PHASE TRANSFORMATIONS IN REGENERATED MICROCRYSTALLINE CELLULOSE FOLLOWING DISSOLUTION BY AN IONIC LIQUID

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Phase transformations in microcrystalline cellulose (MCC) were studied following dissolution of 5, 10, and 20 wt. % MCC in the ionic liquid 1-butyl-3-methylimidazolium formate (BMIMFmO) and regeneration *via* water. BMIMFmO was found to be useful as a non-derivatizing solvent for cellulose without the need for any pre-treatment. Wide angle X-ray scattering indicated that a phase transformation from cellulose I to either a poorly crystalline form of cellulose I and/or cellulose II occurs during regeneration after dissolution in BMIMFmO. The dissolution time affected the resulting microstructure of the regenerated cellulose. Thermogravimetric analysis showed that regeneration from the ionic liquid lowers the decomposition onset temperature and increases the char yield when compared with the as-received MCC.

Keywords: Microcrystalline cellulose; Dissolution; Regenerated cellulose; Ionic liquid

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INTRODUCTION

There has been a growing interest in developing new types of composite materials entirely based on cellulose for the replacement of synthetic polymers derived from non-renewable resources. A new class of monocomponent biocomposite known as all-cellulose composites has emerged in recent years, largely based on the pioneering work of Nishino *et al.* (2004). In particular, cellulose itself is prone to excessive shrinkage during regeneration from the solvent, which currently limits all-cellulose composites to the form of a solid thin film or low density foam. The shrinkage during cellulose regeneration can be reduced by increasing the cellulose concentration (C_{cell}) in solution. However, higher C_{cell} also increases the viscosity of the solution, hindering ease of processing (Duchemin *et al.* 2007). If all-cellulose composites are to play a more prominent role in replacing non-renewable plastics, new eco-friendly dissolution pathways need to be explored that offer improved dissolving power and low viscosity.

Investigations into room temperature ionic liquids (RTILs) as solvents for cellulose have rapidly been increasing (Rogers *et al.* 2003; Swatloski *et al.* 2002; Zhang *et al.* 2005). The reader is also referred to a recent review of ionic liquids and their interaction with cellulose. In general, RTILs have tunable physicochemical properties, negligible vapour pressures, thermal stability over a wide range of temperatures, and have the potential to reduce current dependencies on volatile organic compounds (VOCs) (Rogers *et al.* 2005).

Previous work by the authors has shown that dissolution of up to C_{cell} = 20 wt. % (MCC) was possible in more traditional DMAc/LiCl solvent systems (Duchemin *et al.* 2007). However, cellulose concentrations of up to 25 wt. % can be dissolved in 1-butyl-3-methylimidazolium chloride (BMIMCl) using microwave heating (Swatloski *et al.* 2002). The chloride present in BMIMCl is assumed to be responsible for interrupting the extensive intermolecular and intramolecular hydrogen bonding network present in cellulose – a mechanism similarly found in solutions of cellulose and DMAc/LiCl (Striegl 2002). Swatloski *et al.* (2002) showed that the solubility of cellulose decreased with increasing size of the cation such as when the imidazolium ring comprises lengthy alkyl groups. Intensive interactions between cellulose and RTIL occur if the salt solution has small, strong polarizing cations and large polarisable anions. More recently, Fukaya *et al.* (2006) found the strong hydrogen bond acceptability of 1,3-dialkylimidazolium formates is appropriate for the dissolution of cellulose. Moreover, they reported relatively low viscosities for 1,3-dialkylimidazolium formates compared with 1-allyl-3-methylimidazolium chloride (AMIMCl). However, this work did not provide any details on any phase transformations after cellulose regeneration.

In this work, the dissolution and regeneration of microcrystalline cellulose (MCC) was achieved using 1-butyl-3-methylimidazolium formate (BMIMFmO). The effect of the initial concentration of MCC (C_{MCC}) in BMIMFmO on phase transformations in the final regenerated cellulose was examined, and the mechanism of dissolution of cellulose in BMIMFmO is discussed.

