Nanocellulose in Spun Continuous Fibers: A Review and Future Outlook

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ABSTRACT: Continuous fibers are commonly manufactured for a wide variety of uses such as filters, textiles, and composites. For example, most fibrous reinforcements (e.g., carbon fiber, glass fiber) for advanced composites are continuous fibers or yarns, fabrics, and preforms made from them. This allows broad flexibility in design and manufacturing approaches by controlling fiber orientation and architecture. However, there has been growing interest in preparing continuous fibers from biobased materials such as plants. Of particular recent interest are nanocelluloses, which are projected to be less expensive than many other nanomaterials and have the potential to be produced in large volumes. They also have an impressive strength-to-weight ratio and have so far shown few environmental, health, and safety concerns in their unmodified state. However, efficient and effective use of nanocellulose in continuous fibers is challenging and a variety of approaches have been explored in which nanocellulose dispersions are either spun directly or in combination with polymers. Methods such as wet spinning, dry spinning, melt spinning, and electrospinning have been investigated. To better understand the body of knowledge of this new and growing area, various approaches are reviewed and a perspective on what the future holds is provided.

KEYWORDS: Nanocellulose, cellulose nanofibrils, cellulose nanocrystals, fiber, spinning

1 INTRODUCTION

Through successive cycles of evolution, nature has developed methods to precisely assemble complex, hierarchical structures while using a limited amount of building blocks, elegantly meeting a wide variety of functional needs [1]. One of the most common load-bearing architectures found in nature are fibers, which can be found in such varied materials as spider silk, plant cell wall microfibrils, and the collagen in the fibrous tissues of animals [2].

In man-made materials as well, continuous fibers are commonly manufactured for a wide variety of uses such as filters, textiles, and composites. For example, most fibrous reinforcements (e.g., carbon, glass) for advanced composites are continuous fibers or yarns, fabrics, and preforms made from them. This allows broad flexibility in design and manufacturing approaches by controlling fiber orientation and architecture. However, to explore new possibilities and to meet a variety of environmental and societal goals, there is growing interest in transitioning to biobased materials. Therefore, it is not surprising that there has been considerable effort investigating the spinning of continuous fibers from such sources as plant fibers, cellulose solutions, and nanocellulose.

For example, natural bast fibers, such as flax, hemp and jute, are sufficiently long enough to be made into continuous reinforcing yarns or rovings using modified textile technologies [3]. Some mechanical performances of these yarns or rovings tend to fall short of the more commonly used continuous synthetic fibers such as glass fibers. For example, strength properties are generally less. However, natural fibers have low density and they are of interest because of their specific properties (i.e., property divided by the material density) and their damping abilities. These rovings or yarns can be directly sold as reinforcement or can be fabricated into mats, fabrics, and prepregs for use in applications such as automotive components or sporting goods [3, 4]. However, the potential of these reinforcements in advanced composites is ultimately limited by the inherent properties and natural variability of the natural fibers used to produce the continuous fibers, yarns, and fabrics [5]. Also, there are challenges in balancing the processability and the
mechanical performance of spun natural fibers. For example, yarns must have a sufficiently high level of twist so that they have the integrity to be handled by textile machinery or composite processing equipment. However, this twist increases misalignment and limits mechanical performance and must be minimized [6].

Continuous fibers can also be spun from solutions of cellulose, which is the main structural component of plants. These regenerated cellulose fibers have been spun from cellulose solutions for over a hundred years [7]. Although they have been traditionally used in textiles, there has been growing interest in their use as polymer reinforcements as well [5, 8]. These fibers are attractive partly due to their lower variability than natural fibers such as flax [5]. Regenerated cellulose fibers are made by several technologies that first dissolve cellulose and then precipitate it during fiber production. While their mechanical performance is still typically less than glass fiber, new regenerated cellulose fibers with high orientation and crystallinity have recently been developed that show significant improvements. For example, a recent experimental regenerated cellulose fiber yielded a tensile modulus and strength of about 46.6 GPa and 1170 MPa [9], which is well above the 10.8–22.2 GPa and 340–780 MPa reported for commercial regenerated celluloses [5]. Since its density is only about 1.5 g/cm³, the specific modulus of some of these new regenerated celluloses is comparable to E glass fiber, which has a density around 2.5 g/cm³ [10]. However, the crystalline structure of regenerated cellulose (referred to as Cellulose II) is different from that of cellulose in its native state (i.e., Cellulose I). While reported values for the mechanical performance of these two types of crystal structures vary considerably and depend on the measurement technique, the values for Cellulose I are clearly considerably higher [11].

