Dissolution of Cellose with Ionic Liquids

Richard P. Swatloski, Scott K. Spear, John D. Holbrey, and Robin D. Rogers*

*Center for Green Manufacturing and Department of Chemistry, The University of Alabama,
Tuscaloosa, Alabama 35487*

Cellulose is the most abundant biorenewable material, with a long and well-established technological base.[1] Derivitized products have many important applications in the fiber, paper, membrane, polymer, and paints industries.

Cellulose consists of polydisperse linear glucose polymer chains (Figure 1) which form hydrogen-bonded supramolecular structures;[2] cellulose is insoluble in water and most common organic liquids. The growing willingness to develop new cellulosic materials results from the fact that cellulose is a renewable resource, although many of the technologies currently used in cellulose processing are decidedly nongreen.[3] For example, viscose rayon is prepared from cellulose xanthate (production over 3,000,000 tons per year) utilizing carbon disulfide as both reagent and solvent. Most recently, processes using more environmentally acceptable nonderivitizing solvents (N-methylmorpholine-N-oxide (NMNO) and phosphoric acid) have been commercialized. Solvents are needed for dissolution that enable homogeneous phase reactions without prior derivitization.[4]

Graenacher[5] first suggested in 1934 that molten N-ethylpyridinium chloride, in the presence of nitrogen-containing bases, could be used to dissolve cellulose; however, this seems to have been treated as a novelty of little practical value since the molten salt system was, at the time, somewhat esoteric and has a relatively high melting point (118 °C). We were interested in examining whether other solvents that would now be described as ionic liquids (ILs)[6] would dissolve cellulose and, especially, whether the availability of a wide and varied range of ILs, coupled with the current understanding of their solvent properties,[7] would allow flexibility and control in the processing methodology, with increased solution efficiency and reduction or elimination of undesirable solvents.

Ionic liquids, containing 1-butyl-3-methylimidazolium cations ([C₄mim]⁺) were screened with a range of anions, from small, hydrogen-bond acceptors (Cl⁻) to large, noncoordinating anions ([PF₆]⁻) also including Br⁻, SCN⁻, and [BF₄]⁻. In addition, variations in cation alkyl-substituent from butyl through octyl were investigated for the chloride salts. Dissolution experiments were carried out using cellulose-dissolving pulps (from cellulose acetate, lyocell, and rayon production lines), fibrous cellulose (Aldrich), and Whatman cellulose filter papers. The cellulose samples were added to the ionic liquids without pretreatment, in glass vials, and heated without agitation on a heating plate or in a domestic microwave oven.

Table 1 summarizes the results obtained using high MW dissolving pulp (DP ≈ 1000). Stirring cellulose in the ILs under ambient conditions did not lead to dissolution, although the cellulose fibers were wetted by the ILs. However, on heating to 100−110
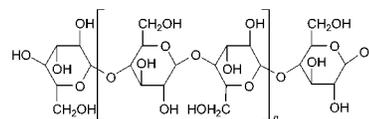

Figure 1. A cellulose polymer chain, n is typically 400−1000.

Table 1. Solubility of Dissolving Pulp Cellulose in Ionic Liquids

| ionic liquid	method	solubility (wt %)
[C₄mim]Cl	heat (100 °C)	10%
	(70 °C)	3%
[C₄mim]Cl	heat (80 °C) + sonication	5%
[C₄mim]Cl	microwave heating 3−5-s pulses	25%, clear viscous solution
[C₄mim]Br	microwave	5−7%
[C₄mim]SCN	microwave	5−7%
[C₄mim][BF₄]	microwave	insoluble
[C₄mim][PF₆]	microwave	insoluble
[C₆mim]Cl	heat (100 °C)	5%
[C₈mim]Cl	heat (100 °C)	slightly soluble

°C, cellulose slowly dissolved in the Cl⁻-, Br⁻-, and SCN⁻-containing ILs to yield increasingly viscous solutions.

