

# High Modulus Regenerated Cellulose Fibers Spun from a Low Molecular Weight Microcrystalline Cellulose Solution

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KEYWORDS microcrystalline cellulose, ionic liquid, anisotropy, fiber spinning, alignment, mechanical property.

ABSTRACT: We have developed a novel process to convert low molecular weight microcrystalline cellulose into stiff regenerated cellulose fibers using a dry-jet wet fiber spinning process. Highly aligned cellulose fibers were spun from optically anisotropic microcrystalline cellulose/1-ethyl-3-methylimidazolium diethyl phosphate (EMImDEP) solutions. As the cellulose concentration increased from 7.6 wt% to 12.4 wt%, the solution texture changed from completely isotropic to weakly nematic. Higher concentration solutions (>15 wt%) showed strongly optically anisotropic patterns, with clearing temperatures ranging from 80 °C to 90 °C. Cellulose fibers were spun from 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose solutions. The physical properties of these fibers were studied by Scanning Electron Microscopy (SEM), Wide Angle X-ray Diffraction (WAXD) and tensile testing. The 18.0 wt% cellulose fibers, with an average diameter of ~20 μm, possessed high Young's modulus up to ~22 GPa, moderately high tensile strength of ~305MPa, as well as high alignment of cellulose chains along the fiber axis confirmed by X-ray diffraction. This process presents a new route to convert microcrystalline cellulose, which is usually used for low mechanical performance applications (matrix for pharmaceutical tablets and food ingredients, etc.) into stiff fibers which can potentially be used for high performance composite materials.

## INTRODUCTION

Cellulose is a polysaccharide consisting of long linear chains of  $\beta$ -(1, 4)-D-glucose units<sup>1</sup>, which is the most abundant and renewable polymer in the world with an annual biosphere production about  $90 \times 10^9$  metric tonnes<sup>1</sup>. As a biopolymer it possesses desirable mechanical properties<sup>1</sup>, such as high molecular order, as well as excellent renewability, biodegradability and biocompatibility<sup>2</sup>. However, the multiple hydroxyl groups on cellulose form intra- and inter-molecular hydrogen bonding, holding the chains firmly together side-by-side thus making it relatively insoluble in most traditional solvents such as water, ethanol and acids<sup>1, 3</sup>. In addition, hydrophobic interactions may contribute to this insolubility<sup>4</sup>.

Viscose process and Lyocell process are the two main methods for manufacturing regenerated cellulose fibres. The Viscose process needs multiple steps to manufacture regenerated cellulose fibres including use of chemical derivatization using high aggressive carbon disulphide solvent. This makes the process more expensive and environmentally hazardous (Hermanutz et al, Macromol. Symp. 2008, 262, 23–27). Lyocell process (which uses N-Methylmorpholine N-oxide, NMMO solvent) is proposed as alternative for the Viscose process. The solvent used in Lyocell process is thermally unstable and required significant financial investment in safety technology. Also the regenerated cellulose fibre produced in Lyocell process shows severe fibrillation. Over the past decade new generation of solvents for cellulose called ionic liquids (ILs) have attracted much attention for their chemical and thermal stabilities<sup>3</sup>, high decomposition points, low vapour pressures, low flammability<sup>4</sup>, excellent recoverability (> 99.5%) and reusability<sup>5-6</sup>. The anions in ILs can form hydrogen bonds with hydroxyl hydrogen and oxygen atoms in cellulose, which break down the hydrogen bonding network thus contributing to the dissolution of cellulose<sup>7-8</sup>.

Unlike the Viscose process, the ionic liquids can dissolve cellulose in one-step without need of chemical derivatization. They are thermally more stable than NMMO used in Lyocell process and avoid the problem of fibrillation of regenerated cellulose fibres. Although the ionic liquids are expensive solvents, due to their less aggressive nature (unlike solvents used in Viscose and Lyocell process), ability to dissolve cellulose in one step and higher thermal stability they do not require large financial investment in safety equipment and auxiliary. They can be easily recycled with high recycling efficiency. Hence they can potentially be an attractive alternative to traditional Viscose process despite of their initial high cost.

Recently, some researchers have reported the formation of optically anisotropic solutions by dissolving cellulose in ILs<sup>14-15</sup>. It is well known that anisotropic solutions can greatly improve the spinnability of fibers<sup>16</sup>; the regenerated fibers produced from such solutions possess excellent mechanical properties due to their intrinsic, highly oriented and rigid molecular backbones as well as strong intermolecular hydrogen bonds<sup>17</sup>. Northolt *et al.* produced very good quality cellulose fibers from an anisotropic solution of cellulose in phosphoric acid with a modulus of 44 GPa and tensile strength of 1.7 GPa<sup>18</sup>. However, a relatively complex mixing process was used in their study, involving orthophosphoric acid, pyrophosphoric acid, polyphosphoric acid, phosphorus pentoxide, and water.

In this study, a low molecular weight microcrystalline cellulose, which is usually used for applications requiring low mechanical properties (medical tablets, food-stuffs, etc.), is used to spin fibers with a high tensile modulus from optically anisotropic solutions, using a phosphate based

ionic liquid as a solvent. The concentration of microcrystalline cellulose dissolved in the ionic liquid was optimized to achieve optically anisotropic solutions to improve the alignment of cellulose chains. Similarly, a high fiber extrusion/winding ratio was used to further improve this alignment to obtain high modulus cellulose fibers. The manufacturing process established in this study has great potential to produce regenerated cellulose fibers for the composites industry by introducing sustainable and renewable fibers with enhanced mechanical performance.

## EXPERIMENTAL METHODS

### **Materials and Dissolution Method**

Highly pure microcrystalline cellulose (MCC), VIVAPUR101, with a viscosity-averaged degree of polymerization (DP) between 200 and 220<sup>14, 19</sup>, was purchased from JRS Pharma GmbH & Co. KG (Rosenberg, Germany). Ionic liquid (IL) 1-Ethyl-3-Methylimidazolium Diethyl Phosphate (EMImDEP) was purchased from Sigma-Aldrich (713392, Gillingham, UK). A magnetic stirrer hotplate (Fisher scientific, Loughborough, UK) with an oil bath was used for the preparation of cellulose solutions. The dissolution process was carried out in a fume hood. 7.6 wt% (2.3 g), 12.4 wt% (3.7 g), 15.2 wt% (4.6 g) and 18.0 wt% (5.4 g) of cellulose were added to 30 g EMImDEP and heated at 95 °C with magnetic stirring at 100 rpm for 24 h, respectively.

### **Characterization of Cellulose/EMImDEP Solutions**

Small amounts of 7.6 wt%, 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose/EMImDEP solutions were pressed to form thin films between two glass slides<sup>19</sup>. These films were placed on a Linkam PE120 thermoelectrically-controlled stage connected to an EHEIM professional 3 water filter for cooling. The observation of optical anisotropy and clearing temperatures of cellulose solution films

was conducted using an Olympus BX51 polarized optical microscope with a PixeLINK PL-B625 camera with a  $\times 10$  objective. The films were heated at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  from  $25\text{ }^{\circ}\text{C}$  to  $90\text{ }^{\circ}\text{C}$  ( $\pm 0.1\text{ }^{\circ}\text{C}$ ), maintaining a fixed temperature for 5 min before taking the polarized optical micrographs. Micrographs were taken at  $25\text{ }^{\circ}\text{C}$  first, then at  $10\text{ }^{\circ}\text{C}$  increments from  $30\text{ }^{\circ}\text{C}$  to  $60\text{ }^{\circ}\text{C}$ , and then at  $5\text{ }^{\circ}\text{C}$  increments from  $60\text{ }^{\circ}\text{C}$  to  $90\text{ }^{\circ}\text{C}$  (see supplementary information section Figure S1-3).

### **Fiber Spinning of Cellulose**

Specifically-designed fiber spinning equipment (Rondol, UK), which consists of a vertical ram extruder, a water bath and a haul off unit, was used for the dry-jet wet fiber spinning of the regenerated cellulose fibers (Figure 1).

