Coaxial Spinning of Oriented Nanocellulose Filaments and Core–Shell Structures for Interactive Materials and Fiber-Reinforced Composites

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ABSTRACT: Spinning filaments from nature’s own high-performance building block, cellulose nanofibrils (CNFs), requires additional considerations compared to conventional manmade fibers commonly made from polymer solutions or melts. We herein utilize the colloidal properties of the highly anisotropic CNFs and demonstrate the preparation of core–shell filaments using a coaxial nozzle. The nanofibril dispersion is passed through the core channel, and the sheath flow consists of a functionalizing solution. The flow rates of the suspensions/solutions are carefully controlled to create an extensional flow at the exit of the nozzle, allowing orientation of the nanofibrils into continuous filaments that are then extruded into a fixation bath before drying. The self-assembly mechanism relies on the control of the colloidal stability of carboxymethylated CNFs altered by pH or ionic strength changes. In the simplest approach, HCl is used in the sheath flow to assemble the accelerated CNFs in the core flow, leading to an irreversible association of the nanofibrils into an oriented filament. The filaments are continuous and homogeneous, with a dry diameter of approximately 20 μm. The orientation of the CNFs in the spun filament was investigated by wide-angle X-ray scattering, and an orientation index of 0.79 is achieved. The tensile strength of the filaments is 431 ± 89 MPa, the Young’s modulus is 19.2 ± 3.4 GPa, and the strain at break is 7.4 ± 1.3%. Core–shell structures are also prepared by incorporating active materials such as carbon nanotubes in the sheath flow. The resulting filaments show a thin shell of a conductive nanotube network covering a core of cellulose nanofibrils, and the conductivity of such structures reaches 1000 S cm⁻¹, opening up opportunities for composites and interactive materials.

KEYWORDS: filament, colloidal stability, cellulose nanofibrils, spinning, core–shell

INTRODUCTION

The interest and knowledge in the synthesis and use of nanometer-sized particles and fibers have expanded over the last decade. Together with the societal growing demand for a broader use of bio-based and renewable resources, this has triggered the emergence of a new class of materials, including wood-based nanomaterials, suggested as a potential candidate to fulfill the criteria of both being renewable and constituting high-performance building blocks in interactive, and fiber-reinforced composites.1,2 Cellulose nanofibers (CNFs) are obtained by defibrillating cellulose-rich wood-based fibers by chemical and mechanical treatments. Most commonly, the chemical treatment of these fibers is performed through carboxymethylation3 or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation,4 which significantly facilitates fibrillation through mechanical treatments such as grinding or homogenization where shear forces act to delaminate and isolate individual nanofibrils. The chemical treatments result in a negative surface charge of the liberated nanofibrils, which typically are 4 nm in width and up to a few μm in length.5

Because of their high aspect ratio and surface charge, CNFs form gels or volume-spanning arrested states, i.e., colloidal glasses, already at low concentrations, and the decrease in pH and/or increase in ionic strength will drastically influence their colloidal behavior.6,7 CNFs can be used to self-assemble into different types of materials with remarkable properties such as dense films, membranes, or porous foams and aerogels. These materials can then further be functionalized by surface treatment, adsorption of polymers and nanoparticles, and in situ polymerization, which makes CNFs a building block of major interest in the design of renewable functional materials.8–11

Received: August 13, 2020
Accepted: September 17, 2020
Published: September 17, 2020
From an engineering point of view, it is challenging to assemble nanofibers into an organized hierarchical structure as nature does. However, with extensive knowledge of fibril characteristics, such as morphology, size, aspect ratio, electrostatic charge, dispersive properties, and colloid stability, it is possible to assemble strong and oriented microscopic or macroscopic structures stabilized by secondary interactions between the nanofibrils. One route to achieve this is to wet spin CNF filaments by extruding a nanofiber dispersion into a fixation bath, which results in continuous filaments with a high degree of alignment. Apart from the CNF aspect ratio and charge, the solid content, shear rate, and drying conditions have been shown to significantly affect the properties of the spun filaments.11 Provided that the mechanical treatment processes for preparing CNF are energy-efficient,15 the use of water-based CNF systems in filament spinning could be a way to prepare cellulose I filaments and to circumvent the dissolution, regeneration, and spinning of cellulose, often requiring more aggressive solvents and processes.15 It is also possible to dry spin CNF filaments by extruding highly viscous CNF gels into air. However, the resulting filaments tend to have irregular and noncircular cross sections and diameters up to 200 μm.17

