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# Upcycling of cellulosic textile waste with bacterial cellulose via Ioncell® technology

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# ABSTRACT

Currently the textile industry relies strongly on synthetic fibres and cotton, which contribute to many environmental problems. Man-made cellulosic fibres (MMCF) can offer sustainable alternatives. Herein, the development of Lyocell-type MMCF using bacterial cellulose (BC) as alternative raw material in the Ioncell® spinning process was investigated. BC, known for its high degree of polymerization (DP), crystallinity and strength was successfully dissolved in the ionic liquid (IL) 1,5-diazabicyclo[4.3.0]non-5-enium acetate [DBNH][OAc] to produce solutions with excellent spinnability. BC staple fibres displayed good mechanical properties and crystallinity (CI) and were spun into a yarn which was knitted into garments, demonstrating the potential of BC as suitable cellulose source for textile production. BC is also a valuable additive when recycling waste cellulose textiles (viscose fibres). The high DP and Cl of BC enhanced the spinnability in a viscose/BC blend, consequently improving the mechanical performance of the resulting fibres, as compared to neat viscose fibres.

# 1. Introduction

The high demand of textiles and apparel has led to a continuous increase in the production of textile fibres and filaments, which reached 118.6 million metric tons in 2022 [1]. Amidst the stagnant production of cotton (24 % market share), the global market is dominated by unsustainable synthetic fibres (up to 60 %) [2–5]. The majority of synthetic fibres are made of non-renewable sources, are not biodegradable and have a low recycling rate, while the cultivation of cotton requires substantial amounts of arable land, water, fertilizers and pesticides [6]. To reduce the environmental impact associated with the production of textile fibres, man-made cellulosic fibres (MMCF) are attracting increasing attention as alternative sources for textiles [7].

Globally, only 6 % of textiles are produced by MMCF, its production involving either derivatization of cellulose or direct dissolution [5]. The most common MMCF are viscose-types (5.8 million tonnes in 2022 [5]), despite the environmental concerns (high amount of chemical usage) associated with their production [8]. The viscose process comprises multiple steps in which the cellulose is degraded intentionally to arrive at solutions suitable for wet spinning. Lyocell is one promising alternative process in which a direct solvent such as *N*-methylmorpholine *N*-oxide (NMMO) monohydrate is used for direct dissolution without prior chemical derivatization of the cellulose. Highly oriented fibres (with good mechanical performance) are obtained using this process and >99 % of the solvent is recovered [9,10]. The global Lyocell capacity is continuously increasing (from ca. 300 kt in 2019 to ca. 400 kt in 2022), which reflects the increasing demand for more sustainable regenerated cellulose fibres [11,12]. Despite of being a promising technology, NMMO is known to be sensitive to high temperatures (higher than 120 °C) in the presence of transition metal ions. Stabilizers such as propyl gallate are used to prevent thermal runaway reactions of NMMO during cellulose dissolution [13].

More recently, the direct dissolution of cellulose in ionic liquids (ILs) has been explored. These are defined as salts (i.e. consisting of a cation and an anion) with a melting point below 100 °C [14]. The appropriate selection of anions and cations allows to tuning the IL properties and the

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ability to dissolve biopolymers in a selective way [14]. During dissolution, the anions of the IL compete with the cellulose intermolecular hydrogen bonds whereas the cations stabilize the negatively charged units, enhancing solubility [6,15]. Several studies demonstrated that imidazolium-based ILs are effective for cellulose spinning, yet induce some cellulose degradation at higher temperatures (>90 °C) [14,16]. Additionally, anions like halides were found to be highly corrosive [17,18]. More recently, non-imidazolium-based ILs such as 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]) were proposed as solvent in Lyocell-type spinning [17]. Despite the known toxicity and biodegradability concerns associated with most ILs, Ruokonen et al. [19] found [DBNH][OAc] to be non-harmful in cytotoxic tests. Nevertheless, virtually full recovery and recyclability of the IL is imperative. Promising steps towards this direction were reported earlier for [DBNH] [OAc] [20]. Despite reoccurring concerns related to the costs of ILs, there is no real market yet that would provide actual bulk prices. Several serious industrial endeavours to upscale IL operations will likely also change the availability of ILs and their costs in the future [14]. These superbase-based ILs show a high cellulose dissolution capacity (17% m<sub>cellulose</sub>/m<sub>dope</sub>), with great spin stability using dry jet-wet spinning [17,21–23]. The resulting fibres, also known as Ioncell fibres, have shown competitive mechanical and structural properties when compared to other commercial MMCF [14,17,21]. Contrarily to NMMO monohydrate dopes, those obtained with [DBNH][OAc] can be prepared and spun at lower temperatures (70-90 °C), reducing energy consumption and preventing cellulose degradation [17].

Another concern related to the increasing use of MMCF is associated to the concomitant consumption of plant-based cellulose. While proving to be a good source for the production of high-performance textiles fibres, such as Tencel and Ioncell, environmental issues arose, such as the increasing need for intensive deforestation and wood (chemically-based) processing. To guarantee a sustainable supply of cellulose for MMCF, alternative sources have to be explored. Bacterial cellulose (BC) could be one alternative, produced via bacterial fermentation, e.g. by the genus *Komagataeibacter*, through agitated or static fermentation [24]. While BC is well known for its high-purity, crystallinity, degree of polymerization (DP) and mechanical performance, its production still needs to be improved due to low yields and high processing cost with the current fermentation systems [25–29].

BC has been applied mostly in the biomedical, food and cosmetic sectors [27–29]. However, interest in using BC in the textile industry is growing. The research community has been exploring ways to create high quality textiles, using BC. For instance, Kaminski et al. [30] and Fernandes et al. [31] demonstrated ways of developing modified BC to manufacture "ready-to-use" fabrics and leather, respectively. Another promising approach concerns the development of regenerated BC fibres [32,33]. In the literature, the high DP of BC (around 1000-2500) is described as a challenge for producing a high quality and spinnable dope. While a high DP is often related to a superior mechanical performance, its processing (mainly dissolution) was proven to be challenging as only low concentrations of BC were successfully dissolved [34,35]. Conversely, this limitation may be diminished if [DBNH][OAc] IL is used, since several studies reported effective dissolutions (and spinning) of high DP cellulose (as high as 1200) [21,36].

Only small amounts (10 % of the total global fibre production) of textiles are recycled. Most of the garments are incinerated or end up in landfills [22,37,38]. Responding to this alarming situation, the European Commission presented a strategy for the development of sustainable and circular textiles. Among different goals to be achieved, one addresses the effort to achieve "durable, repairable and recyclable textiles, to a great extent made of recycled fibres, free of hazardous substances, produced in respect of social rights and the environment". Hence, there is an urgent need for sustainable solutions that enable the recycling of end-of-life fibres. Recycling cellulosic fibres may be challenging as end-of-life cotton, viscose or Lyocell can show a wide range of DP. Laundering, UV-irradiation, or other environmental impacts can

cause a significant DP reduction during the lifetime of the textile. Mechanical and/or chemical treatment of the textile waste leads to further cellulose depolymerization (as low as DP 300), which limits their applicability for the production of recycled MMCF. One way to compensate for these low DP fibres is to blend them with high DP cellulose, such as BC, to improve the viscoelastic properties of the resulting solution and further its spinnability by broadening the molar mass distribution [34,37]. More recently, our team [39] has shown that through blending of BC with varying DP it was possible to spin Lyocell-type fibres using NMMO monohydrate as solvent. This study showed the potential of BC as cellulose source, yet fibres spun entirely from BC might not be economically feasible for still some time. Cellulose with high DP offers unique properties for MMCF, and BC emerges as a "model" of high-DP cellulose with high purity (other sources of high-DP cellulose such as cotton waste may represent cheaper alternatives but are difficult to source consistently in high purity and with similar DP), showcasing the potential to serve as an additive for the upcycling of end-of-life fibres.

