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Regenerated bacterial cellulose fibres

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Abstract

The global shortage of cotton for textile production, forces the exploitation of forests´ lignocellulosic biomass to produce man-made cellulosic fibers (MMCF). This has a considerable environmental impact, pressing the textile industry to search for new sustainable materials and to the development of sustainable recycling processes. Bacterial cellulose (BC), an exopolysaccharide produced by fermentation, could represent such an alternative. In particular, we tested the possibility of improving the mechanical properties of cellulose filaments with a low degree of polymerization (DP) by combining them with high DP from BC, so far exploited to little extent in the textile field.

In this work, BC with different degrees of polymerization (DP_{cuoxam}) (BC_{neat}: 927; BC_{dep}:634 and BC_{blend}: 814) were dissolved in *N*-methylmorpholine-*N*-oxide (NMMO) and their spinnability was studied. The rheological behaviour of the dopes was assessed and all were found to be spinnable, at suitable concentrations (BC_{neat}:9.0%; BC_{dep}:12.2%; BC_{blend}:10.5%). A continuous spinning was obtained and the resulting filaments offered similar mechanical performance to those of Lyocell. Further, the blending of BC pulps with different DPs (BC_{blend}, obtained by combining BC_{neat} and BC_{dep}) allowed the production of fibres with higher stiffness (breaking tenacity 56.4 $CN.tex^{-1}$) and lower elongation (8.29%), as compared to samples with more homogeneous size distribution (neat BC and depolymerized BC).

Keywords

Bacterial Cellulose; NMMO; Degree of Polymerization; Mechanical properties

Introduction

The increasing demand for textile products forces the industry to constantly adapt its sources and manufacturing [1]. The most used synthetic fibre is currently polyester, followed by cotton [2]. Although these are interesting materials due to their low production cost, they carry a high environmental impact [2]. Synthetic fibres are used for a short period of time while taking years to degrade. Also, their recycling rate is still low, being often disposed in landfills [3]. Cotton crops require high amounts of pesticides and large amounts of water (global water footprint of 5,730 $m^3.ton^{-1}$ for crop production) [2,4]. An alternative to cotton (natural cellulose fibres) and synthetic based fibres are the Man-Made Cellulose Fibres (MMCF, also known as regenerated cellulose fibres). MMCF are from wood biomass and have been extensively studied and are

commercially available [5]. There are several methods for the development of MMCF, including well-established processes such as Acetate, Viscose, Cuprammonium and Lyocell, as well as experimental approaches such as Ioncell (or other Lyocell type process using ionic liquid as cellulose solvent), carbamate or LiCl/DMAc [2]. These production processes differ primarily in [2,6,7]: i) The selection of the solvent—some involving cellulose derivatization (e.g., acetate cellulose [8] and viscose [2]), while others employ direct dissolution (N-Methylmorpholine N-oxide (NMMO) [9,10], LiCl/DMAc [8] and ionic liquids [11]); ii) The type of fibre spinning—wet spinning versus dry-jet spinning (with an air gap between the spinneret and the regeneration bath). The cellulose-based solution is extruded through a spinneret, followed by cellulose regeneration via coagulation in a bath containing an antisolvent. Subsequently, the fibres are subjected to drawing and then gathered as continuous fibres or cut into staple fibers, with lengths ranging from 1 to 40 cm.

One of the most promising processes is Lyocell, whereby cellulose is dissolved in *N*-Methylmorpholine *N*-oxide (NMMO), followed by dry-wet spinning in a water-based coagulation bath [9,12]. In its monohydrate form (water content of 13.3% (m/v)), NMMO is a polar organic solvent with a great capacity for dissolving cellulose [9,13]. Cellulose dissolution is a complex process, being dependent on the amount of cellulose, water, NMMO, temperature, degree of polymerization (DP) and mechanical agitation [10,12,14]. It includes two stages, swelling and gradual dissolution layer by layer, whereby the water originally linked to cellulose is replaced by NMMO [8]. Celluloses with DPs (higher than 1000), low temperatures (80-90°C) and poor mechanical agitation during dissolution are known to decrease the efficiency of the process. Also, high temperatures (e.g., higher than 120 °C), may cause undesirable and auto-catalytically NMMO degradation [15]. Stabilizers such as isopropyl gallate are used to prevent NMMO's thermal degradation [16]. Despite its complexity, the dissolution zone in the phase diagram is well established at temperatures between 80 and about 100 °C for plant celluloses with a DP of 550-650 [12].

Plant celluloses are most commonly used as raw material for the development of regenerated cellulose fibres. Despite being recognized as the next generation of renewable biomass for high-performance textiles, environmental issues are a concern, namely due to intensive deforestation and wood (chemically-based) processing. Bacterial Cellulose (BC), synthesized by *Komagataeibacter* sp. via fermentation, may represent a new resource for manufacturing MMCF. Although BC faces challenges regarding cost-effective scaling up, its production offers lower environmental impact and may provide a valuable option for the production of textiles with special properties or combined with recycled fibres to improve their properties. The development of regenerated BC fibres has so far been explored to very little extent. Gao et al., [17] managed to dissolve neat BC in NMMO monohydrate (NMMO.H_2O), using a cellulose concentration of 7% m/m (DP = 2700). The resulting regenerated fibers had a cellulose II crystalline structure, lower degree of crystallinity (native BC: 74.14% vs regenerated BC fibres: 60.83%), smaller crystallites (size of the planes (101), (10-1) and (002) was 80, 120 and 81 Å, and 26, 30, 54 Å, respectively for native and regenerated BC), but higher thermal stability than neat BC (decomposition started at 320 °C for RBC and 300 °C for native BC). Yet, these fibers had lower tenacity (5-15 cN.tex^{-1}) and elasticity (3-8 %) than commercial Lyocell counterparts (Tenacity: 40-44 cN.tex^{-1}; Elongation: 14-16%) [17]. Makarov et al. [18] used an alternative process (developed at the All-Russian Scientific-Research Institute of Polymer Fibres) [19,20] for Lyocell fibre production. High-melting

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hydrate forms of NMMO were used for the dissolution of cellulose, at 105 °C, under compression, shearing and forced plastic flow. Neat BC (DP = 1500) was dissolved at a maximum concentration of 6% m/m, the produced fibres presenting similar mechanical performance to those of Lyocell and Viscose fibres [2,18]. Considering these studies [17,18], dissolving BC in NMMO was found to represent a major processing issue, due its high DP (around 1,000-2,000). Although high DPs have a positive effect on the fibre stiffness, it undesirably influences the solubility of BC in different solvents (including NMMO). Very high DPs also increase the viscosity of the dope, potentially hindering its preparation and a proper spinning [21].

