interfibrillar repulsive forces.⁸³ This can be achieved either through oxidation (usually employing 2,2,6,6-tetramethyl-piperidinyl-1-oxyl radical (TEMPO) region selective oxidation) or adsorption of charged polyelectrolytes (*e.g.* carboxymethyl cellulose, treatment).^{47,90}

2.3.2 Acid hydrolysis. Acid hydrolysis has been used to extract the crystalline particles from a variety of cellulose sources: PF, WF, MCC, tunicate, algae, and bacteria. Though the mechanism of acid hydrolysis is incompletely understood, the process preferentially removes (hydrolyze) the amorphous regions within the cellulose microfibrils. In general, the “purified” starting material is mixed into deionized water with a given concentration of acid. Sulfuric acid is most typically used as it produces a negative surface charge on the particles, leading to more stable suspensions,^{7,16} but other acids have also been used (hydrochloric,^{59,92} maleic,⁹³ *etc.*). After reacting for a set amount of time, the mixture is diluted with deionized water to quench the reaction. This mixture then undergoes a series of separation (centrifugation or filtration) and washing/rinsing steps followed by dialysis against deionized water to remove the remaining acid or neutralized salt. A final centrifuge separation or filtration step can be used to remove any larger agglomerates in the final cellulose nanoparticle suspension. Ultrasonic treatments can be used to facilitate dispersion of the crystalline cellulose in the suspension. Acid hydrolysis process is described in detail elsewhere.^{46,94–97}

2.4 Cellulose particle types

The cellulose particle nomenclature has not been standardized and because of this there is an inconsistent use of terms in the literature to describe a given set of cellulose particles. Within this review, a nomenclature consistent with current trends in terminology is used. Nine particle types are considered to describe the main cellulose-based particles, which typically differ from each other based on cellulose source materials and the particle extraction method. Each particle type is distinct, having a characteristic size, aspect ratio, morphology, crystallinity, crystal structure, and properties. We use the term cellulose nanoparticles (CN) to broadly refer to several of the particle types that have at least one dimension in the nanoscale (MFC, NFC, CNC, t-CNC, AC and BC). For comparison purposes micron and macrosized scaled particles (WF, PF, and MCC) are also defined. Table 2 summarizes several

Table 2 Summary of cellulose I particle types and cellulose II

Particle Type	Particle size			Cross-Section	Crystallinity ^a (%)	I β (%)	References
	Length (μm)	Width (nm)	Height (nm)				
WF and PF	>2000	20–50 (μm)	20–50 (μm)	—	43–65	—	12
MCC	10–50	10–50 (μm)	10–50 (μm)	—	80–85	—	96, 100
MFC	0.5–10's	10–100	10–100	—	51–69	10–66	57, 85, 86, 374
NFC	0.5–2	4–20	4–20	—	—	—	87, 90, 101, 125, 283, 375
CNC	0.05–0.5	3–5	3–5	Square	54–88	68–94	46, 49, 95, 97, 374, 376
t-CNC	0.1–4	~20	~8	Parallelogram	85–100	76–90	46, 63, 76, 62, 248, 374, 377
AC					>80%	12	
(Valonia)	>1	~20	~20	Square	—	36–42	67–69
(Micrasterias)	>1	20–30	5	Rectangular	—	—	65, 69
BC					65–79	12	
(Acetobacter)	>1	30–50	6–10	Rectangular	63	3–27	73, 79, 378
(Acetobacter) ^b	>1	6–10	6–10	Square	—	53	73
Cellulose II	Filament	—	—	Cylindrical	27–43	—	12

^a Degree of crystallinity relative to cellulose. ^b Chemical addition during culturing.

particle characteristics, and Fig. 9 shows characteristic images of each particle type. It should be noted that within each particle type there is a distribution of lengths, width, and percent crystallinity. This is likely a result of several factors, some of which are, (i) the inherent variability of biological processes results in statistical variability in the formation of the crystals, (ii) the type and severity of the given particle extraction process, and (iii) the differences in measurement technique used⁶ and the quality of the data analysis. A brief description of each particle type is given here.

2.4.1 Wood fiber (WF) and plant fiber (PF). WF and PF are the largest of the particle types, and have dominated the paper, textile and biocomposites industries for centuries.^{29,98} The purified particles (bleached Kraft pulp, dissolving pulp, *etc.*) consist of individual wood or plant cells that are 10's of microns in diameter, millimetres in length, have a high percent cellulose, and a relatively low crystallinity (43–65%). WF and PF contain a hierarchical structure.^{24,99}

2.4.2 Microcrystalline cellulose (MCC). MCC is a commercially available material used for applications in the pharmaceutical (tablet binder-, one brand name is Avicel) and food industries, and is prepared by acid hydrolysis of WF, back-neutralization with alkali, and spray-dried. The resulting particles are porous, ~10–50 μm in diameter, have a high cellulose content, a higher crystallinity, and are composed of aggregate bundles of multi-sized cellulose microfibrils that are strongly hydrogen bonded to each other.¹⁰⁰ Usually the MCC aggregates are broken up into smaller micron-sized rod-like particles (1–10 μm in length) prior to use in composites (Fig. 9b).

2.4.3 Microfibrillated cellulose (MFC). MFC is produced *via* mechanical refining of highly purified WF and PF pulps. MFCs have been used as a thickening agent in the food and cosmetics industries.⁸⁵ The MFC particles are considered to contain multiple elementary fibrils each consisting of 36 cellulose chains arranged in the I β crystal structure (Fig. 7), have a high aspect ratio (10–100 nm wide, 0.5–10's μm in length), are ~100% cellulose, and contain both amorphous and crystalline regions.

2.4.4 Nanofibrillated cellulose (NFC). NFC particles are finer cellulose fibrils produced when specific techniques to facilitate fibrillation are incorporated in the mechanical refining of WF and PF (see section 2.3.1).^{47,83,90,101} NFCs are reminiscent of elementary fibrils in the wood and plant cellulose biosynthesis process and are considered to consist of 36 cellulose chains arranged in I β crystal structure, and have a square cross-section (Fig. 7), have a high aspect ratio (4–20 nm wide, 500–2000 nm in length), are ~100% cellulose and contain both amorphous and crystalline regions. The differentiation of NFC from MFC is based on the fibrillation process that produces finer particle diameters. However, in the literature MFC and NFC terminology are sometimes used interchangeably, which may lead to some confusion.

2.4.5 Cellulose nanocrystals (CNC). CNCs are rod-like or whisker shaped particles remaining after acid hydrolysis of WF, PF, MCC, MFC, or NFC.^{49,95,97} These particles have also been named nanocrystalline cellulose, cellulose whiskers, cellulose nanowhiskers and cellulose microcrystals (in the early literature). CNCs have a high aspect ratio (3–5 nm wide, 50–500 nm in length), are ~100% cellulose, are highly crystalline (54–88%), and containing a high fraction of I β crystal structure (68–94%). CNCs resemble whiskers because of the tapering at the ends of the crystals most likely a result from the acid hydrolysis process (Fig. 3c and 9e). Ideally, CNC are reminiscent of the crystalline regions within the elementary fibrils of the wood and plant cellulose biosynthesis process and are considered to consist of 36 cellulose chains arranged in I β crystal structure and have a square cross-section with (110)_m and (1 $\bar{1}$ 0)_m terminating surfaces (Fig. 10a).⁴⁶ Alternatively, Ding and Himmel¹⁰² have proposed for maize cellulose, a 36 cellulose chain elementary fibril having a hexagonal shaped cross-section with (100)_m, (110)_m, and (1 $\bar{1}$ 0)_m terminating surfaces and heterogeneous structure containing a I β crystalline core and layers of subcrystalline sheaths.

Outside of these ideal CNC structures, there is considerable variability in the particle shape, length and width even when a consistent acid hydrolysis condition is used.^{49,95,97} Interestingly, XRD studies of MFC show the crystalline regions within have a height/width of 4–5 nm and lengths of ~20 nm,³⁰ these lengths are much smaller than the resulting

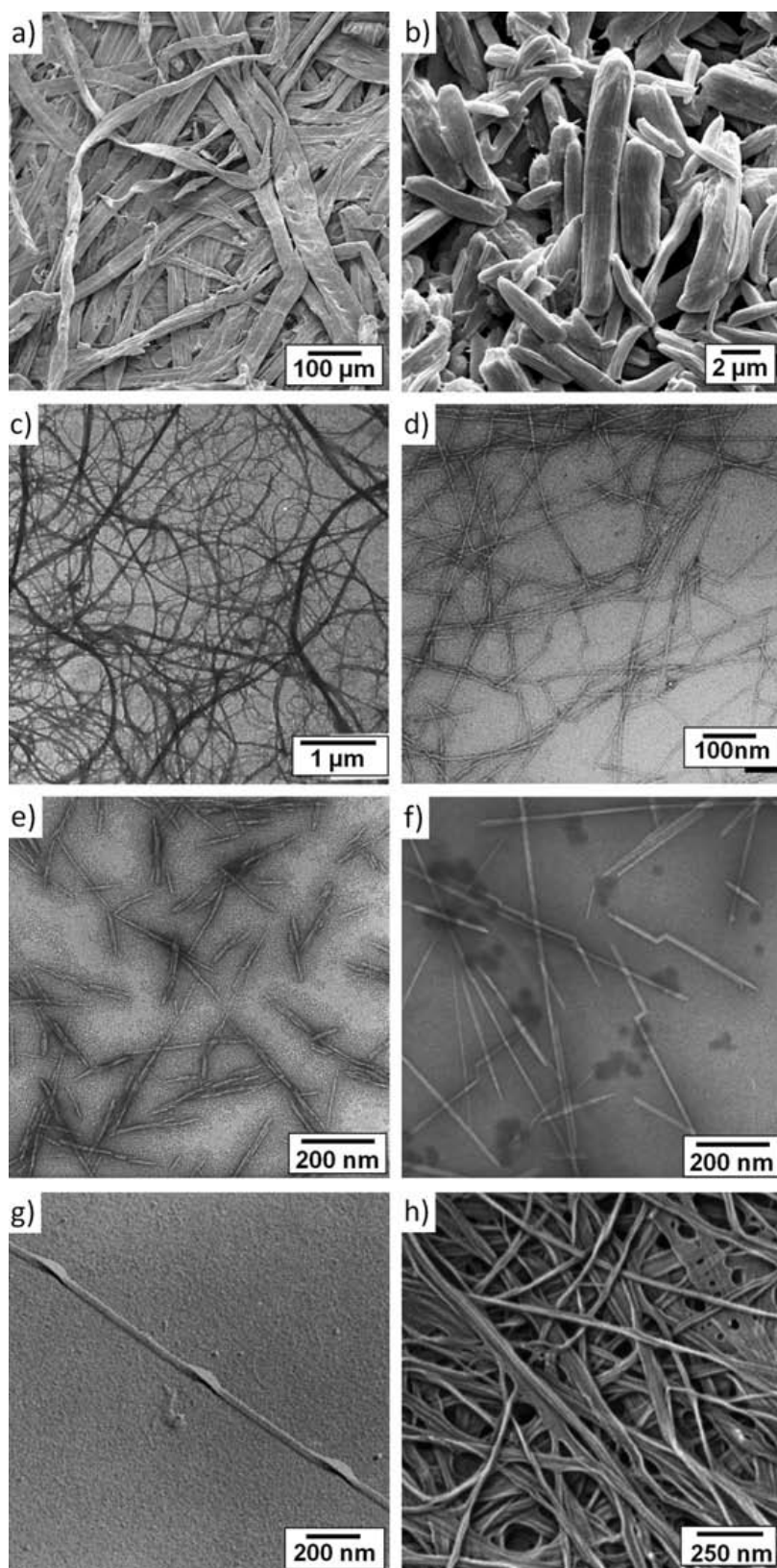


Fig. 9 Several cellulose particle types, (a) SEM image of WF, (b) SEM image of MCC that has been deagglomerated, (c) TEM image of MFC,⁵⁷ (d) TEM image of TEMPO-NFC,¹⁰¹ (e) TEM image of wood CNCs, (f) TEM image of t-CNC, (g) TEM of AC,⁶⁶ (h) SEM image of BC.³³² See section 2.4 for definition of particle types. Reprinted with permission, (c) from ref. 57 © 1997 John Wiley & Sons, (d) from ref. 101 © 2007 American Chemical Society, (g) from ref. 66 © 1997 Springer Science+Business Media B.V., (h) from ref. 332 © 2007 American Chemical Society.

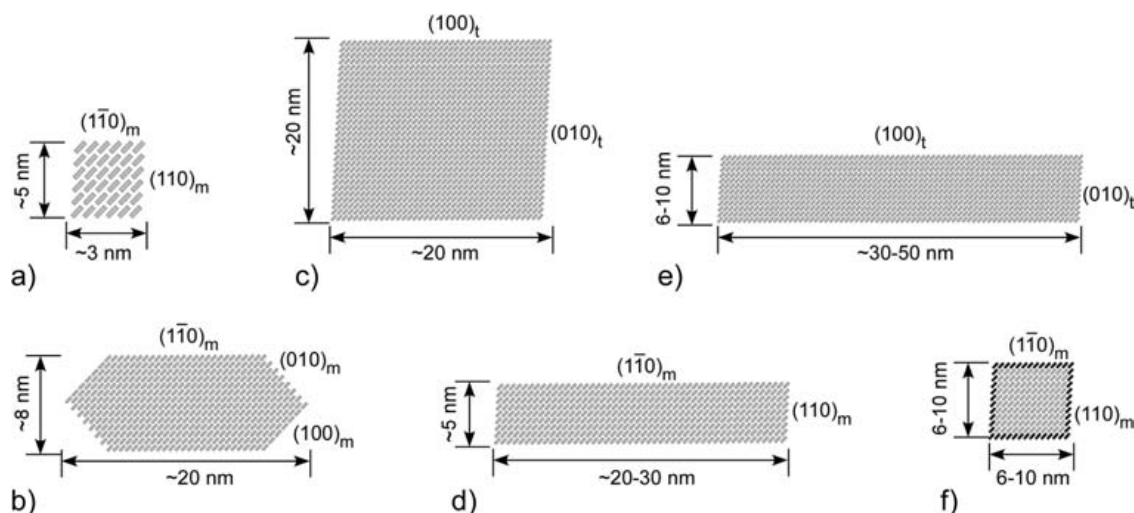


Fig. 10 Schematics of idealized cellulose particle cross-sections showing terminating surfaces and crystal structure (m = monoclinic, t = triclinic) for (a) wood CNC⁴⁶ and elementary fibril (or NFC) cross-section, (b) t-CNC,^{46,62,63} (c) AC *Valonia*,^{67,68} (d) AC *Micrasterias*,⁶⁵ (e) unmodified – BC - *Acetobacter*,⁷³ and (f) modified –BC - *Acetobacter*.⁷³ Each grey box represents a cellulose chain looking down the chain-axis.

extracted CNC particles, suggesting that either the crystalline regions are longer than that estimated in XRD or that the CNC particles consist of crystalline and amorphous regions arranged in series. Other effects are also observed, for example, along the CNC length there are typically step-wise increases (~ 2 – 4 nm) in width or height, which may have resulted from incomplete hydrolysis between crystallites or from “peeling” of small segments of the fibril during hydrolysis, resulting in CNCs composed of multiple elementary crystals (Fig. 7c). Also, if the hydrolysis is inadequate, incomplete removal of the amorphous regions can occur resulting in decreased crystallinity and a change in particle morphology. Likewise, by increasing the severity of the hydrolysis (increase reaction time or reaction conditions), it is possible to depolymerize the crystalline cellulose and the length of the particles will decrease,^{46,94,95} which reduces the aspect ratio⁹³ and can even result in spherical particles.¹⁰³ Additionally, CNCs strongly agglomerate such that they stack up in parallel giving an apparent increase in particle width.⁴⁶ However, this agglomeration can result from the sample preparation method used for a given measurement technique, such as the evaporative deposition of CNC suspensions on a specimen holder for TEM or AFM measurements.

2.4.6 Tunicate cellulose nanocrystals (t-CNC). Particles produced from the acid hydrolysis of tunicates are called t-CNCs. We differentiate t-CNCs from other CNCs because of differences in particle morphology, crystal structure and mechanical properties (Fig. 9f). The ribbon-like shaped t-CNCs have a height of ~ 8 nm, a width of ~ 20 nm, a length of 100–4000 nm (typical aspect ratios 70–100), are $\sim 100\%$ cellulose, are highly crystalline (85–100%), and contain a high fraction (76–90%) of $I\beta$ crystal structure. The advantage of t-CNCs is that they are highly crystalline and have the largest aspect ratio of any CNC. The ideal morphology is a parallelogram-shaped cross-section, and a $I\beta$ crystal structure, but it has been shown that acid hydrolysis used to extract the t-CNC partially erodes the parallelogram-shaped

cross-section, such that the resulting cross-section is a distorted hexagon with $(110)_m$, $(010)_m$ and $(100)_m$ terminating surfaces and the $(1\bar{1}0)_m$ being the largest facet (Fig. 10b).⁶² Along the crystal length there is a 180° twist with a pitch of 2.4–3.2 μm .⁴⁶ T-CNCs are also observed to agglomerate such that they stack in parallel.⁴⁶

2.4.7 Algae cellulose particles (AC). AC particles are the microfibrils extracted from the cell wall of various algae by acid hydrolysis and mechanical refining (Fig. 9g). The resulting microfibrils are microns in length, have a large aspect ratio (greater than 40) with a morphology depending on algae: two contrasting examples are *Valonia* and *Micrasterias*.^{67,68} *Valonia* microfibrils have a square cross-section (~ 20 nm by ~ 20 nm) with $(100)_t$ and $(010)_t$ terminating surfaces, with primarily $I\alpha$ crystal structure (Fig. 10c). *Micrasterias* microfibrils have a rectangular cross-section (~ 5 nm by ~ 20 – 30 nm) with $(110)_m$ and $(1\bar{1}0)_m$ terminating surfaces, where $(1\bar{1}0)_m$ is the largest facet, with primarily $I\beta$ crystal structure (Fig. 10d). Along the crystal length there is a 180° twist with a pitch of 700 nm.⁶⁶

2.4.8 Bacterial cellulose particles (BC). BC particles are microfibrils secreted by various bacteria that have been separated from the bacterial bodies and growth medium (Fig. 9h). The resulting microfibrils are microns in length, have a large aspect ratio (greater than 50) with a morphology depending on the specific bacteria and culturing conditions. Typically, *Acetobacter* microfibrils have a rectangular cross-section (6–10 nm by 30–50 nm), terminating surfaces of $(010)_t$, and $(100)_t$ with $(100)_t$ being the largest facet,⁷³ and have primarily $I\alpha$ crystal structure (Fig. 10e). However, by altering the culture conditions (stirring, temperature, and additives) it is possible to alter the $I\alpha/I\beta$ ratio and alter the width of the microfibrils.^{32,73} Additives have been shown to interfere with the aggregation of the elementary fibrils into the normal ribbon assembly⁷⁵ and these modified BC microfibrils have a square cross-section (~ 6 – 10 nm cross-section) with $(110)_m$, and

(110)_m terminating surfaces, and have primarily Iβ crystal structure (Fig. 10f).^{32,73,104,105} This change in morphology has been linked to the decrease in the proportion of Iα in the microfibril,¹⁰⁶ in which the Iβ preferentially forms in the isolated elementary fibrils that are free from constraint present when aggregated in the normal microfibril ribbon assembly. It has been suggested that this added constraint is necessary for the formation of the metastable Iα phase.¹⁰⁴

2.5 Deviations in idealized CN structure

Several factors may cause deviations from the idealized CN structures: statistical variety of the crystallite formation within the cellulose source materials, the effects of the extraction process, a large surface area to volume ratio, and the coexistence of Iα and Iβ polymorphs. These variations will alter how particles interact with the local environment and will modify their mechanical properties. In general, the deviations in the crystal structure can be grouped into three categories: percent crystallinity, Iα/Iβ ratio, and lattice defects.

2.5.1 Percent crystallinity. The crystallinity of CNs can vary based on the initial amorphous content determined by biosynthesis, the induced changes in cellulose chain order caused by the extraction process and the higher mobility of cellulose chains on the particle surfaces. Generally, cellulose elementary fibrils consist of alternating crystalline and amorphous regions either along their length (Fig. 3b and 7d) or in the transverse direction,⁶ the ratio of which is dependent on the cellulose source. Thus for fibrillated CN types (MFC, NFC, AC, and BC) the retained amorphous regions should lower the percent crystallinity as compared to the CNCs that are extracted from them. It should be noted that the measured percent crystallinity will vary based on the measurement method used, as summarized by Park *et al.*¹⁰⁷

Induced amorphous structures can be produced *via* mechanical refining, which mechanically damages particles, roughens surfaces, and causes cellulose chain disorder in the surface region.⁸¹ Other amorphous structures can be induced by the existence of a surface as compared to bulk.⁴ Solid-state NMR spectroscopy confirmed that the cellulose chain conformations were different between the surface chains and the interior chains, with only the interior chains being truly crystalline.^{90,108} Additionally, molecular modeling has shown that the hydrogen bonding configuration is different for surface chains than interior chains,^{42,108} and that the mobility of surface chains allows them to shift outside of the cellulose I lattice.⁴² Considering this, the ratio of exterior/interior chains is likely to influence percent crystallinity, and the contribution will be dependent on the cross-sectional size of the given particle type. For the idealized cross-sections given in Fig. 10, the exterior/interior chains for the different particle types are: 20/16 for CNC and NFC, 92/358 for t-CNC, 134/1036 for AC (*Valonia*), 110/322 for AC (*Micrasterias*), 162/690 for BC (*Acetobacter*), and 48/120 for modified BC (*Acetobacter*). With the smaller cross-sectional area for wood CNCs and NFC, as compared to t-CNCs, the high fraction of surface chains suggests the possibility of lower crystallinity.

2.5.2 Coexistence of Iα and Iβ polymorphs. Many aspects of the Iα and Iβ polymorphs coexisting within CNs are still controversial, resulting partially from difficulties in structural characterization of individual CNs. The Iα/Iβ ratio is not fixed for a given CN type, but in general CNCs and t-CNCs have high Iβ fractions, whereas some AC (*Valonia*) and BC (*Acetobacter*) have high Iα fractions (see section 1.1). The Iα polymorph is metastable and can be converted to Iβ,^{31,34–36,77} and for BC (*Acetobacter*) by altering culturing conditions it is possible for Iβ to be the dominate polymorph (Fig. 10e and f).^{32,73,104} The Iα and Iβ nanodomains within a given CN type have been considered to occur in three configurations: Iβ core surrounded by Iα,¹⁰⁴ alternating along the CN axis,^{35,70} and alternating laterally across the CN cross-section.^{35,70} Additionally, it is unclear if the Iα to Iβ conversion may also alter the Iα and Iβ nanodomain configuration.¹⁰⁹ The affect of the Iα/Iβ ratio and the Iα-Iβ nanodomains arrangement on mechanical properties is unclear (see section 3.1). However, it is conceivable that differences in the cellulose chain arrangement within the Iα and Iβ polymorphs will affect the inter-hydrogen bonding within CNs and may affect mechanical properties, as predicted in atomistic modeling.^{44,110}

2.5.3 Structural defects. Three general structural defects within the crystalline regions can be characterized as: (i) point defects, (ii) line defects, and (iii) area defects. Point defects are considered to be localized voids or altered bonding along a single cellulose chain that is located within a crystalline region. Line defects result from the extraction or insertion of extra cellulose chain(s) within the cellulose crystal (this is similar to crystal dislocations). Area defects result from the boundaries between the Iα-Iβ crystal structures within a single crystal,^{35,70,104,109} the disorder of cellulose chains located at the CN surface,^{42,90,108} and low angle off-orientation between two crystalline regions within the same CN particle.^{46,75} This latter case is considered different from two independent crystals having an incoherent interface. No systematic studies relating CN structural defects to mechanical properties have been done.

3. Properties of cellulose nanoparticles

3.1 Mechanical properties of cellulose nanoparticles

There is limited understanding of the intrinsic mechanical properties of CNs. The small particle size combined with the limited metrology techniques available to characterize these organic materials along multiple axes has made quantitative mechanical properties measurement extremely challenging. Additionally, several factors may influence the measured mechanical properties and will contribute to the wide distribution the reported values, either between different particle types, but also for a given particle type. These factors include: crystal structure (Iα, Iβ, II), percent crystallinity, anisotropy, defects, and the property measurement methods and techniques. Thus, it is crucial to consider these factors when comparing reported properties of a given particle type.

The mechanical properties of several cellulose particle types are summarized in Table 3. To the author's knowledge no mechanical tests on individual MFC, NFC or AC particles

Table 3 Properties of cellulose based materials

Material	E_A (GPa)	E_T (GPa)	σ_f (GPa)	ε_f (%)	Technique	Reference
WF	14–27	—	0.3–1.4	4–23	Tensile	379
PF	5–45	—	0.3–0.8	1.3–8	Tensile, Raman	8, 24, 25, 380, 381
MCC	25 ± 4	—	—	—	Raman	381
MFC & NFC	N/A	—	—	—		N/A
CNC						
plant	57, 105	—	—	—	Raman	121
wood	—	18–50	—	—	AFM indentation	111
t-CNC	143	—	—	—	Raman	118
Acid ^a	151 ± 29	—	—	—	AFM-3pt bend	63
TEMPO ^a	145 ± 31	—	—	—	AFM-3pt bend	63
	—	9 ± 3	—	—	AFM indentation	112, 113
BC	78 ± 17	—	—	—	AFM-3pt bend	119
	114	—	—	—	Raman	120
Cellulose Iβ						
Experimental	120–138	—	—	—	XRD	114–117
	220 ± 50	15 ± 1	—	—	IXS	114
Modeling	110–173	—	—	—		Table 4
	137–168	10–50	7.5–7.7	—		43, 44, 122, 382
Cellulose Iα						
Modeling	128–155	5–8	—	—		44, 110
Cellulose II						
Experimental	9–90	—	0.2–1.0	—	Raman	123, 380
Modeling	98–109	17–31	4.9–5.4	—		44, 123, 383

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).^a Treated t-CNCs.

have been done. Most work has focused on elastic properties, and because of the anisotropy within crystalline cellulose (*i.e.* non symmetric structure of the cellulose chain and its arrangement within the crystal structure, Fig. 4 and 10), there will be differences in the mechanical properties as a function of direction with respect to the cellulose crystalline structure. Most experimental studies have focused on the elastic properties along the more readily measurable axial direction of the cellulose crystal. Recently, measuring the elastic properties in the transverse direction of individual CNs has also been attempted.^{111–113} Throughout the manuscript the following terminology is used for elastic modulus along the cellulose crystal axial direction (E_A), and cellulose crystal transverse direction (E_T).

The elastic properties of cellulose I crystalline regions have been investigated since the mid 1930's, either by theoretical evaluations or by experimental measurements. Theoretical evaluations have primarily investigated the role of cellulose crystal structure, the critical contribution of intramolecular and intermolecular hydrogen bonding, and different theoretical approaches to modeling the elastic properties (see section 5). The elastic properties of cellulose I crystalline regions have traditionally been experimentally measured using *in situ* tensile tests combined with XRD to measure strain. In these tests, bulk sized specimens consisting of parallel aligned cellulose microfibrils bundles (typically flax fibers) were loaded along the fibril axis direction. The small axial strains in the crystalline cellulose structure measured in XRD were used to calculate E_A . Since XRD only samples lattice displacements in the crystalline regions, it provides a measurement of the crystalline properties, E_A = 120–138 GPa.^{114–117} This technique assumes perfect load transfer and perfect orientation of the cellulose crystals within the microfibril along the axis of loading, this is unlikely and E values reported may under estimate the true

property. Similarly, inelastic X-ray scattering (IXS) of cellulose microfibrils, measures the sound velocity as a function of acoustic phonon dispersion through the crystalline regions and avoids the perfect load transfer issues described for the XRD method.¹¹⁴ The resulting measured axial elasticity is much larger, E_A = 220 ± 50 GPa, and the transverse elasticity can also be measured E_T = 15 ± 1 GPa. One should use caution in applying these measured properties to CNCs. Even though the CNCs are considered to be the extracted crystalline regions within cellulose microfibrils, the influence of the particle extraction process has not been accounted for in these XRD and IXS studies. Note that XRD and IXS can be directly applied to CNCs, instead of microfibrils, so that the effect of the extraction process can be measured.

Elastic modulus of individual CNC, t-CNC, and BC particles have been measured, either in the axial direction, E_A ,^{63,118–121} and/or in the transverse direction, E_T .^{111–113} Tunicate CNCs have been used as idealized particles because of their longer length, larger cross-section (Fig. 10), higher crystallinity, higher volume fraction of I β and uniform particle morphology (see Table 2). Iwamoto *et al.*⁶³ used atomic force microscopy (AFM) three-point bending where the AFM-tip, used as the third loading point, measured the applied force and the bending displacement of individual t-CNCs bridging nanoscale grooves fabricated on a substrate. A total of 32 t-CNCs were tested. The measured elastic moduli of t-CNCs extracted by either acid hydrolysis or TEMPO, was E_A = 151 ± 29 GPa, and E_A = 145 ± 31 GPa, respectively. Beside the wide scatter in the data, these measurements have other errors as it is extremely difficult to measure the exact t-CNC cross-section, which has a strong influence on the calculated E_A . Šturcová *et al.*¹¹⁸ used *in situ* combination of tensile test experiments with Raman spectroscopy to calculate E_A = 143 GPa (distribution was not given) for t-CNC.

