

STUDY OF CO-SOLVENT EFFECT ON THE DISSOLUTION OF CELLULOSE IN IONIC LIQUID AND THE PROPERTIES OF REGENERATED CELLULOSE FIBRES

Chenchen Zhu^{1*}, Anastasia Koutsomitopoulou¹, Jeroen Van Duijneveldt², Kevin Potter¹

¹ Bristol Composites Institute (ACCIS), Department of Aerospace Engineering, University of Bristol, Bristol BS8 1TR, UK. Email: Chenchen.Zhu@bristol.ac.uk; An.Koutsomitopoulou@bristol.ac.uk; K.Potter@bristol.ac.uk. Web: <http://www.bristol.ac.uk/composites/>.

² School of Chemistry, University of Bristol, Bristol BS8 1TS, UK. Email: J.S.Van-Duijneveldt@bristol.ac.uk. Web: <http://www.bris.ac.uk/chemistry/people/jeroen-s-van-duijneveldt/index.html>.

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ABSTRACT

We have developed a novel and economy process to dissolve high concentration of microcrystalline cellulose in ionic liquid using dimethyl sulfoxide (DMSO) as co-solvent, and to produce strong regenerated cellulose fibres from the solution. Highly aligned cellulose fibre has been dry-jet wet spun from optically anisotropic microcrystalline cellulose/1-ethyl-3-methylimidazolium diethyl phosphate (EMIImDEP)/dimethyl sulfoxide (DMSO) solution. The 20.8 wt% cellulose solution shows strongly optically anisotropic patterns, with a clearing temperature of ~100°C. The cellulose fibre possesses an average diameter of 28.6 µm, moderately high Young's modulus of 27.8 GPa, and tensile strength of 387.7 MPa. This process presents a new route to convert a high concentration of microcrystalline cellulose into strong fibres, while reduces the processing time and cost significantly, which can potentially be used as high-performance fibres for composite materials as well as precursors for carbon fibres.

1 INTRODUCTION

As the main component of plants [1, 2], cellulose is the most abundant polymer in nature, with an annual biosphere production of about 90×10^9 metric tonnes [3, 4]. It is also considered as an environmentally friendly and biocompatible product with numerous advantages, including renewability, biodegradability and biocompatibility [5]. Even though cellulose is an inexpensive polymer that possesses excellent properties, it is not utilised for large-scale applications in the textiles and composites industries. This is due to its high rigidity, insolubility in nearly all aqueous and organic solvents (water, ethanol, methanol, etc.) [6], as well as the inability to be molten, which is caused by its complex intra- and inter-molecule hydrogen bonding network [7, 8]. The use of traditional solvents for the dissolution of cellulose, such as aromatic and halogenated solvents, has decreased noticeably in organic synthesis and industrially chemical processes due to their safety factor, which requires a careful selection of the reaction medium [9].

Over the past few decades, ionic liquids (ILs) have received numbers of attention for their chemical and thermal stabilities [10], high decomposition points, low vapour pressures, excellent recoverability (>99.5%), reusability [11], as well as their dissolution performances as the new class of benign solvents for cellulose [10, 12-20]. Among all ILs, imidazolium-based ILs stand out owing to their relatively high thermal stabilities, low melting points, moderate viscosities [21, 22] and non-flammability [23, 24]. Based on the studies of previous researchers, both anions and cations of ILs are involved in the cellulose dissolution process [6, 7, 18, 25, 26]. A dissolution mechanism of cellulose in IL was proposed [27] and expanded [28] to all imidazolium-based ILs (Figure 1). The anions of imidazolium-based ILs could form strong hydrogen bonds with the hydroxyl hydrogen atoms of cellulose, while the cations of imidazolium-

based ILs could establish weaker hydrogen bonds with the hydroxyl oxygen atoms of cellulose, resulting in the deconstruction of the cellulose hydrogen bonding network [26]. ILs with phosphate anions have been reported to perform well in the dissolution of cellulose under mild conditions, in addition to their high abilities as hydrogen bond acceptors [29]. Thus, 1-ethyl-3-methylimidazolium diethyl phosphate (EMImDEP) has been selected as the solvent for cellulose in this study.