2 NANOCELLULOSE

Nanocellulose (NC) represents a new class of cellulose-based material that may have potential in continuous fibers. It can be extracted from trees, plants, some marine creatures such as tunicates, and certain bacteria or algae [11]. NC is not a single material type but a family of materials with very different characteristics, largely due to differences in preparation methodology and source. Here, we focus on plant-derived nanocelluloses. These nanocelluloses are projected to be less expensive than many other nanomaterials and have the potential to be produced in large volumes [12]. They also have an impressive strength-to-weight ratio and have so far shown few environmental, health, and safety concerns in their unmodified state [12]. The two main categories of plant-derived NC are briefly described below. More detailed information can be found in recent reviews [11, 13–19].

Cellulose nanocrystals (CNCs), also called cellulose whiskers, nanowhiskers, or nanorods, are produced by transverse cleavage of cellulose by acid hydrolysis. This results in high modulus, rod-like structures with aspect ratios of around 10–100 but which depend on the source of the cellulose and the exact preparation conditions [11]. Plant-based sources yield crystallites with diameters of about 5 nm and lengths of hundreds of nanometers [20] whereas tunicate and algae yield crystallites with diameters of 10–20 nm and lengths up to several micrometers. CNCs prepared from a high purity wood pulp are shown in Figure 1a.

Severe, mechanical refining of highly purified pulps results in a fibrillated form of cellulose with fibril widths on the same order of magnitude as the cellulose microfibrils in the original pulp. This microfibrillated cellulose (MFC) has more of a network structure than CNCs. Certain preprocessing steps can be used to weaken hydrogen bonding and facilitate fibrillation. For example, a common pretreatment uses a 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) catalyst to mediate the oxidation of native cellulosics, which greatly reduces the energy required to fibrillate the resulting product and form NC [21]. Cellulose nanofibers, nanofibrillated cellulose, and cellulose nanofibers (Figure 1b) are terms that are sometimes used to describe fibrillated cellulose with a finer structure or to reflect that the fibril diameters are of nanoscale dimension. However, the use of the terms is inconsistent and the variability between samples of fibrillated cellulose due to differences in preparation methods, starting materials, etc., or even variability within samples make clear distinction by means of fibril diameter difficult. Here we use the term cellulose nanofibrils (CNFs) for this type of NC. An image of CNFs by mechanical means after a TEMPO-mediated oxidative pretreatment is shown in Figure 1b.

Spinning of continuous fibers from NC is an intriguing option because it has the potential to effectively use the one-dimensional nature and very fine dimensions of NC while maintaining its Cellulose I structure.
Unlike the cellulose-based fibers previously mentioned (natural fibers, regenerated cellulose), NC can be made into continuous fibers of submicron diameter. This reduction in fiber diameter results in continuous nanofibers with intriguing characteristics such as very large surface area, transparency, and fine, controllable porosity when made into mats [22]. Because of these characteristics, nanofibers are being considered in applications such as filters, sensors, optical electronics, catalysts, and tissue scaffolding [23].

However, efficient and cost-effective preparation of continuous NC fibers is challenging and a variety of approaches have been investigated that either spin fibers from 100% NC dispersions or from NC combined with polymers. To date most of the research on continuous NC fibers has focused on monofilaments or electrospun fibrous mats, either directly spinning fiber from NC dispersions or combining NC with a polymer. Wet-, dry-, melt- and electro-spinning methods have been used as well as specialty processes (e.g., microfluidics) to produce continuous fibers. Much of this research is quite recent. For example, initial, rudimentary exploration of what might be possible in terms of spinning of 100% NC dispersions had not even been attempted before 5 years ago [2, 24]. However, because of the rapidly growing body of knowledge, it is useful to summarize what has been learned so far. Various spinning approaches, their use with NC, and the future outlook are reviewed and discussed below.

3 FIBER SPinning

At its most basic level, approaches to spinning that have been used with nanocellulose involve forcing dispersions, solutions, or melts through a needle, die, or spinneret with fine holes to form fibers. The various approaches used with NC are summarized schematically in Figure 2 and mostly involve solution spinning methods (e.g., wet spinning, dry spinning), melt spinning, and electrospinning. These are introduced below and further details of their particular application to nanocellulose are reviewed in subsequent sections.

