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Coaxial spinning of all-cellulose systems for enhanced toughness: filaments of oxidized nanofibrils sheathed in cellulose II regenerated from a protic ionic liquid

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ABSTRACT: Hydrogels of TEMPO-oxidized nanocellulose (TO-CNF) were stabilized for dry-jet wet spinning using a shell of cellulose dissolved in 1,5-diazabicyclo[4.3.0]non-5-enium propionate ([DBNH][CO₂Et]), a protic ionic liquid (PIL). Coagulation in an acidic water bath resulted in continuous core-shell filaments (CSF) that were tough and flexible: average dry (and wet) toughness of ~ 11 (2) MJ m⁻³ and elongation of ~ 9 (14) %. CSF morphology, chemical composition, thermal stability, crystallinity, and bacterial activity were assessed using scanning electron microscopy with energy dispersive X-ray spectroscopy, liquid-state nuclear magnetic resonance, Fourier transform infrared spectroscopy, thermogravimetric analysis, pyrolysis gas chromatography-mass spectrometry, wide angle X-ray scattering and bacterial cell culturing, respectively. The coaxial wet spinning yields PIL-free systems carrying on the surface the cellulose II polymorph, which not only enhances the toughness of the filaments but facilitates their functionalization.

INTRODUCTION

Material industries are facing a critical period because they must comply with the current demands of advanced and smart production, with new functionalities and minimum environmental impact. Thus, under the guidelines of sustainable development, associated manufacturing needs to

apply a strategy based on the principles of the circular economy. Bio-based materials and, in particular, cellulose nanomaterials (CNMs) have become excellent candidates in this regard, as they could partially replace materials based on non-renewable resources. Indeed, CNMs enable high-performance, green functional materials with a broad spectrum of applications, e.g., electronics, biomedical and tissue engineering scaffolds, coatings, food, textiles, and even in daily use goods ¹⁻⁸.

Cellulose resources have the potential of becoming a platform to develop novel CNMs with high mechanical performance since nanocellulose, in its cellulose I crystalline phase, possess an elastic modulus of about 150 GPa and 18-50GPa in the longitudinal and transverse directions, respectively^{9,10}. The regioselective C6 oxidation of nanocellulose fibers can be additionally catalyzed by the use of the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) nitroxyl radical to produce hydrogels with high transparency¹¹, an extensive degree of fibrillation ¹², and low cytotoxicity ¹³. These TEMPO-oxidized cellulose nanofibers (TO-CNF) are suitable for applications in diverse fields such as packaging ^{3,4,14-16}, textiles ¹⁷⁻²⁰, biosensing and bioelectronics ^{21,22}, fire retardancy ²³, wound dressing and cell delivery ²⁴⁻²⁶, among others³.

Despite its excellent mechanical properties, materials derived from nanocellulose and, in particular, TEMPO-oxidized nanocellulose, have several drawbacks inherent to its nature. For instance, these materials are mostly hydrophilic owing to the high concentration of hydroxyl and carboxylate groups; this causes mechanical instability of the formed materials under wet/humid conditions, and exhibit rather low aspect ratios compared to dissolved polymers. The limited aspect ratio makes it difficult to create oriented structures of cellulose nanofibrils by drawing ^{27,28}. Many attempts to overcome hydrophilicity challenges have been made through approaches such as surface stabilization ²⁹, cross-linking ^{14,29,30}, and hydrophobization ³¹; moreover, composites and

blending with different materials have been proposed to improve drawability using polymers (polyvinyl alcohol, polylactic acid, polypropylene)³², gelatin³³, silk protein³⁴, phenolic resins³⁵, or oxidized starch³⁶. Nevertheless, until now such modifications imply the permanent addition and mixing of nondegradable components or molecules different to cellulose or its derivatives. Since traditional wood pulp producers are the most likely industrial complexes utilized for the bulk production of CNMs³⁷, a continuous filament entirely composed of cellulose is desirable, offering a broad spectrum of functionalities and new environmentally friendly materials³.

In the present study, the processability of a TO-CNF hydrogel is enhanced by enclosing it inside a supportive shell of a cellulose solution. This approach even allows accessing dry-jet wet-spinning, which has previously been challenging to accomplish for TO-CNF¹⁹, unless nanocellulose is used as a minor additive in polyvinyl alcohol³². Herein, the simultaneous extrusion of dissolved cellulose and TO-CNF hydrogels²⁸ leads to the production of core-shell filaments (CSF) with an external regenerated cellulose shell and an inner layer (core) composed exclusively of TO-CNF material. The proposed method is expected to provide at least the following three advantages and characteristics:

(1) Nanofiber alignment: the shear forces during the dope extrusion contribute to the alignment of the nanofibers, as discussed extensively previously^{19,27,28}. Besides, the employment of a stabilizing shell dope and an air gap allows for drawing, which creates extensional forces that can orient the structure even more effectively^{27,38,39}. Generally, the alignment of CNF plays a crucial role in improving mechanical properties³⁰; thus, conforming well-aligned filaments from nanocellulose has the potential to enhance the strength and toughness²⁸. In this sense, Mittal et al.^{38,40} have recently obtained fibers by extrusion and flow-assisted techniques and suggested, based

on Young's modulus (86 GPa) and tensile strength (1.57 GPa), that the CNF exhibited enhanced mechanical properties as compared to cotton fibers and other non-cellulosic biopolymers.

(2) A broad range of applications: the production of filaments with several layers by the simultaneous spinning of different materials brings more opportunities for functionalization compared to homogeneous filaments, having in mind specific uses¹⁹. For instance, it is possible to functionalize the outer and inner layers separately. In general, the coaxial wet spinning allows for the use of an inner core material that is not typically spinnable on its own, owing to the confinement within the shell. Thus, this system is not only limited to TO-CNF hydrogels but can be applied to stabilize also other structural or functional materials with poor spinnability. This technique has been used recently for producing yarn supercapacitors for high energy density, and safe wearable electronics^{41–43}, absorbent nanofibrils⁴⁴, multifunctional resistive-heating and color-changing filaments⁴⁵, flame retardant fibers²³ and conductive cable fibers made with carbon nanotubes⁴⁶. Potentially, it can even be used for smart textiles production⁴⁷.

(3) Use of recyclable IL: regenerated cellulose spinning is performed industrially by the dissolution of the pulp and regeneration using, for example, the well-known Viscose or Lyocell process or others which may present issues related to toxicity, explosion/flammability, hazards and non-recyclable chemical reagents/byproducts^{17,48–52}. From 2002, Ionic Liquids (ILs) were described to dissolve cellulose⁵³, and ever since ILs are increasingly investigated for the production of biopolymer-based composite materials and regenerated fibers^{53–60}. The interest in ILs relies on their flexibility as solvating agents, low explosive hazard (low volatility), and tolerance to many chemistries, as compared with the current industrial processes solvents (i.e., sodium hydroxide, urea, carbon disulfide and N-methylmorpholine-N-oxide (NMMO))^{53–60}. Recently, a new class of ILs has been utilized for the dry-jet wet spinning of cellulose

multifilaments, this process, Ioncell™^{61–64}, is based on the family of Protic acid-base conjugate Ionic Liquids (PILs), which are relatively simple to synthesize and possible to recycle by distillation. The distillation is carried out under vacuum conditions, establishing a temperature-dependent, conjugated–unconjugated acid-base equilibrium for the ionic species precursors, allowing a recovery up to 99% of the PIL^{65–67}.

