Study of Cellulose-Rich Materials Recovered After Dissolution of Sulphite Pulp from South African Eucalyptus Wood in [C$_2$mim][OAc]/co-Solvent Mixtures

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Biomass processing in ionic liquids (ILs) is a promising technology but involves the simultaneous optimization of many variables in parallel. Here we investigated how dissolution of dissolving wood pulp in IL molecular co-solvents affects the structure of lignocellulosic materials. Mixtures of the IL 1-ethyl-3-methylimidazolium acetate ([C$_2$mim][OAc]) and dimethylsulfoxide (DMSO) or dimethylformamide (DMF) were used to dissolve South African eucalyptus raw (unbleached) and final (bleached) pulp and regenerated cellulose was obtained by addition of a 1:1 (v/v) water/acetone mixture. The regenerated cellulose materials were characterized by SEM, FTIR, TGA, and PXRD. The results showed that addition of co-solventsled to increased dissolution yields, presumably due to reduction of the IL viscosity facilitating faster dissolution of the wood materials. The selection of the co-solvent for the mixtures did not have a significant influence on the recovered materials, whose characteristics such as crystallinity and thermal stability depended only on the source material. Co-solvents did affect the purity of the recovered material, with DMF appearing to lead to greater contamination. Co-solvent addition is a viable approach for dissolution of dissolving wood pulp without affecting the quality of the recovered material providing removal and recovery of the spent solvents can be optimized.

Keywords: Cellulose, Dissolving Wood Pulp, Ionic Liquids, Co-Solvents

Introduction

With increasing governmental regulations in the industry, the need to implement green processes in order to minimize waste production is becoming increasingly important. The use of ILs as green replacements for conventional solvents will offer potential benefits over the existing dissolution methods. ILs exhibit advantages such as non-volatility, easy recyclability, non-flammability, and thermal stability.[1-2] The discovery that ILs can dissolve wood and cellulose provides new opportunities to utilize cellulose/pulp.[3-5]Among the different kinds of ILs have been reported as cellulose solvents in literature[2], the ILs based on alkyl phosphate and acetate anions with lower viscosities have the ability to dissolve cellulose under mild conditions.[6] For example, 1-ethyl-3-methylimidazolium acetate ([C$_2$mim][OAc]) was

demonstrated to be able to dissolve biomass more efficiently than other ILs.[7-8]Dissolution of cellulose in ILs such as [C$_2$mim][OAc] is attributed to their ability to break the extensive network of hydrogen bonds existing in cellulose through interactions between the IL anions and hydroxyl protons of glucose[3]cellulose allowing it to diffuse into the interior of the biopolymer, which then results in its complete dissolution.[9] It has been reported that the addition of an organic co-solvent to the IL modifies the dissolution of cellulose.[10]Since the dissolution of cellulose by ILs containing acetate is mainly determined by the hydrogen-bond interactions between acetate anions and the hydroxyl protons of cellulose, the aprotic solvents (*e.g.*, dimethylsulphoxide, DMSO, or dimethylformamide, DMF) can interact with the ions of the IL, breaking the ionic clusters of the ions in the IL, and thus generating ion pairs and free anions of the IL to interact with the biopolymer.[11-12]Therefore, cellulose can be dissolved in the IL/co-solvent systems at ambient temperature

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with high solubility. These solvent systems are reported to show many advantages such as, non-derivatization, low viscosity, and high dissolution speed.[13] New research in the field of IL-based biomass processing tends to focus on the qualities of the final material such a pulp yield or percent delignification as readily understood metrics of a process.[14] However, the major challenges facing development of this technology pertain to the front end – biomass dissolution and IL recovery. There is a need for research that systematically investigates the effects of a variable on as many aspects of cellulose dissolution as possible.

In the present work, we investigate the effects of the two aforementioned co-solvents, DMSO and DMF, on processing of bleached and unbleached dissolving pulp in $[C_2mim][OAc]$. The regenerated cellulose was characterized by FT-IR, PXRD, SEM, and TGA. The study also investigated the effects of co-solvation on yield, purity, particle morphology, and thermal stability of the recovered cellulose.