7.6 wt%, 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose/EMImDEP solutions were transferred into a removable extruder barrel and degassed in a vacuum oven at  $80\text{ }^{\circ}\text{C}$  under 800 mbar for 18 hours to remove bubbles before spinning. After evacuation, the solution in the extruder barrel was put back into the extruder which was also heated to  $80\text{ }^{\circ}\text{C}$ . Fiber spinning started 5 min after the solution was transferred into the extruder. All solutions were injected through a  $150\text{ }\mu\text{m}$ -diameter nozzle into the water bath. The air gap between the nozzle and the surface of the water bath was 3 cm. We were unable to form continuous fibers with the 7.6 wt% cellulose/EMImDEP solution. Therefore, only cellulose fibers spun from 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose/EMImDEP solutions are reported. The extrusion velocity ( $V_1$ ) was 0.4 m/s while the haul off unit was continuously winding the coagulated fiber downstream at a winding velocity ( $V_2$ ) of 2.1 m/s (draw ratio = 5.3). After spinning, the fibers were immersed in tap water for two days to remove the ionic

liquid solvent, with a change of water every 24 h. Then the fibers were rolled and dried in a fume hood for a further 48 h.

### **Characterization of Cellulose Fibers**

The solvent was completely removed during processing, which was confirmed via FTIR in a previous study<sup>12</sup>.

The diameter measurements and the observations of the outer surfaces of cellulose fibers were carried out using a TM3030 Plus tabletop Scanning Electron Microscope (SEM) produced by HITACHI (Berkshire, UK). Five filaments of each of the 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers were mounted onto a sample holder, without silver coating. Three SEM images from three different locations of each fiber filament were obtained. From these images, three diameters were measured from three different locations along each filament using the ImageJ software package. Thus, 45 different locations' diameters were measured for 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers, respectively. Average SEM diameters and standard deviations were then determined (see supplementary information section Figure S4). The outer surfaces of 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers were also observed from these SEM micrographs.

To observe the cross-sections of the fibers before and after tensile testing, SEM analysis was conducted. All fiber filaments were prepared using an Agar Scientific high resolution sputter coater with 15 nm-thick silver coating. The cross-sections of fibers before tensile testing were obtained using liquid nitrogen. The cross-sectional areas of coated filaments were revealed (see supplementary information section Figure S5) and further observed using a JEOL IT300 SEM.

Wide Angle X-ray Diffraction (WAXD) patterns of single fiber filaments were obtained with an exposure time of 10 hours. A SAXSLAB GANESHA 300 XL SAXS system in the School of

Physics at University of Bristol was used for this study, consisting of an X-ray generator producing Cu K $\alpha$  radiation with a wavelength of 0.154 nm, a sample stage and a detector inside a vacuum chamber, as well as data reduction and analysis software (SAXSGUI and IDL). The beam stop was 2 mm, the beam size was 0.8 mm, and the sample-to-detector distance was set at 100 mm. Single fiber filaments were mounted straight and tight on a sample holder, which was located on the sample stage between the X-ray generator and detector.

### **Mechanical Properties of Cellulose Fibers**

Three gauge lengths (12, 20 and 30 mm) of fibers were used for mechanical properties measurements in order to account for machine compliance and end effects (see supplementary information section Figure S6 and S7), according to ASTM standard C1557. Tensile testing was carried out using a Dia-stron LEX820 single fiber tester (Hampshire, UK), containing a 20 N capacity load cell with a resolution of 0.5 mN. The tensile samples were prepared by mounting a single fiber filament between two plastic tabs. These tabs were located on a 20-slot linear plastic cassette with three different gauge lengths of 12, 20 and 30 mm. Every single fiber filament was located straight and tightly on tabs using DYMAX 3193 UV adhesive (Wiesbaden, Germany). The tabs were clamped horizontally between a fixed jaw and a movable jaw on the fiber tester. All tensile samples were tested at the same strain rate of 10 %/min. Tensile testing was controlled using the UvWin PC application. Tensile load and displacement data points were recorded automatically with an interval of 50 ms during the testing. Tensile strength and breaking strain were calculated from these data using Equations 1 and 2, where  $\sigma$  is the tensile stress,  $\epsilon$  is the tensile strain,  $F$  is the tensile load,  $d$  is the fiber diameter,  $A$  is the fiber cross-sectional area,  $l$  is the displacement, and  $l_0$  is the initial gauge length.

Ten samples for each gauge length were prepared and tested to failure for 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers, respectively.

$$\sigma = \frac{F}{A} = \frac{4F}{\pi d^2} \quad (1)$$

$$\varepsilon = \frac{l}{l_0} \quad (2)$$

To study the effects of water on the properties of cellulose fibers, 18.0 wt% cellulose fibers were merged in water for 24 hours. Ten wet 18.0 wt% fiber filaments were mounted and glued on plastic tablets with a gauge length of 20 mm using UV adhesive for tensile testing, which took about one hour. After this preparation, the ten fiber filaments became nearly dry. Their diameters were measured using SEM method. The ten filament samples were tested to failure.

## RESULTS

### **Anisotropy Study of Cellulose/EMImDEP Solutions**

The cellulose/solvent solution films were observed with a polarized optical microscope. When the solutions are heated above the clearing temperature ( $T_c$ )<sup>20</sup>, the solution becomes isotropic and the anisotropy pattern disappears. To study  $T_c$ , 7.6 wt%, 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose/EMImDEP solutions were heated from 25 °C to 90 °C, while polarized optical micrographs were taken at different temperatures, respectively. The anisotropy of

cellulose/EMImDEP solutions diminished gradually as the temperature increased and finally disappeared at  $T_c$ .

When the concentration of cellulose was 7.6 wt%, the solution was isotropic and appeared completely dark between crossed polarizers at 25 °C and 80 °C (Figure 2A). When the concentration of cellulose rose to 12.4 wt%, a weakly nematic texture appeared at 25 °C and disappeared at 80 °C (Figure 2B). When the concentration of cellulose further increased to 15.2 wt%, strong optical planar textures as a typical sign of anisotropy were observed at 25 °C and also disappeared at 80 °C (Figure 2C). When the concentration of cellulose rose to 18.0 wt%, the optical planar textures of cellulose/EMImDEP solutions became even stronger at 25 °C compared to 15.2 wt% solutions, and the textures still existed after the solution was heated to 80 °C (Figure 2D). The  $T_c$  of 18.0 wt% cellulose/EMImDEP solution was found to be between 85 °C and 90 °C (Figure 3). The  $T_c$  for 12.4 wt% and 15.2 wt% solutions were found to be lower than 18wt% cellulose solution (see supplementary information Figure S1 and S2).

### **Diameter Measurements of Cellulose Fibers**

SEM images of 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose were taken for diameter measurements (Figure 4A-F). Their average diameters as obtained from images are given in Table 1. With the same draw ratio, no significant differences in the average diameters were observed for 12.4 wt% ( $22.0 \pm 1.4 \mu\text{m}$ ), 15.2 wt% ( $23.1 \pm 1.1 \mu\text{m}$ ), and 18.0 wt% ( $20.8 \pm 3.0 \mu\text{m}$ ) fibers (see supplementary information Figure S4 and S5).

### **Outer Surface Observation of Cellulose Fibers**

SEM micrographs of the outer surfaces of cellulose fibers were taken (Figure 5A-C). For 12.4 wt% fibers, there were obvious serrations on the outer surface (Figure 5A), as seen for viscose

fibers<sup>21</sup>. For a 15.2 wt% fiber, the serrations seem to diminish in size (Figure 5B), but for the 18.0 wt% fiber, the serrations are not present at all and a smooth outer surface is observed (Figure 5C). It is known that the solution dope concentration affects the counter diffusion process between ionic liquid and water in the coagulation bath, which further influences the microscopic structures and mechanical properties of spun fibers<sup>22</sup>. This might be the reason why the fiber outer surface became smoother and the serrations reduced as the cellulose concentration was increased to 18.0 wt%.

### **SEM Analyses for Fracturing Cross-sections of Cellulose Fibers**

The cross-sections (perpendicular to the fiber axis) of the cellulose fibers before (Figure 6A-C) and after (Figure 7A-F) tensile testing were observed using SEM. Before tensile testing, all cross-sectional shapes of the fibers appear close to circular, similar to NMMO-type fibers, and different to the serrated shape of viscose fibers. All fibers appear to have uniform structure throughout the cross-section without any visible large size voids. After tensile testing, the cross-sections of cellulose fibers remain circular without obvious necking behavior (Figure 7). As demonstrated, the cellulose fibers are more apt to lateral slitting like NMMO fibers instead of ductile fracture like viscose fibers<sup>23</sup>, as the increase of cellulose concentration (Figure 7).