In work at hand, we demonstrate the suitability of BC as additive to use low-DP cellulose textile waste as raw materials for MMCFs. The dissolution of BC using [DBNH][OAc] was first optimized, considering the BC concentration and the rheological behaviour of the prepared dopes. Spinning trials were done under different conditions to achieve the best performing fibre. Then, the process was scaled to collect larger amounts of staple fibres for yarn spinning and knitting into garments, as a demonstration that BC is a suitable candidate for textile production via the Ioncell® technology. Finally, we show that BC can be used to enable chemical recycling of textile waste with a very low DP. Viscose fibres, representing cellulosic textile fibres with the lowest DP, were re-spun into virgin fibres using BC as additive. Several solutions in [DBNH] [OAc] were prepared with different amounts of BC to assess the overall performance of the final regenerated cellulose fibre comprising viscose and BC.

#### 2. Materials and methods

#### 2.1. BC pulp preparation

BC membranes from HTK Food Co., Ltd. (Ho Chi Minh City, Vietnam) were washed with a sodium hydroxide solution (0.1 M) twice for 24 h, at room temperature. Then, BC membranes were washed with distilled water several times until the pH of the filtrate became neutral. To obtain a BC pulp, the membranes were cut into cubes and wet-ground with a hand-blender. Then, the concentration was adjusted to 0.5 % m/v and mechanically processed with a blender (Moulinex TYPE LM935) (6 times for 5 mins each time, allowing cooling between each period). Then, the BC pulp was air dried at 50 °C and milled using a high-speed grinding machine 600G. The pre-processing conducted on BC membranes to yield a powder is essential for opening the fibres before drying, thereby preventing fibre agglomeration and hornification, which is known to aggravate dope preparation. Prehydrolysis kraft (PHK) pulp (Stora Enso, Enocell) was milled to a powder with Fritsch pulp with 0.5 mm mesh. Viscose fibres, obtained from Kelheim Fibres GmbH, were milled using a Wiley Mini Mill 475-A.

Before processing, the dry matter content of each pulp was determined as described by the ISO 638:2008 standard. Three samples (from each pulp) of 0.1 g were weighed and dried at 105  $^{\circ}$ C for 24 h. Afterwards, dried samples were cooled down in a desiccator and weighed, and the dry matter content was determined.

# 2.2. Estimation of the degree of polymerization

The DPs of all cellulose pulps, which is correlated with the intrinsic viscosity, were characterized according to SCAN-CM 15:88. BC (96 % m/m, dry basis), PHK (92 % m/m, dry basis) and viscose fibres (95 % m/m, dry basis) were each dissolved using cupriethylenediamine aqueous solution (CED, CAS:14552–35-3, M:, CuC<sub>4</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>; Oy FF-Chemicals

Ab). Preliminary testing on BC, PHK and viscose showed intrinsic values bellow 650 mg.L<sup>-1</sup>. Consequently, about 250 mg of each sample was weighed into plastic bottles with five copper rods and further filled with 25 mL deionized water. The plastic bottles were shaken for 30 min in a Kauko Lehtinen shaking device, at room temperature (RT). Then, 25 mL of CED was added (yielding a final concentration of around 0.005 g. mL<sup>-1</sup>) and again shaken for 30 min, for cellulose dissolution at RT. All samples were then placed in a 25 °C water bath (Mistral Multi-stirrer) before measurement. The intrinsic viscosity of all solutions was measured using a capillary viscometer. Then, the determined intrinsic viscosity was used to estimate the DP using formula (1) (described in SCAN-CM 15:88):

$$\mathsf{DP} = \left(\frac{\eta}{Q}\right)^{\frac{1}{\alpha}} \tag{1}$$

where *Q* and *a* parameters, are defined as follows:when DP < 950, Q = 0.42 and a = 1;when DP > 950, Q = 2.28 and a = 0.76;

#### 2.3. [DBNH][OAc] preparation

1,5-Diazabicyclo[4.3.0]non-5-ene (99 %, CAS: 3001-72-7, M: 124.18,  $C_7H_{12}N_2$ , Fluorochem, UK) and acetic acid (glacial, 100 %, CAS: 64–19-7, M: 60.05,  $C_2H_4O_2$ , Merck, Germany) were used as received. [DBNH][OAc] was prepared (in a customized 6 L reactor) by slowly adding equimolar amounts of acetic acid to DBN at 70 °C under constant stirring [17].

# 2.4. Preparation of spinning dopes

Before dissolution, [DBNH][OAc] was first melted at 70 °C in a water bath. Then, the melted [DBNH][OAc] was transferred to a customized kneader system, pre-heated to 75-85 °C. Then, the air-dried BC pulp (dry matter content of 96%m/m) was slowly added, with manual stirring, to a final concentration (dry  $m_{cellulose}/m_{dope}$ ) of 10 %, 12 % and 13 %. For the recycling of viscose fibres, blends of viscose and BC were prepared, maintaining the total cellulose concentration at 16 % (dry  $m_{cellulose}/m_{dope}$  ). Blends with (%viscose/%BC) 16 %/0 %, 14 %/2 %, 13 %/3 % and 12 %/4 % (labelled as Vis16, Vis14BC2, Vis13BC3, and Vis12BC4 respectively) were prepared for spinning trials. The mixtures were stirred (30 rpm) at 75–85 °C under reduced pressure (50–60 mbar) until complete dissolution was observed (> 180 min). Each produced dope was then filtered by means of a hydraulic press filtration device (200 bar, metal filter fleece, 5–6  $\mu$ m absolute fineness, Gebr. Kufferath AG, Germany) to remove residual undissolved particles and impurities. The filtered solutions were shaped to the dimensions of the spinning cylinder and kept in a cold room (4 °C) until use [17].

# 2.5. Spinning trials

PHK pulp, BC and blended BC/viscose fibres were spun using a smallscale customized dry-jet wet spinning unit (Fourné Polymertechnik, Germany) [23]. The solid, shaped [DBNH][OAc]-cellulose dopes were loaded into the cylinder and the samples were heated to 70  $^\circ\text{C}$  for melting. Dopes were then extruded at 55-85 °C (depending on the rheology data of each dope, as described later) through a single hole spinneret (100 µm diameter, length-to-diameter ratio of 0.2). The produced filaments passed a 0.5-1.0 cm airgap, were immersed into a water coagulation bath and collected at godets utilised for stretching the filaments via the variation of the take-up speed. The air gap distance, immersion depth inside the water bath, deflection angle, the retention distance of the filament bundle and the temperature of the coagulation bath (5 °C) were kept constant throughout all spinning trials. The extrusion rate was fixed at 1.3 m/min, while the take-up velocity of the godet was varied from 6 to 23 m.min<sup>-1</sup>, resulting in draw ratios (DR = vtake-up/vextrusion) of 5.0 to 18.