The textile industry urgently needs new sources of fibre to meet the needs of a growing world market [11]. The development of technologies for textile fibres recycling may represent a solution, addressing the environmental issues related to the accumulation of huge amounts of used textiles. Therefore, the European Commission unveiled a strategy focused on production of sustainable and circular textiles. One particular goal is the development of "durable, repairable and recyclable textiles". These textiles are intended to consist predominantly of recycled fibers, free of harmful substances, and to be manufactured in accordance with social and environmental principles. Currently, the recycling rate of textiles is still low, due to ineffective processes [22]. Mechanical and chemical treatments are used for this purpose, but these are severe and each reutilization cycle further degrades the fibres by significantly lowering their DP (often bellow 300), thus deteriorating the fibres' mechanical properties [22]. A crucial objective in achieving sustainable MMCF production involves adapting the processes of regenerated fibers by incorporating recycled cellulose, sourced by end-of-life fibres (such as cotton, hemp, linen, Viscose, or even Lyocell). We hypothesise that BC, with high DP, may play a relevant role in this scenario, by contributing to the improvement of the recycling process through the combination of high DP BC with low DP recycled fibres [23].

To our knowledge this approach has never been studied so far and therefore the effect of BC's DP on its dissolution in NMMO, spinning and mechanical properties of the resulting fibres were analysed. Depolymerisation of BC was optimized by adapting the mercerization and ageing steps from the Viscose process. Then, BC samples (with different DPs) were dissolved and spun through dry-jet spinning. The blending of BC with different DPs was carried out in order to see its effect on the rheological behaviour (dope) and mechanical performance (fibre). This way, testing the hypothesis that the combination of celluloses with different DP may improve the properties of the final product. A rheological and mechanical characterization of the prepared dopes, and regenerated cellulose fibres was performed.

2.Materials and Methods

2.1 BC pulp preparation

Commercial BC membranes from HTK Food Co., Ltd. (Ho Chi Minh City, Vietnam) were washed by immersion in a sodium hydroxide solution (0.1M) twice, for 24h, at room temperature. Then, the BC was washed for several times with distilled water until the pH became that of the distilled water, yielding pure BC. In order to obtain a BC pulp, the membranes were cut into cubes and wet-ground with a hand-blender. Then, the BC concentration was adjusted to a final value of 0.5% w/v and mechanically processed with a blender

(Moulinex TYPE LM935) (6 times for 5 mins each time, allowing cooling between each period), to improve its dissolution in NMMO. Then, the BC pulp was concentrated to c.a. 10% w/v through centrifugation (Multifuge XR3, Thermo Fisher) at 18,000 rpm, at room temperature, followed by filtration (using vacuum pump (Millipore, Model WP6122050)); the dry matter content of each pulp was recorded. A fraction of the pulp was kept until use and another subjected to depolymerisation, as described further.

2.2. Optimization of the BC depolymerisation

BC depolymerisation was carried out through a mercerization and aging step as described by Jinzarli et al., [24,25]: never dried BC pulp (10% w/w) was first dispersed in NaOH solution with 5M to a final BC concentration of 2 %w/w. Each alkaline BC suspension was then subjected to constant magnetic stirring (600 rpm) at 50 °C for 60 min. Then, the mercerized BC was concentrated through centrifugation (18,000 rpm, at room temperature) up to 8-10 % w/v, and poured in a rotary evaporator (Heidolph VV2000) (at 50°C, without vacuum) for the aging step, under constant agitation, for 4h. Afterwards, the BC was washed with distilled water, with several filtrations, until the pH became that of the distilled water. The depolymerised BC was then freeze dried in a freeze drier (Coolsafe 100-9 Pro, Labogene, Allerød, Denmark) at -100°C and 0.025 mbar. The DP of all samples was characterized as described in section 2.3

2.3. Estimation of the Degree of Polymerisation

The average degree of polymerisation (DP) of the BC pulp was also determined using cuoxam, according to an internal standard specification used at Thüringisches Institut für Textil- und Kunststoff-Forschung (TITK). For this purpose, the intrinsic viscosities in cuoxam $[\eta]_{cuoxam}$ (unit: ml/g) were detected by means of a capillary viscometer and the DP_{cuoxam} was calculated according to the following equation:

$$DP_{cuoxam} = 2 * [\eta]_{Cuoxam} \quad (1)$$

This method is normally used to access Lyocell pulps which typically have DP values in the range of 500 - 650. Due to the high DP of BC, small deviations from the used linear relation between the intrinsic viscosity and the DP_{cuoxam} cannot be ruled out.

2.4. Dope preparation of BC NMMO

Three BC dopes were prepared, using pulps with different DPs. BC pulps with a DP_{cuoxam} of 634, 758 and 927 were labelled as, respectively, BC_{dep}, BC_{blend} and BC_{neat}. BC_{neat} refers to neat BC pulp (without any depolymerisation), BC_{dep} refers to the depolymerised BC (see section 2.2.) and BC_{blend} refers to a blend of the previous ones (62% w/w of neat BC and 38% w/w of depolymerised BC). Concerning the BC_{dep}, a mixing step was made before its dissolution in NMMO: the BC was dispersed in deionized water with an ultra-turrax mixer (DIAX 900, Heidolph Germany) and then concentrated with a vacuum filter (with a glass filter).