### **Wide Angle X-ray Diffraction of Cellulose Fibers**

Figure 8A-C shows the two dimensional WAXD diffraction patterns for single cellulose fibers. A narrow strip of intensity on each WAXD pattern was taken for the regrouping, which was much less than the radial width of all peaks. Radial scanning data (intensity against  $2\theta$ ) were obtained and are reported in Figure 8D. The Bragg peaks shown only occur for a cellulose II structure, a widely known crystal structure of regenerated cellulose after dissolution<sup>10, 24-26</sup>.

Two Bragg peaks appear at 20.6 ° and 21.6 ° corresponding to the reflection planes (110) and (020) respectively, and a small peak at 28.8 ° corresponding to the (103) plane. A secondary peak appears at 12.7° corresponding to the cellulose( $\bar{1}10$ ) plane, indicating a structural transformation into cellulose II (Figure 8B). The shift of the main (110) peak from 22.5° of cellulose I to 20.6 ° of regenerated cellulose is evidence for a non-recoverable change in the cellulose lattice structure after regeneration due to the diffused IL<sup>27</sup>.

For regenerated cellulose, cellulose II is the most common structure, possessing an ideal monoclinic P2<sub>1</sub> structure with unit parameters of a = 0.801 nm, b = 0.904 nm, c = 1.036nm,  $\alpha = \beta = 90^\circ$  and  $\gamma = 117.1^\circ$ <sup>28</sup>. Unit cell dimensions were calculated for our fibers using the measured q-spaces of the( $\bar{1}10$ ), (110), (002), (020) and (103) planes from the WAXD patterns. The measured unit parameters of cellulose in our fibers were found to be a = 0.78 nm, b = 0.90 nm, c= 1.03 nm and  $\gamma = 117.2^\circ$  for the 12.4 wt% fiber, a = 0.78 nm, b = 0.90 nm, c= 1.03 nm and  $\gamma = 116.9^\circ$  for the 15.2 wt% fiber, and a = 0.78 nm, b = 0.90 nm, c= 1.03 nm and  $\gamma = 116.0^\circ$  for the 18.0 wt% fiber. Our values appear to differ somewhat to those published in the literature (particularly for the a-axis) which may be due to a large number of diffraction intensities overlapping each other in the X-ray data for the cellulose II structure<sup>29</sup>.

The fraction of crystalline material in cellulose fibers, or crystallinity, can be estimated using the crystallinity index (CrI) developed by Segal<sup>30</sup> in Equation 3.

$$CrI (\%) = \frac{I_{total} - I_{am}}{I_{total}} \times 100 \quad (3)$$

where  $I_{total}$  is the total scattered intensity at the main peak, and the  $I_{am}$  is the minimum scattered intensity between the main and secondary peaks for cellulose<sup>31</sup>. To use CrI, an assumption that

there is only a single crystalline phase along with an amorphous phase has been applied<sup>32</sup>. For cellulose II structure in regenerated cellulose fibers in our work, the main peak appears as a doublet composed of (110) and (002) peaks at 20.6 ° and 21.6 °, and the secondary peak appears at 12.7 ° corresponding to ( $\bar{1}10$ ) plane<sup>33-34</sup> (Figure 8D). Therefore, the CrI of 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers are calculated using  $I_{110}$  and  $I_{am}$  (Figure 8D) after subtraction of the background signal measured without cellulose, which are 65.0%, 66.8% and 64.4% correspondingly (Table 1). It appears that the cellulose fibers with different cellulose concentrations in this work have similar crystallinities (~65%) when produced under the same condition. The CrI of cellulose in our fibers are higher than most native cellulose in plants<sup>35</sup>, similar as the cellulose fibers regenerated by Rehatekar et al.<sup>10</sup>, but lower than the potassium hydroxide treated liquid crystalline cellulose fibers reported by Kim's group<sup>34</sup>.

In a stretched fiber, the cellulose chains have a preferred orientation with their longitudinal axes parallel to the deformation direction, which appear as concentrated intensity as two arcs in the diffraction ring, in the azimuthal direction (Figure 8A-B). The intensities of the diffraction rings corresponding to the cellulose ( $\bar{1}10$ ) planes were plotted as a function of azimuthal angle and fitted using a Lorentzian function (Figure 8E). The full width at half maximum (FWHM) is the difference in angle across the peak where the intensity is 50% of the maximum value<sup>36</sup>. The FWHM of cellulose peaks corresponding to the( $\bar{1}10$ ) planes were calculated as an indication of the degree of alignment of cellulose chains in all fibers, and found to be 24, 25, 21°, respectively (Table 1). The lower the value of FWHM, the higher is the degree of alignment of the cellulose chains<sup>37</sup>. The regenerated cellulose fibers appear to possess aligned cellulose chains, as exhibited by the sharp azimuthal peaks in Figure 8E.

The “orientation parameter”,  $f$ , first proposed by Hermans<sup>38</sup>, can be used to characterize the extent of cellulose crystallite orientation in our fibers. This parameter is defined as the mean coefficient of the second-order Legendre polynomial,  $P_2(\cos \theta)$ , where  $\theta$  is the polar disorientation angle of a crystallite relative to the fiber axis and the angle brackets indicate an average over all crystallites (Equation 4)<sup>39</sup>. The cellulose crystallites would have a perfect orientation perpendicular to the fiber axis when  $f = -0.5$ , and a perfect orientation parallel with fiber axis when  $f = 1.0$ . For a uniaxial fiber,  $f$  may be measured directly from the azimuthal intensity distribution,  $\rho(\phi)$ , of a paratropic peak (i.e. one resulting from planes parallel to the crystallite axis) in the X-ray diffraction pattern (Equation 5).

$$f = \langle P_2(\cos \theta) \rangle = \frac{(3 \langle \cos^2 \theta \rangle - 1)}{2} \quad (4)$$

$$f = \langle P_2(\cos \theta) \rangle = (-2) \frac{\int_0^\pi \rho(\phi) P_2(\cos \phi) \sin \phi d\phi}{\int_0^\pi \rho(\phi) \sin \phi d\phi} \quad (5)$$

where the factor of -2 arises because the center of the peak is at right angles to the fiber axis<sup>40</sup> and only tilts of the crystallites in the plane containing the X-ray beam and the fiber axis broaden the diffraction peak.

Another commonly used measure<sup>41</sup> of the orientational order is  $\langle \sin^2 \theta \rangle$  which is closely related to  $f$  (Equation 6), where the angle  $\theta$  is the crystallite angle. For a uniaxial fiber, this can be measured directly from the azimuthal intensity distribution,  $\rho(\phi)$ , of a diatropic peak (i.e. one resulting from planes perpendicular to the crystallite axis) by Equation 7.

$$\langle \sin^2\theta \rangle = \frac{2}{3}(1-f) \quad (6)$$

$$\langle \sin^2\theta \rangle = \frac{\int_0^\pi \rho(\phi)\sin^3\phi d\phi}{\int_0^\pi \rho(\phi)\sin\phi d\phi} \quad (7)$$

However, for a paratropic peak (i.e. one resulting from planes parallel to the crystallite axis) from a uniaxial fiber the equation becomes:

$$\langle \sin^2\theta \rangle = 2 \langle \sin^2\Delta\phi \rangle = 2 \frac{\int_0^\pi \rho(\phi)\cos^2\phi\sin\phi d\phi}{\int_0^\pi \rho(\phi)\sin\phi d\phi} \quad (8)$$

where, again, the factor of 2 arises because only tilts of the crystallites in the plane broaden the diffraction peak and  $\Delta\phi$  is measured from  $\phi = \pi/2$ . In the literature, the spread of a paratropic peak,  $\langle \sin^2\Delta\phi \rangle$ , rather than the spread of the crystallites,  $\langle \sin^2\theta \rangle$ , is often evaluated and used as an experimental observable to gauge the quality of orientation<sup>42</sup>. It can be calculated directly from  $f$  (Equation 9).

$$\langle \sin^2\Delta\phi \rangle = \frac{(1-f)}{3} \quad (9)$$

The orientation parameter values for the cellulose fibers were calculated from the intensity distribution in a ring containing the ( $\bar{1}10$ ) peak, with background estimated from adjacent rings and subtracted using IDL. The value of  $f$  was calculated from Equation 5. The highest orientation function ( $f$ ) value was observed for 18 wt% fibers (0.80) as shown in Table 1, indicating very good orientation of the cellulose chains along the fiber axis compared to the fibers produced previously by the groups of He<sup>13</sup> ( $f= 0.71$ ) and Sixta<sup>43</sup> ( $f= 0.73$ ).