The work at hand explores the potential of the Ioncell™ technology for the coaxial spinning with TO-CNF to obtain stabilized filaments or fibers with enhanced mechanical properties in dry-jet wet-spinning conditions. This CSF may be suitable for applications in fields such as packaging, textiles, biomedical, flexible electronics, among others^{3,7}. Therefore, the present study focuses on the spinnability of CSF composed of 2 wt% TO-CNF hydrogel (core) and a cellulose solution in PIL (shell), illustrating their synergistic effect on mechanical performance. The dopes solid content concentrations were selected according to previous studies, showing optimal rheological properties and spinnability behavior at 2 wt% solid content^{27,28,44,68}. Furthermore, the morphology, chemical composition, thermal stability, and antibacterial activity of the produced filaments are discussed, with reference to the spinning dopes used.

MATERIALS AND METHODS

Prehydrolysis Kraft birch pulp from Stora Enso (Enocell™ was used for dissolution into the PIL for shell formation, and Kraft bleached birch pulp from a Finnish pulp mill UPM (kappa number 1; DP 4700; fines-free) was used to prepare the TO-CNF hydrogels for core formation. The PIL superbase precursor 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, CAS No. 3001-72-7, purity = 99%, Fluorochem U.K) and propionic acid (CAS No. 79-09-4, purity > 99%, Sigma Aldrich) were used to synthesize the PIL [DBNH][CO₂Et] following a procedure reported elsewhere⁶⁹. Milli Q® type

I water from Merck was used for the nanofibers suspension and wet spinning coagulation baths. Poly(ethyleneimine) solution (PEI), used for fiber attachment in AFM analysis, was prepared from Sigma Aldrich PEI 50 % w/v commercial reagent (CAS No. 9002-98-6). Accordingly, the birch pre-hydrolysis kraft pulp was dissolved and regenerated using the PIL [DBNH][CO₂Et] in a modified setup to Ioncell™ processing conditions^{61–66}. The ([DBNH][CO₂Et]) has shown to be a cellulose-dissolving IL with no significant toxicity issues^{70–72}. However, some cellulose-dissolving ILs have shown significant toxicities; mainly those long hydrophobic side-chain substituted ILs that are capable of interacting with cell membranes and can act as neurotoxins⁷³. In addition, ILs are currently rather expensive chemicals and must be recycled to high degrees. Therefore, the presence of any residual IL in the filaments should be avoided. Regarding the toxicity of TO-CNF filaments, as mentioned before, they have shown low cytotoxicity compared to unmodified nanocellulose fibers¹³; additionally, a previously reported study⁷⁴ about fibers anionic surface functionalities using the embryonic zebrafish, revealed that the surface chemistry in CNF and TO-CNF had a minimal influence on the overall toxicity of nanocellulose materials.

TO-CNF preparation. TEMPO-oxidized cellulose nanofibrils were prepared using the following reagents acquired from Sigma-Aldrich: 2,2,6,6-Tetramethylpiperidine-1-oxyl or TEMPO (CAS No. 2564-83-2, purity > 98%), sodium bromide NaBr (CAS No. 7647-15-6, purity > 99%), sodium hypochlorite NaClO (CAS No. 7681-52-9, reagent grade), sodium hydroxide NaOH (CAS No. 1310-73-2, purity > 99%). The TEMPO-oxidation of the cellulose fibers was made following the procedure described elsewhere^{75–79}. In particular, the procedure reported by Orelma et al.⁸⁰ has been followed, starting from milled and sieved 45g cellulose. The original pulp hard sheets were milled using a Wiley mill with a 1 mm sieve; the pulp was then oven-dried to a constant weight at 105°C. The resulting fibers were washed and filtered several times until neutral

pH. For each gram of dry pulp, 0.13 mmol TEMPO and 4.65 mmol NaBr were dispersed in deionized water for 3.7 L total volume and then stirred until complete dissolution. The pulp was added to the previous solution and mixed for one and a half hours with a magnetic stirrer (~700 rpm) adjusting pH to 9 (with NaOH) and then dissolving 5 mmol/g(dry_pulp) of NaClO in the solution. The pH was then adjusted to 10 by the dropwise addition of NaOH 0.5M solution. After the addition of NaClO, the reaction proceeded for 90 minutes at room temperature until the pH was stable (when pH remains constant, the reaction was finished). Finally, 10 ml of ethanol were added to stop oxidation, and the treated pulp was filtered, water-washed three times, and 1 wt% solid content samples were prepared in sodium form, adjusting the pH=9 by the addition of NaOH. Lastly, the oxidized pulp was homogenized in a microfluidizer (1 pass at 2000 bar, Microfluidics M-110P™, International Corporation, USA). TO-CNF fibers solid content was above 2 wt%; the final solid content was then adjusted by vacuum evaporation at 60°C and 200 mbar. After this step, the morphology and charge of TO-CNF fibers were characterized by AFM and conductometric titration respectively.

Cellulose dissolution in ([DBNH][CO₂Et]). Birch pre-hydrolysis kraft pulp hard sheets were milled using a Wiley mill with a 1 mm sieve; the fluffy pulp was then oven-dried to a constant weight at 105°C and stored in a desiccator. The ([DBNH][CO₂Et]) PIL was dried at 80°C under vacuum (200 mbar). The dissolution was carried out in a hot plate magnetic stirrer at 400 rpm and 80°C. Previous the cellulose addition, the PIL was heated to 80°C before the gradual addition of cellulose. The complete dissolution of 2 wt% of cellulose was carried out for 2 hours, reaching a clear, viscous solution.

CSF spinning. Previously prepared TO-CNF hydrogel (2 wt%) dope and the dissolved cellulose dope (2 wt %) were separately homogenized and de-aired in a planetary centrifugal mixer

(THINKY AR-250, JAPAN), and subsequently transferred to the pumping syringes (Henke Sass Wolf, 60ml, Luer lock, soft jet ®). The wet spinning system (Figure 1) includes one stainless steel coagulation bath (9 cm x 9cm x 62 cm), two pumps (CHEMYX, Model NEXUS 6000, and CHEMYX, Model FUSION 6000, USA) for syringes connected to one coaxial dispensing needle (Ramé-Hart Instrument CO, shell needle gauge 15 outer diameter $\Phi_o = 1.83$ mm, and inner diameter $\Phi_i = 1.37$ mm, and core needle outer diameter $\Phi_o = 0.889$ mm, and inner diameter $\Phi_i = 0.584$ mm). The spinning dopes were injected into the regeneration bath, leaving an air gap of 2 cm, allowing for possible cellulose orientation²⁰. The regeneration occurs in acidic conditions (pH = 2, HCl), thus promoting the protonation of TO-CNT and thus facilitating its coagulation, according to previous studies^{19,30}.