Before dissolution, the dry matter content of BC_{neat} or BC_{dep} was determined to be 10.3% and 96.0%, respectively. Then, BC pulps (BC_{neat}, BC_{blend} or BC_{dep}) were transferred into a kneader reactor (PML 8, Netzsch, Germany) to be mixed with NMMO (Ravago Chemicals) solvent (60% w/v) and propyl gallate 0.6 % (w/w$_{BC}$). The distillation of water (swelling and dissolution step) from the mixture was made under constant kneading

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(80-100 rpm), jacket temperature of 95°C and a reduced end-pressure of 20-30 mbar. When the dope reached its monohydrate form (13.3 ± 4% w/w of H_2O), NMMO began to interact with the hydroxyl groups of the cellulose, dissolving it [10]. The process was considered complete when a clear amber coloured dope was obtained (without any visible gel or fibrous particles) (Figure 1-C). Equation 3 was used to determine the final BC concentration:

$$Solid\ content\ (\%) = \frac{mBC}{msolution\ final}\ \ (2)$$

Figure 1 here please

2.5. Dry-wet-spinning

A lab scale dry-wet spinning module (self-construction by TITK) (Figure 2) was used for the development of the BC fibres. Each of the produced dopes were transferred into the storage tank of the laboratory spinning line and the dope was left at 85 °C standing overnight to remove air bubbles. Then, each solution was spun at 80 - 95 °C (depending on the dopes solid content) through the spinneret holes (with 7 x 80 holes for staple fibres and 4 x 80 holes for filament, 90 μm spinning hole diameter) with a varying extrusion velocity (9.75-13 m/min) and a godet speed of 30 m/min. The generated spinning capillaries passed through an air gap (about 10 mm length) before entering in the coagulation bath (water at room temperature). After filament formation, the multi filament bundle was collected and drawn at the following draw - ratios (DR, ratio between the collecting and extrusion velocity): DR of 2.3; 3.1 and 2.7 for BC_{neat}, BC_{dep} and BC_{blend}, respectively. Concerning BC_{neat} and BC_{dep}, the fibres were cut to a predetermined length of 38 mm (resembling staple fibres of cotton), washed multiple times with water and air dried at 70 °C until equilibrium moisture content. The BC_{blend} was collected as a multi filament yarn, where additional washing steps and drying godets (rotating) at 90 °C were used, before winding.

Figure 2 here please

2.6. BC & RBC characterisation

Determination of the solids content by precipitation, washing and drying

The solids content of the dope was determined by gravimetry after precipitation, washing and drying of the cellulose. About 2 g of the dope were accurately weighted, pressed out into a film and washed out the NMMO. Then the cellulose was air dried (105°C) and weighed.

Optical characterisation of the cellulose dopes by polarization microscopy

The optical characterisation of the spinning dopes was carried out using polarization microscopy. A Keyence digital microscope VHX-6000 series and a Zeiss Axiolab light microscope with 10-fold magnification lens were used. A small sample of the dope was placed on a cleaned glass slide and cover slipped and then placed in an oven at 105 °C for 1 h to form a thin uniform film.

Rheological characterisation of the cellulose dopes

The rheological characterisation of the dope was carried out by means of the rotation rheometer HAAKE MARS II, using a cone/plate measuring system (C35/4°). The measurement of the zero shear viscosities occurred by creep tests at shear stress of 90 Pa, applying a measuring temperature of 85 °C. Oscillation mode measurements at 4 different temperatures (60/85/95/110 °C) were carried out for the calculation of the master curves at a reference temperature of 85°C as well as the determination of the values for cross over between storage and loss modulus, plateau modulus and relaxation time spectra determination. Rheological polydispersity was determined from the ratio of zero shear viscosities (η_0) and complex viscosities at the cross over ($\eta*\#$):

$$U\eta = \left(\frac{\eta 0}{\eta *\#}\right) - 1 \ (3)$$

Mechanical characterization

BC staple fibers were left for 48h in controlled conditions, humidity of 65% ± 4% and temperature of 20°C ± 2°C. Then, the fibers were subjected to a single-Fibre tester (FAVIMAT+; Textechno Class 1 acc) for breaking force, elongation at break and loop tenacity measurements. For the determination of the linear density, a gravimetric method was used: 10 sets of 50 fibre were tested, using a 30 mm bundle length. For the breaking force and elongation at break, 50 single fibres were tested, with 10 mm gauge length, using a pre-load of 0.60 cN/tex and test speed of 10 mm/min (according to standards DIN EN ISO 5079:2021-02 and DIN 53843 T2:1988-03) [26,27]. For the loop tenacity, the similar specifications were used, with the exception of test speed, which was of 5.0 mm/min (according to standard DIN 53843 T2:1988-03) [27].

Statistical analysis

Statistical analysis was supported with Prism version 9.4.1 (GraphPad Software, La Jolla California USA), using one-way ANOVA and Tuckey's post hoc analysis for pairwise comparison of more than two means. Mean differences were considered statistically non-significant (ns) when p-value was higher than 0.05 (95% of interval of confidence). The default statistical confidence level was set at 95% ($P< 0.05$) in all tests.

3. Results & Discussion

3.1. BC Depolymerization and dope characterization

BC have a DP of about 1,000, whereas the pulp used in the Lyocell process normally have a DP of 550-650. It is well known that high DP values increase the dope's viscosity. This may compromise the spinning process, hindering the use of high draw ratios and subsequently the fibre performance (specially the mechanical performance). Thus, in this work we analysed in more detail the effect of the DP on the quality of regenerated (Lyocell) BC fibers. Although not used industrially in the Lyocell process, mercerization was adopted in this study to depolymerize BNC in small scale. Mercerization involves an alkaline treatment with sodium hydroxide, to swell the pulp; then, the alkali BC concentrated up to 10% cellulose is allowed to react with oxygen by stirring the dispersion, aging for 4 hours.