For comparison with literature values,  $\langle \sin^2 \Delta\phi \rangle$  was also calculated using Equation 9 and the results are given in Table 1. This parameter has been previously utilized to determine the crystalline orientation parameter of PBO (poly-p-phenylene benzobisoxazole) fibers<sup>44</sup>. Crystalline orientation is inversely proportional to the value of the orientation parameter, and therefore, for a perfect orientation,  $\langle \sin^2 \Delta\phi \rangle$  is equal to zero. The  $\langle \sin^2 \Delta\phi \rangle$  values for our fibers are shown in Table 1. The lowest orientation parameter ( $\langle \sin^2 \Delta\phi \rangle = 0.07$ ) i.e. highest orientation of crystallites along the fiber axis was observed for the 18 wt% fibers. The orientation parameter of our 18 wt% fibers (0.07) indicates lower orientational order than the cellulose fibers ( $\langle \sin^2 \Delta\phi \rangle = \sim 0.01$ ) regenerated from a liquid crystalline cellulose solution reported in literature<sup>45</sup>. Lyocell cellulose fibers have also been reported to possess a lower orientation parameter of 0.05 at the center of the fiber, indicating a higher crystallite orientation along the fiber axis<sup>46</sup>.

### **Tensile Testing of Cellulose Fibers**

Typical tensile stress-strain curves for 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers with a gauge length of 20 mm are shown in Figure 9. It is found that, as the cellulose concentration increased from 12.4 wt% to 15.2 wt%, the mechanical properties (Young's modulus, tensile

strength, and breaking strain) of cellulose fibers did not show any obvious differences. As the cellulose concentration further increased to 18.0 wt%, both Young's modulus and tensile strength of cellulose fibers significantly increased (Figure 9 and Table 2), while the breaking strain remained similar.

With the same increment in cellulose concentration (2.8 wt%), the increase in Young's modulus was significantly different for 15.2 wt% and 18.0 wt% cellulose fibers. When the concentration of cellulose increased from 12.4 wt% to 15.2 wt%, Young's modulus only increased slightly from 15.8 GPa to 16.2 GPa. When the concentration further increased to 18.0 wt%, Young's modulus rose from 16.2 GPa to 22.8GPa. As cellulose concentration increased from 12.4 wt% to 18.0 wt%, the tensile strength of cellulose fibers increased from 207.3-215.5 MPa to 252.3-304.7 MPa. Meanwhile, the breaking strain for fiber samples with different gauge length exhibited no change (Table 2).

The properties of 18.0 wt% cellulose fibers before and after wetting were compared as shown in Table 3. After wetting in water for 24 hours, the swelling of cellulose fibers was determined by the increment of fiber diameter from 20.8  $\mu\text{m}$  to 25.4  $\mu\text{m}$ . Meanwhile, a moderate reduction on the mechanical properties of cellulose fibers (5.9 GPa in Young's modulus and 67 MPa in tensile strength) was also observed (Table 3).

## DISCUSSION

In this study, the cellulose/EMImDEP solution appeared isotropic for a cellulose concentration of 7.6 wt%, weakly nematic for a concentration of 12.4 wt% and anisotropic at 15.2 wt% and 18.0 wt%. Song *et al.* studied the anisotropic behaviors of MCC/AMImCl<sup>15</sup> and MCC/EMImAc<sup>19</sup> solutions. Their solutions possessed similar isotropic forms at lower concentrations (at 7 wt%), at

lower threshold concentrations (9-10 wt%) appeared to show a weak optical texture and at higher concentrations (11-18 wt%) gave a strong optical texture. Boerstael *et al.* reported that the  $T_c$  of cellulose solutions increases as the concentration of polymer increases<sup>20</sup>, which is named lyotropic behavior<sup>47</sup>. The anisotropic appearance may be attributed to an increase in the alignment of cellulose chains during dissolution and the resistance for the migration into a random state; this is thought to be due to the high shear viscosity of the cellulose/EMImDEP solution and the large number density of cellulose<sup>3,47</sup>. When the concentration of cellulose in our study was 7.6 wt%, the  $T_c$  of cellulose/EMImDEP solution was lower than room temperature which is hard to observe under a polarized optical microscope. When the concentration of cellulose is 12.4 wt% or higher, the  $T_c$  of cellulose/EMImDEP solution increased above room temperature, and the nematic texture of solution appears under polarized light. Upon heating, the shear viscosity of the anisotropic solution decreased while the cellulose molecules became disordered. Finally, the solution reached an isotropic state at  $T_c$ . This inversely proportional anisotropy-temperature performance is named thermotropic behavior. Under the collective effect of thermotropic and lyotropic behaviors, the anisotropy of the cellulose solutions diminished gradually as temperature increased and finally disappeared at 80 °C for 12.4 wt% and 15.2 wt% solutions, while the anisotropy disappeared at an increasing temperature of  $85\text{ °C} < T_c < 90\text{ °C}$  for 18.0 wt% solution.

The  $T_c$  of 11.4 wt% cellulose/phosphoric acid solution obtained by Boerstael *et al.* was as low as 45 °C<sup>20</sup>. Song and his group conducted similar observations of anisotropic transitions on 16 wt% MCC/AMImCl solutions with a similar range of  $75\text{ °C} < T_c < 80\text{ °C}$ <sup>15</sup>, as well as on 14 wt% MCC/EMImAc solution with a range of  $75\text{ °C} < T_c < 85\text{ °C}$ . Therefore, the 18.0 wt% cellulose/EMImDEP solution prepared in this study possessed a higher  $T_c$  than most previous studies, indicating better self-accessibility of cellulose chains dispersed in EMImDEP.

The difference in  $T_c$  of 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose/EMImDEP solutions also indicates that during the fiber spinning process at 80 °C, the 12.4 wt% and 15.2 wt% fibers were produced from isotropic solutions, while 18.0 wt% fibers were produced from an anisotropic solution. This could be the reason why the mechanical properties of 18.0 wt% cellulose fibers were significantly higher than those of 12.4 wt% and 15.2 wt% cellulose fibers.

The fibers reported in this study, which were regenerated using low molecular weight (~220) cellulose, showed moderately high Young's modulus (~22 GPa) and tensile strength (~305 MPa). We have compared these values with other natural polymer fibers and fiber-based materials (balsa wood, wool, bone, worm silk and spider silk, etc.) and currently-used commercial viscose (Figure 10). The average Young's modulus (for 18.0 wt% fibers) is higher than all these fibers, however the tensile strength is lower than silk fibers from silkworms and spiders. Our cellulose fibers also showed good mechanical performance compared with regenerated cellulose fibers from higher DP cellulose using ionic liquid as solvents reported by some of the previous researchers (Table 1). The regenerated cellulose fibers from MCC/AMImCl solution reported by Luo *et al.* had a much lower tensile strength of 73.8 MPa<sup>14</sup>. Lim *et al.* wet-spun cellulose fibers from a rice straw cellulose/NMMO solution, with a much lower Young's modulus in the range 11.0-13.0 GPa, but tensile strength similar to our fibers (280.0-400.0 MPa)<sup>48</sup>. He *et al.* dry-jet wet spun cellulose fibers from a 14.5 wt% cellulose/AMImCl solution (cellulose DP=650) with Young's moduli as low as 5.1 GPa and a lower strength of 204.0 MPa<sup>13</sup>. Rahatekar *et al.* dry-jet wet spun cellulose fibers using EMImAc from a smaller spinneret (120 μm) at a draw ratio of 1.5, with a finer diameter of 23.2 μm, yielding fibers with a Young's modulus of 13.1 GPa and strength of 198.0 MPa<sup>10</sup>. Sixta *et al.* have recently manufactured cellulosic fibers (Ioncell-F) with a very good Young's modulus (23.4 GPa) and tensile strength (~694.0 MPa)<sup>43</sup>. However, they used a high DP

cellulose (DP 1095) and their spinning procedure used a different IL as a solvent, without forming an anisotropic solution before fiber spinning. The manufacturing method developed in this study will be very useful to convert low molecular weight waste cellulose, which is normally used for medical tablets, food-ingredient, etc., to fibers with good mechanical properties which could be used in the composite engineering industry.

