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Interfacial polyelectrolyte complex spinning of cellulose nanofibrils for advanced bicomponent fibers

Matti S. Toivonen,† Sauli Kurki-Suonio,† Wolfgang Wagermaier,§ Ville Hynninen,† Sami Hietala,# and Olli Ikkala†*

† Molecular Materials, Department of Applied Physics, Aalto University (previously Helsinki University of Technology), P.O. Box 15100, FIN-00076 Aalto, Espoo, Finland

§ Max Planck Institute of Colloids and Interfaces, Department of Biomaterials, D-14424 Potsdam, Germany

#Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 HY, Helsinki, Finland

* Corresponding author: Olli.Ikkala@aalto.fi

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ABSTRACT. Fiber spinning of anionic TEMPO-oxidized cellulose (TOCN) nanofibrils with polycations by interfacial polyelectrolyte complexation is demonstrated. The formed fibers were mostly composed of cellulose nanofibrils and the polycations were a minor constituent, leading to yield and ultimate strengths of ca. 100 MPa and ca. 200 MPa, and Young’s modulus of ca. 15 GPa. Stretching of the as-formed wet filaments of TOCN/polycation by 20 % increased the Young’s modulus, yield strength, and ultimate tensile strength by approximately 45, 36 and 26 %, respectively. Importantly, feasibility of compartmentalized wound bicomponent fibers by simultaneous spinning
of two fibers of different compositions and entwining them together was shown. This possibility was further exploited to demonstrate reversible shape change of a bicomponent fiber directly by humidity change, and indirectly by temperature changes based on thermally dependent humidity absorption. The demonstrated route for TOCN-based fiber preparation is expected to open up new avenues in the application of nanocelluloses in advanced fibrous materials, crimping, and responsive smart textiles.

**Introduction**

Cellulose nanofibrils (CNF, also denoted as cellulose nanofibers, nanofibrillated cellulose, NFC, or sometimes microfibrillated cellulose, MFC) have drawn much attention in recent years due to their attractive combination of high mechanical and optical properties, renewability, availability, biocompatibility, and thus their potential for new advanced functional materials.\(^1\)-\(^5\) TEMPO-oxidized cellulose nanofibrils (TOCN) are a subcategory of CNFs which are chemically modified to possess abundant carboxylic acid groups on their surface and thus negative charge at neutral pH conditions.\(^6\),\(^7\) Due to their high density surface charge, TOCNs can be disintegrated from pulp with relatively low energy consumption to result in well-dispersed fibrils with very small diameters (typically 3 – 5 nm).\(^6\),\(^7\)

Versatility of CNF has been demonstrated in forming a myriad of versatile materials including transparent and water-resistant nanopapers,\(^8\),\(^9\) nanostructured foams,\(^10\) cell-growth supporting hydrogels,\(^11\) mechanically robust and transparent aerogels and membranes.\(^12\)-\(^14\). Fibers based on CNF or TOCN have aroused particular interest in the nanocellulose research community, due to the inherent suitability of cellulose to form strong fibers.\(^15\)-\(^22\) Especially, wet-spinning of CNF into a non-solvent (i.e. coagulation bath such as ethanol or acetone) has been widely explored and exploited.

Inspiration derived from biological materials has been a prominent lead of thought in the realm of material science in recent decades.\(^23\)-\(^25\) Of biosynthesized fibers, spider silk has inspired multiple works for novel, tough and strong fibers, due to its excellent mechanical properties albeit being processed in aqueous and ambient conditions at near neutral pH.\(^26\),\(^27\)
Wool is another biosynthesized fiber with several attractive properties and of significant commercial relevance. Individual wool fibers coil spontaneously into a spring-like morphology, commonly known as crimp, and this tendency endows some of the elasticity, porosity and thermal-insulation of wool-derived materials. Crimp arises partially from the bicomponent fiber structure of two differing protein composition biosynthesized and assembled side-by-side into a single wool fiber. The differing compositions observed in the wool fiber cause spontaneous crimping of the fiber through differential stress relaxation. Recognition of the mechanism behind the crimping behavior of wool has led to wool-inspired synthetic self-crimping fibers and further to a number of approaches for reversibly crimping fibers, where differential swelling or thermal expansion of the different components were exploited, mostly described in patent literature, whereas very few scientific publications on reversibly crimping fibers are available. One attractive direction of applications for such fibers has been responsive textiles that are able to reversibly change air permeability. The mentioned fibers have all been processed with conventional fiber spinning processes typically utilizing special spinnerets.