Melt spinning is the most common method for commercial production of polymer fibers and is often the most economical. Not surprisingly, it is used in spinning most commodity plastics. In melt spinning, molten plastic is pumped under high pressure through the spinneret. In solution spinning methods (e.g., wet spinning or dry spinning), a viscous solution of polymer (sometimes called a spinning dope) is used rather than a melt. While the solution spinning methods tend to be more expensive than melt spinning methods, they often result in greater mechanical performance by carefully controlling the level of molecular entanglement, which can result in more highly drawn fibers. In dry spinning, the dope is forced through the spinneret and solvent is removed by evaporation, often in a hot atmosphere. In wet spinning, the material leaving the spinneret is submerged in a liquid where the solvent is either removed through diffusion or through precipitation by chemical reaction [25]. The fiber is then dried to remove remaining liquid. Regardless of the spinning method, high molecular alignment is induced by drawing the fiber immediately after the spinneret, by drawing the fiber farther down the spinning line or in a separate step (e.g., by reheating and stretching melt-spun fiber), or by some combination of the two. This high induced molecular alignment is key to high stiffness and strength. For example, Figure 3 shows the large effect of draw ratio on the tensile properties of polyvinyl alcohol. Sometimes aspects of the different spinning methods are combined. For example, a specialized wet spinning method that has been used with nanocellulose is dry-jet-wet spinning. In this approach, the spinning dope is extruded through an air gap between the spinneret and coagulation bath where threadline tension can induce molecular orientation.

Figure 2 The various approaches that have been used to prepare continuous fibers.
spinning these NC dispersions. Spinning can be seen as somewhat of a biomimetic, albeit less sophisticated, analogue to nature’s approach to organizing NC into fibrous architectures. Researchers also have noted that wet-spinning is a promising alternative technique for fast and efficient dehydration of CNF dispersions. Water removal is a common bottleneck when fabricating cellulose nanopapers from CNFs and is usually performed by ultrafiltration and drying processes that are very slow [29]. Rather than CNCs, CNFs have exclusively been used to spin 100% NC dispersions because of the high aspect ratio and fibril entanglement/interaction that is necessary. Most CNFs investigated have been mechanically prepared after a TEMPO-mediated oxidative pretreatment (TEMPO CNFs).

The CNF dispersions can be spun into a coagulation bath containing a solvent such as acetone, ethanol, isopropanol, or THF (i.e., wet spun), which results in rapid skin formation and water removal by solvent exchange [2]. Iwamoto et al. [24] first reported spinning of NC dispersions with the goals of controlling NC alignment and fabricating a new type of cellulose fiber. The researchers wet spun TEMPO CNFs prepared from wood pulp at rates between 0.1 to 100 m/min into acetone, followed by drying at 105 °C under weak tension. Increased CNF alignment and an overall increase in modulus and strength were found with increased spinning rate. Interestingly, very different results were found when spinning CNCs with higher aspect ratio prepared from the mantle of a tunicate, a marine invertebrate. The authors reported more circular cross section than with wood pulp-derived CNCs but also a higher solution viscosity as well as lower alignment, higher porosity, and a reduction in modulus and strength with spinning rate. At about the same time, Walther et al. [2] also wet spun 100% TEMPO CNFs and demonstrated how the fibers could be functionalized for hydrophobicity, conductivity, and magnetism. These early fibers showed evidence of some porosity [2] and some were only nominally circular in diameter or even had a distorted tubular shape at high spinning rates [24]. This suggests that improvements could be made by greater understanding and more careful control of water removal, NC alignment, densification, and bond formation processes.

Torres-Rendon et al. [29] focused on wet stretching to improve previously wet spun/dried fibers of TEMPO CNFs. Dry fibers were first allowed to relax in water and then were wet stretched to a maximum of 28% draw followed by immediate coagulation in acetone and eventual drying under restraint. The authors argued that the improved alignment and mechanical performance of the resulting wet-drawn fibers over the original fibers resulted from stretching in a more uniformly swollen state (i.e., after relaxation in a water

![Figure 3](image.png) Effect of alignment on the tensile properties of oriented polyvinyl alcohol films containing 5% CNFs. DR = draw ratio [47].

This approach can result in fibers with improved molecular alignment compared to conventional wet spinning [26].

In electrospinning, a large electric field is applied between the spinneret and a conductive collector, resulting in uniaxial elongation of a jet of polymer melt, emulsion or (more often) a solution or dispersion [27]. Since thus far electrospinning with NC has only involved solutions and dispersions (not melts), its use with NC has really been as a specialized version of dry spinning. Due to rapid solvent evaporation and substantial stretching and whipping processes, the jet cross section can be reduced by up to six orders of magnitude during jet flight, resulting in very fine fibers, often of nanoscale diameter [27]. Processing variables (e.g., voltage and distance between emitter and collector, humidity) and spinning solution properties (e.g., conductivity, viscosity, surface tension) can have large effects on fiber and mat characteristics [28]. One of the main disadvantages of electrospinning is its low spinning rate, which negatively affects economics. Consequently, much of the recent interest has focused on increasing throughput and its use in high performance and specialty applications that might prove economical [27].