Additionally, for BC spinning at larger-scale, another dry-jet wet spinning unit (Fourné Polymertechnik, Germany) was used. The shaped [DBNH][OAc]-BC dope was extruded at 65–80 °C through a multi hole spinneret (200 & 400 holes; 100  $\mu$ m diameter, length-to-diameter ratio of 0.2), using the same conditions as above. The extrusion rate was fixed at 3.5 m.min<sup>-1</sup>, while the take-up velocity of the godet was varied from 7 to 63 m.min<sup>-1</sup>, resulting in draw ratios (DR) of 2.0 to 18. The collected filaments (small and large unit) were cut into 4 cm segments for yarn production and 10 cm pieces for analysis. All the fibres were washed with hot water (60 °C) and air dried at ambient temperature.

# 2.6. Yarn spinning

Yarn spinning was performed as described by Michud et al., [40]. Firstly, the staple fibres were treated with target amount of 0.25 % m/ m<sub>fibre</sub> of lubricant; 80/20 % of Afilan CVS (ARCHROMA, Switzerland) and Leomin PN (ARCHROMA, Switzerland), respectively. The fibres were submerged into a solution (liquor ratio of 1:20) comprising Afilan CVS (0.677 g.L<sup>-1</sup>) and Leomin PN (0.233 g.L<sup>-1</sup>) and heated at 45 °C for 5 min (manually stirred). Then, the fibres were pressed to reach 300 %pick-up and air dried. Next the fibres were opened using a Mesdan Lab Trash Analyzer 281C (Mesdan SpA, Italy) and left overnight in a conditioned room (65 % RH; 20 °C). The opened fibres were fed into batches of 25 g for carding (carding machine 337 A, Mesdan SpA, Italy) and rolled into slivers using Stiro lab 3371 (Mesdan SpA, Italy) for roving, stretching and doubling. Slivers were drafted twice, in the second one two slivers were combined and drafted together. Finally, two doubled slivers were combined into roving. The roving was then ring spun (Ring Lab 82BA; SER.MA.TES srl, Italy) into a 20 tex yarn (Nm 50, Ne 30). The yarn had Z torsion and the number of twists per meter (TPM) was 700. The calculated twist multiplier expressed in Ne was 3.26. The linear density of the spun yarn was determined from 10-m skeins (n = 6; expressed in tex).

#### 2.7. Knitting & bleaching

The knitting of the yarn was done in a Stoll ADF 32 W E7.2 (14gg), where 4 samples were developed, two samples with an "interlock" pattern (stitch size: NP5 and NP6 = 9.5; sample size: 150 stitches, 400 rows) and two samples with a "racking & single knit" pattern (stitch size: NP5 and NP6 = 10.0 (mock rib + racking), NP22 = 11.0 (single knit); sample size: 120 stitches, 200 rows) [41]. Additional samples were knitted using a Knotyong machine Labknitter 297E (Mesdan SpA, Italy), for bleaching assays. The bleaching was carried out under the following conditions: the samples were submerged in a container with a solution comprising 2.0 g.L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (29.7 %; CAS: 7722-84-1 M: VWR), 7.0 g.L<sup>-1</sup> Na<sub>2</sub>SiO<sub>3</sub> (Na<sub>2</sub>O: 7.5–8.5 %; SiO<sub>2</sub>: 25.5–28.5 %, CAS: 1344-09-8, VWR), 0.5 g.L<sup>-1</sup> NaOH (99.1 %, CAS: 1310-73-2; M: VWR) and 1.8 g.L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> (99.8 %, CAS: 144–55-8 M: VWR). Then, these containers were placed in a Testex Infrared lab dyeing machine TD130 and subjected to a temperature of 90 °C for 2 h.

# 2.8. Dope & fibre characterisation

#### 2.8.1. Molecular weight distribution

As previously described by Pitkänen et al., [42] the molecular weight distribution was measured with gel permeation chromatography (GPC) using a Dionex Ultimate 3000 HPLC system equipped with a Shodex DRI (RI-101), and a Viscotek/Malvern SEC/MALS 20 multi-angle light scattering (MALS) detector. About 0.05 g of each pulp/sample was subjected through a solvent exchange process, consecutively using water, acetone, and DMAc (4 mL of each reagent). The contact between pulp/sample and each solvent was maintained overnight for effective activation. After solvent exchange, cellulose samples were dissolved in LiCl/DMAc (90 g.L<sup>-1</sup>) and stirred overnight, to ensure full dissolution. The samples were then diluted (from 90 g.L<sup>-1</sup> to 9.0 g.L<sup>-1</sup>). The diluted

samples were filtered using 0.2 µm filters onto plastic vials before measurements. 100 µL of each sample solution was placed into the four columns system (PLgel MIXED-A) operating at a flowrate of 0.75 mL. min<sup>-1</sup>. A narrow polystyrene standard (Mw = 96,000 g.mol<sup>-1</sup>, D = 1.04, refractive index increment,  $\partial n/\partial c$ , 0.146 mL.g<sup>-1</sup>) was used to obtain the detector constants for MALS and DRI, whereas a broad polystyrene sample (Mw = 248,000 g.mol<sup>-1</sup>; D = 1,73) was applied to test the calibration of the detectors. A  $\partial n/\partial c$  value of 0.136 mL. g<sup>-1</sup> was used for celluloses in 0.9 % LiCl in DMAc. After GPC analysis, the parameters weight-average molar mass (Mw), number-average molar mass (Mn), polydispersity index (Mw/Mn) and the proportion of long cellulose chains (DP > 2000) and short cellulose chains (DP  $\langle 100 \rangle$  were obtained.

# 2.8.2. Optical characterisation of the cellulose dopes by polarization microscopy

The optical characterisation of the spinning dopes was carried out using polarization microscopy. A Zeiss Axio with heating stage microscope ( $10 \times$  magnification lens) was used. A small sample of the dope was placed on a cleaned glass slide (with cover), and heated to 80 °C for 15 min before optical observations.

# 2.8.3. Rheological characterisation of the cellulose dopes

The rheological characterisation was carried out as described by Michud et al., [34] with slight modifications. An Anton Paar Physica MCR 302 rheometer with a plate-plate geometry of 25 mm diameter and 1 mm gap size was used. The rheological behaviour was determined by dynamic frequency sweep tests from 100 to  $0.01 \text{ s}^{-1}$ , at varying temperatures (50–90 °C). Zero shear viscosity ( $\eta_0^*$ ) and crossover points (G' = G'') were determined by using the Cross model assuming the validity of the Cox-Merz rule [43].

#### 2.8.4. Mechanical characterisation

Fibre testing was carried out in accordance with EN ISO 5079 and EN ISO 139 standard procedures. The fibres were conditioned overnight at a relative air humidity of 65 % and 20 °C. Next, the fibres were subjected to a single-fibre tester (Textechno Herbert Stein Favigraph) for the measurement of linear density (titre), tenacity and elongation at break in conditioned (RH 65 % & T 20 °C) and wet state (fibres soaked for 10 s before measurements). Tensile testing was done under the following settings: 20 fibres per sample; gauge length of 20 mm; 20 cN maximum capacity of load cell; test speed of 20 mm.min<sup>-1</sup>.

The mechanical properties of the yarn were determined (following ISO 2062) using MTS400 tensile tester set with a 50 N load cell. The testing speed was 250 mm.min<sup>-1</sup>, and the gauge length was 250 mm.