Experimental

Materials

The IL $[C_2mim][OAc]$, with a purity of > 95 %, was purchased from IoLiTec (Tuscaloosa, AL). Before use, the IL was dried at 50 °C under high vacuum for 12 h (final water content, determined by Coulometric Titration Karl Fischer, was 10435 ppm). The solvents acetone, DMSO and DMF (99.9 % purity) were purchased from Sigma Aldrich (St. Louis, MO) and were used as received. Nylon membrane filter papers, 10 and 0.8 µm, were purchased from Sterlitech Corporation (Kent, WA). Deionized (DI) water was acquired from an in-house system (Culligan Water Systems, Rosemont, IL, USA) with a typical resistivity of 17.4 MΩ·cm at 20 °C. The pulp samples were obtained from a mill in South Africa. Once received, the pulp samples were dried at 50 °C for 12 h under vacuum, ground using a mortar and pestle, and then stored in a desiccators until use.

Dissolution of biomass and regeneration of cellulose

The previously dried and ground raw or final pulp samples (1 g) was added into a 20 mL glass vial containing $[C_2mim][OAc]$/DMSO or $[C_2mim][OAc]$/DMF mixtures (25 wt% co-solvents) to get a final concentration *ca.* 5 wt%. Dissolution was achieved by magnetic stirring at 120 °C for 6 h in an oil bath. After dissolution time, the solution was cooled to room temperature and 50 mL water/acetone mixture (1:1, v/v) was added. The mixture was stirred for 1 h and then centrifuged for 10 min at 700rpm (Clays Adams centrifuge, Becton Dickinson and Company, Franklin Lakes, NJ). The top liquid phase was removed, while awhitish material settled at the bottom of the centrifuge tube. The whitish material was transferred to a 250 mL beaker, where it was washed three times with 50 mL water/acetone mixture. After washings, the material was filtered using a Nylon membrane filter (10 µm pore size), and oven-dried at 80 °C for 1 h. The dried weight of the precipitate was recorded and the percentage recovery of the biomass (wt %) was calculated using equation (1).

$$yield(\%) = \frac{mass\ of\ regenerated\ biomass}{mass\ of\ pulp} x100\% \qquad \dots (1)$$

Characterization techniques

Infrared spectra of regenerated cellulose samples from $[C_2mim][OAc]$/DMF or DMSO mixtures were collected using a Bruker Alpha ATR-FTIR spectrometer, and spectra were obtained in the range of 400–4000 cm^{-1}. Before characterization, the regenerated cellulose samples were cut and ground into very small particles. SEM images of the regenerated cellulose samples were taken at 300x magnification using a Jeol 6310 Electron Probe analyzer SEM instrument operated at 5-10 kV accelerating voltage. Prior to imaging, the samples were sputter-coated with gold to make the fibres electrically conductive, thus avoiding degradation and build-up of charge on them. The diffraction patterns of the regenerated cellulose samples were obtained using a Bruker D2 Phaser Powder XRD instrument. The patterns were recorded using a Cu-Kα radiation at 30kV and 10 mA, over a 2θ from 5 to 40º. For each sample, a thin layer of neat powder was loaded onto a single crystal silicon low background sample holder. Thermogravimetric analysis was performed with a MT TGA/DSC Star 1 system (Mettler-Toledo, Columbus, OH). Approximately 10mg of the regenerated cellulose samples were placed in the pans and analysis was carried out by the Thermo Analyzer at a heating rate of 5 °C/min under continuous nitrogen flow in a temperature range from 25 to 600 °C, with an isotherm process at 75 °C for 30 min to remove any absorbed water.