## CONCLUSIONS

We have developed a novel manufacturing method for stiff regenerated cellulose fibers spun from an anisotropic solution of low molecular weight cellulose dissolved in EMImDEP. 18.0 wt% cellulose/EMImDEP solution appeared highly anisotropic with a strong sign of anisotropy and clearing temperature ( $T_c$ ) between  $85\text{ }^\circ\text{C} < T_c < 90\text{ }^\circ\text{C}$ . Scanning Electron Microscopy graphs demonstrated that the cellulose fibers possessed circular, dense and homogeneous cross-sections, without any visible voids. The Wide Angle X-ray Diffraction and mechanical testing of fibers spun from 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose solution confirmed that 18.0 wt% cellulose fiber possessed the highest molecular alignment and therefore mechanical properties (Young's modulus  $\sim 22$  GPa; tensile strength  $\sim 305$  MPa). Despite using a low molecular weight cellulose we were able to achieve superior tensile modulus from our fibers compared to previous studies which used higher molecular weights. These findings open up a potential route to convert low performance cellulose waste into high performance engineering fibers.

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### **Author Contributions**

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

### **Funding Sources**

This research work is funded by Engineering and Physical Science Research Council (EPSRC, grant code EP/L017679/1).

### **ACKNOWLEDGMENT**

We would like to acknowledge funding from the Engineering and Physical Science Research Council (EPSRC, grant code EP/L017679/1). We thank Jon Jones for help with Scanning Electron Microscope studies carried out in the Chemical Imaging Facility, University of Bristol. The Scanning Electron Microscope and the Ganesha X-ray scattering apparatus used for this work were supported through an EPSRC Grant “Atoms to Applications” Grant ref. EP/K035746/1.

### **ASSOCIATED CONTENT**

## \*Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

## Notes

The authors declare no competing financial interest.

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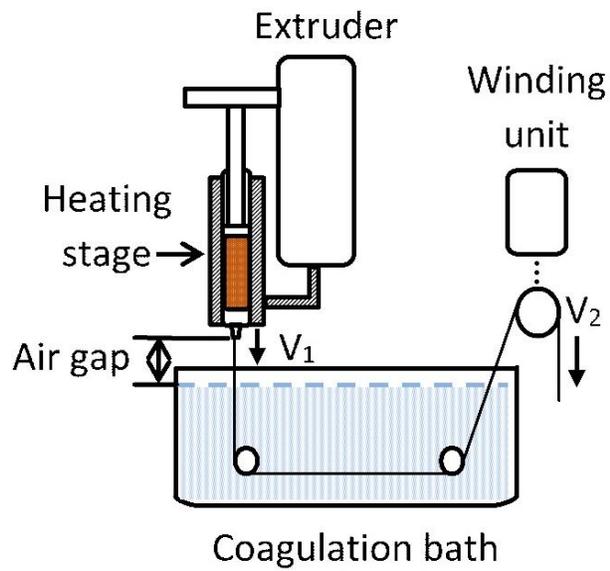
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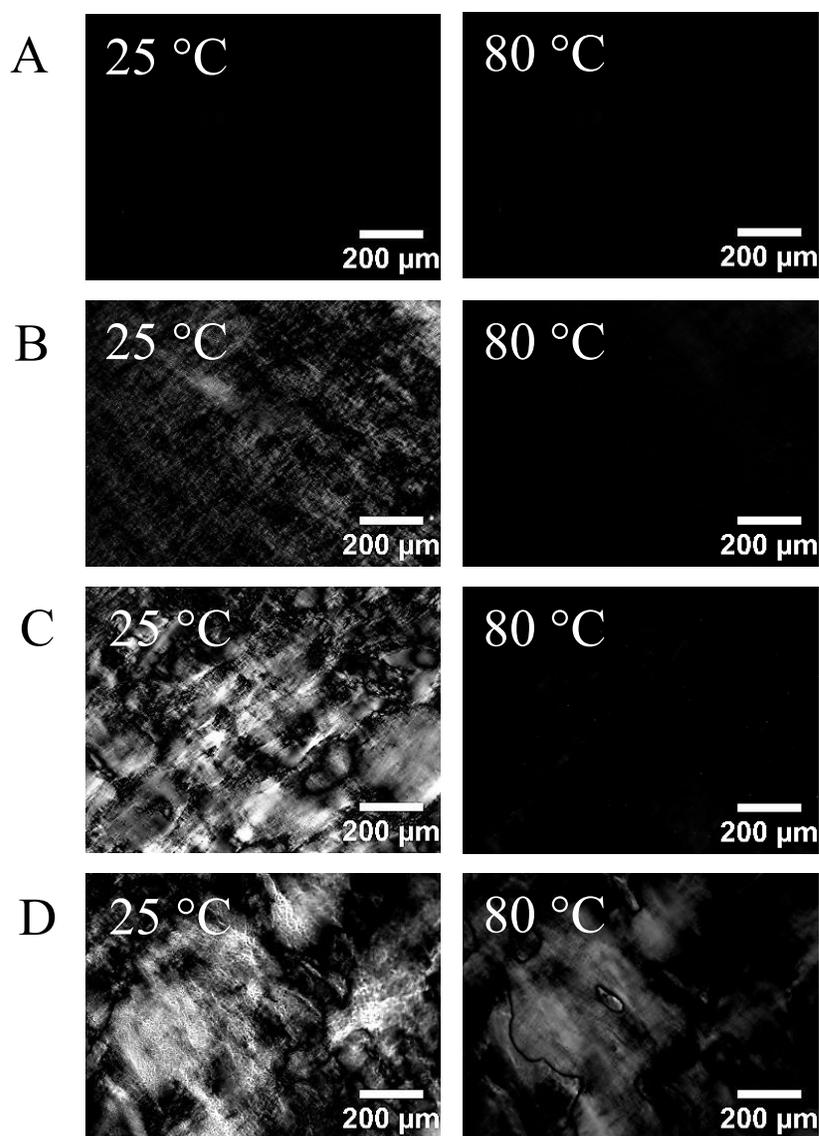
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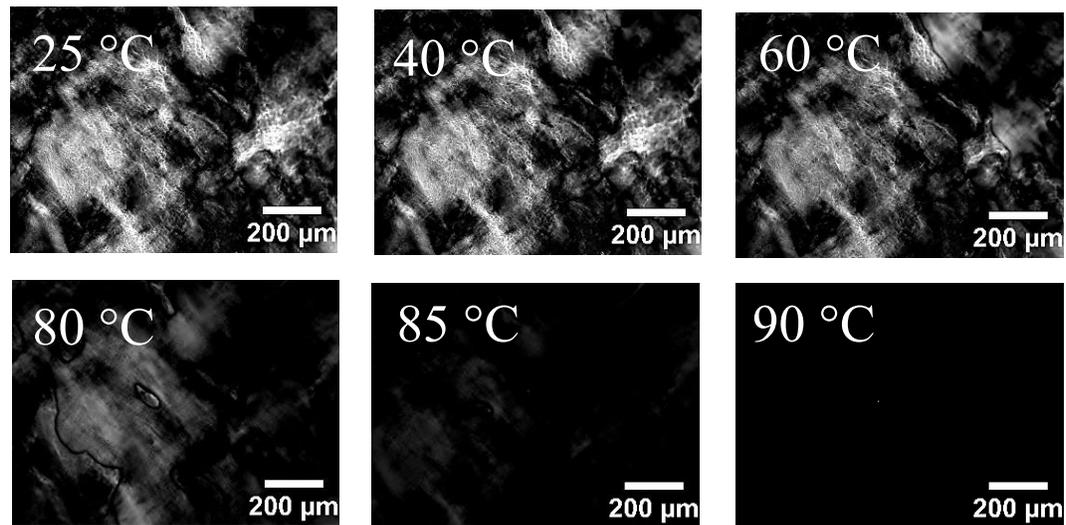
FIGURES