Following the inspiration from the bicomponent fiber structure of wool has led us to consider alternate pathways to imitate such a side-by-side fiber structure embedded into CNF-based fibers. Necessities for the chosen processing route are strong adsorption of the components and clear spatial segregation, i.e. compartmentalization in the final fiber. Appropriate material choices can be further expected to result in not only strong fibers but added functionalities, such as humidity or temperature-responsive curling and crimping. For this end facile variation of the composition of the fiber constituents is also desirable.

Interfacial polyelectrolyte complexation (IPC, sometimes termed complex coacervation) spinning can be recognized as an attractive route for these ends. IPC spinning is based on the spontaneous formation of a self-assembled continuous filament upon mechanical drawing of the interface of two solutions with oppositely charged polyelectrolytes and was first reported in 1998 by Yamamoto et
When appropriately set up the IPC spinning process is reminiscent of the interfacial polymerization of nylon-6 often seen as a science demonstration for students, see schematic representation in Figure 1. The attractive features of IPC include fully aqueous, environmentally friendly processing and feasibility of spinning multicomponent fibers. This combination of characteristics have been recognized as beneficial for preparation of fibers for biomedical applications. As an additional benefit, large scale high throughput IPC spinning has been demonstrated to be feasible. While IPC spinning of colloidal materials such as carbon nanotubes and protein amyloids into strong fibers has been shown, IPC spinning of CNF-based fibers remains yet to be demonstrated.

In this work we have prepared and characterized TOCN-based fibers through IPC spinning of the anionic TOCN with a polycation, namely poly(diallyldimethylammonium chloride) (PDADMAC) and chitosan. We have demonstrated spinnability and the stretchability of the wet filaments and after drying characterized the resulting structures, compositions and the mechanical properties of the fibers. Lastly we demonstrate the feasibility of forming well-compartmentalized TOCN-based bicomponent fibers with a side-by-side structure and show preliminary evidence for possibility of preparing humidity-driven, and indirectly thermally-driven, reversibly crimping TOCN-based bicomponent fibers.

Experimental

**Materials.** TOCN was prepared from never dried birch pulp by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation. More accurately, the never-dried cellulose was suspended at a consistency of approximately 1.3 wt. % in water containing TEMPO (0.017 wt. %) and sodium bromide (0.17 wt. %). The TEMPO-mediated oxidation was induced by addition of 13% NaClO at room temperature under gentle agitation. The amount of NaClO was chosen to result in approximately 1.2 mmol/g charge density in the final product. A pH of 10.5 was maintained by addition of 0.5 M
NaOH along the process. The reaction was considered finished when no more decrease in pH was observed. Finally, the pH was adjusted to 7 by addition of 0.5 M HCl. After the oxidation process the oxidized pulp was washed thoroughly with water and disintegrated 3 times through a fluidizer (Microfluidics Corp., Newton, MA, USA) leaving a hydrogel with a consistency of approximately 0.76 wt. %. This gel was further diluted with deionized water to the desired consistency and shaken vigorously to result in a homogenous, transparent dispersion that was stored at 4 °C for further use. Bubbles were removed by bath sonication when necessary. Morphological characterization of the resulting TOCN dispersion by atomic force microscopy (AFM) is shown in Figures S1 and S2. Rheological characterization can be found in Figure S3.

PDADMAC (20 wt. % solution in water, M_w 400-500 kDa), chitosan from crab shells delivered as dry flakes of middle-viscosity (M_w 300-500 kDa, degree of deacetylation 80%), poly(styrene sulfonate) sodium salt solution (PSS, 30 wt. % solution in water, M_w 70 kDa), oleic acid, 37% hydrochloric acid, sodium hydroxide, Reactive Blue 2, and Sulforhodamine B were purchased from Sigma-Aldrich. Deionized water was obtained with a Milli-Q water system from Millipore. The TEMPO-radical was purchased from Alfa Aesar. Melamine-formaldehyde microparticles (mean diameter 4.5 µm, referred to as simply microparticles in the rest of the text) were purchased from Sphere Scientific Corporation.

**Preparation of polycation solutions.** PDADMAC was diluted from a 20 wt. % solution with deionized water to the desired concentration. Chitosan was dissolved at 2 wt. % in 100 mM HCl, which had been diluted with deionized water. The resulting solution was diluted and the pH carefully elevated by dropwise addition of aqueous 30 mM NaOH solution during vigorous stirring with a magnetic stirrer until the concentration of chitosan reached 1 wt. %. No insoluble aggregates were formed. The pH was measured to be 5.8 with an electronic pH meter (6230N, JENCO).
**Preparation of mixture of microparticles and PSS.** 30 wt. % PSS solution was diluted to 1 wt. %. The diluted PSS solution was mixed with the 20 wt. % dispersion of microparticles to reach a mixing ratio of 20:1 (wt./wt.) microparticles to PSS.