The system pumps were operated at a steady flow of 2 mL/min, and 0,6 mL/min for shell and core syringes, respectively and the filament take-up speed over the stainless steel winder (6 cm) was 67,5 cm/min giving a constant draw ratio of $Dw = 1.15$. Figure 1 illustrates the dry-jet-wet spinning setup used.

Figure 1. Coaxial dry-jet-wet spinning setup composed of syringes pumps, coaxial needle, coagulation bath, silicon roller, and stainless steel winder.

Four types of filaments were prepared: (1) **sample SF (shell)**: cellulose+PIL dope shell filament with a hollow core (instead of a core dope, acidic water was pumped through the inner needle), (2) **sample CF (core)**: TO-CNF single-component filaments (without cellulose+PIL shell component), (3) **sample CSFuw (core-shell, unwashed)**: cellulose+PIL dope shell filament with TO-CNF core (filament not washed before drying), and (4) **sample CSFw (core-shell, washed)**: cellulose+PIL dope shell filament with TO-CNF core (post washed with water to remove PIL traces before drying). These four samples were drawn over an air gap into acidic water at the same coagulation bath conditions ($\text{pH} = 2$, $T = 20^\circ\text{C}$, $D_w = 1.15$). After collecting the filaments (with or without additional washing), they were dried at room temperature for 12 h inside a fume wood. Four different filament samples were spun and tested. Table 1 present the sample names and their process conditions.

Table 1. Dry-jet wet spun samples prepared

Sample name	Description	washing with water (2 h)
SF	Shell (Ioncell™)	yes
CF	Core (TO-CNF)	no
CSFuw	CSF not washed	no
CSFw	CSF washed	yes

Table 1 presents the dry samples considered in this work as explained before. The sample CSFuw prepared with the combination of samples SF and CF exhibited a yellowish appearance, thus indicating a presence of residual PIL. Therefore the sample CSFw was prepared, including two hours washing step with deionized water before drying. After the drying step at room temperature, the samples were vacuum dried overnight (60°C, 200 mbar), and their dimensions and surface properties were studied.

Conductometric titration. TO-CNF hydrogel charge was measured by conductometric titration according to standard SCAN-CM 65:0278. The titration was performed using an automatic titration device (Methrom 751 GPD Titrino and Tiamo 1.2.1 software). The titration data were processed with OriginPro 2018b software (OriginLab Corporation, MA, USA). A blank sample (water) was used to exclude systematic error.

Atomic Force Microscopy (AFM). The TO-CNF morphology was analyzed using AFM (Digital Instruments Multimode Atomic Force Microscope, Bruker, UK). The samples were deposited on a silica wafer using a self-prepared solution of 25 mg/ml Poly(ethyleneimine) solution (PEI) and the spin coating technique for a homogeneous distribution on the wafer surface. The sample preparation and analysis were made following reported procedures^{9,81,82}. The analysis was carried out at room temperature (23°C), operating in tapping mode.

Optical Microscope. Optical light microscope images were obtained using a Leica DM 750 Microsystems® microscope, Germany, with an ICC50HD camera. The samples were placed between two glass slides, and the light was adjusted using an external source of light, Lampe Fiber Optic Fi. L-100.

Fourier-Transform Infrared Spectroscopy (FT-IR). FT-IR was performed using a Thermo Fisher Scientific Nicolet Avatar 380 FT-IR spectrometer, in transmittance mode. A bundle of solid filaments was prepared by gluing the extremes with epoxy-resin. Samples were vacuum dried for 16 h before the test. Spectra were acquired for 32 scans in the wave number range from 500 to 4000 cm^{-1} with a resolution of 2 cm^{-1} .

Scanning Electron Microscopy with Energy-Dispersive X-ray spectroscopy (SEM-EDX). Surface morphology and composition of samples were analyzed using SEM-EDX (JEOL JSM-7500FA, Germany) at the Nanomicroscopy Center in Aalto University, Finland. The SEM was equipped with four detectors, including the EDX detector, and possess a resolution of 0.6 - 1.4 nm at 30 - 1 kV. Before imaging, the samples were vacuum dried overnight, frozen, and fractured using liquid nitrogen (for measuring cross-section areas). Finally, the samples were fixed to SEM aluminum stubs using carbon tape and subsequently sputtered using a sputtering device (Emitech K350, Quorum Technologies Ltd, UK) operating at 220 v -50 Hz – 10 A for 1.5 min with an Au/Pt coater disc obtaining layers of ~ 10 nm Au/Pt over the samples. The images were analyzed using SEM EDX software and ImageJ⁸³.

Tensile Test and Morphology. CSF mechanical properties were studied using a Universal Tensile Tester Instron 4204, 1kN load cell, test speed 20 mm/min. Samples were prepared and analyzed according to the ASTM D3822/ D3822M standard, and these were stored before the test in a conditioned room at 50 % R.H at 23°C. For the tests, 30 mm long filaments were cut and

fixed to the Instron clamps using printer paper to hold the sides of the filaments and finally gluing them with Loctite® super glue, and this was to avoid slippage during the test. The thickness of wet samples (immersed in deionized water overnight) was measured using a micrometer (Lorentzen and Wettre Micrometer, Sweden) and repeated ten times in different positions. For the dry samples, filament diameters were measured from SEM images. The equivalent circular diameters of dry filaments were calculated from cross-sectional areas measured from SEM images, while for wet samples, they were measured with the micrometer assuming the filaments possess a circular cross-section. Six replicas of each sample were taken for the mechanical tests, and the results were averaged. The linear density was calculated after measuring the weight of a known length of filament, and from the titer information, the apparent density was calculated, assuming that each filament has cylindrical morphology. The apparent porosity was calculated with reference to the reported density consequently (1.55 g·cm⁻³)⁸⁴ of pure or crystalline cellulose I. Equation 1 and equation 2 were used to calculate the apparent densities and porosities, respectively.

$$\rho_a = \frac{400 \times \text{titer}}{\pi \times D^2} \quad (1)$$

$$\text{Porosity} = \frac{\rho_a}{\rho_c} \times 100 \quad (2)$$

Where, ρ_a is the apparent density ([=] g·cm⁻³), the *titer* is in tex (g·1000 m⁻¹), D is the filament diameter in microns, and ρ_c is the crystalline cellulose density.