4 SPINNING OF 100% NC FIBERS

Preparation of NC results in aqueous dispersions. These dispersions, particularly those of CNFs, are somewhat analogous to the polymer solutions (spinning dopes) used to spin fibers. Rather than long polymer molecules dissolved in a solvent, CNFs are dispersed in water. Therefore, it is perhaps not surprising that some research to date has centered on directly

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bath). This is in contrast to stretching in a coagulation bath, where water content in the fiber changes over time and across the fiber diameter. The TEMPO CNF fibers had superior performance compared to chitin nanofibrils, which were also investigated.

Hooshmand et al. [30] were able to prepare fibers by dry spinning of aqueous dispersions at rates ranging from 72–216 mm/s and containing 8–12% CNFs, concentrations considerably higher than those previously used. The CNFs were prepared by ultrafine grinding and then spun in air, rather than a coagulation bath, thereby eliminating the need for a solvent. Semi-dried fibers were then air-dried while under restraint, resulting in oriented fibers of 100% CNFs. High spinning rate led to slightly improved CNF alignment and the CNF dispersions at the lowest concentration led to the highest density and best mechanical performance.

Håkansson et al. [31] used a very different approach to prepare continuous fibers from CNF. They investigated a combination of hydrodynamically induced fibril alignment (flow focusing) and a surface-charge-controlled gel transition to prepare continuous fibers. While not necessarily a spinning method, it is a potentially interesting method for preparing very fine, continuous fibers of 100% NC with diameters as low as 20 microns. As shown in Figure 4, two perpendicular opposing streams of a sodium chloride solution merge with a core stream of a CNF dispersion, canceling the electrostatic repulsion between the fibrils that originates from the carboxyl groups and forming a gel thread. The gel filament is then soaked in a water bath to remove the electrolytes and then in an acetone bath for fixing. The filament is finally dried under restraint. By controlling variables such as the flow rate of core and sheath solutions and electrolyte concentration, alignment and gelation rates were controlled.

Table 1 summarizes the properties of the continuous 100% CNF fibers prepared by the various methods. Similar information on regenerated celluloses from reference [9] is also provided for comparison, including a relatively recent experimental regenerated cellulose fiber (Bocell) that has very high performance. Given that cross sections of the CNF fibers were not necessarily circular and testing methodology and conditions may differ between the investigations, reported

| Reference | Spinning approach | Nominal diameter (microns) | Herm. order param. | Highest strength achieved (MPa) | Modulus of same (GPa) | Breaking strain (%) |
|-----------|-------------------|-----------------------------|--------------------|-------------------------------|----------------------|-------------------|
| CNF fibers: | | | | | | |
| [24] | Wet | 60 | NR | 332 | 19.1 | 3.1 |
| [2] | Wet | 300 | NR | 275 | 22.5 | 4 |
| [29] | Wet | 250–300 | 0.57 | 289 | 33.7 | 1.6 |
| [30] | Dry | 180 | NR | 198 | 11.2 | 3.6 |
| [31] | Flow focusing | 28 | 0.50 | 490 | 17.6 | 6.5 |
| Regen. cellulose fibers: | | | | | | |
| [9] | Bocell | 11.6 | 0.87 | 1170 | 46.6 | 6.1 |
| [9] | Lyocell A | 9.0 | 0.73 | 624 | 31.2 | 6.8 |
| [9] | Lyocell B | 10.5 | 0.72 | 621 | 30.3 | 7.5 |
| [9] | Lyocell C | 17.3 | 0.70 | 551 | 27.3 | 9.8 |
| [9] | Lyocell D | 26.5 | 0.64 | 472 | 22.4 | 13.7 |
| [9] | Viscose | 10.5 | 0.40 | 423 | 11.5 | 19.0 |

1Hermans order parameter.  
2NR: Not reported.  
3Fibers were further aligned by wet stretching after wet spinning.
properties should be considered approximate and caution should be exercised when making comparisons. Nevertheless, several useful observations may be made. The nominal diameter of the CNF fibers is generally much larger than those of the regenerated celluloses, suggesting less confinement and slower coagulation/gelation in the center of the fibers. This would allow more time for relaxation of any induced orientation. For several of the CNF fibers, alignment of crystalline cellulose within the fibers was determined by X-ray diffraction and Hermans order parameters were determined based on the equatorial (200) reflection [29, 31]. In general, order parameters vary from 0 to 1 as order moves from random to perfect alignment. Table 1 shows that the order parameters for the CNF fibers are below most of those of the regenerated celluloses listed. Rather than an order parameter, several of the researchers determined an orientation index as an alternative in quantifying alignment [24, 30]. Given that these were lower than those found by Torres-Rendon et al. [29], who determined both types of parameters, it does not appear that their fibers were as aligned. Both measures of alignment suggest that there is plenty of room for improvement. The maximum alignment and density that can be practically achieved with 100% CNF fibers and the method to do so are still open questions. Given the lack of alignment, it is not surprising that the moduli and strengths of the CNFs also are generally below those of the regenerated celluloses. However, the modulus of the fibers prepared by Torres-Rendon et al. are higher than those of the regenerated cellulose fibers with comparable alignment, though their strength is lower. Also, the tensile properties of the fibers prepared by flow focusing compare favorably with the regenerated cellulose fibers. While such conclusions need to be verified by direct comparisons using consistent test methodology, the results are intriguing given the early stage of development. Improvements in fiber quality are being actively pursued and it is apparent that such improvements are necessary for continuous CNF fibers to have competitive performance with regenerated cellulose fiber.