A thin mat of t-CNCs was impregnated with epoxy and this composite was subjected to tensile loading. Shifts in the characteristic Raman spectroscopy peak for cellulose I (1095 cm^{-1}) were used to monitor strain along the axial direction of the crystal. The micron sized laser spot size samples several t-CNCs within a single measurement, because of this the resulting Raman shift gives an averaged strain and thus an average value for E_A . Errors associated with this technique likely manifest from the assumed perfect load transfer from the epoxy matrix to the t-CNC and the assumed 2-dimensional (2D) t-CNC network. Rusli *et al.*¹²¹ used a similar technique for CNCs and calculated $E_A = 57\text{ GPa}$, or 105 GPa , depending on whether the CNCs were assumed to be arranged in a 2D or 3D network, respectively. Unlike the previous study, the CNCs were dispersed in epoxy and a bend bar specimen was cast, which suggests that the distribution of the CNCs would be more likely a 3D structure. The lower E_A for CNCs as compared to t-CNCs was considered to result from less efficient stress transferred between the epoxy matrix to the CNC particles because of smaller CNC length, rather than an intrinsic difference in properties. Lahiji *et al.*¹¹¹ and Wagner *et al.*^{112,113} used a combination of high resolution AFM indentation and modeling to measure individual wood CNCs $E_T = 18\text{--}50\text{ GPa}$, and t-CNCs $E_T = 9 \pm 3\text{ GPa}$, respectively. Unfortunately, the associated transverse crystallographic orientation could not be determined. These results are similar to the IXS experimental results¹¹⁴ and the theoretical model calculations.^{43,122} However, such measurements have large measurement uncertainty associated with AFM sensitivity limits, and model assumptions used to extract the mechanical properties.¹¹³

The BC elastic modulus was measured with nearly identical techniques used for the t-CNCs (*e.g.* AFM 3-pt bend and Raman). Similar to t-CNCs, BC can also be considered as an idealized particle because of their longer length, larger cross-section (Fig. 10), high crystallinity, high volume fraction of $I\alpha$ (73–97% see Table 2) and uniform particle morphology. The reported axial elastic modulus, $E_A = 78 \pm 17\text{ GPa}$ and $E_A = 114\text{ GPa}$, were measured by AFM 3-pt bend¹¹⁹ and Raman,¹²⁰ respectively. The difference between these values of BC is likely based on measurement technique issues and assumptions used for property calculations, which typifies the difficulties of property quantification of nanosized particles.

Consensus is emerging that E_A is greater for cellulose I than for cellulose II, as demonstrated with predictive modeling,⁴⁴ and by two comparable Raman spectroscopy studies by Eichhorn and coworkers.^{118,123} In contrast, no consensus has been made regarding the difference in mechanical properties between $I\alpha$ and $I\beta$. Reiling and Brackmann¹¹⁰ predicted E_A to be $\sim 20\text{ GPa}$ larger for $I\beta$ than $I\alpha$, while Eichhorn and Davies⁴⁴ predicted $I\beta$ to be $\sim 6\text{ GPa}$ smaller than $I\alpha$. The contradiction between these two modeling studies is likely based on the different model construct (see section 5 and Table 4). Experimentally, comparisons between t-CNC ($I\beta$ crystal structure) and BC ($I\alpha$ crystal structure) may provide some insight as to the role of $I\alpha$ and $I\beta$ polymorphs on properties. Two comparable Raman spectroscopy studies by Eichhorn and coworkers found that E_A was $\sim 30\text{ GPa}$

greater for t-CNC¹¹⁸ than for BC.¹²⁰ Likewise, comparing the two AFM 3-pt bending studies by Iwamoto *et al.*⁶³ and Guhados *et al.*¹¹⁹ show that the E_A was $\sim 70\text{ GPa}$ greater for t-CNC⁶³ than for BC.¹¹⁹ The higher E_A for t-CNC could be real and likely results from several factors, in particular the higher crystallinity in t-CNC as compared to BC (see Table 2). However, it is also possible that there might be a contribution based on the different $I\beta$ fraction within each particle type. More detailed/systematic studies will be needed to fully examine the effects of $I\alpha$ and $I\beta$ polymorphs on mechanical properties.

3.2 Thermal properties

The thermal properties of CNs are briefly described here in terms of thermal chemical degradation and CTE. The onset of thermal chemical degradation of CNs has been measured using thermogravimetric analysis (TGA), which measures weight loss as a function of temperature for a given heating rate. Typically, the onset of thermal chemical degradation of CNs occurs between $200\text{--}300\text{ }^\circ\text{C}$, depending on heating rate, particle type, and type of surface modification.^{124,125} Petersson *et al.*¹²⁴ completed a series of TGA measurements of freeze dried MCC, CNC (produced *via* sulfuric acid hydrolysis of the same MCC) and chemically modified CNC suspensions. The onset of thermal chemical degradation was $\sim 300\text{ }^\circ\text{C}$ for MCC and $\sim 260\text{ }^\circ\text{C}$ for CNCs. Subsequent chemical modifications to the CNCs were shown to further altered the onset temperature. The CTE of crystalline cellulose in the axial direction has been estimated at $\sim 0.1\text{ ppm K}^{-1}$,^{126–128} which is more than an order of magnitude lower than most metals and ceramics,¹²⁹ but comparable to other high-modulus, anisotropic fibers, such as carbon fibers.

3.3 Liquid crystallinity

It has long been known that cellulose itself is liquid crystalline (LC).¹² Thus, a discussion of liquid crystalline behavior is relevant to CN properties. Such behavior should be expected of any asymmetric rod-like or plate-like particle. Stiff rod-like particles (polymer micro-objects, viruses, rod-like alumina) are known to show liquid crystallinity^{130,131} and CNs are no exception. Other reviews have touched on the subject,^{16,22} we will briefly describe this behavior here. Due to their stiffness and aspect ratio, CNCs can be considered rigid-rods, and therefore, one could expect nematic behavior where the rods align under certain conditions. This is akin to trying to pack pencils—the highest packing density is where the pencils are parallel. As interactions between individual crystals are strong, yet the crystals are readily dispersible, lyotropic (in solution) behavior is observed.^{16,22,132,133} However, cellulose crystallites have a helical twist down the long axis, similar to a screw (Fig. 11a). This twist induces crystal suspensions to attain a helical twist normal to the long axis of the rod (Fig. 11b). Like a screw, a higher packing arrangement is to pack at an angle in order to intertwine the “threads”. Thus, the cellulose crystals take on a chiral nematic or cholesteric phase of stacked planes aligned along a perpendicular axis, with each plane being rotated by a phase angle, which is dependent on concentration.^{132–134} Such alignment can result in optical band-gaps giving

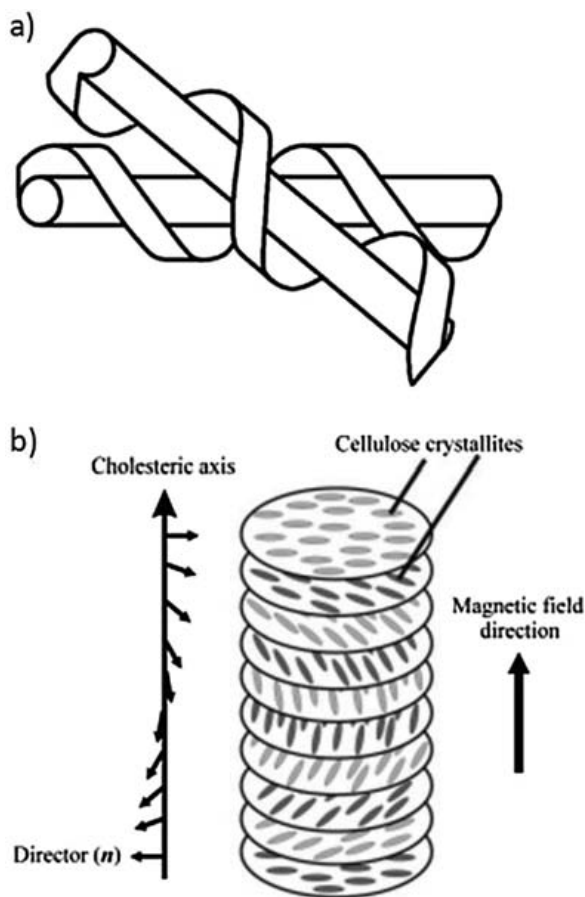


Fig. 11 Chiral nematic structure of CNCs: (a) “screw”-type packing due to the helical twist of the CNC, (b) helical twisting of CNC layers along a cholesteric axis. The cholesteric axis will align in the direction of a magnetic field.¹³³ Reprinted with permission from ref. 133 © 2001 WILEY-VCH.

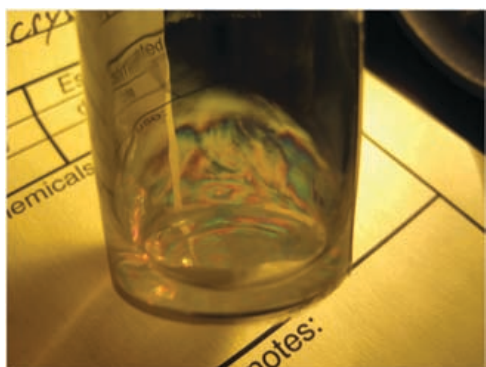


Fig. 12 Birefringent Schlierin structures in CNC suspension viewed between crossed polarizers.

iridescent/pearlescent behavior and phase behavior can be viewed as Schlierin texture (Fig. 12) between crossed polarizers due to the birefringence of individual domains typically producing fingerprint patterns (Fig. 13) for chiral nematic as opposed to domain-like (or cross-like patterns) for simple nematic.^{16,22,134–136}

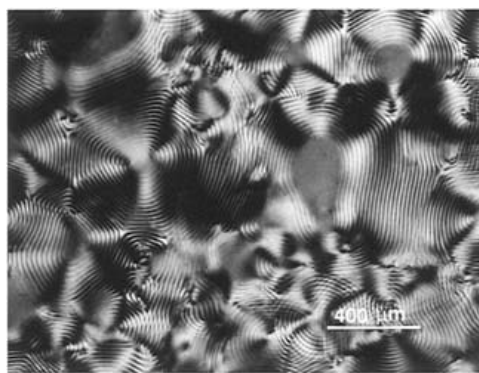


Fig. 13 CNC suspension viewed *via* optical microscopy showing the fingerprint texture of chiral nematic structure as viewed through crossed polarizers.¹³⁴ Reprinted with permission from ref. 134 © 1996 American Chemical Society.



Fig. 14 CNC suspension showing separation into clear isotropic and structured chiral nematic phases as viewed through crossed polarizer.¹³⁴ Reprinted with permission from ref. 134 © 1996 American Chemical Society.

Various factors such as size, shape, dispersity, charge, electrolyte, and external stimuli can affect the liquid crystallinity, pitch, domain size, ordering, and other properties. Simple settling of the crystals will in many cases produce two phases where they separate into a chiral nematic phase and an isotropic phase (Fig. 14) with the longer crystals showing the anisotropy.⁹⁴ Rheological methods (shear),¹³² magnetic fields,^{132,133,137} and electric fields¹³⁸ have all been used to align CNs (CNC, MCC, *etc.*). Physically, studies have shown that a major factor in LC determination is the aspect ratio of the particles.^{103,132} Higher aspect ratios represents more anisotropy and therefore drive a transition to the liquid crystal phase at lower concentrations.¹³² However, it can be expected that at sufficient lengths order will break down as the particles will become less rigid and behave more like worms or strings as opposed to rods. As such, there is little work on ordering in fibrillated particle types, where their length and defects overcome their stiffness. Another factor at play is the ionic strength of the solution. Addition of electrolyte to the suspensions reduces the effective diameter due to screening and lower repulsive forces acting between crystals. Thus increased ionic strength can result in raising the critical lyotropic concentration,¹³⁴ reducing ordering¹³⁹ or a small

reduction in crystal separation, chiral pitch¹³⁴ and eventual agglomeration of the CNs.¹³² Additionally, the phase may change from chiral nematic to simple nematic if there are extremely low levels of electrolyte,¹³⁶ and ordering may be problematic.¹⁴⁰ Changing the counterion of the crystals by using different electrolytes shows that lowest critical concentrations for ordering are attained for smaller counterions (such as H⁺) and highest critical concentrations for largest (Cs⁺, tetrapropylammonium) and differing counterions also change the chiral pitch.¹⁴¹

As the electrostatic double layer around the particles affects the behavior, it is no surprise that the chemistry of the particles also affects the LC behavior. Highly sulfonated nano- and microcrystals have different charge behavior than non-sulfonated hydroxyl surface crystals and so can be expected to give different LC behavior.¹⁴² Interestingly, sulfuric acid and phosphoric acid derived crystals give chiral nematic structure whereas hydrochloric acid derived crystals with post-reaction sulfonation gives a birefringent glassy phase^{133,135} that shows a crosshatch pattern. Other work shows that higher degrees of sulfonation also play a role.⁹⁵

3.4 Rheological properties

When investigating the rheological properties of CNCs, researchers generally either study the gelation properties through viscometric measurements or seek to discover knowledge about the liquid crystallinity and ordering properties of the nanocellulosics through rheological characterization. Here a brief review will be given for the rheological properties of CN suspensions, further details can be found in the following review papers.^{16,17,22} Investigations of liquid crystalline CN suspensions have been performed to determine LC transitions under shear (Fig. 15). CNC suspensions in the dilute regime were shear thinning and this behavior increased as concentration was raised and showed concentration dependence at low rates and very little concentration dependence at high rates. However, at higher concentrations where the suspensions were lyotropic, the suspensions show anomalous behavior with viscosity showing shear-thinning behavior at low rates, a semi-plateau region where the shear-thinning is less pronounced as the rate is raised, and then a precipitous drop in viscosity at a critical rate. The rates at which such transitions in the flow behavior occur are concentration dependant.^{22,143} T-CNC show similar behavior.¹⁴⁴ The explanation for such behavior is that at a critical shear rate, the nanocrystals align due to their rod-like nature, greatly easing their flow. Under enough shear the chirality of the suspensions breaks down in favor of a simple nematic structure. Such behavior has been observed by diffraction/scattering^{132,145} and SEM.¹⁴⁶ Additionally, the time constant of relaxation is highly dependent upon aspect ratio with higher aspect ratios staying aligned for longer times after shear (Fig. 16).¹³²

Time-dependent viscosity measurements have been performed on CNC suspensions (these crystals were MCC as stated in the publication, but from reported TEM size scales of ~500 nm length and ~20 nm width, we will consider them CNCs). Studies were performed investigating the influence of the acid used in hydrolysis.¹⁴⁷ In contrast to the sulfuric acid

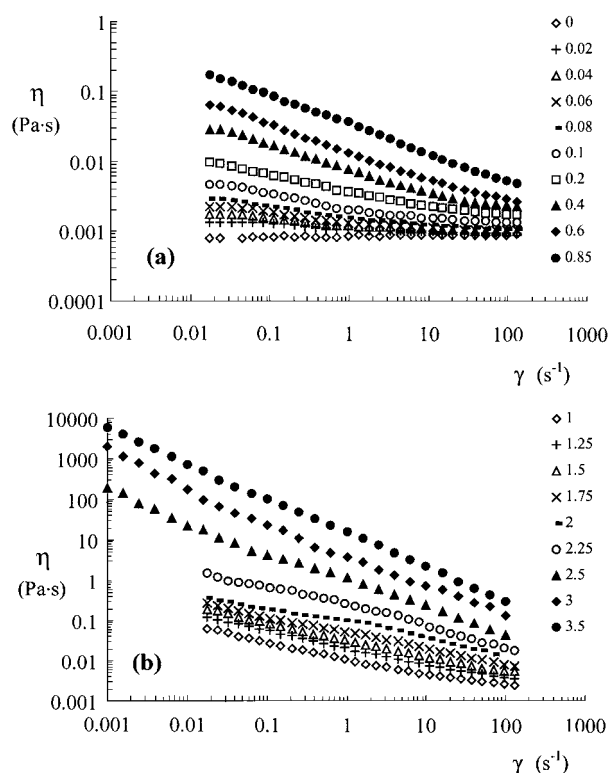


Fig. 15 Viscosity of CNC suspensions as a function of shear rate and for increasing CNC concentration (wt%): (a) increase of concentration in the isotropic at-rest regime up to the lyotropic transition, (b) increase of concentration beyond the lyotropic transition in the anisotropic at-rest regime.¹⁴⁴ Reprinted with permission from ref. 144 © 2000 American Chemical Society.

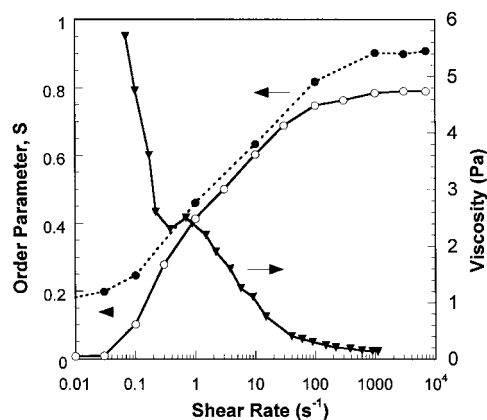


Fig. 16 Order parameter and viscosity of CNCs as a function of shear rate. Open circles are smaller aspect ratio than closed circles. Viscosity is for the smaller aspect ratio particles.¹³² Reprinted with permission from ref. 132 © 1998 American Chemical Society.

treated crystals which showed some shear thinning and no time-dependent behavior, HCl derived crystals showed much higher shear thinning behavior, thixotropy at high concentrations and anti-thixotropy at dilute concentrations. Follow-on studies showed that this was due to the influence of surface charge.¹⁴²

Rheometry measurements (Fig. 17) have also been performed on NFCs prepared *via* TEMPO-oxidation.¹⁴⁸ These NFC

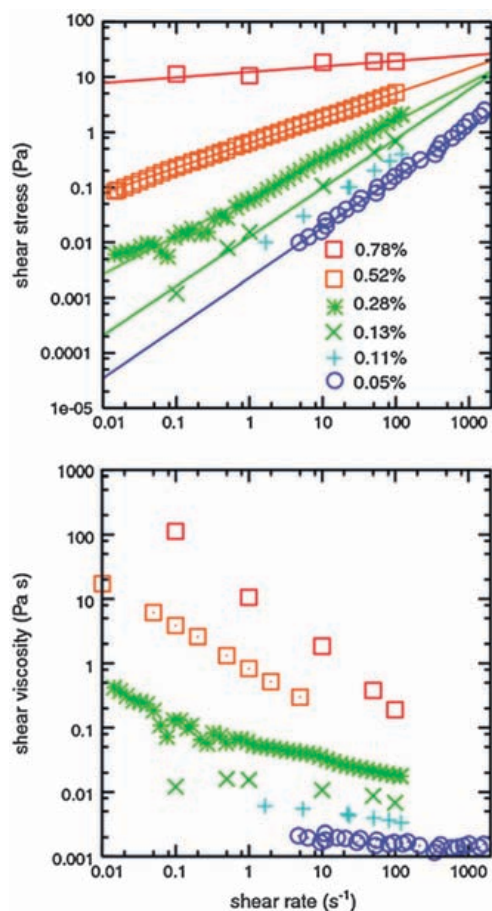


Fig. 17 (a) Shear stress and (b) viscosity as a function of shear rate for a variety of concentrations of NFC (wt%) prepared by TEMPO oxidation.¹⁴⁸ Reprinted with kind permission from ref. 148 © 2008 Springer Science + Business Media B.V.

suspensions also showed shear-thinning behavior following a power-law and thixotropy, which are explained through percolation in the fibrils and flock formation. In this case, gelation was seen to onset (storage modulus > loss modulus) at about 0.5% CN (we assume wt%, although it is not stated).

3.5 Optical properties

At first glance, one would think that CNs would have the same optical response as other cellulosic materials. Based on the cellulose structure—which is comprised of ether, hydroxyl, carbon-carbon, and carbon-hydrogen bonds—the material should not have adsorption in the optical range, and indeed, it does not. Films cast of CNs have excellent transparency (see section 7.7). However, CNs differ from other cellulose materials in three important ways: (1) they are nanoscale in size, (2) individual structures are anisotropic and show birefringence, and (3) depending upon size scale, concentration and aspect ratio, are liquid crystalline (section 3.3).

Birefringence in cellulose based particles should be expected as cellulosic structures are anisotropic at nearly every length-scale- from cellulose chains to WF. Upon fibrillation of WF or PF to CNs, this structure may be preserved. In the case of CNCs, the oriented chains of cellulose are preserved (section 2) thus, CNCs are birefringent, and have refractive indices of

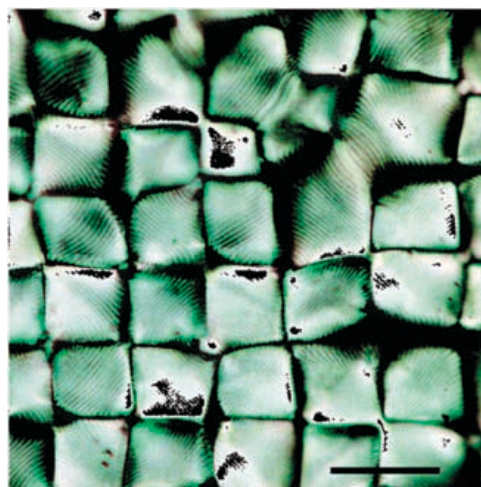


Fig. 18 Parabolic focal conics in CNCs viewed between crossed polarizers.¹⁵¹ Reprinted with permission from ref. 151 © 2005 American Chemical Society.

1.618 and 1.544 in the axial and transverse directions, respectively.¹²⁷

Liquid crystallinity of CNs suspensions coupled to the birefringent nature of the particles, leads to interesting optical phenomena. As the lyotropic LC onset concentration is reached, the particles align creating a macroscopic birefringence. This can be seen through crossed polarizers as the Shlieren texture described in section 3.3. Such solutions can be dried to preserve the domain structure, and between crossed polarizers show colored domains²² and oriented films from spin-coating show classic cross-like patterns of polarization.¹⁴⁹ Optical phenomena also appear prior to LC formation as nanoparticles can form “tactoid” assemblies in dilute solution, which also show birefringence.²² As discussed earlier, the LC behavior is highly dependent upon type and history of the nanoparticle as well as conditions, and therefore so are the optical properties arising from such behavior.

An interesting optical behavior is described by Gray and Roman.^{150,151} It is extremely difficult to align and preserve the chiral nematic structure in films of liquid crystals. However, suitably stabilized, CNs can preserve this structure upon drying to a thick film resulting in parabolic focal conic defect structures that are reminiscent of smectic and lamellar LCs of polymers and lipids.^{150,151} In this case, the chiral structure pitch determines size scales and results in dazzling optical displays as seen in Fig. 18.¹⁵¹

4. Surface chemistry of cellulose nanoparticles

The chemical functionality of CN surfaces dictates CN suspension properties, the composite fabrication processes and the resulting composite properties. This functionality and its modification have been reviewed extensively elsewhere for plant-based fibers,²⁴ cellulose adhesion,²⁰ and CNs.^{7,8,16,17,19,21,27} However, a short discussion will be given here, referring back to these reviews as appropriate.

Surface functionality of CNs can generally be categorized into 3 distinct groups: (1) native surface chemistry of the

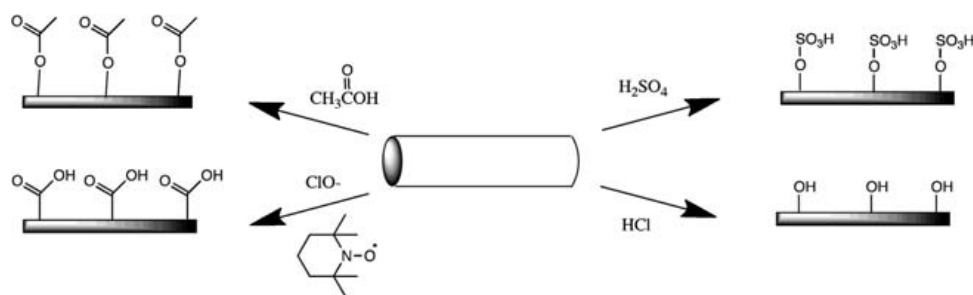


Fig. 19 Common syntheses of CNs provide for distinctive surface chemistries: sulfuric acid treatment provides sulfate esters (top right), hydrochloric acid treatment provides hydroxyl (bottom right), acetic acid provides acetyl (top left), TEMPO mediated hypochlorite treatment provides carboxylic acid (bottom left).

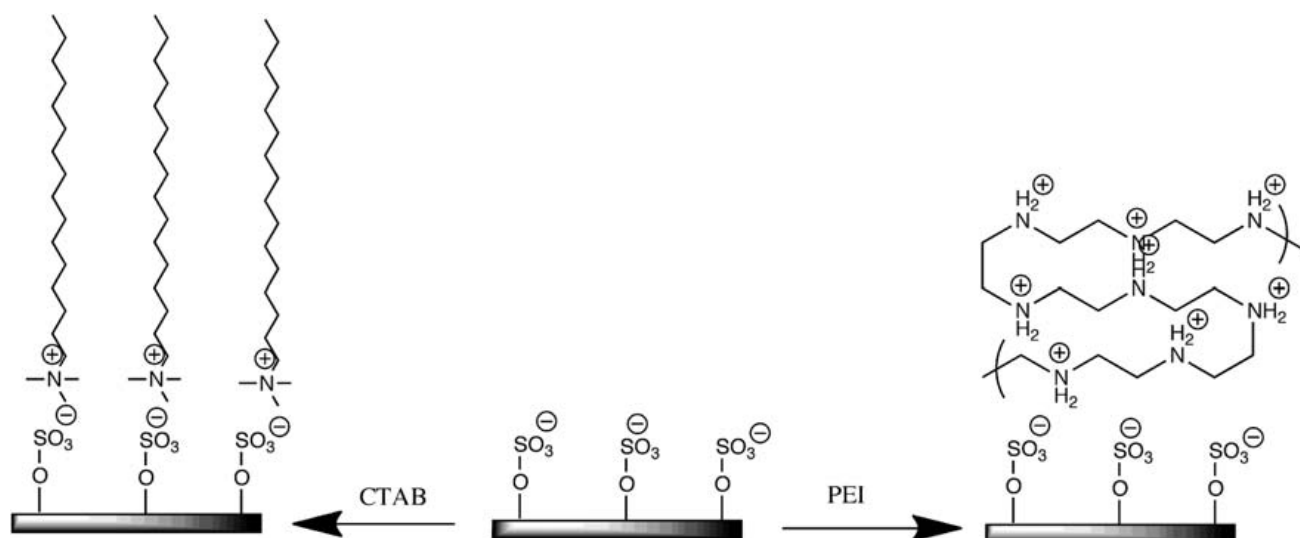


Fig. 20 Electrostatic adsorption to (sulfonated) cellulose nanoparticle examples: (left) cetyltrimethylammoniumbromide (CTAB) surfactant adsorption and (right) polyethylenimine (PEI) layer-by-layer (LbL) electrostatic adsorption.

particles as a result of their extraction or the use of similar methods to treat the surface of the particles (Fig. 19), (2) adsorption to the surface of the particles (Fig. 20), and (3) covalent attachment of molecules or derivatization of the surface (Fig. 21). These modification methods have generally been borrowed from larger pulp and paper processes, and rely on the surface functionality such as hydroxyl groups in native cellulose or on functionality derived from synthesis of the nanoparticles as a “handle” for modification. There is a plethora of research articles on the modification of CNCs because of the effort to disperse and compatibilize them. However, functionalization of fibrillated CN types has been much less reported.