Wide Angle X-ray Scattering (WAXS). After the drying step, samples were stored in a desiccator and collected to form bundles which were next press to form thin films using a manual pellet press (Specac, UK). The thin films X-ray diffractograms were acquired and recorded in a Bruker AXS model D4 Endeavor diffractometer using monochromatic Cu K α radiation (λ = 0.15418 nm). The signal was generated at 40 kV and 20 mA. The intensities were measured in the range of 5° < 2 θ < 90° with a step size of 0.02° and a scan rate of 1 s/step. Crystallinity index,

crystals type, and crystals size were evaluated for all samples. The crystallinity index was determined by the method proposed by Segal et al.⁸⁵ (Eq. 3) and, whereas the apparent crystallite size was calculated using Scherrer's equation⁸⁶ (Eq. 4).

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \quad (3)$$

$$\tau = \frac{K \times \lambda}{\beta \times \cos(\theta)} \quad (4)$$

Where I_{200} and I_{am} are the intensities of the (200) plane and amorphous phase, respectively; K is the Scherrer's constant (0.94); λ is the wavelength in nm; β is the full width at half maximum intensity (FWHM), and θ is the plane angle in radians.

The Z-function of Wada et al.⁸⁷ was used to determine the crystal structure (I_α or I_β) based on the d-spacings of the (110) and ($\bar{1}\bar{1}0$) peaks.

Thermogravimetric Analysis (TGA). The thermal stability of the samples was studied using thermogravimetric analysis, with a Cahn-Versatherm thermogravimetric analyzer (sensitivity of 0.1 μ g). Around 20 mg of each sample was placed in thermogravimetric analysis, to be investigated under Nitrogen flow (50 ml/min) The programmed temperature procedure is maintained at 35°C for 35 min, then increased to 600°C (ramp rate 10°C/min) and finally kept at 600°C for 30 min.

Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC/MS). The chemical composition of samples was investigated by Pyrolysis Gas Chromatography-Mass Spectrometry, using a CDS Analytical Pyroprobe (5200 HPR) coupled to a Perkin Elmer Gas Chromatography (Clarus 690) - Mass Spectrometry (Clarus SQ8T) system. Two milligrams of each sample were pyrolyzed for 12 s, using a sequential pyrolysis procedure at different temperatures (200°C, 300°C, 400°C, 500°C and 600°C) on the same sample.

Pyroprobe equipment was configured as follows: Probe initial temperature (50°C); Probe ramp rate (10°C/ms); Probe final temperature (Desired pyrolysis temp: 200°C, 300°C, 400°C, 500°C or 600°C); Transfer line to GC/MS (280°C); Trap rest temperature (50°C); Trap desorb temperature (280°C); Trap desorb time (3 min). Chromatographic separation of chemical species was performed with an Elite 1701 (30 m × 0.25 mm ID × 0.5 µm DF) capillary column. Programmed GC oven temperature maintained at 40°C for 5 min, then increased to 220°C at 5°C/min. The injection port was kept at 150°C, using 1 ml/min of carrier gas and a split of 50 ml/min. The Clarus SQ8T was operated in SCAN mode ($m/z = 10\text{--}300$ amu); electron energy at 70 eV; transfer line 200°C; ion source at 150°C; and quadrupole mass detector on electron impact ionization mode. High purity helium was used as a carrier and purge gas in the Py-GC/MS equipment. Chromatographic data were processed using Turbo Mass (v6.1.2.2048) and mass spectra laboratory databases (NIST 2017 v2.3).

Liquid-state Nuclear Magnetic Resonance (NMR). The chemical composition of the filaments was studied using liquid-state NMR on the filaments dissolved in the ionic liquid electrolyte, tetrabutylphosphonium acetate ([P₄₄₄₄][OAc]): DMSO-d₆ (1:4 w/w)⁸⁸. To prepare the samples for NMR analysis, typically 50 mg of sample is added to a sealable sample vial and made up to 1 g by addition of stock [P₄₄₄₄][OAc]:DMSO-d₆ (1:4 w/w) solution. The samples were magnetically stirred at RT until they go clear; this typically was over a 1 h period. If the samples did not go clear during that period, the temperature was typically increased to 60 °C. All NMR experiments were recorded on a Bruker AVANCE NEO 600 MHz spectrometer equipped with a 5 mm SmartProbe™. Standard ¹H and diffusion-edited ¹H experiments)⁸⁸ were recorded for all samples to help compare filament composition and impurities. Diffusion-editing has the effect of editing out the fast diffusing species from the spectrum, *i.e.* ionic liquid, and DMSO, but retain the

slow-diffusing polymeric species. ^{13}C and multiplicity-edited heteronuclear single quantum correlation (HSQC) NMR experiments were recorded for the CSFuw sample to help identify the presence of PIL in the sample. NMR data was initially phased and calibrated in Topspin 4. Final images were prepared using Mnova 10 and Powerpoint.

Bacterial Activity. Biomedical and food packaging applications are most relevant to CNMs. In related uses, one problematic bacteria is the highly pathogenic *Staphylococcus aureus*. *S. aureus* is a facultative anaerobe that causes nosocomial diseases worldwide, with high rates of morbidity and mortality ⁸⁹; additionally, *S. aureus* toxins can cause secondary gastrointestinal infection ⁹⁰. Thus, this bacteria was selected for testing growth and biofilm-forming ability. Model films were produced by vacuum filtration ⁹¹ for antibacterial activity, and regenerated cellulose with PIL model films were produced by casting ⁹².

Bacterial cell culture. Tryptone soy agar (TSA) and tryptone soy broth (TSB) were purchased from Becton Dickinson (Heidelberg/Germany). Double distilled water was employed in all media preparations. The bacterial strain used was *Staphylococcus aureus subsp. aureus* Rosenbach (ATCC® 25923). The experimental procedure was performed under sterile conditions in a laminar airflow chamber (Biobase BBS-V1800). The bacterial growth rate was assessed in triplicate trials conducted using 90 mm-Petri dishes with 15 mL of sterile TSA medium, inoculated by spreading 250 μL of an *S. aureus* culture (previously grown in TSB, 0.5 McFarland). In the center of the inoculated plates, a 2.5 cm diameter sterilized disc (121 °C, 15psi, 20 min), was placed, corresponding to each cellulose-derived nanomaterial film. The plates with the film samples were incubated for 12 h at 35°C and then checked to verify bacterial growth under each nanomaterial.

Biofilm formation assay. Five colonies of *S. aureus* of a one day grown TSA culture plate were transferred to sterile TSB medium and incubated for 12h at 37°C, for obtaining a bacterial liquid

culture. Sterile TSB was inoculated with aliquots of 750 μ L from this bacterial liquid culture, containing a sample of 1 cm^2 piece of the sterilized model film sample (121 $^{\circ}\text{C}$, 15psi, 20 min).