5 SPINNING OF NC WITH POLYMERS

To overcome the challenges of spinning 100% NC dispersions (e.g., low gel strength, limited entanglement), some researchers have introduced polymers into NC dispersions or have added NC in small amounts as an additive in spun polymer fibers. These approaches seek to merge NC technology with the significant history and technological development of polymer spinning.

5.1 Melt Spinning

Melt spinning is of considerable interest because of its efficiency, favorable economics, and its wide use for large-volume commodity polymers. However, while conceptually attractive, doing so is challenging and relatively few researchers have used it to spin fibers containing nanocellulose. CNCs at a low level of addition have been exclusively used as they are easier to disperse and have less effect on melt viscosity and melt elasticity. Melt processing of the composites without thermally degrading the CNCs can be difficult due to the low thermal decomposition temperatures of CNCs and the high melting point of most plastics. Drying and dispersing CNCs can be problematic since low-melting-point thermoplastics (e.g., polypropylene, polyethylene) tend to be hydrophobic.

In an attempt to overcome these challenges, John et al. [32] used a solvent blending approach to prepare masterbatches of poly(lactic acid) (PLA) and CNCs. The masterbatch was then diluted with more PLA during extrusion compounding. Multifilament yarns containing up to 3% CNCs were then spun with the resulting compound. Adding CNCs showed only marginal improvements in fiber moduli, no improvement in strength, and a reduction in strain at break. The lack of mechanical property improvement was attributed to poor CNC dispersion and poor adhesion between the CNCs and PLA. Hooshmand et al. [33] compared several techniques for dispersing CNCs in cellulose acetate butyrate (CAB) and found that a sol-gel approach worked best. Subsequent work showed improved modulus and strength in “as-spun” fibers when CNCs were added [34]. While strengths were improved when an additional solid-state process was used to draw the fibers, those without CNC improved more and, consequently, little difference in strength was observed in the final fibers. However, modulus was improved by 32% with 10% addition of CNCs.

5.2 Solution Spinning

While some work has been performed on melt spinning NC-polymer blends, most investigations have centered on solution spinning methods. Solution spinning can avoid challenges such as the low thermal stability of NC and difficulties in dispersing dry NC. Additionally, techniques such as electrospinning can be used to prepare fibers of nanoscale diameter, and fiber mats with beneficial characteristics such as high surface area and a fine, porous structure. Such nanofibers are of great interest and can potentially enable nanocellulose use in new application areas such as filtration, catalysis, and tissue scaffolding [23].
However, spinning with solutions has its own challenges. For example, NC affects spinning dope characteristics, the extent of which depends strongly on NC type. For example, Figure 5 shows the effects of addition of CNCs and CNFs on the viscosity of aqueous polyethylene oxide solutions [35]. The effect of CNFs is especially large due to its entangled network structure, which leads to high viscosity and formation of gels even at low concentrations. As a result, less CNFs are usually added to spinning dopes and more liquid needs to be removed than if CNCs are used.

The two major methods of solution spinning are wet spinning and dry spinning and both have been investigated for preparing continuous fibers from NC. The relevant literature is reviewed below. Despite essentially being a specialized version of dry spinning, electrospinning is reviewed separately because of the amount of activity in the area and its very different nature and areas of application.

### 5.2.1 Wet Spinning

Nanocellulose has been used as a biobased reinforcement for improving wet spun fibers. For example, Endo et al. [36] added CNFs to improve the performance of dry-jet-wet spun polyvinyl alcohol (PVOH) fibers and broaden their use. The addition of CNF was limited to about 1% by weight because higher concentrations led to gelation and poor spinning ability. Dried fibers were drawn in hot air to a maximum total draw ratio of 20. The authors found that the CNFs improved the molecular chain alignment of the amorphous portion of the PVOH polymer but made little difference in the alignment of the crystal fraction. At high draw ratios, the increase in amorphous chain alignment when CNFs were added resulted in higher tensile modulus but little change in strength.