**Atomic force microscopy (AFM) of nanofibrils.** The morphology of the TOCN was investigated using a Dimension 5000 scanning probe microscope with NanoScope V controller (Veeco). The samples were prepared by first diluting a dispersion of TOCN to approximately 0.001 wt. % with deionized water and pipetted onto a clean microscope glass slide. The glass slide was subsequently turned vertical to allow excess dispersion to flow off. The samples were dried at room temperature for 24 hours prior to measurement. The images were scanned in tapping mode in air using silicon cantilevers (NSC15/AIBS) delivered by MicroMash (Tallinn, Estonia). The sizes of the images were 4 × 4 and 8 × 8 µm, and the images were scanned across 10 different parts of the sample. The data was post-processed in order to flatten substrate background and remove streaks from scanning artifacts.

**Rheology of TOCN dispersion and polycation solutions.** Rheological measurements were carried out at 20°C with TA Instruments AR2000 stress controlled rheometer equipped with a double concentric cylinder geometry with stator inner radius of 20 mm. Linear viscoelastic region in the oscillatory experiments was established with amplitude sweep at an oscillation frequency of 1 rad/s. Based on the results, frequency sweeps were then performed at 1 % or 10 % strain. Flow viscosities were measured by controlling the shear rate within 0.1 – 1000 s⁻¹. Strain as a function of shear stress was measured by varying the shear stress from 0.005 to 100 Pa.

**Investigating the feasibility of TOCN/polycation IPC spinning.**

A small droplet (approximately 100 – 300 µL) of the TOCN dispersion was placed on a horizontal polystyrene Petri dish and a droplet of similar size of the polycation (PDADMAC or chitosan) solution was pipetted next to it without the two droplets coming into contact yet at this stage. Subsequently, the two droplets were brought into contact carefully with the tips of tweezers without
further mixing of the droplets. Under the appropriate conditions a gel-like thin membrane formed at the interface of the two droplets preventing further mixing. Spinning was considered feasible, when the membrane at the interface was sufficiently strong to be grabbed with tweezers and dragged upwards to result in the formation of a continuous wet filament. See Supporting Video SV1 for demonstration, the blue droplet is 0.4 wt. % TOCN with Reactive Blue 2 as the dye, the pink droplet is 1 wt. % PDADMAC with Sulforhodamine B as the dye.

**IPC spinning of TOCN/polycation wet filaments.** For constant and controlled spinning speed; a computer-controlled linear stage was used. The complex formation was carried out in a cylindrical well (10 mm deep, 6 mm in diameter) drilled in a PMMA block. The walls of the well were treated with a superhydrophobic coating spray used for car mirrors (Glaco Mirror Coat Zero). This was done to reduce the adsorption of the interfacial complex onto the walls, which seemed occasionally to cause rupture of the filament during spinning. For testing of the effect of the well diameter on the diameter of the dry fiber using the TOCN/Chitosan system, a series of wells 10 mm deep, and 2 – 15 mm in diameter were used.

In a typical preparation procedure, the PMMA block with the well pointing upwards was placed on the linear stage and filled halfway with TOCN dispersion. Polycation solution was pipetted on top of the TOCN dispersion resulting in a nearly horizontal interface at start. The interface was subsequently grabbed with inverted tweezers, which were carefully attached to an immobile support directly above the well. The linear stage was lowered at a constant velocity to produce typically a 180 mm long wet filament that was cut with scissors from the lower end. Lastly, if the wet filaments were not stretched prior to drying, they were secured at the ends to dry in order to prevent curling and longitudinal shrinkage. The ends were first wrapped one or two rounds around a glass rod from both ends and carefully taped to the rod with adhesive tape. The drying was carried out in ambient conditions of 20 °C and relative humidity of approximately 30 %. See Figure 1a for the schematic illustration of the arrangement of the fluids and Supporting Video SV2 for a demonstration of the process. Figure 1c is
a screen capture from the video SV2. In the video the blue droplet is 0.4 wt. % TOCN with Reactive Blue 2 as the dye, the pink droplet is 1 wt. % PDADMAC with Sulforhodamine B as the dye. In the video a similarly superhydrophobized (see above) glass test tube is used to allow for better viewing inside the container.
Figure 1. Schematic representation of (a) process of IPC of TOCN/polycation fibers, and (b) suggested cross-section of formed wet filament with polycation containing solution on the periphery and the formed polyelectrolyte complex membrane at the interface of the two fluids. (c) Screen
capture of video SV2 (see Supporting Information) of IPC spinning using dyed 0.4 wt. % TOCN dispersion (blue) and 1 wt. % PDADMAC solution (pink).