Using the concept of microfluidics, a flow-focusing technique was recently developed and applied, where the main flow (core flow) consisting of a dilute CNF dispersion is exposed to two perpendicular flows (sheath flows). These sheath flows induce an extensional flow field in the core flow, which aligns the nanofibers. The sheath flows consist of a salt solution or dilute acid, which induces self-association of the nanofibers, and the resulting gel thread is extruded in a bath containing deionized water or salt solutions.18 This technique was later improved by implementing an additional sheath flow step: in the first step, the CNF dispersion is aligned using deionized water in the sheath flows, and in the second step, the sheath flows induce both alignment and self-association using HCl before being extruded in a HCl bath.19 This flow-focusing technology was also used to prepare the strongest bio-based filament ever made, so far, as well as bioactive composites.20 This experimental procedure is very versatile and provides a new toolbox for the preparation of many types of specially designed filaments, since the properties can be further improved and tailored by using additives, cross-linkers or additional postprocessing steps.15,19,21,22 Being the state-of-the-art when it comes to a CNF filament in terms of alignment and mechanical properties, this universal method is presently sensitive to processing parameters, and the possibility to scale up the technology has still to be proven.

In this contribution we introduce a facile and scalable route for the extrusion of CNF filaments as well as core–shell filaments. The setup consists in a simple coaxial needle mounted with an extension tube, with the aim of reproducing the three key steps for CNF filament preparation (as provided by the flow-focusing technology): flow acceleration, fibril alignment, and final self-association into a filament.15 The results show that it is possible to prepare continuous filaments of CNF, i.e., cellulose I, with diameters of ca. 20 μm and an orientation index of 0.79. In addition, it is possible to incorporate active nanoparticles and prepare core–shell structures, here demonstrated by fabricating a filament with a CNF core and a shell composed of conductive carbon nanotubes (CNT), reaching conductivities of 1000 S cm⁻¹. Such materials could potentially be used in applications such as nonwovens, textiles, electronic devices, and biomedicine, and the method opens up various possibilities of interactive and composite filaments with a scale-up potential. By using montmorillonite clay in the sheath flow, it is also demonstrated that it is possible to prepare a mineral filament surface while the mechanical properties of the filament are dominated by the CNF core showing similar mechanical properties as a pure CNF filament. Potentially, this filament type could be used in fire protection applications.

### EXPERIMENTAL SECTION

#### CNF Preparation.
Carboxymethylated CNF with a charge of 600 μeq g⁻¹, length up to 1 μm, and diameter of 5−15 nm was provided by RISE Bioeconomy AB (Stockholm, Sweden) and prepared following the previously described procedure.13 Prior to use, the CNF aqueous gel was diluted to 4 g L⁻¹ in Milli-Q water, mixed using an Ultra-Turrax at 12000 rpm for 15 min, and ultrasonicated at 50% intensity for 20 min using Sonics VC 750 equipment.

#### Filament Spinning.
Filaments were prepared using a setup consisting of a coaxial needle, fed with two syringe pumps, and mounted with a silicone tubular extension, which was submerged into a collection bath into which the dispersion is extruded. The coaxial needle is made of an internal needle (inner diameter, 510 μm; outer diameter, 1230 μm) and an external needle (inner diameter, 1570 μm; outer diameter, 2230 μm). The extension is 10 mm long and has a diameter of 735 μm. The flow speeds were set to 8.4 (core flow) and 50 mL h⁻¹ (sheath flow), resulting in a Reynolds number (Re) = 32. The extruded wet filaments were collected using a pair of tweezers and dried at room temperature after being fastened at both ends to a frame. For plain CNF filaments, a CNF suspension of 4 g L⁻¹ was used in the core flow, and HCl (pH 2) was used in the sheath flow as well as in the collection bath. For CNT core–shell structures, sulfonated CNTs (sCNTs) were synthesized adapting a procedure described previously:23 carboxymethylated single wall nanotubes (P3 grade, from Carbon Solutions, Inc., USA) were reacted with 97% sulfuric acid at 250 °C for 18 h. After the reaction, the excess sulfuric acid was washed away by three centrifuge cycles at 4000 rpm for 10 min, and the sCNT suspension was ultrasonicated for 20 min at 75% amplitude using a Sonics VC 750 equipment. Functional filaments were prepared using aqueous 0.1 g L⁻¹ suspension of sCNT or MMT in the sheath flow and adjusted to pH 2 with HCl.