4.1 Functionalization via CN synthesis

For the first group of modification methods, that of extraction-dependent surface functionality, CNCs generally exhibit one of two chemistries at the surface. Degradation by the sulfuric acid forms sulfate esters that give the surface a high acid content. Harsher treatments such as longer treatment time result in higher degrees of sulfation.⁹⁴ A less used synthesis method is hydrochloric acid degradation and this results in hydroxylated surfaces.⁹⁵ Other investigated, but

minor methods have been used as well, such as phosphoric acid and hydrobromic acids.¹⁶ Digestion with Fischer–Speier esterification using acetic acid for digestion and as acid-catalyst has also been performed resulting in an acetylated surface.¹⁵² Sulfuric acid degradation is, by far, the most commonly used method (and therefore the most common surface) as the high sulfate content provides for a highly charged surface that stabilizes nanocrystal dispersion. Owing to this, some groups have used post-synthesis sulfation to further enrich sulfate groups on the crystal surface.¹³⁵

Fibrillated CN types (MFC, NFC) are derived using different methods and show different surface chemistries. Purely mechanical methods such as steam explosion, high-pressure homogenization, and high speed shear, having no oxidant or degradation capacity, produce hydroxylated surfaces similar to native cellulose. Another method that is becoming increasingly common is TEMPO-mediated oxidation coupled with low speed mechanical treatment.⁴⁷ This method uses the 2,2,6,6-tetramethyl-piperidinyl-1-oxyl (TEMPO) radical as a catalyst with a primary oxidant such as hypochlorite to selectively oxidize primary alcohol groups in the cellulose. The oxidation helps to degrade the material such that low speed mechanical treatment fibrillates the mass. The treatment also leaves the surface of nanofibrillated

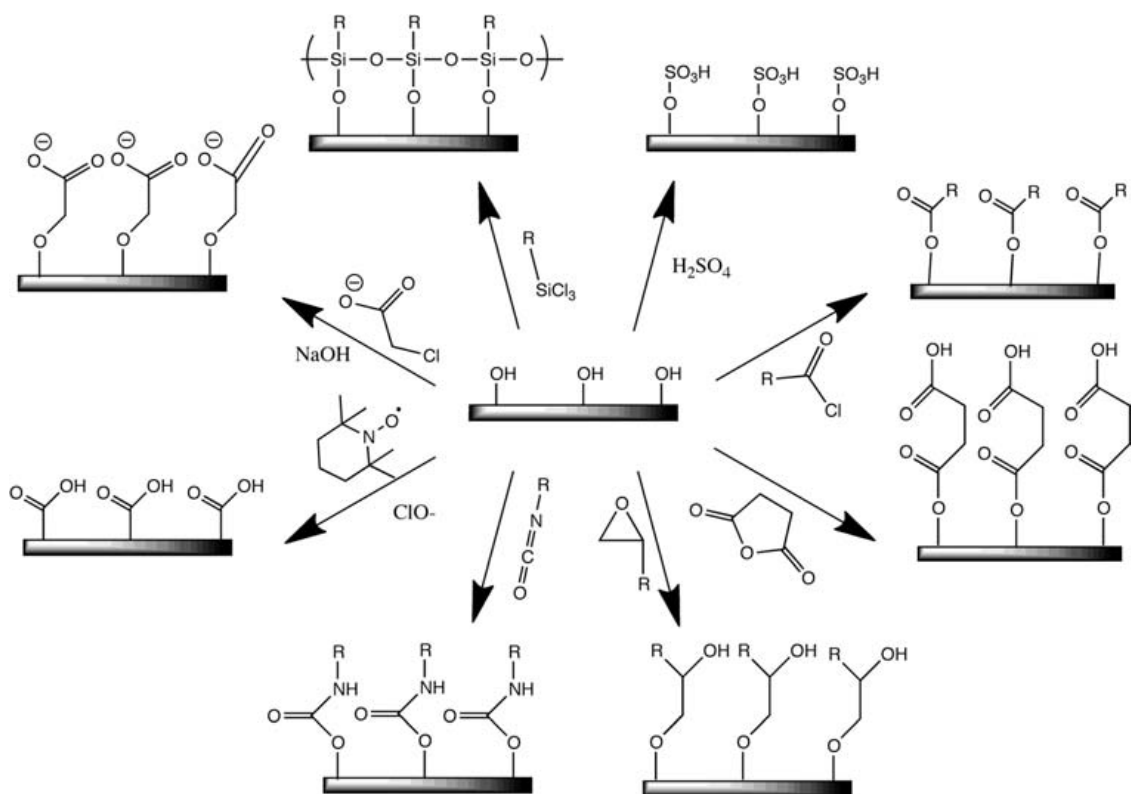


Fig. 21 Common modification chemistries of CN surfaces: (clockwise from top-right) sulfuric acid treatment provides sulfate esters, carboxylic acid halides create ester linkages, acid anhydrides create ester linkages, epoxides create ether linkages, isocyanates create urethane linkages, TEMPO mediated hypochlorite oxidation creates carboxylic acids, halogenated acetic acids create carboxymethyl surfaces, and chlorosilanes create an oligomeric silylated layer.

cellulose with a carboxylic acid surface, due to oxidation of the alcohol groups.

4.2 Functionalization via adsorption

The second subset of modification procedures involves using adsorption to the surface of the particles. Most commonly, electrostatics of some type are used, such as using surfactant to stabilize the nanoparticles. Due to their lack of dispersibility in organic media and polymers, nanocrystalline particle types are very commonly stabilized with surfactants. Sulfuric acid derived CNs provide a charged surface to adsorb surfactants. Such dispersants as stearic acid¹⁵³ and cetyltrimethylammonium-bromide (CTAB)¹⁵⁴ are common. Another common method using adsorptive modification is through the use of electrostatic adsorption of macromolecules. This method is borrowed from the manufacture of paper as it has long been known that cellulose is weakly charged and polyelectrolytes have been used as dry and wet strength additives, anti-static, and other uses. Most commonly, layer-by-layer deposition is used.¹⁵⁵ Non-ionic adsorption/dispersants have also been used.^{156,157} Xyloglucan has a strong, specific adsorption to cellulose, and xyloglucan block copolymers have been used as a non-ionic absorbant/dispersant.¹⁵⁸

Much less electrostatic stabilization is reported for the nanofibrillated cellulose types. This is likely due to the lower surface charge of the most commonly synthesized types—high shear, homogenizer, and steam exploded. However,

dispersants derived from guluronic and mannuronic acids and from ethylene-acrylic acid copolymers have been used.¹⁵⁹ Electrostatic adsorption of macromolecules using amideamine polybase has also been performed.¹⁶⁰ Likely, with the advent of the more easily processed TEMPO-derived NFC, which is more highly charged, the use of electrostatic-driven adsorption methods will increase.

4.3 Functionalization via chemistry modification

The third and last method of surface chemistry modification is through use of direct chemical modification and/or covalent attachment of molecules. Generally, the techniques are the same as those used for many years on cellulose surfaces for such things as wood modification, and natural products chemistry. As cellulose has prodigious hydroxyl groups at the surface, techniques that react with alcohols, *e.g.* isocyanates, epoxides, acid halides, and acid anhydrides are the most common for direct attachment. These reactions can be used to form a host of alternate surface chemistries such as amine, ammonium, alkyl, hydroxyalkyl, ester (acetate, propionate, *etc.*), acid, *etc.* Alternatively, many groups seek to change the chemistry of the hydroxyl group. Borrowing from nanofibrillation techniques, others have resorted to TEMPO-mediated oxidation of HCl derived nanocrystals to convert alcohol groups to carboxylic acid moieties for better dispersibility.^{7,92} Other methods to modify the surface, such as using sulfuric acid, can also be used to form sulfate esters.

For CNCs, these methods are, in many cases, meant to increase dispersibility within organic solvent or polymer resin, the latter to improve mechanical properties. Rather than use simple surfactant or alkyl-based reactant, many groups use covalent attachment paradigms to covalently link polymers to the surface of the nanocrystal in order to increase compatibility with a resin. For example maleated polyolefins, such as polypropylene have been coupled to nanocrystal surfaces using anhydride chemistry.¹⁶¹ Alternatively, grafting-from approaches to grow polymers from cellulose surfaces has been performed.²¹ For example, acid halides have been used to attach bromoesters as initiators for Atom Transfer Radical Polymerization (ATRP) of styrene^{162,163} and Single-Electron Transfer Living Radical (SET-LP) of N,N-dimethylaminoethylmethacrylate.^{164,165} Of interest lately by a variety of groups is the fabrication of biodegradable biocomposites of CNCs with polycaprolactone (PCL) by using surface grafted PCL as a compatibilizer using surface hydroxyls as initiators with a catalyst.^{48,166–168}

Fibrillated celluloses have also seen a variety of surface modification chemistries and generally reproduce those that are used above. Isocyanate,⁵⁰ anhydride,¹⁶⁹ and epoxy¹⁷⁰ have all been used. Borrowing from classic cellulosic chemistry, NFC has been carboxymethylated using the alcohol group as a nucleophile.¹⁷¹ Again, many groups have grafted polymers to the surface of fibrillated cellulose to better compatibilize them with blends both using grafting-to chemistry¹⁷² and grafting-from.¹⁷³ Surfaces have also been silylated using chloro- and alkoxy-silanes.¹⁷⁴ While undoubtedly there is covalent linkage of the silanes to the cellulose surface, such silicon-oxygen-carbon linkages are hydrolytically unstable. However, the bond is likely stabilized by lateral crosslinking of the layer.

5. Atomistic modeling of crystalline cellulose

Since the 1980's, atomic-scale modeling of cellulose has been used to complement experimental measurements of individual cellulose crystals. It has been applied to predict structural, energetic, and mechanical characteristics as well as provide a fundamental understanding of the atomic-scale origins of these characteristics. This section's goal is to summarize the contributions atomistic model-based studies have made to our understanding of cellulose structure and properties. However the subtext is intended to convey the critical relationship between models and their predictions.

This section is divided into two sub-sections. First, we introduce the methods including description of the atomic interaction models, atomic structure and orientation, and numerical simulation techniques. Then, we discuss predictions made using these models including structural, material, and interfacial properties. Most content is limited to models of cellulose I, however, some studies of cellulose II and III are included where necessary to make general comments on modeling methods applied to cellulosic materials.

5.1 Models

5.1.1 Simulation methods. Atomistic modeling of cellulose and cellulose crystals is either molecular mechanics (MM) or molecular dynamics (MD). The primary difference between

MM and MD is that the former is used to study the potential energy associated with a fixed configuration while the latter is used to model atomic and molecular motion.

Molecular mechanics typically refers to energy minimization or geometry optimization wherein the system's configuration (*i.e.* positions of atoms and bonds) is evaluated in terms of its potential energy. The configuration with the lowest energy is statistically the most likely to occur and therefore is assumed to correspond to the most physically representative model. MM methods reported in the cellulose literature may deviate in the specific algorithm used to identify minimum potential energy (*e.g.* steepest-descent or conjugate-gradient), but results tend to be insensitive to this choice. Minimization can also be performed in steps. For example, unit cell side lengths can be varied while the angles are fixed, and *vice versa*, to efficiently identify an optimal crystal structure.¹⁷⁵ Another stepwise MM method is to minimize the atomic positions while the crystal unit cell dimensions and angles are fixed, and then minimize both the atomic positions and the unit cell parameters.⁴⁴

MD simulation is a computational tool used to describe how positions, velocities, and molecular orientations change over time. Each time step the total interaction force on each particle is calculated, numerical integration of acceleration yields particle velocities, and then each particle is moved through a distance equal to its velocity multiplied by the length of the time step. Thus, MD is a computational "experiment" where a system is defined, allowed to evolve, and observations made based on its evolution. The most common ensembles for MD simulations of cellulosic materials are NPT—constant number of atoms, pressure and temperature, and NVT—constant number of atoms, volume and temperature. In either ensemble, the fixed parameters must be controlled. The method by which this control is implemented plays a major role in the simulation and therefore can be expected to significantly affect model predictions. Pressure control algorithms used in NPT simulations reported in the cellulose literature include pressure rescaling (isotropic rescaling of atomic positions) and the Berendsen barostatting method. Although these methods can be used to impose nearly any pressure, studies to-date have only used them to maintain 1 atm. Reported methods of temperature control are much more varied and include velocity rescaling, Berendsen thermostat, Nosé-Hoover thermostat, and Langevin dynamics. Most simulations use these methods to maintain the temperature at 293 or 300 K, although some high temperature studies have been reported and will be discussed in section 5.2.2. A few studies have used ensembles other than NVT or NPT. These include NPH—constant number of atoms, pressure, and enthalpy,¹⁷⁶ and NVE—constant number of atoms, volume and potential energy.^{177,178}

In some cases, MM and MD are used in conjunction to more efficiently explore the available phase space. It is extremely common to use minimization before and during an MD simulation to evaluate the minimum potential energy of a given configuration. Also, MD simulations have been run consecutively in the NVT and NPT ensembles to allow the system to reach its equilibrium pressure and volume independently.^{179,180} Another method, referred to in the literature as high temperature annealing, consists of equilibrating at high

temperatures (typically 500–800 K) then slowly cooling to the target temperature to “encourage” the system to cross potential energy barriers more efficiently.^{175,176,181,182}

5.1.2 Force fields. All predictions made by atomistic simulation are functions of the underlying interaction models, or force fields. It is therefore critical that the force field selected accurately describe the interactions that occur in the modeled molecule. For cellulose, a force field must accurately describe the stretching, bending, and torsion of covalent bonds, electrostatic interactions, van der Waals forces, and particularly important for cellulose, hydrogen bonding.

The most commonly employed force fields for cellulose modeling are MM2/MM3,^{45,183–187} GROMOS,^{181,188–197} CHARMM,^{110,175,177,178,198,199} CVFF/PCFF/COMPASS,^{44,118,123,176,179,180,200–203} AMBER,^{182,204–207} Dreiding,^{43,208,209} and COSMOS.^{210,211} In addition, one force field was developed specifically for modeling cellulose.²¹² These force fields vary in (a) which atomic interactions are modeled, (b) the mathematical form of those interactions, and (c) the parameters fit to the resulting mathematical expressions. The details of a given force field may also vary significantly from one version or release to another, and some force fields allow the user a certain degree of control over model parameters. Examples of definable parameters are cut-off distance (the interatomic spacing beyond which interactions are neglected) and the dielectric constant.

Force fields are often subject to simplifications or approximations to improve computational efficiency. Most commonly employed in the cellulose literature are the united atom model and bond/position constraints. The united atom model is the term used to describe the agglomeration of multiple atoms into a single “interaction site”. This effectively decreases the number of degrees of freedom in the simulation. Most often the united atom model is applied to hydrocarbon systems, such that a carbon atom and its bonded hydrogen atoms become a single “united atom”. In cellulose studies the united atom model is sometimes applied conditionally, either to *only* the aliphatic carbon atoms or to all atoms *except* the hydroxyl hydrogen. Another common method of increasing computational efficiency is to fix bond lengths or atomic positions during the simulation. Bond length constraints (rigidity) have been implemented in models of cellulose for all covalent bonds, or in some cases just covalent bonds involving hydrogen atoms. Positional restraints have been used to fix the distance between chains within a sheet, or fix the positions of atoms in a subset of the chains (usually the interior or exterior chains depending on the focus area of the study).

Among the numerous differences between interaction models, one of the most important for cellulose is hydrogen bonding. As discussed in section 1.2, hydrogen bonding is critical for both the structural and mechanical properties of cellulose crystals. Hydrogen bond models can be broadly categorized into two groups: implicit and explicit. Implicit models combine the standard van der Waals and electrostatic interaction models to capture hydrogen bonding. This widely-used approach is found in some or all versions of CVFF, PCFF, COMPASS, GROMOS, and CHARMM.

The alternative is to explicitly model hydrogen bonding. This typically entails the development of hydrogen-specific parameters for models of (a) covalent bonding (early work only), (b) van der Waals interactions (AMBER), (c) angularly dependent van der Waals interactions (early CHARMM and Dreiding), and (d) dipole–dipole interactions (MM2/MM3). Although the hydrogen bond model selected can have a significant influence on simulation predictions, the advantages of using one approach over another have not yet been conclusively determined.

5.1.3 Modeling structures. After a force field is selected an initial configuration, *i.e.* the initial spatial positions of all atoms and their corresponding bonds, must be identified. The process by which the positions of atoms in a single cellulose repeat unit are duplicated to become the initial positions of a model cellulose crystal is summarized below (adapted from Baird *et al.*²⁰⁹):

(a) *Repeat unit:* Transform a cellobiose molecule into a repeat unit (Fig. 3a) by making the terminal hydrogen bonded to the oxygen atom at one end of the molecule a “head linkage” and the terminal hydrogen bonded to the oxygen atom at the other end of the molecule a “tail linkage”.

(b) *Chain:* Link the desired number of repeat units “head” to “tail”; Adjust hydroxymethyl conformations to be uniformly *tg* or *gt*.

(c) *Unit cell:* Place chains in a unit cell where the dimensions of the cell, offset of neighboring chains along the chain axis, and direction and orientation of chains relative to the cellulose surface are identified from the literature.

Application of the above procedure requires information about the expected positions of atoms in the repeat unit and parameters that define the crystal unit cell. Particularly in MM simulations where positional changes are minimal, correct initial placement of atoms is critical to obtaining accurate simulation results. For example, it has been shown that chain stiffness values can differ by ~35% when predicted by energy minimization using the same force field with slightly different initial atomic positions.⁴⁴ This is somewhat less of an issue for MD simulations in which atoms can move according to Newtonian dynamics; however it certainly can have an impact depending on the restraints placed on the system and the predictions that are being made.

Defining the initial configuration for an atomistic model also requires information about the cellulose crystal unit cell which is typically obtained from experimental studies using diffraction based techniques (X-ray, neutron, and electron). The majority of reported atomistic models of cellulose I α and I β have drawn from a small subset of experimental studies. The three most commonly cited experiment-based sources for I β unit cell data are: Gardner and Blackwell⁴¹ cited by ref. 43,110,175,183,189,190,208, Woodcock and Sarko²¹³ cited by ref. 45,177,184, and Nishiyama *et al.*³⁷ cited by ref. 178,180,194–197,200,202,204,205. Unit cell data for I α is most often obtained from Sugiyama *et al.*³⁹ cited by ref. 45,110,177,181,185,192,193,212 or Nishiyama *et al.*³⁸ cited by ref. 204 and 211. Note that the I α and I β unit cell data from Nishiyama *et al.*^{37,38} are given in section 1.1. In some cases the initial positions for an I α model are obtained by manually

adjusting coordinates from an I β initial configuration using $(a,b,c)_{I\beta} \rightarrow (1/2a-1/2b-1/4c, 1/2a+1/2b-1/4c,c)_{I\alpha}$ where a, b, and c are the dimensions of the unit cell. More recent studies, particularly from research groups with more than one paper on cellulose modeling, use atomic positions from previously reported models as the starting point for new simulations.

A few studies have used molecular modeling to investigate the properties of amorphous as opposed to crystalline cellulose. An initial configuration of amorphous cellulose can be identified by a Monte Carlo-type method wherein cellulose molecules are randomly inserted into the simulation box, but only energetically favorable insertions are accepted.^{179,200}

Unfortunately the level of detail available from atomistic simulations also limits the overall number atoms (and therefore system size) that can be modeled. The computational time required for an MD simulation scales with up to the square of the number of atoms. As the efficiency of both hardware and software have improved, so has the number of atoms that can be realistically modeled (Table 4). Early work was limited to a single cellulose repeat unit with the united atom approximation (e.g. Tashiro and Kobayashi).²⁰⁸ As computational capabilities improved, the upper limit on atoms was increased more than an order of magnitude. For example, a limit of 700 atoms enabled modeling of seven cellotetraose molecules.¹⁸⁵ Recent studies have been able to model many more atoms. For example, Fig. 22 shows a typical atomistic model of I β crystalline cellulose containing 4 $\times$ 8 $\times$ 8 unit cells, or 43 264 atoms.

In general, three types of systems are modeled: finite number of finite length cellulose chains (mini-crystals), finite number of infinite length cellulose chains, and infinite number of infinite length cellulose chains. The term infinite here refers to applying periodic boundary conditions such that the system is “effectively infinite”. Selection of one of these models is driven by the goal of the simulation. As discussed in the previous paragraph, computation time limits the total number of atoms that can be modeled. Therefore, the choice of how to use those limited number of atoms to the best advantage is extremely important. Mini-crystal is the term used to describe a model containing many relatively short cellulose chains placed in a non-periodic simulation cell. Previous studies have

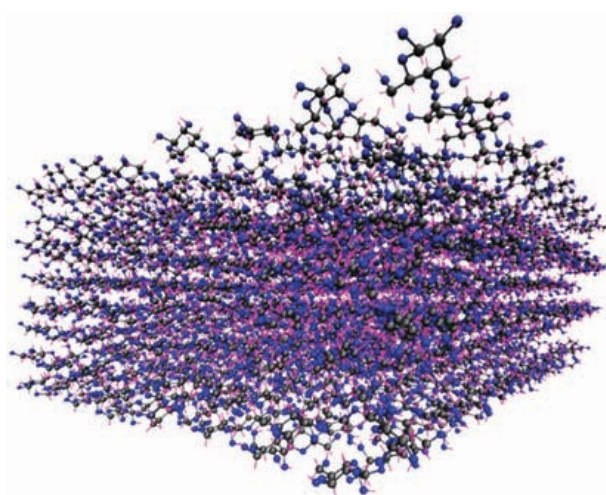


Fig. 22 Atomistic model of I β crystalline cellulose: 4 $\times$ 8 $\times$ 8 unit cells. Atoms represented as grey spheres (Carbon), blue spheres (Oxygen), and pink lines (Hydrogen).

referred to groups of between 5 and 48 chains as mini-crystals.¹⁹⁴ The advantage of mini-crystal models is they enable the model crystal cross-section to approach that of measurable cellulose crystals. These types of models have been used successfully to predict the relative stability of different cellulosic forms as well as important structural features such as the fiber twist. However, the disadvantage of mini-crystal models is their necessarily short axial length, which not only limits prediction of some properties, but also can introduce so-called “end effects” into the simulation.¹⁷⁹ The alternative to the mini-crystal is to introduce periodic boundary conditions in one or more coordinate direction to simulate infinite length. Modeling infinite length in the axial direction is extremely useful because it more correctly captures the aspect ratio of real cellulose crystals whose length is significantly larger than its cross sectional area. Models with periodic boundary conditions in all directions are useful because they enable investigation of the “bulk” structure of the crystal. Because these models have an infinite cross-section, however, they cannot be used to study surface effects or twisting (cellulose twist introduced in section 2.4). Lastly, models of a finite

Table 4 Summary of atomic modeling predictions of axial elastic modulus of cellulose I β

Study	Year	Structure (referenced atomic position data)	Force field	Method	E_A (GPa)
Tashiro and Kobayashi ²⁰⁸	1985	Single chain (41)	Dreiding (explicit H bonds)	MM	172.9
Kroon <i>et al.</i> ¹⁸³	1986	Single chain (41)	MM2 (explicit H bonds)	MM	136
Tashiro and Kobayashi ⁴³	1991	Single chain (41)	Dreiding (explicit H bonds)	MM	167.5
Reiling and Brackman ¹¹⁰	1995	1 $\times$ 1 $\times$ 1 unit cell crystal (41)	CHARMM (explicit H bonds)	MM & NVT MD	148
Kroon-Batenburg and Kroon ¹⁹⁰	1997	3 $\times$ 3 $\times$ 2 unit cell crystal (41)	GROMOS (implicit H bonds)	MM	136
Neyertz <i>et al.</i> ²¹²	2000	3 $\times$ 2 $\times$ 2 unit cell crystal [personal communication]	Custom (implicit H bonds)	NPT MD	115.2
Štuncová <i>et al.</i> ¹¹⁸	2005	Single chain (384)	COMPASS (implicit H bonds)	MM	145
Eichhorn and Davies ⁴⁴	2006	Unit cell crystal (37)	COMPASS (implicit H bonds)	MM	149
Tanaka and Iwata ²⁰¹	2006	1 $\times$ 1 $\times$ 10 unit cell crystal (385)	COMPASS (implicit H bonds)	MM	110.53
		4 $\times$ 4 $\times$ 10 unit cell crystal (385)	COMPASS (implicit H bonds)	MM	124.6
Bergensträhle <i>et al.</i> ¹⁹⁴	2007	4 $\times$ 4 $\times$ 8 unit cell crystal (37)	GROMOS (implicit H bonds)	NVT MD	156

E_A = elastic modulus in axial direction.

number of infinite length chains are useful because they incorporate the axial dimension while enabling surface effects. However, they are limited in the number of chains that can be modeled and so tend to have unrealistically small cross-sections.

5.2 Predictions

5.2.1 Crystal structure. The most commonly reported results from MM or MD-based studies of crystalline cellulose are those that define the structure of the unit cell. As discussed in section 1.1, the crystal structures of cellulose I α and I β are determined by the side lengths and angles of the unit cell. In most cases, the predicted crystal structures are compared to experimental measurements as part of the model validation process. At a minimum, these comparisons are made for the axial length of the crystalline cellulose unit cell, often referred to in the literature as the *c*-spacing. The degree of accuracy of this predicted length is considered to be a significant indicator of the validity of a given model. More recent studies have evaluated model validity in terms of the other unit cell dimensions and angles. Experimental comparisons include those to nuclear magnetic resonance ^1H NMR¹⁸⁸ and ^{13}C NMR,^{181,195,210,211} XRD ($^{123}\text{-Cellulose II}$ only), Raman spectroscopy,¹¹⁸ and neutron crystallography.⁴²

Another widely predicted structural characteristic is the transition between different crystal forms including transitions between different phases (*e.g.*, cellulose I α and I β) and orientations (*e.g.* “parallel-up” and “parallel-down” as defined in section 1.1). Transitions are typically induced in molecular models by changing the temperature, introducing a solvent, or explicitly shifting the positions of atoms in the structure. Resulting structures are then evaluated in terms of their minimum energy before, during, and after the induced transition. A few references report predictions of other structural features: twist,^{178,204–206} pucker,^{179,190,193,206} and persistence length.¹⁹¹

As discussed in section 1.2, hydrogen bonding is critical to the structural stability of crystalline cellulose. Atomistic modeling provides the unique capability to “count” the number of hydrogen bonds, a value that can be used to evaluate structure stability and the likelihood of transitions between structures. The difficulty in utilizing this information is the lack of a consistent definition of a hydrogen bond. A hydrogen bond is typically identified by the distance between

hydrogen and acceptor and (sometimes) by the angle between donor, hydrogen, and acceptor. For example, inter and intra molecular hydrogen bonds have been identified as those where $\text{H}\cdots\text{O} < 2.4 \text{ \AA}$,¹⁹⁰ $\text{H}\cdots\text{O} < 2.5 \text{ \AA}$ and $\text{O-H}\cdots\text{O} > 135^\circ$,^{181,192} $\text{H}\cdots\text{O} < 3.195 \text{ \AA}$,²¹² $\text{H}\cdots\text{O} < 2.5 \text{ \AA}$ and $\text{O-H}\cdots\text{O} > 120^\circ$,¹⁷⁹ $\text{H}\cdots\text{O} < 3 \text{ \AA}$ and $\text{O-H}\cdots\text{O} > 90^\circ$,¹⁸⁷ $\text{H}\cdots\text{O} < 3.5 \text{ \AA}$ and $\text{O-H}\cdots\text{O} > 150^\circ$,¹⁹⁴ and $\text{H}\cdots\text{O} < 3.5 \text{ \AA}$ and $\text{O-H}\cdots\text{O} > 135^\circ$.²⁰⁶

5.2.2 Material properties. Molecular modeling has been used to predict a variety of cellulose material properties. The most frequently reported are elastic properties because they can be calculated using molecular models relatively easily and are experimentally measurable. Predictions of the elastic modulus in the axial (chain) direction for I α or I β have been reported from atomistic model-based studies for more than 20 years now; one of the first studies was reported in 1985.²⁰⁸ Unfortunately it has been difficult to compare elasticity predictions due to variation in the model structures and methods. This effect is illustrated for I β in Table 4.

The most common method for calculating axial modulus *via* molecular simulation is illustrated by the schematic in Fig. 23. First, the equilibrium axial length, z_0 , of one or more cellulose chains is calculated. Then, the simulation cell is extended, Δz , (typically a tensile strain) in the axial direction by some small amount. The magnitude of this extension varies in the literature, but the limiting value, above which cross-sectional area changes cannot be ignored, has been estimated to be 5% of the chain length.²⁰¹ Total applied strain is an important parameter and has been shown to affect calculated elasticity.³⁹³ The minimum potential energy of the extended system is then calculated using MM (or in a few cases as a time average from MD). This process is repeated to generate a plot of energy as a function of axial length, z . The data are fit to a harmonic^{110,175,183} or third order polynomial^{44,118} equation. The derivative of this function yields force, which can be divided by area to obtain stress (note that this area is somewhat an arbitrary determination in single chain systems). Axial modulus is then the slope of the linear relationship between stress and strain.³⁹³ In an alternate energy density method, the same simulation procedure is performed, but the modulus is taken to be twice the slope of the linear relationship between energy density (change in energy divided by volume) and the square of the strain.²⁰¹

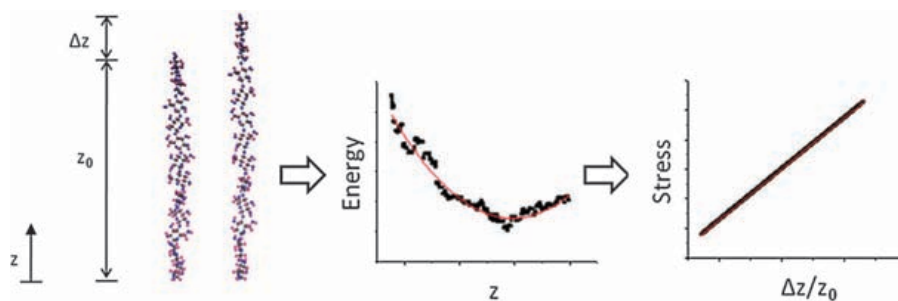


Fig. 23 Illustration of the most widely used method for calculating the axial modulus of cellulose using molecular simulation. (a) Snapshots of a single cellulose chain at its equilibrium and strained lengths; color scheme same as in Fig. 22. Representative plots of (b) potential energy as a function of chain length and (c) the corresponding stress as a function of strain. Variables are defined in the text.

A few studies of elastic properties have used other methods. In one case, the system was strained, and then an MD simulation run from which the internal stress was directly calculated as a time average of the pressure virial. The elastic modulus was then the calculated stress divided by the imposed strain.¹⁹⁴ Another approach was to directly apply stress and calculate the strain.²¹² This method was implemented by running an MD simulation in the NPT ensemble and systematically varying the imposed pressure.

All the above methods assume constant cross-sectional area, and therefore do not capture Poisson contraction that may occur as a result of the applied tension. Parameters that quantify elastic properties with and without the assumption of constant area have been differentiated as “chain stiffness” and “chain modulus”, respectively.⁴⁴ A few studies have also reported full elastic constant matrices.^{43,44,176} These methods are based on the continuum concept of elasticity and report a fourth order tensor. Elastic properties calculated from the full elasticity matrix can differ from those obtained using the methods described in the previous paragraphs because there is no assumption of constant area.⁴⁴

Even if the same method is employed, it is nearly impossible to compare predicted elastic properties from one study to another because of the differences between the models.³⁹³ Significant variation has been found even within the same force field “family” where elastic properties obtained using COMPASS, PCFF, and various versions of CVFF (with the same $4 \times 4 \times 10$ unit cell structure) were found to differ from one another by up to $\sim 25\%$.²⁰¹ One critical aspect of a model in terms of elastic properties is hydrogen bonding. Molecular simulation has shown that (numerically) removing hydrogen bonds can cause predicted elastic properties to decrease on the order of 50 to 60%.^{43,183,208} Furthermore, it is the intramolecular hydrogen bonding (as opposed to intermolecular) that is critical for elastic properties.⁴³ More recently it was shown that removal of hydrogen bonds resulted in a decrease of between 14% and 26% in the $I\alpha$ chain stiffness, while for $I\beta$ it caused either a 15% decrease or a 7% increase in chain stiffness depending on the initial atomic coordinates.⁴⁴ Further it has been found that cooperative hydrogen bonding plays a critical role such that omitting inter-chain hydrogen bonding (as is necessarily the case for a single chain) will affect intra-chain hydrogen bonding.²¹⁴

In addition to force field, the model structure has been shown to affect elastic property predictions. One example of this difference was illustrated by a comparison between models of $1 \times 1 \times 10$ and $4 \times 4 \times 10$ $I\beta$ unit cells. With the same force field (COMPASS) and simulation method, the axial modulus of the larger unit cell were $\sim 11\%$ greater than that of the single chain.²⁰¹ That same work found that the effect of force field on elasticity was less significant for the larger system. As mentioned previously, an MM simulation does not enable the system to deviate far from its initial configuration. Thus, most of the elastic property calculations based on MM are highly dependent on the choice of configuration. A comprehensive study of this effect was recently performed for cellulose $I\alpha$, $I\beta$, and II with two different initial configurations for each.⁴⁴ The difference between initial configurations was quantified by the equilibrium unit cell length in the chain

direction (c-spacing). For $I\alpha$, a 1.5% difference in the c-spacing resulted in 12% elasticity variation, while for $I\beta$, a 0.1% difference in c-spacing resulted in 22% elasticity variation.

