Spin of Cellulose Nanofibrils into Filaments: A Review

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1. INTRODUCTION
The transition toward the future bioeconomy poses increasing demands on renewable materials. Preferably, these materials should originate from bioresources with minimum dependence on high-grade arable land, water and pesticides. Lignocellulose could respond to this demand, owing to its abundance combined with the inherent strength of cellulose assemblies. However, to become economically feasible, lignocellulose-based materials need to reach or surpass the mechanical performance and processability of their fossil-based counterparts; added functionalities can also provide a competitive edge. Spinning of cellulose nanofibrils (CNF) has been suggested as a suitable method to produce cellulose filament material and to harness optimally their inherent strength. Furthermore, spinning can be combined with functionalization routes that may enable new properties in CNF and their filaments.

This review presents a summary of the recent developments in CNF spinning. First, we introduce the essential qualities of CNF and their role in determining the mechanical properties of wood fibers and man-made cellullosic materials. Second, an overview is presented of the conventional methods for spinning polymeric materials. Following, we report on the spinning methods that have been used so far with CNF. In particular, we analyze the impact of CNF quality, spinning parameters and optional additives on filament properties. Finally, key applications for CNF filaments are introduced.

2. CELLULOSE NANOFIBRILS
The properties of CNF have been extensively reviewed elsewhere. In brief, cellulose nano- and microfibrils are strong, lightweight, chemically versatile and biodegradable. Furthermore, they can be produced from abundant lignocellulosic resources. However, large scale processing remains challenging if controlled structure and characteristics of the CNF-derived material are demanded. The high hydrophilicity or water affinity of CNF together with the absence of melting transition of cellulose further limits adoption of traditional polymer processing techniques, including melt-spinning.

In nature, the strength properties of plant tissues correlate with the helix or microfibril angles characteristic of their fiber cell walls. This refers to the angle (φ in Figure 1a) between the fiber axis and that of the individual microfibrils that orient as layered assemblies. In locations requiring higher stiffness, plant fibers display lower microfibril angles. As an illustration, Figure 1b indicates the decline of wood fiber stiffness with increasing microfibril angle. This is explained by the anisotropy of the cellulose crystallites that constitute the elementary fibrils. Indeed, the Young’s modulus of a cellulose crystal is estimated to be up to 160 GPa in the longitudinal direction but only 8–57 GPa in the transverse direction. Following the principle of orientation control in plants, the performance of man-made cellullosic materials is expected to depend on the cellulose crystallite alignment. For example, nanopaper stiffness has been increased by 223–405% and tensile strength by 37–162% by unidimensional stretching by 30–60% of the original dimension. This observation is likely related to the higher degree of alignment of CNF. Such an effect, however, is difficult to implement because stretching has to be applied slowly in order to avoid breaking of the nanopaper. A potentially faster effect occurs during spinning of CNF, which aligns the nanofibrils by hydrodynamic
shear inside a spinneret. This alignment can be further enhanced by drawing. As such, the following section introduces the existing spinning techniques, including those that can be implemented for CNF processing.

3. CONVENTIONAL SPINNING TECHNIQUES

Filaments, considered here as continuous fibers of indefinite length, can be formed by various spinning techniques. Synthetic and cellulosic filaments are predominantly produced through melt- or solvent-spinning. Solvent spinning techniques can be further classified into dry-spinning, wet-spinning and dry-jet wet-spinning. In any kind of spinning, the polymer precursor is first molten or dissolved to produce a spinning dope, which is then extruded through a forming element (i.e., spinneret). Solidification of the dope is achieved through cooling, evaporation of the solvent or precipitation in an antisolvent. These techniques are referred to as melt-, dry- and wet-spinning, respectively. Another widely reported method is electrospinning, which, in its simplest form, draws a polymer solution under the influence of an electric field.

The optimal spinning technique for a particular polymer is selected based on the polymer melting point, melt stability or solubility in organic and/or inorganic solvents. The filament-forming ability of a particular polymer dope is commonly referred to as spinnability. To assess the spinnability of a dope, a number of factors needs to be considered, such as flow behavior, rheology, melt flow index (for melt-spun polymers), crystallization, phase transition, solvent/solvent system behavior and structure development.

Synthetic filaments are typically melt-spun from polymers such as polyester, polyethylene, polyamide (nylon) and polypropylene. Melt-spinning has become prevalent because it is based on a simple extrusion process where no addition or removal of solvent is required. Obviously, melt-spinning requires melt processability, which is more typical for polymers derived from petroleum, such as polyolefins.

In contrast, lignocellulosic biomass represents a more sustainable alternative, for example, by using streams from wood and nonwood pulping processes for dope preparation and regeneration. This type of man-made cellulose filaments are expected to become increasingly relevant because the market for cellulosic textiles is expected to surpass the production capacity of cotton. We note that cellulose derivatives, such as cellulose esters, can also be spun into filaments after dissolution, mostly using dry-spinning techniques. A recent report describes even the spinning of microscopic wood fibers without any dissolution.

Today, most man-made cellulosics are produced by the viscose process, involving xanthogenation, dissolution in caustic soda, adjustment to a relatively low dope viscosity, extrusion and regeneration in sulfuric acid. As an alternative that bypasses the cellulose derivatization step, the Lyocell process dissolves cellulose directly in an organic solvent such as N-methylmorpholine N-oxide (NMMO). Lyocell filaments are produced by dry-jet wet-spinning through an air gap to achieve drawing before regeneration. Consequently, compared to viscose filaments, lyocell filaments often show a superior mechanical performance. Other solvents, such as ionic liquids, have also been investigated as a means to reduce chemical hazards and enable novel functionalizations of the filament.