**Stretching of wet TOCN/polycation filaments.** For increasing alignment of the TOCN fibrils in the fiber, the wet filaments were stretched prior to drying. The upper end of the filament was attached to an immobile support while the lower end was clamped to a weight supported by the linear stage. The length of the free wet filament was measured and the linear stage was then lowered at rate which corresponded to a strain rate of 4% / min. When a desired strain was reached, the linear stage stopped and the filament was allowed to dry while both ends were secured at the ends to prevent curling and longitudinal shrinkage.

**Spinning of bicomponent fibers.** For demonstrating feasibility of IPC spinning of bicomponent fibers, a 0.2 wt. % TOCN dispersion, a 1 wt. % chitosan solution at pH 5.8 and a mixture of microparticles and PSS were used, where the microparticles were incorporated within PSS to allow differentiation between the formed compartments in the SEM micrographs. Droplets of the TOCN dispersion and the mixture of microparticles with PSS were placed approximately 2 cm apart on a PTFE sheet. Adjacent to both of these droplets were placed droplets of the chitosan solution. The droplet of TOCN dispersion and the adjacent droplet of chitosan solution were brought carefully into contact with the tips of tweezers and the resulting polyelectrolyte complex interface was drawn as a wet filament onto a glass rod. The same was repeated with the droplets of the mixture of microparticles and PSS and the adjacent droplet of chitosan so that the formed filament was drawn onto the glass rod approximately 1 cm apart from the TOCN/Chitosan filament. Next the PTFE sheet with the droplets was rotated at 60 rounds per minute while the glass rod was slowly elevated manually. Thus the two filaments were wrapped around each other while simultaneously new filament was drawn out from the droplet interfaces.

For preliminary testing of reversibly crimping bicomponent fibers, a similar process as described above was used with the difference that a 1 wt. % sodium oleate solution was used instead of the
mixture of microparticles and PSS. The sodium oleate solution was prepared by weighing oleic acid in a flask and adding an equimolar amount of 100 mM NaOH solution. The pH was measured to be approximately 7. The turbid sodium oleate solution was complexed with 1 wt. % chitosan solution and spun to give one component of the fiber. The other component was spun from 0.2 wt. % TOCN dispersion and 1 wt. % chitosan solution.

**Reversible self-crimping driven by environmental conditions.** The shape change of bicomponent fibers, composed of a TOCN/Chitosan filament and a chitosan-oleate filament and prepared as described above, was investigated separately as a function of the surrounding relative humidity at constant temperature and as a function of temperature in dry conditions. The fibers were suspended vertically with the upper end attached to a substrate. The substrate was placed in an environmental chamber with a continuous supply of air of controlled humidity.

For cycling the environmental relative humidity no heating was applied and the temperature was constant at 20 °C. The relative humidity was cycled by supplying either dry (10 %) or humid (80 %) air into the chamber until the relative humidity was equilibrated at the given value. Similarly for cycling the temperature, the absolute humidity was kept constant constant corresponding to a relative humidity of 10 % at 20 °C, while the temperature was cycled between 25 and 70 °C. For this purpose the fiber was attached directly onto the surface of a hotplate which was turned on its side for the sample to hang freely. The hotplate was covered with a large Petri dish so that the air surrounding the sample was sealed from the surrounding conditions in order to minimize convection and keep the temperature around the fiber constant.

For both types of experiments, when the reading from the thermometer or the humidity sensor was equilibrated at the desired temperature or relative humidity, a photograph of the sample was taken with intervals of five minutes to ensure that no further shape change was observed between subsequent photographs. At this state the sample was assumed to be equilibrated and a photograph of
the equilibrated shape of the fiber was recorded, after which temperature or the relative humidity was changed to the other extreme.

To further demonstrate the possibility of reversible shape change of the bicomponent fiber driven indirectly by temperature changes, the fiber was placed at a moderate, constant absolute humidity corresponding to 30 % relative humidity at 20 °C. Subsequently, the temperature was cycled between 20 and 60 °C and photographs were recorded at both extremes as described above.

**Tensile properties.** The fibers were cut in pieces approximately 1.5 cm long and glued from both ends onto small pads of abrasive paper (ca. 3 mm x 4 mm) leaving a 10 mm long section of fiber available for standard tensile tests. The diameters of fibers were measured with an optical microscope (Leica MZ6 equipped with a Leica DFC420 camera) and the cross-section was assumed to be circular. The values of cross-sectional surface area were confirmed to be in good accordance with those obtained with SEM from cross-sectional views of fractured fibers. The prepared samples were equilibrated 48 h prior to measurement in 50 % relative humidity in a custom-made humidity chamber inside which also the tensile tester was located. For the measurement the samples were clamped to the tensile tester (Tensile/Compression Module 5kN with 100N load cell, Kammrath & Weiss GmbH) and stretched until fracture with a rate of elongation of 0.5 mm/min and original gauge length of 10 mm. Number of samples characterized and analyzed of each type of sample were four or five and the diameters of fibers tested were typically between 50 and 60 micrometers, see Table S1.

