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DISSOLUTION OF NATURAL POLYMERS IN IONIC LIQUID

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The investigation is aimed to study the interaction of natural polymers (Avicel, wood, "beech" cellulose) with the ionic liquid (EMIM Cl) and their structural features before and after regeneration process. The observed dissolution mechanisms are fully controlled by the physical and chemical organizations of the macromolecular chains. Experimental data evidence less crystalline resulting regenerated polymers from ionic liquid.

INTRODUCTION

Cellulose constitutes the most abundant, renewable polymer resource available today worldwide, mostly being combined with lignin and other polysaccharides (so called hemicelluloses) in the cell wall of wood and woody plants. Cellulose is converted by large scale industrial processing into cellulose derivatives (ethers and esters) and regenerated materials (fibers, films, food casing, membranes, and sponges, among others).

Cellulose derivatives 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 ($ZnCl_2/H_2O$, $Ca(SCN)_2/H_2O$)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.[2, 3]

The need to implement 'green' processes in order to prevent pollution and waste production, and to utilize renewable resources, is becoming increasingly important. The use of ionic liquids as 'green' replacements for conventional organic solvents has been demonstrated in chemical, biochemical and separation processes[4] and offer potential benefits over existing bioresources extraction processes.

Ionic liquids are used in electrochemistry, organic synthesis, enzymatic biocatalysis, extraction, and catalytic reactions.[5, 6] Possibility of their use for dissolving natural polymers is also examined.[7-10] Interest in ionic liquids arises from their high polarity, electrical conductivity, and the possibility of preparing molecules of varied structure. They exist in the liquid state in a wide temperature range and are characterized by low vapor pressure. In addition, they are thermally stable and incombustible.

Ionic liquids were suggested for the dissolution of cellulose, Swatloski et al.[11] showing that concentrated solutions of cellulose can be prepared in imidazolium-based ionic liquids. Ionic liquids can also be used for dissolving other

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carbohydrates[7], silk fibroin[8, 9], wool keratin[10], as well as lignin and lignocellulose.[12, 13]

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. It has been found that cellulose can be dissolved in ionic liquids without derivatization in high concentrations, up to 30 wt% is possible although solutions containing 5wt% cellulose in ionic liquid are easy to prepare and handle. The greatest solubility was obtained using 1-butyl-3-methylimidazolium chloride as the solvent, this showing the higher dissolving power compared to the ionic liquids with the same cation but with other anions.[14]

Cellulose can be regenerated from the ionic liquid solution in a range of structural forms with a relatively homogeneous microscopic morphology 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.

The present investigation is aimed to study the interaction of natural polymers (microcrystalline cellulose, wood, cellulose separated from "beech" wood) with the ionic liquid (EMIMCl). Results from structural investigation upon initial and regenerated natural polymers by means of FTIR spectroscopy and X-ray diffraction are discussed.

RESULTS

Solubility screening

In this paper, we report preparation of gel type materials from solution of cellulose and lignocellulose in EMIMCl (Figs.1-2), which are composed of cellulose, EMIMCl, and water. The films were obtained by casting the solution onto a glass plate, followed by reconstitution by the addition of water.

a b

Fig. 1 – Photographs of gelation process (a) and the obtained gel material (b) for microcrystalline cellulose.

a b c d

Fig. 2 – Photographs of dissolution of beech sawdust (a, b), respectively beech cellulose (c, d) in ionic liquid.

FTIR analysis

Fig. 3 shows the Fourier transformed IR spectra of initial substrates and after regeneration from ionic liquid. The absorption band at 1 430 cm^{-1} is assigned to the CH_2 scissoring motion in cellulose. The absorption band at 897 cm^{-1} is assigned as C–O–C stretching at the β-(1→4)-glycosidic linkage in cellulose.[15]