Spinning of CNF offers the opportunity to produce a renewable filament without the need for cellulose dissolution and regeneration. Provided that the energy consumption is limited during CNF preparation, the absence of dissolution chemicals signifies a reduced environmental impact. Current results suggest that CNF-based filaments with competitive mechanical performance can be produced. Different approaches have been recently reviewed for wet-, dry-, melt- and electrospinning of CNF and CNF–polymer combinations.

The following sections analyze the findings so far regarding the effects of various spinning parameters on CNF filament properties. This analysis is limited to wet- and dry-spinning, which are the only techniques applied on CNF spinning from hydrogels without added polymers. When possible, the results obtained for CNF are compared to existing knowledge for conventionally spun polymers. Especially, regenerated cellulose filaments are considered here as reference systems because of their chemical similarity, even though critical comparison needs also to account for characteristic cellulose size, crystallinity as well as preparation issues.

4. CNF HYDROGEL PARAMETERS

A number of parameters related to the CNF dope has been realized to affect the performance of the CNF-based filaments. This section discusses first the CNF aspect ratio, which is influenced by the CNF source and pretreatment. Subsequently, the effect of CNF solids content is introduced and the possibilities discussed to associate the aspect ratio and solids content by studying CNF crowding factor and rheology.

4.1. CNF Source. The aspect ratio or slenderness (i.e., fibril length per fibril width diameter) of the fibrils used for spinning basically depends on the source material (plant species, for example) as well as the process used for fiber isolation. Furthermore, CNF qualities can be tailored by pre- and post-

Figure 1. Schematic illustration of the microfibril angle ϕ in a wood cell (a). Tensile stiffness of wood fibers as a function of microfibril angle (b). Data are collected from several studies examining samples from different wood species and tissues. The respective symbols refer to different preparation techniques.
treatments associated with the mechanical fibrillation, such as enzymatic or chemical pretreatment (for instance, to increase the electrostatic charge). These parameters affect both the cost of the CNF and the ensuing filament properties.

Films prepared from CNF derived from different wood species differ in mechanical properties: CNF obtained from long (softwood or gymnosperms) tracheids produce films with slightly higher tensile strengths, lower Young’s moduli and much higher breaking elongations than those originated from short fibers (from hardwood or deciduous species). This implies that the CNF origin or source, in turn, influences CNF spinning and filament properties. In fact, CNF isolated from both softwoods and hardwoods have been used to produce filaments by spinning but, unfortunately, have not been compared under same processing conditions. Moreover, the method used to isolate the fibers that are then converted into CNF, is most likely relevant, even though such a topic has not been addressed either.

As an alternative to virgin wood fibers, CNF can be liberated from cellulose-rich bioresources such as soybean pods, needle leaf, rice straw, sugar beet, pineapple leaves and banana rachis. CNF from banana rachis has been dry-spun into filaments with remarkable mechanical properties (Young’s modulus up to 12.6 GPa and tensile strength up to 222 MPa). These properties are comparable to those of cotton fibers (Young’s modulus 5.5–12.6 GPa and tensile strength 287–597 MPa). This implies that diverse raw materials, even residual biomass stream or recycled materials, can be potentially used for CNF spinning. However, it is expected that the mechanical properties of CNF derived from recycled fibers are of relatively lower quality given the reduced aspect ratio from the shortening of the fibrils during each processing step in their lifecycle.

An interesting alternative as a filament source is CNF produced from microorganisms, algae and the sea animal tunicate. Tunicates can synthesize cellulose microfibers with a width of 20 nm. After oxidation with 2,2,6,6-tetramethylperidinyl-1-oxyl (TEMPO), these microfibers can be liberated, reaching aspect ratios of more than 500. This is much higher than that for CNF produced from wood, which have aspect ratios <200 and thus present lower hydrogel viscosity. Indeed, filaments wet-spun from dopes of these two CNF hydrogels have very different structure and mechanical properties. At low flow velocities (0.1–1 m/min), tunicate-based filaments have higher Young’s moduli and tensile strengths than those of wood-based filaments. Conversely, at a high flow velocity (10 m/min), this trend is reversed. Nevertheless, filaments produced from tunicate CNF display a more regular, circular cross section and grooved surfaces, compared with those spun similarly from wood CNF, which may form hollow structures with irregular cross section and smooth surfaces (Figure 2). Interestingly, tunicate-based filaments also show higher toughness, as explained by their high aspect ratio. Apparently, the extension of the long, entangled fibrils dissipates energy efficiently. Furthermore, the high degree of crystallinity of tunicate CNF can also positively contribute to the mechanical performance.

Figure 2. Scanning electron micrographs of surfaces (a, c) and cross sections (b, d) of filaments spun from wood CNF (a, b) and tunicate CNF (c, d) at a flow velocity of 10 m/min.

4.2. CNF Pretreatment. In addition to the raw material selection, the CNF morphology and thus CNF filament properties are most likely influenced by pretreatment. Three different pretreatment options have been reported for CNF intended for spinning: no pretreatment, TEMPO-oxidation and carboxymethylation (see Table 1). However, systematic investigation of the effect of pretreatment has been limited to one study comparing the properties of filaments prepared from unmodified and TEMPO-oxidized CNF. In this study, TEMPO-oxidation was found to enhance fibril orientation during wet-spinning because of the elevated fibril aspect ratio and surface charge, which cause both entanglement and osmotic repulsion between the fibrils. Possibly, this also explains why the highest Young’s modulus for undrawn filaments (23.6 GPa, see Table 1) has been achieved by TEMPO oxidized CNF. However, it should be noted that the values obtained from distinct references cannot be reliably compared due to the differences in the spinning and tensile testing conditions.