Dissolution rates could be significantly improved by heating in a microwave oven. In a typical procedure to prepare a 10 wt % solution, 0.5−1.0 g of fibrous cellulose was placed in a glass vial and [C₄mim]Cl ionic liquid (10 g) was added as a liquid at 70 °C (i.e., above the melting point). The vial was then loosely capped, placed in a microwave oven, and heated with 3−5 s pulses at full power. Between pulses, the vial was removed, shaken or vortexed, and replaced in the oven. A clear, colorless, viscous solution was obtained. ILs are heated with exceptional efficiency by microwaves,[8] and care must be taken to avoid excessive heating that induces cellulose pyrolysis. The decomposition appears to be more rapid in contact with the ILs than for isolated cellulose under equivalent conditions.

Solutions containing up to 25 wt % cellulose can be formed as viscous pastes in the chloride-containing ILs, although compositions between 5 and 10 wt % cellulose are more readily prepared. The greatest solubility was obtained using [C₄mim]Cl as the solvent. When high concentrations of cellulose (>10 wt %) were dissolved in [C₄mim]Cl, the viscous solutions obtained were optically anisotropic between crossed polarizing filters and displayed birefringence. The formation of liquid crystalline solutions of cellulose may have useful applications for the generation of new, advanced materials.[9] High-strength materials that conserve anisotropy in the solid phase are especially desirable, yielding enhanced mechanical properties.

Nonderivitizing solvents for cellulose effect dissolution by disrupting and breaking the intramolecular hydrogen-bonding network. For dimethylacetamide (DMAC)/LiCl solvents, complexation of lithium ions by DMAC mobilizes chloride ions which

* To whom correspondence should be addressed. E-mail: rdrogers@bama.ua.edu.
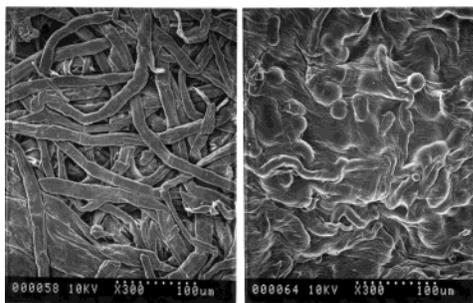
Figure 2. SEM micrographs of the initial dissolving pulp (left) and after dissolution in [C$_4$mim]Cl and regeneration into water (right).

Figure 3. Thermal decomposition profiles of (i) regenerated cellulose and (ii) original dissolving pulp. Samples were heated in platinum sample containers under a nitrogen atmosphere at 10 °C min^{-1}.
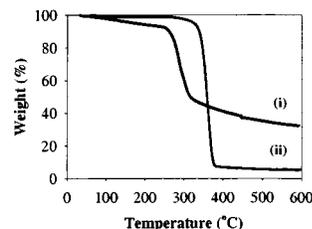
interact with the cellulose hydroxyl groups. In a typical 10 wt % LiCl/DMAC solution, free chloride ion concentration is about 6.7 mol %. In contrast, [C$_4$mim]Cl has a chloride concentration almost 3 times as high, (approximately 20 mol %). In all these cases, the chloride ions are nonhydrated.

We speculate that the high chloride concentration and activity in [C$_4$mim]Cl is highly effective in breaking the extensive hydrogen-bonding network present, thus allowing for much quicker dissolution times, and the ability to dissolve higher concentrations of cellulose than the traditional solvent systems. The longer-chain substituted ionic liquids ([C$_6$mim]Cl and [C$_8$mim]Cl) appear to be less efficient at dissolving cellulose. This may be due to the reduced effective chloride concentration within these liquids; however, the choice of IL can also be a compromise between solubilizing power and rheological properties; when cooled to room temperature, [C$_8$mim]-Cl is a (viscous) liquid, whereas [C$_4$mim]Cl forms a crystalline solid.

The presence of water in the ionic liquid was shown to significantly decrease the solubility of cellulose, presumably through competitive hydrogen-bonding to the cellulose microfibrils which inhibits solubilization. When water was added to the IL at concentrations greater than ca. 1 wt % (approximately 0.5 mole fraction H$_2$O) the solvent properties were significantly impaired, and cellulose was no longer soluble. Hydrogen-bonding properties are important in solvents for the dissolution of cellulose. For example, anhydrous and monohydrated NMNO are good solvents; however, when completely hydrated by two or more waters, NMNO is no longer a good solvent for cellulose.[10] Similarly, the ability of molten inorganic salt hydrates[11] to dissolve cellulose depends on the degree of ion hydration and is thought to occur via coordinating the cellulose hydroxyl groups to the metal cation (when deficient in water).