#### Imaging.
An S-4800 field emission scanning electron microscope (FESEM) (Hitachi, Tokyo, Japan) was used to image the filaments.

#### Tensile Test.
The filament mechanical properties were tested by performing uniaxial tensile tests at 50% RH and 23 °C using an Instron 5566 universal testing machine (Norwood, MA, USA) equipped with a 50 N load cell. The span length was 10 mm, and the samples were tested at a rate of 5% min⁻¹. For the evaluation of mechanical properties, the filaments were assumed to be cylindrical, and their diameters were evaluated by SEM imaging. A total of at least 10 specimens were tested for each configuration: Re = 32 and Re = 64.

#### Wide-Angle X-Ray Scattering.
Wide-angle X-ray scattering (WAXS) measurements were performed using an Anton Paar SAXSpoint 2.0 system (Anton Paar, Graz, Austria) equipped with a Microsource X-ray source (Cu Kα radiation, wavelength 0.15418 nm) and a Detecor 2D CMOS Eiger R1 M detector with 75 × 75 μm pixel size. A beam size of approximately 500 μm diameter was used at a sample temperature between 25 and 29 °C with a beam path pressure of about 1–2 mbar. The sample-to-detector distance (SDD) was 111 mm. The filaments were mounted on a solid sampler (Anton Paar, Graz, Austria) mounted on a VarioStage (Anton Paar, Graz, Austria). Three to five filament fragments were mounted together in order to maximize the signal-to-noise ratio. The measurements were performed under vacuum. For each sample, five frames each of 17 min duration were read from the detector, giving a total measurement time of 1.4 h per sample. For all samples, the relative transmission was determined and used for scaling of the scattering intensities.

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1. [Link](https://dx.doi.org/10.1021/acsnano.6b02192)
2. [ACS Appl. Nano Mater.](http://www.acsanm.org)
software used for instrument control was SAXSdrive version 2.01.224 (Anton Paar, Graz, Austria), and postacquisition data processing was performed using the software SAXSanalysis version 3.00.042 (Anton Paar, Graz, Austria).

The orientation was determined from the data corresponding to the (2 0 0) crystal plane of cellulose at 15.3 nm⁻¹. The orientation index and order parameters were calculated from the azimuthal integration of the intensity, following the procedure described more in details in previous studies. Also, using the following equation, where \( W_{1/2} \) is the full width at half of the maximum of the azimuthal intensity profile:

\[
\text{orientation Index} = \frac{180 - W_{1/2}}{180}
\]

**Electrochemical Evaluation.** The electrochemical evaluation of the sCNT-modified filaments was performed with a Biologic VSP potentiostat (Biologic Science Instruments, Seyssinet-Pariset, France) using an approximately 2 cm long filament having 1 M KCl as the electrolyte, an Ag/AgCl electrode as the reference, and a platinum plate as the counter electrode. In order to facilitate handling and contacting, the sCNT-functionalized filament was supported on a glass slide and contacted by adding a small amount of conducting glue. The cyclic voltammetry was performed for potentials between 0.1 and 0.5 V at 10 mV s⁻¹.

**RESULTS AND DISCUSSION**

**Preparation of Filaments Using the Coaxial Flow.** The alignment and assembly of CNFs into filaments is achieved by a coaxial setup as depicted in Figure 1a,b. The core flow consists of a CNF dispersion, and the sheath flow (similar to flow-focusing) consists of a HCl solution at pH 2. Both components are flowing through the coaxial nozzle until they come in contact, followed by acceleration due to a contraction of the diameter of the flow channel. This induced flow acceleration causes the high-aspect-ratio fibrils to orient in the flow direction and in addition, the nano fibrils are self-associated by protonation of the carboxyl groups on the nano fibrils induced by the low pH of the sheath flow. The protonation decreases the electrostatic repulsion between the oriented charged fibrils, which brings them so close together that van der Waals forces will dominate their interaction, locking the oriented filament structure into a continuous gel thread. As can be seen in Figure 1c, the gel thread that is extruded into the bath is homogeneous and regular, showing potential for continuous and larger scale filament preparation. The filament is picked up manually from the extrusion bath (Figure 1d) and dried at room temperature by fixing the ends of a piece of the gel thread to a frame. During the drying process, the diameter decreases by a factor of 10 (Figure 1e), and the equilibrium dry content is reached after a few minutes. Mesoscale structures can be observed on the surface of the dry filaments, similarly to what can be observed when wood fibers are dried and show surface wrinkling, which is probably due to the formation of a moisture gradient during the final stages of drying, leading to surface wrinkling.