The supposed positive effect of TEMPO-oxidation may be related to the observation that the spinning of dissolved cellulose is facilitated by increased degree of polymerization (DP), which somewhat corresponds to the aspect ratio, at least at the molecular level. Cellulose solution with a high DP can be drawn more easily than that from a low-DP solution and thus spun into a stronger and stiffer regenerated filament. Presumably, the tension applied on a CNF filament during drying has a stronger aligning effect on TEMPO-oxidized CNF, which have higher aspect ratios.

As a drawback of TEMPO-oxidized CNF filaments, their higher specific surface area and surface charge make them more sensitive to water. Obviously, the strength of CNF filaments deteriorates in wet conditions; however, on a relative basis, unmodified CNF filaments remain more than three times stronger in wet conditions compared to those produced from TEMPO-oxidized CNF, as shown by both Table 1 and ref 24. If the high surface area and charge are employed to maximize mechanical performance, the simultaneously increased sensitivity to water needs to be addressed by other methods, such as cross-linking or hydrophobization (section 6).

Carboxymethylation typically leads to surface charge levels between those of unmodified and TEMPO-oxidized fibrils. This pretreatment could be expected, therefore, to produce fibrils that could be spun into filaments with stiffnesses higher than...
unmodified but lower than TEMPO-oxidized. However, confirming this would require additional work comparing CNF with different surface charges spun and tested in exactly similar conditions. For instance, variances in the spinning conditions lead to diversity in cross-sectional morphologies, which again influence the results of tensile testing. Also, the measured mechanical behavior depends on the deformation rate during testing, temperature and relative humidity, which have to be kept constant in order to produce comparable results.

4.3. Solid Volume Fraction in CNF Hydrogels. For unmodified CNF, filament mechanical performance has been shown to increase with decreasing solids content in the CNF dope, until approaching the limit of spinability (apparent viscosity on the order of 1 Pa s at the shear rate applied in the spinneret). For dry-spun CNF filaments, dilution of the CNF dope clearly improved mechanical performance, even though it had no significant effect on filament orientation. Similarly, in the case of wet-spun CNF filaments, dilution was found to increase orientation only slightly and inconsistently. On the other hand, it increased stiffness by up to 80% and tensile strength by up to 140%. Apparently, a higher free volume in the CNF hydrogel allows for slightly better fibril alignment during spinning, though the ensuing filament performance is more strongly influenced by other factors such as discontinuities and defects that form more easily in a concentrated hydrogel. The negative effects of hydrogel concentration, to an extreme, compromise spinnability.

Likewise, at extremely low solids contents, CNF ceases to form a continuous filament or allow for high drawing. Moreover, dry-spinning of diluted CNF dispersions produces deformation (flattening) of the forming filament after contact with reeling surfaces, as seen in Figure 3. The lowest solids contents used so far to successfully wet- and dry-spin unmodified CNF are 1.47% and 3%, respectively. TEMPO-oxidized CNF can be spun even at lower solids contents: minimum 1% and 0.82% for wet- and dry-spinning, respectively. This is possible because of the more effective fibril entanglement arising from a higher fibril aspect ratio. Changing the wet-spinning system from a syringe needle to a flow-focusing channel allows further decreasing the CNF solids to as low as 0.3%. For filaments obtained from regenerated cellulose, the effect of cellulose precursor loading seems to be the opposite to what is described above for CNF: more concentrated cellulose solution leads to an improved crystallinity, orientation and strength of the obtained filament. The concentration-enhanced strengthening and stiffening in filaments have been explained by the better entanglement between the cellulose chains. This highlights the rheological differences between individual, dissolved cellulose chains and a colloidal suspension of fibrils. CNF display more long-range interactions, which can, assumedly, offset orientation and packing uniformity, particularly in concentrated suspensions.

Nevertheless, CNF and dissolved cellulose both benefit from increased freedom of individual fibrils or molecules. When cellulose filaments were regenerated from solutions in phosphoric acid with varying concentrations, the stronger phosphoric acid lead to a stronger filament than more diluted acid. This was explained by the increasing “dissolution power” with increasing phosphoric acid concentration. However, the strengthening of the filament with strengthening of the phosphoric acid occurs because of effects different from those of high crystallinity or orientation. This finding confirms that, for the development of filament strength, the quality and uniformity of the cellulose packing may be even more important than orientation.

4.4. CNF Crowding Factor and Rheology. The effects of CNF aspect ratio and solids content have been proposed to be summarized as the effect of osmotic pressure, which is governed by fibril surface charge and crowding effects. The fibrillar crowding can be quantified via a crowding factor N, defined originally for fibers in papermaking suspensions, according to eq 1.

\[ N = \frac{2}{3} C_v \left( \frac{L}{d} \right)^2 \]

where \( C_v \) is fibril volumetric concentration and \( L/d \) aspect ratio. The exact determination of the crowding factor is prevented by the fact that CNF aspect ratio is not usually reported in studies on CNF spinning. Nevertheless, aspect
ratios for CNF from unmodified wood, TEMPO-oxidized wood and TEMPO-oxidized tunicate can be roughly estimated to be 50,24 200 and 500,32 respectively. With these assumptions, it can be expected that CNF hydrogels in studies related to spinning (in the absence of drawing and other external effects) have been wet-spun under conditions of crowding factors ranging between 2224 and 1111.32