Environmental conditions will also have an effect on cellulose elastic properties. Limited simulation work has been done to investigate these effects although a few studies have considered the influence of temperature. The predicted elastic properties of $I\beta$ were found to be the same using either MM (which is effectively at 0 K) or MD run at 300 K. However, the change from an MM to an MD model of $I\alpha$ resulted in an axial modulus decrease of 34 GPa.^{110,175} MD simulation also revealed that increasing the temperature from 300 to 500 K will decrease the modulus of $I\beta$ by 39 GPa.¹⁹⁴

Material property predictions other than elasticity have been limited mostly to characterizations of the thermal response of cellulose. The CTE was predicted for cellulose $I\beta$ from MD simulations run in the NPT ensemble at temperatures from 280–320 K.¹⁹⁴ Molecular dynamics simulations in the NPH ensemble have also been used to predict the CTE and specific heat at constant temperature of cellulose II.¹⁷⁶ Lastly, for amorphous cellulose only, a transition at 650 K observed in plots of specific volume vs. temperature obtained from NPT simulations was identified as the glass transition temperature.¹⁷⁹

5.2.3 Solvent and interfacial topics. Models have been used to investigate the interaction of cellulose with other materials. These studies can be divided at a high level into two groups: interactions with a liquid solvent and interactions with other polymeric materials.

Most solvent studies are focused on water (exceptions being studies of benzene²⁰³ and cyclohexane¹⁹⁷). Because of the large number of solvent molecules necessary to effectively study the effect on crystalline cellulose, these studies typically employ united atom model-type approximations. For water, simple interaction-site models keep each molecule in a rigid geometry and describe the interaction between molecules using pair-wise Coulombic and van der Waals expressions. The most common of these models reported in the cellulose literature are TIP3P, used by ref. 110,178,200,203–207 and SPC, used by ref. 188,191–193,195–197,202. Both of these models are three-site models in which each water molecule contains three sites for the electrostatic interactions, a partial positive charge on the hydrogen atoms that is exactly balanced by a negative charge on the oxygen atom, and van der Waals interactions calculated with a single interaction site located at the oxygen atom.

The initialization process for systems that include solvents is typically some variation of the following procedure: First, atoms in the cellulose chains are placed in their crystal structure-dependent minimum energy positions. Then the extents of the simulation cell are increased and the new volume filled with solvent molecules at the desired density (e.g. water at 0.998 g cm^{-3}). Lastly, the system is equilibrated in two steps: the positions of the cellulose atoms are fixed while the solvent molecules are allowed to approach their minimum energy configuration; and then all positional restraints are released to allow the entire system to approach equilibrium.

The resultant system is characterized in terms of (a) cellulose-solvent interactions, (b) changes in the solvent due to the cellulose, and (c) changes in the cellulose due to the presence of the solvent. The strength of the interaction between solvent and solute is determined by calculating the potential energy of the system and, sometimes, the number of hydrogen bonds formed between the cellulose and water (as discussed in section 5.2.1 the criteria used to identify hydrogen bonds is somewhat inconsistent). Additional insights are gained by breaking the total potential energy down into its component parts (van der Waals, bond, angle, *etc.*) to investigate which terms are dominant. The effect of cellulose on water is usually investigated by calculating the average radial distribution function of the water. Some studies have used the radial distribution function to characterize the water structure relative to specific surfaces, referred to as solvent accessible surfaces.^{178,193} In one study, instead of surrounding the cellulose with water, a water droplet was introduced into the model. This enabled investigation of the solvent accessible surfaces in terms of the contact angle.²⁰² Lastly, studies have shown that water induces changes in the crystal structure itself, including affecting the twist. A recent structural observation was that the crystal size increased due to the solvent, a phenomenon referred to as swelling.^{200,204,205,207}

A few studies have also been reported in which the interaction of cellulose and another polymeric material was investigated. These studies have, to this point, been focused on characterizing molecular interactions in terms of the various surfaces of crystalline cellulose. Reported cellulose-polymer interaction simulations include models of lignin (*threo* guayacyl β -O-4 dimer) with the (110)_m, (1 $\bar{1}$ 0)_m, (200)_m, (010)_m faces of cellulose I β ,^{198,199} polymers (EVA0, EVA75, EVA100) with the (110)_m and (1 $\bar{1}$ 0)_m faces of cellulose I β ,¹⁸⁰ and benzophenone with (200)_m, (110)_m, (1 $\bar{1}$ 0)_m faces of cellulose I β and amorphous cellulose, with and without water.²⁰⁰ In these studies, the interactions between cellulose and an adjacent molecule (note that this does not refer to the formation of covalent bonds) are characterized in terms of interaction energies, density profiles, and orientation changes. In another study, the interaction between a cellulose crystal and a single cellulose chain was characterized by numerically pulling the chain away from a surface and calculating the pull-off force as a function of the initial chain orientation.¹⁹⁷ Lastly, the potential for chemical grafting as a means of strengthening the interaction between cellulose and a polymer matrix was investigated by grafting caprolactone onto the surface of a cellulose crystal and studying the relationship between caprolactone density and work of adhesion.¹⁹⁶

6. Analytical modeling of engineered cellulose materials

The “nano” hypothesis is that using nanoscale phases within a composite will result in new materials with properties not attainable in conventional composites. The potential for realization of useful nanocomposites must derive from one of two phenomena. First, the nanoscale phases themselves might have excellent properties. Most experiments show that nanocrystalline cellulose is stiffer and stronger than their

natural fiber or organic source (see Table 3). If CNs are built into a composite with the proper structure, those properties might translate into excellent composite properties. Second, nanocomposites might derive excellent properties from nanoscale phenomena not present in conventional composites. A potential basis for “nano” effects might be the interface. The amount of interface in nanocomposites greatly exceeds the amount in a composite with the same content but having larger phases. If this extra interface can enhance properties, the nanocomposite might exhibit unique properties. The advancement of CN composites will require combined experimental and modeling research efforts to exploit the excellent properties of CN reinforcements and to understand and exploit any possible nanoscale phenomena for property enhancement. Some obvious questions arise. Can CN composites be made that exploit the excellent properties of CN reinforcements? Will interfacial effects help or hinder the development of CN composites? Will new nanoscale phenomena be discovered that can be exploited? Progress on these and related questions should be guided by modeling the mechanical and physical properties of CN nanocomposites.

Since the 1990's, various analytical modeling approaches have investigated the effect of CN fillers within polymer matrices on effective nanocomposite properties. Most of the effort has focused on using analytical models to understand the “unusual” reinforcing effect of low concentration (less than 30 wt%) CN in low-modulus (rubbery) polymers.²¹⁵ Typically, mean field (Halpin-Tsai,²¹⁶ Halpin-Kardos,²¹⁷ *etc.*) and percolation (connected CN network within the matrix) approaches^{218,219} have been used, as previously reviewed.^{5,8,16,19} This section reviews the basic science behind modeling composite properties and then uses those concepts to critically evaluate prior models used for CN composites. The primary goal is to use conventional continuum mechanics methods and to evaluate the best application of those methods for CN composites. A secondary goal is to evaluate whether scaling issues, such as the large increase in interface, might be important. This continuum-mechanics approach does not deny the possibility of undiscovered nano-effects playing a role in nanocomposites. Rather, it focuses on what should be possible given what is known now by using only continuum mechanics. If new nano-effects are discovered that change those mechanics, then new modeling should explore those effects. But, if the “great potential” of CN composites is contingent on the discovery of unknown nano-effects, one should be aware that “Life has a malicious way of dealing with great potential.”²²⁰

6.1 Elastic properties by continuum mechanics

There are two strategies for solving nanocomposite mechanics problems. One approach is to consider a specific observed structure with known phases and evaluate its properties. This approach works best when an exact solution is possible. For example, the classic Eschelby analysis can solve for an elliptical inclusion in an infinite matrix.²²¹ For more complicated structures, finite geometries, interacting phases, *etc.*, exact solutions are impossible and composite micro-mechanics always involves approximations (*e.g.*, Mori-Tanaka,²²²

Halpin-Tsai,²¹⁶ etc.). Complicating issues can alternatively be studied numerically (finite element analysis, FEA) by considering a representative volume element (RVE) of the structure. Both approximate and numerical methods give a single approximate answer to a specific structure. It is difficult to judge if the approximations are valid or if any errors will make the true result higher or lower. More importantly when developing new materials, it is difficult to judge the possibility for potential materials to have much worse or much better properties than predicted by analyses. An alternative approach is to develop upper and lower bounds to the mechanical properties.^{223,224} The upper bound is the maximum possible property for a composite of given phase content and properties regardless of the phase geometry. Similarly, the lower bound is the minimum possible mechanical property. This approach is valuable for new materials and valuable tool for avoiding claims of a potential for impossible results (e.g., those exceeding upper bounds).

This review evaluates existing rigorous bounding methods that are applicable to CN composites modeling. It begins with elementary bounds for a 3D random composite of arbitrary phase geometry (section 6.1.1). These equations assume no knowledge about structure. The next two sections introduce structure (2D and 1D structures in section 6.1.2) followed by fiber length and interface effects (section 6.1.3). The bounds on a 1D composite with short fibers and interface effects can be viewed as a unit cell for a composite of well-dispersed CN fibers. This unit cell forms the basis for various mean field methods described next (section 6.1.4). Finally, these existing bounding methods are used to evaluate mean-field modeling methods for CN composites. In general, the discrepancies between modeling and experiment in prior CN studies using mean-field methods (as previously reviewed^{5,8,16,19}) can be attributed to poor modeling assumptions rather than to an observation of new nano-effects, such as percolation effects. The bounding approach can evaluate expectations for percolation effects in CN composites (section 6.1.5).

6.1.1 Elementary upper and lower bounds. The classic view of upper and lower bounds is the model of springs in parallel or series, which are known as the Voigt and Reuss bounds, respectively.²²⁴ This elementary approach can be extended to 3D solids by averaging elements of the stiffness or compliance matrices instead of a 1D model of springs.²²³ As explained by Hashin,²²³ these provide rigorous upper and lower bounds to the effective properties of composites, but they may not be the optimal bounds. In other words, it might be possible to find an improved upper bound that is *lower* than the elementary upper bound, or an improved lower bound that is *higher* than the elementary lower bound.

Elementary bounds of a statistically isotropic, 3D composite with random CN orientation within a polymer matrix are described first. This model assumes that an RVE of this composite is an isotropic material (*i.e.* all possible orientations of the CN phase are equally likely). The CN phase, however, is anisotropic and is commonly approximated as transversely isotropic (CNs can be treated as orthotropic, but the resulting equations are much more complex and for many properties, although not all, the final results are similar). The upper and

lower bound properties for 3D random composites are then found by averaging stiffness and compliance matrix elements over all possible orientations for the axial direction of the CN crystal.^{224,225} The final results are most directly expressed as bounds on the effective bulk and shear moduli (K_c and G_c) of the composite. The averaging equations derived in Christensen²²⁴ and Watt and Peseinick,²²⁵ for anisotropic CN fibers properties are added here with an isotropic matrix phase to give:

$$\left(\frac{V_f}{K_T} + \frac{V_m}{K_m}\right)^{-1} \leq K_c \leq \frac{V_f}{9}(E_A + 4K_T(1 + \nu_A)^2) + V_m K_m \quad (1)$$

$$\left(\frac{V_f}{15}\left(\frac{1}{K_T} + 6\left(\frac{1}{G_A} + \frac{1}{G_T}\right) + \frac{3(1 + 4\nu_A)}{E_A}\right) + \frac{V_m}{K_m}\right)^{-1} \leq G_c \leq \frac{V_f}{15}(E_A + 6(G_A + G_T) + K_T(1 - 2\nu_A)^2) + V_m G_m \quad (2)$$

Here E_A , K_T , ν_A , G_A , and G_T are axial modulus, transverse bulk modulus, axial Poisson's ratio, and axial and transverse shear moduli of the transversely isotropic CN, K_m and G_m are the bulk and shear moduli of the isotropic matrix, and V_f and V_m are volume fractions of CN and matrix. The bounds on the axial modulus can be found from the bounds on K_c and G_c and using a standard relation between E , K , and G for isotropic materials:²²⁶

$$\frac{9K_c^l}{1 + \frac{3K_c^l}{G_c^l}} \leq E_c \leq \frac{9K_c^u}{1 + \frac{3K_c^u}{G_c^u}} \quad (3)$$

where superscripts *l* and *u* refer to lower and upper bounds on bulk and shear moduli.

For a sample plot, consider the results for CN fibers ($E_A = 150$ GPa) in a matrix of either a glassy polymer ($E_m = 2.5$ GPa) or a rubbery polymer ($E_m = 0.1$ GPa). The upper and lower bounds for E_c are shown in Fig. 24 (additional material properties in the caption). This modeling illustrates several important points. First, the bounds when using a glassy polymer are fairly close. This result implies that

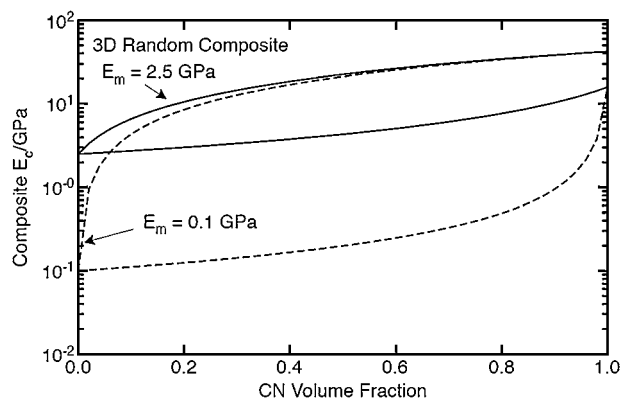


Fig. 24 Elementary upper and lower bound modulus for 3D random CN composite with glassy ($E_m = 2.5$ GPa, $\nu_m = 0.33$) or rubbery ($E_m = 0.1$ GPa, $\nu_m = 0.47$) matrix containing CN filler ($E_A = 150$ GPa, $K_T = 7.6$ GPa, $\nu_A = 0.25$, $G_A = 15$ GPa, $G_T = 3.8$ GPa).

no matter how you make a statistically isotropic CN composite, the expected modulus will be confined to a range of about one half an order of magnitude. For example, a CN/glassy matrix composite with 10% CN must have a modulus between 2.7 and 6.6 GPa. Second, the region between these upper and lower bounds encompasses all possible phase geometries. In other words, within that half order of magnitude are structures with either perfect dispersion or agglomerated phases, structures with either nanofibrils or macroscopic fibrils, and structures with either a percolated network or no network. Although working to achieve nanocomposites with good dispersion or a percolated structure might move the results within the bounds, such modification cannot lead to “unusual” levels of reinforcement that exceed this upper bound.

Many results with CN fillers focus on large increases in modulus of rubbery polymers. These large relative increases are predicted by the elementary bounds. For example, the upper bound for a 10% CN/rubbery matrix composite is 4.3 GPa, which is a 43-fold increase on the base matrix. But conclusions based on relative modulus can be misleading. The absolute increment in modulus attributed to the CN phase is nearly identical for the glassy and rubbery matrices. For the 10% CN composite, the upper bound for the glassy matrix is 4.1 GPa higher than the base matrix while it is 4.2 GPa higher for the rubbery matrix. In other words, the CN is contributing essentially an identical amount of reinforcement for the two matrices. The large relative increase when using a rubbery matrix is because the matrix modulus is low and not because the CN has initiated a new mechanism for nanoreinforcement.

These elementary bounds are trivial bounds and sophisticated modeling (e.g., Hashin-Shtrikman^{227–229} or numerical methods) could shift the bounds closer together, but would not expand the opportunity for higher properties. Two effects that might expand the bounds at a given CN volume fraction would be to change CN–matrix interfacial properties, or to increase the CN orientation. Interfacial properties will have an influence if the CNs constrain the matrix or modify crystal structure (when using semicrystalline matrices^{230–232}) in a thin layer around the fibers such that the local matrix modulus increases. Since the entire matrix can be close to CN in a well-dispersed nanocomposite, the effect could be significant. The CNs may increase a glassy matrix modulus slightly. The effect is more likely to be dramatic for rubbery matrices. These changes could shift all bounds to higher values. But, the contribution of the CNs would be unlikely to change (as it did not change when matrix modulus increased 25 fold from 0.1 GPa to 2.5 GPa, see Fig. 24). On the other hand, a stiffening of the interphase region might be vitally important and useful for stress transfer;²³³ this possibility is discussed in section 6.1.3. Perhaps more significant would be if the CN orientation changed from 3D random to a more ordered structure. This effect is discussed next in section 6.1.2.

6.1.2 Statistically isotropic (2D) composite films and unidirectional (1D) composites. The next level of structure to consider is a CN film such that all CN fibers lie in the plane of the film. In this example, the bulk composite would be statistically isotropic for in-plane properties (2D). The analysis

of this structure can be done by the same methods used for the 3D composite except averaging is done over all orientations within the plane of the film.^{217,224} The equations for in-plane tensile and shear moduli are:

$$\left[\frac{V_f}{8} \left(\frac{3}{E_T} + \frac{1}{G_A} + \frac{3 - 2\nu_A}{E_A} \right) + \frac{V_m}{E_m} \right]^{-1} \quad (4)$$

$$\leq E_c \leq 4V_f U_2 \left(1 - \frac{U_2}{U_1} \right) + V_m E_m$$

$$\left[\frac{V_f}{2} \left(\frac{1}{E_T} + \frac{1}{G_A} + \frac{1 + 2\nu_A}{E_A} \right) + \frac{V_m}{E_m} \right]^{-1} \quad (5)$$

$$\leq G_c \leq V_f U_2 + V_m G_m$$

$$U_1 = \frac{E_A(3 + 2\nu'_A) + 3E_T + 4G_A(1 - \nu_A\nu'_A)}{8(1 - \nu_A\nu'_A)} \quad (6)$$

$$U_2 = \frac{E_A(1 - 2\nu'_A) + E_T + 4G_A(1 - \nu_A\nu'_A)}{8(1 - \nu_A\nu'_A)} \quad (7)$$

The final level of structure is to assume that all CNs are oriented in the same direction to produce a unidirectional composite (1D). First consider the CNs to be long enough to be treated as continuous fibers. The most rigorous model for analysis of continuous fiber, unidirectional composites is the concentric cylinders model developed by Hashin.^{223,234} This model is a bounding model that is applied to an approximate structure for an unidirectional composite; the only approximation is that the CNs are allowed to have variable diameters such that 100% of the volume can be filled with concentric cylinders. The resulting composite properties are transversely isotropic with five independent mechanical properties. Remarkably, the upper and lower bounds for four of the five properties coincide, which implies the model provides an exact solution to the approximate (but reasonable) structure. The equations for axial modulus, axial Poisson's ratio, axial shear modulus and the transverse modulus are:

$$E_A^c \approx E_A V_f + E_m V_m \quad (8)$$

$$\nu_A^c \approx \nu_A V_f + \nu_m V_m \quad (9)$$

$$G_A^c = G_m + \frac{V_f}{\frac{1}{G_A - G_m} + \frac{V_m}{2G_m}} \quad (10)$$

$$K_T^c = K_m + \frac{V_f}{\frac{1}{K_T - K_m} + \frac{V_m}{K_m + G_m}} \quad (11)$$

The fifth property, which can be given as either E_T^c or G_T^c is bounded, rather than exact, and the expression is more complicated (see elsewhere for details^{223,224,235}). The equations above for E_A^c and ν_A^c used approximately-equal signs because an additional term related to difference in Poisson ratios between the CN and the matrix has been omitted. The full expressions are given in Hashin,²²³ but the extra terms are usually negligible and therefore were omitted here for simplicity.

The upper bound moduli for 3D, 2D (film), and 1D (unidirectional) CN composites (with the same mechanical properties as used for Fig. 24) are shown in Fig. 25. As more order is imposed on the structure, the potential modulus

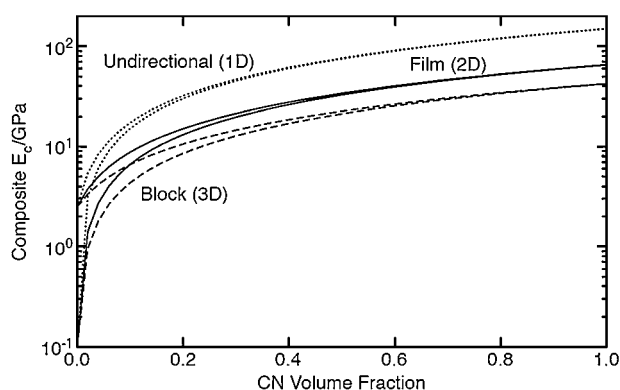


Fig. 25 Upper bound modulus for 3D random (dashed), 2D film (solid) and 1D unidirectional (dotted) composites, showing the influence of CN orientation on predicted composite properties. The upper curve of each set is for a glassy polymer ($E_m = 2.5$ GPa, $\nu_m = 0.33$); the lower curve is for a rubbery polymer ($E_m = 0.1$ GPa, $\nu_m = 0.47$). The CN properties used were ($E_A = 150$ GPa, $K_T = 7.6$ GPa, $\nu_A = 0.25$, $G_A = 15$ GPa, $G_T = 3.8$ GPa).

increases. For example, upper bound modulus for a 10% CN composite in a glassy matrix ($E_m = 2.5$ GPa) ranges through 6.6 GPa, 8.8 GPa, and 17.2 GPa, for 3D, 2D, and 1D composites, respectively. The 3D composite achieves modulus in all directions while the 2D and 1D only achieves high modulus in the plane of the film or along the direction of the fibers, respectively. These predicted results are supported by experimental testing of CN composites that have measured up to 3–4 times higher composite E with increased particle alignment.^{236,237} Gindl and Keckes²³⁶ produced preferentially aligned CNC-cellulose composites (~25 wt% CNC, 75 wt% cellulose II) that had elastic moduli of 33.5 GPa (see section 7.1.2). The result show 1D order leads to higher modulus and is similar to the 1D upper bound (depending on assumptions about moduli of CNC and the cellulose matrix). For neat BC films, Bohn *et al.*²³⁷ aligned neat BC films by drawing and was able to span a range from 2D planar order to approaching 1D order. The modulus increased about three fold (from 10 GPa to 33 GPa), which is similar to the expected increase (*i.e.* three fold) due to 1D *vs.* 2D particle alignment (see Fig. 25).

6.1.3. Fiber aspect ratio and interface effects. Two important properties for all short-fiber reinforced composites are the fiber aspect ratio and the quality of the interface between the fibers and the matrix. Both of these effects have been incorporated into the concentric cylinders model introduced in section 6.1.2. The detailed analysis can be reduced to simply replacing the fiber axial and shear moduli by effective moduli (as derived elsewhere^{238,239}):

$$E_A^* = E_A \left(1 - \frac{\tanh \beta \kappa}{\beta \kappa} \right) \quad (12)$$

$$G_A^* = \frac{G_A}{1 + \frac{2G_A}{r_f D_s}} \quad (13)$$

The fiber axial modulus is evaluated by calculating the average stress in the fibers accounting for a stress transfer region at the fiber ends.²³⁸ This effect can be modeled accurately using

shear-lag theory where the parameter β is a stress transfer rate and κ is the fiber aspect ratio (length/diameter).^{240–242} CN aspect ratios can be estimated from the data given in Table 2, for example; MFC (~10–100), NFC (>100) CNCs (~5–50), t-CNC (~70–100), and BC (20–100). Shear-lag methods originated with the work of Cox,²⁴³ but the shear-lag parameter proposed by Cox is known to be inaccurate (despite its continued misuse in modeling).^{242,244} Old shear-lag methods can be fixed by replacing β with a new result that provides accurate stress transfer rate in terms of phase properties (derived elsewhere^{240–242}), which for solid fibers is:

$$\beta^2 = \frac{2}{E_A E_m \frac{V_m}{4G_A^*} - \frac{1}{2G_m} \left(\frac{V_m}{2} + 1 + \frac{1}{V_m} \ln(V_f + \chi) \right) + \frac{V_m}{r_f D_s}} \quad (14)$$

Here r_f is the CN cross-sectional radius and D_s is an interfacial stiffness parameter²³⁹ (see below). The term $\chi = 0.009$ is a universal constant that allows use of this β equation in the limit as V_f approaches zero, while older shear-lag models cannot be used at low volume fractions. This constant was determined numerically and works for any ratio of moduli between the fiber and the matrix and for both isotropic and anisotropic fibers.²⁴⁴

The fiber axial shear modulus, as well as the shear-lag β that influences tensile modulus, are altered to account for fiber/matrix interface effects.^{233,244} This change uses the interface analysis method for composites introduced by Hashin.²³⁹ The approach is to define interface parameters (such as D_s above) that relate to a displacement discontinuity at the fiber/matrix interface. The simplest model assumes a linear relation between axial displacement discontinuity ($[w]$) and interfacial shear stress (τ_{int}):

$$[w] = \frac{\tau_{int}}{D_s} \quad (15)$$

where D_s is an interfacial stiffness property. An interface property of $D_s = \infty$ implies zero discontinuity or a “perfect” interface. An interface property of $D_s = 0$ implies zero interfacial shear stress or a debonded interface. All other values of D_s define an “imperfect” interface; the higher the value, the faster the rate of stress transfer and therefore the better the interface for maximal stiffness properties of the composite.

Fig. 26 shows E_A^* for a 1D composite found using E_A^* as a function of fiber aspect ratio for CN properties ($V_f = 10\%$, $E_A = 150$ GPa, $r_f = 5$ nm) in a glassy matrix ($E_m = 2.5$ GPa) and various values of the interfacial stiffness property. As D_s decreases, the axial modulus drops significantly and the CN reinforcement goes from an effective material that works well with aspect ratios 10 and up to a material that provides virtually no reinforcement (when $D_s = 86$ GPa mm⁻¹). Modeling thus predicts that the development of effective CN composites will rely on an interface with a high D_s , or more physically, on an interface that can transfer stress from the matrix to the CN as rapidly as possible.²³³

This large role for the interface suggests measuring D_s would be useful, but that is a difficult task for nano-reinforcements. The value of $D_s = 86$ GPa mm⁻¹ was used because that is a result measured for the interface between micron-sized HM carbon

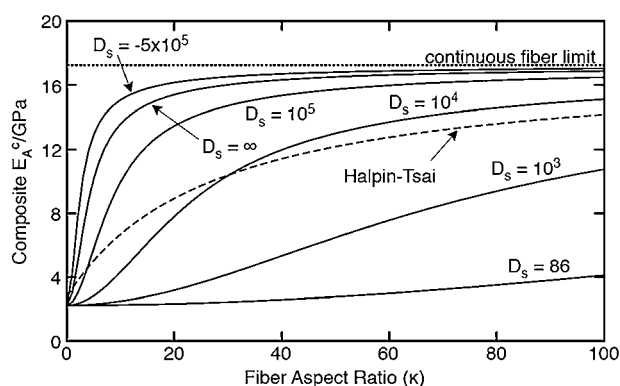


Fig. 26 The 1D composite modulus for CNs ($V_f = 10\%$, $E_A = 150$ GPa, $K_T = 7.6$ GPa, $\nu_A = 0.25$, $G_A = 15$ GPa, $G_T = 3.8$ GPa, $r_f = 5$ nm) of various aspect ratios (0–100) in a glassy polymer matrix ($E_m = 2.5$ GPa, $\nu_m = 0.33$) as a function of interfacial stiffness (D_s in GPa mm⁻¹). Both particle aspect ratio and interfacial stiffness influence the predicted composite modulus. The horizontal dotted line is the continuous fiber limit. The dashed line is the prediction by the Halpin-Tsai equation using $\zeta = 2\kappa$ (it is only one curve because the equation does not account for interface effects).

fibers in an epoxy matrix.²⁴⁵ The interface quality for CN composites is unknown. Fortunately, interactions between CN filler and a matrix could potentially stiffen the layer of matrix on the CN surface. When stiffening occurs, the interface might become better than “perfect.” In imperfect interface modeling, this phenomenon would correspond to a negative displacement discontinuity and a negative D_s .²⁴⁶ Fig. 26 shows one result for negative D_s showing that CNs that stiffen the interphase region may provide an excellent composite even with small aspect ratios. Because of the larger amount of interface in nanocomposites, they could potentially reinforce better than larger-scale fillers. Negative values of D_s are limited to the regime where the denominator in β^2 is positive; a zero denominator corresponds to the limit of a rigid interphase region.²³³

The above modeling for E_A^* used shear-lag analysis because this approach has been shown by comparison to numerical methods to be an accurate upper bound to aligned short-fiber composites.²³³ Much prior work on modeling for CNs has used the Halpin-Tsai equation²¹⁶ instead. For example, as reviewed by Samir *et al.*⁵ (after correcting a typo), the Halpin-Tsai equation predicts the 1D composite modulus to be:

$$E_A^c = \frac{E_A + \zeta(E_A V_f + E_m V_m)}{E_A \left(\frac{V_f}{E_A} + \frac{V_m}{E_m} \right) + \zeta} \quad (16)$$

This empirical equation predicts modulus in terms of an unknown structure parameter, ζ . A common suggestion to account for fiber aspect ratio is to select $\zeta = 2\kappa$,²¹⁶ but the resulting equation is not based on rigorous elasticity and does not agree well with either shear-lag analysis or numerical models (see dashed line in Fig. 26). In terms of upper and lower bounds, the Halpin-Tsai equation has limiting values of $E_A^c = E_V = E_A V_f + E_m V_m$ for $\zeta \rightarrow \infty$ and $1/E_A^c = 1/E_R = (V_f/E_A) + (V_m/E_m)$ for $\zeta \rightarrow 0$; i.e., the limiting values are the simplistic Voigt upper (E_V) and Reuss lower (E_R) bounds. Unfortunately, its relative position between upper and lower

bounds depends on the modulus ratio E_A/E_m . That position can be expressed as

$$\frac{E_A^c - E_R}{E_V - E_R} = \frac{\zeta}{\zeta + V_f + V_m \frac{E_A}{E_m}} \quad (17)$$

Thus, the Halpin-Tsai result will trend to lower bound predictions for high modulus ratio (common in nanocomposites based on rubbery matrices); this limit is not accurate for aligned, short-fiber composites. For reinforcement of glassy polymers, Halpin-Tsai moves closer to other models (see curve for $E_A/E_m = 60$ in Fig. 26). Besides inaccuracy at high modulus ratio, the Halpin-Tsai equation has no information about fiber anisotropy or about the quality of the interface. Any prior model that relied on the Halpin-Tsai equation can be improved by using the concentric cylinders model instead.