Peng et al. [37] were able to spin fibers at higher CNF concentrations using a similar CNF type but with a lower aspect ratio. The authors found not only an effect on polymer crystal orientation but also found matrix reinforcement when CNFs were added. This was evident by an increase in strength as well as the presence of fiber-matrix stress transfer as determined by Raman spectroscopy. Since X-ray diffraction (XRD) was used to measure polymer orientation, it was the orientation of the crystal fraction that was investigated and found to change. This was different from the finding of Endo et al. that only the amorphous fraction was affected by CNF addition [36]. These differing results may be due to the already very high PVOH crystal orientation in the neat PVOH fibers in the work of Endo et al. or to differences in fiber processing variables (e.g., wet draw ratios, hot air drawing temperatures). Peng et al. found an optimal level of about 3% CNFs, which resulted from the combined effects of alignment and CNF reinforcement (see Figure 6) [37]. Adding small amounts of CNFs increased alignment but as the CNF content was increased over 2%, CNF network formation began to inhibit alignment, eventually offsetting any additional gains in CNF reinforcement. Similar trends were found in other work on oriented films of the same material [38].

Uddin et al. [39] found that adding CNCs also increased orientation of the crystal fraction of PVOH as well as improved the modulus and the strength of the fibers. An XRD technique showed efficient stress transfer at modest CNC content, above which the efficiency was diminished, possibly due to CNC agglomeration. However, reduction in PVOH and CNC alignment was also found at high CNC levels. The optimal CNC concentration was determined to be around 5% by weight. Figure 7 shows a comparison of the mechanical properties of these NC-PVOH fibers.

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**Figure 5** Viscosity (η) vs shear rate (γ) of dispersions of PEO with (a) CNCs and (b) CNFs. Reprinted with permission from [35]; Copyright 2014 American Chemical Society.
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Figure 6 Comparisons of CNF weight ratio and crystal orientation effects on ultimate fiber strength.

Figure 7 Comparison of NC-PVOH fibers from reference [39] with unoriented [40–46] and oriented [38, 47] films of NC-PVOH from elsewhere in the literature.

with unoriented and oriented films of NC-PVOH from elsewhere in the literature [38, 40–47]. The large effect of increased alignment can clearly be seen. Also, the CNC fiber contents of the NC-PVOH fibers are included to show its relative effect, which is a combination of reinforcement, alignment, and possibly effects on crystallization as well.

In an intriguing approach, Liu and Yao [48] investigated the spinning of an all-cellulose composite fiber. They used a temperature-sensitive solvent system to prepare a wet-spun regenerated cellulose fiber containing up to 12% CNCs. By controlling solvent temperature they sought to avoid dissolution of the CNCs when they were added to a previously prepared solution of dissolved cellulose. An optimal CNC content of 9% resulted in large improvements in modulus and strength while maintaining a high breaking strain. However, since the mechanical performance of the unreinforced fiber was quite low (likely due to the low draw of 20%), even with these large improvements, the modulus of the composite fiber reached only slightly more than 4 GPa and was quite low compared to other regenerated cellulose fibers (cf. Table 1). However, after a nearly 230% increase, strength was comparable [5]. Further optimization (e.g., greater molecular alignment) may further improve performance.

5.2.2 Dry Spinning

Dry spinning of NC-polymer composites is also possible and has the advantage of eliminating the need for a coagulation bath. Chen et al. [49] investigated dry-spun cellulose acetate fibers with up to nearly 50% CNCs added. Fiber diameter generally increased with CNC content as did CNC alignment, which plateaued at a maximum order parameter of about 0.7 as determined by X-ray diffraction. Maximum improvement of tensile properties occurred at 34% CNC by weight, where strength and elastic modulus were increased by 137 and 637%, respectively. The authors suggested that above the critical 34% CNC content, further increases were prevented by defects resulting from CNC agglomeration, porosity, or uneven diameter and cross-sectional shape.

5.2.3 Electrospinning

Aside from being a conceptually simple and versatile technique, electrospinning offers several other potential advantages from a fiber preparation standpoint with regard to NC [50]. The large electrostatic fields and the shear forces in the liquid jet during electrospinning help induce alignment of both polymer chains and NC. Also, the extreme confinement because of the very small fiber diameter contribute to alignment [51]. The solvent removal is very rapid because of the very fine fiber diameter of the jet. This has the potential to rapidly lock in the high polymer and NC alignment and avoid the longer drying times that can result in relaxation in the center of larger diameter fibers spun by other methods [29].