These bacterial-immersed nanomaterial pieces were incubated for 16 h at 37 $^{\circ}\text{C}$ under continuous agitation (100rpm). The film pieces were transferred and washed three times, with fresh sterile water each time (30 mL, manual agitation), to discharge the planktonic bacterial cells that were loosely adhered to their surfaces. Finally, the film pieces were placed in sterile flasks with 20 mL of physiological saline serum. They were then sonicated (ELMA E 60 H sonicator, UK) for 5 minutes at 37 kHz and 150 watts, in a cold water bath ⁹³.

The bacterial cell count was performed by serial dilutions from the flasks suspensions, transferring them to TSA for quantification, after overnight incubation at 37 $^{\circ}\text{C}$. Two independent series of dilutions with physiological saline serum were performed from the sonicated flasks suspensions. After incubation, the bacterial colony-forming units (CFU) per 1 cm^2 of the respective cellulose-derived nanomaterial, was recorded.

Proper sterility controls were run in parallel, i.e., 1 cm^2 piece of the sterilized (121 $^{\circ}\text{C}$, 15 psi, 20 min) model film, was immersed in sterile inoculum-free TSB, and further processed accordingly. Differences between the samples in terms of their bacterial count was assessed using Tukey's test ($P < 0.05$). These analyses were performed with the InfoStat/L software package Statistica 7.0 (Stat Soft Inc., Tulsa, OK, USA).

RESULTS AND DISCUSSION

TO-CNF properties. AFM morphology and conductometric surface charge were assessed to identify if the TO-CNF fibers were properly produced, and to discriminate these fibers from common CNF. Furthermore, morphology and surface charge densities are key properties to

determine self-assembly behavior, and rheological properties in suspensions (e.g., high surface charge density will increase colloidal stability and reduce the energy required for mechanical defibrillation)⁷. TO-CNF was characterized after processing in a microfluidizer, figure S1 (see supporting information) presents an AFM image of TO-CNF and the corresponding hydrogel conductometric plot obtained after titration. Figure S1a indicates that the produced TO-CNF possess a high polydispersity in length and width. Fibrils of several microns in length and a width of 24.5 (6.5) nm and aspect ratio > 100 are similar to previously reported TO-CNF analyzed by AFM and Transmission Electron Microscopy (TEM)^{8,9,11}. Figure S1b presents conductometric titration data for the TO-CNF hydrogels. The final charge value obtained after water blank correction was 1.36 (0.05) mmol_{COOH}/g_{pulp}, comparable to other reports indicating typical carboxylate group contents ≤ 1.7 mmol/g⁷⁵⁻⁷⁹.

CSF morphology. The surface morphology of the filaments, their length, and cross-section areas were analyzed with SEM and optical microscopy. Figure 2 shows SEM images of dried samples (Figure 2a-2d) and the corresponding optical microscope images of wet samples (Figure 2e-2h).

Figure 2. Morphology of spun filament samples assessed by SEM: a) SF, b) CF, c) CSFuw, d) CSFw; and the corresponding optical microscopy images of wet filaments: e) SF, f) CF, g) CSFuw, h) CSFw. The yellow lines indicate examples of points at which the cross-section area and diameters were measured. SF filaments were prepared by extrusion coagulating solvent in the inner section of the needle and cellulose dissolved in PIL in its outer shell (forming a hollow filament that partially collapsed under SEM observation).

Figure 2 includes the morphology of the dry filaments (Figures 2a-2d) as well as their optical microscope images in the wet condition (after soaking in deionized water overnight, Figures 2e-2g). From Figure 2, it is observed that filament shape and dimension strongly depend on the composition of the dope and whether the filament was wet or dry. TO-CNF filaments (CF) with diameters $\sim 35 \mu\text{m}$ swelled extensively ($420 \mu\text{m}$, a 12-fold increase in diameter) after soaking in water overnight (Figures 2b, 2f). TO-CNF filaments displayed irregular surfaces with flocculated TEMPO-oxidized nanofibrils (Figure 2b); this behavior indicates a poor fibrils alignment, opening the door in future works for optimizing fibers alignment by the manipulation of different variables (e.g., coagulation bath temperature and take-up speed)³⁰. On the other hand, the filaments

produced from the shell component, sample SF (hollow filaments), were less prone to swelling with water, exhibiting a swelling ratio of ~ 6 (Figures 2a, 2e). Unfortunately, within the scope of this study, all the stresses generated in the drying process could not be controlled. As such, the hollow filaments tended to collapse. However, this is a remarkable result that can be developed in the future for applications such as vessels, channels, or insulating textile fibers.

The observations above encouraged the combination of both filaments (SF and CF) in the core-shell or coaxial configurations. Figure 2c shows the morphology of core-shell filaments made with the combination of both components. These filaments present a smooth surface and a regular cylindrical shape (flattening on one side is explained by the drying on the winder). Importantly, Figure 2c indicates strong interfacial adhesion of TO-CNF and regenerated cellulose filaments (shell). However, these filaments displayed a yellowish appearance (suggesting the presence of residual PIL); therefore, the CSFw samples were prepared (Figure 2d, 2h) and exhibited the same morphology of the unwashed samples. Table 2 summarizes the morphology results.

Table 2. Filament morphology and physical properties, including filaments diameters, shell thickness, linear density, or titer in tex units (grams per 1000 meters), apparent density, and porosity. Values in parenthesis are the respective standard deviations from five measurements.

Sample	Equivalent diameter dry [μm]	Diameter wet [μm]	Shell thickness dry [μm]	Titer [tex]	Apparent density [$\text{g}\cdot\text{cm}^{-3}$]	Porosity
SF	281 (13)	240 (2)	17 (3)	82 (13)	0.13	92
CF	35 (10)	163 (9)	-	13 (5)	1.34	14
CSFuW	253 (67)	243 (2)	35 (15)	110 (24)	0.22	86
CSFw	208 (26)	209 (2)	40 (17)	84 (13)	0.25	84

Table 2 presents the filament morphologies. It is important to point out that the equivalent circular diameters for the dry filaments were calculated from SEM images of cross-sectional areas, while the wet diameters were measured with a micrometer assuming circular cross-sections. Sample SF as mentioned before, exhibited hollow regions that collapse after drying; therefore, images were measured when clear cross-sectional areas were obtained. The TO-CNF hydrogels (CF) packed more densely in filaments with a porosity of 14 %. The regenerated cellulose produced in all cases filaments with high linear density (titer > 80 tex) but loose packing (porosities > 80 %). The results are similar to those reported by Olsson et al.^{60,94} for wet spinning of cellulose filaments using ILs. Table 2 reveals that the washing step facilitates shrinking by ~ 18% with respect to the unwashed filaments (compare CSFw and CSFuw), indicating that the presence of residual PIL might cause swelling and influence the strength properties.

Mechanical performance. The filament's mechanical properties were evaluated from tensile tests. Table 3 summarizes the results for dry and wet samples.