**Scanning electron microscopy (SEM).** Dry fibers were fractured in uniaxial tension as described in the section above for tensile properties, and subsequently attached to an aluminum stub with carbon tape and sputtered with a 5 nm platinum film (Emitech K100X). Imaging was carried out with a Zeiss Sigma VP scanning electron microscope at 1-2 kV acceleration voltage.

**Fourier transform infrared (FTIR) spectroscopy.** The spectra were recorded using a ThermoNicolet 380 spectrometer and ATR method on a diamond crystal. The spectra were collected from both fresh dried fibers and separately dried pure starting compounds.
Wide-angle x-ray scattering (WAXS). WAXS measurements were performed at the µSpot beamline at BESSY II (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung, Helmholtz-Zentrum Berlin, Germany). The energy exposure used was 15 keV using a silicon 111 monochromator and a beam size of 100 µm. Fibers were attached to sample holders and mounted on a motorized stage, enabling positioning of the fibers perpendicular to the beam path. Three points along the fibers were measured. Sample-to-detector distance was 299.5 mm, detector width 225 mm, number of pixels 3072 x 3072 and the 2θ scale was calibrated using a quartz powder sample as a reference.

After subtraction of air scattering from the diffraction pattern, azimuthal intensity distribution profiles for 20 values ranging from 18.2° to 18.6° (intensity maximum at 18.4°), wherein lies the (004) reflection, were integrated. The baseline of the azimuthal intensity profiles was further adjusted to zero for computation of two kinds of orientation parameters, the Hermans orientation parameter (S) and Degree of Orientation (Π), according to the equations 2 – 4:52,53

\[ S = \frac{3}{2} \langle \cos^2 \phi \rangle - \frac{1}{2} \]  
(2)

with

\[ \langle \cos^2 \phi \rangle = \frac{\sum_\theta I(\theta) \sin \theta \cos^2 \phi}{\sum_\theta I(\theta) \sin \theta} \]  
(3)

\[ \Pi = \frac{180° - \text{FWHM}}{180°} \]  
(4)

where FWHM is the full-width at half-maximum. It is important to note that the equations (2) and (3) hold for the (004) reflection which is a diatropic peak, but not for the (200) reflection which is a paratropic peak.54

Results and discussion

The feasibility of spinning a fiber from the complex interface of a TOCN dispersion and a polycation solution (i.e. PDADMAC or chitosan) was investigated for a variety of concentrations. The experiment consisted of bringing individual droplets of the two components in contact and
attempting to draw out a continuous wet filament from the formed interface. If a filament longer than 5 cm was possible to be drawn, the composition was considered feasible. The results are collected in Figure 2 and Table S2. The feasibility of fiber spinning requires the formed gel-like interface to withstand the stresses exerted on it during the spinning process. As highlighted with the striated region in Figure 2 the general trend was that the lower the concentrations of both components, the more likely the combination was to be spinnable. However, subjectively an optimal region for robust and reproducible IPC fiber spinning was found at TOCN concentrations in the range of 0.1 to 0.4 wt. % and polycation concentrations in the range of 0.1 to 2 wt. %, as highlighted by the hatched region in Figure 2. Factors that seemed to reduce the spinnability, and even impede it, were the excessive resistance to flow of either component and reduced bridging of the TOCN fibrils when the polycation-to-TOCN concentration ratio was high. Especially at high concentrations of TOCN the fiber spinning was either challenging or impossible due to gelation of the dispersion above a critical concentration. 

While the rheology of the polycation solutions (see Figure S3a) may be a factor affecting the spinnability of the composition, the shear stress and strain at which the TOCN gel yields was interpreted to be the most important parameter in this respect (see Figure S3b). Surprisingly, all tested combinations of TOCN with chitosan concentrations were found to be spinnable. This contrast between PDADMAC and chitosan may be due to stronger bonding of the chitosan to TOCN via sugar-sugar interactions in addition to the ionic interactions. For further investigations the TOCN concentration was chosen as 0.4 wt. % and both polycation concentrations were chosen as 1 wt. %.
Figure 2. Fiber spinning feasibility of various concentrations of TOCN and polycations. Feasible spinning conditions are shown for TOCN/PDADMAC with closed black circles and for TOCN/Chitosan with open red diamonds. Concentrations where spinning was not feasible are shown for TOCN/PDADMAC with black crosses. For TOCN/Chitosan all tested concentrations were found feasible for fiber spinning. The striated area roughly describes the concentration range where IPC spinning was considered most feasible. The hatched pattern further highlights the approximate region of concentrations that could be subjectively described as robust to spin good quality fibers repeatedly. The accurate values of concentrations can be found from Table S2 in the Supporting Information.