As observed in Table 1, the DP of BC$_{neat}$ was approximately 978 ± 45, bellow the values reported in the literature [28]. Yet, the difference may be due to the use of different methodologies for measuring the intrinsic viscosity (e.g., solvent used) and the equation for calculating the DP. After mercerization and aging, a

significant reduction in DP was observed (BC_{dep} further reduced to 608 ± 47), as expected. As described in the literature, cellulose treatment with NaOH leads to its conversion to soda cellulose (mercerization), reducing the DP as well as the crystallinity [29], the DP reduction being favoured by the presence of oxygen [24]. The study conducted by Strunk et al. [30] and the patent authored by Jinzarli et al. [25] that also demonstrated a substantial depolymerization of cellulose (of about 2 times its initial molecular weight) after the aging process. In order to produce a pulp with higher polydispersity, a third pulp (BC_{blend}) was prepared by mixing BC_{neat} with BC_{dep} (as detailed in section 2.4).

All BC pulps (BC_{neat}, BC_{blend} or BC_{dep}) were successfully dissolved using NMMO, with no observed undissolved particles (Figure 3). For each case, the final BC concentration of the obtained dope was adjusted according to the estimated DP_{cuoxam}, as well as to previous rheological characterization in smaller scale dopes: 9.0 % for BC_{neat}, 12.2 % for BC_{dep} and 10.5% for BC_{blend} (Table 1). The dopes were characterized for their rheological behaviour (Table 1). Concerning the zero-shear viscosity (η_0), the lowest value obtained was of 4,951 Pa.s for BC_{dep}, followed by BC_{blend} and BC_{neat} with 20,470 Pa.s and 21,780 Pa.s, respectively (table 1). For spinning, the η_0 is commonly targeted to 5,000 - 10,000 Pa.s, at 85°C. This means that both BC_{neat} and BC_{blend} dopes were out of range, while BC_{dep} dope was in the lower limit. As observed in Table 1, BC_{neat} with higher DP highly affected the η_0 of the dope, which consequently limited its concentration for dissolution in NMMO (cellulose concentration in standard pulps is 13%). Considering BC_{dep}, higher DP (between 600-650) or higher cellulose concentrations should increase the η_0. Importantly, a direct comparison of the obtained dopes cannot be made, as, along with differences in the DP, they differ in their concentration.

Figure 3 here please

Table 1 here please

Despite the η_0 values being out of range, other important rheological parameters should be considered, such as the storage modulus (G'), the angular velocity (ω) at cross over point, the plateau modulus (Gp), the rheological polydispersity (Uη) and the relaxation time. As observed in Table 1, the combination of high BC concentrations and lower DP (BC_{dep}: DP 553 and 12.2%BC) led to higher cross-over ω (5.64 rad/s), higher G' (4,755 Pa at cross-over) and higher Gp (30,100 Pa), as compared to the dope using untreated BC (BC_{neat}) (ω: 0.60 rad/s; G': 2,352 Pa; Gp: 22,300 Pa). The BC_{dep} showed similar viscoelastic properties (G', G'' and cross-over point, COP) when compared to common dissolution pulps [21]. BC_{neat} and BC_{blend} dopes exhibited similar elastic and viscous behaviour, being lower to those observed with BC_{dep} (Table 1 and Figure 4). As mentioned, the higher DP of BC_{neat} limited its concentration used for the dope preparation (Table 1). Consequently, at a lower concentration of cellulose (composed mainly of higher cellulose chains), the elastic and viscous behaviour of the dope decreased. Hence, the cross-over point between G' and G'' is observed at lower ω, G' and G'' values (Figure 4). Despite these differences in behaviour, a cross over between G' and G'' was still observed, where the dope shows elastic behaviour, important for spinnability (Table 1 and Figure 4). Moreover, a broader weighted relaxation time spectrum was observed for BC_{neat} and BC_{blend}, when compared

to BC_{dep} (Table 1; Figure 4). Relaxation times within 1.00s was obtained for BC_{dep}, falling within the typical range for standard pulps (when dissolved in NMMO) [21]. However, pulps with a high DP (BC_{neat} and BC_{blend}) exhibited higher relaxation times (Figure 4). For BC_{dep}, a much lower intensity was observed, with the maximum being shifted to lower relaxation time values. Dopes containing longer cellulose chains (such BC_{neat} and BC_{blend}) needed a longer relaxation time. As a result, the dopes' elastic properties (G'>G'') manifest at slower movements (lower angular velocities). Conversely, the depolymerized BC dope exhibited quicker recovery post-deformation (shorter relaxation times), meaning that the exhibiting elastic behaviour (G'>G'') occurs at higher angular velocities (Figure 4 and Table 1 for ω at crossover).

In short, differences in the rheological characterization between depolymerized BC and neat BC were verified. However, BC_{blend} (containing 62% m/m of BC_{neat} and 38% m/m of BC_{dep}), showed similar rheological characteristics to those obtained with BC_{neat}. A slight decrease in η_0 as well as an increase in storage modulus and plateau modulus is observed, mostly related to the decrease in DP (to approximately 800) and the presence of different polymeric chains sizes, resulting from the blending of BC_{neat} and BC_{dep} pulps.

Figure 4 here please

3.2. Spinning

A dope with good spinnability is mainly characterized by the ability to stretch a filament through the air gap for better cellulose alignment along the chain axis. An important feature for aligning the cellulose is the draw ratio (DR) (also known as filament stretching) characterized by the ratio between take-up and extrusion velocity [22,32]. All BC dopes were considered stable during spinning, being continuously spun for 60, 50 and 360 min, for BC_{neat}, BC_{dep} and BC_{blend}, using a DR of 2.3, 3.1 and 2.7, respectively.

After spinning, 148 g of BC_{neat} and 67 g of BC_{dep} staple fibres were collected. For BC_{blend} , a filament yarn (320 single filaments x 1.5 dtex 2 bobbins of 2,600 and 2,980 m) was collected (Figure 2).