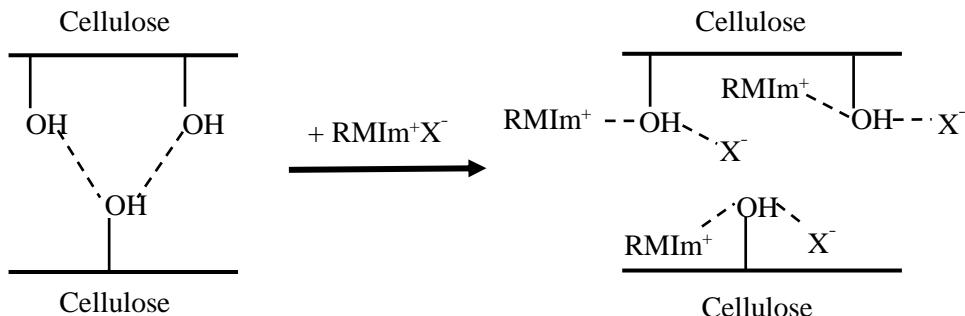


Figure 1: Dissolution mechanism of cellulose in imidazolium-based ionic liquids. R = alkyl group. X= ionic liquid anion.

Co-solvents have been reported to be able to improve the dissolution of cellulose working together with ILs [6, 30], by effectively reducing the dissolution time, temperature [31], and the viscosity of cellulose solution without the precipitation of cellulose [32]. With the addition of relatively cheap co-solvent, the cost in cellulose solvent can be significantly decreased due to reduced quantity of ionic liquid required for dissolution. Moreover, numbers of researchers have reported that mixing co-solvent with IL under specific conditions can increase the hydrogen bond accepting ability of IL while decrease the hydrogen bond donating ability of IL [6, 30], thus can potentially contribute to the properties of regenerated cellulose fibres by improving the dissolution of cellulose. Minnick et al. [6] have compared the effects of multiple co-solvents (dimethyl sulfoxide, dimethylformamide, and 1,3-dimethyl-2-imidazolidinone) on the solubility of cellulose in EMImDEP at 25 °C. According to his study, the addition of all three co-solvents increased the hydrogen bond accepting ability of EMImDEP (in loadings less than 50 mass%) and decreased hydrogen bond donating ability. However, considering the safety requirement and the cost, dimethyl sulfoxide (DMSO) stands out as the best option. DMSO is a low cost (12 GBP per litre) polar aprotic solvent, which is miscible in a wide range of organic solvents including ILs [6, 30, 32]. With the addition of DMSO, the fibre spinning process can be further eased with the reduction of solution viscosity.

In this study, we have investigated the Kamlet–Taft (K-T) parameters, including hydrogen bond accepting ability or basicity (β), hydrogen bond donating ability or acidity (α), dipolarity/polarisability (π^*) and electronic transition energy (Et (30)) of DMSO/EMImDEP mixtures with different ratios at various temperature (30 °C and 60 °C) to determine the best addition ratio of DMSO to improve the cellulose dissolution in EMImDEP. The birefringent behaviour of 20.8 wt% cellulose/EMImDEP/DMSO solution was observed using a polarised optical microscope. Regenerated cellulose fibres were manufactured using dry-jet wet fibre spinning, and tensile tested. This study presents a controllable and cost-effective route to manufacture regenerated cellulose fibres using IL/co-solvent mixtures.