EXPERIMENTAL METHODS

Materials

Microcrystalline cellulose (MCC) with an average diameter of 50 µm was used as-received (Avicel PH-101, Fulka) without any further modification. The MCC was dried under vacuum at 90°C for 6 hr before being used. All other chemicals were reagent grade and used without further purification.

Preparation of BMIMFmO

BMIMFmO was synthesized *via* a hydroxide intermediate anion (Fukaya *et al.* 2006). An aqueous solution of the chloride anion RTIL was passed through a column filled with anion exchange resin (Amberlite IRA-400) loaded with hydroxide anion to give a 1-butyl-3-methylimidazolium hydroxide aqueous solution. The basic aqueous solution was then neutralized using formic acid (Fig. 1).

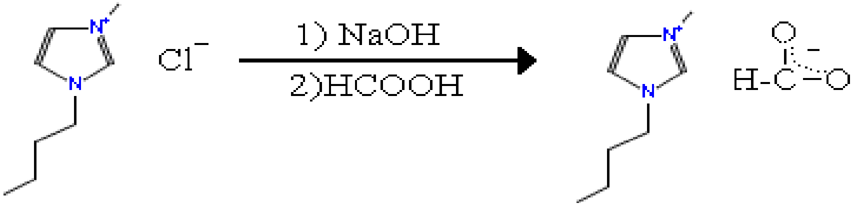

Figure 1. Conversion of BMIMCl to BMIMFmO.

Acid was added in 0.5 mL portions while the pH was monitored using universal pH paper. BMIMFmO was formed upon removal of water with a rotary evaporator. The BMIMFmO was then dried under vacuum at 70°C for 48 hr. It was noted that precipitation of AgCl did not occur following additions of $AgNO_3$ aqueous solution to the RTIL. Viscosity measurements were carried out with Brookfield DV-I prime viscometer at 25°C under nitrogen.

Dissolution of MCC

MCC was added to 20 mL of BMIMFmO in a flask to give solutions with C_{MCC} = 5, 10, and 20 wt. %. C_{MCC} is expressed as a percentage weight of the total weight (*i.e.* cellulose and BMIMFmO). Dissolution was carried out by stirring at 100°C for 15 min, resulting in a solution that was optically clear. The solution was poured into glass Petri dishes. After the completion of this procedure, the samples were taken out of the oven and placed for 1 h on the laboratory bench in order to be cooled to room temperature and exposed to ambient moisture. This step increased the solvent viscosity and also stopped the dissolution process (Duchemin *et al.* 2007; Liebert *et al.* 2008). The partially regenerated cellulose was then immersed in a beaker of water for 48 hr at 20°C, in which the water was replaced every 24 hr. Residual RTIL was removed by further thorough rinsing of the specimen with water. The specimens were finally dried for 48 hr in a vacuum oven at 60°C.

Materials Characterisation

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction of cellulose and regenerated cellulose was performed using a Philips PW1729 X-ray diffractometer with Ni-filtered CuK_α radiation (λ = 0.154178 nm), operating at 50 kV/40 mA with 2θ increased in steps of 0.02° at a scan speed of 0.02°/s over the range of 5 to 50°. The X-ray intensity curves were smoothed over 100 adjacent points, using the adjacent averaging smoothing function in Origin Pro 7.5, and plots were then area-normalized. Diffraction peaks were assigned according to the monoclinic unit cell after Sugiyama *et al.* (1991). The Scherrer equation was used to calculate crystallite thickness by using the half-width at half height of the peak assigned to (200) planes,

$$D = k\frac{\lambda}{B\cos\theta} \tag{1}$$

where D is the crystal thickness, λ the radiation wavelength, θ the diffraction angle, and B the full width of the diffraction peak measured at half maximum height prior to smoothing. The correction factor, K, was set to 0.9 (Murdock 1930). The crystallinity index of cellulose (CrI) was calculated using the following equation,

$$CrI = 100(I - I') / I \tag{2}$$

where I is the height of the peak assigned to the (200) planes of cellulose I, typically located in the range 2θ = 21° to 22° (Ishii *et al.* 2003; Isogai *et al.* 1989), and I' is the height measured at 2θ = 18°, which is where the maximum appears in a diffractogram of amorphous cellulose obtained by ball milling (Mann 1962).