Results and Discussions

Dissolution and regeneration of cellulose

The dissolution and regeneration results are shown in Table 1. The data show that the addition of co-solvent sled to improved pulp yields. The yields of cellulose recovered from the pulp samples after dissolution in pure [C2mim][OAc] were low comparable: this in agreement with that previously reported in the literature.[15] The low yield is possibly due to the higher viscosity of the solution which impedes penetration into the fibre matrix and thus retards the speed of dissolution of cellulose.[16] The addition of co-solvents reduced the viscosity of the mixture, and this accelerated the dissolution process.[15,17] DMSO and DMF showed differences in performance, with DMF consistently leading to higher pulp yields. The literature contains mixed interpretations on the origin of this difference. Earlier, it was reported that cellulose solubility on similar ILs/co-solvent mixtures followed the trend [C4mim][OAc]/DMSO (15.0%) > [C4mim][OAc]/DMF (12.5%), suggesting DMSO should lead to greater solubility and, therefore, greater regenerated cellulose yield. However, interactions strongly depend on the concentration and type of IL in the mixture. On the other hand, while both DMSO and DMF have high dielectric constants and would be expected to interact strongly with the IL ions[18], DMSO is more polar than DMF and would be expected to engage in stronger ion-dipole interactions. This then results in reduction of cellulose solubility, because DMSO forms competing hydrogen bonds to the macromolecular chains of cellulose.[20] Yet more factors such as coagulation could have their own effects and perhaps reverse the correlation between co-solvent and pulp yield. Pulp yields from the two pulp fibres also differed, with the final pulp generating consistently higher yields that the unbleached pulp. This may be due to the lower amounts of hemicelluloses and lignin present in the bleached pulp compared to those present in the unbleached pulp. For example, the total lignin content was 3.60 *vs.* 1.40 wt% for raw and final pulp, respectively.

Characterization of the recovered cellulose rich materials

The FTIR spectra of cellulose regenerated after dissolution in [C2mim][OAc]/co-solvent mixtures resembled that reported for typical lignocellulosic materials.[11,19] Lignin was not detected on the regenerated cellulose materials using FTIR, as evidenced by the absence of aromatic skeletal vibrations of lignin around 1587 and 1506 cm^{-1} nor the characteristic peak of the carbonyl groups of lignin *ca.* 1730 cm^{-1}. Thermogravimetric analysis (TGA) was used to investigate whether the differences in pulp type or processing affected the purity or thermal stability of the recovered cellulose Figure 1. Samples were heated from 35 to 600 °C at a rate of 5 °C/min with a 30 min isotherm at 75 °C, which is typically sufficient to remove volatiles such as water. The cellulose regenerated from both pulp samples dissolved in [C2mim][OAc]/DMSO reached stable masses at the end of the isotherm up until the onset of the first decomposition step. Both pulp samples treated with DMF show continued mass loss after the isotherm. Although both DMSO and DMF are high boiling solvents, it appears that DMF is more difficult to remove. Additionally, by comparing the relative amounts of volatiles (mass lost prior to the decomposition event beginning *ca.* 163 °C) and decomposition products (mass lost after the decomposition event) to the total mass loss Figure 2, the usage of DMF is correlated with a greater amount of volatile mass. From this it can be seen that, although both co-solvents are high boiling, DMF leads to greater contamination of the regenerated material than DMSO, which can be removed. When the fraction of remaining mass lost during the
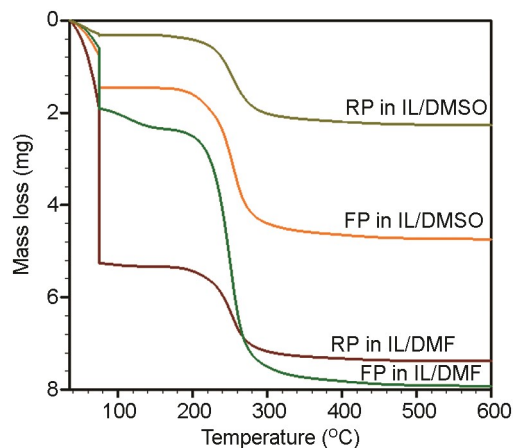
Table 1 — Percentage yield of regenerated cellulose after dissolution of raw and final pulp samples in [C2mim][OAc]/DMSO and DMF mixtures

IL or IL/co-solvent mixtures	% Raw (unbleached) pulp	% Final (bleached) pulp
[C2mim][OAc]	10.54 %	35.29 %
[C2mim][OAc]/DMSO	15.25 %	41.88 %
[C2mim][OAc]/DMF	36.25 %	49.89 %