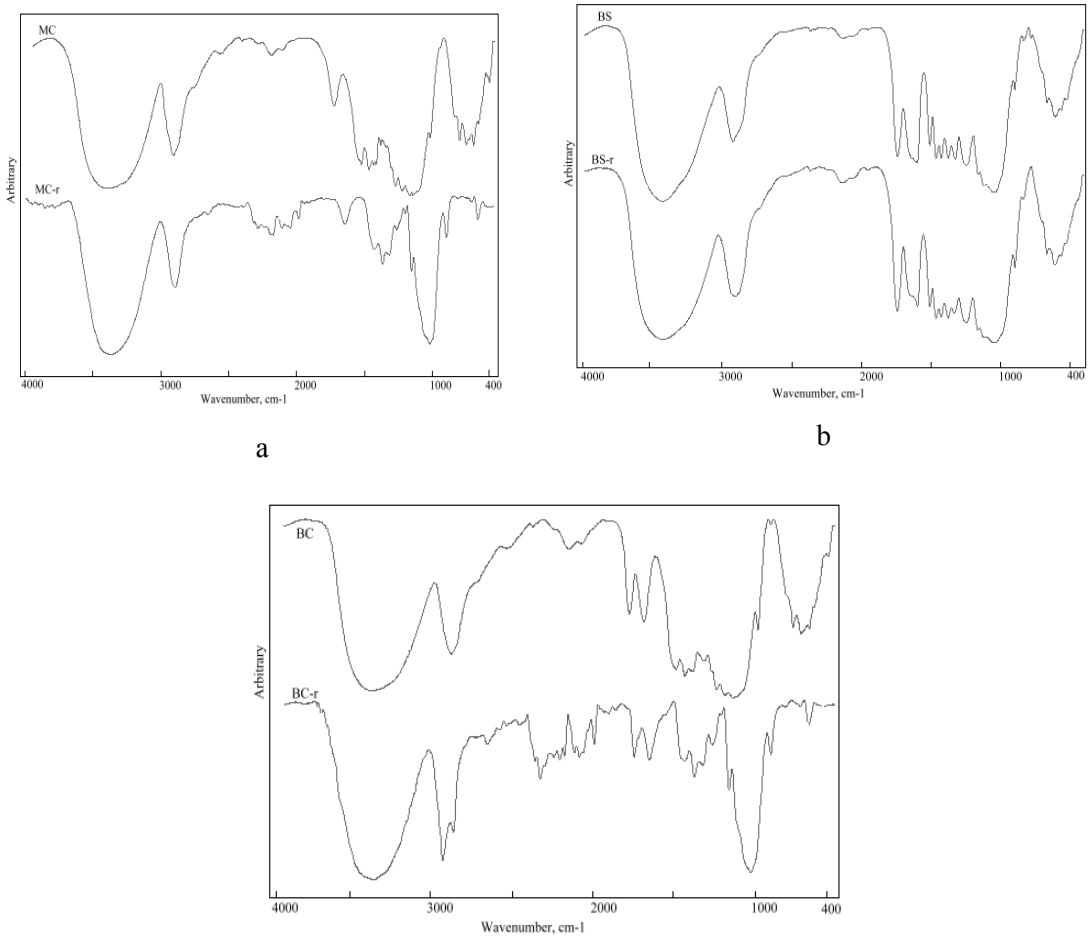
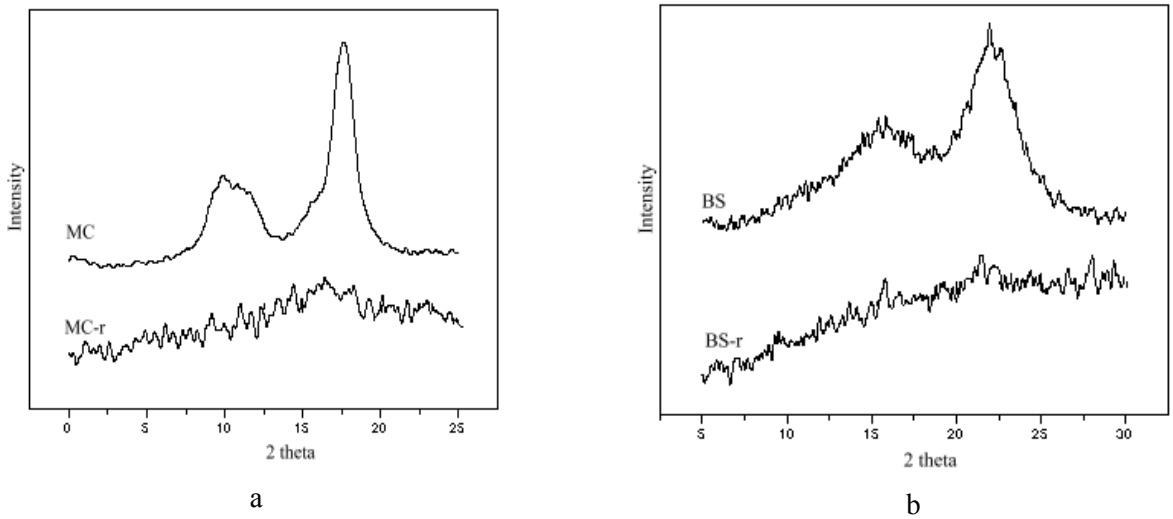
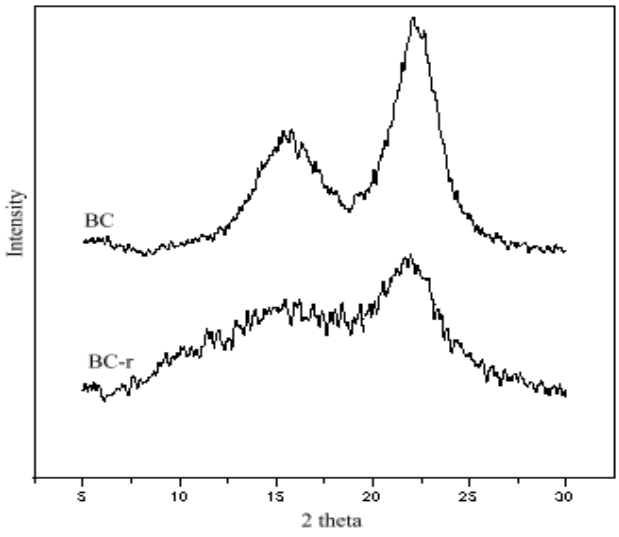