6.1.4. Mean field theory for well-dispersed composites.

Most prior modeling efforts for CN composite properties has used the so-called mean-field theory. This theory is a special case of elementary bounds but imposes some restrictions on geometry and therefore will give tighter bounds. It is a building block approach that proceeds as follows: First analyze a short-fiber composite with aligned fibers. Although this step has commonly been done for CN composites using the Halpin-Tsai equations,^{5,8} it is better done with the concentric cylinders model combined with shear-lag and imperfect interface models (see section 6.1.3). This unit cell is then averaged over its possible orientations to find composite properties. This averaging can be done using the bounding methods above for 3D, 2D, or 1D composites. Since the matrix is already included in step 1, the equations above are used by setting $V_f = 1$ and then replacing the CN mechanical properties (E_A , G_A , etc.) with the aligned, short-fiber composite properties from step 1.

This approach was described by Halpin and Kardos²¹⁷ who input the results from step 1 (using the Halpin-Tsai equation²¹⁶) into a quasi-isotropic laminate analysis. A laminate analysis is averaging stiffness elements and a quasi-isotropic layup is identical to averaging all orientations in a plane. Thus, the Halpin-Kardos results are identical to the 2D-composite upper bound on E_c in eqn (4) with $V_f = 1$ and aligned short-fiber composite properties replacing CN properties. Because Halpin and Kardos derived aligned short-fiber composite properties from a Halpin-Tsai equation, their final results are not an upper bound. Their method can be improved by replacing the Halpin-Tsai equation with a concentric cylinder model. With this change, the upper and lower bounds in eqn (1) to (5) with $V_f = 1$ extend the Halpin-Kardos mean-field method to true upper and lower bounds and to both 2D and 3D composites. Because the mean-field model forces each individual fiber to be surrounded by matrix before being averaged into the composite, it physically approximates upper and lower bounds to a well-dispersed composite with a specific fiber aspect ratio. By including imperfect interface properties, the model can include interface effects as well. In short, it is the current state-of-the-art for analytical modeling of CN composites.

Fig. 27 compares upper and lower bound mean-field theory to experimental results by Capadona *et al.*²⁴⁷ The experiments

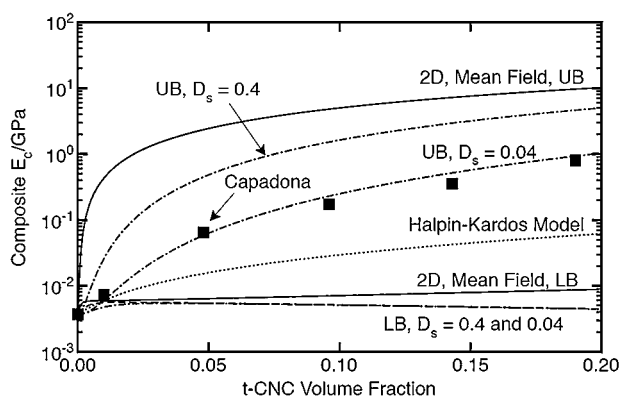


Fig. 27 Comparison of upper and lower bounds mean-field theory for a 2D CN composites applied to the experimental results by Capadona *et al.*²⁴⁷ The solid lines are upper and lower bounds with perfect interface ($D_s = \infty$), while the dashed lines are the bounds with imperfect interface ($D_s = 0.04$ and 0.4 GPa mm^{-1}). The dotted line is the Halpin-Kardos model. The properties used were for CN ($E_A = 143 \text{ GPa}$, $K_T = 7.6 \text{ GPa}$, $\nu_A = 0.25$, $G_A = 15 \text{ GPa}$, $G_T = 3.8 \text{ GPa}$, $r_f = 5 \text{ nm}$, $\kappa = 85$) and the EO-EPI rubbery matrix ($E_m = 0.0037 \text{ GPa}$, $\nu_m = 0.45$).

were for t-CNC fibers ($E_f = 143 \text{ GPa}$) in a rubbery ethylene oxide–epichlorohydrin copolymer (EO-EPI, $E_m = 0.0037 \text{ GPa}$) matrix. As expected the experimental results fall between the upper and lower bounds. Fig. 27 also shows mean-field calculations using the Halpin-Kardos²¹⁷ approach when it is based on the Halpin-Tsai equation.²¹⁶ As shown in the previous section, this model is closer to the lower bound than the upper bound. Thus, an observation that experiments exceed the Halpin-Kardos model is the expected result and not an observation of “unusual” amounts of CN reinforcement. The dashed lines show upper and lower bounds as a function of interface quality. As the interface quality drops, both the upper and lower bounds get lower.

When compared to more accurate models, the question about these CN composite results (and similar results with other rubbery matrices^{215,248–251}), is not why do they exceed the Halpin-Kardos model, but rather why are the results significantly below the theoretical upper bound? The experimental results can be “fit” by setting the imperfect interface parameter to $D_s = 0.04 \text{ GPa/mm}$. This fit suggests that CN fibers slip easily in this rubbery matrix and that slippage keeps the modulus low. This possibility, however, would need confirmation by independent measurement of D_s between t-CNC and the EO-EPI matrix. Another possibility is that the bounding equations are too far apart and more advanced modeling would bring them closer to experiments. First, the mean-field bounds can be narrowed by using the Hashin-Shtrikman bounding method.^{227–229} This classic work was used to bound the mechanical properties of polycrystalline metals and frequently found extremely narrow bounds.²²⁸ A new mean-field analysis could be implemented in the same procedure by treating it as a polycrystalline material with the aligned-short-fiber composite properties as the anisotropic crystal properties. These composite properties belong to the symmetry group for hexagonal crystals; the Hashin-Schtrikman method for hexagonal crystals has been solved²²⁵ and therefore could be

directly applied to CN composites. A second approach to improving the bounds would be to introduce more information about the structure and then use new modeling or numerical methods to calculate properties. This type of modeling may eventually be important for analysis CN composites, especially when using rubbery matrices.

6.1.5 Percolation concepts in mechanical properties.

Percolation concepts in CN composite have been used for explaining the observed exceeding of mean-field results (e.g., Halpin-Kardos²¹⁷), and have been previously reviewed.^{5,8,10,16,19} The concept of percolation deals with the development of a connected network in a multiphase system.²⁵² At low concentrations, no network is formed. As the concentration of the percolating phase increases, it will eventually reach the percolation threshold defined as the first development of a connected network (V_{fc}). Its significance in composites is that some effective properties will increase dramatically and rapidly for concentrations above the percolation threshold. Its significance in nanocomposites including a fibrous phase is that the percolation threshold decreases as the fiber aspect ratio increases.²⁵³ Thus the percolation threshold and the subsequent rapid increase in properties can be shifted to very low concentrations by using high aspect ratio nanofillers. Percolation is most dramatic in high-contrast composites. The property contrast when modeling mechanical properties of CN composites is not very large. For CNs in a glassy matrix, the ratio of filler modulus to matrix modulus is on the order of $150/2.5 = 60$ or less than two orders of magnitude. The property contrast for a rubbery matrix might be $150/0.1 = 1500$ or higher. For comparison, percolation effects are commonly observed in electrical conductivity where the property contrast between a conductive phase and an insulating phase is effectively infinite.

For CN composites, the bounding methods give insight into the role of percolation in composite properties. The development of a percolated network is recognized as a change in structure at the percolation threshold. The definition of bounding methods is that they give the upper and lower bounds for *all* possible structures. Thus, by definition, the structures both below and above the percolation threshold are confined to remain between those bounds. In other words, percolation cannot provide a mechanism for developing properties beyond upper bound calculations, but it can provide a structure that allows the properties to move between those bounds.

Some results on mechanical percolation in t-CNC composites are in the work of Favier *et al.*^{215,248–250} and of Dubief *et al.*²⁵¹ Favier *et al.* reinforced an emulsion polymerization of styrene and butyl acrylate with t-CNC and measured the modulus as a function of volume fraction at 325 K , which is 50 K above the matrix T_g . The matrix shear modulus at this temperature is about 0.00005 GPa . Dubief *et al.* used t-CNCs in a poly(β -hydroxyoctanoate) (PHO) matrix and looked at modulus at 285 K , which is also 50 K about their matrix T_g . The PHO matrix had a slightly higher modulus of $E_m = 0.0004 \text{ GPa}$ (or $G_m = 0.00013 \text{ GPa}$). These experimental results along with upper and lower shear-modulus bounds for a 2D, mean-field model, a Halpin-Kardos²¹⁷ mean field model, a fit to a percolation model from

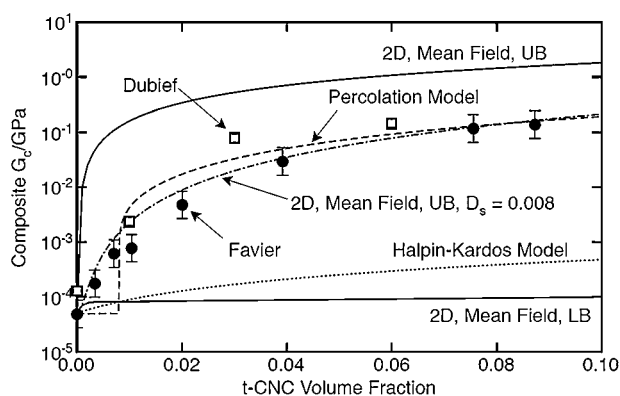


Fig. 28 Comparison of upper and lower bounds mean-field theory for 2D CN composites applied to the experimental results by Favier *et al.*,^{215,249} and Dubief *et al.*.²⁵¹ The solid lines are upper and lower bounds with perfect interface ($D_s = \infty$), while the dot-dashed line is the upper bound with imperfect interface ($D_s = 0.008 \text{ GPa mm}^{-1}$). The dotted line is the Halpin-Kardos model, and the dashed line is the percolation model. The properties used for CN ($E_A = 143 \text{ GPa}$, $K_T = 7.6 \text{ GPa}$, $\nu_A = 0.25$, $G_A = 15 \text{ GPa}$, $G_T = 3.8 \text{ GPa}$, $r_f = 5 \text{ nm}$, $\kappa = 85$) and the styrene and butyl acrylate rubbery matrix ($E_m = 0.00015 \text{ GPa}$, $\nu_m = 0.45$).

Takayanagi,^{218,219} and a fit to 2D, upper bound model with an imperfect interface, are all plotted in Fig. 28. The modeling calculations used the matrix properties from the Favier *et al.* experiments. A 2D model was used because the t-CNCs were assumed to lie in the plane of their thin films.^{215,249} As expected, the experiments and the percolation predictions fall between the upper and lower bounds. Indeed, the Takayanagi percolation model is based on this concept because it combines simplistic lower bound and upper bound results in parallel with the fraction of upper bound properties increasing rapidly after the percolation threshold (fit to $V_{fc} = 0.008$ for these results). The original references compared only to the Halpin-Kardos mean-field result, which Fig. 28 shows is essentially a lower bound model. That model is not a good tool for analysis of CN nanocomposites with rubbery matrices.

The question remains—is percolation a relevant mechanism in CN composites? The observation of experimental results exceeding Halpin-Kardos,²¹⁷ mean-field calculations is a common basis for claiming a percolation effect. A critical evaluation of that model, however, shows it is an approximate lower bound result, and thus exceeding it is the expected result. An alternate justification of percolation is that experimental results fit the Takayanagi percolation model. Although data qualitatively fit such models, no CN results to date show compelling evidence of the very rapid increase in modulus at a finite percolation threshold volume fraction, V_{fc} . In fact these experiments can be “fit” better by a 2D, mean-field model with imperfect interface parameter set to $D_s = 0.008 \text{ GPa/mm}$ (see Fig. 28). Just as fits to a percolation model do not demonstrate a percolation effect, however, fits to an imperfect interface model do not demonstrate an interface effect. Both possibilities need to be studied further, such as by independent experiments to measure D_s . Prokhorova *et al.*²⁵⁴ have recently presented a new percolation-based model and used it to analyse the same

experiments on tunicate fibers in rubbery matrices as a function of CN volume fraction.

Some more compelling evidence of percolation in CN composites and its break down by water uptake has been reported.^{49,247,255} Garcia de Rodriguez *et al.*⁴⁹ investigating the effects of relative humidity (RH) exposure (0–98% RH) on the water uptake and T_g of CNC-polyvinyl acetate composite and suggested percolation effects and/or preferential water uptake at CNC surfaces. Capadona *et al.*²⁴⁷ incorporated t-CNC into a rubbery ethylene oxide-epichlorohydrin matrix. Evidence of percolation in their results comes not from an observation of exceeding mean-field results or of fitting percolation models (both of which they claimed) but rather from their observation of switchable modulus by absorption of water. The initial and dry composites developed a modulus around 0.8 GPa (at 19% t-CNC), which is, as expected, below the mean-field upper bound (see Fig. 28). By adding water, the modulus dropped to 0.020 GPa. A percolation interpretation is that the water changed the structure by disrupting the percolated network resulting in the modulus changing from closer to the upper bound to closer to the lower bound. A potential non-percolation interpretation is that the water induced interfacial slippage (or equivalently viscous flow in the matrix, which could affect properties the same way as interfacial slippage) to dramatically reduce modulus. By either mechanism, the ability to reversibly change stiffness by addition or removal of water opens up potential CN applications.

6.2 Other properties

Besides bounding of stiffness properties, other relevant properties of CN composites can be modeled, such as failure properties and transport properties. The experimental research on fracture and transport properties of CN composites have been summarized in section 7.5.2, and sections 7.8 and 7.9, respectively. However, we are not aware of specific modeling results on these properties of CN composites. The modeling of CN composites can build on existing failure and transport properties modeling of other nanocomposite systems. The interest in modeling failure and transport properties is that they are more likely to have scaling effects, or new nano-effects, than are stiffness properties.

Composite failure can occur by many potential mechanisms, such as matrix failure, fiber failure, interfacial debonding, cavitation of particles, alteration of crack paths, shear banding, and more. Each of these mechanisms may require separate modeling methods. Furthermore, because the thermodynamics for failure are different than for stiffness, the bounding approach used for stiffness does not work for failure. In nanocomposites, scaling in failure properties can be traced to the development of damage zones or plastic zones around a crack tip.²⁵⁶ These zones have a size and therefore the size of fillers has an influence. A goal for nanocomposites is to develop systems that can dissipate energy on much smaller scales than crack tip plasticity zones. Such materials could be used to develop composites or adhesives with enhanced toughness. This potential has been realized, to a modest extent, by adhesives reinforced with silica nanoparticles.^{257,258} Although debate remains on the details, modeling suggests

that particle debonding and plastic void growth contribute most to the toughening.^{257,259} Modeling also confirms the existence of a scaling effect (smaller particle size leads to greater plastic void growth energy) and highlights the importance of good dispersion (as particles agglomerate the toughening effect diminishes).²⁵⁹ These modeling results may be useful for CN fracture properties as well.

The interest in nanocomposite membranes is because experimental results show that transport properties can be altered in “unusual ways” by the addition of nanofillers.²⁶⁰ Modeling of transport properties requires modeling of diffusion processes through phases and effects of interfaces on that diffusion. Merkel *et al.*,²⁶⁰ looked at the permeability of methane through poly(4-methyl-2-pentyne) (PMP) as a function of volume fraction of nanoscale fumed silica. As the amount of filler increased the permeability *increased* more than a factor of three, rather than decrease as predicted by continuum models. They concluded the deviation from modeling was caused by interface effects and the large amount of interface in nanocomposite materials. Although this model was not for a CN nanocomposite, it suggests membranes with CN fillers might have interesting properties. First, CN will differ from impenetrable fillers, especially for hydrophilic penetrants. This difference might open up applications not available to other nanofillers. Second, for an analogous interface effect, the CN must interact with the polymer to change the polymer's free volume at the interface. A negative interaction that increases free volume and decreases T_g would be a good choice to enhance permeability. A positive interaction that decreases free volume and increases T_g would be a good choice to enhance barrier properties. Section 6.1 pointed out that the interface is important for mechanical properties as well and that unless the interface has positive interactions, the CN is unlikely to be an effective reinforcement material. These two modeling results suggest that enhancing permeability and stiffness are incompatible goals. The more a nanofiller increases permeability, the worse it will perform for reinforcement. In contrast, membranes with enhanced barrier properties and stiffness should be possible.

7. Engineered cellulose nanoparticle materials

Since the 1990's there has been increased research of neat CN films and CN composites having engineered properties (mechanical, thermal, optical, barrier, *etc.*). These engineered CN materials are being considered for use in transparent film applications,¹²⁵ barrier film applications,¹²⁵ loudspeaker membranes,²⁶¹ and polymer matrix thermal and mechanical reinforcements.⁷ Researchers have generally approached the utilization of CNs from two viewpoints: One is to add CNs of various types to polymers (CN reinforced polymer matrix composites) and compare the results to the unfilled neat polymer. The other viewpoint is to start with 100% cellulose materials (neat CN films) and modify, or plasticize, them (modified/composite CN films) and compare the results to neat CN films. The properties of both composite types are strongly dependent on the CN network formation. The differentiation between CN reinforced polymer matrix composites and modified/composite CN films is herein arbitrarily based

on the CN weight fraction, in which the former has <30 wt% cellulose particles, while the latter has >70 wt%. These two compositional ranges characterize two extreme spectrums in CN composites and as shown in the bound analyses of section 6 (Fig. 24 and 25) there are considerable differences in the predicted composite properties within these two groups.

Four types of CN engineered materials are reviewed in this section; cellulose reinforced polymer matrix composites (section 7.1), neat cellulose films (section 7.2), modified/composite films (section 7.3), and aerogels (section 7.4). The mechanical, thermal, optical, water sorption and barrier properties of CN engineered materials produced from several cellulose particle types (MFC, NFC, CNC, t-CNC, and BC) are also summarized in sections 7.5, 7.6, 7.7, 7.8, and 7.9. The BC engineered materials are described in greater detail in section 8. Lastly, a brief summary is given regarding CN-hybrid composites for additional composite functionality (section 7.10).

7.1 CN reinforced polymer matrix composites

Research on low CN concentration (<30 wt%) reinforced matrix composites produced from MFC, NFC, CNC, t-CNC, AC, and BC has been extensively reviewed.^{1,2,5,7–10,16,19,27} and the reader is referred to these earlier reviews for the detailed descriptions. This section provides a brief summary of composite processing and the role of particle alignment on properties.

7.1.1 Processing. The paradox of CN reinforced polymer matrix composites processing is that it is desirable to have both a fine CN dispersion while also forming a CN network structure in which the degree at which the CN particle touch can be controlled. One direction of research has focused on producing composites with maximized and reproducible properties by developing processing routes that maximize a fine CN dispersion (*i.e.* avoiding large-scale CN agglomeration, which increases the effective particle size and lowers the CN-matrix interface area). In contrast, the other direction of research has focused on the formation of CN network structures and on altering the CN-matrix interface to maximize the reinforcement of a given polymer (section 6). Four processing techniques have been used to make CN reinforced polymer matrix composites: solution casting,^{5,7,16} melt-compounding,^{7,8,16,27} partial dissolution,⁸ and electrospinning.^{156,168,262–266}

(a) *Solution casting.* In general, the CNs are dispersed within a given medium (0.05–5 wt% solids), typically water, but various organic mediums have also been used and then polymer solutions are mixed with the CN dispersion. By controlling the cellulose/polymer wt% ratio in the mixture, a range of composite compositions (0/100 to 100/0) can be produced.^{267,268} Composite films can be produced from this mixture *via* three general techniques, casting on a suitable surface followed by evaporation, freeze-drying and compression molding, or freeze-drying, extruding, and then compression molding the mixture. Various modifications of this method (*e.g.* CN surface functionalization, *etc.*) have been developed to improve CN dispersion and are summarized elsewhere.^{7,16} Alternatively, solution casting of CN suspensions has been

used to produce neat CN films with high porosity (density $\sim 0.2\text{--}0.9\text{ g cm}^{-3}$) (see section 7.2.1) that are subsequently infiltrated with a polymer resin. The resulting CN reinforced polymer matrix composites retain an interconnected CN network²⁶⁹ (see section 8.1 for BC composites).

(b) *Melt-compounding*. In general, this process involves the incorporation of CNs into thermoplastic polymers by using thermal-mechanical mixing (compounding), the extrusion of the melt mixture, and optional compression molding into specific test specimen geometries as previously summarized.^{7,8,16,27} Careful control of processing parameters is needed to minimize CN degradation resulting from shear stresses and temperatures involved in the process. Research efforts have focused on improved dispersion of CNs within the matrix polymer (polylactic acid^{270,271}) as shown in Fig. 29.

(c) *Partial dissolution*. This process is closely associated with the processing of “all-cellulose” or “self-reinforced” polymer composites, in which cellulose particles or fibers reinforce a cellulose II (regenerated cellulose) polymer matrix as previously summarized.⁸ For CN reinforced cellulose II matrix composites, this process typically involves the formation of neat CN film (see section 7.2.1), and the subsequent formation of the cellulose II matrix phase by the partial dissolution of the starting neat CN network and the subsequent precipitation of cellulose II. The partial dissolution occurs by immersing the starting neat CN film in a solution of N,N-dimethylacetamide (DMAc) for a set time. This “activated” film is then immersed in a solution of lithium chloride/DMAc solvent for a set time to selectively dissolve the CN surfaces. Afterwards, the partially dissolved film is rinsed to remove the DMAc and initiate the precipitation of cellulose II, dried and compression molded ($\sim 1\text{ MPa}$, $50\text{ }^{\circ}\text{C}$). By varying the processing conditions (*i.e.* dissolution time, *etc.*) the properties of the composite can be modified. Note that “all-cellulose” composites have also been produced *via* solution casting a mixture of CN suspensions within a medium of dissolved cellulose.^{236,272}

(d) *Electrospinning*. Electrospinning is a variation on fiber spinning. Spinning is typically done by pushing a polymer melt or solution through a small orifice, then coagulating the polymer in a solution or drying atmosphere. In electrospinning a high voltage is applied between the orifice and a “target” which can be just a conductive plate (which produces a non-woven mat of fibers) or the fiber can be wound onto a spool.²⁷³ This process produces micrometre to nanometre-scale fibers. In general, CNs are dispersed within a given medium (typically 0.05–5 wt% solids) and then polymer solutions (poly(acrylic acid),²⁶⁴ polyethylene oxide,²⁶² PMMA,²⁶⁶ *etc.*) are mixed with the CN dispersion. By controlling the cellulose/polymer ratio in the mixture a range of compositions can be produced. In laboratory electrospinning, the solution/suspension is typically held in an insulated syringe (at a set temperature) with a metallic needle and upon the application of pressure and high voltage (10–30 kV), a jet of solution is accelerated out toward a target (*e.g.* vertical plate, continuous spooler) at a given distance (10s of cm) under a given set of environmental conditions (*e.g.* temperature, atmosphere, *etc.*). The solvent

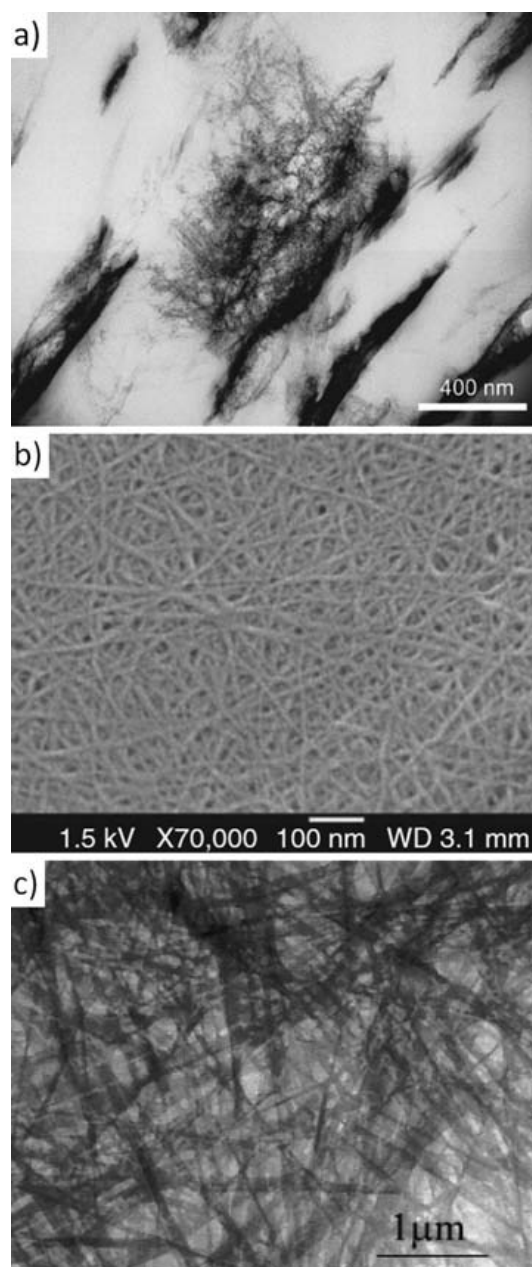


Fig. 29 Images of CN films and composites showing the CN particle distribution. (a) TEM image of CNC reinforced PLA matrix composite (5 wt% CNC), showing both CNC agglomeration and dispersion.²⁷¹ (b) SEM image of NFC neat film surface,¹²⁸ (c) TEM image of a 50/50 composite of t-CNC/silk fibroin produced from solution casting.²⁸⁴ Both (b) and (c) show interconnected CN network structure typical of such films. Reprinted with permission, (a) from ref. 271 © 2007 Koninklijke Brill NV, (b) from ref. 128, (c) from ref. 284 © 2002 John Wiley & Sons.

evaporates as the fiber moves between source and collector and the polymer coagulates, forming a composite fiber. The CN reinforced fibers can then be further dried and/or can undergo additional treatments (*e.g.* heating to crosslink the matrix polymer). Research efforts have focused on improved alignment of CNs along the fiber length,^{262–264} tailored CN–matrix interfacial properties, and improved mechanical properties.^{262,264}

7.1.2 Properties. The properties of CN reinforced matrix materials are summarized in Table 5 and in sections 7.5, 7.6, 7.7, 7.8, and 7.9. It is well known in composite theory that alignment of high aspect ratio filler particles improves mechanical properties (see section 6.1.2). This section summarizes two studies that have investigated the influence of CN alignment on mechanical properties in CN reinforced polymer matrix composites. Preferential alignment of CNs within a matrix material has been achieved by a strong magnetic field²⁷⁴ and mechanical drawing.²³⁶ Kvien and Oksman²⁷⁴ applied a magnetic field (7 Tesla) during solution casting of a CNC/PVA suspension (2 wt% CNC), and were able to lock in the preferential alignment of the CNCs. The CNC particle alignment was perpendicular to the field direction as determined from analysis of fracture surfaces that were ion etched to remove the PVA matrix. Additionally, dynamic mechanical tests showed property anisotropy when testing the sample in parallel (storage modulus, $E' = 4.2 \pm 0.06$ GPa) and transverse ($E' = 6.2 \pm 0.2$ GPa) directions with respect to the magnetic field direction during sample processing. The higher storage modulus in the transverse direction, agrees with the higher axial CNC alignment in this direction. Gindl and Keckes²³⁶ mechanically stretched solution cast all-cellulose composites (~25 wt% CNC, 75 wt% cellulose II). The cast composite films were first water-swollen by immersing in distilled water for 5 min, after which the films were placed in a tensile testing machine and stretched to either 10, 25 or 50% strain along a single axis. The degree of CNC alignment was quantified by XRD and a calculation of an order parameter, f_c , where $f_c = 1$ indicates complete parallel orientation, while $f_c = 0$ indicates random orientation. The results demonstrated that a high degree of CNC orientation could be achieved with this process, and that it was directly related to the amount of mechanical stretching. The properties along the stretching direction were shown to change as the degree of mechanical stretching increased: random, 0% strained CNC/Cellulose II films ($f_c = 0.00$, $E = 9.9$ GPa, $\sigma_f = 202$ MPa, $\varepsilon_f = 16.1\%$), and the highly aligned, 50% strained CNC/Cellulose II films ($f_c = 0.29$, $E = 33.5$ GPa, $\sigma_f = 428$ MPa, $\varepsilon_f = 2.3\%$). This study compares well with analytical modeling predictions in which for a given reinforcement volume fraction, as the reinforcement orientation changes from 2D (*i.e.* random within the plane of the film) to 1D (perfectly aligned) there is a large increase in the composite's Young's modulus (see section 6.1.2). These studies demonstrate the utility of preferential CN particle alignment for the development of composites with high

stiffness and strength, and the comparison with the upper bounds shown in Fig. 25 suggests the possibility for further property improvements.