Fig. 1 — TGA curves of regenerated cellulosic material from raw and final pulps (RP and FP, respectively) after dissolution with [C2mim][OAc]/co-solvent mixtures.
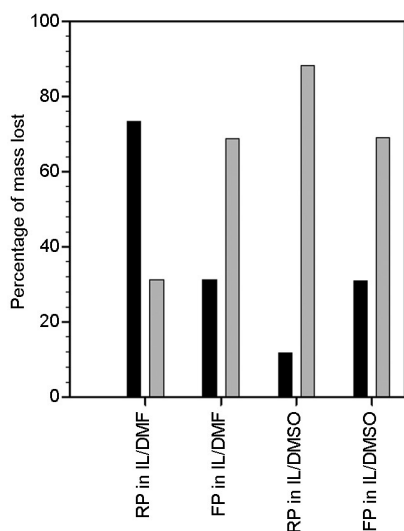
Fig. 2 — Percent of mass lost prior to the decomposition event (beginning ca. 163 °C, black bars) and decomposition products (after the decomposition event, grey bars) of the regenerated cellulosic material from raw and final pulps (RP and FP, respectively) after dissolution with [C$_2$mim][OAc]/co-solvent mixtures.
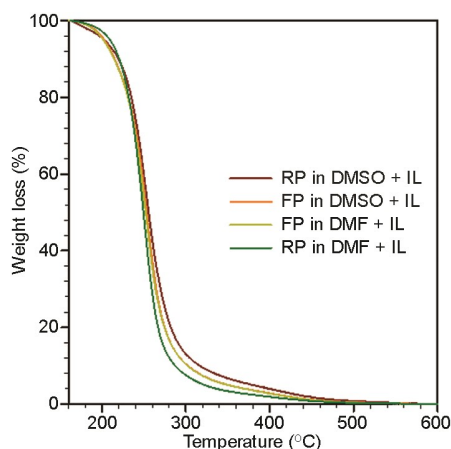

Fig. 3 — TGA curves normalized for the remaining mass lost during the decomposition for the regenerated cellulosic material from raw and final pulps (RP and FP, respectively) after dissolution with [C$_2$mim][OAc]/co-solvent mixtures.

decomposition is normalized for the four samples Figure 3, it can be seen that they all follow very similar profiles. This indicates that after volatiles are removed, the remaining materials are all very similar in composition, lose mass at approximately the same rate (as a function of temperature) and yield the same fraction of char. Neither the choice of auxiliary solvent nor bleaching of pulp is found to have an effect on decomposition of the recovered cellulose. This also suggests that the auxiliary solvents are completely removed prior to the decomposition event, as if either were still present their different

decomposition pathways would be reflected in differences in the rate of mass loss. Analysis using powder X-ray diffraction indicates that the regenerated cellulose samples exhibit typical diffraction patterns of cellulose II, which conserve the (1,-1,0)crystalline peaks of cellulose II at 11.8° and 20.0°.[1,12] There are no obvious differences between diffraction patterns correlated with changing the co-solvent. Samples prepared from final pulp show slightly greater diffraction centered roughly at 27.5°. This suggests that the crystallinity of the final form is correlated with the composition of the pulp but not the composition of the dissolving solution. Such a result suggests that source material and coagulation conditions completely determine the crystallinity of the final material for these systems. SEM microscopy was used to study the detailed morphology of the regenerated cellulose samples. The fibrous structure of bleached eucalyptus pulp is normally easily visible at this magnification[2] and is completely absent in the recovered materials. This supports complete destruction of the original structure during the dissolution process. The SEM images suggest that particles obtained by raw pulp may be larger than those from final pulp, but both have essentially random shapes and surface morphologies consistent with the rapid coagulation method. As with the PXRD, neither treatment method appears to affect the form of the final material.

Conclusions

The study illustrates the importance of a full characterization of a new material resulting from new separation and recovery techniques, including those based on ILs. The addition of a co-solvent to the [C$_2$mim][OAc] solution increased the yields of the cellulosic material regenerated from Southern African eucalyptus raw and final pulps, in comparison with those obtained using only [C$_2$mim][OAc]. It appears that co-solvents reduce the viscosity of the ILs thus facilitating their penetration into the pulp matrix to enable rapid dissolution. Characterisation of the regenerated matter from the dissolved material showed the presence of mainly cellulose. Co-solvent addition is a viable approach for dissolution of dissolving wood pulp without affecting the quality of the recovered material providing removal and recovery of the spent solvents can be optimized.

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