Figure 5 here please

Afterwards, the DP_{cuoxam} was estimated once again, as shown in Figure 5. All regenerated BC fibres displayed a similar DP_{cuoxam} to that of the corresponding BC pulp (p >0.05). Although a minor decline in the degree of polymerization of RBC fibers was observed, its non-significance (p >0.05) validates that there was no substantial depolymerization of the BC during its dissolution and spinning into highly oriented fibres, proving that all BC pulps were successfully dissolved in NMMO.

3.3. Mechanical Properties

The collected RBC fibres were analysed with the goal of understanding the effect of DP and of the size distribution on the mechanical properties of the fibres. Table 2 displays the linear density, breaking force, breaking tenacity, elongation at break, initial modulus and loop tenacity of the RBC fibres, as well as data collected from the literature (Lyocell fibres).

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Table 2 here please

Significant differences (p<0.05) between RBC fibres were obtained, mainly on the linear density and elongation at break and loop tenacity. RBC$_{blend}$ fibres presented the lowest linear density and elongation at break, followed by RBC$_{neat}$. There were no significant differences (p>0.05) observed between RBC$_{neat}$ and RBC$_{dep}$ in terms of the breaking force, breaking tenacity, initial modulus and loop tenacity. In turn, RBC$_{blend}$ presented the highest stiffness (breaking tenacity and initial modulus) (p<0.05). From these results, it is perceived that varying the DP and consequently the concentration of BC did not affect the overall mechanical performance of the RBC fibres (Table 2). On the other hand, importantly, the blending of pulps with different DPs significantly improved the mechanical performance. This finding is aligned with studies conducted by Michud *et al.* [33] and Härdelin et al., [34], where the authors noted that the presence of cellulose chains with broad Mw distribution enhances the intermolecular entanglement. This phenomenon influences then the viscoelastic characteristics of the dope, enhancing the drawing during the spinning process, impacting positively in the fibre alignment. All these improvements collectively contribute to an overall superior mechanical performance. Despite the high stiffness of RBC fibres, lower initial modulus (higher deformation under initial stress) and loop tenacity was obtained on RBC fibres. The values reflect the lower orientation of the cellulose molecules due to the lower DR applied during spinning.

Other parameters to be considered are the BC concentration in the spinning solution and the applied draw ratio. For BC$_{dep}$, the amount of BC used (12%) was near that of the one used in standard Lyocell process (13%), but was lower in the case of BC$_{blend}$ (10.5%) and BC$_{neat}$ (9.0%), since the amount of BC was adjusted depending on the DP. Consequently, the ability to stretch the fibre during spinning was also limited. The applied DRs were on the lower end (between 2-3) of the standard values used for commercial Lyocell (between 2-10) [35]. In order to collect fibres with low linear density (1.3-1.5), higher DRs should be applied. However, the stretchability of the spinning solution at higher DRs was limited due to the high DP of BC. For that reason, the selected DR (for each dope), represented the maximum DR without compromising the spinning. Additionally, using lower drawing ratios avoids fibrillation, as reported by Cui et al. [35]. However, the lack of stretching (lower DR) may have influenced the overall mechanical performance. As reported in the literature, the stiffness and elasticity may be tuned by the DR during spinning. Higher DR leads to lower linear densities, which consequently leads to lower elongation at break and higher tenacity [36,37]. The high fibre stretching increases the crystallinity, birefringence and orientation, enhancing the fibre stiffness (initial Young's modulus and tenacity), yet compromising elasticity [9,35]. Even so, as discussed above, very overall good mechanical properties could be achieved using BC$_{blend}$. Furthermore, the observed differences between the various samples may also be attributed to the different fibre spinning procedures. Both RBC$_{neat}$ and RBC$_{dep}$ were collected as staple fibres, whereas RBC$_{blend}$ was collected continuously into yarn bobbins (section 2.5). Differences in the mechanical properties due to Lyocell fibre processing (staple fibres vs fibre tow) were elsewhere reported [38]. These differences may also be caused by different drying conditions. More specifically, staple fibres could be dried as nearly independent single fibre (without any counterforce), whereas

filaments would be dried as a fibre bundle, causing filament-filament-friction and reconditioning of predried bundles wound up on bobbins.

When compared to Lyocell fibres, RBC$_{blend}$ showed higher resistance (higher breaking tenacity), lower elongation at break and lower loop tenacity (Table 2). The differences encountered between RBC$_{blend}$ and Lyocell may be related to the advantage of using a more polydisperse pulp.

Finally, the developed RBC fibres were compared with cotton, polyester and MMCF (such as Lyocell, Ioncell and viscose), regarding their tenacity and elasticity (Figure 6).

Figure 6 here please

The developed RBC fibres stand out for their high tenacity, when compared to all other fibres. RBC$_{blend}$ presented a tenacity comparable to that of polyester. On the other hand, both viscose and polyester have higher elasticity than RBC fibres (Figure 6). The production of BC fibres using NMMO is not novel [17,18], yet the mechanical properties obtained with RBC$_{blend}$ were superior when compared with those reported in the literature.

The findings indicate that BC fibres, which possess higher stiffness, may be useful in the development of strategies for recycling end-of-life fibers through blending. A substantial volume of waste cellulosic textiles (including MMCFs, cotton or linen) degraded by their extensive use and repeated washing is being generated [44, 45]. This waste consists of cellulose with reduced chain length, posing challenges for recycling using viscose or Lyocell-type spinning methods. One approach to circumvent these difficulties involves the incorporation of high DP cellulose (such as BC) to increase the average chain length and widen the molar mass distribution. Spinnable dopes can be developed for Lyocell, facilitating the upcycling of textile waste. Despite its drawbacks in terms of current poor cost-effectiveness and yield at a large scale, BC stands out due to its purity (mainly composed of water and cellulose) and low ecological footprint, as evidenced by the findings in the studies conducted by Forte et al., [46] and Costa et al., [47]. Although technological breakthroughs are still necessary to make BC available at lower cost and at very large scale to match the textile industry needs for new raw materials, it may represent an alternative source of cellulose with high DP. Various fibers were already upcycled, such as hemp waste [48], newspaper [49], paper & cardboard [50], and cotton scraps [51], using Ioncell® and Lyocell technologies. These recycling methods could benefit from small additions of BC to improve both their strength and flexibility.