2 EXPERIMENTAL METHODS

2.1 Materials and dissolution method

Highly pure microcrystalline cellulose (MCC), VIVAPUR101, with a viscosity-averaged degree of polymerization (DP) between 200 and 220 [33, 34], was purchased from JRS Pharma GmbH & Co. KG (Rosenberg, Germany). Ionic liquid (IL) 1-ethyl-3-methylimidazolium diethyl phosphate (EMImDEP) was purchased from IoLiTec Ionic Liquids Technologies (IL-0052, Tuscaloosa, US). Dimethyl

sulfoxide (DMSO) was purchased from Fisher Scientific (D/4121/PB08, Leicestershire, UK). Reichardt's dye 30 (RD) and 4-Nitroaniline (NA) were purchased from Sigma-Aldrich (272442, 185310, Gillingham, UK). N, N-Diethyl-4-nitroaniline (DENA) was purchased from Santa Cruz Biotechnology (SC-281564, Dallas, US). The dispersion and dissolution processes were carried out in a fume hood. A magnetic stirrer hotplate (Fisher Scientific, Loughborough, UK) with an oil bath was used for the preparation of EMImDEP/DMSO solvent mixtures and cellulose/EMImDEP/DMSO solution.

2.2 Analysis of EMImDEP/DMSO solvent mixtures

K-T analysis was conducted on an Agilent 8453 UV-visible spectrophotometer with a 10-mm path length glass cuvette. The measurements were conducted at 30 °C and 60 °C, as maintained for three min with an increment of every 10 °C by an Agilent temperature-controlled cell holder to approximately 0.1 °C. Three dyes including NA, DENA, and RD were used to obtain the wavelength of maximum absorption. Homogeneous dye solutions for spectroscopic analysis were prepared by first dissolving the dyes in pure DMSO or EMImDEP. The DMSO/EMImDEP mixtures were prepared gravimetrically at 100, 90, 70, 50, 30, 10 and 0 %. The absorptions were background corrected using exactly same solvent mixtures without dyes.

From the spectroscopic data, the K-T parameters hydrogen bond accepting ability or basicity β , hydrogen bond donating ability or acidity α , dipolarity/polarisability π^* , and electronic transition energy $E_T(30)$ were calculated using Equation 1-5:

$$\nu_{max}(cm^{-1}) = \frac{10^7}{\lambda(nm)} \quad (1)$$

$$E_T(30) = \frac{28592}{\lambda_{max}(RD)} \quad (2)$$

$$\pi^* = 0.314(27.52 - \nu_{max}(DENA) * 10^{-3}) \quad (3)$$

$$\alpha = 0.0649 E_T(30) - 2.03 - 0.72 \pi^* \quad (4)$$

$$\beta = 11.134 - \frac{3580}{\lambda_{max}(NA)} - 1.125 \pi^* \quad (5)$$

2.3 Preparation of cellulose/EMImDEP/DMSO solution

20.8 wt% (6.24 g) of cellulose were added to 30 g EMImDEP/DMSO (mass fraction= 7:3) mixture and heated at 100 °C with magnetic stirring at 100 rpm for six hours.

2.4 Characterisation of cellulose/EMImDEP/DMSO solution

Small amounts of 20.8 wt% cellulose/EMImDEP/DMSO solution was pressed to form a thin film between two glass slides [33]. The film was 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 film was conducted using an Olympus BX51 polarised optical microscope with a PixeLINK PL-B625 camera with a $\times 10$ objective. The film was

heated at a heating rate of 10 °C/min from 25 °C to 100 °C (± 0.1 °C), maintaining a fixed temperature for five min before taking the polarised optical micrographs. Micrographs were taken at 5 °C increments from 25 °C to 100 °C.

2.5 Fibre spinning of cellulose

A bespoke fibre spinning equipment, which consists of a vertical compressing extruder with a load cell of 10000 N, a water bath and a haul-off unit, was used for the dry-jet wet fibre spinning of the regenerated cellulose fibres (Figure 2).