Microstructural observations

The Pt/Pd coated surfaces of specimens were observed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7000F) at an accelerating voltage of 20 kV.

Thermal analysis

The thermal stability and decomposition behaviour of the as-received and regenerated MCC was investigated using thermogravimetric analysis (TGA) (SII TG/DTA6200, TA Instruments). Each sample was analyzed in a platinum pan using N_2 as the purge gas. Temperature scans were carried out from 30 to 600°C at a rate of 10°C/min using a sample weight of 5-10 mg.

RESULTS AND DISCUSSION

Cellulose dissolution did not occur by BMIMFmO at room temperature, and only some swelling of cellulose was observed. However, cellulose dissolution was rapid above 60°C. From the work carried out here, it appears that BMIMFmO dissolves cellulose at lower temperatures (60°C) compared with BMIMCl (80°C) (Fukaya *et al.* 2006). Solvent systems for cellulose such as DMAc/LiCl and NaOH/H_2O generally require an activation step that acts to swell the cellulose structure (Spange *et al.* 1998; McCormick 1985). As for other RTILs, it was also found that MCC dissolves readily in BMIMFmO without the need for any activation step. It is clear that the cellulose dissolution pathway for RTILs, such as BMIMFmO, offers an easier processing route to all-cellulose composites through a reduction in the number of processing steps.

Interaction between the RTIL and hydroxyl groups of cellulose is crucial for dissolution of cellulose. The presence of water in the cellulose-RTIL solution or methylation of the hydroxyl groups decreased the solvating power of the RTIL (Zhang *et al.* 2005, Armstrong *et al.* 1999). To dissolve cellulose, hydrogen bond basicity (β) is necessary to weaken the intermolecular and intramolecular hydrogen bonds of the cellulose chains. BMIMFmO possesses stronger hydrogen bond basicity than chloride salts as also indicated by a lower viscosity.

BMIMFmO was found to have a relatively low viscosity of 55 cP at 25°C when compared with 1,3-dialkylimidazolium formates (66-117 cP), BMIMCl (460 cP), and AMIMCl (2090 cP) (Zhang,*et al.* 2005, Fukaya *et al.* 2006). The lower viscosity of BMIMFmO may be due to the small ion size and “flatness” of both the anion and cation. The relatively low viscosity of the cellulose-BMIMFmO solution should improve the efficiency of cellulose dissolution by enhancing the diffusion of the solvent into the crystalline regions of the cellulose. It is known that cellulose does not dissolve in RTILs containing non-coordinating anions (Swatloski *et al.* 2002). Thus, requirements for dissolution appear to include the presence of a strongly coordinating anion. A possible mechanism for dissolution in BMIMFmO is that above a critical temperature dissociation of the ion pairs (*i.e.* [BMIM]$^+$ and HCOO$^-$) results in the formate anions and [BMIM]$^+$ cation complexes interacting with the proton and oxygen of the hydroxyl groups, respectively. Further work using solid-state ^{13}C NMR is necessary to determine the precise mechanism of dissolution.

The X-ray diffraction intensity curves of the as-received MCC and regenerated cellulose (5%, 10%, and 20%) are shown in Fig. 2. Peaks at 2θ = 15.18, 16.88, 22.68, and 34.88 in the diffractogram for MCC were also consistent with peaks in published WAXS diffractograms for cellulose I (Ishii *et al.* 2003; Isogai *et al.* 1989). Following dissolution and subsequent regeneration using water, the regenerated cellulose exhibited diffraction peaks at 2θ = 21.8° and 12.32°, indicating the presence of cellulose II. These results indicate that the transformation from cellulose I to cellulose II occurred after the dissolution and regeneration in BMIMFmO. This phenomenon has also been reported in most other known solvent systems for cellulose (Raymond *et al.* 1995; Koplak 1976). Cellulose III was not formed, because Cellulose III, when prepared from cellulose I, shows a strong WAXS peak 2θ = 20.7 and a weaker peak 2θ = 11.7 (Isogai 1989), but the latter was not observed.