Fig. 3 – FTIR spectra for cellulosic substrates: microcrystalline cellulose (a), beech wood sawdust) (b), respectively beech cellulose (c).

X-ray diffraction

The crystalline structure of the cellulose materials initial and regenerated from ionic liquid was investigated by X-ray diffraction (Fig. 4).





c

Fig. 4 – XRD diffractograms of microcrystalline cellulose MC (a), beech wood sawdust BS (b), respectively beech cellulose BC (c), initial and regenerated from EMIM Cl.

DISCUSSION

FTIR analysis

As shown in Fig. 3, the absorption band at 1 430 cm^{-1} was strong for initial substrates, but weak for those treated with EMIM Cl. It appears that the initial substrates possess a structure of cellulose I crystal type. This is in accord with the well-known fact that almost all native celluloses in the higher plants have the crystal structure of cellulose I. The cellulose I structure was transformed into amorphous or cellulose II structure in the presence of ionic liquid. The absorbance values at 1430 cm^{-1} and 897 cm^{-1} are quite sensitive to the crystal structure of cellulose in lignocellulosic materials. Thus, the absorbance ratio A1 430/A897, which is known as crystallinity index[16] or lateral order index (LOI), has been used to reflect the cellulose I fraction in the substrate structure.[17] The FTIR spectra show characteristic cellulose peaks around 1 000-1 200 cm^{-1}.[18, 19] Band near 1 160 cm^{-1} is representative of the anti-symmetric bridge stretching of C-O-C groups in cellulose and hemicelluloses, and the band near 1 318 cm^{-1} can be ascribed to CH_2 wagging vibrations in the cellulose and hemicelluloses. The band at 1 635-1 640 cm^{-1}, which has been attributed to the absorbed water bending vibrations, significantly decreased in the presence of ionic liquids.

Another two infrared ratios were calculated: (1) $A_{1372\ cm\text{-}1}/ A_{2900\ cm\text{-}1}$, which is known as the total crystallinity index (TCI) [15], respectively (2) $A_{3308\ cm\text{-}1}/ A_{1330\ cm\text{-}1}$ known as hydrogen-bond intensity (HBI).[17] These parameters closely related to the crystal system and the degree of intermolecular regularity are presented in Table 1.

A high index value indicates that the material has a high crystallinity and an ordered structure. The TCI values significantly decreased for substrates MC and BC in the presence of ionic liquids (Table 1). This indicates that a part of the crystalline structure of cellulose was transformed into amorphous form. Thus, the ordered well crystalline phase and the degree of intermolecular regularity were affected by the presence of ionic liquid through changing the substrate structure.