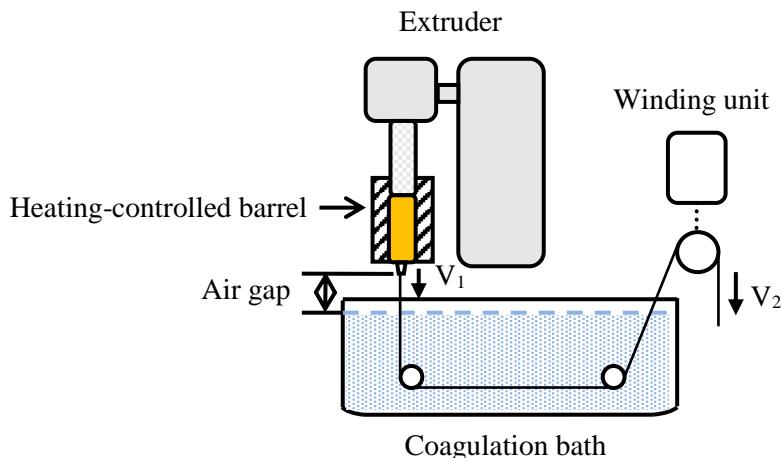


Figure 2: Schematic representation of dry-jet wet fibre spinning process for cellulose fibre with constant extrusion velocity (V_1) and winding velocity (V_2).

20.8 wt% cellulose/EMImDEP/DMSO solution was transferred into a removable extruder barrel and degassed in a vacuum oven at 100 °C under 800 mbar for 2 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 100 °C. Fibre spinning started 5 min after the solution was transferred into the extruder. The solution was injected through a 150 µm-diameter nozzle into the water bath. The air gap between the nozzle and the surface of the water bath was 3 cm. The extrusion velocity (V_1) was 0.33 m/s while the haul off unit was continuously winding the coagulated fibre downstream at a winding velocity (V_2) of 1.33 m/s (draw ratio= 4). After spinning, the fibre was immersed in tap water for one day to remove the EMImDEP/DMSO solvent. Then the fibre was rolled and dried in a fume hood for a further 48 h.

2.6 Diameter measurement of cellulose fibre

Five cellulose fibre samples were prepared for diameter measurement. The samples were prepared by mounting a single fibre filament between two plastic tabs. These tabs were located on a 20-slot linear plastic cassette with a gauge length of 20 mm. Every single fibre filament was located straight and tightly on tabs using DYMAX 3193 UV adhesive (Wiesbaden, Germany).

The diameter measurement was conducted using Dia-stron FDAS770 fibre dimensional analysis system. For each sample, the diameters were measured from five different locations along the filament. Thus, 25 different locations' diameters were measured for 20.8 wt% cellulose fibre.

2.7 Tensile testing of cellulose fibre

Tensile testing was carried out using a Dia-stron LEX820 single fibre tester (Hampshire, UK), containing a 20 N capacity load cell with a resolution of 0.5 mN. Eight 20.8 wt% fibre samples were prepared for tensile testing using the same method as the diameter measurement samples mentioned above. The tabs holding the single filament were clamped horizontally between a fixed jaw and a movable jaw on the fibre tester. All tensile samples were tested at the same strain rate of 10 %/min.

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 6 and 7, where σ is the tensile stress, ε is the tensile strain, F is the tensile load, d is the fibre diameter, A is the fibre cross-sectional area, l is the displacement, and l_0 is the initial gauge length.

$$\sigma = \frac{F}{A} = \frac{4F}{\pi d^2} \quad (6)$$

$$\varepsilon = \frac{l}{l_0} \quad (7)$$

3 RESULTS AND DISCUSSIONS

3.1 Kamlet-Taft (K-T) analysis of EMImDEP/DMSO solvent mixtures

The K-T analysis results are as shown in Figure 3. Pure DMSO has moderate hydrogen bond accepting abilities ($\beta = 0.78$ at 30 °C, Figure 3A) and correspondingly low hydrogen bond donating abilities ($\alpha = 0.15$ at 30 °C, Figure 3B) compared to pure EMImDEP ($\beta = 1.18$, $\alpha = 0.50$ at 30 °C). Therefore, it does not compete with the EMImDEP anion for interactions with the hydroxyl groups on cellulose.