Fibrous polymer mats containing up to 50% NC have been electrospun, although much lower concentrations are more common. CNCs have almost exclusively been used as the NC component due, in part, to the fact that the large viscosity increases with CNF addition make electrospinning more difficult and tend to result in larger diameter fibers. A variety of polymers have been investigated as matrices. For example, CNCs have been added to clear polymers such as polystyrene [28] and poly(methyl methacrylate) [51] to try and improve performance in applications where transparency is important. Use of biobased polymers, such as poly(lactic acid) [52] and cellulose acetate [53–55], results in 100% biobased composites. Others
have investigated adding NC to biocompatible polymers (e.g., poly(ε-caprolactone) [56], poly(acrylic acid) [57], poly(ethylene oxide) [58, 59], poly(vinyl alcohol) [60–66]) to positively impact spinning and performance of electrospun mats for biomedical applications (e.g., tissue engineering). CNCs have also been added to poly(vinylidenefluoride-co-hexafluoropropylene) [67] as a reinforcement and to reduce the pore size of pressed electrospun mats for membrane distillation. Blends of polymers (poly(vinyl alcohol)/lignin blends [68]) have also been investigated. Additionally, all cellulose composites have been electrospun by blending CNCs with cellulose acetate and then stripping the acetyl groups from the spun mat by alkaline hydrolysis [54]. Others have shown how stable CNC-inorganic particle dispersions could be electrospun with polyvinyl alcohol into magnetically active mats that could potentially be used in separation applications [66].

Where necessary, techniques involving solvent exchange [51], chemical grafting [56], and surfactants [28] have been employed to adequately disperse NC into polymer and improve the bonding between them. The type of approach depends largely on the matrix material selected and desired application and outcome. The dispersion of NC in the polymer is often challenging. In fact, several have noted that, even when compatible, water-soluble polymers have been used, NC dispersion is not necessarily complete [57, 58].

Adding NC to polymers has a variety of effects on the spinning of electrospun mats. It can improve the conductivity of the electrospinning solution (e.g., due to the negative charges on sulfate groups of unmodified CNCs [51]), which can reduce fiber diameter [65]. However, viscosity can also increase with NC addition, especially at high loadings, which can increase fiber diameter. As a result, sometimes it is necessary to dilute the spinning solution to offset these increases and to stay within a reasonable processing window, especially when investigating a wide range of CNC content [51]. These types of trade-offs, along with the variety of polymers, differing solution formulations (e.g., CNC concentrations, CNC modifications), and spinning approaches and conditions, make further broad generalizations on the effects of NC addition on electrospinning difficult. Even relatively minor changes in the chemistry of polymer matrices can significantly affect electrospinning. For example, Peresin et al. [65] compared electrospun cellulose nanocomposites made with a highly hydrolyzed (2% nominal residual acetate groups) and partially hydrolyzed (12% nominal residual acetate groups) polyvinyl alcohol. The degree of hydrolysis had large effects on solution properties (e.g., surface tension, viscosity, and conductivity) and the two polymers were affected differently by CNC addition. For example, adding CNCs to the highly hydrolyzed polyvinyl alcohol reduced fiber diameter, but had no clear effect when partially hydrolyzed polyvinyl alcohol was used.

Much of the research has centered on the effects of CNC on the improvement of mechanical properties. These effects are usually measured by testing the electrospun mats rather than the fibers themselves, since the mat properties are usually of most interest in the final application and since it is far easier to do so. Consequently, effects are due to a combination of changes in material behavior (e.g., polymer reinforcement, nucleation or inhibition of matrix crystallization) as well as mat structure (e.g., fiber orientation, porosity) and interfiber bonding. One exception, however, is the work by Dong et al. [51] who measured the fiber moduli of individual electrospun poly(methyl methacrylate) (PMMA) fibers with various quantities of CNCs by nanoindentation techniques. The authors found modest increases in storage moduli with addition of the first 17% of the CNCs.

However, others have shown large effects on mechanical properties of electrospun mats with CNC addition, particularly in biocompatible and/or water-soluble polymer matrices. This may prove useful for biomedical applications where improvements in matrix properties are often needed and the economic feasibility of electrospun mats is considered more possible. Lee and Deng [61] showed that adding 15% CNCs to a highly hydrolyzed polyvinyl alcohol doubled the tensile modulus and increased the strength by 86% in random electrospun mats. Peresin et al. [65] showed a 4-fold increase in storage modulus at 125 °C (above the glass transition temperature) when 15% CNCs were added to a similar polymer but a much smaller effect was seen at room temperature. Lu and Hsieh [57] added CNCs to poly(acrylic acid), a matrix with abundant carboxylic acids along the polymer chain that can hydrogen bond with the CNC surfaces and that can form ester linkages with CNC when heated. They found that Young’s modulus and tensile strength were improved up to 35-fold and 16-fold, respectively, prior to heat treatment when 20% CNCs were added. Heat crosslinking more than doubled the increases in mechanical performance. Herrera et al. [53] showed that adding only 1% CNCs to cellulose acetate resulted in a 10-fold increase in storage modulus of the electrospun mats made from it. The authors suggested that the reductions that they found in storage modulus with further addition of CNCs (up to 5%) might be due to CNC agglomeration.