However, even though CNF is spinnable at a variety of crowding factors, no conclusion has been shown for the effect of crowding factor on filament properties. So far, crowding factor has only been demonstrated to have two alternative contributions to filament properties: stronger filaments can be spun either by decreasing the crowding factor by diluting unmodified wood CNF, or by increasing the crowding factor through enhancing the CNF aspect ratio via TEMPO-oxidation.24 Probably, unmodified CNF are prone to aggregate due to low interfibrillar electrostatic repulsion (high friction) and thus benefit from dilution. Furthermore, interfibrillar friction can be further decreased by increasing the surface charge through TEMPO-oxidation. Also, elevated fibril surface charge and crowding factor are associated with a high osmotic pressure, which can favor the alignment of TEMPO-oxidized fibrils through repulsive forces (occurring in conditions of frequent interfibrillar contact) as well as through forcing fibrils to pack more efficiently during coagulation and drying.24 However, confirming the connection between CNF crowding factor and filament properties would require comparable experiments on a variety of crowding factors, generated by varying both solids content and aspect ratio.

In addition to the well-grounded and also the more speculative correlations discussed so far for CNF hydrogel dope and filament properties, upscaling of the spinning process requires an easy and experimental way to predict the spinnability of a given dope. For example, viscosity of the dope at the shear rate applied in the spinneret would be simpler to measure than the aspect ratio and solids content. In the case of unmodified hardwood-based CNF, strong filaments have been associated with an apparent viscosity of ~2 Pa s (2% solids content, shear rate 200 s−1).24 This is slightly lower than the usual zero shear viscosity for a viscose dope (5–20 Pa s) and orders of magnitude lower than that for a Lyocell dope (5000–30000 Pa s).39 Similar screening of other types of CNF and spinning systems would be helpful to relate more universally the rheology of the dope with the spinnability and to be able to have some level of prediction through simple experiments.

5. CNF SPINNING PARAMETERS

In addition to the hydrogel properties, the CNF filament properties can be controlled via adjusting the spinning conditions. This section analyses the parameters related to the spinning process, including the shear rate and drawing followed by coagulation and drying.

5.1. Shear Rate. Shear forces in the spinneret induce CNF alignment. Thus, adjusting the shear rate in the spinneret can influence the ensuing filament structure. Calculating the exact shear rate and assuming it as constant is unrealistic due to the complex rheological behavior of CNF as well as the variety of the reported flow-generating equipment, including a syringe pump,12,22,32 an extruder,26 a capillary rheometer,30 and even a 3D printer.25 Nevertheless, because most of the spinning studies have used a single orifice spinneret with a circular cross section and constant diameter, the average shear rate ẏ can be estimated by eq 2.

\[ \dot{y} = \frac{\nu}{r} \]

(2)

where \( \nu \) is average flow velocity and \( r \) is spinneret radius. Figure 4 displays the mechanical properties achieved by wet-spun, wood-based CNF filaments aligned mainly by shear (i.e., with no drawing). In this figure, Young’s modulus, tensile strength and breaking elongation are plotted against the shear rate in the spinneret (eq 2). Data from ref 32, marked in Figure 4 by connected squares, include four shear rates that were systematically generated by varying the flow velocity.

As shown in Figure 4a, the Young’s modulus generally increases with shear rate. A similar trend is observed for the tensile strength (Figure 4b), though, at shear rates above 200
s⁻¹, the tensile strength appears to reach a plateau level at slightly above 300 MPa. This stiffening and strengthening of the filament with increasing shear rate has been explained by the tendency of shear forces in the spinneret to align fibrils along the filament axis, producing a more oriented structure.²² It should be noted, however, that tunicate CNF-based filaments with Young’s moduli and tensile strengths of the order of 20 GPa and 400 MPa, respectively, have been produced despite a low shear rate.²³ This may be related to the high aspect ratio of tunicate CNF, as explained in section 4.1. When the shear rate on wood CNF was increased above 300 s⁻¹ by increasing the flow velocity, the ensuing extreme shear caused the filaments to become hollow (Figure 2b).²² This was explained by “cylindrical coalescence” of the tangentially assembled wood CNF sheets forming the filament.³²

The increased orientation at high shear is expected to decrease the breaking elongation of the filaments. However, the available data do not conclusively support this expectation, according to Figure 4c. Apparently, the filament flexibility varies more heavily depending on the detailed conditions used in the respective studies. For example, nonuniform coagulation along the filament has been proposed as a reason for low breaking elongation.³²

The mechanical strengthening achieved with high shear has also been shown for dry-spun filaments produced by varying the flow velocity.³⁰ In this case, the maximum shear rate (576 s⁻¹) and best performance (tensile strength 222 MPa) were achieved with a flow velocity of 0.288 m/s through a spinneret with a diameter of 1 mm.³⁰ However, another report on dry-spinning, which used an extremely high shear rate (204 000 s⁻¹, velocity 11 m/s, diameter 0.108 mm), only attained a tensile strength of 145 MPa (in the absence of drawing).³⁰ This seems to point out to more complex relationships that exist between dope type and process conditions or also the possibility that an optimum spinning shear exists beyond which the mechanical performance begins to decline. For example, in the first case discussed above for dry-spinning, the spinneret length was 20 mm,³⁰ while, in the second case, the extremely high shear rate was generated in a short spinneret with a length of only 8 mm.²³ Thus, a very short residence time inside the spinneret may have been insufficient to induce CNF alignment.