The IPC spun wet filaments were handleable, flexible and transparent. A typical filament was able to support at least 20 cm of its own weight, which was generally more than 95% water. The TOCN dispersion and the polycation solution alone were flowing fluids that could not be handled as such semi-solid objects as the wet filaments. This leads us to suggest, in accordance with most previous works, that at the interface of the two components forms a load-bearing strong skin that prevents diffusion of the polycation deep into the filament, resulting in a core-shell structure. The majority solid component was interpreted to be TOCN based on the color of the wet filament (see Figure 1c) when using dyed TOCN dispersion (blue) and polycation solution (pink, PDADMAC).
This interpretation is further supported by FTIR spectra of the dried fibers and their respective components in Figure 3, SEM images of the cross-section of the fiber later in Figure 5a,d, and radial intensity profiles of WAXS diffractograms in Figure S4.

The FTIR spectra of dried TOCN/polycation fibers and their respective components are shown in Figure 3. Notably the spectra of the fibers follow that of the pure TOCN very accurately, which suggests that the majority component of the dry fiber is TOCN. The presence of PDADMAC in the TOCN/PDADMAC fiber is, however, recognizable as a shoulder in the TOCN/PDADMAC spectrum in the 1460 to 1480 cm\(^{-1}\) region. Similarly, in the TOCN/Chitosan spectrum the dip observed for TOCN at 1090 cm\(^{-1}\) is weaker due to the signal from the chitosan component.

\[\text{Figure 3. FTIR spectra of dried TOCN/polycation fibers and of their respective components.}\]

Stretchability of the wet filaments was investigated as stretching is known to induce orientation and hence enhance anisotropic mechanical properties.\(^{17,61}\) The wet filaments were stretched at 4 % / min until rupture and the strain-at-break was recorded. The highest strains-at-break were reached with chitosan reaching 35 %, but a more repeatable 20 % was reached while using either PDADMAC or chitosan as the polycation. The relatively low stretchability of the wet filaments was interpreted to result from failure of the complex coacervate skin, where low reversibility of multivalent ionic crosslinks did not allow further stretchability. How to allow higher plastic deformability to the
coacervate skin is a question of interest to consider in further work, if higher stiffness and strength are to be attempted.

**Figure 4.** Polarized optical microscope images of a representative TOCN/polycation fibers with crossed linear polarizers at 45° angle to the axis of the fiber.

