Processing Cellulose with Ionic Liquids

Occurring at a volume of some 700 billion tons, cellulose is earth’s most widespread natural organic chemical and therefore our most important bio-renewable resource. Together with lignin, cellulose occurs as main part of every lignocellulosic biomass. It is produced by biosynthesis on land (wood, grasses) and in sea (algae) as component of plant cells in quantities of approximately 75 billion tons per year.

But out of these 75 billion tons nature renews every year, only 0.2 billion tons are used as feedstock for further processing – mainly for the pulp and paper industry. As feedstock for chemical processes only the very small amount of 0.005 billion tons per year (respectively 0.007%) is utilized. This is surprising and in a way disappointing as well, as the by nature given properties of the cellulose biopolymer should be a very good basis for manufacturing polymeric materials based on renewable feedstock.

![Diagram showing the composition of biomass](image)
A more intensive exploitation of cellulose as a bio-renewable feedstock has to date been prevented by a strong focus on petrochemical raw materials, but also by the lack of suitable solvents. The majority of cellulose today is processed by using carbon disulfide (CS₂) as a solvent - mainly leading to the well known viscose fibres produced worldwide in amounts of 2.5 million tons per year. The principle disadvantage of the CS₂ process is given by the fact that this process is not a physical dissolution process. Cellulose is dissolved here after derivatization as sodium xanthate and the major drawback results from the need of equimolar quantities of auxiliaries like sodium hydroxide and sulfuric acid leading to significant amounts of waste and efforts in waste treatment.

Dissolution of cellulose in Ionic Liquids

It was Robin Rogers with his research team at the University of Alabama who in 2002 applied Ionic Liquids to the dissolution of cellulose. In particular, with using 1-Butyl-3-methyl-imidazolium chloride (BMIM Chloride) he was the first to be able to dissolve cellulose in technically useful concentrations by physical dissolution in an inert solvent without using any auxiliaries. From today's point of view this has to be seen as major breakthrough in opening opportunities for a broader utilization of cellulose from natural feed stocks. In 2005 BASF licensed the exclusive use of various intellectual property rights from the University of Alabama.

Starting with BMIM Chloride, BASF set up a broad screening for the dissolution of cellulose in Ionic Liquids. The dissolution of cellulose (5 to 25 wt.-%) was investigated by including a broad range of cellulosic raw materials from different sources and also applying different dissolving techniques.

The dissolution process seems to be mainly driven by the anion of the ionic liquid. Anions such as halides, carboxylates or phosphates seem to be able to very effectively break down interchain hydrogen bonds within the cellulose structures. The presence of water decreases the solubility through competitive hydrogen bonding processes.
1-Ethyl-3-methyl imidazolium acetate (EMIM Acetate) turned out as one of the most preferred solvents for cellulose dissolution and processing as it is liquid at room temperature, offers relatively low viscosity and high dissolving power - even in the presence of up to 10wt.-% of water.

Furthermore, EMIM Acetate is not acutely toxic, shows no corrosion against stainless steel and is highly miscible with water. The only limitation in using EMIM Acetate is the limited thermal stability of this ionic liquid. During processing of EMIM Acetate temperatures below 150°C should be applied – otherwise the decomposition of the imidazolium salt will lead to significant material losses.

Regeneration of the cellulose and recycling of the ionic liquid
By adding water or any other solvent miscible with the ionic liquid, like methanol, ethanol or acetone, the dissolved cellulose can be coagulated and regenerated quantitatively. The regenerated cellulose has almost the same DP as the initial pulp, but the morphology changes significantly. The degree of crystallinity can be manipulated by putting more or less stress on the regenerating material. Without any stress, cellulose is obtained as nearly amorphous polymer – giving the opportunity to manufacture amorphous cellulosic materials.

After washing with water any remains of ionic liquid can be easily removed due to the very high affinity of ionic liquids to water. Depending on the size of the particles the content of ionic liquid is between <0.1 and <1% – determined through measuring the nitrogen contents by elemental analysis.

After separation of the cellulose, a water respectively solvent containing Ionic Liquid is obtained. Both water and solvent can be removed for example by evaporation under reduced pressure getting the ionic liquid back, which can then be reused for the dissolution step. Additional purification steps will be necessary after a couple of regenerating cycles in order to remove impurities.

This opens broad opportunities for various processes on re-shaping cellulose:
Cellulose Derivatives
Homogenous derivatization of cellulose has always been an important objective in polymer research. The advantages are: more options in introducing functional groups and better control of the degree of polymerization – resulting in more opportunities to design new products as for example thermoplastic cellulosic materials. Additional opportunities are given by combining cellulosic with synthetic polymers in blends or composites.

T. Heinze and his coworkers for example have investigated the acylation and carbanilation of cellulose in ionic liquids. The homogenous reaction path allows mild reaction conditions, low excess of reagents, short reaction times and an easy controlling of the degree of substitution (DS). Another opportunity for carrying out the derivatization of cellulose in homogenous reactions is the high chemical stability of the ionic liquids, which allows using highly active reagents as for example ketenes or diketenes.

Fractionation of biomass with ionic liquids
Most of the cellulose in nature is part of lignocellulosic biomass with three major constituents: cellulose, hemicelluloses and lignin. The first step of any utilization of cellulose as raw material or chemical feedstock therefore needs to be the separation from the other components and especially from lignin leading to chemical grade pulp or dissolving pulp which is used as feedstock for all man-made cellulosics. Sources for lignocellulosic biomass are softwood and hardwood species as well. Among the delignification and purification processes today the acid bisulfite and the prehydrolysis Kraft pulping processes are most important. Alternative pulping processes with lower levels of environmental pollution and energy consumption are in development, but have not been commercialized yet.

Ionic Liquids offer new opportunities here, as they are able to dissolve lignocellulosic biomass partially or in total. For example, with subsequently adding solvents and water, lignin and cellulose / hemicelluloses can be obtained as separate fractions. As described above, the cellulose is got back as more or less amorphous material, which shows a much higher reactivity - for example in the enzymatic hydrolysis to glucose.
An alternative concept by utilizing ionic liquids in biomass fractionation might be to dissolve biomass as it is and to carry out a specific degradation of cellulose to the degree of polymerization required for further processing or even down to mono sugars. After separation from the mixture, cellulose can be further processed by reshaping, derivatization or blending, whereas the mono sugars might be processed to (cellulosic) bioethanol. In any of these processes ionic liquids can be expected as valuable tools due to their ability to dissolve cellulose.

Conclusion and Outlook
Cellulosic Polymers have a good chance for further increase in production volume in future – especially if long term prices for petrochemical feedstock would further increase. Ionic liquids might be valuable tools to achieve this as they allow combining the given advantages of natural fibres with processing and modification of them leading to new, even more advantageous materials.