**Morphology and Properties of Coaxially Spun Filaments.** The morphology and structure of the filaments is investigated by scanning electron microscopy (SEM), and the collected images are shown in Figure 2a–c. The filaments show a circular cross section and a regular shape along their axis. Some mesoscale structures can be observed at the surface of the filaments, similar to what was previously observed. The cross-sectional images reveal a dense and homogeneous cellulose network throughout the filament. In order to characterize and quantify the alignment of the CNF in the filaments, wide-angle X-ray scattering (WAXS) is used, and the results are displayed in Figure 2d–f. From the resulting diffractogram and integrated intensity, an orientation index of 0.79 and an order parameter of 0.63 were obtained. Considering the specimen preparation, WAXS measurements are performed on a bundle of several filaments in order to optimize the signal-to-noise ratio, and the values obtained are actually an underestimation of the orientation and show that the filaments prepared by coaxial spinning are in line with the filaments obtained by the flow-focusing technology, although slightly below the highest reported orientation index (0.86) for carboxymethylated nanocellulose fibrils with similar charge density. This difference is suggested to be due to a difference in the filament diameter, given that the diffusion of protons and thus the gelation is faster in the case of a filament with a smaller diameter, and this limits the possibilities of fibril reorientation after the acceleration step. The larger filaments obtained using the coaxial setup hence allows more time for reorganization.

Tensile testing of the fabricated filaments is performed to evaluate the mechanical properties. Due to the size and fragility of the filaments, each specimen is mounted on a paper frame in order to avoid any stress prior to testing. In parallel, a fragment of each specimen is saved for diameter analysis using SEM imaging. A representative stress/strain curve is shown in Figure 3. The tensile strength is 431 ± 89 MPa, the modulus is 19.2 ± 3.4 GPa, and the strain at break is 7.4 ± 1.3%. These values are very similar to the first results reported for flow-focused
filaments but lower than the latest and highest reported values for a similar CNF starting material, highlighting the crucial effect of a slight difference in degree of orientation in the mechanical properties of the final filament. Another configuration is also tested, where all flow speeds are doubled up, as well as the extension tube length, giving rise to a Reynolds number twice as high as the reference configuration, i.e., Re = 64. In this case, some discontinuities in the spinning process are observed, whereas no gain in the mechanical properties is obtained: the tensile strength is 288 ± 24 MPa, the Young’s modulus is 14.3 ± 2.8 GPa, and the strain at break is 8.1 ± 1.8%.

**Preparation and Functionality of Filaments Prepared Using Sheath Flows of Functional Components.** Due to the coaxial design of the setup, it is possible to prepare filaments with a core–shell structure. Adding active materials in the shell at pH 2 gives rise to a filament with a dense CNF core and a thin shell of the active material added. As an example, conductive CNT–CNF filaments have been fabricated (Figure 4a). As pristine CNTs or carboxymethylated CNTs could not form a stable colloidal dispersion at the required low pH, instead, sulfonated CNTs (sCNTs) were used. Using the same settings as for the plain CNF system but passing a pH 2 sCNT suspension in the sheath flow results in the formation of a core (CNF)–shell (sCNT) filament with similar morphology and dimensions as the CNF filaments. SEM imaging (Figure 4b,c) of the cross section of such core–shell structures shows a dense CNF core coated with a thin sCNT layer. For the nonsputtered specimens, SEM images reveal a sharp sCNT-covered surface, whereas charging can be observed in the core, showing that the core is composed of a nonconductive CNF and that sCNTs can only be found onto the surface of the filament (Figure S1).

CNTs could not form a stable colloidal dispersion at the required low pH, instead, sulfonated CNTs (sCNTs) were used. Using the same settings as for the plain CNF system but passing a pH 2 sCNT suspension in the sheath flow results in the formation of a core (CNF)–shell (sCNT) filament with similar morphology and dimensions as the CNF filaments. SEM imaging (Figure 4b,c) of the cross section of such core–shell structures shows a dense CNF core coated with a thin sCNT layer. For the nonsputtered specimens, SEM images reveal a sharp sCNT-covered surface, whereas charging can be observed in the core, showing that the core is composed of a nonconductive CNF and that sCNTs can only be found onto the surface of the filament (Figure S1).