Cellulose could be precipitated from the IL solution by the addition of water, or other precipitating solutions including ethanol and acetone. The macroscopic morphology of the regenerated cellulose varied depending on how the contacting of the IL solution and the regeneration liquid is achieved. To explore the scope for processing of cellulose from ILs, we prepared monoliths, fibers, and films by forming into an aqueous phase. Rapid mixing of the IL solution with an aqueous stream results in precipitation of cellulose as a powdery floc. By extrusion of the IL/cellulose solution into water, thin fibers and rods were prepared.

The regenerated materials were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and size exclusion chromatography (SEC). Scanning Electron Microscopy (SEM) was used to observe the bulk structure, scanning electron micrographs of dissolving pulp and regenerated cellulose are shown in Figure 2. The dissolving pulp shows fibers at 300× magnification in the SEM. After regeneration, the morphology of the material was significantly changed, displaying a rough, but conglomerate texture in which the fibers are fused into a relatively homogeneous macrostructure. SEC indicated that the dissolving pulp could be solubilized in [C$_4$mim]Cl and regenerated from water without significant change in the degree of polymerization or polydispersity.

TGA curves are shown in Figure 3 for dissolving pulp regenerated from [C$_4$mim]Cl. Rapid decomposition in a narrow temperature range from 350 to 360 °C is observed for the initial cellulose sample. The regenerated sample exhibits a lower onset temperature for decomposition, but gives a higher char yield (nonvolatile carbonaceous material) on pyrolysis, indicated by the high residual masses after the decomposition step.

This research has shown that ILs can be used as nonderivatizing solvents for cellulose. ILs incorporating anions which are strong hydrogen bond acceptors were most effective, especially when combined with microwave heating, whereas ILs containing 'non coordinating' anions, including [BF$_4$]$^-$ and [PF$_6$]$^-$ were nonsolvents. Chloride containing ILs appear to be the most effective solvents, presumably solubilizing cellulose through hydrogen-bonding from hydroxyl functions to the anions of the solvent.

References

(1) *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1993; Vol. 5, p 476.
(2) Finkenstadt, V. L.; Millane, R. P. *Macromolecules* 1998, *31*, 7776−7783.
(3) Johnson, D. C. In *Cellulose Chemistry and its Application*; Nevell, T. P., Zeronian, S. H., Eds.; E. Horwood: Chichester, 1985; p181.
(4) (a) Augustine, A. V.; Hudson, S. M.; Cuculo, J. A. In *Cellulose Sources and Exploitation*; Kennedy, J. F., Philipps, G. O., Williams, P. A., Eds.; E. Horwood: New York, 1990; p59. (b) Dawsey, T. R. In *Cellulosic Polymers, Blends and Composites*; Gilbert, R. D., Ed.; Carl Hanser Verlag: New York, 1994; p157.
(5) Graenacher, C. Cellulose Solution. U.S. Patent 1,943,176, 1934.
(6) See, for example: (a) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* 2001, *3*, 156−164. (b) Holbrey, J. D.; Seddon, K. R. *Clean Prod. Proc.* 1999, *1*, 223−236. (c) Gordon, C. M. *Appl. Catal. A* 2001, *222*, 101−117. (d) Sheldon, R. A. *Chem. Commun.* 2001, 2399−2407.
(7) Holbrey, J. D.; Visser, A. E.; Rogers, R. D. In *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; VCH−Wiley, 2002. In press.
(8) Varma, R. S.; Namboodiri, V. V. *Chem. Commun.* 2001, 643−644.
(9) Boerstoel, H.; Maatman, H.; Westerink, J. B.; Koenders, B. M. *Polymer* 2001, *42*, 7371−7379.
(10) Maia, E.; Peguy, A.; Perez, S. *Acta Crystallogr. B* 1981, *37*, 1858.
(11) Leipner, H.; Fischer, S.; Brendler, E.; Voigt, W. *Macromol. Chem. Phys.* 2000, *201*, 2041−2049.

JA025790M