Table 3. Filament mechanical performance in the dry and wet (*) state. The standard deviation is shown in parenthesis. CSFw and CSFuw correspond to the unwashed and washed CSF, respectively,

Sample	Description	Elastic modulus (GPa)	Tensile strength (MPa)	Elongation (%)	Toughness (MJ·m ⁻³)
SF	Hollow	0.37 (0.08)	63 (9)	7.6 (2.5)	3.6 (1.6)
CF	TO-CNF filament	38 (3)	449 (91)	2.5 (0.8)	8.4 (4)
CSF _w	CSF(washed)	10.4 (1)	172 (27)	8.8 (2)	11.4 (1.9)

CSF _{UW}	CSF (unwashed)	3.5 (0.6)	64 (9)	14.5 (3.5)	6.8 (1.9)
SF*	SF wet sample	0.14 (0.3)	16 (4)	14.3 (1.6)	1.2 (0.4)
CF*	CF wet sample	6.1 (3.7)	58.6 (13)	1.3 (0.5)	0.4 (0.1)
CSFw*	CSFw wet sample	0.35 (0.04)	22 (4)	13.7 (4)	2 (0.1)
CSFuw*	CSFuw wet sample	0.08 (0.03)	8 (2)	18 (5)	0.9 (0.4)

The main observation in Table 3 is the remarkably high tensile strength and Young's modulus of the TO-CNF filaments (CF): 449 MPa and 38 GPa, respectively. These values exceed those reported for TO-CNF filaments spun in coagulation baths (we note that better values have been obtained by using microfluidic flow-focusing systems³⁸). The excellent mechanical strength of TO-CNF filaments may be explained by the enhanced interfibrillar affinity induced by the decreased surface charge via the protonation of the carboxylate groups^{19,23,30} combined with the alignment that occurs in the air gap, this effect persists even in the wet state were the TO-CNF filaments exhibited an average strength of 58.6 MPa. Ling et al.⁹⁵ have studied the effect of different non-solvents and electrolytes on the formation properties of TO-CNF filaments, from this studies and using quartz crystal microgravimetry (QCM), they have shown that carboxylate groups from TO-CNF surface suffer a protonation under exposition to acidic environment; subsequently, this protonation promotes water release and coagulation of TO-CNF. Nonetheless, this acidic environment seems not to affect unmodified cellulose⁹⁵.

Additionally, high elongations and tensile strengths in wet conditions have been observed for CSF up to 18% and 22 MPa respectively; with a toughness up to 2MJ/m³, this indicates that the shell increases the fiber elongation percentage; although its combination with the TO-CNF core does not improve the elastic modulus of such fibers. One possible way to overcome this issue in future works might be to promote crosslinking between both layers while optimizing the drawing

ratio, producing densely packed and aligned coaxial filaments. Figure 3 compares the mechanical performance of TO-CNF filaments in dry (CF) and wet (CF*) conditions as well as those of the respective washed filaments (CSFw, CSFw*).

Figure 3. TO-CNF and CSF mechanical performance in: dry conditions CF (black line), CSFw (green line) and wet conditions CF* (grey-area), and CSFw* (green-area)

From Table 3 and Figure 3, it is possible to notice that wet coaxial filaments (CSFw*) were more water-stable and flexible compared to wet TO-CNF filaments (CF*), understanding water stability and flexibility as the production of tough filaments that possess high elongation percentage allowing their stretchability under wet conditions. In spite of this, there is a significant decrease in tensile strength for wet CSF filaments (both washed and unwashed) compared to dry filaments,

and this behavior can be attributed to the water adsorbed by CSF fibers. The reduction of mechanical properties under wet conditions has been reported to CNF fibers ²⁸, and it has shown to be more critical in the presence of TO-CNF fibers due to their high affinity with water; therefore, a drastic decrease in tensile strength and elastic modulus in wet conditions compared to dry conditions are expected ²⁸. Nevertheless, CSF washed samples (both in wet and dry conditions) presented higher elastic modulus, tensile strength, and toughness compared to the respective unwashed samples, and this was attributed to the presence of PIL in the CSFuw samples. It has been reported for CNF films, that the presence of PIL and water in cellulose causes plasticization, increasing the elongation percentage and decreasing the elastic modulus, and tensile strength ⁹¹. Hence, washing is a critical step to maintain a balance in mechanical properties, understanding mechanical balance as the conservation of elastic modulus, tensile strength, and elongation percentage to produce tough fibers; contrarily, the presence of PIL produce a mechanically unbalanced filament with high elongation percentage but very low toughness.

The main feature from Figure 3 is that CSF owes its toughness to the high elongation, more evident in the wet state (the TO-CNF filaments were unstable). Compared to TO-CNF filaments, the coaxial samples exhibited higher elongations and toughness (wet and dry states) (see radar chart in Figure 4 for properties in the dry state).

Figure 4. Radar chart of mechanical properties (elongation %, toughness, tensile strength, and Young's modulus) of filaments in dry condition: SF (green), CF (black), CSFw (red), and CSFuW (cyan).

According to Figure 4, the TO-CNF filaments (CF) are tough (8.4 MJ·m⁻³) but have little elongation (2.5 %) compared to that of the CSFuW samples (14.5 %). In sum, CSFs are flexible and water-stable filaments, and their mechanical performance is affected by the presence of residual PIL as it has been discussed in this section and reported earlier for CNF films ⁹¹. The sample crystal structure, thermal stability, and composition were studied to inquire further into this subject.

CSF structure, thermal stability, and composition. So far, we have shown that TO-CNF and regenerated cellulose are compatible and produce stable CSF. However, the cellulose regeneration and the dry-jet wet spinning technique might cause changes in the cellulose crystal structure, thermal stability, and composition. These aspects were studied by using WAXS, TGA, Py-GC/MS, SEM-EDX, FT-IR, and liquid NMR.

For XRD analysis, two reference samples were prepared according to a previous study, corresponding to CNF and TO-CNF films ⁹¹. Figure 5 presents XRD patterns for reference (CNF, TO-CNF) and all filament samples.

Figure 5. XRD Patterns: a) acid-coagulated core-shell filaments (CSFuw), b) acid-coagulated core-shell filaments after water washing (CSFw), c) shell filaments (SF), d) TO-CNF core filaments (CF), e) TO-CNF film blank sample, f) CNF film (blank sample).