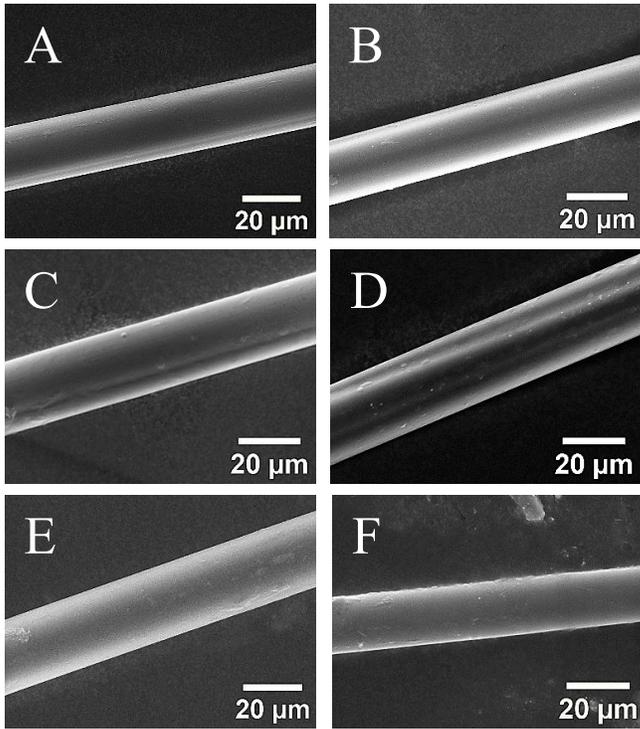
**Figure 1.** Schematic of dry-jet wet fiber spinning process for cellulose fiber with constant extrusion velocity ( $V_1$ ) and winding velocity ( $V_2$ ).



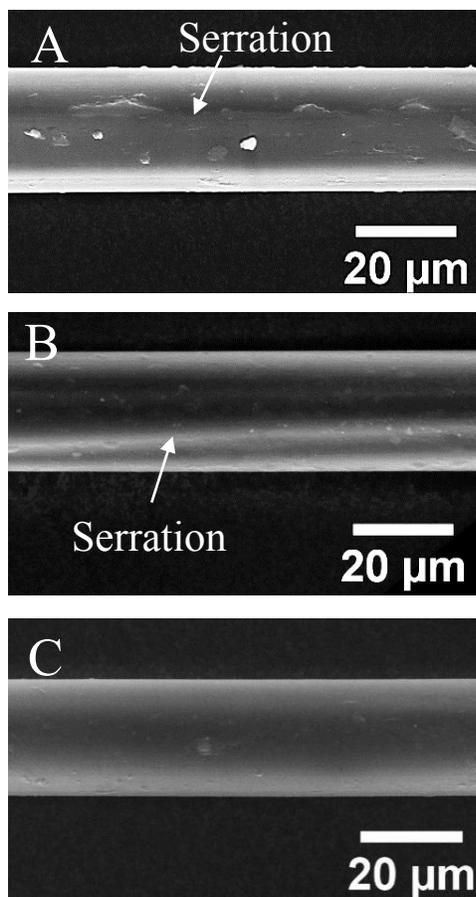
**Figure 2.** Typical polarized optical micrographs of (A) 7.6 wt%, (B) 12.4 wt%, (C) 15.2 wt% and (D) 18.0 wt% cellulose/EMImDEP solutions at 25 °C and 80 °C.



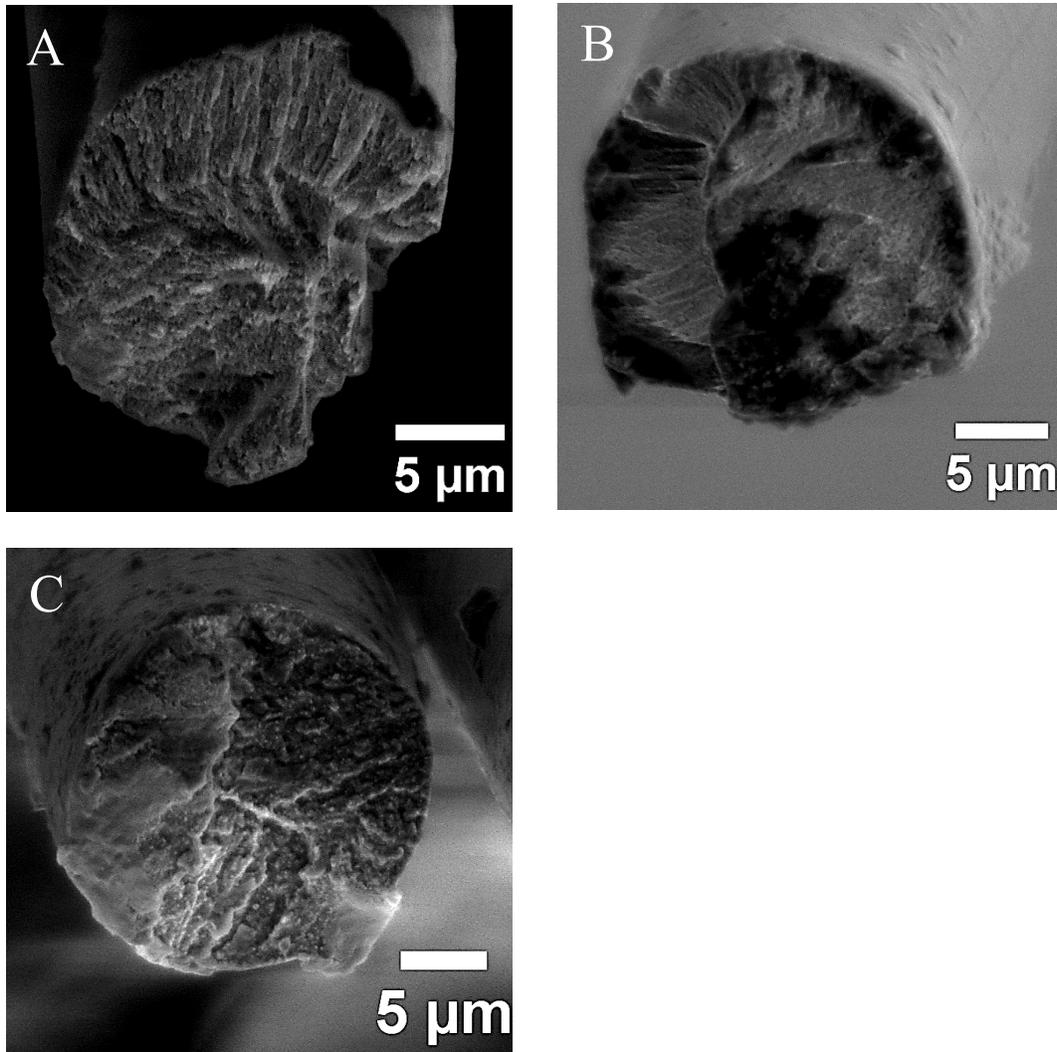
**Figure 3.** Typical anisotropy transition of 18.0 wt% cellulose/EMImDEP solution heated from 25 °C to 90 °C.