The thicknesses of the produced fibers were highly constant (see Figure 4 and S5 for qualitative reference) and repeatable under appropriate conditions. As shown in Figure S6 with the TOCN/Chitosan composition, linear control over the resulting dry fiber diameter was achieved by varying the diameter of the well used for the two solutions during the spinning process when the well diameter was 7 mm or less. When using a well with a diameter larger than 7 mm, the dry fibers showed diameters smaller than what would be expected from the linear relation observed at smaller well diameters. We expect that this is a result of a larger volume-to-surface ratio in the wet filament when increasing the diameter of the well. As suggested above in this work and in earlier literature, the as-spun, wet filament is supported mainly by the formed complex skin at the interface. Thus, the components that are not adsorbed to the inner surface of the skin of the wet filament are free to flow downwards due to gravitational forces as if in a soft capillary. However, if the diameter of the wet filament is very small, capillary forces overcome gravitational forces, thus prohibiting mass transport down the filament. The gel-like properties of the inner TOCN-phase are also likely to reduce the tendency of the core-component to flow.
The cross-sections of the fibers when observed in the SEM showed typically nearly circular and non-hollow morphology, see insets in Figure 5a,d (larger images available in Figure S7 in the Supporting Information). An important feature to note is that a very thin region along the surface of the fiber can be recognized to display a more smooth texture, a part of which is encircled in images in Figure 5a,d. We consider this to be composed of the polyelectrolyte complex skin and possibly a small amount of free polymer dried on the surface of the skin. The surface texture along the side of the fibers shows the typical surface structure reported for IPC spun fibers, often called the nervation/veining pattern, as shown in Figure 5b,c,e,f. Some orientation can qualitatively be estimated to occur as the surface textures appear more aligned when the fibers have been drawn by 20 % before drying, in Figure 5c,d, in contrast to no pre-stretching, in Figure 5b,e.
Figure 5. Close-ups of SEM images of the cross-sectional fracture surface of individual (a) TOCN/Chitosan and (d) TOCN/PDADMAC fibers. Insets in both images show the nearly circular shape of the cross-section, see large high-resolution versions of the inset images in Figure S7. Notice the encircled thin skin formed by the cationic polymers, now folding on the fracture surfaces. This can be best viewed in the electronic version of the Supporting Information in Figure S7. Side views of TOCN/Chitosan in (b) and (c), and TOCN/PDADMAC in (e) and (f) show the veining / nervation pattern of the surface. Fibers in (b) and (e) have not been stretched as wet filaments, whereas the fibers in (c) and (f) have been stretched 20 % prior to drying.
The mechanical properties of the dried filaments were characterized in uniaxial tension at a relative humidity of 50%. The representative stress-strain curves of fibers of TOCN with chitosan or PDADMAC with and without 20% stretching of the wet filament prior to drying are shown in Figure 6. The differences in mechanical properties between fibers made using either PDADMAC or chitosan were minor. The unstretched fibers typically displayed a Young’s modulus of approximately 15 GPa, a yield strength between 90 and 100 MPa and an ultimate tensile strength near 200 MPa. A slight difference in ultimate strain was observed as the unstretched TOCN/PDADMAC fibers ruptured at 7.6% and the TOCN/Chitosan fibers at 9.2%. The stretching of the wet filament had the expected effect of increasing the Young’s moduli (by 53 and 33% for TOCN/PDADMAC and TOCN/Chitosan, respectively), yield (36 and 39%) and ultimate tensile strengths (18 and 26%) while reducing the ultimate strain (46 and 41%) as has been observed in previous works. Comparing still to other CNF spinning methods, IPC spinning of TOCN/polycation fibers resulted in slightly higher ultimate strains and similar or somewhat reduced Young’s modulus, yield and ultimate tensile strengths when compared to those produced by extrusion and coagulation or dry spinning as reported in the literature (see Table S1). Fibers produced with microfluidics and oriented with flow-focusing show yield and ultimate tensile strengths notably higher, although Young’s modulus remains similar to that of IPC spun TOCN/polycation fibers. Orientation parameters computed from WAXS diffractograms suggest that the changes in the mechanical properties are due to increased orientation of the CNF in the fiber due to stretching prior to drying by 20% as the degree of orientation increased from 0.790 and 0.744 to 0.839 and 0.853 for TOCN/PDADMAC and TOCN/Chitosan fibers, respectively. These values are similar to those reported for CNF-based fibers prepared by extrusion into a coagulation bath. The WAXS diffractograms can be seen in Figure S8 and the orientation parameters are summarized in Table S3.

One important fact to note about the process used here is that there is no extrusion step, where the CNF gel is sheared by flow through a capillary, such as a syringe needle or tubing. Shearing has been
recognized to induce orientation in CNF dispersion.\textsuperscript{16,55} Without shear the fibrils orient only by lateral contraction during drying, by stretching when applied, and possibly by self-assembly at the interface. This would suggest that the combination of the IPC spinning with shear-induced orientation prior to complexation and stretching could lead to further advances in the anisotropic mechanical properties.

![Figure 6](image.png)

**Figure 6.** Tensile stress-strain curves for TOCN/PDADMAC (red) and TOCN/Chitosan (black) fibers with either 0 (dashed line) or 20 \% (solid line) stretch of the wet filament before drying. Characterization was carried out at 50\% relative humidity. For averages and standard deviations of mechanical properties see Table S1 in Supporting Information.

Spinning of bicomponent filaments is next addressed using model compounds. A tightly bound, helical and strictly compartmentalized hybrid structure was formed when two separate polyelectrolyte complex filaments were spun simultaneously and twisted together to dry (see Figure 7). One filament was composed of TOCN complexed with chitosan and the other was composed of chitosan complexed with a mixture of microparticles with PSS to allow differentiation between compartments. Constituents of the latter filament were selected for illustration purposes; i.e. for highlighting the well-compartmentalized and helical structure of the formed hybrid filament. The facile preparation of such structures is expected to open avenues of research for environmentally friendly preparation of advanced compartmentalized functional fibers.
Figure 7. SEM micrographs of a loosely helical bicomponent fiber produced by simultaneous spinning of two polyelectrolyte complex filaments and twisting them together to dry. One compartment is composed of TOCN complexed with chitosan and the other is composed of a mixture of microparticles and PSS complexed with chitosan. The microparticles are used in order to visualize the compartmentalization along the fiber.