CNF hydrogel flow in the spinneret can also be characterized by the Reynolds number Re:

\[
Re = \frac{\rho v d}{\mu}
\]

where \( \rho \) = hydrogel density, \( v \) = flow velocity, \( d \) = nozzle diameter and \( \mu \) = hydrogel viscosity at the applied shear rate. Because most studies do not report CNF viscosity, comparison based on Re is only limited. Nevertheless, the maximum Re can be estimated in a case with an exceptionally wide spinneret (diameter 2 mm) and fast flow velocity (126 mL/min or 2.7 m/s).²⁶ These conditions correspond to an approximate shear rate of 2675 s⁻¹ (eq 2). At this shear rate, the utilized TEMPO-oxidized CNF (solids content 1%)²⁵ can be expected to have a viscosity of at least 0.01 Pa s because the viscosity of unmodified CNF at a similar dilution remains at ~0.1 Pa s at 1000 s⁻¹.²⁴ This assumption yields a maximum Re = 535, which remains below the maximum Re for laminar flow in a cylindrical pipe (2300). Thus, all the spinning experiments reported so far feature laminar flow conditions. Interestingly, the study carried out with the highest Re also reported exceptionally poor mechanical properties before filament stretching (Young’s modulus 8.2 GPa, tensile strength 118 MPa).²³ This implies that approaching the turbulent flow regime may disturb filament formation (formation of eddies, etc.).

Design of the spinneret and flow conditions should also take into account the more complex CNF flow features, such as shear banding, wall slippage, plug flow behavior and flocking.⁴⁰ For example, instead of a needle-type of spinneret, a hyperbolically contracting spinneret could enhance the extensional flow and thus potentially align CNF even more effectively.³³ Furthermore, hydrodynamic spinnerets with fluids forming the spinneret walls can essentially eliminate the shear and achieve CNF orientation almost fully by extensional forces (section 5.2).²³ As flow models for CNF develop, spinneret design by simulation is expected to have a great impact on our knowledge for enhancing processing parameters and filaments properties.

Naturally, if the shear rate is increased by reducing the spinneret diameter, filament becomes thinner. Thin filaments are beneficial for several applications, such as composite materials, which benefit from a high aspect ratio of reinforcement fibers. However, if spinnerets with very small diameters are used, clogging is also more likely to occur because of the aggregates and flocs that form in CNF hydrogels and dispersions.⁴⁰ The thinnest spinneret reported for CNF spinning had a diameter of 108 μm.²⁶ Conventional spinnerets used in the spinning of polymer solutions or melts feature multiple orifices with diameters in similar size range, from 10 to 500 μm.¹⁴ The cross-sectional geometry of the orifices can be varied in order to alter the filament properties. Such aspects remain ready for testing with CNF hydrogels.

5.2. Filament Drawing.

The extent of drawing during spinning is quantified by the draw ratio, i.e., ratio between the filament take-up velocity and the flow velocity at the spinneret. Draw ratios >1 result in stretching that axially aligns polymer chains along the filament, which results in an oriented structure. Tensile strength and stiffness are typically improved with high draw ratios as a result of the enhanced alignment. Simultaneously, breaking elongation tends to decrease. Feasible draw ratios are determined by the rheological and coagulation behavior of the spinning dopes.

Due to a relatively low aspect ratio, CNF cannot be drawn during spinning as easily as dissolved polymers. Thus, an alternative approach is necessary for creating the extensional flow necessary for effective fibril alignment. Three possibilities have been reported: wet-stretching,²⁵ flow-focusing²¹ and dry-spinning with an oil layer on a collector capstan.²⁶ A wet-stretching setup is depicted in the inset of Figure 5a. This approach immerses a dry filament in water and uses the plasticity of the wet CNF filament to stretch it slowly. Wet-stretching improves the orientation parameter of the filaments up to 20% (from 0.48 to 0.57), leading to an improvement by more than 300% in filament Young’s modulus (from 8.2 to 33.7 GPa) and close to 150% in tensile strength (from 118 to 289 MPa). Stress-strain curves of filaments prepared with different extents of wet-stretching are presented in Figure 5a.

A flow-focusing system is illustrated in the inset of Figure 5b. At the intersection of three microfluidic channels, the core flow of the CNF dispersion (central vein) is subjected to sheath (shell) flows colliding with it from the sides. When the sheath flows have higher velocities than the core flow, they create an extensional flow in the core. The sheath flow is selected to induce gelification of the CNF dispersion, thus facilitating the locking of the aligned fibril structure already before coagulation.
The tensile strength and ductility (increasing area under stress–strain curve). This indicates that, although both systems enhance fibril alignment, flow-focusing contributes more effectively to the uniformity of the packing structure of CNF. This could explain how flow-focused filaments avoid the brittleness that wet-stretched filaments suffer from.

Both wet-stretching and flow-focusing suffer from an extremely low process speed. In contrast to wet-spinning, where the flow velocity can be even higher than 160 m/min,\textsuperscript{23} flow-focusing is limited to a spinning speed of 450 mm/min.\textsuperscript{21} Wet-stretching allows for maintaining the original spinning speed but adds an additional process step, proceeding at only 5% of deformation per minute.\textsuperscript{23} The limited process speeds can markedly raise the cost for effectively orienting CNF in filaments.