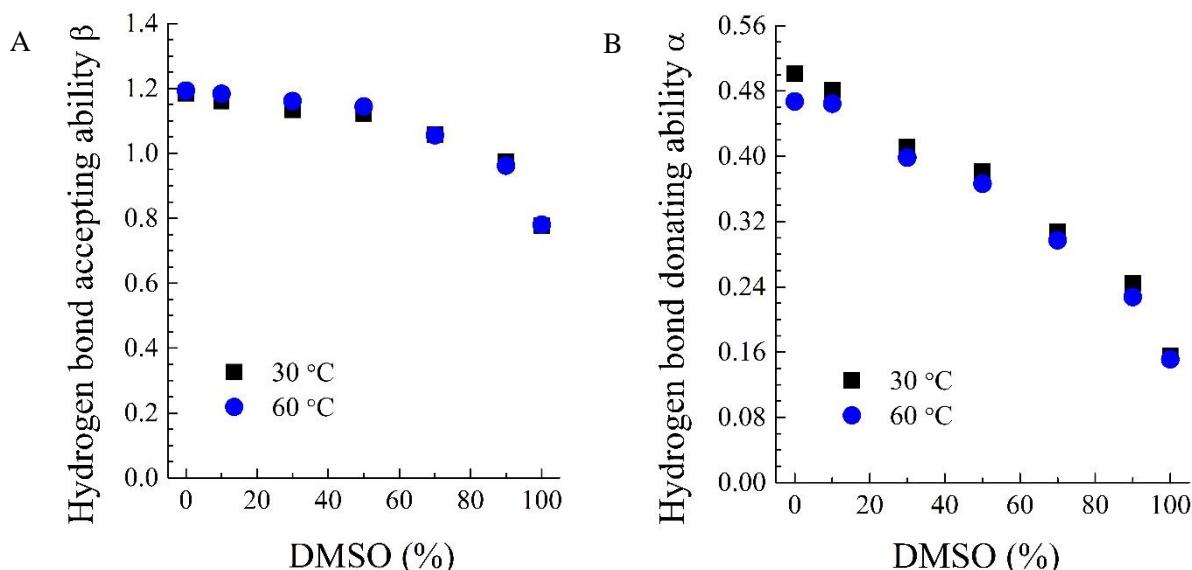


Figure 3: (A) Hydrogen bond accepting ability or basicity (β), and (B) hydrogen bond donating ability or acidity (α) of EMImDEP/DMSO solvent mixtures at 30 °C and 60 °C.

The β values for the EMImDEP studied here are dominated by the nature of the anion [35], which are proportional to the ability of EMImDEP anions to form strong hydrogen bonds with the hydroxyl hydrogen atoms of cellulose. The α values are largely determined by the nature of the EMImDEP cation, but there is also a smaller anion effect [35]. At 30 °C and 60 °C, K-T probes suggest that the hydrogen bond accepting strength of EMImDEP decreases slowly when the DMSO is less than 50 wt%, then reduces sharply as DMSO wt% further increases (Figure 3A). Meanwhile, the α value decreased upon the addition of DMSO (Figure 3B), which may be due to two reasons: 1. the low α values of the pure DMSO, and 2. the imidazolium cation of EMImDEP is better solvated, reducing the interactions with the dyes and potentially also with the anion [6]. The two essential characteristics required to improve the dissolution of cellulose are the increased hydrogen bond accepting ability and decreased hydrogen bond donating ability. Considering the β and α results comprehensively, 30 % is determined as the best addition ratio of DMSO in EMImDEP/DMSO mixture for the cellulose dissolution.

3.2 Anisotropy study of cellulose/EMImDEP/DMSO solution

The 20.8 wt% cellulose/EMImDEP/DMSO solution (EMImDEP: DMSO= 7:3) film was observed with a polarised optical microscope.

At 25 °C, strong optical planar textures as a typical sign of anisotropy were observed (Figure 4). 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 might be due to the high shear viscosity of the cellulose/EMImDEP/DMSO solution and the large number density of cellulose [7, 36].