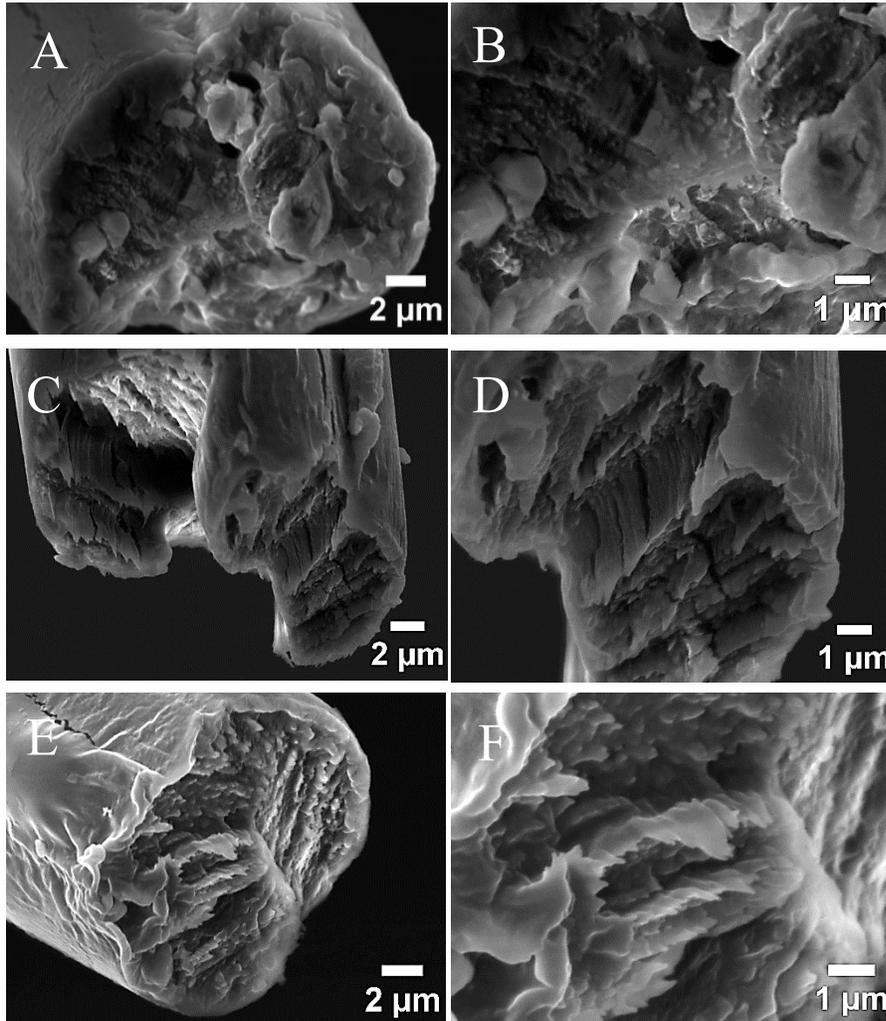
**Figure 4.** Typical SEM micrographs of (A-B) 12.4 wt%, (C-D) 15.2 wt% and (E-F) 18.0 wt% cellulose fibers for diameter measurement.



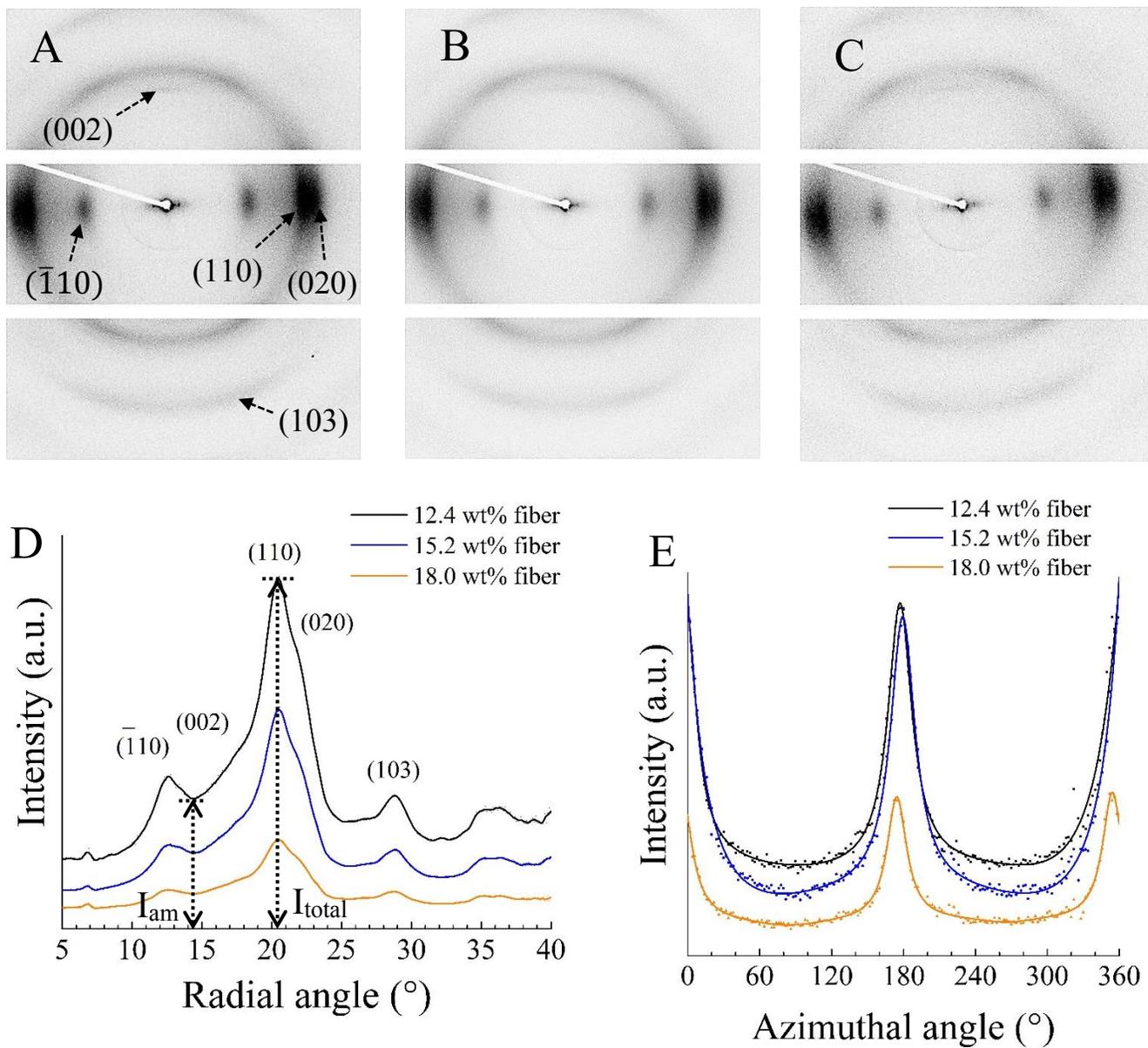
**Figure 5.** Typical SEM micrographs of the outer surfaces of (A) 12.4 wt%, (B) 15.2 wt% and (C) 18.0 wt% cellulose fibers.



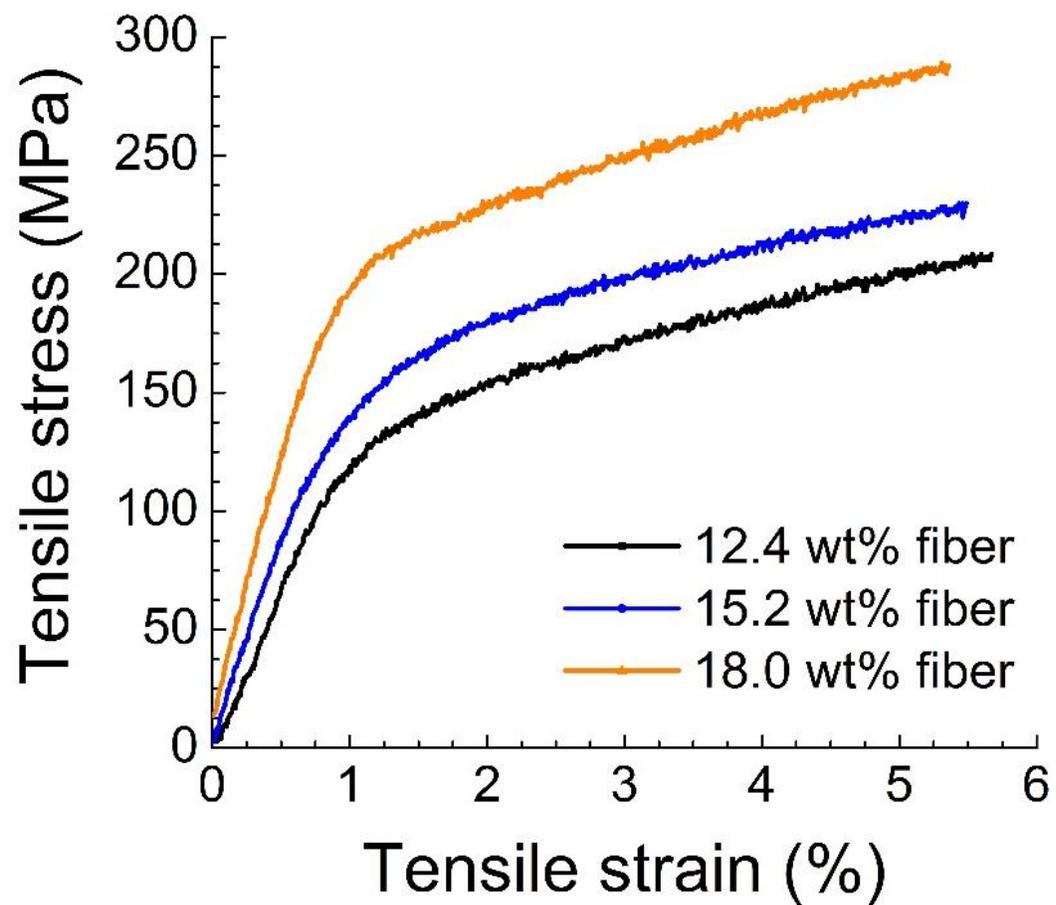
**Figure 6.** Typical SEM images of cross-sections of (A) 12.4 wt%, (B) 15.2 wt% and (C) 18.0 wt% cellulose fibers fractured using liquid nitrogen.