# 2.8.5. Birefringence

Three fibres (from each sample) with similar linear density to its average ( $\pm$  0.1 dtex) were attached to a microscope slide and observed with a Zeiss Axio Scope.A1 microscope with a Zeiss Tilting Compensator B. The thickness of the fibre was determined from the linear density and the assumption of a density of 1.5 g/cm<sup>3</sup>. The total orientation factor  $f_t$  was determined by dividing the birefringence with 0.062, the maximum birefringence of cellulose [44].

# 2.8.6. Scanning electron microscopy

The morphology of PHK and BC fibres were analysed using scanning electron microscope (Zeiss; Sigma VP), with a variable pressure and a 5 kV operating voltage. For cross-section imaging, the samples were prepared as follows: a bundle of fibres was immersed in water and subsequently frozen with liquid nitrogen. The ice was then shattered, to collect the cryo-fractured fibres [40]. After drying, the fibres were vertically attached to SEM sample holders and sputter-coated with 80 Au/20 Pd (5 nm thickness) in a Quorum 150R S plus sputtering device.

# 2.8.7. Carbohydrate & elemental analysis

The national renewable energy laboratory (NREL) protocol was

followed for the determination of structural carbohydrates and lignin in the samples [45]. About 0.30 g of each sample (duplicates) was submitted to acid hydrolysis, using  $H_2SO_4$  72 % ( $\nu/\nu$ ). Firstly, 3 mL of  $H_2SO_4$ 72 % (v/v) was added to the sample and heated to 30  $^\circ$ C for 60 min (stirred every 5 min). Then, the resulting suspension was diluted to 4 % of H<sub>2</sub>SO<sub>4</sub>. Simultaneously, a sugar recovery standard was prepared (composed of glucose (1000 mg), mannose (50 mg), galactose (50 mg), and xylose (50 mg)) to be used as reference. The samples and sugars were hydrolysed in a Systec DE-23 autoclave at 121 °C for 60 min, after which the samples were filtered through VitraPOR Borosilicate 3.3 crucibles. The remaining residue was dried and weighed for the determination of the acid insoluble non-saccharides, whereas the filtrate was diluted with milli-Q water by a factor of 100 and measured in a Dionex ICS-3000 HPAEC-PAD. For solubilized lignin quantification, samples were measured by UV-spectrometry (Shimadzu UV-2550) at a wavelength of 205 nm.

# 2.8.8. Brightness

The brightness and colour were measured with a SpectroScan (16130–818) and Spectrolino by GretagMacbeth, following the methods of the ISO 2470-1:2009 standard. Five scans were performed on each sample (bundle of fibres or knit), with the sample positioned above a white surface. The scans were taken at various locations on the bundle/knit. The measurements were conducted using a polarized filter, D65 illumination and an observer angle of  $10^{\circ}$ .

# 2.8.9. XRD measurements

The crystalline properties of the fibres were measured by XRD with a Xenocs Xeuss 3.0 X-ray diffractometer in transmission mode. Bundles of fibres were placed on sample plate and scanned for WAXS analysis, using a CuK $\alpha$  radiation ( $\lambda = 1.5406$  Å operated at 50 KV/0.6 mA combined with a Dectris Eiger2 R 1 M detector (detector – sample distance: 56 mm)). After data collection, scattering profiles were corrected by subtracting a blank measurement (air scattering) [23]. The Segal crystal linity index (CI; %) was determined by the following equation:

$$Cl[\%] = \frac{lt - la}{lt} * 100$$
<sup>(2)</sup>

where "It" is the total intensity of the (020) peak at 21.7° 20, and "Ia" is the amorphous intensity at  $16^\circ$  20 for cellulose II.

#### 2.9. Statistical analysis

Statistical analysis was supported with Prism version 9.4.1 (Graph-Pad Software, La Jolla California USA), using t-student analysis for unpaired comparison of two means. Mean differences were considered statistically non-significant (ns) when the *p*-value was higher than 0.05 (95 % of interval of confidence). The default statistical confidence level was considered to be 95 % (P < 0.05) in all tests.

# 3. Results & discussion

# 3.1. BC - Ioncell® fibre production

#### 3.1.1. Degree of polymerization & GPC

The quality of the regenerated fibres (in particular their mechanical performance) is connected to the macromolecular properties of the cellulosic constituents such as the intrinsic viscosity and molar mass distribution (weight fraction of short and long-chain molecules). The viscosity and key-parameters derived from the molar mass distribution for BC, viscose and standard PHK pulp (Enocell) as reference are summarized in Table 1.

The BC displayed a slightly lower intrinsic viscosity and a lower weight-average molar mass as compared to values found in literature (BC: 919 mL.g<sup>-1</sup>, 564–752 kDa (Table 1) [46,47]. However, the BC

#### Table 1

Viscosity, degree of polymerization and molar mass distribution of BC and PHK pulp.

Sample	[η] mL. g <sup>-1</sup>	DP <sub>v</sub> *	M <sub>w</sub> kDa	M <sub>n</sub> kDa	PDI M <sub>w</sub> / M <sub>n</sub>	DP < 100 %	$\begin{array}{c} DP > 2000 \\ \% \end{array}$
BC pulp	$\begin{array}{c} 646 \\ \pm \ 18 \end{array}$	$\begin{array}{c} 1686 \\ \pm 15 \end{array}$	585.0	527.3	1.1	1.9	28.5
PHK pulp	$\begin{array}{c} 414 \\ \pm 1 \end{array}$	$\begin{array}{c} 939 \ \pm \\ 1 \end{array}$	147.5	78.5	1.9	1.5	8.1
Viscose fibre	$\begin{array}{c} 175 \\ \pm 5 \end{array}$	$\begin{array}{c} 417 \pm \\ 3 \end{array}$	48.0	21.4	2.3	19.0	$\textbf{3.9}\times \textbf{10}^{-2}$

degree of polymerization calculated from the intrinsic viscosity.

samples have been obtained from different sources - different strains and different cultivation conditions, hence the differences observed were not unexpected. However, the cellulose chains in BC pulp were longer ([n]: 630.4 mL.g<sup>-1</sup>; DP: 1632) than those in PHK pulp ([η]: 414.2 mL.g<sup>-1</sup>; DP: 939). This is also seen in the molar mass distribution (Fig. S1), with  $M_n$ and Mw of BC being higher, yet the molar mass distribution was narrower, resulting in a lower polydispersity index. As expected, the substrates also differed in their share of long cellulose chains. BC pulp is comprised of approximately 29 % of cellulose chains with a DP > 2000, whereas PHK only accounted for 8 %. Only low amounts of short cellulose chains, often attributed to small cellulose chains or hemicellulose (only on plant cellulose) were found in both pulps (about 1-2 %). Despite the longer cellulose chains, BC appears to be suitable for dissolution in [DBNH][OAc] and subsequent spinning, since the intrinsic viscosity is close to the values of 400–500 mL.g<sup>-1</sup>, considered optimal for Ioncell® technology [21,34].

As expected, the viscose fibres intended for recycling (in Section 3.3.) had much shorter cellulose chains ([ $\eta$ ]: 175 mL.g<sup>-1</sup>; DP: 417) compared to BC and PHK (Table 1). In addition to the lower molecular weight (both Mw and Mn; 19 % of DP < 100), the cellulose in viscose fibres also exhibited a wider molar mass distribution (Mw/Mn of 2.3) than BC and PHK (Table 1).

