IONIC LIQUIDS FOR THE DISSOLUTION AND REGENERATION OF CELLULOSE.

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Cellulose derivatives (Figure 1) have many important commercial applications in the fiber, paper, membrane, polymer and paints industries. However, there are only a limited number of common solvents in which cellulose is soluble;[1] solvents include, carbon disulfide, *N*,*N*-dimethylacetamide/lithium chloride (DMAC/LiCl), concentrated inorganic salt ($ZnCl/H_2O$, $Ca(SCN)_2/H_2O$) and mineral acids (H_2SO_4/H_3PO_4), or molten salt hydrates ($LiClO_4.3H_2O$, NaSCN/KSCN/LiSCN/H_2O). The efficiency of existing methods for dissolving and derivitizing cellulose can be significantly improved by the availability of suitable solvents for refined and natural cellulose; such an example is *N*-methylmorpholine-*N*-oxide (NMMO), used as a solvent for non-derivitizing dissolution of cellulose for the production of lyocell fibers.

With increasing governmental regulations in industry, the need to implement 'green' processes in order to prevent pollution and waste production, and to utilize renewable resources, is becoming increasingly important.[2] The use of ionic liquids as 'green' replacements for conventional organic solvents has been demonstrated in chemical, biochemical and separation processes[3] and offer potential benefits over existing bioresource extraction processes.

We have investigated the use of ionic liquids for the dissolution of cellulose with the view to facilitating cleaner processes, with increased efficiency and a reduction, or elimination, in the use of environmentally undesirable solvents. It has been found that cellulose can be dissolved in ionic liquids without derivitization in high concentrations, up to 30 wt% is possible although solutions containing 5 wt% cellulose in ionic liquid are more easy to prepare and handle. The greatest solubility was obtained using 1-butyl-3-methylimidazolium chloride as the solvent, other non-chloride containing ionic liquids may be used. This offers the basis to explore and develop new, improved solvent systems.

Ionic liquids containing halide anions have been shown to be strongly hydrogen-bonding whereas, for example, hexafluorophosphate containing ionic liquids are not. This study has shown that ionic liquids can be used as non-derivitizing solvents for cellulose. The ability of the ionic liquids to dissolve cellulose varies significantly with the size and polarizability of the anion present, and also with the nature of the cation. Chloride-containing ionic liquids appear to be the most effective solvents, presumably solubilizing cellulose through hydrogen-bonding from hydroxyl functions to the anions of the solvent.

Cellulose can be regenerated from the ionic liquid solution in a range of structural forms with a relatively homogeneous microscopic morphology (Figure 2) by simply contacting the cellulosic solution with water. This allows, a simple, benign system for the processing of cellulose into fibers, monoliths and membranes and has potential environmental and cost advantages over current processing methodologies, which make use of volatile organic solvents. We will compare solvents traditionally used for cellulose dissolution with ionic liquids, and describe methods for cellulose regeneration. Results from regenerated cellulose, as well as important intermolecular forces will be discussed.

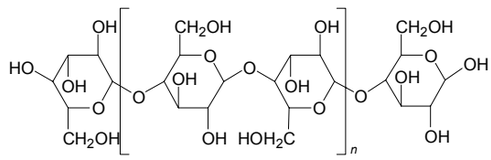

Figure 1. Molecular structure of the cellulose polymer chain, *n* is typically 400-750

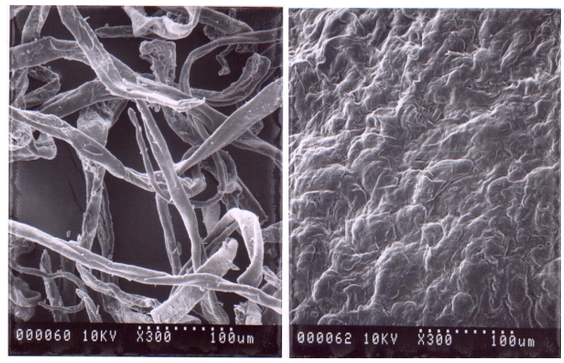

Figure 2. Electron micrograph of fibrous cellulose before (left), and after (right), dissolution and regeneration from the ionic liquid, $[C_4mim]Cl$.

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1 Heinze, T.; Liebert, T. *Prog. Polym. Sci.*, **2001**, *26*, 1689.

2 Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998.

3 Holbrey, J. D.; Visser, A. E.; Rogers, R. D. "Solubility and Solvation in Ionic Liquids", in *Ionic Liquids in Synthesis*; eds. Wasserscheid, P; Welton, T. VCH-Wiley, 2002.