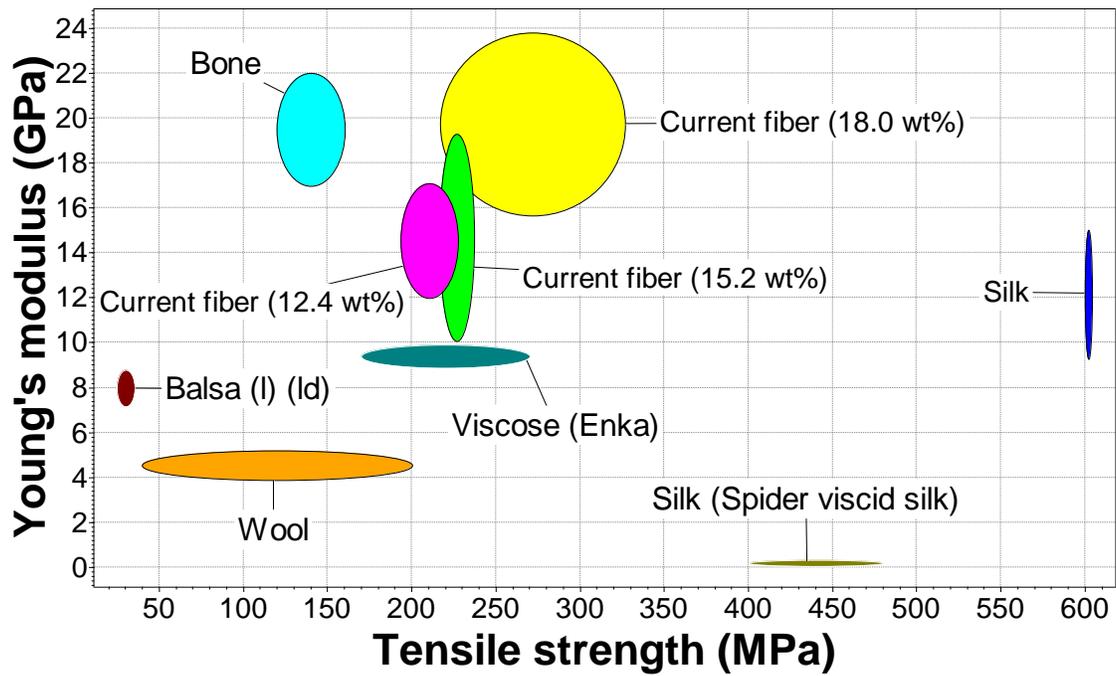
**Figure 7.** Typical SEM images of fractured surfaces of (A-B) 12.4 wt%, (C-D) 15.2 wt% and (E-F) 18.0 wt% cellulose fibers after tensile testing.



**Figure 8.** Typical WAXD patterns of (A) 12.4 wt%, (B) 15.2 wt% and (C) 18.0 wt% cellulose fibers, as well as their (D) radial scanning data and (E) azimuthal scanning data from the  $(\bar{1}10)$  peak.



**Figure 9.** Typical tensile stress-strain curves for 12.4 wt%, 15.2 wt% and 18.0 wt% regenerated cellulose fibers.



**Figure 10.** Mechanical properties of 12.4 wt%, 15.2 wt% and 18.0 wt% regenerated cellulose fibers, compared to natural polymer fibers (Balsa, wool, bone, worm silk and spider silk) as well as commercial viscose (Enka<sup>TM</sup>) cellulose fibers<sup>49</sup>.

TABLES

**Table 1. Degree of polymerization (DP), average SEM diameter, crystallinity index (CrI), full width at half maximum (FWHM), orientation function ( $f$ ), magnitude of the orientation parameter  $\langle \sin^2 \Delta\phi \rangle$  data of the  $(\bar{1}10)$  azimuthal peaks, best Young's modulus and corresponding tensile strength of 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers, compared to regenerated cellulose fibers reported by previous researchers.**

Material	DP	Diameter ( $\mu\text{m}$ )	Young's modulus (GPa)	Tensile strength (MPa)	CrI (%)	FWHM of $(\bar{1}10)$ peak ( $^\circ$ )	$f$ of $(\bar{1}10)$ peak	$\langle \sin^2 \Delta\phi \rangle$ of $(\bar{1}10)$ of peak
12.4 wt% cellulose fibers	200-220	22.0 ( $\pm 1.4$ )	14.8 ( $\pm 2.3$ )	215.5 ( $\pm 11.9$ )	65.0	24	0.77	0.08
15.2 wt% cellulose fibers	200-220	23.1 ( $\pm 1.1$ )	15.7 ( $\pm 1.6$ )	226.4 ( $\pm 10.0$ )	66.8	25	0.76	0.08
18.0 wt% cellulose fibers	200-220	20.8 ( $\pm 3.0$ )	22.4 ( $\pm 1.4$ )	304.7 ( $\pm 12.7$ )	64.4	21	0.80	0.07
Luo et al <sup>14</sup>	200-220	300-400	---	73.8 ( $\pm 2.2$ )	---	---	---	---
Lim et al <sup>48</sup>	---	5-10	11-13	280-400	---	---	---	---
He et al <sup>13</sup>	650	---	5.1	204.0 ( $\pm 6.0$ )	---	---	0.71	---
Rahatekar et al <sup>10</sup>	820	23.2 ( $\pm 1.8$ )	13.1 ( $\pm 1.1$ )	198.0 ( $\pm 25.0$ )	62	---	---	---
Sixta et al <sup>43</sup>	1026 - 1133	---	23.4 ( $\pm 3.5$ )	~694.0	---	---	0.73	---

**Table 2. Young's modulus, tensile strength and breaking strain of 12.4 wt%, 15.2 wt% and 18.0 wt% cellulose fibers with different gauge length of 12, 20 and 30 mm.**

<b>Material</b>	<b>Gauge length (mm)</b>	<b>Young's modulus (GPa)</b>	<b>Tensile strength (MPa)</b>	<b>Breaking strain (%)</b>
<b>12.4 wt% cellulose fibers</b>	12	13.5 ( $\pm 1.5$ )	207.3 ( $\pm 13.6$ )	5.0 ( $\pm 0.2$ )
	20	14.4 ( $\pm 0.5$ )	212.2 ( $\pm 16.6$ )	5.5 ( $\pm 1.2$ )
	30	14.8 ( $\pm 2.3$ )	215.5 ( $\pm 11.9$ )	5.0 ( $\pm 0.1$ )
<b>15.2 wt% cellulose fibers</b>	12	15.0 ( $\pm 2.3$ )	232.4 ( $\pm 4.6$ )	4.9 ( $\pm 0.1$ )
	20	15.7 ( $\pm 1.6$ )	226.4 ( $\pm 10.0$ )	5.7 ( $\pm 1.1$ )
	30	14.7 ( $\pm 4.6$ )	226.0 ( $\pm 6.4$ )	4.7 ( $\pm 0.4$ )
<b>18.0 wt% cellulose fibers</b>	12	19.3 ( $\pm 3.1$ )	290.0 ( $\pm 36.3$ )	5.6 ( $\pm 0.7$ )
	20	22.4 ( $\pm 1.4$ )	304.7 ( $\pm 12.7$ )	6.5 ( $\pm 0.7$ )
	30	18.9 ( $\pm 3.2$ )	252.3 ( $\pm 35.2$ )	5.2 ( $\pm 0.8$ )

Insert Table of Contents Graphic and Synopsis Here