Figure 5 has been divided into two sections, the first three plots (a, b, and c) shows the typical cellulose II polymorph signals, while the last three plots (d, e and f) shows the typical cellulose I signals^{96,97}. CNF, TO-CNF, and CF present a monomodal diffraction intensity centered at 22.5 °, corresponding to the cellulose I (200) Miller index and diffraction intensity at 14.8 ° corresponding to the (1 $\bar{1}$ 0) and (110) Miller (Figure 5), which can be taken as an indication that they retained the cellulose I polymorph⁹⁶. For the samples that included regeneration of the dopes with dissolved cellulose in PIL (SF, CSFuw, CSFw), the cellulose I polymorph signal is missing, with the appearance of the cellulose II hydrate polymorph⁹⁷. This latter observation is evident from the bimodal peak intensity around 22 ° corresponding to the (110) and (020) Miller indices of cellulose II hydrate. Besides, the SF and CSFw samples have diffraction intensity around 12 ° corresponding to the (1 $\bar{1}$ 0) Miller index of cellulose II hydrate. This d-spacing corresponds to the separation of cellulose chains in the H-bonding plane by water molecules⁹⁷. In contrast, sample CSFuw did not exhibit this intensity. As the CSFuw sample contains a significant amount of residual [DBNH]⁺, it is reasonable to conclude that PIL is still bound to cellulose as an intermediate stage of the regeneration. However, residual PIL was quickly removed by washing with water, yielding cellulose II hydrate (CSFw). Table 4 summarizes the XRD findings.

Table 4. Crystalline forms (allomorphs), crystal size, and crystalline index of the reference films and filament samples.

Lattice Planes								
Sample	(1 $\bar{1}$ 0) ^a	(110) ^a	(020) ^b	(200) ^c	$\tau_{(200)}$ (nm)	CrI (%)	Z- function value	Cellulose type
CNF (reference)	15.6	16.5	-	22.5	5.5	80	-66	I β
TO-CNF (reference)	14.8	16.5	-	22.6	4.7	81	-5.2	I β
CF	14.7	15.9	-	22.4	5.2	85	-33	I β
SF	12.1	20.5	21.9	-	-	87	-	II hydrate
CSFw	12.1	20.3	22.0	-	-	91	-	II hydrate
CSFuw	-	20.3	22.4	-	-	71	-	II-PIL

^a in cellulose I β and cellulose II hydrate, ^b in cellulose II hydrate, ^c in cellulose I β .

The XRD results suggest that the cellulose crystal structure is affected during the production of the CSF by the dry-jet wet spinning with ionic liquids. These results are in line with previous reports confirming structural changes of cellulose due to ILs. For example, Freire et al. ⁹⁸ indicated the change from native cellulose (I) to type II polymorph; they attributed such change to the disruption caused in intra- and intermolecular hydrogen bonds by dissolution in IL. This allomorph possess an expanded crystal structure along (1 $\bar{1}$ 0) direction that might increase its reactivity ⁹⁹; in particular, this has been shown in the case of enzymatic hydrolysis ⁹⁹. Table 4 shows the crystallinity index for all samples, and such values are higher than expected; notwithstanding, XRD can over-predict CI values up to 30% ¹⁰⁰, additionally low fibrillated cellulose with low surface area < 100 m²/g can reach similar values ¹⁰⁰. Furthermore, Olsson et al. ⁵⁹ reported that for samples that have been highly dissolved, i.e., samples with low water- and cellulose content, a maximum conversion to cellulose II could be seen together with an increase in CI measurements.

According to the discussion above for crystallinity, the thermal performance of the cellulose filaments is expected to change. The thermogravimetric analysis combined with a Py-GC-MS were

carried out to study the thermal stability and the chemical composition of each sample. The thermogravimetric analysis in nitrogen atmosphere of the samples and their constituents are presented as thermogravimetric profiles (TG, Figure 6a) and their first derivative (DTG, Figure 6b).

Figure 6. (a) Thermogravimetric profiles (TG) and (b) first derivative of TG curve (DTG) for the filament samples: SF, CF, CSFw, CSFuw, and CNF (reference sample) in the 50-575 °C range.

The weight loss for all samples (Figure 6a) indicates degradation in the temperature range tested, exhibiting a weight loss > 80 % for temperatures above 350°C. Samples CF, CSFw, and CSFuw containing TO-CNF showed two degradation steps; the first starts at about 50°C and proceeds very fast until 150°C, which is probably due to the loss of water or PIL in the filament, followed by further dehydration reactions at the higher temperatures. The second step takes place in the 150 - 250°C temperature range. In this step, both CSFw and CSFuw display one peak with a small shoulder. The small shoulder at ~ 160 °C for CSFuw and ~ 190 °C for CSFw are partly attributed to sodium anhydroglucuronate degradation¹⁰¹. The main peaks attributed to the cellulose nanofiber degradation appears at 170°C for SF, 186°C for CSFuw, 209°C for CF, 215°C for CSFw, and

215°C for CNF. From these results, it is clear that TO-CNF filaments possess lower thermal stability compared to unmodified cellulose fibers; this is due to the introduction of sodium carboxyl groups^{101,102} and the reduction of crystallinity and complex morphology of the regenerated cellulose. In conclusion, CSFw filaments presented a slightly improved thermal stability (215°C), compared to the unwashed CSFuw samples (186°C), and TO-CNF filaments (209°C).

It is possible to conclude that the mixture of cellulose and TO-CNF fibers affect coaxial filament's thermal stability. Furthermore, it is evident that the thermal stability depends not only on the differences in crystallinity but chemical composition. Therefore, the Py-GC/MS analysis was carried out for all samples at 200, 300, 400, and 600°C (see supporting information) to identify the chemical species after pyrolysis (see Figure S2 in the supporting information for a group of Py-GC/MS profiles, obtained at 300°C). As seen in Figure S2 and Table S1, a distinctive peak around 8.8 min was registered for the SF and CSFuw samples, corroborating that the washing step was crucial and effective in removing residual PIL in sample CSFw. To further confirm this observation and to determine the regioselectivity of the PIL retention, the composition of the filament at the surface level was assessed by SEM-EDX and FT-IR.

Surface composition of CSF. Cross-sectional areas of CSFuw and CSFw samples were tested with EDX to corroborate whether PIL remains in the filaments. Figure 7 shows a typical SEM-EDX image and elemental composition profile for sample CSFuw. For each sample (CSFw and CSFuw), five different random cross-sectional areas of $\approx (20 \times 20 \mu\text{m})$ were checked at core and shell positions with the EDX detector, and results were averaged. The relative mass percentage of C, O, N, Au, Pt, and Cl were measured. Table 5 summarizes EDX results in the core and shell positions for samples CSFw and CSFuw.

Figure 7. SEM-EDX analysis of a CSFuw filament: a) cross-section, b) elemental nitrogen distribution, c) EDX C, N, O, Au, and Cl atom's profiles.

Table 5. CSF cross-sections elemental composition by SEM-EDX C, O, N, Cl were selected since they are fingerprint components to identify the presence of ([DBNH][CO₂Et]) or HCl.