By using SEM images, the thickness of the CNT film can be estimated to 100 nm. Assuming this thickness all along the...
filament, a conductivity of 1000 S cm\(^{-1}\) is obtained. CNF–sCNT core shell filaments are also evaluated electrochemically, and a typical cyclic voltammogram as well as galvanostatic cycling experiment are shown in Figure 4d,e. The CV plot shows a supercapacitor-like square-shaped response, characteristic of carbon materials, and the cycling shows a stable response, showing that the surface of the filament is coated with a thin homogeneous and percolating film of CNT, giving rise to a typical supercapacitor behavior.

The versatility of the coaxial nozzle to produce different core–shell structures was also demonstrated by switching the sheath flow from sCNTs to a stable dispersion of montmorillonite clay (MMT) at pH 2. The continuous process for filament preparation using the coaxial nozzle was unaffected by the switch to an MMT dispersion, and the prepared filaments were of the same dimensions as when the sheath flow was only HCl or sCNTs (Figure 5a). The MMT-containing filaments displayed diameters similar to the HCl-prepared filaments of approximately 20 \(\mu\)m in the dry state. This suggested that there was no extensive incorporation of MMT into the CNF core, and this was corroborated by SEM images of the filament surface, which indeed showed that MMT sheets were tightly packed on the surface of the filament, see Figure 5a,b, and the surface structure was smoother compared to the CNF-only filaments. The presence of MMT on only the surface was further corroborated by observations of the cross sections of the MMT-coated filament, which showed that the MMT was deposited only on the surface of the filament. The two morphologies, CNFs and MMT, are clearly distinguishable in Figure 5b. This is similar to that observed for the sCNTs, which were also only deposited on the surface of the spun filament. The MMT coating consisted of only a few MMT sheets stacked on top of each other covering the whole filament surface, see Figure 5b. The MMT-coated filaments were mechanically evaluated and revealed that no detrimental effect on the mechanical properties by using MMT in the sheath flow was induced, and the properties were in the same range as HCl-formed filaments. This coverage of the filaments with a distinct layer of MMT might be interesting for the preparation of fire-retardant filaments, but this was beyond the scope of the present work.

CNT and MMT coaxial fibers shown in the present investigation are among the wide range of potential interactive material and composites that can be achieved by using the coaxial nozzle spinning and careful control of the colloidal stability of nanoparticle aqueous suspensions. As compared to electrospinning, a common technique used to prepare coaxial fibers, the presented method offers great advantages such as the possibility to work with environmentally friendly water-based systems as well as to isolate, spin, and process single continuous filaments, opening up potential upscaling application where continuous filaments can be extruded, dried, and rolled in a continuous process.

**CONCLUSIONS**

This work demonstrates the feasibility of using a coaxial flow setup having only a core flow of CNF dispersion and a sheath flow of dilute HCl in order to continuously spin filaments of aligned CNFs with potential application in interactive and composite materials. Although the separate flows are brought into direct contact with each other in the extension tube and the CNFs start to interact due to the decreased pH, there is enough time for the CNFs to align due to the acceleration of the flows in the extension tube, also without any prior alignment of the CNFs in the core flow. The produced CNF filaments displayed an orientation index of 0.79 and an order parameter 0.63. The tensile strength of the filaments reached 431 ± 89 MPa, a Young’s modulus of 19.2 ± 3.4 GPa, and a strain at break of 7.4 ± 1.3%. The coaxial setup also enabled the use of sheath flows of colloidal dispersions stable at pH 2. Functional filaments were spun having sulfonated CNTs and montmorillonite clay platelets deposited as thin layers on the entire surface of the spun filaments by using CNT and montmorillonite dispersion as sheath flows. The conductivity of the CNT-coated filament reached values of 1000 S cm\(^{-1}\) and was demonstrated to work as a supercapacitor electrode with a distinct square-shaped cyclic voltammogram. The possibility of preparing MMT-coated CNF filaments opens up for using the coaxial setup to prepare filaments for other applications, for example, as flame-retardant materials where the CNF–MMT combination has earlier shown promising results.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c02192.

SEM image of a nonsputtered core–shell CNF–CNT filament (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
A.M. acknowledges the Knut & Alice Wallenberg Foundation and Research for funding. J.E. acknowledges the Swedish Energy Agency through the Modulit project (grant no. 37716-1), and Vinnova through the Digital Cellulose Centre for financial support. L.W. and L.D.S. acknowledge the Wallenberg Wood Science Center for funding through the KAW 2018.0452-WWSC 2.0, Grant. Dr. Anita Teleman and Dr. Frédéric Pouyet are acknowledged for their assistance in WAXS measurements.

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