On the other hand, Figure 8a shows the reversible shape-change of a slightly twisted bicomponent fiber composed of a TOCN/Chitosan filament and a chitosan-oleate filament upon changing the relative humidity at constant temperature. When the bicomponent fiber is cycled between 10 and 80 % relative humidity a small, yet observable change in the shape of the fiber occurs reversibly. The behavior is interpreted to result from selective absorption and desorption of water to and from the more hygroscopic TOCN/Chitosan component of the fiber.\(^{62}\) The possibility of a shape change driven by differential thermal expansion was also considered, but this was not observed upon cycling of the temperature in dry conditions (see Figure S9 in Supporting Information).\(^{8,63}\) But interestingly, thermally reversible shape change was achieved indirectly as the humidity absorption changes as a function of temperature (see Figure 8b). These results are taken to serve as preliminary evidence of the potential of IPC spun reversibly crimping bicomponent fibers. The authors recognized that further
optimization of the described structure does not fit the scope of this work and warrants further research for textile applications and even for soft robotics.

**Figure 8.** Photographs of reversible shape change of a wound bicomponent fiber of chitosan-oleate fiber wound with a TOCN/Chitosan fiber upon cycling of environmental conditions. (a) Cycling of relative humidity between 10 and 80 % at a constant temperature of 20 °C leads to a small, yet discernible and reversible, change in the shape of the fiber. This serves as preliminary evidence of the potential of such fibers to undergo humidity-driven reversible crimping. (b) Thermoreversible shape change caused indirectly via temperature dependent humidity absorption. The temperature is cycled between 20 and 60 °C at a constant environmental absolute humidity corresponding to a
relative humidity of 30 % at 20 °C. The contrast has been increased artificially for clarity. The length of the fibers shown is approximately 20 cm and diameter 50 µm.

**Conclusions**

Aqueous interfacial polyelectrolyte complex spinning of TOCN-based fibers was demonstrated using IPC of TOCN with polycations, namely chitosan and PDADMAC. Upon contact of the TOCN dispersion and the polycation solution a polyelectrolyte complex interface formed rapidly between the two fluids. This polyelectrolyte complex interface was shown to be spinnable from a variety of concentrations. Reduced bridging of TOCN-fibrils by high polycation-to-TOCN ratio or excessive resistance to flow (i.e. high viscosity or gelation) by the constituent phases were interpreted as reasons preventing fiber spinning. Using a vertical arrangement of the two fluid phases, where TOCN phase was underneath, resulted in wet filaments composed mostly of TOCN in water and an interfacial, thin skin on the periphery composed of the polyelectrolyte complex of TOCN and the polycation. The skin was interpreted to be the main load bearing component in the formed wet filament. These wet filaments were found to be stretchable up to 35 % prior to drying. After drying the fibers showed non-hollow, dense and circular cross-sections when observed in the SEM.

The uniaxial tensile mechanical properties obtained with the fibers spun using IPC were of the same order as comparable CNF and TOCN fibers described in the literature using extrusion and coagulation. Taken the very simple process, the present interfacial polyelectrolyte complex spinning could allow a useful platform for optimization. Stretching of the wet filament prior to drying resulted in a similar change in mechanical properties as previously reported for comparable systems, namely with an increase in Young’s modulus, yield stress and ultimate tensile strength, accompanied with a reduction of elongation-at-break.

Importantly, the present concept allows a facile extension to scalable multicomponent fibers without need to design extrusion nozzles. Fabrication of helically wound TOCN-based bicomponent fibers was demonstrated. The bicomponent fibers were strictly compartmentalized and the different
components were tightly bound to each other. Selective incorporation of a more hydrophobic component into one of the compartments and cycling of relative humidity at constant temperature led to a reversible deformation of the fibers. Similarly, due to thermally dependent humidity absorption, also thermoreversible shape changes were shown.

The authors believe that the approach presented here could open feasible routes for achieving high performance TOCN-based fibers, and advanced functional fibers based on the diverse possible compositions of the bicomponent fibers demonstrated.

**Supporting Information Available**

Supporting information contains additional material about the morphological and rheological properties of the TOCN material, the feasibility investigation of IPC spinning of TOCN/polycation fibers, effect of well diameter used for IPC spinning on the diameter of the resulting dry fiber, WAXS diffractograms of TOCN/polycation fibers, orientation parameters, numeric values of mechanical properties with comparison to the relevant literature, evidence for the negligible role of temperature on the reversible shape change of the fibers. Supporting information contains also videos demonstrating the IPC spinning of the fibers. This material is available free of charge via the Internet at http://pubs.acs.org/.

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