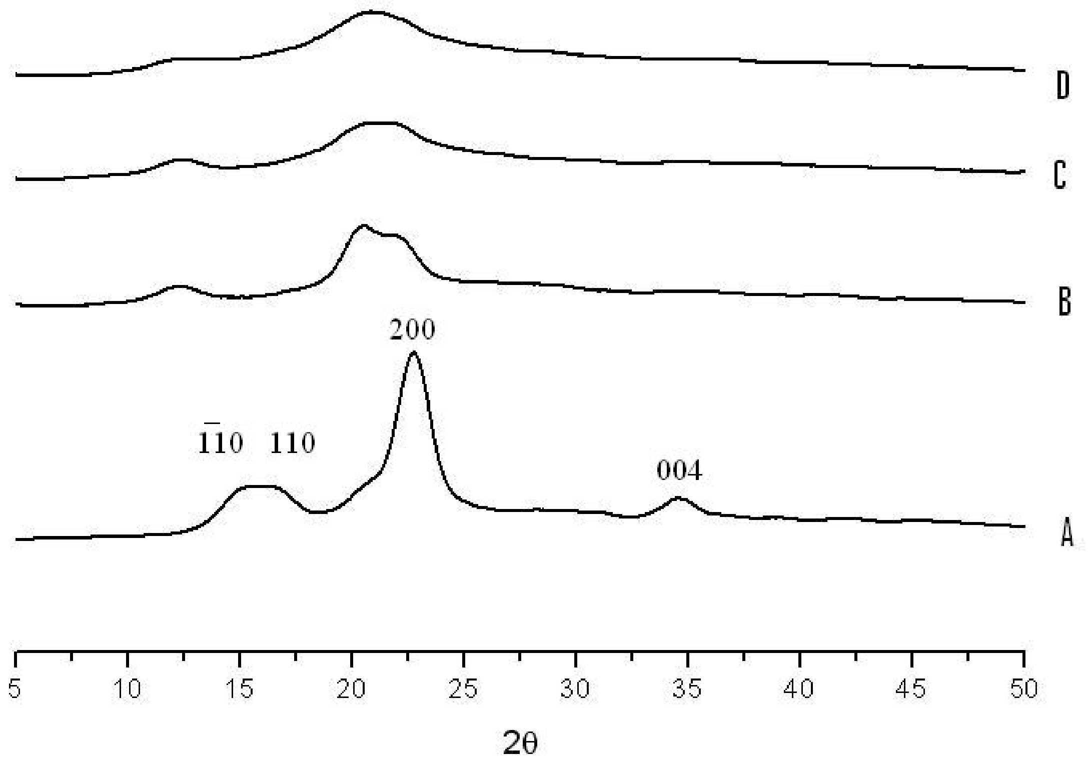

Figure 2. WAXD intensity curves of (A) as-received MCC and regenerated cellulose with C_{MCC} of (B) 20, (C) 10, and (D) 5 wt. % after dissolution in BMIMFmO for 15 min.

The crystallite thickness in the (200) direction (perpendicular to the fiber axis) was determined. The crystallite thickness decreased from 5.31 nm for the as-received MCC to 2.1 nm for C_{cell} = 5 wt. %. Thus, an increase in cellulose concentration in the solution resulted in an apparent increase in crystallite thickness. Furthermore, increasing the dissolution time from 15 min to 4 hr was observed to decrease the crystallite thickness in the sample with C_{cell} = 5 wt. % from 2.1 to 1.52 nm.