A faster setup for drawing CNF during dry-spinning is illustrated in the inset of Figure 5c. This approach capitalizes on an oil layer between the collecting capstan and the filament, which allows the filament to glide on the surface and thus balance the stretch it experiences through the drawing and dewatering. In this manner, filament tensile strength has been improved by up to 52% (from 145 to 220 MPa) compared to an undrawn filament, as confirmed by Figure 5c.\textsuperscript{26} Furthermore, a production speed of 66 m/min has been achieved.\textsuperscript{26} This is already on the level of a typical spinning rate in a single orifice in a viscose spinning line (20–150 m/min).\textsuperscript{42} Feasible production volumes can be achieved through multiple spinnerets. For example, a typical viscose spinning line comprises 150–400 individual spinnerets, each containing 1–500–14 000 orifices.\textsuperscript{42}

Wet-stretching, flow-focusing and lubricated dry-spinning have attained maximum draw ratios of 1.28, 1.15 and 1.7, respectively. These are close to the values typically applied in the viscose process (1–2.5)\textsuperscript{43} but they are lower than normally applied on more highly drawn man-made cellulosics (e.g., 8.4 for lyocell\textsuperscript{35} or 15 for Ioncell-F)\textsuperscript{34} or during melt-spinning of synthetic polymer filaments (e.g., up to 6 for polyester).\textsuperscript{13} In the case of regenerated cellulose filaments, drawability has been shown to correlate with the DP.\textsuperscript{44} For example, lyocell with a DP of 550 can be drawn more than viscose with a DP of 300, resulting in stronger and more crystalline filaments.\textsuperscript{44} CNF have aspect ratios of 25–500,\textsuperscript{7} depending on the precursor material and the preparation method used (section 4.1). Thus, attainable draw ratios can be expected at levels similar to those in the viscose process. Increasing the drawing to a similar extent than that of Lyocell or Ioncell-F would require an increase in the effective aspect ratio, such as using a multicomponent system, modifying or blending CNF with a high-DP polymer.

Even when CNF is drawn by wet-stretching, the filament orientation index reaches a plateau at slightly above 80%.\textsuperscript{23} This further highlights the possible need for modifying the CNF or blending it with additives to enable more effective orientation under extensional flow. Nevertheless, better alignment does not fully imply better mechanical performance because the filaments are also influenced by other factors such as frequency of defects and cellulose crystallinity. Thus, a moderate alignment may suffice to achieve strong filaments, provided the CNF are homogeneous, defect-free and highly crystalline.

5.3. Coagulation and Drying. Coagulation refers to the counter diffusion of solvents between the dope and the surrounding media in the coagulation bath.\textsuperscript{45} The removal of water from the CNF dispersion and the counter-diffusion of the coagulant result in hemisolid CNF filaments. The diffusion

Figure 5. Mechanical properties achieved with alternative drawing systems for CNF filaments: Wet-stretching with SR = draw ratio – 1 (a).\textsuperscript{21} Flow-focusing with D undrawn, A–C drawn with different salinity conditions in the bath and sheath flow (b).\textsuperscript{21} Lubricated dry-spinning with constant capstan rotation at 11 m/s, nozzle speed varied to create draw (c), reprinted with permission from ref 26. Copyright 2016 Springer Science+Business Media Dordrecht.
rates of water and the coagulant impact the filament surface morphology, internal structure and subsequent properties. A suitable coagulant for CNF needs to be miscible in water and have a moderate polarity and hydrogen bonding ability. During drying, the coagulant is removed from the filament by evaporation while the filament contracts heavily. The drying conditions may also influence the properties of the filament.

In the case of lyocell, cellulose chains align mainly during coagulation and drying. Similar effects can be expected to orient CNF, too. However, most of the existing reports have ignored coagulation and drying and focused instead on the orient CNF, too. However, most of the existing reports have been shown in the case of a lyocell process. This is challenging due to the weakness of the cellulosic filament in the bath as well as the length of the coagulation time.

The significant contributions of coagulation and drying have been shown in the case of a filament spun via a flow-focusing channel, coagulated without tension and dried with tension. A maximum order parameter of 0.4 for CNF inside the channel was reported in this case. This maximum orientation relaxed down below 0.2 while the CNF traveled downstream in the channel. Curiously, the final dry filament had an order parameter of 0.5. This implies that even the flow-focusing channel specifically designed for optimally orienting CNF had less effect on the alignment than coagulation and drying combined. Thus, better understanding to optimize these issues is expected to bring beneficial effects.

A related study on regenerated cellulose has compared the impact of the coagulant selection by using two consecutive coagulation baths (Figure 6). The first coagulation bath was filled with ethanol to cause cellulose regeneration and initial coagulation. The solvent in the second bath was changed in order to generate different types of secondary coagulation. Even though this latter coagulation was applied to regenerated cellulose, it gives an indication about how similar solvents would act on CNF. For instance, it was concluded that methanol would produce the highest mechanical performance and a smooth surface (Figure 6b). The authors also compared three of the coagulants used previously for CNF: acetone, ethanol and isopropyl alcohol. Among these, both ethanol and isopropyl alcohol resulted in moderate tensile strength and breaking elongation whereas acetone produced a stronger and more brittle regenerated cellulose filament with a cracked surface (Figure 6c). Interestingly, glycerol was found to produce highly flexible filaments. This observation suggests that a new type of flexible CNF filament could be possible by changing the coagulant.

The coagulation time has been reported to be from 5 min to 12 h, but no study has systematically examined its effect. Considering that at least several minutes may be necessary for coagulation of CNF dispersions, there is an indication that this step is rate-limiting in wet-spinning. In comparison, the outer surface of the viscose dope stream coagulates in fractions of a second when entering in contact with the antisolvent (sulfuric acid). This allows for relatively small coagulation baths (less than 1 m deep). Impropractically large baths for CNF coagulation could be avoided by thinning the filament by spinneret design. However, small orifice spinneret can suffer from more frequent clogging, which again slows down the spinning process through lost time.