Indeed, additional research is still needed to validate the benefits of blending BC with other low DP fibres, as this study focused on blending BC with different DPs. Nevertheless, these initial studies have already yielded promising results for upcoming studies into the chemical recycling of end-of-life fibres. Moreover, the application of BC to promote the recyclability of other fibres allows for a more feasible prospect for the large-scale application of BC in the textile industry [52,53].

4. Conclusions

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Our findings demonstrated that a high DP – non-depolymerized – BC can be spun through the Lyocell process, in contradiction to the common believe that only depolymerized cellulose can be regenerated into high quality fibres. However, the depolymerised BC allowed its dissolution at higher concentrations (up to 13% with DP 500-600). All BC pulps were continuously spun (up to 360 min), with no major losses. The resulting fibres have shown interesting mechanical performance, particularly RBC$_{blend}$, where higher stiffness was observed. In sum, the blending of BC with different cellulose chains (different DP) improved the mechanical performance of the regenerated cellulose fibres. This demonstrates that BC (a source of long cellulose chains) may be an additive for recycled cellulosic waste materials (with low DP), blending the two materials through dissolution and spinning. Thus, BC may play a relevant role in improving the properties of recycled textile waste and thus it can be considered a promising source of cellulose for textile applications.

Conflicts of Interest: The authors declare that they have no conflict of interest.

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Figure captions

Figure 1. A - Mixture of wet BC and NMMO in the vessel; B – aspect of the mixture during dope preparation; C - BC spinning dope;

Figure 2. Large laboratory spinning line (upper section); Lower section: A- Filament extrusion from the spinning nozzle, through an air gap into a water bath; B- Drawing and drying rollers; C- Fibre collector

Figure 3. Microscopic images (polarized light) of the different BC dopes (scale division 200 μm);

Figure 4. On the left, master curves of the spinning dopes from neat and depolymerized BC; triangles - storage modulus; squares - loss modulus; open circles - Complex viscosities; on the right, weighted relaxation time spectra of the spinning dopes

Figure 5. DP_{cuoxam} estimation of BC pulps and BC regenerated fibres (RBC); ns- non significant

Figure 6. Breaking tenacity ($CN.tex^{-1}$) vs elongation at break (%) of RBC fibres, lyocell [2,24,39], viscose [24,40,41], Modal [40, 42], Super 3 cord [32], Ioncell [32,41,43], cotton [40,42] and polyester [40]

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Table 1. BC, dope and rheological characterization

	Sample	BC_{neat}	BC_{dep}	BC_{blend}
Pulp	DP_{cuoxam} BC	978 ± 45	608 ± 47	836 ± 46
Dope	Solid content (wt %)	9.0	12.2	10.5
Rheological	Zero shear viscosity (85°C), η_0 (Pa.s)	21,780	4,951	20,470
	Angular velocity, ω (cross over) (rad/s)	0.60	5.64	0.82
	Storage modulus, G' (cross over) (Pa)	2,352	4,755	2,672
	Plateau modulus, Gp (Pa)	22,300	30,100	26,200
	Rheological polydispersity, $U\eta$	2.9	3.2	3.5
	Relaxation time, λ_m at H*m (s)	11	1.75	13.8

Table 2. Mechanical properties of RBC fibres and Lyocell (from literature)

Sample	RBC_{neat}	RBC_{dep}	RBC_{blend}	Lyocell [30,38]
Draw-ratio	2.3	3.1	2.7	2.0-10.0
Linear density (dtex)	1.7 ± 0.04^a	1.7 ± 0.02	1.5 ± 0.02^c	1.3-1.7
Breaking force (CN)	7.8 ± 1.6^{ab}	8.2 ± 8^{bc}	8.6 ± 1.5^{bc}	-
Breaking tenacity (CN.tex^{-1})	46.4 ± 9.5^{ab}	48.0 ± 10.6^{ab}	56.4 ± 9.5^c	40-48
Elongation at break (%)	10.9 ± 1.4^a	12.1 ± 1.9^b	8.3 ± 1.1^c	10-16
Initial modulus (CN.tex^{-1})	$978 \pm 287^{*ab}$	$1,119 \pm 273^{*ab}$	$1,917 \pm 334^{*c}$	2,500-2,700
Loop tenacity (CN.tex^{-1})	14.5 ± 3.5^{abc}	15.7 ± 3.8^{ab}	12.8 ± 3.6^c	18-20

* Modulus 0.5%-0.7%, related to bundle linear density; for the same row, the different superscript letters indicate statistically significant differences (p<0.05); RBC- Bacterial cellulose regenerated fibres;

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Declaration of interests

☒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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
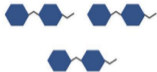
Graphical abstract