Table 1. WAXD Data for As-Received and Regenerated Cellulose

Sample	2θ (200)	2θ (110)	B° (200)	D (nm)	C_{Ir} (%)
MCC	22.7	15.08	1.526	5.31	69
%5MCC	21.80	12.32	1.602	2.10	54
%10MCC	21.78	12.35	3.576	2.26	61
%20MCC	21.84	12.3	3.848	5.03	64
%5MCCT *	21.85	12.92	5.322	1.52	54

*after 4h. dissolution

The crystallinity index *CrI* calculated from Eq. (2) decreased from 69% for MCC to 54% after 5% MCC solutions regenerated (Table 1), and the full widths B at half maximum height were 1.526 and 3.848, giving crystal thicknesses of 5.3 nm and 2.1 nm, respectively, according to Eq. (1). Compared to the original cellulose, the intensity of diffraction peaks of the regenerated cellulose was reduced significantly. In other words, the crystallinity of this regenerated cellulose was lower than the original cellulose as shown in Table 1. This phenomenon means that, in the dissolution process, RTILs rapidly broke intermolecular and intramolecular hydrogen bonds and destroyed the original crystalline form.

The WAXS diffractograms for regenerated cellulose showed a peak at 2θ = 21.8° that progressively developed into a distinct diffraction peak with increasing cellulose concentration in the solvent (Fig. 2). The peak was more distinct in composites prepared with a dissolution time of 4 h compared with 15 min. (Fig. 3).

In samples processed with the longest dissolution time of 4 h, the WAXS pattern of the regenerated cellulose showed decreased intensity of the characteristic crystalline cellulose peaks. Gindl and Keckes (2006) also observed a peak at 21.8° for all-cellulose composites, that they assigned to regenerated cellulose. Duchemin et al. (2007) observed a similar peak in a WAXS diffractogram of cellulose produced by dissolving cellulose II in LiCl/DMAc and regenerating it. A single broad band was observed, characteristic of an amorphous material. This may indicate a slow breakdown of the cellulose with increasing dissolution time. These results indicate that the degree of crystallinity (and hence, microstructure) of the cellulose can be manipulated during the regeneration process to manufacture materials with varying mechanical properties. The diffractogram of MCC (Fig. 2) showed a peak assigned to the (004) planes. This peak was weak or absent in diffractograms of regenerated cellulose prepared with the greatest degrees of transformation (*e.g.* the lowest diffractogram in Fig. 2.)

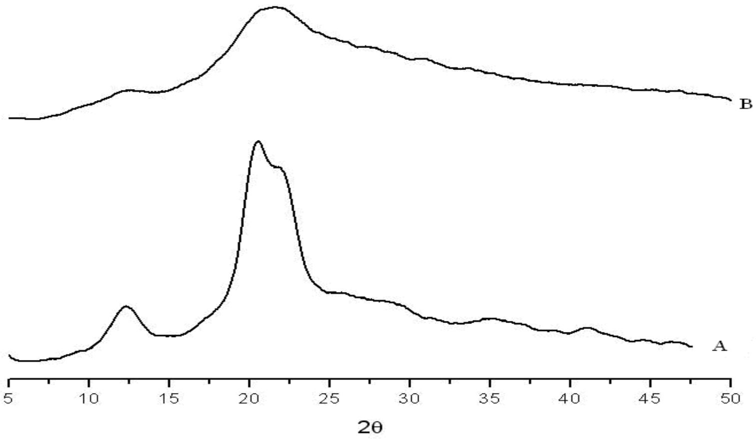

Figure 3. WAXD intensity curves of regenerated cellulose (C_{MCC} = 5%) as a function of dissolution times of (A) 15 min and (B) 4 hr.