Filaments spun from CNF are normally dried in ambient conditions. As a more thorough alternative, drying has also been performed at 105 °C for 1 h. Compared to other studies, the increased drying temperature produced little effect on the mechanical properties of the filament. This observation shows that increasing the temperature to 105 °C can be used to reduce the time during the drying process without negatively affecting the wet-spin filament.

In the case of dry-spinning, drying becomes even more critical because the water inside the filament has not been exchanged with any other, more volatile solvent. Dry-spin filaments have been dried through two alternative procedures. Dry-spin filaments can be initially dried at room temperature and then heated to 105 °C for 2 h to remove the residual moisture. Alternatively, if the filament is dry-spin on a rotating capstan, the rotation can be continued, thus taking advantage of the air flow created on the filament surface. This latter alternative leads to sufficient drying in only a few minutes. Regardless of the conditions, filament needs to be dried under a weak tension to avoid longitudinal shrinkage and curling during drying.

6. ADDITIVES

As mentioned above, to attain new filament properties that cellulose lacks, such as water stability, spinning of CNF is insufficient without additives. Additives can be applied by mixing with the CNF hydrogel (water-dispersive additives) or by dispersion in the coagulation bath (hydrophobic additives), though the latter approach requires an extended coagulation time. Alternatively, filaments can be exposed to the additives after spinning by immersion or vapor-phase deposition. The ability of the filament to retain the additive depends on the interaction between CNF and the added component. The addition of other components to CNF filaments has mainly focused on improving the filament’s wet strength. Relative to their dry strength, CNF filaments have wet tensile strengths of only 0.7% or 1.8%. For filaments produced from TEMPO-oxidized CNF, the wet strength is even smaller, 0.3% of the dry strength. Overcoming this limitation has been attempted by

Figure 6. Schematic illustration of regenerated cellulose fiber spinning line with two coagulation baths: 1, cellulose solution; 2, screw extruder; 3, spinneret; 4, roller; 5, first coagulation bath; 6, second coagulation bath (a). Scanning electron micrographs of cellulose fiber surfaces regenerated first in ethanol, second in methanol (b) and acetone (c). Reprinted with permission from ref 36. Copyright 2013 The Korean Fiber Society and Springer Science+Business Media Dordrecht.
modifying filament surfaces through vapor-phase deposition with chlorosilanes.\textsuperscript{33,47} This approach is effective to reduce the water affinity of the filaments, by increasing substantially the water contact angle and can be also effective in achieving omniphobicity.\textsuperscript{47} Photographs of pristine and chlorosilane-modified wet filaments are presented in Figure 7.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Pristine and chlorosilane-modified CNF filaments exposed to water immediately (a)\textsuperscript{37} and after 4 h of soaking (b). Reprinted with permission from ref 33. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.}
\end{figure}

However, the hydrophobicity of a filament surface fails to manifest in terms of long-lasting improvement in wet strength.\textsuperscript{47} This conclusion implies that additives in the filament bulk are necessary to enable filaments to retain more of their performance in wet conditions. As an example, glutaraldehyde has been added to wet-spun CNF filaments in order to cause covalent cross-linking between adjacent fibrils.\textsuperscript{25} The cross-linked filaments retained up to 40\% of their dry strength in wet conditions. In addition to higher wet strength, additives have also been used to attain optical transparency, magnetic activity\textsuperscript{33} and electrical conductivity.\textsuperscript{22,33} Also, a CNF filament can act as a support for stem cells\textsuperscript{25} or be carbonized to achieve high conductivity by adding reduced graphene oxide as a carbonization template.\textsuperscript{48}

In principle, any modifications or treatments reported to work in the case of CNF films\textsuperscript{16−5,19,49} can probably be adapted for CNF filaments, too. Furthermore, in addition to incorporating the additives inside the filament structure, filament itself can be cut into sections and blended with other components, thus achieving a composite structure where filament sections function as macroscopic reinforcements. Possibilities for this and other kind of applications building on CNF filaments will be discussed in the next section.

7. APPLICATIONS

Owing to the availability of the CNF source material together with its high strength and stiffness, low weight and biodegradability, CNF filaments may be used in a wide variety of applications. Furthermore, filaments may be functionalized to produce conductive, magnetic, bioactive or flame-retardant structures. Generally, three main application areas can be identified: composites, nonwovens and textiles.

CNF have been employed in various composite structures owing to their exceptional mechanical properties. Starting from small amounts of microfibrillar cellulose added to thermoplastics,\textsuperscript{50} the research of cellulose nanocomposites has progressed to a variety of structures with different material combinations and processing techniques. These bionanocomposites have been reviewed extensively elsewhere.\textsuperscript{22,50,51} However, research in this area has focused on the utilization of colloidal suspensions, without an intermediate spinning phase. To manufacture high quality reinforcements, the source material often has to be processed into a continuous fiber product such as filament or yarn.

Utilizing spun filaments allows for increased control of the directionality of the composite structure. Individual filament sections can be aligned, thus optimizing the tensile strength in a desired direction. In composite applications, matrix selection needs to take into account the hydrophilicity of the CNF filament surface. This challenge can be overcome by using surface treatments and additives to enable use of hydrophobic matrices (section 6). As CNF filaments can be modified to reduce opacity,\textsuperscript{33} they can be even used in transparent composites. Furthermore, conductive CNF filaments have applications in bioelectronics, sensing and damage monitoring of composite structures.