#### 3.1.2. Dope characterisation

All BC dopes (with concentrations of 10-13 %) dissolved readily in [DBNH][OAc], with no undissolved particles remaining in the dope after filtration (Fig. S2). Undissolved cellulosic particles were found on the filter, which, although being in trace amounts only, might have contributed to a slight decrease in the final cellulose concentration. The concentrations reported in Tables 2 and 3 refer to the theoretical values without considering any variations caused by the filtration of undissolved particles. The dopes were characterized by rheological measurements, in order to compare them with the reference material (PHK) and values from literature (Fig. 1), and to determine the appropriate spinning conditions. The rheological properties of the PHK pulp solution was found to be in line with the literature [17], in spite of the slight differences of the average molecular weight:  $\eta_0$  decreased from 30,000 Pa.s to 15,000 Pa.s with increasing temperature (70 °C - 90 °C); the dynamic moduli at the cross over point (COP - cross over between the storage and loss modulus) was around 4000 Pa (70  $^\circ C$  – 90  $^\circ C)$  and  $\omega$ increased from 0.7 to  $2.5 \text{ s}^{-1}$ , respectively.

#### Table 2

Dry-jet wet spinning of  $\ensuremath{\mathsf{PHK/BC}}\xspace{-[DBNH]}\xspace{-[DBNH$ 

Cellulose concentration (%)	Optimal T [°C]	Maximum DR	Continuous spinning*
PHK 13 %	68	12	DR 8
BC 10 %	58	8	DR 6
BC 12 %	70	14	DR 13
BC 13 %	77	18	DR 18

\* Fibre collected for >4 min;

The zero-shear viscosity ( $\eta_0$ ) increases with the polymer concentration in the dope and decreases with the processing temperature. When compared to PHK (13 %), only the dope with 10 % BC had a lower  $\eta_0$ , yet similar at higher temperatures (T > 70 °C) (Fig. 1a). In general, as reported by Sixta et al., [17], the targeted  $\eta_0$  for cellulose-[DBNH][OAC] dopes is between 25,000–35,000 Pa.s (Fig. 1a - highlighted in green). For the dope with BC 10 %, the optimal  $\eta_0$  was reached at 60 °C, whereas for the standard dope (PHK) this is observed between 65 and 70 °C. When the BC concentration was increased up to 12 % and 13 %, the optimal temperatures for spinning increased to 70–75 °C and 75–85 °C, respectively (Fig. 1a).

All dopes showed a visco-elastic behaviour, displaying a cross over between storage and loss moduli (COP), although at different angular frequencies and dynamic moduli (Fig. 1b and c). The viscoelastic properties are influenced by the molar mass distributions of the polymeric solute. The BC based dopes displayed lower dynamic moduli (PHK 13 % - 3500-4300 Pa vs BC 13 % - 2500-3000 Pa) and lower angular frequencies (PHK 13 % - 0.60-3.16 s<sup>-1</sup> vs BC 13 % - 0.032-0.47 s<sup>-1</sup>) across all temperatures tested. Increasing the concentration from 10 % to 12 % led to higher dynamic moduli (from  $\cong$  1500 to  $\cong$  2500 Pa) and lower angular frequencies (more noticeable at higher temperatures) (Fig. 1b and c). Dopes with BC 12 and 13 % presented similar dynamic moduli, yet  $\omega$  was slightly higher for BC 12 % (Fig. 1b and c).

In short, PHK and BC dopes have distinct rheological properties. Having higher DP and longer cellulose chains, BC shows an increased  $\eta_0$  (and higher optimal spinning temperatures, up to 80–85 °C), but a lower overall elasticity, when compared to the dope prepared with PHK. These rheological features provide information about the optimal spinning conditions, mainly extrusion temperature and ability to stretch the filaments in the air gap [17].

#### 3.1.3. Fibre spinning

Spinning trials, using a monofilament spinning device, were performed in order to pre-evaluate the spinnability performance of each material produced. The spinnability of any dope may be defined, according to the draw ratio (DR) achievable, as: DR < 2 non-spinnable, 2-8 poor, 8–14 good, >14 excellent [37]. Targeting a high DR, the spinning of each material was optimized by: i) varying the temperature of extrusion, taking in account the rheology data; ii) by varying the godet speed while collecting the regenerated cellulose fibres, in order to assess the maximum DR as well as the time stable spinning until filament rupture. The main results regarding the spinning trials are illustrated in Table 2. As observed in the rheology data, the predicted optimal temperature for spinning BC was higher compared to PHK and increased with the BC concentrations. Optimal spinning conditions were found at slightly lower temperature than estimated from the rheology data (Fig. 1 and Table 2). The maximum DR of the PHK pulp reference material was 12, yet stable spinning for longer period of times was only possible at DR10 and DR8. These DR values are lower than those reported by Sixta et al., [17], where a maximum DR of 18 using 13 % PHK was possible. The discrepancy in results is due to different spinning set-ups. Herein, a monofilament device was used, in which the single fibre is more susceptible to external disturbances. Despite these limitations, excellent spinnability was achieved with BC-based dopes, particularly for the higher concentrations tested, a maximum DR of 18 being reached for 13 % BC.

After the optimization of the BC concentration on a monofilament spinning device, fibres were spun from a 13 % BC-[DBNH][OAc] solution on a larger multifilament unit to validate the spinnability on a larger scale and to characterize the fibres comprehensively. The respective dope had a higher  $\eta_0$  than the same dope produced at a smaller scale (Table 3). This difference in  $\eta_0$  is attributed to more efficient dissolution provided by the larger equipment, slightly increasing the total amount of dissolved cellulose on the dope, and consequently increasing the  $\eta_0$ . To compensate for this increase in viscosity, the total cellulose content was reduced (12 %), which provided the target viscosity of 25,000–35,000

#### Table 3

Large scale spinning of BC-[DBNH][OAc]; optimal temperature; maximum DR; continuous spinning at specified DR.

Parameters	Cellulose on dope (%)	BC 13 % Small scale	BC 13 % Small scale		BC 13 % Large scale		BC 12 % Large scale	
Rheological	Temperature [°C] Zero shear viscosity, η <sub>0</sub> (kPa.s) Angular velocity, ω (COP) (rad/s) Dynamic moduli, (COP) (Pa)	80 30.9 0.31 2700	85 26.0 0.40 2700	80 43.9 0.24 3100	85 35.9 0.33 3200	80 41.0 0.25 3100	85 33.4 0.34 3100	
Spinning	Optimal T [°C] Maximum DR Spinning	77 18 Continuous (DR 14)		80 14 Continuous (DR12)		82 18 Continuous (DR16)		



**Fig. 1.** Rheological properties of PHK/BC-[DBNH][OAc] dopes: a) Zero shear viscosity ( $\eta_0$ ) vs. temperature, estimated from PHK/BC [DBNH][OAc] dopes (optimal  $\eta_0$  highlighted in green); b) dynamic moduli at COP at different temperatures; c) angular frequency at COP at different temperatures.



Fig. 2. Tenacity (cN.tex<sup>-1</sup>), elongation at break (%) and linear density (dtex) of all collected fibres, from different dopes produced at different DR, using mono- or multifilament spinning; "Dry"- conditioned fibres at 65 % RH, 20 °C; "Wet" – fibres submerged in water for 10 s prior testing.