7.2 Neat CN films

Neat CN films consist of an interconnected CN network structure that is held together by extensive hydrogen bonding (Fig. 29). Compositionally, these neat films are 100 wt% cellulose particles, but have remnant porosity from the gaps within the cellulose particle network.

7.2.1 Processing. Neat CN films have typically been produced using solution casting techniques from suspensions containing either MFC,^{56,57,80,81,275–281} NFC,^{81,87,261,267,268,282,283} CNC,⁵² or t-CNC.^{161,284} To the authors' knowledge there have been no studies on neat AC films. In general, the CNs are dispersed within a given medium (0.05–5 wt% solids), typically water, but may also be various organic mediums. Neat films can be produced by casting on a suitable surface (either solid surface, or filter membrane). The remaining dispersing medium is removed either by evaporation, vacuum filtration, pressing or a combination of these three, typically completed at moderate temperatures (less than 150 °C).^{282,285} The neat films are typically 25–100 µm thick and the remnant porosity results in a film density of 0.8–1.5 g cm⁻³. Mechanical pressing up to 160 MPa has been used to further densify neat CN films.²⁸³ The CNs are isotropically oriented in the plane of the film, resulting in isotropic (independent of testing direction) in-plane film properties. Neat films with higher porosity (density ~0.2–0.9 g cm⁻³) can be produced by either freeze-drying²⁶⁹ or solvent exchange,^{282,286,287} in which the water dispersing medium is exchanged with a lower surface energy solvent (methanol, ethanol, acetone, *etc.*), and during evaporation the lower meniscus forces (as compared to that produced from water) results in less CN consolidation. Incidentally, such porous structures can be infiltrated with a polymer resin to make CN reinforced polymer matrix composites that retain the interconnected CN network (section 7.1.1).

7.2.2 Properties. Several properties of neat CN films have been investigated, in particular, mechanical,^{52,56,57,80,81,87,161,261,267,275–277,279–284} thermal stability,^{81,87,281,283} optical,^{125,283,288} water sorption,^{261,267,275} and barrier,²⁸⁰ and are summarized in the corresponding sections 7.5, 7.6, 7.7, 7.8 and 7.9. Reviewed in this section is the influence of mechanical fibrillation on particle size and the

Table 5 Mechanical properties of cellulose particle reinforced polymer matrix composites (<30 wt% CN)

Particle Type	E (GPa)	σ_f (MPa)	ε_f (%)	WF (MJ m ⁻³)	Bending strength (MPa)	CTE (ppm K ⁻¹)	References
MCC	1.2–10	20–202	2.7–180	29–50	—	—	236, 323, 324, 330, 335
MCC ^a	33.5	428	2.3	6	—	—	236
MFC	0.093–10	1.7–113	1–400	0.4–86	—	27–31	8, 50, 58, 269, 276, 290, 329–331, 333
NFC	0.003–6.2	5–92	1.7–970	0.7–150	—	12–28.5	53, 54, 83, 91, 267, 292, 386
CNC	0.0007–3.9	1.5–218	1.9–986	1.2–102	—	—	48, 50, 51, 58, 270–272, 324
t-CNC	0.0005–6	0.2–50	0.5–285	0.35–35	—	—	143, 284, 387, 388
BC	0.355–11	21–188	3.5–30	1.3–16	—	4–38	286, 287, 362, 389

E = Young's modulus, (tensile testing). σ_f = tensile strength (tensile testing). ε_f = strain to failure (tensile testing). WF = Work of Fracture: area under stress-strain curve. (tensile testing).^a Composite with high MCC orientation, tested in direction of MCC particle alignment.

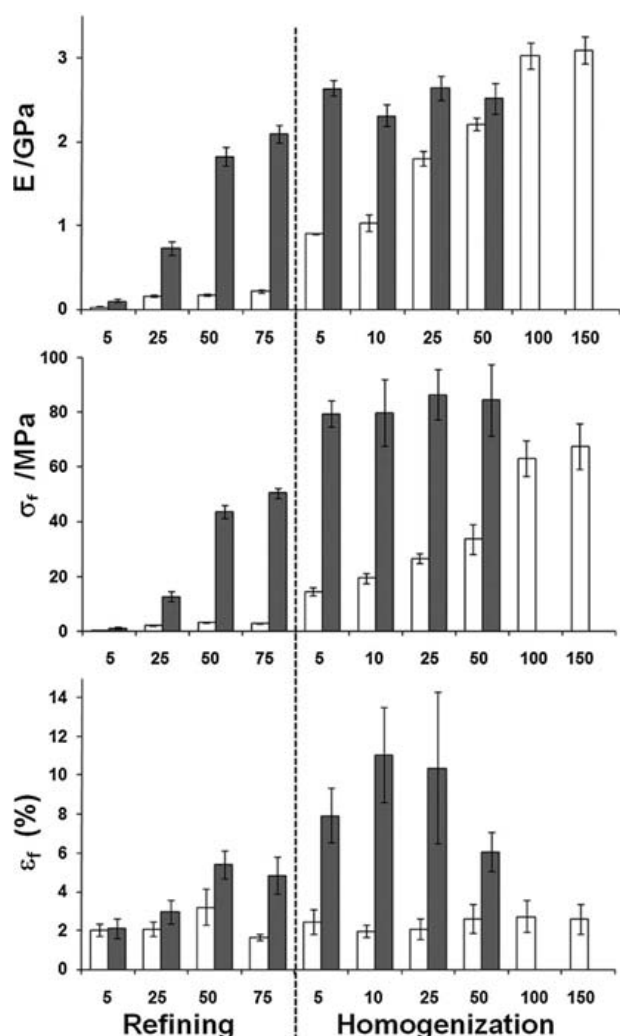


Fig. 30 Influence of mechanical fibrillation of WF, softwood (open bars) and hardwood (shaded bars) on mechanical properties of CN films.⁸⁰ The numbers on the *x*-axis refer to the number of passes through the specific mechanical treatment, either the refining or homogenization. Materials that have been homogenized initially went through the refining process 75 times. Reprinted with permission from ref. 80 © 2009 American Chemical Society.

corresponding change in neat CN film properties.^{57,80,81,275} In general, as the degree of fibrillation increased (from WF to MFC to NFC) the mechanical properties of the film increased (Fig. 30). However, excessive mechanical processing can reduce properties.^{80,81} Stelte and Sanadi⁸⁰ used an initial refining and subsequent high-pressure homogenization to fibrillate dried WF from either softwood or hardwood. By varying the number of cycles during refining (5–75) or homogenization (5–150), the resulting particle size was altered, such that after 75 refining cycles and 10 homogenization cycles particles had diameters in the 10–25 nm range. The fibrillation process was much faster for softwood WF and resulted in neat MFC and NFC films with higher properties and larger strain to failure as compared to MFC and NFC from hardwood WF. Iwamoto *et al.*⁸¹ showed that increased passes for mechanical fibrillation lowered the degree of crystallinity within the MFC or NFC and was believed to attribute to the lower

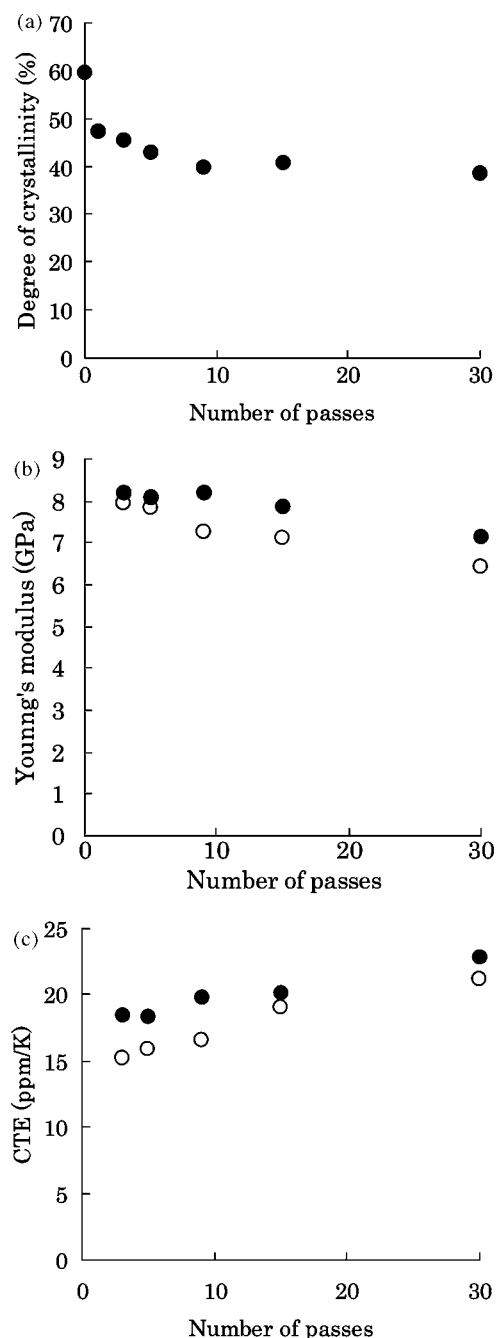


Fig. 31 Influence of mechanical fibrillation (number of passes through the grinder) of WF on (a) degree of crystallinity, (b) Young's modulus of neat (open circles) and composite films (filled circles), and (c) CTE of neat and composite films. Composite films were produced from infiltrating acrylic resin into preformed neat films, resulting in only small changes in film properties. Reprinted with kind permission from ref. 81 © 2008 Springer Science + Business Media B.V.

Young's modulus and higher CTE in the resulting neat films (Fig. 31).

7.3 Modified and composite CN films

In general, most investigations into modified and composite cellulose films have a CN concentration greater than 70 wt%

and have focused on improved properties relative to the neat CN films, which tend to be brittle, or in the case of optical properties, show low transmission properties.

7.3.1 Processing. Modified and/or composite CN films from MFC,^{56,269,275,277–279,289–291} NFC,^{81,87,90,125,261,267,268,285,292} CNC,²⁹³ and t-CNC^{161,284} have been produced by three main processing routes: solution casting of surface modified CNs, solution casting with water soluble polymers, and the subsequent modification of preformed neat CN films.

(a) *Solution casting.* Both solution casting processes follow the method described in section 7.2.1. In the first case the starting CNs have altered surface chemistry either from the extraction process or subsequent chemical treatments (e.g. TEMPO regioselective oxidation),^{90,125,161} where the changes in surface chemistry alters the CN–CN interaction in the final film. For the second case the starting cellulose particle suspension is mixed with a water-soluble compound (glycerol,²⁶⁷ glycerol-amylopectin,²⁶⁷ silk fibroin,²⁸⁴ polyvinyl alcohol,⁵⁶ and phenol-formaldehyde⁵⁶), which remains in the final structure after the evaporation of the aqueous dispersing medium. By controlling the cellulose/polymer wt% ratio in the solution, a range of composite compositions (0/100 to 100/0) can be produced. Composite films can be produced from this mixture *via* three general techniques, casting on a suitable surface followed by evaporation, freeze-drying and compression molding, or freeze-drying, extruding, and then compression molding the mixture.

(b) *Modification of neat films.* Modification of preformed neat CN films is typically completed by partially or completely filling the remnant porosity with a given chemical (NaOH²⁷⁹) or resin (melamine formaldehyde,²⁶¹ acrylic,^{81,87,285,287,292} epoxy,²⁹⁴ phenol-formaldehyde^{269,277–279,289}). The resulting composites retain the CN network structure and the CN–CN interaction. Typically, dried CN films are pressure infiltrated (~ 0.1 MPa) with the desired resin, then films are dried at elevated temperatures (less than ~ 100 °C), and can be hot pressed (5–30 MPa, less than 200 °C) for further densification.^{261,269} The cellulose/matrix ratio can be controlled by varying the amount of porosity in the starting neat CN film prior to infiltration and by adjusting the concentration of resin within the carrier solvent (e.g. methanol) used to facilitate impregnation into the neat CN film.^{277,278,289} Additionally, laminate CN film composites have been produced by stacking several (5–25) modified/composite CN films and compression molding (~ 15 –150 MPa, less than 200 °C) them.^{277–279,289}

7.3.2 Properties. Several properties of modified/composite CN films have been investigated, including mechanical,^{56,81,87,125,161,261,267,269,275,277–279,284,285,289,290} thermal stability,^{81,87,125,285} optical,^{81,125,285} water sorption,^{261,268,289} and barrier,¹²⁵ and are summarized in the corresponding sections, 7.2, 7.3, 7.4, 7.5 and 7.6. Reviewed in this section are studies that have directly compared neat CN films to their modified/composite CN film counterparts in terms of mechanical,^{56,81,87,161,261,267,284} optical,⁸¹ and CTE^{81,87,287}

properties. The specific effect of the modification/composite on CN film properties is highly dependent on the specific chemical treatment, the matrix material and the process by which it was incorporated into the CN network, namely solution casting or modification of preformed neat CN films.

(a) *Solution casting.* Solution casting of composite CN films alters the CN network formation and the CN–CN interface properties, resulting in large differences in film properties as compared to that of the neat CN film.^{56,267,284} Noishiki *et al.*²⁸⁴ compared neat t-CNC films ($E = 10$ GPa, $\sigma_f = 40$ MPa, $\epsilon_f = 0.5\%$) to a series of composite t-CNC/silk fibroin films (0–90 wt% t-CNC). The 50–90 wt% t-CNC/silk fibroin composites had a slightly lower Young's modulus, but increased tensile strength (300–500%) and strain to failure (400–800%) as compared to the neat films. Material properties peaked at 70–80 wt% t-CNC (Fig. 32). Leitner *et al.*⁵⁶ compared neat MFC films ($E = 9.3$ GPa, $\sigma_f = 104$ MPa, $\epsilon_f = 3.2\%$) to a series of composite MFC/PVA or MFC/PF films (0, 50, 70 and 90 wt% MFC). The 90 wt% MFC/PVA films ($E = 7.7$ GPa, $\sigma_f = 84$ MPa, $\epsilon_f = 1.7\%$) had diminished properties, while 90 wt% MFC/PF films ($E = 9.5$ GPa, $\sigma_f = 127$ MPa, $\epsilon_f = 2.9\%$) had similar or improved properties compared to the neat films. Improved performance of the

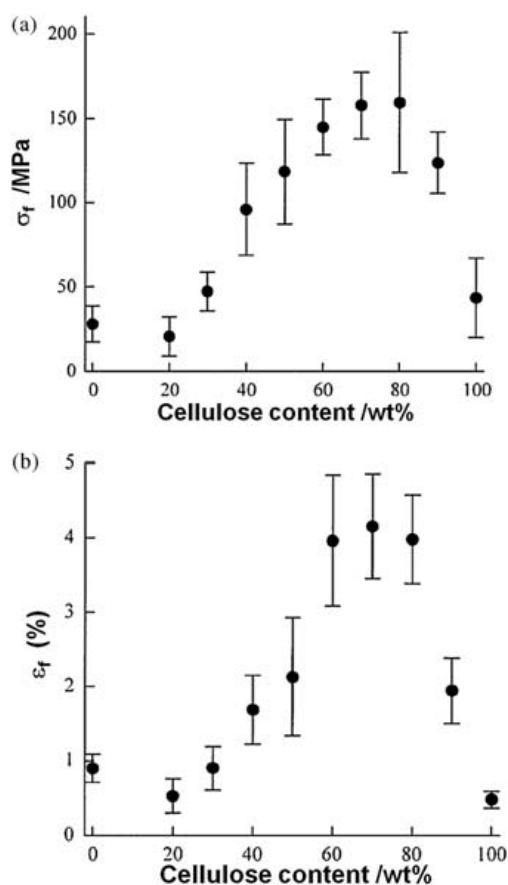


Fig. 32 Mechanical properties of t-CNC/silk fibroin solution cast composite films showing that the maximum composite properties are reached at ~ 70 –80 wt% t-CNC concentration.²⁸⁴ (a) Tensile strength, and (b) strain to failure. Reprinted with permission from ref. 284 © 2002 John Wiley & Sons.

MFC/PF films was attributed to stronger interfibrillar bonding. As the MFC wt% decreased there was a corresponding decrease in mechanical properties (E , σ_f and ε_f). Svagan *et al.*²⁶⁷ compared neat NFC films ($E = 13.0$ GPa, $\sigma_f = 180$ MPa, $\varepsilon_f = 2.1\%$) to a series of composite NFC/glycerol-amylopectin starch films (0–70 wt% NFC). The 70 wt% MFC composite films ($E = 6.2$ GPa, $\sigma_f = 160$ MPa, $\varepsilon_f = 8.1\%$) were much less stiff but had nearly a 400% increase in the strain to failure.

(b) *Modification of neat films.* The modification of preformed neat CN films can have modest influences on the mechanical properties as compared to that of the neat CN films^{81,87,261,279,287} (Fig. 31). Nakagaito *et al.*²⁷⁹ immersed dried neat MFC films ($\rho = 0.99$ g cm⁻³, $E = 9$ GPa, $\sigma_f = 140$ MPa, $\varepsilon_f = 5\%$) into aqueous NaOH solutions (5 wt% or 20 wt%) and showed that the mechanical properties of the resulting dried films were altered as a function of NaOH concentration (5 wt% treatment: $\rho = 1.01$ g cm⁻³, $E = 10$ GPa, $\sigma_f = 145$ MPa, $\varepsilon_f = 6.3\%$ and 20 wt% treatment: $\rho = 1.1$ g cm⁻³, $E = 8.5$ GPa, $\sigma_f = 155$ MPa, $\varepsilon_f = 11.5\%$). The resulting increases in tensile strength and the strain to failure also contributed to an increased work of fracture. Henriksson *et al.*²⁶¹ infiltrated neat NFC films ($\rho = 1.34$ g cm⁻³, $E = 14.0$ GPa, $\sigma_f = 104$ MPa, $\varepsilon_f = 2.6\%$) with melamine formaldehyde, which increased the Young's modulus and tensile strength of the composite film, but lowered the strain to failure ($\rho = 1.36$ g cm⁻³, $E = 16.1$ GPa, $\sigma_f = 142$ MPa, $\varepsilon_f = 1.4\%$). Similar trends were observed by Iwamoto *et al.* for acrylic resins.^{81,87} Iwamoto *et al.*⁸¹ infiltrated neat NFC films ($\rho = 1.31$ g cm⁻³, $E = 6.4$ GPa, $\sigma_f = 5$ MPa, $\varepsilon_f = 2.2\%$, CTE = 22 ppm K⁻¹) with acrylic resin and the resulting composite film had only small changes in properties ($\rho = 1.38$ g cm⁻³, $E = 7.2$ GPa, $\sigma_f = 80$ MPa, $\varepsilon_f = 1.9\%$, CTE = 23 ppm K⁻¹). Iwamoto *et al.*⁸⁷ also infiltrated neat NFC films ($\rho = 1.3$ g cm⁻³, $E = 14.9$ GPa, $\sigma_f = 240$ MPa, $\varepsilon_f = 3.2\%$, CTE = 8.9 ppm K⁻¹) with acrylic resin and the resulting composite film had only small changes in properties ($\rho = 1.4$ g cm⁻³, $E = 15.8$ GPa, $\sigma_f = 272$ MPa, $\varepsilon_f = 3.0\%$, CTE = 10.4 ppm K⁻¹). The large difference in the neat CN films between these two studies may be associated with differences in the starting cellulose source and mechanical fibrillation process. The Iwamoto *et al.*⁸⁷ study used never dried holocellulose pulp that was fibrillated with only a single pass through a grinder, the resulting NFC likely had much less mechanical damage and the remnant hemicellulose may have improved NFC–NFC bonding, both of which would improve the mechanical properties of the neat films.

7.4 Cellulosic aerogels

Aerogels are highly porous materials that can have extremely low densities (0.01–0.4 g cm⁻³), high surface areas (30–600 m² g⁻¹),²⁹⁵ low thermal transport, and have the potential to be engineered for a wide variety of applications.²⁹⁶ Cellulose-based aerogels were developed during the 1950's by Stamm and co-workers.^{297,298} However, little further development occurred until the 2000's. Most research efforts have been in aerogel processing and in some isolated cases the subsequent functionalization of the aerogel *via* coatings. This

section will discuss cellulose-based aerogels with nanoscale dimensions fabricated from three different starting materials: cellulose solutions,^{299–314} MFC,^{315–318} and CNC.^{295,319,320} While aerogels from cellulose solutions are not strictly nanomaterials, they are included here for completeness and comparison with other aerogels.

7.4.1 From cellulose solutions. The processing of cellulose aerogels from cellulose solutions involves three main steps: the dissolution of the starting cellulose (various solvents and cellulose source materials can be used), the precipitation of cellulose, and solvent removal while avoiding cellulose consolidation/agglomeration (this can be done by supercritical drying, freeze drying, rapid decompression, *etc.*). An additional step that may also be included is the subsequent treatment of the cellulose aerogel for new functionality. Varying any step in this process will alter the aerogel that is formed. For example, the density of the cellulose aerogel is typically directly proportional to the concentration of cellulose in the original solution. The resulting cellulose that is formed during the precipitation process (often called regenerated cellulose) has the cellulose II crystal structure (see section 1.1), which has lower mechanical properties than the cellulose I crystal structure (see Table 3). Research has been active in each of the steps listed above, resulting in cellulose aerogels with a range of densities 0.01–0.26 g cm⁻³, and having a nanoscale structure. A more detailed description of several of these studies follows.

Aerogels from pure cellulose were reported by Jin *et al.*,³⁰⁰ who regenerated cellulose fibers from a calcium thiocyanate solution, freeze-dried the regenerated solution and found nanoscale fibers in an aerogel with a density approaching 0.02 g cm⁻³. They tried rapid freeze drying by pouring the regenerated solution onto a cold metal plate. This gave rise to asymmetric porosity as the porosity was related to the rate of ice crystal formation.³⁰⁰ The same dissolution method was reported by Hoepfner *et al.*,³⁰¹ but supercritical CO₂ drying was utilized, and densities down to 0.010 g cm⁻³ were obtained. The article also shows a good comparison of the differences between cryogels (produced by freeze drying) and aerogels (produced by supercritical drying).

The Aerocell program in Europe, a consortium of ten partners investigating cellulose aerogels, has completed fairly comprehensive investigations regarding cellulosic aerogels, from regenerated *N*-methylmorpholine-*N*-oxide (NMMO) solutions, and additional routes.^{302,303,305} NMMO was also used by Liebnert *et al.*,^{304,305} with *N*-benzyl-morpholine-*N*-oxide used as the stabilizing agent to prevent discoloration. Densities from 0.05 to 0.26 g cm⁻³ were obtained. They found they could regenerate the cellulose from NMMO using DMSO or DMSO/ethanol mixtures and remove these solvents with liquid CO₂. This gave a finer pore structure compared to water and skipped the step of solvent exchange from water to a CO₂ soluble solvent. Recent activity in this area has focused on developing biomedical implants from cellulose aerogels.^{306,307} An alternative to NMMO solvent, Gavillon and Budtova³⁰⁸ used cold NaOH and produced cellulose aerogels with a similar pore structure.

Cai *et al.*^{309–311} used either NaOH/urea or LiOH/urea to dissolve cellulose from a variety of sources. Regeneration was accomplished with aqueous acid or ethanol. Nanoscale fibrous aerogels were obtained with surface areas up to $485 \text{ m}^2 \text{ g}^{-1}$ for samples from cotton pulp.^{309–311} This same dissolution system was used to prepare aerogels containing metal nanoparticles. The most successful was silver nitrate, which was reduced *in situ* by the cellulose to give silver nanoparticles imbedded in the cellulose aerogel. Gold and platinum imbedded nanoparticles were also obtained, but required a borohydride reducing agent.³¹²

Ionic liquids have been used as the cellulose solvent and the corresponding aerogels produced. Tsiptsias *et al.*³¹³ used 1-allyl-3-methylimidazolium chloride for the cellulose dissolution. Nanoporous, *i.e.*, mostly microporous ($<2 \text{ nm}$) and mesoporous ($2\text{--}50 \text{ nm}$) aerogels were obtained with densities down to 0.058 g cm^{-3} . They also used rapid decompression of the supercritical CO_2 to foam the materials. Pore sizes in the tens to hundreds of microns were obtained in this case. Aaltonen and Jauhiainen³¹⁴ used 1-butyl-3-methylimidazolium chloride for the cellulose dissolution and regenerated in aqueous ethanol baths. They obtained a cellulose aerogel with a density of 0.048 g cm^{-3} . Additional materials were studied, including spruce wood and mixtures of cellulose with lignin and xylan. Certain combinations of materials and processing produced a number of aerogels. The aerogels from wood appeared to be more variable than the other samples.

7.4.2 From MFC. Aerogels from MFC have come largely from Scandinavia. Paakko *et al.*³¹⁶ showed MFC aerogel formation using either rapid freeze drying and drying by vacuum freezing, followed by sublimation (Fig. 33). The porosity was observed to be hierarchical, with nanoscale pores in sheets of agglomerated MFC and macroscale pores between the sheets. Densities ranged to 0.020 g cm^{-3} . However, BET surface areas were only $20\text{--}66 \text{ m}^2 \text{ g}^{-1}$. An additional experiment was performed by coating the MFC with polyaniline-dodecylbenzene sulfonic acid *via* solvent casting from toluene. The resulting composite showed a moderate conductivity of

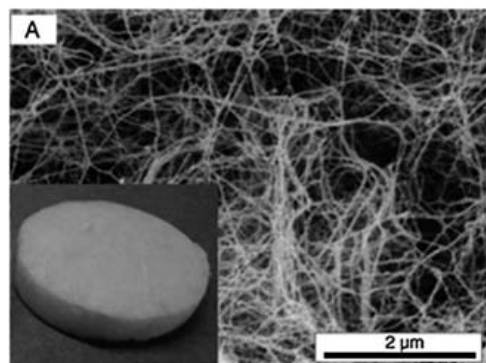


Fig. 33 SEM image of an MFC aerogel prepared from freezing MFC suspension in liquid propane and subsequent drying and show the fine nanoscale structure and high volume fraction porosity. Insert is a low magnification optical image showing the 3 mm thick MFC aerogel specimen.³¹⁶ Reprinted with permission from ref. 316 © The Royal Society of Chemistry 2008.

$\sim 10^{-2} \text{ S cm}^{-1}$.³¹⁶ While there are few reports from this group in the literature, activity has been high with recent conference presentations.^{317,318} Additionally, MFC aerogel functionalization was reported by Ikkala *et al.*³¹⁵ who used atomic layer deposition to coat an MFC aerogel with titanium oxide. The resulting organic/inorganic hybrid composite was extremely hydrophobic with a contact angle of $130\text{--}140^\circ$.

7.4.3 From CNC. Aerogels from CNCs are sparsely reported in the literature.^{295,319,320} An interesting approach was used in the processing of t-CNC reinforced matrix polymer nanocomposites; t-CNC aerogels were formed by gelling in acetone and then supercritical drying. A polymer solution was then infused into the aerogel structure and subsequently dried. The result, after compression molding, was a t-CNC-filled nanocomposite with a well-dispersed t-CNC network structure. This approach is suitable for polymers and solvents not otherwise compatible with CNCs.³¹⁹ Heath and Thielemans²⁹⁵ report aerogels fabricated from cotton CNCs which were produced using sulfuric acid hydrolysis. Their reported densities range from 0.078 to 0.155 g cm^{-3} . The hydrogels were prepared from rapidly frozen, then freeze-dried CNCs by sonication in water using a relatively low ultrasonic power. This resulted in apparent agglomeration based on the SEM images shown in the article. However, the BET surface areas are among the highest reported for cellulose-based aerogels and the TEM image shows extensive nanoscale structure, even though the contribution of micro and mesopores to the total porosity is small. Thus the fabrication method, while retaining a nanoscale structure, results in a largely macroporous aerogel. The authors report minimal shrinkage during drying, which bodes well for applications since uncontrollable shrinkage is an issue in aerogel formation. Recent activity in this area points to more developments in the future.³²⁰

7.5 Mechanical properties

The mechanical properties of CN reinforced polymer matrix composites, neat CN films, and modified/composite CN films are summarized in Tables 5, 6, and 7, respectively. Several factors have been shown to contribute to the mechanical properties of CN neat films and composites.^{321,322} (1) The CN properties and that of any matrix material,^{267,276,292} (2) The degree of CN in-plane orientation,^{236,237,274} (3) The density of CN–CN contacting points within the CN network,^{275,277,278} (4) Interfacial properties, either CN–CN^{57,87,90,267,279} and/or CN–matrix,^{161,291} (5) The CN volume fraction,^{267,269,276,280,282,323} (6) CN morphology/size,^{54,56,57,80,81,87,91,269,275,276,279,289,323,324} and (7) Moisture content.^{8,57,247,282} The large number of factors that can modify the CN structure within the neat films and composites provides an opportunity to engineer for a wide variety of final composite properties. This is evident in the overlap in the properties between the different CN structures and between different CN particle types. In general, all of these factors are currently understudied with respect to their relationship to the given mechanical properties of the final CN composite.