Bacterial Cellulose (BC) → BC dope → BC dry-jet spinning
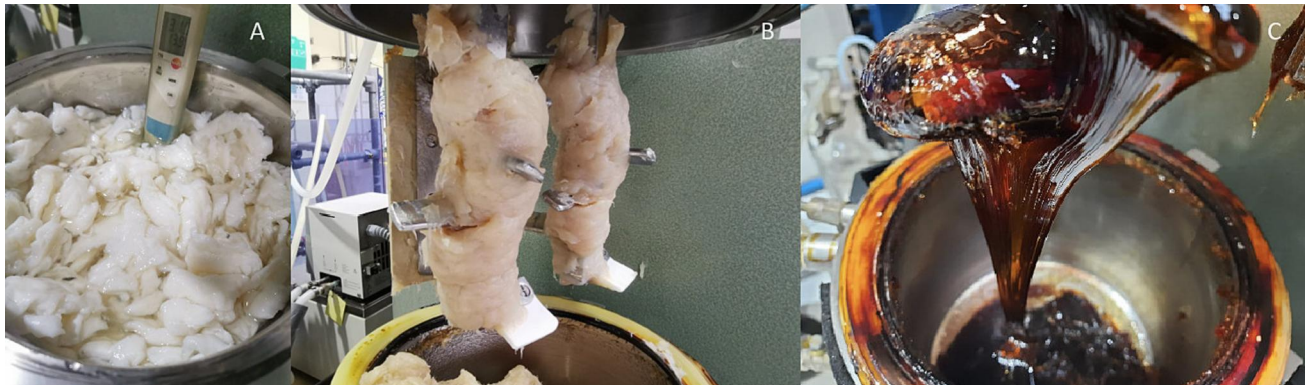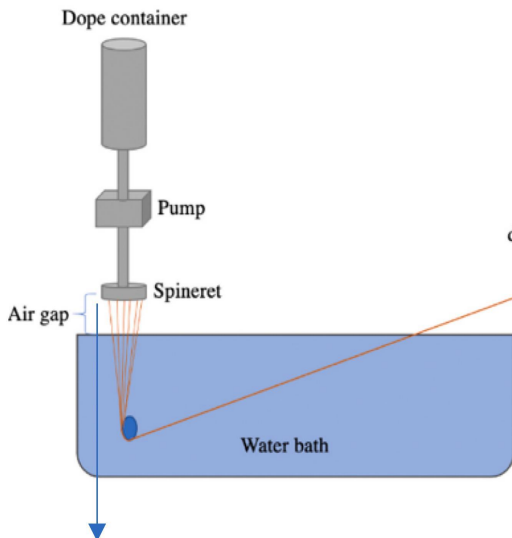
DP effect