The TGA results were characterized by a small mass loss near 100°C due to loss of some retained moisture. All samples exhibited a single pronounced decomposition event, followed by a more gradual loss of mass. The as-received MCC exhibited decomposition in a narrow temperature range from 318-350°C. It was observed that dissolution in the RTIL decreased the onset temperature for decomposition of the regenerated MCC (Fig. 4). After dissolution in the RTIL, the onset of decomposition for C_{MCC} = 5, 10, and 20 wt.% shifted to 212°C, 225°C, and 238°C, respectively, indicating that an increasing C_{MCC} increases the thermal stability of the regenerated MCC. This observed change in thermal stability was also evidenced by increasing char residue remaining after 500°C from 7.9% for the as-received MCC to 12.8%, 16.1%, and 21.2% for C_{MCC} = 5, 10, and 20 wt.%, respectively. The variation in char residues qualitatively suggests variations in the morphology and degree of polymerization (DP) of the celluloses regenerated from the RTIL (Calahorra *et al.* 1989).

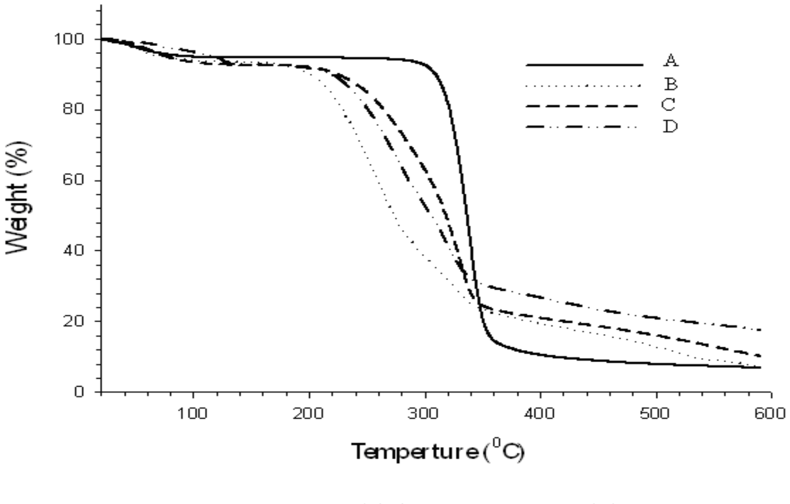

Figure 4. Thermal decomposition curves of (A) as-received MCC and regenerated cellulose after dissolution in BMIMFmO for 15 min for C_{MCC} of (B) 5%, (C) 10% and (D) 20%.

The MCC/RTIL solutions were found to form a gel after being cooled down to room temperature. Thus, it is quite easy to prepare a transparent soft material (Fig. 5) by casting the as-prepared MCC/RTIL solution into a plastic mold and cooling it to room temperature. In addition, the RTIL in the gels could be extracted out by rinsing the MCC /RTIL gels in water.

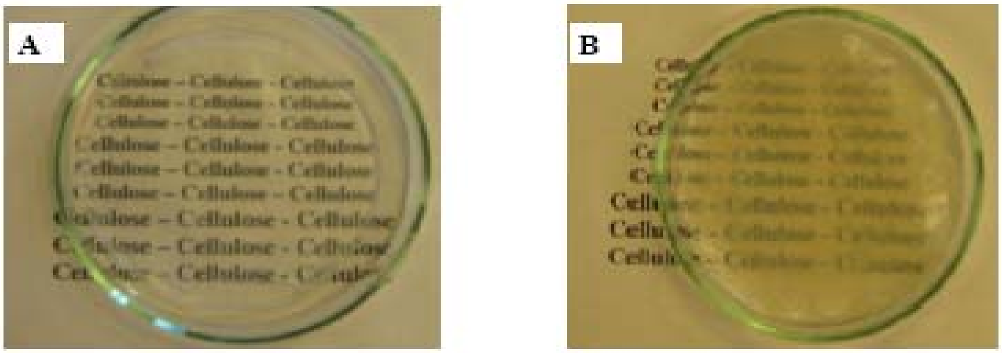

Figure 5. Photographs of regenerated cellulose (CMCC = 5%) as a function of dissolution times of (A) 4 hr and (B) 15 min.