Table 6 Mechanical properties of neat cellulose films (100 wt% CN)

Particle type	E (GPa)	σ_f (MPa)	ε_f (%)	WF (MJ m ⁻³)	Bending strength (MPa)	CTE (ppm K ⁻¹)	References
WF^a	4–9	45–80	2	0.6–0.8	—	—	56, 275
MFC	1–17.5	30–155	2.5–11.5	2.3–4.7	165–255 ^b	15–25	56, 57, 80, 275, 277, 279–281
NFC	6–15	95–240	2–10	1–15	—	2.7–22	81, 87, 90, 125, 261, 267, 268, 282, 283, 285
CNC	6	—	—	—	—	—	52
t-CNC	5–10	40–70	0.5–5	2.8	—	—	161, 284
BC	10–35	87–510	1.1–4.4	0.4–12	—	2–3	11, 79, 277, 321, 322, 326, 327, 353, 359, 362, 390
Cellulose II							
-Cellophane	3.7–5.4	75–125	—	—	—	—	391
-Fiber	55	1800	—	—	—	—	383

E = Young's modulus, (tensile testing, or 3pt bend testing). σ_f = tensile strength (tensile testing). ε_f = strain to failure (tensile testing). WF = Work of Fracture: area under stress-strain curve. (tensile testing).^a Kraft paper, 60g mm⁻². ^b Laminated composites several films stacked and bonded together and testing in 3pt bending.

Table 7 Mechanical properties of modified/composite cellulose films (> 70 wt% CN)

Particle type	E (GPa)	σ_f (MPa)	ε_f (%)	WF (MJ m ⁻³)	Bending strength ^a (MPa)	CTE (ppm K ⁻¹)	References
MFC	5–19	60–200	1.6–12	0.6–3.2	180–380	10–14	56, 269, 275, 277–279, 289–291
NFC	4–17	80–290	0.8–11	1.4–9	—	10–23	81, 87, 261, 267, 268, 285, 294
t-CNC	0.5–11	16–160	1.5–7.7	0.1–2.6	—	—	161, 284
BC	5–25	300–510	3–4	5–12	350–420	8–10	277, 286, 334, 362

E = Young's modulus, (tensile testing, or 3pt bend testing). σ_f = tensile strength (tensile testing). ε_f = strain to failure (tensile testing). WF = Work of Fracture: area under stress-strain curve. (tensile testing).^a Laminated composites several films stacked and bonded together and testing in 3pt bending.

7.5.1 Mechanical properties. The Young's modulus and tensile strength of crystalline cellulose I β , cellulose reinforced polymer matrix composites, and cellulose neat and modified/composite films are compared to other material systems *via* “Ashby plots” (Fig. 34). Each generalized region represents a particular material class (metals, ceramics, wood, *etc.*) and is based on experimental measurements.³²⁵ The wood regions are based on the most common wood species used in industry, having a density of 0.4–0.9 g cm⁻³, and are separated based on testing orientation with the configuration of the wood grain (*i.e.*, perpendicular- $\perp$, or parallel- $\parallel$). The crystalline cellulose regions, CN reinforced matrix composite region, neat and modified/composite CN film regions are based on the data given in Tables 3, 5, 6, and 7, respectively. The results of MFC, NFC, CNC, and t-CNC were grouped together as there was extensive overlap in the measured properties. BC films were considered separately. Although cellulose crystals have high axial properties ($E \sim 150$ GPa, $\sigma_f \sim 7000$ MPa), this has yet to be fully exploited in CN neat films and composites, in which the properties are typically well below the theoretical upper bounds (see section 6). For example, CN films with 70–100 wt% CNs in a 2D random in plane CN-orientation have a potential upper bound of $E = 50$ –60 GPa, while composites with highly aligned CNs in a single direction (*i.e.*, 1D), have an upper bound potential of $E = 100$ –150 GPa (see Fig. 25). Currently, the maximum elastic modulus measured for 2D random in-plane CN orientation was $E = 25$ –35 GPa for BC neat films.^{322,326,327} Possible factors contributing to the lower mechanical properties in CN neat films and composites are: low interfacial properties of CN–CN and/or CN–matrix

(factor 4 in section 7.5), low particle aspect ratio (factor 6), and for 1D case lower than expected CN alignment (factor 2).

When the density, ρ , is factored in for cellulose particles (1.6 g cm⁻³), CN reinforced polymer matrix composites (1–1.5 g cm⁻³), neat CN films (0.8–1.5 g cm⁻³) and modified/composite CN films (0.9–1.5 g cm⁻³) the specific mechanical properties become comparable to other structural materials (metals, ceramics, and composites), as shown in Fig. 35 for specific Young's modulus (E/ρ) and specific tensile strength (σ_f/ρ). Only studies that specifically reported both density and mechanical properties data were used to construct the BC region²⁷⁷ and CN region,^{80,81,90,125,261,267,275,277,279,280,282,283} while the CN matrix reinforced composite region was based on the results listed in Table 5 with an assumed density of 1.2 g cm⁻³. The Ashby plot shown in Fig. 35 is useful for assessing materials to be used in applications with high stiffness and strength at minimal weight, such as in the automotive and aerospace industries. With the high axial properties of crystalline cellulose, producing composites with highly aligned CNs will increase properties in the aligned direction^{236,237} and the resulting properties may be closer to properties typical for glass fiber reinforced polymer composites. For example, Gindl and Keckes²³⁶ mechanically stretched solution cast all-cellulose composites (see section 7.1.2), had high properties with only ~ 25 wt% CNs ($E = 33.5$ GPa, $\sigma_f = 428$ MPa). With a composite density of 1.4 g cm⁻³ (obtained through private communication with authors) the specific properties would be ($E/\rho = 24$ GPa (g cm⁻³)⁻¹, $\sigma_f/\rho = 305$ MPa (g cm⁻³)⁻¹), which would be within the midpoint of the composite region. This demonstrates the utility of preferential CN particle

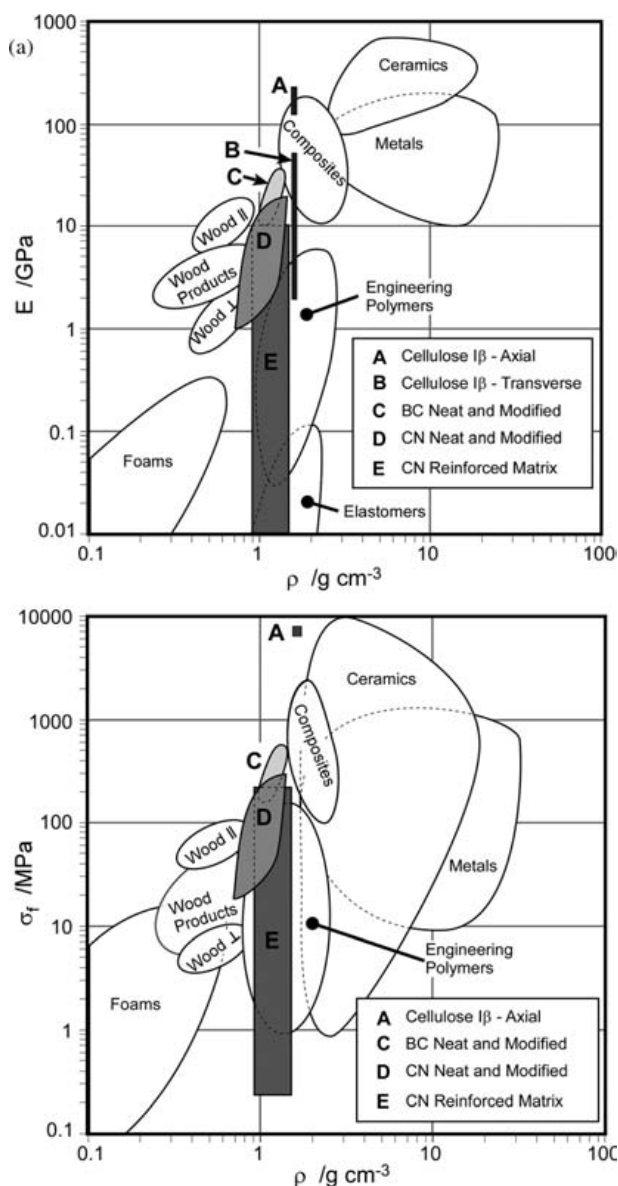


Fig. 34 Ashby plots showing of crystalline cellulose I β (axial and transverse directions) regions, BC neat and modified/composite films, CN neat or modified/composite films of various cellulose particle types (CNC, t-CNC, MFC, and NFC), and CN reinforced polymer matrix composites (less than 30 wt% CN). (a) Young's modulus versus density, and (b) tensile strength versus density.

alignment for the development of composites with high specific stiffness and strength.

7.5.2 Fracture properties. Fracture properties of CN structures and composites have been investigated to a lesser extent than elastic modulus, typically only the work-to-fracture and SEM images of fracture surfaces are given. The work-to-fracture, which is qualitatively related to toughness, is determined by measuring the area under the stress-strain curve, and represents the energy imparted into a material up to the point of fracture. Tough materials have high work-to-fracture, while brittle materials have low work-to-fracture values. For a material to be tough, it must have both high

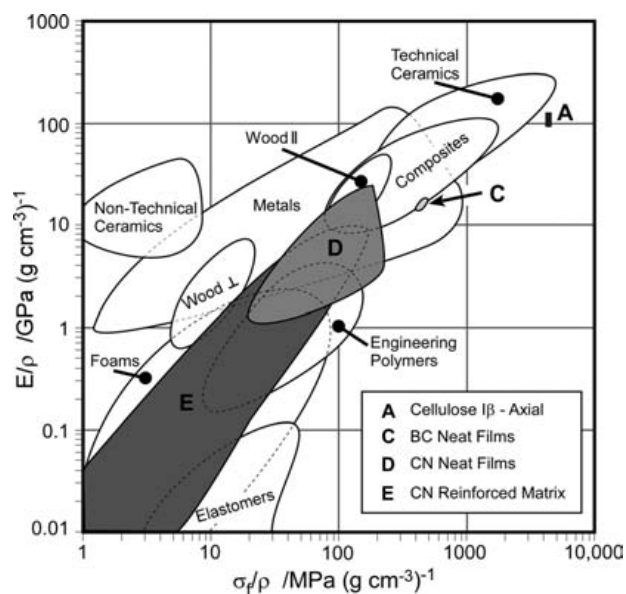


Fig. 35 Ashby plot of specific modulus (E/ρ) versus specific strength (σ_t/ρ). Regions of crystalline cellulose I β , BC neat films, neat films of either CNC, t-CNC, MFC, and NFC, and CN reinforced matrix composites (less than 30 wt% CN) are shown.

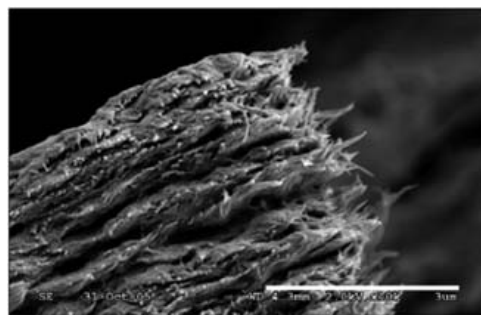


Fig. 36 FE-SEM image of a fractured cross-section of a cellulose composite film, showing the parallel stacking of thin cellulose layers.²⁶⁷ Reprinted with permission from ref. 267 © 2007 American Chemical Society.

strength and large strain to failure. CN structures and composites have work-to-fracture values that are within the range of 0.4–150 MJ m⁻³. The work-to-fracture has been shown to be strongly influenced by the CN volume fraction and CN–CN bond strength.²⁶⁷ The fracture surfaces of NFC^{261,267} and BC^{11,79,322,328} films typically show a stacked structure of many parallel layers (~200 nm thick) each consisting of a dense CN network (Fig. 36). Some researchers have concluded that the stacking behavior results from the CN film processing.^{79,322,328} Other researchers suggest this appearance could result from the combined effects of the fracture mechanism, the random-in-plane orientation of CNs, and the stronger intralaminar CN interaction as opposed to the interlaminar interactions.²⁶⁷

7.5.3 Role of particle type. Considering the CN neat films and composite literature as a whole, it is difficult to assess the advantages between different CN particle types as there is

considerable overlap in the measured properties as shown in Tables 5, 6, and 7 and in Fig. 34. Only direct comparisons can identify trends in the role of a particular cellulose particle type (WF, PF, MCC, MFC, NFC, CNC, BC) on mechanical properties. A few select studies have completed direct comparison for CN reinforced polymer matrix composites,^{50,54,58,91,269,276,324,329–331} neat films,^{56,275,276} and modified/composite films.^{277–279,289} The advantage of these direct comparisons is in artifact minimization resulting from differences in sample preparation, characterization and mechanical testing methods that typically vary between researchers and labs. In addition, for matrix reinforced composites, the matrix polymer is held constant.

For matrix reinforced polymer composites having 0.1–30 wt% CN reinforcement, the resulting properties are dictated by the matrix material, but the cellulose network can strongly influence the properties (section 6). Several types of comparisons have been made: WF versus MFC,^{269,329,331} WF versus NFC,⁹¹ MCC versus MFC,³³⁰ MCC versus CNC,³²⁴ MFC versus CNC,^{50,58,83} MFC versus CNC,⁸³ and NFC versus CNC.⁸³ In general, WF reinforced matrix composites had lower Young's moduli, tensile strengths, and strains to failure as compared to MCC and MFC reinforcements. MFC reinforced matrix composites had higher Young's moduli and tensile strengths compared to MCC and CNC reinforcements, while CNC reinforced had greater strains to failure. CNC reinforced matrix composites had a higher Young's modulus, tensile strengths, and strains to failure compared to MCC reinforcement. The specific polymer matrix did not appear to alter these general trends, but the mechanical properties of the matrix influenced the overall composite properties (see factor 1 described in section 7.5). Additionally, Zimmermann *et al.*⁵⁴ investigated the role of NFC from five different sources on the properties of NFC–hydroxypropyl cellulose (HCP) composites (1, 5, 10, and 20 wt% NFC). This work also confirmed that the degree of cellulose fibrillation (WF, PF and MFC vs. NFC) was found to significantly influence the resulting composite properties, namely, the finer structured NFC showed 2.5 time higher Young's modulus, and 4 times higher stiffness as compared to WF or MFC. The role of NFC from five different sources did not appear to have much influence on Young's modulus ($E \cong 1.5$ GPa), while there may have been a small influence on tensile strength.

For neat and modified/composite films the cellulose network dictates the resulting properties, thus some overlap in properties is to be expected. Most comparisons have been made between WF and MFC in neat films^{56,275} and in modified/composite films.^{278,279,289} In general, neat and modified/composite films from MFC, as compared to WF, have increased Young's moduli, tensile strengths, moduli of rupture, strains to failure, and work-to-fracture. There have also been comparisons between MFC and BC in modified/composite films in which BC films were shown to have higher Young's moduli and tensile strengths, but similar to lower strains to failure.²⁷⁷ The higher properties for the BC composite films was believed to be associated with the more uniform, continuous and in-plane orientation of the BC network as compared to the MFC network.

7.6 Thermal property

The thermal properties of CN structures and composites are both limiting (in terms of thermal stability) and enabling (in terms of CTE) with regard to potential applications, and has been previously reviewed.¹⁰ Recent research on the thermal stability^{52,125,261,267} and CTE^{81,87,125,269,281,283,285,286,292,294,332} of CN reinforced polymer matrix composites, neat CN films, and modified/composite CN films are briefly summarized below and in Tables 5, 6, and 7, respectively.

7.6.1 Thermal stability. Thermal degradation of cellulose materials or the reduction in mechanical properties at elevated temperatures is one of the major issues that limit CN applications. The onset of thermal degradation of CNs typically occurs at ~ 200 – 300 °C (section 3.2) and provides an upper limit to the application and processing temperatures appropriate for CN-based products. However, if CNs have been chemically modified (*e.g.*, sulfate esters introduced during hydrolysis by H_2SO_4 or carboxylation *via* TEMPO-based oxidation) the onset temperature of thermal degradation will likely change. For example, for NFC neat and modified films, Fukuzumi *et al.*¹²⁵ showed that the onset of thermal degradation, as measured by thermal gravimetric analysis (TGA) of modified films made from TEMPO-oxidized NFCs were ~ 100 °C lower than those of neat NFC films (~ 300 °C).

Dynamic mechanical thermal analysis (DMTA) has been the most reported technique for evaluating the response of the mechanical properties of CN structures and composites to temperature. DMTA has been used to characterize changes in the loss and storage moduli (E'), and the internal friction factor as a function of increasing temperature, typically within the range of -100 to ~ 200 °C. The internal friction factor (loss modulus divided by storage modulus), assesses the damping of the material, while the storage moduli assesses the stiffness of the material. DMTA has been used to test CN reinforced polymer matrix composites,^{5,52,267,333} neat CN films,²⁶¹ and modified/composite CN films.²⁶¹ For CN reinforced polymer matrix composites the cellulose particle network throughout the matrix (percolated network structures described in section 6) improves the thermal stability of mechanical properties as compared to the neat matrix polymer.^{5,52} The greatest stabilization occurs for temperatures greater than the matrix glass transition temperature, T_g . The composite T_g is unchanged from that of the neat polymer, but at temperatures above T_g , the composite has higher storage and loss moduli. The stabilization effect has been demonstrated for various cellulose particle types (t-CNC, MFC, MCC, and NFC) and increases with increases in cellulose particle concentration (0.5–70 wt%) within the matrix.^{52,267,333} The thermal stability of cellulose reinforced matrix composites is described in greater detail in prior review papers.^{5,16,19}

The thermal stability of the mechanical properties of neat CN films²⁶¹ and modified/composite CN films²⁶¹ have only been investigated by a few studies. The DMTA study by Henriksson *et al.*²⁶¹ demonstrated that it is possible to tailor the thermal mechanical properties of neat CN films by infiltrating the remnant porosity within the film with a resin material. By directly comparing neat NFC films to neat NFC

films infiltrated with melamine formaldehyde (MF), the role of MF on the NFC film properties was determined. Neat NFC films had a large decrease in storage modulus from 7.5 GPa to 3.5 GPa with increasing temperature (25–225 °C). The inclusion MF increased the storage modulus ($\sim +2$ GPa) and decreased the internal friction factor over the entire temperature range; the extent was dependent on the concentration of MF addition.

The thermal conductivity of matrix polymer resins can be increased by the inclusion of a cellulose particle network structure. Shimazaki *et al.*²⁹⁴ produced NFC (58 wt%)-epoxy matrix reinforced composite that had thermal conductivity of $1.0 \text{ W m}^{-1} \text{ K}^{-1}$, which was 3–5 times higher than the neat epoxy matrix. The increased thermal conductivity of the NFC composites provides the capability to dissipate more heat for a given input heat flux, which lowers the composite temperature and thus improves the thermal stability both chemically and mechanically.

7.6.2 Coefficient of thermal expansion (CTE). The low CTE of crystalline cellulose, estimated at $\sim 0.1 \text{ ppm K}^{-1}$,^{126–128} makes CNs ideally suited for uses in neat and composite structures in which a low CTE is desirable and has recently been reviewed.¹²⁸ One area of applied research is the development of support materials for flexible transparent displays.²⁹² Support materials not only need to be transparent (section 7.3), but also need to have the in-plane CTE match the display electronics (typically less than 20 ppm K^{-1}).¹²⁸ Polymer based substrate materials have been considered, but the CTE of most polymers is too large. For example, the CTE of neat acrylic resin²⁸⁶ and epoxy resin¹²⁸ are 86 ppm K^{-1} and 120 ppm K^{-1} , respectively. The in-plane CTE of neat CN films has been measured for BC^{286,332} ($\sim 2\text{--}3 \text{ ppm K}^{-1}$), NFC¹²⁵ ($\sim 2.7 \text{ ppm K}^{-1}$), and MFC²⁸¹ (from bamboo = $\sim 25 \text{ ppm K}^{-1}$ and from SW = $\sim 15 \text{ ppm K}^{-1}$). The Ashby plot of the CTE versus Young's modulus is given in Fig. 37, and shows how crystalline cellulose I β , neat and modified/composite CN films, and CN matrix reinforced composites compare to other material systems. The crystalline cellulose regions, CN reinforced matrix composite region, neat and modified/composite CN film regions are based on the data given in Tables 3, 5, 6, and 7, respectively. The results of MFC, NFC, CNC, and t-CNC were grouped together as there was extensive overlap in the measured properties. BC neat films were considered separately. The CTE of CN reinforced matrix composite films can be tailored to the desired application and, as shown in Fig. 37, can be used to lower the CTE of engineering polymers by over an order of magnitude. The CN composite CTEs are dependent on several factors: The CTE of the matrix phase,^{81,87,292} the mechanical properties of the matrix phase (see section 8.5.1),^{287,292} the CN network,²⁸⁶ the CN-CN bond strength,⁸⁷ cellulose volume fraction,^{269,286} and the directionality of measurement (in-plane versus out-of-plane).²⁸⁷ The improvement in composite CTE only occurs in-the-plane of the film, the out-of-plane CTE is greater than that of the neat resin.²⁸⁷ The in-plane CTE of CN composite films have been measured for BC^{286,287,334} ($\sim 4\text{--}10 \text{ ppm K}^{-1}$), NFC^{285,292,294} ($\sim 12\text{--}30 \text{ ppm K}^{-1}$), and for MFC²⁶⁹ ($\sim 10\text{--}30 \text{ ppm K}^{-1}$).

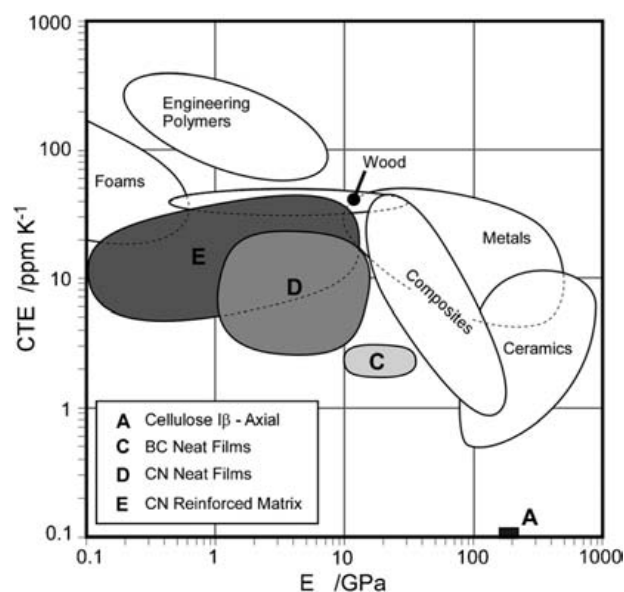


Fig. 37 Ashby plot of CTE versus Young's modulus. Regions of crystalline cellulose I β , BC neat and modified/composite films, CN neat or modified/composite films of various cellulose particle types (CNC, t-CNC, MFC, and NFC), and CN reinforced matrix composites (less than 30 wt% CN) are shown.

7.7 Optical transmittance properties

Several studies have investigated the transmittance of CN reinforced polymer matrix composites,^{285–287,292,294,335} neat CN films,^{125,127,283} and CN modified/composite films,^{127,285,286,292,294,332,334,336} and has recently been reviewed.¹²⁸ A schematic plot of transmittances as a function of wavelength illustrates several factors which influence the optical transmittances of films (Fig. 38). These include: The wavelength of the light, the cellulose particle size,^{81,87,285} film thickness,²⁸⁶ cellulose fraction,^{286,335} index of refraction mismatch between cellulose and matrix (or porosity in neat structures),^{127,336} and the film surface roughness.²⁸³ Typically transmittance has been measured in the wavelength range of 200 nm to 1000 nm, which encompasses the full range of the visible spectrum of 390–750 nm. To minimize scattering it is

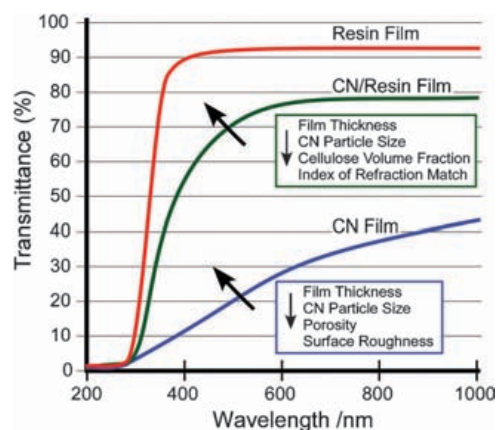


Fig. 38 Schematic plot showing trends of light transmittance as a function of wavelength for neat polymer and cellulose films and resulting composite.

desirable to use a particle size that is less than 1/10th the wave length of interest.¹²⁷ Reduction in transmittance increases with the film thickness and wt% of cellulose content.²⁸⁶ For neat films the transmittance is typically below 50% over the entire range of wavelengths,^{127,283} but TEMPO oxidized NFC films have shown transmittance of greater than 80%.¹²⁵ This poor transparency is primarily attributed to light scattering caused by the high fraction of porosity 20–40% within the films combined with the large differences in the refractive indices between cellulose (1.618 along the fibril and 1.544 in the transverse direction¹²⁷) and the porosity. By filling the porosity with refractive index matching resins (epoxy, acrylic, phenol-formaldehyde), it is possible to increase the transmittance to greater than 80% over most of the visible spectrum (Fig. 38).^{127,334,336}

7.8 Water sorption

Water sorption is one of the major issues that limits applications for cellulose based materials, as this impacts dimensional stability, mechanical property stability, and chemical stability and has been recently reviewed.¹⁹ There have been several studies that have investigated the moisture sorption and retention of CN reinforced polymer matrix composites,^{19,49,55,268,293,332} CN neat,²⁶¹ and CN modified/composite films.^{261,289} The accessible hydroxyl groups on the surface of cellulose particles are generally regarded as the initial site of water sorption and thus susceptibility to property loss. However, for matrix materials that readily adsorb water, *i.e.* starch based polymers, the CN networks can decrease water vapor sorption and water diffusion as a function of increased CN volume fraction as compared to the neat polymer matrix material.^{55,268} Additionally, in comparison to solid wood, neat CN films have a lower equilibrium moisture content over the entire range of relative humidity (0–100% RH).²⁶¹ Water sorption can be significantly lowered in modified/composite films by either chemical treatments and/or infiltrating the porosity with a matrix resin.²⁶¹ These generally reduce the number of hydroxyl groups accessible to water molecules. However, Nakagaito and Yano²⁸⁹ showed that water retention in hot pressed MFC phenol-formaldehyde laminated composites was insensitive to changes in resin content (2.5–28%, assumed to be wt%). They also showed that water retention increased with increased degree of WF fibrillation (*i.e.*, number of mechanical treatments as described in section 2.3.1), which corresponded to an increased exposed cellulose surface area. Composites made with the finest fibril diameter had over four times the water retention as compared to composites made with the starting softwood pulp fibers (*i.e.* before any mechanical treatments).²⁸⁹

7.9 Barrier properties

CN-based materials, both neat and modified/composites, have attracted interest as barrier films with potential uses in filtration and packaging applications and has been previously reviewed.^{7,10} Barrier property investigations have primarily focused on water vapor transmission^{55,324} and oxygen permeability,^{7,125,280,335} but there has been some limited work on permselective properties as well.³³⁷ Water vapor barrier

properties for reinforced matrix composites show that the addition of cellulose particles typically increases water permeability (the exception is for matrix materials that readily adsorb water see section 7.8). Thermal treatments (120 °C for 3 h) have also been shown to decrease water vapor permeability up to 11% in carboxylated CNC composites.³²⁴ Oxygen barrier properties have been studied for CN reinforced matrix composites,^{7,335} CN neat films,²⁸⁰ and modified/composite films.¹²⁵ Petersson and Oksman³³⁵ showed that the addition of 5 wt% MCC to PLA increased oxygen permeability by over 3 times. In contrast, Fukuzumi *et al.*¹²⁵ significantly lowered the oxygen permeability of 25 μm thick PLA film ($746 \text{ mL m}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$) by depositing on top of the PLA film a 0.4 μm TEMPO-NFC film. The resulting permeability of the two layer structure was $1 \text{ mL m}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$. Since barrier properties are linked to factors that influence the tortuous path of the diffusing species through the film, the permeability difference observed between the above two studies may be based on several factors, such as, reinforcement shape, concentration, orientation, crystallinity, porosity, and interphase effects. Similarly, Syverud and Stenius²⁸⁰ demonstrated that neat MFC films (20–30 μm thick) had low oxygen permeability of $\sim 17 \text{ mL m}^{-2} \text{ day}^{-1}$. For modified atmosphere packaging, the oxygen transmission rate should be below 10–20 $\text{mL m}^{-2} \text{ day}^{-1}$.²⁸⁰ These two latter studies have demonstrated the potential of neat and/or modified cellulose films for oxygen barrier applications. Barrier properties against hydrophobic chemicals were demonstrated by Paralikar *et al.*³³⁸ Here poly(vinyl alcohol) films reinforced with carboxylated CNCs showed improved barrier properties against trichloroethylene. Thielemans *et al.*³³⁷ investigated the permselective properties of neat CNC films as a function of the diffusing species charge. Rotating-disk electrode measurements were used to study the diffusion of positively-charged species, $\text{Ru}(\text{NH}_3)_6^{3+}$, neutrally-charged species, FeOH , and negatively-charged, IrCl_6^{3-} . The negatively-charged sulfate surface groups on CNCs, a byproduct from their extraction process, produced electrostatic repulsion mechanism that inhibited the transfer of negatively-charged species through the CNC network.