Pa.s [17]. This dope showed excellent spinnability (DR8 until DR16) [37], with higher fibre breakage being noticed only at DR18. Dopes with a BC concentration of 13 % could only withstand a maximum DR of 14, yet a stable continuous spinning was possible at lower DR (8, 10 and 12) (Table 3). Fibres for further testing and yarn spinning were spun at DR 8 (to obtain fibres with a linear density between 1.0 and 2.0 dtex).

#### 3.1.4. Fibre characterisation

The collected fibres were analysed in terms of their mechanical performance, birefringence, crystallinity and chemical composition. The mechanical properties of the collected fibres from all produced dopes (mono- and multi-filament spinning) are presented in Fig. 2. These properties include linear density, breaking tenacity, and elongation at break, under both standard and wet conditions.

The tenacity of the PHK fibres under standard conditions was similar to values reported for Ioncell fibres earlier [17,37] but generally slightly lower than for BC fibres collected at each maximum DR (BC 10 % - DR 7; BC 12 % - DR 13 and BC 13 % - DR 18) (p < 0.05). Although not statistically significant among all BC fibres, there is an upward trend in tenacity values (ranging from 52 to 57 cN tex<sup>-1</sup>) with increasing cellulose content and DR (Fig. 2). The incorporation of higher concentrations improves the elasticity in the filaments prior to coagulation, which helps to withstand higher DRs [17,21,48,49]. As expected, an increasing DR resulted in a lower elongation, as well as lower linear densities (as low as 0.79 dtex at DR 18). Most BC fibres exhibited lower elasticity compared to PHK fibres (p < 0.05), except for BC 12 % DR 10 and BC 13 % DR 14 fibres (p > 0.05). The intrinsic properties of the given pulps also affected the overall mechanical performance of the resulting fibres. The presence of longer cellulose chains in BC (Table 1) contributed to the development of stiffer fibres. Other relevant studies reported the same outcome when using cellulosic materials with higher [ŋ] and Mw [17,21,50]. Concerning the used spinning setup, fibres produced in a multi-filament spinning device showed better performance, with significantly improved elongation (multi-filament: 10.46-12.08 % vs. mono-filament: 7.98-9.51 %), while maintaining similar tenacity levels (ranging between 52 and 57 cN tex $^{-1}$ ). These fibres outperformed the ones reported for Ioncell process (using standard PHK), especially in terms of tenacity (PHK: 40-47 cN tex<sup>-1</sup> vs BC: 52-57 cN tex<sup>-1</sup>) [17,21,23,34]. The mechnical properties also surpassed those of BC-Lyocell fibres previously reported in the literature (a detailed comparison is shown in Table S2) [32,33,39].

The measurements in wet state showed the same trends for the tenacity, elongation and linear density dependence on the DR and dope concentration. The fibres spun with the monofilament unit had a lower tenacity and higher elongation under wet conditions (Fig. 2). These differences between wet and dry conditions are typical for MMCFs and

can be attributed to the fibre's ability to absorb water upon exposure. The less oriented amorphous regions within the fibre are more prone to moisture absorption, as the hydrogen bonds become more accessible for water. Consequently, after water exposure, the fibre's capacity to with-stand axial external forces diminishes, leading to reduced tenacity and increased elongation at break [50]. This difference was less pronounced for the fibres produced through multi-filament spinning (dope BC 12 %). Tenacity and elongation were similar under both dry and wet conditions, indicating a higher crystallinity and less accessible hydrogen bonds to absorb water in the BC fibres.

To understand the improved mechanical performance achieved with BC fibres, the structure was further studied with regards to total orientation (determined via the fibres' birefringence), crystallinity index and morphology (by SEM) (see Fig. S5). Concerning total orientation, no significant differences were found between PHK and BC fibres, or between samples obtained with different DR (Fig. 3; p > 0.05). Although, generally, high DRs lead to better fibre alignment, the total orientation reaches a plateau value already at moderate DRs [17]. Herein, all fibres showed a similar total orientation which was comparable with those reported for other Ioncell and Lyocell fibres, and higher than those of viscose and modal [34,52].

The degree of crystallinity differed more significantly between BC and PHK fibres (BC: 54–66 % vs PHK: 41 %). The Segal crystallinity index found for the PHK fibres was slightly higher than in other PHK fibres reported in the literature (32–37 %) [11,17,21,37]. The BC fibres are more crystalline than PHK fibres, reflected in the toughness, with increased tenacity and lower elongation (Figs. 2 and 3). Also, a fibre structure with more ordered crystalline regions impacts on the total orientation of the fibre (Fig. 3), apart from the DR used for spinning [53]. The crystallinity of BC decreased slightly with increasing DR in the small spinning unit, although changes were largely within the magnitude of the standard deviation of each value (Fig. 3). From this data, it is perceived that BC fibres presented a highly oriented and cohesive structure, without any impurities, confirmed also by SEM (Fig. 3).

The spun fibres (multifilament) were further characterized in terms of their chemical composition, namely elemental analysis, carbohydrate analysis, DP and molar mass distribution, to track any potential polymer degradation during the dissolution and spinning processes (Table 4). The amounts of carbon and hydrogen remained the same in the BC pulp and fibre, being also in line with values reported by Tomé et al. [54] and Volova et al. [55] (Table 4). Compared to PHK [56], BC is composed only of cellulose (no hemicellulose or lignin), which may also affect the overall performance of the fibre. Only very low amounts of nitrogen were found in the fibres, showing that [DBNH][OAc] was removed efficiently from the fibres after spinning (Table 4). Carbohydrate analysis revealed similar amount of cellulose in both BC pulp and fibre



Fig. 3. Total orientation and crystallinity of all collected fibres;

#### Table 4

Elemental analysis (% nitrogen, carbon, hydrogen; sulphur); carbohydrate analysis (% cellulose; acid insoluble matter) and DP estimation of BC pulp and BC fibres (collected at DR 8 from multifilament spinning trials);

Analysis		BC pulp	BC fibres
	Nitrogen (%)	$0.081\pm0.004$	$\textbf{0.098} \pm \textbf{0.006}$
Elemental analysis	Carbon (%)	$43.26\pm0.02$	$42.01 \pm 0.74$
	Hydrogen (%)	$6.23\pm0.04$	$6.17 \pm 0.04$
Corbobydrata apolyzia	Cellulose (%)	94.89	93.16
Carbonyurate analysis	Non-saccharides	5.11	6.84
	$DP_v$	$1686\pm15^a$	$1660\pm8^{\rm b}$
	M <sub>w</sub> (kDa)	585	446
Depolymerization	M <sub>n</sub> (kDa)	527	407
Depotymenzation	PDI (M <sub>w</sub> /M <sub>n</sub> )	1.11	1.10
	DP < 100 (%)	1.92	11.71
	DP>2000 (%)	28.45	21.37

"a" "b" - t-student statistical difference.

(around 90 %). The total amount of residue (non-saccharides) found in the BC pulp was around 5 %, attributed to components from the fermentation and washing processes. In the fibre, the amount of non-identified residues slightly increased to 6.84 %, associated to the dissolution and spinning process. Regarding depolymerisation during dissolution and spinning of BC, the DP was found to be similar between pulp and BC regenerated fibres, yet some depolymerisation was seen in both the intrinsic viscosity (DP) (p < 0.05) and GPC data (Table 4). Both M<sub>w</sub> and M<sub>n</sub> decreased after dissolution and spinning of BC, leading to an increase in the fraction of short chains (DP < 100: from 1.92 % to 11.71%) and, consequently a decrease in the fraction of long chains (DP > 2000: from 28.45 % to 21.37 %) (Table 4). Indeed, some depolymerisation occurred on BC during dissolution with [DBNH][OAc] and spinning [57], yet not being significant to decrease the average DP.