Traditional fiber reinforcements, such as glass and carbon fibers, have been used as weaves with different tow sizes. Filaments spun from CNF correspond to similar type of reinforcing elements. Considering that the CNF filament thickness can vary between the scales of dozens and hundreds of micrometers (Figure 3), combining several filaments into a tow will be possible with thinner filaments. However, when using thicker ones, tow preparation will become unnecessary in many cases.

Natural fibers such as hemp, ramie, flax and jute have been extensively researched in the context of composite reinforcement. Because these fibers are sufficiently long, they can be cut into staple, if necessary, and spun into yarns that can, in turn, be used to reinforce composites. Natural fiber-based mats, fabrics and prepregs are used to produce a wide variety of composite structures. However, to produce these yarns, individual fibers need to be twisted together. This twisting reduces the processing properties of the laminate, impedes impregnation and decreases the compaction of the reinforcement.\textsuperscript{32,53} Moreover, the inherent variability of natural fibers and partly damaging processing methods limits their use in composites.\textsuperscript{54}

By spinning nanoscale fibers into filaments with controlled spinning parameters this variability may be reduced. Furthermore, CNF filament can avoid the negative effects of twisting because it can be produced directly to the desired length and thickness without the need to twist several filaments together.

Cellulose-based products such as pulp and viscose are widely used to produce nonwovens, which can be used in, e.g., filters, surgical gowns, wipes, packaging and geotextiles. Many
processes such as wet-laying, foam-forming and air-laying can be used to produce different nonwoven structures. To maintain the nonwoven macrostructure, the fibers need to be bound together mechanically (entanglement), chemically (with adhesives) or thermally (melting). Mechanical binding with cellulosic materials has been of special interest because it enables cost efficient production of biodegradable structures. To achieve a strong structure through entanglement, longer fibers are necessary. Although natural or regenerated fibers may be used, the properties of CNF filaments introduce a possibility to develop stronger nonwovens with a lowered environmental impact.

The increased demand for textile fibers arising from global population growth can potentially be met with low environmental impact by adopting lignocellulosic raw materials in fiber production. In textile production, filament properties have a strong impact on two-dimensional structures such as knitted or woven fabrics. It is, therefore, presumable that strong woven or knitted structures for certain textile applications may be manufactured out of CNF filaments. Naturally, further research is required to investigate the knittability and weavability of CNF-based filaments.

Further research is also necessary to uncover new uses and viable business opportunities for CNF filaments. Particularly, interdisciplinary collaboration is necessary to explore the possibilities of this new material in terms of both material science and real-life applications. Explorative prototyping between experts on design, engineering and business can identify new viable product opportunities. Examples on this type of approach are underway in the case of fiber yarns spun from wood fibers,\(^5^6\) Ioncell-F fibers, cellulose derivatives 3D printed on textiles,\(^5^5\) CNF, synthetic nacre and foam-formed wood fibers.\(^5^0\) Four of these examples are illustrated in Figure 8.

8. CONCLUSIONS

Filaments spun from CNF have shown promising mechanical properties, though challenges remain in upscaling their production and in achieving properties such as stability in water and humidity. For optimal spinning, the following conditions should be aimed at:

- High CNF aspect ratio; though, on the other hand, a high aspect ratio makes water stability more challenging to achieve
- Low CNF solids content, especially if using unmodified CNF (target the apparent viscosity of the CNF dispersion close to 2 Pa s at the system shear rate)
- High shear rate in the spinneret (on the order of hundreds of s\(^{-1}\))
- Adding drawing in the process and restricting the time for CNF to relax back to a disordered structure
- Capitalization on the beneficial effects of coagulation and drying (further work needed to execute this in practice)
- Selection of additives based on application

The improvements achieved in filament stiffness and strength by adjusting the CNF properties and shear rate originate mainly from improved fibrillar uniformity and packing inside the filament. The extent of fibrillar orientation along the filament axis correlates only slightly with the mechanical performance. Nevertheless, in the case of drawn filaments, better fibril alignment correlates with enhanced stiffness and strength.

 Naturally, the priorities regarding the CNF material and spinning process might change depending on the intended application. For example, if a flexible and stretchable filament is desired, the conditions mentioned above should be adjusted appropriately. Further development of CNF spinning is, therefore, recommended with an application-oriented approach.

[Figure 8. Examples on novel uses for cellulosic materials: knitted fabric based on Ioncell-F fibers dyed combining reactive dyes with residual lignin in the fibers (a); fabric with controlled stretch accomplished via a 3D printed cellulose derivative (b); composite structure composed of a triaxially knitted net and CNF film (c); wood fiber-based foam-formed structures (d). Images: Eeva Suorlahti.

Samples: Marjaana Tanttu, Yibo Ma, Shirin Asaadi, Michael Hummel, Herbert Sixta, Aalto Chem; Marjo Määttänen, Airi Särkkälähti, Ali Harlin (a); Marjaana Tanttu, Tiia-Maria Tenhunen, Tuomas Hänninen (b); Tiina Härkäsalmi, Minna Hakalahti, Tiia-Maria Tenhunen, Tuomas Hänninen (c); Jukka Itälä, Tiina Härkäsalmi, Jukka Ketoja, Jani Lehmonen (d).]

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**Notes**

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**ABBREVIATIONS**

- CNF = cellulose nanofibers
- TEMPO = 2,2,6,6-tetramethylpiperidine 1-oxyl
- DP = degree of polymerization

**REFERENCES**