The modifications to the bulk structure of regenerated cellulose are shown from scanning electron micrographs of the initial untreated samples (Fig. 6(a)) and cellulose regenerated from the BMIMFmO (Fig. 6(b)). After regeneration, in all cases, the morphology of the cellulose changed to exhibit a roughened surface. It can be seen that the free surface and fracture surface of the regenerated cellulose display uniformity from the interior to the surface, indicating a dense texture ((Swatloski *et al.* 2002). Different from the structure of the cellulose regenerated from NaOH/H_2O, no porous structure was observed (Zhang *et al.* 2002). The SEM data indicate that the MCC can be solubilized and regenerated with a relatively homogenous macrostructure.

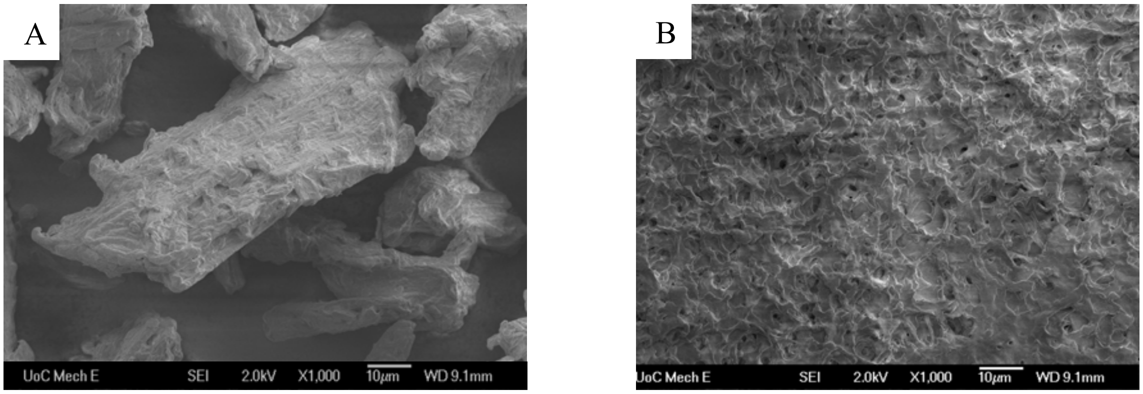

Figure 6: Scanning electron micrographs of the A) free surface of the as-received MCC and B) fracture surface of regenerated cellulose (C_{MCC} = 5%) dissolved in BMIMFmO for 15 min.

Ninety percent of the RTIL could be recovered from the first precipitation bath after an overnight drying step at 130°C followed by 48 h at 100 °C in a fan oven. This result is encouraging and it compares favorably with the work of other authors (Tsioptsias *et al.* 2008). It was also calculated that the MCC samples lost approximately 6% of their total mass throughout the production process, suggesting that some of the most readily dissolvable forms of MCC were dispersed in the BMIMFmO and possibly degraded within the solvent, which could be correlated to the slight yellow–brown coloration of the RTIL after recovery. The decomposition of MCC in the BMIMFmO could induce some complications in the solvent recycling process that requires further study.

CONCLUSIONS

In summary, a novel ionic liquid of BMIMFmO was found to be effective as a powerful, non-derivatizing single-component solvent for cellulose. BMIMFmO possesses low viscosity and high hydrogen-bonding characteristics suited to the processing and dissolution of crystalline cellulose. Unactivated MCC was rapidly dissolved in BMIMFmO. On the basis of the fact that BMIMFmO is thermostable and non-volatile, this process of dissolution and regeneration of cellulose seems to be a promising "green process" for the preparation of regenerated cellulose materials. Both WAXS and TGA results suggested that the crystalline structure of cellulose was mostly disrupted in the material. The transformation to cellulose I to cellulose II was observed by X-ray diffraction for the regenerated cellulose. The crystallinity index of the regenerated cellulose is slightly increased with an increase in MCC concentration in RTILs, but does not change with increasing time of dissolution. Crystallite dimensions of the regenerated MCC were increased with an increase in MCC concentration in RTILs and decreased with time.

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