# 3.2. Yarn & knitting of BC

The staple fibres spun with the multifilament spinning unit (collected at DR 8) exhibited good mechanical performance (tenacity of 53 cN.  $tex^{-1}$ ; elongation of 12 %, and titre of 1.5 dtex), a high orientation and a low amount of impurities (Figs. 2 and 3), and were converted into a yarn using a laboratory ring-spinning unit. It is difficult to compare yarns spun on a laboratory scale with commercially produced products using industrial yarn spinning devices. Therefore, a couple of benchmark staple fibres (both experimental and commercial) were selected to produce reference yarns: Ioncell® fibres spin from PHK pulp, viscose, and Tencel.

The BC-fibre yarn had a tenacity, elongation, and yarn count of 25.3  $cN.tex^{-1}$ , 7.8 % and 19.8 tex, respectively. The tenacity was slightly

lower than in the case of yarn spun from PHK-pulp Ioncell® fibres are reported by Michud et al. [40]: tenacity of  $34.4 \text{ cN.tex}^{-1}$  and 7.4 % of elongation at a yarn count of 27 tex. However, BC yarn outperformed both Tencel (tenacity, elongation and yarn count of 26 cN.tex<sup>-1</sup>, 9 % and 20 tex, respectively) and viscose yarns (tenacity, elongation and yarn count of 17 cN.tex<sup>-1</sup>, 18 % and 31.5 tex, respectively) [40,58]. The yarn was then knitted into small fabrics (Fig. 4). Recently, the company *Nanollose* also produce fabrics from BC using Lyocell and Viscose processes [59], and by depolymerization through mercerization to achieve suitable spinnable solutions [60].

MMCFs are usually off-white due to chromophore formation during the spinning process and undergo subsequent bleaching stages to arrive at white fibres. Cellulose reducing ends are prone to chromophore formation during dissolution and spinning in Lyocell and viscose operations. Colour measurements (using CIE Lab system) were done to monitor the colour of the fibres and knitted fabrics. Comparing fibres spun at DR8 and DR18, the brightness seemed to increased slightly at higher DR (Table 5). However, this might be an effect of the reduced fibre diameter which alters light scattering and reflectance. The original BC fabric (unbleached) presented a vellowish hue with reduced lightness. Dissolution, filtration, and spinning at temperatures of 80-85 °C may have led to aforementioned chromophore formation. The same discolouration was noticed by Parviainen et al. [20] after treating cellulosic substrates in [DBNH][OAc]. A standard bleaching procedure allowed to remove most of the yellowish colour (b\* decreased from 14.8 to 9.1; L\* increased from 79.7 to 81.7) (Table 5).

# 3.3. BC to enable recycling of low-DP textile waste

At present, industrial BC cultivation and isolation is still limited by high operational costs and low BC yields [49,61,62]. Nevertheless, the

# Table 5

Colour measurement (CIELAB colour space) of BC fibres and the resulting knit: where  $\Delta E = \left(\Delta L^2 + \Delta a^2 + \Delta b^2\right)^{0.5}$ , L\* represents the lightness value from black to white, a\* the green to magenta opponent colours and b\* the blue to yellow opponent colours.

Sample	L*	a*	b*	$\Delta E^1$
BC fibres (DR8) BC fibres (DR18) BC fabric (unbleached) BC fabric (Bleached)	$\begin{array}{c} 82.4 \pm 1.7 \\ 84.6 \pm 1.5 \\ 79.7 \pm 0.9 \\ 81.7 \pm 0.6 \end{array}$	$\begin{array}{c} 2.8 \pm 0.5 \\ -0.9 \pm 0.3 \\ 2.4 \pm 0.2 \\ 1.4 \pm 0.1 \end{array}$	$\begin{array}{c} 7.3 \pm 0.3 \\ 7.0 \pm 1.2 \\ 14.8 \pm 0.2 \\ 9.1 \pm 0.3 \end{array}$	4.27 (>2.0) 6.10 (>2.0)

 $1~\Delta E<$  1.0: Not perceptible by the human eye;  $\Delta E=$  1–2: Perceptible through close observation;  $\Delta E=$  2–10: Perceptible at a glance.



Fig. 4. On the left: picture of fibres, yarn and knitted BC; on the right: unbleached vs bleached knitted BC samples.

industrial production of BC bears great potential for output increase, for example with regards to strain improvement through genetic engineering, optimization of the water usage and recycling, process automation, etc. Thus, although BC-based textiles and garments are unlikely to become a commercial alternative in the near future, already now BC could be a viable and valuable additive in the recycling of cellulosic textile waste with low DP. The depolymerization of cellulose in textiles made from cotton, MMCFs, hemp, linen, etc. is inevitable and largely random. The extent of chain length reduction depends on the wear and wash history of the respective product [63,64]. All spinning processes (viscose or Lyocell-type) require cellulosic solutes with a certain average molar mass and molar mass distribution to produce spinnable solution. If the DP of the starting material is too high, it can be adjusted by simple degradation [37]. However, if the DP is too low then a cellulose additive is needed to increase the average chain length and broaden the molar mass distribution. Viscose fibres represent such a challenging substrate because already virgin viscose fibres have a low DP which further reduces during for instance washing [65]. Blending small amounts of BC to viscose fibres can change the rheological properties of the resulting solution to increase the spinnability and, eventually, the properties of the spun fibres. The overall cellulose concentration was kept at 16 weight-%. Starting from a solution consisting of only viscose fibres, the BC content was gradually increased until the solution contained 12 % viscose and 4 % BC. Table 6 summarizes the spinning trials of the dopes prepared from a mixture of viscose fibres and BC. Their rheological properties were assessed through frequency sweeps like in the case of pure BC solutions (see Fig. S6 and S7). The particular behaviour of the complex viscosity did not allow to use the Cross model to calculate the zero-shear viscosity. Overall, the addition of BC to viscose as main cellulosic substrate had little influence on the complex viscosity. However, BC did change the visco-elastic behaviour of the solutions as reflected by the dynamic moduli. The storage and loss moduli represent the elastic and viscous portion of the cellulose solution and are both frequency dependent. At low angular frequency the loss modulus is usually higher. As the frequency is increased the storage and loss moduli intersect at the so-called crossover point (COP) at which the solution behaves predominantly elastically. The COP represents a relaxation time which relates to the molecular weight of the cellulose and is shifted to higher angular frequencies upon increase of temperature or decrease of cellulose concentration [66]. At 50 °C, the 16 % viscose solution did not show a COP which would indicate the transition from dominantly viscous to elastic behaviour. The presence of small amounts of BC (< 4 %) did not change this. However, upon the addition of 4 % BC such a transition becomes visible at 1.2 s<sup>-1</sup> (Fig. S7). At higher temperatures than 50 °C, also the solution of viscose fibres showed a COP at angular frequencies  $>10 \text{ s}^{-1}$ , which is shifted towards lower frequencies when BC is added. Earlier, a COP at ca. 1  $s^{-1}$  and 5000 Pa was found as indicator for good spinnability [17,34].