Sample	location	%relative mass percentage			
		C	N	O	Cl
CSFw	Core	52.6 (0.8)	0	47 (0.6)	0.4 (0.3)
	Shell	56 (5)	0	42 (6)	1.9 (1)
CSFuw	Core	54.1 (0.4)	14.3 (2)	28.4 (2.6)	3.18 (1)
	Shell	52 (1.2)	14 (6)	29 (9)	5 (2)

The presence of C and O atoms can be attributed to the cellulose, nanocellulose, and PIL, but N atoms are only attributed to [DBNH][EtCO₂] PIL since the test was carried out in vacuum. The presence of Cl atoms is attributed to the residual acidic water coming from the coagulation bath and adsorbed into the filaments. Au/Pt atoms are related to the sputtering procedure. Additionally, the carbon relative mass percentage is higher than reported¹⁰³, and this could be attributed to uncovered regions coming from the carbon tape used to fix the samples over the SEM aluminum stubs. CSFw samples relative mass percentage clearly shows that two hours washing was enough to remove residual PIL from the shell and core layers and to reduce Cl. The total elimination of chloride ions would require more extended washing or higher temperatures and vacuum conditions. Unwashed filaments show that PIL not only remains in the shell layer but quickly diffuses and concentrates in the core layer; this process probably occurs during coagulation in the bath. This observation indicates that during coagulation, the IL diffuses bi-directionally outward from the shell to the coagulation bath and inward to the core; simultaneously, the HCl ionic species diffuse radially throughout the whole filament and triggers effective coagulation of the TO-CNF. The SEM-EDX analysis is complemented by FT-IR study of the filament's surface chemical composition.

Figure S3 (see supporting information) shows FT-IR spectroscopy data for cellulose nanopaper (reference) and filament samples CF, CSFw, and CSFuw. In sum, FT-IR results demonstrate that the washing step is essential at removing the [DBNH][EtCO₂]. However, it is necessary to confirm the results from SEM-EDX experiments that showed potential diffusion of PIL inside the filament. Therefore, liquid-state NMR analysis was performed. To identify impurities in the regenerated filaments, CF, CSFuw, and CSFw were dissolved in a ionic liquid electrolyte,

tetrabutylphosphonium acetate ($[P_{4444}][OAc]$):DMSO- d_6 (1:4 w/w) ⁸⁸ for liquid-state NMR analysis. Figure 8 shows stacked 1H spectra for the filaments.

Figure 8. 1H spectra in $[P_{4444}][OAc]$:DMSO- d_6 (1:4 w/w) at 65 °C of: a) acid-coagulated core-shell filaments (CSFuw), b) acid-coagulated filaments (CF), & c) acid-coagulated core-shell filaments after water washing (CSFw).

As expected, the polymeric cellulose and xylan resonances are present in the spectra. However, there are additional sharp signals in the CSFuw sample, characteristic of low molecular weight species, in addition to the $[P_{4444}][OAc]$ signals. Additionally, Figure 9 shows multiplicity-edited HSQC spectrum of acid-coagulated core-shell filaments (CSFuw) in $[P_{4444}][OAc]$:DMSO- d_6 (1:4 w/w) at 65 °C

Figure 9. Multiplicity-edited HSQC spectrum of acid-coagulated core-shell filaments (CSFuW) in $[P_{4444}][OAc]:DMSO-d_6$ (1:4 w/w) at 65 °C: a) aliphatic region showing the presence of clear resonances corresponding to $[DBNH]^+$ and $[P_{4444}][OAc]$ (1H trace), b) polysaccharide aliphatic region showing clear presence of AGUs and AXUs (diffusion-edited 1H trace).

HSQC of the sample indicates impurities such as $[DBNH]^+$ (Figure 9). The peaks from the 1H spectra (Figure 9a) are consistent with propionate anion (triplet at 1.0 ppm and a quartet at 2.2 ppm). In the washed sample (CSFw), the 1H spectra show only traces of $[DBNH]^+$, indicating that the washing step was suitable for these materials. A possible application for these filaments is related to textiles and biomedical fields. It is essential to explore the activity towards bacteria of the synthesized materials. In the following section, *S. aureus* bacteria activity was explored.

Bacterial Activity. Plate bacterial assays for CSF model films indicated the growth of *S. aureus* and the formation of biofilms (Figure S4 and S5, see supporting information). Compared to the washed sample, CSFw, more limited biofilm formation occurred on CF and CSFuW, which can be explained by the presence of sodium carboxylate groups and residual PIL, respectively. Growth inhibition and antibiofilm properties of CNMs have been described against *S. aureus* upon chemical modification by the addition of bactericidal agents such as lysozyme and nisin¹⁰⁴ and

titanium-aluminium-niobium-gentamicin ¹⁰⁵. Moreover, cellulose/nanocellulose filters grafted with a zwitterionic poly(cysteine methacrylate) ¹⁰⁶ have shown inhibition of biofilm formation and potential for water treatment applications. When addressing bacterial behavior, such modifications are appropriate. Indeed, Dederko et al. 2018 ¹⁰⁷ have recently demonstrated that pathogenic bacteria (including *S.aureus*) can slowly degrade nanocellulose (of bacterial origin). On the other hand, the behavior of beneficial bacteria towards materials should be studied, bearing in mind that their biofilms or their biosurfactants, could avoid subsequent pathogenic superficial colonization.

CONCLUSIONS

CSF was prepared using the dry-jet wet spinning with a coaxial nozzle. The coaxial spinning improved the TO-CNF hydrogel spinnability, as the surrounding cellulose solution in PIL [DBNH][EtCO₂] supported the filament formation in the air gap and bath. Acidic water was an effective coagulant for both TO-CNF and dissolved cellulose. In the ensuing CSF, the regenerated outer layer improved the thermal and wet stability. Compared to the TO-CNF filaments, CSF was less brittle and more flexible, elongation increased from 2 to 18 %. The optimization of the process (coagulation bath temperature, PIL, and water diffusivity, drawing ratio, among other variables) is expected to allow improved properties and design of filaments for different applications. Reported studies suggested that PILs are efficient solvents and simultaneous low-cost catalysts for transesterifications reactions of cellulose ^{108,109}; therefore, this opens multiple possibilities of functionalization for the regenerated cellulose layer. In particular, the cellulose II hydrate polymorph on the surface of CSF suggests a potential for further functionalization of the filaments, through increased reactivity.

ASSOCIATED CONTENT

Supporting Information.

SEM-EDX data, and Py-GC/MS table information for all samples at 200, 300, 400, 500 and 600°C (dataset online: DOI: 10.17632/jzvtvbxmvcw.2). Py-GC/MS chromatograms at 300°C, main products from samples pyrolysis, FT-IR results, and *S. aureus* plate growth in contact with CSF based films, diffusion-edited and ¹H liquid-state NMR spectra for key samples, full NMR experimental (Supporting_Information.PDF).

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Enhanced toughness in filaments wet-spun from TEMPO-oxidized cellulose nanofibrils through synergistic effect with a regenerated cellulose shell

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Coaxial fiber