Upon heating, the shear viscosity of the anisotropic solution decreased while the cellulose molecules became disordered. Finally, the solution reached an isotropic state at the clearing temperature (T_c). When the solutions are heated above T_c [37], the solution becomes isotropic, and the anisotropy pattern disappears. This inversely proportional anisotropy-temperature performance is named thermotropic behaviour. In this study, the T_c of 20.8 wt% cellulose/EMImDEP solution was found to be about 100 °C (Figure 4).

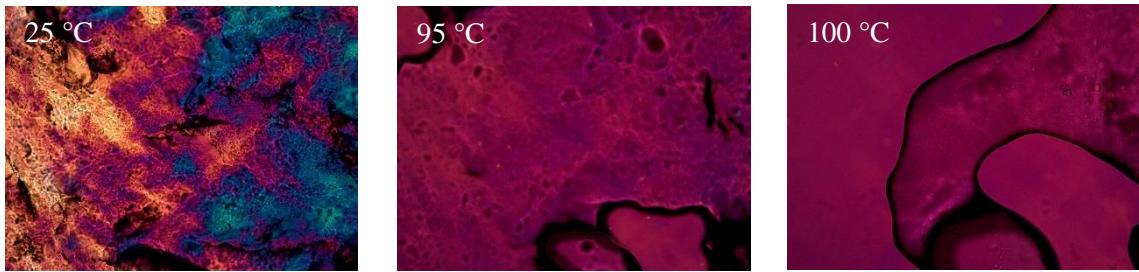


Figure 4: Typical polarised optical micrographs of 20.8 wt% cellulose/EMImDEP/DMSO solution.

3.3 Diameter and tensile analyses of cellulose fibre

The diameter measurement and tensile testing results of 20.8 wt% cellulose fibre with a gauge length of 20 mm are shown in Table 1.

Table 1: Diameter measurement and tensile testing results of 20.8 wt% cellulose fibre.

Engineering constant	Unit	Average value
<i>Diameter (d)</i>	[μm]	28.6± 0.3
<i>Young's modulus (E)</i>	[GPa]	27.8± 1.1
<i>Tensile strength (TS)</i>	[MPa]	387.7± 7.0
<i>Breaking strain</i>	[%]	4.6± 0.5

The tensile properties of 20.8 wt% cellulose fibre ($E= 27.8$ GPa, $TS= 387.7$ MPa, $d= 28.6$ μm) are significantly higher than the 18 wt% cellulose fibre reported in our previous study ($E= 22.4$ GPa, $TS= 304.7$ MPa, $d= 20.8$ μm) [20]. This is because a higher concentration of cellulose could be successfully dissolved with the addition of DMSO, resulting an overall major contribution to the properties of the novel regenerated cellulose fibres developed in this study. Moreover, the processing time (solution preparation and degassing) to produce the cellulose fibre has been significantly reduced from 42 hours in our previous study [20] to only 8 hours, which boosts the manufacturing efficiency remarkably.

4 CONCLUSIONS

We have developed a novel manufacturing method for strong regenerated cellulose fibres spun from an anisotropic solution of low molecular weight cellulose dissolved in EMImDEP using DMSO as co-solvent. 20.8 wt% cellulose/EMImDEP/DMSO solution appeared highly anisotropic with a strong sign of anisotropy and clearing temperature (T_c) about 100 °C. The regenerated cellulose fibre, with an

average diameter of 28.6 μm , demonstrates very good mechanical properties (Young's modulus= 27.8 GPa; tensile strength= 387.7 MPa). Despite the significant reductions in processing time (80 % decrease) and cost in the solvent (30 % decrease), we could dissolve higher concentration of cellulose in EMImDEP, and achieve superior tensile modulus and strength from our fibres compared to previous study that used EMImDEP as the only solvent. These findings open up a potential route to improve the dissolution of cellulose in the ionic liquid and produce high-performance engineering fibres.

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