7.10 CN-hybrid composites and templates

Additional functionality to CN composites can be achieved through subsequent modification of individual CNs or the CN networks. Three techniques are briefly introduced here: fluorescent labeling, creating “receptor sites”, and the incorporation of inorganic nanoparticles into the CN networks. For fluorescent labeling, fluorophores are either covalently attached or noncovalently associated with the CN surface. The newly functionalized CNCs are being studied for uses in bioimaging applications,³³⁹ and pH sensing.³⁴⁰ Receptor sites involve chemically functionalizing the CN surface so that they respond to a given stimuli. Bonne *et al.*³⁴¹ have used boronic acid binding sites as “receptor sites” along CN networks to develop membranes for spectrophotometric or electrochemical detection. These functionalized CNC networks were produced *via* solution casting of boronic acid dendrimer with CNCs. The incorporation of inorganic

nanoparticles onto CNs and into CN networks have potential uses in biosensors, catalysis, photovoltaics, filters and antimicrobial applications. For these applications it is important that the inorganic nanoparticles are uniformly dispersed and well bonded to the CN surface. A variety of electroless deposition techniques have been used to precipitate various inorganic nanoparticles (copper,¹⁵⁴ silver,^{154,342} gold,^{154,343} gold-silver,³⁴⁴ nickel,³⁴⁵ platinum,¹⁵⁴ selenium,³⁴⁶ porous titania,³⁴⁷ cadmium sulfide,³⁴⁸ zinc sulfide,³⁴⁸ and lead sulfide³⁴⁸) directly out onto the surface of CNCs,^{344–347} t-CNCs,^{154,348} NFCs,³⁴³ and BCs.³⁴² The advantage of the CN networks is that they not only provides mechanical support but also help disperse the inorganic nanoparticles by providing a template surface to nucleate precipitation.

8. Engineered bacterial cellulose materials

The BC literature has been previously reviewed in detail,^{8,11–14} but a brief review is given here. Bacterial cellulose is fairly unique compared to the other cellulose microfibril sources in that there is an accessible route to alter the BC microfibril biosynthesis process and the starting microfibril configuration within the pellicle (Fig. 39), which is often retained in the final engineered BC materials. The resulting mechanical properties of engineered BC materials are strongly linked to their multi-stage processing methods. There are three general engineered BC materials that will be reviewed: hydrogel based structures, neat BC films, and modified BC films (*e.g.* composites).

8.1 General processing of bacterial cellulose materials

The general processing of engineered BC materials can be considered to occur in four main stages: (1) BC culturing, (2) pellicle management, (3) water removal, and (4) chemical modification. For stage 1, the biosynthesis of BC occurs in culture solutions, generally in a bioreactor, in which bacteria secrete cellulose microfibrils, producing an interwoven web of fibrils that is a hydrogel, as described in detail elsewhere.^{14,72,349} The hydrogels are composed of entangled cellulose microfibrils formed from the random motion of the bacteria,²⁸⁷ contain upwards of 99% water, and are called pellicles. Variation in culture conditions (bacteria type,¹⁴ nutrients,⁷² temperature,⁷² pH,⁷² and agitation^{14,327}) alters the biosynthesis process,¹¹ which in turn alters the BC microfibril morphology (Fig. 10f) and network configuration within the pellicle.^{14,327} The changes in BC microfibril morphology and network configuration both alter the properties of the pellicle and the engineered BC materials produced from the pellicle.³²⁷ The shape of the pellicles can be altered by changing the shape of the bioreactor (*i.e.* the gel conforms to the bioreactor shape), stirring conditions and the thickness of the gel increases with increasing culture time.¹¹

For stage 2, pellicle management refers to any process imparted on the pellicle up until the point of water removal. To remove the bacteria from the pellicles, the pellicles are washed by boiling in a low concentration ($\sim 2\%$) NaOH bath for several hours, after which it is rinsed under running water for several days. Additional NaOH and NaClO treatments have also been used for further purification of the BC microfibrils.^{11,321,350} Mechanical treatments have been used to alter

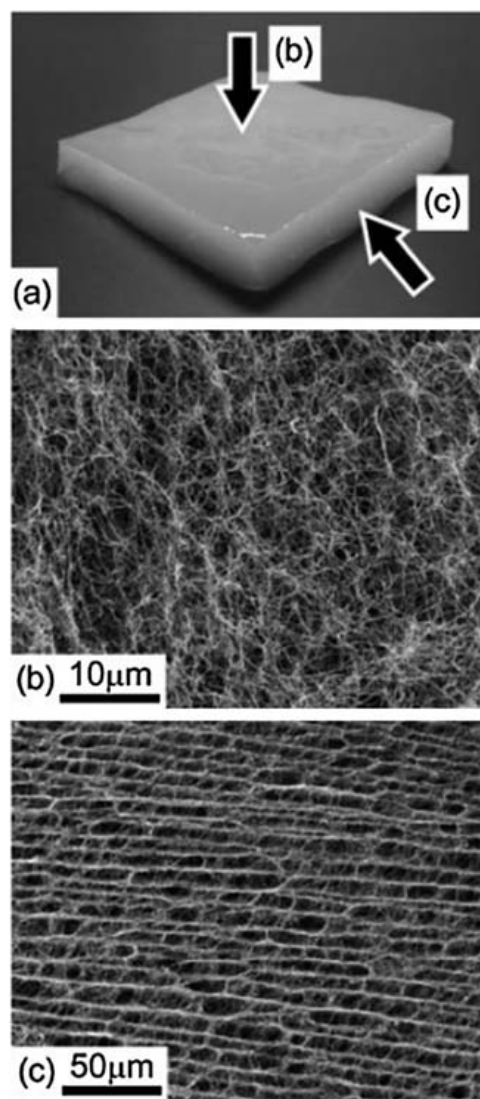


Fig. 39 Images of BC pellicle. (a) optical image of BC pellicles showing the directionality for images b and c. Field-emission SEM image showing the (b) the low density in-plane BC network, and (c) the transverse structure.²⁸⁷ Reprinted with permission from ref. 287 © 2008 WILEY-VCH.

the BC microfibril network structure within the pellicle. Mechanical defibrillation treatments can be used to break up to the entangled BC networks,^{79,277,350} while stretching treatments can be used to induce preferential microfibril alignment within the pellicle.^{237,351,352}

For stage 3, once the pellicle is formed and purified, a sample is cut from the gel-like sheet. Water removal either by evaporation or a combination of pressing and evaporation collapses the gel-network and produces a dense film ($\sim 1.0 \text{ g cm}^{-3}$). Pressing methods typically involve placing a gel sheet between stainless steel mesh and/or non-woven fabrics to facilitate the escape of water.¹¹ The resulting films have a through-film thickness made up of many parallel stackings of thin cellulose sheets, or layers, each consisting of a dense microfibril network.^{11,79,322,328} For producing BC composite films with lower microfibril contents (*i.e.* 1–40 wt% BC), solvent exchange (replacing water with acetone or ethanol, *etc.*)

or freeze drying minimizes the BC microfibril consolidation that occurs during water evaporation.^{286,287} Combined with compression treatments of the pellicle, the resulting thickness of the dried structure or film can be controlled.²⁸⁶

For stage 4, chemical modification to the BC microfibril network can be achieved at three points along the engineered BC material processing, (i) during stage 1, (ii) during stage 2, and (iii) after stage 3 (*i.e.* to dried BC structures or films). Any combination of these modification routes can also be used to make BC composites (see section 8.4). The addition of various chemicals during stage 1 (*i.e.* water soluble polymers,³²⁶ dithiothreitol,³⁵³ nalidixic acid,³⁵³ 2-mercaptoethanol,³⁵³ xyloglucan,³⁵² pectin,^{352,354} sodium alginate³²⁸) alters the morphology and configuration of the BC microfibrils (Fig. 10f) and the properties of the pellicles. The chemicals are designed to remain bonded to the BC microfibrils and are retained in the final engineered BC material. Since these chemicals are bonded to the entire BC microfibril surface during pellicle formation, it is possible to tailor the microfibril-microfibril bonding strength, and thus alter the properties of the resulting composite film. Chemical modification during stage 2 involves aqueous chemical treatments to the pellicle to modify the BC surface (*e.g.* acetylation treatments,³⁵⁵ poly(vinyl alcohol) (PVA)³⁵⁶). The chemicals are either covalently bonded to the BC substrate or adsorbed on the BC surface as the water is removed by evaporation. The resulting material can have very different properties from the original BC. The final case involves infiltration/impregnation of resins (acrylic,^{127,286,334,336} phenolic,²⁷⁷ epoxy, *etc.*) into the dried and porous BC substrate after stage 3 with a subsequent cure and/or solvent removal protocol to form a composite material.

8.2 Bacterial cellulose hydrogel structures

Hydrogels are hydrophilic network structures that can absorb from 20% to one thousand times their dry weight in water.³⁵⁶ Polyvinyl alcohol is one polymer system that shows this behavior, as does the BC pellicle, which is used to make the BC hydrogel structures. The ability of BC networks to hold high volume fractions of water has been considered to be one reason why BC implants do not elicit any foreign body reaction.¹⁴ BC hydrogel structures are showing great potential for biological applications (*e.g.* cardiovascular implants, wound and burn dressings, and tissue regeneration scaffolding).^{12–14,349,357}

BC hydrogel structures result after the stage 2 processing described in section 8.1. The BC biosynthesis process is conducive to the direct formation of 3D objects. By varying cultivation techniques and the geometry or type of bioreactor, it is possible to make the desired BC network structure, BC/water balance, and the bulk 3D shape of the hydrogel (*e.g.* bulk materials, films, balls, and tubes).^{12,14} The tubular shaped BC hydrogels are being developed for cardiovascular implants, in which the high mechanical properties and the fine control of the tubular structure (outer and inner diameters, surface quality, *etc.*) have been shown to be advantageous.^{13,349} There is a need to develop materials that not only have biocompatibility, but have similar mechanical properties as the tissues they are replacing. Despite the high water content

(upwards of 99%) the hydrogels have reasonable mechanical properties as a result of the BC microfibril network structure, and can be altered by chemical treatments, which allows for engineered properties.^{352,354,356,358} The properties of BC hydrogel structures can be tailored similarly to the general description given in section 8.1. One specific example is given here. Astley *et al.*³⁵² produced neat BC hydrogels (~95% water, $E = \sim 14.0$ MPa, $\sigma_f = \sim 2$ MPa, $\epsilon_f = \sim 20\%$). The inclusion of either xyloglucan³⁵² or pectin^{352,354} to the culture solutions (*i.e.*, Stage 1 in section 8.1) lowered both the E (~ 0.05 – 1 MPa) and σ_f (~ 0.05 – 1 MPa), while increasing the ϵ_f by ~ 200 – 400% .^{352,354}

8.3 Neat bacterial cellulose films

Neat BC films are being considered for uses in high stiffness acoustic diaphragms.³²² Neat BC films are the result after the stage 3 processing described in section 8.1 and the resulting mechanical properties are strongly linked to their multi-stage processing method. The mechanical properties of neat BC films are summarized in Table 6. The high mechanical properties of neat BC films are believed to result from the properties of individual BC microfibrils, the ultrafine ribbon structure resulting in more extensive hydrogen bonding, the high in-plane orientation and “three-way branching points” of the microfibril networks.⁷⁹ Several neat BC film processing variables have been shown to strongly influence the resulting film mechanical properties, such as, pellicle purification,^{11,321} pressing pressure,^{79,359} drying temperature,⁷⁹ pellicle defibrillation,^{79,277,350} and alignment of BC microfibrils.²³⁷ The combined purification treatments of NaClO and/or NaOH have been shown to increase the elastic modulus of BC films from 15 GPa up to 30 GPa.^{11,321} It is believed that these treatments remove impurities and promote stronger hydrogen bonding between BC microfibrils (increased interfacial properties as described in section 6.1.3). The application of low pressure during the water removal stage (Stage 3 in section 8.1) is beneficial for properties; however, at pressures greater than 50 MPa, σ_f and ϵ_f can be degraded, which has been attributed to introduced defects within the BC network structure and within the BC microfibrils.^{11,79} Drying films at temperatures greater than room temperature increases film properties,³⁶⁰ however, additional drying above ~ 100 °C has minimal influence on properties.⁷⁹ The mechanical refining of pellicles breaks up the very fine microfibrillar network structure^{79,277,350} and can cause agglomeration of the microfibrils into micron sized particles. The mechanical properties of neat BC films produced from the disintegrated BC pellicles were shown to have lower E ^{79,277} and σ_f ,^{79,277} but have a larger ϵ_f and work of fracture.³⁵⁰ Mechanical alignment of BC microfibrils within the pellicles has been shown to have a significant effect in increasing E and σ_f of neat BC films tested along the axis of the microfibril alignment.²³⁷ Subsequent hot pressing (70 °C at 10, 50, or 100 MPa) of dried BC films have shown increased E , σ_f , ϵ_f , and work of fracture.³⁵⁹

8.4 Modified bacterial cellulose films and composites

Modified BC films and composites are being considered for uses in acoustic diaphragms,^{72,322} new paper products

(that include either copper, calcium carbonate, or activated carbon particles),³²² and transparent film displays^{128,361} to name a few. These films result from the stage 4 processing described in section 8.1. BC modified or composite films have been processed by either the addition of various chemicals during Stage 1 (*i.e.* water soluble polymers,^{326,360} dithiothreitol,³⁵³ nalidixic acid,³⁵³ 2-mercaptoethanol,³⁵³ sodium alginate³²⁸), or after Stage 3 in which the dried film was subsequently chemically treated,³⁶² or infiltration/impregnation with acrylic resins^{127,286,334,336} or phenolic resins.²⁷⁷

The mechanical properties of BC composite films are summarized in Table 7. The addition of a matrix phase has been shown to alter the mechanical properties with respect to the neat BC films.^{277,326,360} However, identifying the specific role of the matrix phase on altering BC film mechanical properties remains elusive. Direct comparisons between neat BC films and composite films is challenging since BC composite films typically have a lower volume fraction of BC microfibrils, there is typically a change in the fibril morphology (Fig. 10f), and there can be changes in the resulting microfibril network structure. The addition of a matrix phase has been shown to improve the film E , but there are corresponding decreases in the film σ_f and ϵ_f .²⁷⁷ The study by Tajima *et al.*³⁶⁰ produced BC composite films with the addition of carboxymethyl cellulose, methyl cellulose or polyethylene glycol into the BC culture stage. The reported dynamic elastic moduli of the resulting composite films were up to 90 GPa. Impressive as this is, there have been no studies to corroborate these findings. In addition, this exceeds the theoretical upper bound for 2D random in-plan CN orientated films (see Fig. 25).

8.5 Optical and thermal expansion properties

BC networks have been used in the development of transparent displays as a reinforcement phase since it causes low light scattering and imparts low thermal expansion properties to the composite. There have been several studies that have investigated the transmittance^{127,286,287,332,334,336} and CTE^{286,287,332,334} of neat and BC modified/composite films, and have been recently summarized.¹²⁸ A general description of the thermal and optical properties has been provided in section 7.6 and section 7.7, respectively. Additional details specific to the BC neat films and composites are given here.

8.5.1 Thermal expansion properties. BC composite films are being used as the support for transparent displays as it is possible to match the in-plane CTE to that of the display electronics (typically less than 20 ppm K⁻¹).¹²⁸ BC networks are ideally suited for uses in neat and composite structures in which a low CTE is desirable. The in-plane CTE of neat BC films are $\sim 2\text{--}3$ ppm K⁻¹,^{286,332} and can be further lowered to 1 ppm K⁻¹ through acetylation treatments.³³² BC networks have been used to lower the CTE of neat acrylic resin²⁸⁶ and epoxy resin,¹²⁸ 86 ppm K⁻¹ and 120 ppm K⁻¹, respectively (Fig. 40). Even for BC additions of less than 10 wt% the in-plane CTE of the composite film is less than half that of the neat matrix polymer. For BC-acrylic composite films with ~ 60 wt% BC the in-plane CTE was decreased to $\sim 8\text{--}10$ ppm K⁻¹.^{286,334} Additionally, by using acrylic resins with lower Young's moduli it has been shown that for the

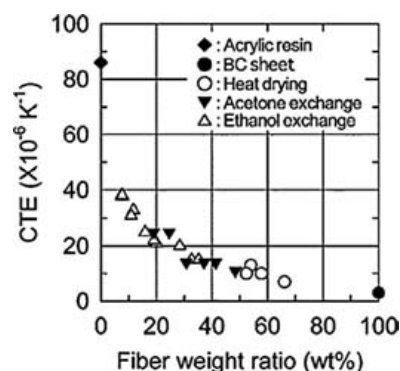


Fig. 40 CTE schematic plot showing trends for neat acrylic resin and BC films and resulting composites as a function of BC microfibril wt%, based on the results from ref. 286. Reprinted with permission, from ref. 286 © 2006 American Institute of Physics.

same volume fraction BC the in-plane CTE of the composite is lower.²⁸⁷ Specifically, for composites with $\sim 35\text{--}40$ wt% BC, the CTE was 4 ppm K⁻¹ and 38 ppm K⁻¹ when acrylic resins with Young's moduli of 0.025 GPa and 2.5 GPa were used, respectively.²⁸⁷

8.5.2 Optical properties. In general, the transmittance of BC films and composites has been shown to be dependent on the wavelength, film thickness,²⁸⁶ cellulose fraction,²⁸⁶ and index of refraction mismatch between cellulose and matrix.^{127,336}

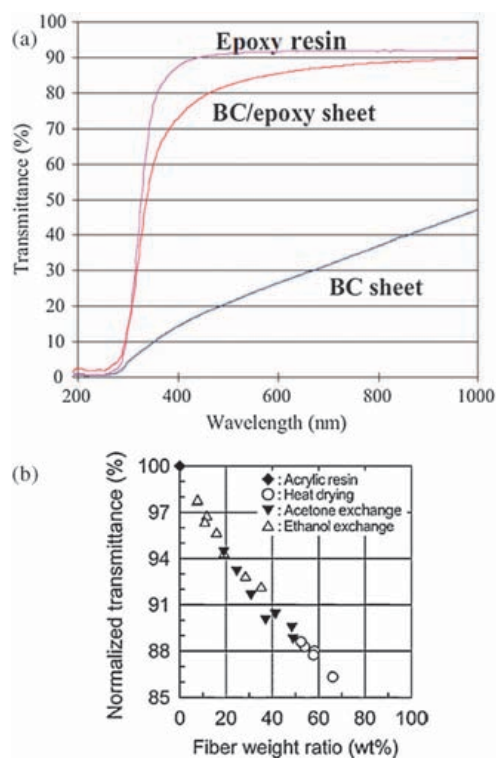


Fig. 41 Light transmittance schematic plots showing trends for neat polymer and BC films and resulting composites. (a) Transmittances as a function of wavelength for epoxy resin,²⁸⁸ (b) transmittance as a function of BC microfibril wt% within composite.²⁸⁶ Reprinted with permission, (a) from ref. 288 © 2005 WILEY-VCH, (b) from ref. 286 © 2006 American Institute of Physics.

For neat BC films the transmittance is below 50% over this entire range.¹²⁷ By filling the porosity within the neat BC films and structures with refractive index matching resins (epoxy, acrylic, phenol-formaldehyde), it is possible to increase the transmittance to greater than 80% over most of the visible spectrum (Fig. 41).^{127,334,336} Interestingly, the improvement in transmittance of BC composite films was insensitive to the refractive index of resins from 1.492 to 1.636 at 20 °C, and were insensitive to the small changes in refractive index resulting from temperature increases up to 80 °C.³³⁶ Acetylation treatments, used to reduce hygroscopicity of BC microfibrils, have been shown to improve or degrade the transparency of composite films, dependent upon the matrix resin,³³⁴ and on the extent of acetylation.³³² Comparatively, the transmittance of neat acrylic and epoxy resins are ~92%, and the addition of any wt% BC microfibrils is shown to lower the transmittance, most notably in the wavelength range of 300–600 nm.^{127,286,287,336}

9. Grand challenges

9.1 Cellulose nanoparticles

9.1.1 Cellulose nanoparticle processing. As reviewed in section 2 there is a wide variety of different CN types (MFC, NFC, CNC, t-CNC, BC, and AC) that have been studied in recent years and each have their own research grand challenge areas. In general, four grand challenges can be identified for CNs as having the greatest potential for expanding their use in new composite materials: decrease the internal damage in CNs as a result of the extraction process, narrow the particle size range for a given CN processing methodology, decrease the cost of the extraction process, and scaling up production to industrial quantities. The extraction of CNs from a given source material has the inadvertent effect of altering the percent crystallinity, particle morphology, and possibly introducing new defects within the CN (see section 2.5). By minimizing these defects the resulting CN is likely to retain higher tensile, elastic and thermal properties. For example, the use of pretreatments (*e.g.* TEMPO, never dried source material, and/or retained hemicellulose) to facilitate the fibrillation of WF and PF to NFC and/or MFC has led to lower amounts of mechanically induced damage to the CN (see section 2.3.1).

Processes controlling the CN size distributions from a given extraction process have to date mostly used filtration to truncate the distribution on the high end. Developing extraction processes with tighter controls on CN particle size distributions (length, width, aspect ratio) will provide more control in CN suspensions, CN-surface functionalization, CN-polymer blends, and in the design and processing of CN composites.

Decreasing the cost of CN production would increase the number of markets appropriate for CN based applications. Efforts to reduce costs could focus on increasing CN yield, decreasing energy input, decreasing chemical usage and recycling/reuse of processing chemicals. Pretreatments have improved MFC and NFC processing by decreasing the number of “passes” through mechanical refiners, but the additional costs of TEMPO or other chemical treatments, need to be considered. New catalysts and/or recovery processes

hold the potential of breakthroughs in CN production costs. For BC, there is a need to reduce the time required for growing the cultures and improve the understanding of the genetics involved to allow for improved production and products.

Scaling-up CN processing from laboratory size quantities to pilot plant quantities is a needed first step toward industrial scale CN-composite processing. The availability of larger CN quantities allows applied research in the processing of larger sized CN-composite samples (10s to 100s of cm in dimensions), which are more realistic in terms potential products as compared to the much smaller laboratory scales (typically less than 1cm in size). Pilot plant facilities have been made or are in the design stage for CNC processing (FPIInnovations,³⁶³ Domtar,³⁶⁴ Bio Vision Technology Inc,³⁶⁵ and USDA—Forest Service Forest Products Laboratory³⁶⁶), and MFC processing (Innventia,³⁶⁷).

9.1.2 Cellulose nanoparticle functionalization. There are three grand challenges that can be identified as having the greatest potential for significant contribution: compatibilization, control, and cost. As reviewed in section 4, a variety of chemical functionalization methods have been studied. For the most part these have focused on compatibilization. While much work has been done to compatibilize CNs with matrix materials, this issue is still mostly unsolved. As is true of composite science in general, the performance of composite materials is quite complicated and the various parameters involved can be quite interactive. CN-based composites are no exception. Nevertheless, improving the dispersion of CNs in polymer matrices, improving the interfacial characteristics of the composite and improving strength and stiffness without sacrificing toughness remain significant challenges. Compatibilization touches on all these characteristics.

The second grand challenge is to control CN properties, *i.e.* to develop the means to produce CNs with tightly controlled size and aspect ratio, minimized crystal defects and controlled surface chemistry. Such control will allow for repeatable, optimized materials with few defects, currently an issue in production.

The last grand challenge in CN chemistry is cost. A factor in the cost of CN production is the low yield when starting from plant (or animal, in the case of tunicates) based raw materials, as opposed to bacterial sources. Additionally, the viscosity of CN dispersions rapidly build with concentration, forcing dilute CN content during processing and functionalization. In addition to increased capital costs for production, this can also lead to excessive waste. While cellulose is generally inexpensive, the cellulose pulp and paper industry is extremely cost sensitive, raising barriers to commercialization. At the research level, the dilute amounts mean larger reactor sizes to provide the requisite amounts for pilot or large-scale research, which raises the capital cost of research. For example, while TEMPO mediated fibrillation drastically lowers the mechanical action for NFC production, TEMPO is relatively expensive, toxic and raises the chemical costs—alternatives are needed.

9.1.3 Cellulose nanoparticle characterization. Two grand challenges can be identified as having the greatest potential for significant contribution: CN structure characterization, and

CN nanomechanical properties measurement. The extraction of CNs from their respective source materials, likely imparts damage to the crystal structure and thus the properties of the resulting CN will be altered compared to those measured (or predicted) for idealized cellulose crystal structures. While the cellulose crystal structures are generally well known, the characterization of CNs is lacking, in particular the percent crystallinity, location of amorphous regions (*i.e.* on CN surface or throughout core), the I α /I β ratio, location of I α and I β regions within the CN (*i.e.* at the surface, or at the core), the identification of defects, and CN surface chemistry. Improved structural understandings of CNs will facilitate the development of models for the design of improved products.

There is a need for the development of standardized measurement methods and reporting for CN mechanical properties (elastic, tensile strengths, interfacial, *etc.*). This will help sort out whether the source of the wide distribution in the reported CN mechanical properties (see Table 3) is due to fundamental properties of the CN or different measurement techniques. While the reported properties for CNs are on par with atomistic model predictions (see section 5), they are too variable for conducting fundamental research on structure-property relationships. For example, the wide property distribution makes it difficult to directly compare properties as a function of particle type or CN extraction process, as well as to choose appropriate input values for continuum modeling. Nanomechanics of individual CNs is a huge challenge, as the small size scale pushes the limits of sensitivity of current methodologies (atomic force microscopy, *etc.*). Progress has been made in the elastic property measurements; however, more work is needed to quantify the uncertainty in the measurements.¹¹³

9.2 Atomistic modeling

This review has shown that atomistic modeling has contributed to our understanding of cellulosic materials and, more importantly, that there will be many more opportunities for this method going forward. There are three high-level research directions that can be identified as having the greatest potential for significant contribution: standardization of methods and reporting, study of a greater range of environmental conditions, and direct comparison/validation with experimental measurements. The first, methods and reporting standardization, is perhaps more of a necessity than an opportunity. Inconsistencies between simulation methods, models, and results were evident throughout section 5. It is absolutely critical that researchers not only understand how what goes in (method details) affects what comes out (model predictions), but that this relationship is reported. In addition, atomistic modeling of cellulose has, to this point, been limited in the range of environmental conditions under which studies are performed. The effect of conditions such as pressure, temperature, and humidity are well known to affect material properties and investigation of these effects has significant potential to improve our understanding of CN technology. Lastly, extending the applicability of molecular modeling from a research method to a design tool necessarily requires that model predictions be validated. Experimental validation thus

far has been primarily qualitative and limited to a subset of features including axial crystalline unit cell length and elasticity. However, as the capabilities and accuracy of both experimental techniques and modeling methods improve, there will be significant potential for research efforts towards direct, quantitative comparison between measurement and prediction.

9.3 Analytical modeling

Analytical models, in particular conventional continuum methods, provide an excellent basis for probing the potential of CN nanocomposites (see section 6). The upper and lower bound results already give useful benchmarks for evaluation of experimental results. Mean field approaches, like Halpin and Kardos (but using concentric cylinder model rather than Halpin-Tsai model), give refined upper bounds and can evaluate the role of CN aspect ratio and CN/matrix interface. Experimental results that exceed any of these upper bounds should be treated with skepticism, unless a unique “nano” effect can be discovered and modeled to explain them. Prior “unusual” reinforcement effects of CNs have typically been explained in terms of the formation of CN network structure, *via* percolation theory. With careful modeling, however, these results, as all results should, also fall between the upper and lower bound of continuum models. In contrast, an interphase near the particle surface can play a significant role. The amount of interface in nanocomposites greatly exceeds the amount in composites with the same amount of large-scale reinforcement. If CN-polymer interactions change the mechanical properties of the matrix in the interphase region, new property variations are expected. Modeling predicts a role for this interphase in stress transfer and in transport properties. A grand challenge, therefore, is a thorough investigation into the role of the CN–CN and/or CN–matrix interphase regions on CN nanocomposite properties. A good starting point would be experimental methods to character the interphase such as measurement of the D_s parameter incorporated into mechanical property modeling.

9.4 CN films and composites

Three grand challenges can be identified for the further development of CN films and composites: Interface characterization and mechanics, characterization of CNs within the matrix polymer and role of hierarchical structure on resulting macroscopic properties. As described in section 6 conventional continuum analytical modeling methods can predict the upper and lower bounds of properties, in which narrower bounds are achieved by the inclusion of the contribution of interfaces. More work is needed to develop the characterization tools and then to characterize CN–CN and CN–matrix interfaces (geometry, thickness, properties, *etc.*), which can be used as input values used for various models. For CN reinforced polymer matrix composites, characterization of the CN configuration within the matrix polymer is challenging. The CN distribution (*e.g.* finely dispersed, or aggregated) within the matrix will have a strong influence on the mechanical properties (see section 6). Conventional imaging techniques (transmission electron microscopy-TEM, scanning electron

microscopy-SEM, *etc.*) have had limited success, due to difficulties in differentiation between the CN and matrix material. Further developments in imaging or characterization techniques or protocols are needed. The ability to relate how the variation in properties at various length scales influences the final macroscopic properties of CN films and composites, would give insight on the design of such materials. For example, if it was possible to modify either the CN–CN or CN–matrix interface and assess the change in interfacial properties, this information could then be used to predict the macroscopic properties of CN films and composites.

Additionally, the potential of CN based materials and composites are limited in potential consumer applications because of water sorption (see section 7.8), thermal stability (see section 7.6), and cost issues. Approaches need to be developed to investigate new cost effective mechanisms to alter the hygroscopic nature of CNs and maximize their thermal stability. This will likely require research efforts in which atomistic models are combined with targeted experiments.

9.5 Creativity

While it is tempting to focus on applications for CNs that utilize the vast production capability of the pulp and paper industry, or to couple CN production with bioenergy production, or to focus on “stronger, stiffer” composites for building materials applications, the places where CN technology naturally fits in the marketplace may be elsewhere. Thinking outside the box and exploring new and unusual applications may provide for a quicker adoption of CN-based technology in a world that is rapidly becoming greener and more sustainable and turning to cellulose and other natural products for answers.

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