Mechanical Performance

Graphics Abstract

Figure 1

Spinning Step

Whashing step

Dope container
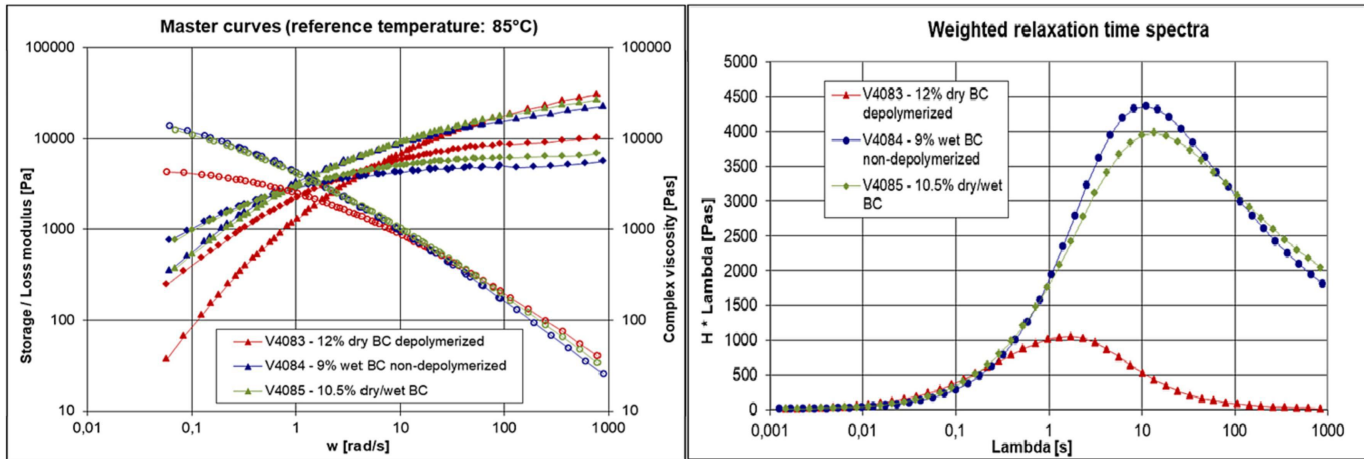
Pump

Spineret

Air gap

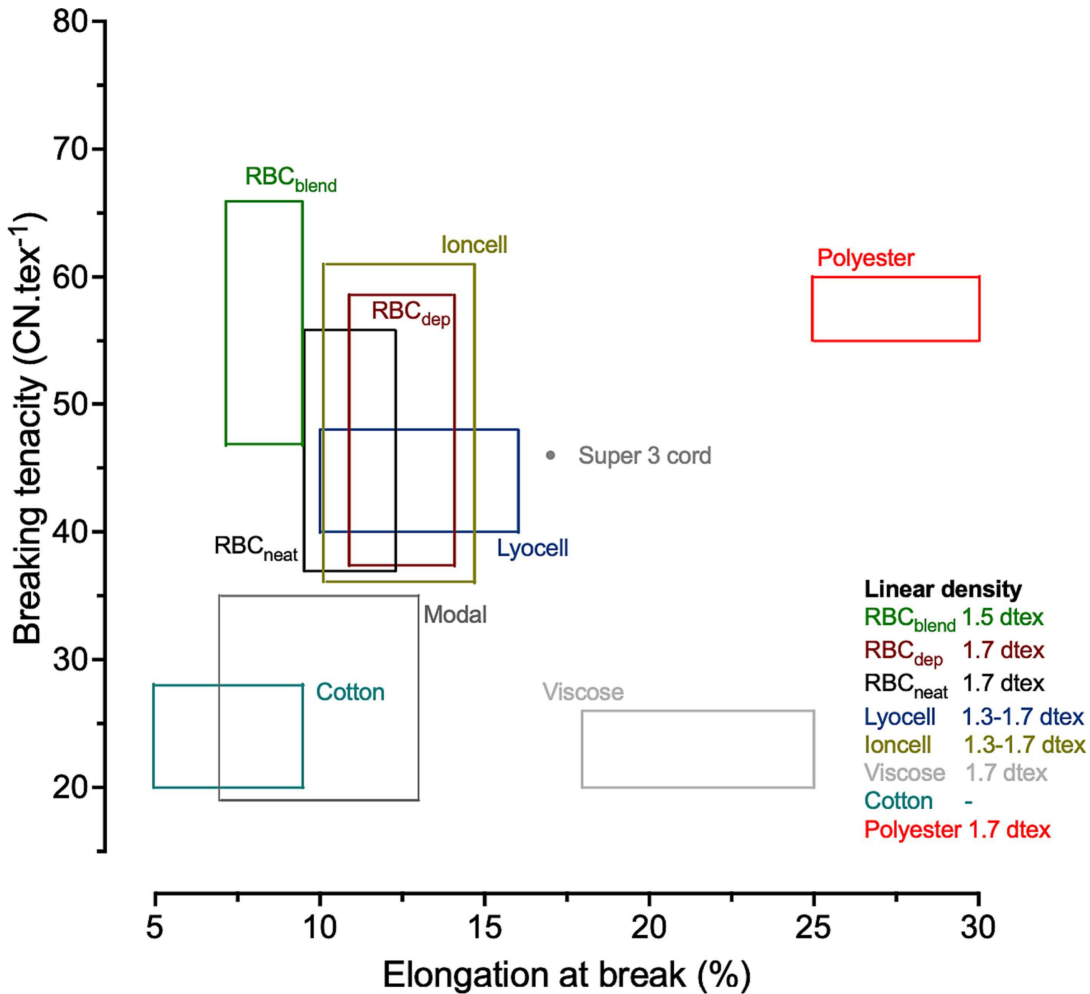Water bath

drag rollers

Regenerated BNC fibre

A

B

C
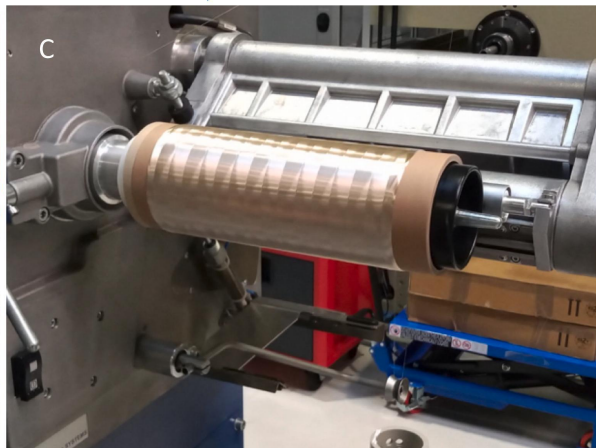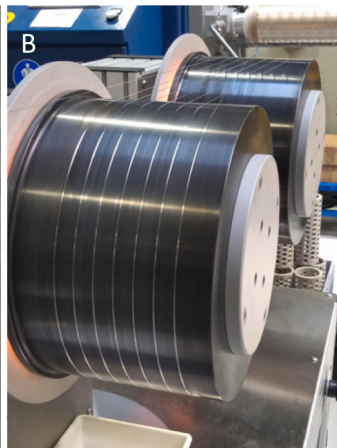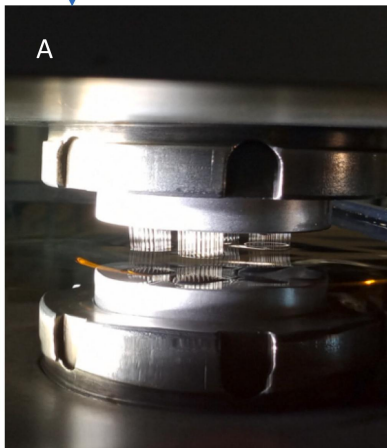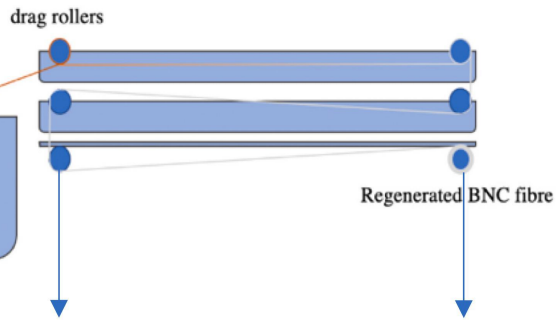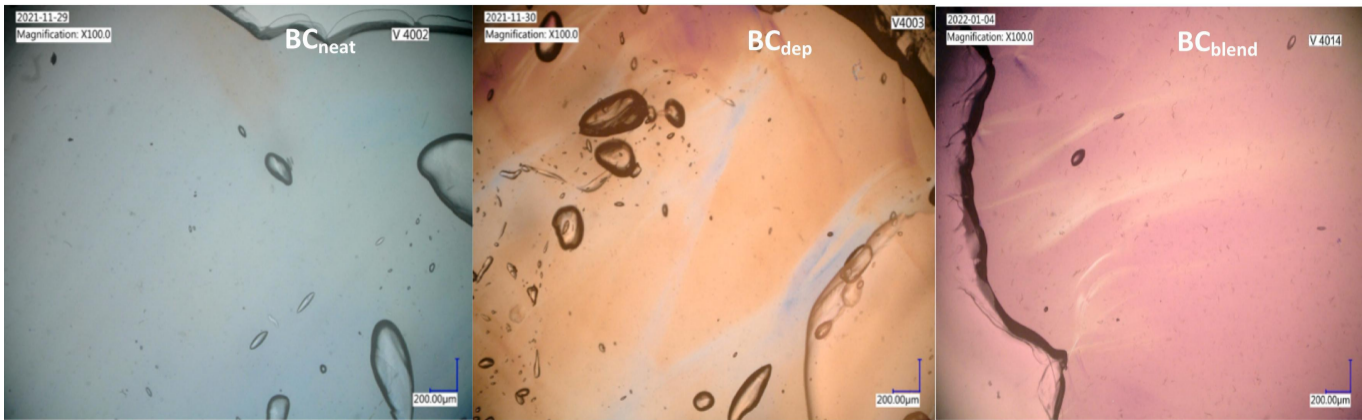
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6