Spinning of pure viscose fibre solution was challenging, where a

#### Table 6

Dry jet-wet spinning parameter for the viscose/BC-solutions: optimal temperature for spinning, maximum DR achieved; DR that allowed for stable continuous spinning.

Cellulose concentration (%)	Optimal T [°C]	Maximum DR	Spinning	
Viscose 16 %	50	8	Non- Continuous	
BC 13 %	80	18	Continuous*	(DR8)
Viscose 14 % BC 2 %	80	13	Continuous*	(DR 8)
Viscose 13 % BC 3 %	80	13	Continuous*	(DR 8)
Viscose 12 % BC 4 %	78	13	Continuous*	(DR 8)

\* Fibre collected for >4 min;

maximum DR of 8 was reached but could not be sustained over a longer period of time (Table 6). The addition of BC improved the spinnability of the dopes. It allowed for a continuous spinning, and higher maximum DRs of 13 were reached in viscose-based dopes with 2-4% (m<sub>BC</sub>/m<sub>dope</sub>) of BC. The optimal spinning temperature increased (up to 80 °C) with the addition of BC (as compared to the optimal spinning temperature of 50 °C for the pure 16 % viscose dope). Table 7 summarizes the intrinsic viscosity (and calculated DP values) of the various blends. As expected, a higher share of BC in the fibres led to an increase in intrinsic viscosity. The presence of longer cellulose chains from BC increased both the viscosity (Fig. S6) and the viscoelasticity (Fig. S7), important factors that contribute to the dry-jet wet spinnability of the dope [17,32]. Michud et al. [32] showed that an increase in the cellulose molar mass had a significant impact on the rheological properties due to improved entanglement of the cellulose chains [67]. This affected directly the spinnability of the resulting solutions.

Fig. 5 depicts the mechanical and structural properties of the spun fibres, which showed their typical dependence on the DR. Higher DRs led to a decrease in linear density and elongation, but increase in fibre orientation and tenacity, as was also the case for pure BC fibres and reference fibres spun from PHK pulp (Figs. 2 & 3). The standard viscose fibres used as a substrate had a tenacity of 22–26 cN tex<sup>-1</sup>, elongation at break of 20–25 %, and linear density of 1.7 dtex. The recycled viscose fibres obtained through the Ioncell process exhibited a tenacity of 24.13 cN tex<sup>-1</sup>, elongation at break of 8.27 % and linear density of 3.13 dtex.

The linear density of the recycled viscose fibres is higher than DR8 fibres spun from pure BC (Fig. 2) because of the higher polymer concentration. Also, Lyocell-type fibres have a higher molecular orientation than viscose fibres, reflected in the reduction of the elongation [17]. The incorporation of BC improved the mechanical properties notably. Even small amounts of BC increased the tenacity significantly. This is in line with earlier studies by Michud et al. [34] in which the molar mass distribution of the cellulosic solute was varied systematically. A higher share of long-chain molecules was found to improve the tenacity, which was also observed here upon the gradual increase of BC.

The strength properties of MMCFs decrease with increasing moisture content. As mentioned already earlier, water loosens the hydrogen bonds between the cellulose strands, in particular in the more accessible amorphous areas. Therefore, the tenacity of standard viscose fibres can drop up to 50 % of its conditioned value upon exposure to water. In addition, the pronounced skin-core structure of viscose fibres causes structural inhomogeneities across the fibre cross section, amplifying the effect of water on the mechanical properties of the fibre. Due to the higher crystallinity of Lyocell-type fibres the wet-to-dry ratio of the tenacity is much higher ( $\geq$ 0.8). Fibres spun from pure viscose loose strength in the wet state due to the low DP of the cellulose and also the moderate orientation at low DR of 8. However, the wet-to-dry ratio is still significantly above 0.5. The addition of BC and increase in DR also improves the wet strength as seen earlier [17,34].

These results highlight the potential of BC as a high-DP cellulose substrate that offers high mechanical performance to Ioncell fibres, representing a valuable additive for chemical recycling of cellulosic textile waste with lower DP. Other cellulosic materials with high DP such as cotton waste may offer similar properties, but waste refining

#### Table 7

Viscosity and the average degree of polymerization of the used pulps and produced fibres.

Sample		[η] mL g <sup>-1</sup>	$DP_v$
Pulps	BC pulp Viscose pulp	$\begin{array}{c} 630\pm14\\ 175\pm5\end{array}$	$\begin{array}{c} 1632\pm11\\ 417\pm3 \end{array}$
Fibres	Vis16 Vis14BC2 Vis13BC3 Vis12BC4	$163 \pm 2$ $199 \pm 1$ $234 \pm 6$ $243 \pm 5$	$\begin{array}{c} 388 \pm 1 \\ 474 \pm 0.5 \\ 558 \pm 4 \\ 576 \pm 3 \end{array}$



Fig. 5. Tenacity (cN.tex<sup>-1</sup>) (conditioned and wet state), elongation at break (%) (conditioned and wet state), linear density (dtex), and total orientation of spun fibres.

requires additional chemicals and energy, and the resulting product quality might fluctuate. Conversely, a comprehensive comparison between BC and plant-based celluloses (including cotton, dissolving wood pulp) should be carried out in the future encompassing: a life cycle analysis gauging the environmental impact and a cost analysis to understand the economic viability of all materials as additives for cellulosic waste upcycling. Regardless whether BC is a viable source of cellulose for textiles, this study provides insight on the i) behaviour of high-DP dopes and its spinning performance; ii) production of a garment from BC based filaments; iii) strategies for end-of-life fibre recycling, with BC representing a model high-DP cellulose.

#### 4. Conclusions

In this study, bacterial cellulose (BC) was successfully dissolved and dry-jet wet spun into textile fibres using [DBNH][OAc] as the solvent. Despite the high DP and molecular weight of BC, the resulting solutions had visco-elastic properties that allowed for air gap spinning and draw ratios. The resulting fibres revealed remarkable mechanical performance (breaking tenacities between 52 and 57 cN.tex<sup>-1</sup>; elongation at break ranging from 10 % to 12 %, and linear density down from 1.5 dtex to 0.83 dtex), with high crystallinity (up 60%) and high total orientation (about 0.7). Fibre spinning trials were successfully scaled and the obtained staple fibres were spun into a yarn and further knitted into a small sample fabric as a proof of concept. To date, only the company Nanollose in cooperation with Birla Cellulose produced textile fibres using BC, however in blends with dissolving-grade wood pulp [60]. Scaling the production of BC is still challenging and larger quantities at competitive costs are not yet available. However, small amounts of BC could be a valuable additive for the chemical recycling of cellulosic textile waste with low DP. The gradual incorporation of small amounts of BC can change the molar mass distribution sufficiently to improve the spinnability of waste consisting of for instance viscose staple fibres and to improve the mechanical properties of the resulting fibres.

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# CRediT authorship contribution statement

Francisco A.G.S. Silva: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. Inge Schlapp-Hackl: Writing – review & editing, Supervision, Investigation, Formal analysis. Nicole Nygren: Writing – review & editing, Investigation. Senni Heimala: Writing – review & editing, Investigation, Formal analysis. Anna Leinonen: Investigation, Formal analysis. Fernando Dourado: Writing – review & editing, Supervision. Miguel Gama: Writing – review & editing, Supervision, Formal analysis, Conceptualization.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2024.132194.

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#### International Journal of Biological Macromolecules 271 (2024) 132194

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