A variety of approaches have been explored to facilitate alignment of electrospun nanofibers to produce oriented fiber mats with improved directional properties [50]. For example, Dong et al. [51] spun oriented mats of PMMA with up to 41% CNCs using a rotating
drum as a collector. Lee and Deng [61] used a similar approach for CNC composites with a PVOH matrix. Herrera et al. [53] used two metal sheets with an insulating gap between them to align their cellulose acetate composite fibers.

In addition to using the mats themselves, it is possible to infuse such mats with thermosetting resins. The resulting composites are somewhat of a fine diameter analogue to oriented thermoset laminates reinforced with glass or carbon fiber. For example, inspired by recent carbon nanotube research by Lionetto et al. [69], we recently investigated a two-step procedure for preparing aligned, NC-reinforced thermosets. The two-step approach is based on: 1) spinning of aligned, electrospun fibers of polymer and NC, and 2) resin impregnation of the fibers by a thermoset matrix in which the polymer is readily soluble. Figure 8 shows an image of an aligned electrospun mat of NC and polymer. Figure 9 shows the differing optical behavior with orientation when strips of the final composite are placed between cross polarizers with printed paper underneath. The dissolution of the polymer component in the electrospun mat and the retention of CNC alignment in the final composite have been confirmed by XRD. Determination of the effect of CNC orientation on the mechanical performance of the composites is ongoing.

6 FUTURE OUTLOOK

Overall, the vision for use of NC in continuous fibers is still very much in an embryonic stage. The first attempts at preparing continuous fibers from 100% NC were only 5 years ago. However, initial work is intriguing both in terms of the simplicity of the methods of fabrication as well as the variety of functionalities possible due to the ease and abundant knowledge of cellulose chemistry. Also, the tensile properties of some of the fibers that have been prepared compare favorably with those of regenerated cellulose fibers at comparable alignment. However, it will ultimately be necessary to determine how best to maximize this alignment to improve mechanical performance (e.g., through smaller fiber diameter and better confinement of the NC). Also, it will be necessary to optimize CNF bonding and reduce voids and the performance of the fibers needs to be benchmarked against other continuous cellulose fibers. Improvement of fiber quality may require more sophisticated, NC-specific approaches that go beyond traditional polymer spinning approaches. For instance, such work has already begun with new, flow-focusing methods that are currently being explored [31]. Other nanomaterials have evolved similarly. For example, early solution spinning technologies for preparing continuous carbon nanotubes have been displaced by more effective solid-state methods such as spinning from vertically grown arrays (Figure 10), processes that are unique to carbon nanotubes [70]. Identifying and developing efficient new methods for preparing continuous fibers from NC dispersions will be a major research challenge.

Also, NC has been used in combination with polymers, which helps overcome issues such as the limited...
entanglement and the low gel strength of NC dispersions. A variety of spinning approaches have been investigated, including melt spinning and various solution spinning methods.

Melt spinning with nanocellulose-polymer blends is particularly challenging since low melt temperature thermoplastics are required due to the low thermal stability of NC. Unfortunately, these plastics tend to be highly nonpolar and commodity-based, which makes NC dispersion and compatibility difficult and often not cost effective. Solution spinning techniques can overcome some of these challenges by using the NC in solution. Wet spinning, dry spinning, and electrospinning have been explored and NC has been found to reinforce matrices and favorably affect alignment under optimal conditions. Electrospinning has been by far the most commonly explored method for spinning of polymer-NC solutions. When added to polymer spinning dopes CNCs can have a large influence on the quality and performance of electrospun mats. The very fine fibers, high surface areas, and fine porosity of these electrospun mats lend themselves to applications in the catalysis, filtration, and biomedical fields, or as sensor or actuators, for example. These applications represent a major departure from those typically found for cellulosic fibers but perhaps most effectively use attributes of NC such as very fine diameter, transparency, high mechanical performance, ease of functionalization, and its apparent biocompatibility. However, there is still much work to be done with respect to research and development needs, the specifics of which depend on the area of application. Additionally, it will be necessary to address overarching issues of NC use such as continued efforts related to environmental health and safety, growth of commercial infrastructure, and characterization and standards development, for example [12].

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