Table 1

Crystallinity indexes and hydrogen bonding intensity of cellulosic materials under study

Cellulosic material	TCI (1372/2900)	LOI (1430/897)	HBI (3308/1330)
MC initial	1.269	1.514	1.502
MC regenerated from EMIM Cl	0.662	1.332	5.555
BS initial	1.243	2.845	1.993
BS regenerated from EMIM Cl	1.164	2.061	1.560
BC initial	1.369	1.738	0.676
BC regenerated from EMIM Cl	0.297	1.106	5.750

X-ray diffraction

The diffraction of cellulosic materials without EMIM Cl is characterized by a strong magnitude peak at around 23º (2θ) attributed to cellulose.

In comparison with the XRD profile of initial substrates, the diffraction peaks due to crystalline structure of cellulose nearly disappeared in the XRD profile of the regenerated material. However, some diffraction peaks, probably attributed to crystalline regions of cellulose, are still observed at around 23°. The XRD results indicate that the crystalline structure of substrates regenerated from ionic liquid is mostly disrupted. Moreover, the existence of non-crystalline structures in the material can be assumed by the appearance of the broad diffraction peaks in the range of 15-19°.

EXPERIMENTAL

Materials

Ionic liquid (EMIM Cl; mp 87°C) was screened for its ability to dissolve cellulose and lignocellulose. It was purchased from Fluka (Germany). Since it is hygroscopic or unstable in water, EMIM Cl was dried thoroughly in a drying oven at 80°C for at least 10 h. As substrates, cellulose and lignocellulose were used. One kind of cellulose was chosen, microcrystalline cellulose Avicel, which features the typical fiber structure. This substrate originates from hardwood pulp and was obtained from Sigma-Aldrich (Deisenhofen, Germany), being used without further purification. As wood source a hardwood was chosen, namely common beech (*Fagus sylvatica* L.), obtained from local sawmills, wood sawdust being produced by sawing and sieving in the range 0.40-0.65 mm in length. Cellulose separated from beech wood was also used as substrate.

Solubility tests

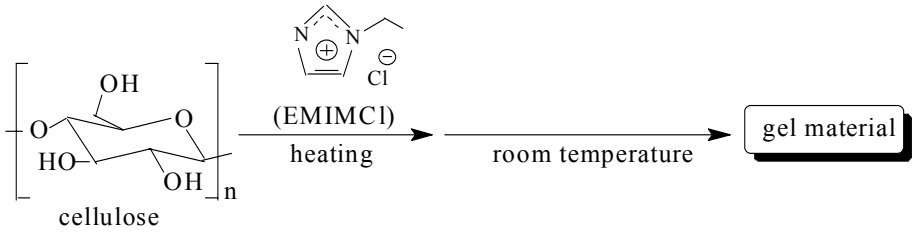
Dissolution experiments were conducted in vials. These vials contained 1 mL EMIM Cl and 10% (w/w) Avicel, or lignocellulose substrates (beech sawdust, beech cellulose) – Scheme 1. They were loosely capped and continuously shaken for 8h at 1 000 rpm and heated using the thermo-mixer MR Hei-Standard (Heidolph Instruments, Schwabach, Germany). The temperature was kept constant at 90 °C. Precipitation of dissolved cellulose and lignocellulose was achieved by pipetting 1 mL water to the solution with subsequent vortexing.

FTIR analysis

The Fourier Transformed Infrared spectroscopy (FTIR) analysis was performed using a Bruker Vertex 70 spectrophotometer. The spectral resolution was 4 cm-1 and the scanning range varied from 400 to 4 000 cm^{-1}.

X-ray diffraction

The X-ray diffraction data were obtained by means of a Bruker AD8 ADVANCE X-ray diffractometer, with a conventional copper target X-ray tube set to 60KV and 50 mA. The X-ray source was Cu Kα radiation. Data were collected for diffraction angle 2θ ranging from 6 to 35°.



Scheme1 – Dissolution of microcrystalline cellulose with EMIM Cl.

CONCLUSIONS

Ionic liquid (EMIM Cl) was screened for its ability to dissolve cellulose and lignocellulose. Structural investigation upon initial and regenerated natural polymers was performed by means of FTIR spectroscopy and X-ray diffraction.

The FTIR spectra showed characteristic cellulose peaks around 1 000-1 200 cm^{-1}. The ordered well crystalline phase and the degree of intermolecular regularity were affected by the presence of ionic liquid through changing the substrate structure.

In comparison with the XRD profile of initial substrates, the diffraction peaks due to crystalline structure of cellulose nearly disappeared in the XRD profile of the regenerated material. The XRD results indicate that the crystalline structure of substrates regenerated from ionic liquid is mostly disrupted.

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