PRESWELLING OF CELLULOSE PULP FOR DISSOLUTION IN IONIC LIQUID

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The effect of cellulose preswelling with dimethyl sulfoxide (DMSO), dimethylformamide (DMF), formamide (FA), diethyl ether (DEE) and ethyl acetate (EAc) on cellulose dissolution in the ionic liquid (IL) 1-butyl-3-methylimidazolium acetate (BMIMAc) was studied. The solutions were analyzed by ^{1}H and ^{13}C NMR spectroscopy and rheological methods. The preswelling of cellulose accelerated its dissolution in the IL without significant changes of the degree of polymerization. Volatile, aprotic and organic liquids appeared to be the most effective at cellulose activation.

Keywords: cellulose, activation, swelling, ionic liquids, dissolution

INTRODUCTION

The invention of simple and environmentally friendly processes of manufacturing using abundant natural polymers, such as cellulose, could create new areas for its applications. However, native cellulose possesses a highly ordered molecular structure with a network of strong intra- and intermolecular hydrogen bonds and it is difficult to dissolve in the majority of known solvents.

Imidazolium cation based ILs are known to be efficient direct cellulose solvents.[1-3] The high polarity and electron donor–acceptor properties of ILs lead to strong hydrogen bonding upon cellulose solvation.[4] Ionic liquids have some advantages in comparison with other cellulose solvents, for example, their negligible vapour pressure and inflammability.[1,5,6] 1-Butyl-3-methylimidazolium chloride and acetate appear to be the most efficient for cellulose dissolution. It is possible to reach 10 wt% and higher concentrated solutions of cellulose in such ILs.[7,8] High temperature treatment (90-110 ^{o}C) and prolonged time of cellulose dissolution can also be applied due to the ILs' thermal and chemical stability. It should be noted that these conditions may affect the cellulose degree of polymerization (DP) and mechanical properties of the final products.

Pre-activation of cellulose by weakening its intermolecular structure is necessary to increase the efficiency of the dissolution process, decrease the time for dissolution and thereby reduce the degree of cellulose degradation. The current methods of cellulose activation can be divided into 4 main groups: 1) physical, 2) mechanical, 3) chemical, and 4) biological.

Cellulose can be mechano-chemically activated by breaking up the intra- and intermolecular hydrogen bonds through shear and compression forces.[9] It can be expected that such kind of activation dramatically decreases cellulose DP.

Defibration by steam explosion[10,11] makes the cellulose structure more amorphous, disrupting most of intra- and intermolecular hydrogen bonds. However, this method is expensive and has been poorly studied until recently.

The enzymatic treatment of cellulose also activates it and makes dissolution easier.[12]

This treatment is a relatively effective, but prolonged process. Moreover, there are also other methods, such as pretreatment with IL and consequent enzymatic hydrolysis.[13] Overall however, the most common and easy method for cellulose activation is preswelling.

During preswelling, the strong hydrogen bonds in the cellulose structure are disrupted and the cellulose structure becomes looser and amorphous.[14-16] Preswelling of cellulose with water is currently used in commercial processes, such as the Lyocell process. This method is ecologically safe and inexpensive, however has limited efficiency. The use of other swelling agents, especially volatile ones, could erode the environmental advantages of using ILs. However, it can be justified by the role they play in regulating the depolymerization of cellulose and therefore, the effect on the properties of the final product.

Ideally, during such dissolution processes, the molecules of swelling agents, absorbed by the cellulose, should be replaced by the molecules of the main solvent. Different factors affect the essentially opposite processes – absorption of the swelling agent and its replacement. Cellulose swelling is controlled by polymer–swelling agent interaction and depends mainly on donor–acceptor properties, polarity and molecular volume of the swelling agents.[17-19] The strength of the polymer-swelling agent interaction is a challenging parameter, since it should be strong enough for efficient swelling, but weak enough to support the replacement process. From this point of view, the volatility of the swelling agent can play an important role in the dissolution of cellulose in ILs performed at high temperatures and therefore, a volatile swelling agent could be easily replaced by the main solvent under these conditions.

The aim of this research was to define the regularities of processes that take place in the system cellulose–solvent–protic/aprotic swelling agent and to study the influence of swelling agents with different physical and chemical properties on the effectiveness of cellulose dissolution in 1-butyl-3-methylimidazolium acetate and the properties of the final cellulose product – the film. Low molecular organic liquids of different nature, polarity and boiling temperatures were used as swelling agents. NMR spectroscopy was used to understand the role of the swelling agent in the cellulose dissolution process.

EXPERIMENTAL

Solvents and reagents

High purity wood-derived chemical cellulose pulp, Alicell-Super (Western Pulp Inc, Canada) was used as a polymer. The main solvent used with the cellulose pulp was the ionic liquid, 1-butyl-3-methylimidazolium acetate (BMIMAc), from Sigma-Aldrich, Germany. The solvents selected as swelling agents, namely, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), formamide (FA), ethyl acetate (EAc), and diethyl ether (DEE), were supplied by POCH S.A., Poland. Selected properties of these swelling agents are presented in Table 1. The NMR standards used, deuterated dimethyl sulfoxide DMSO-d_6 and deuterated nitromethane CD_3NO_2, were obtained from Sigma-Aldrich, Germany. All materials were used as received without any further purification.

Dissolution of cellulose

Cellulose was swollen using 5 wt% swelling agents at 20 °C over the course of 1 hour and then dissolved in the ionic liquids at 110 °C to obtain solutions with cellulose concentrations of 2 and 5 wt%. Despite the time of cellulose dissolution depending on the swelling agent used, the time of temperature treatment was kept equal for all samples. The duration of temperature treatment was chosen on the basis of experimental data and corresponded to the longest dissolution time amongst the studied samples. Transparency, being an indicator of complete dissolution, was checked using an optical microscope.

Method of cellulose film preparation

Cellulose films were obtained from cellulose solutions (0.5 mm) cast onto a warm glass pad. The cast solutions were coagulated in distilled water at 20 °C and then rinsed with water to remove unwanted solvents. Three washing steps were carried out at intervals of 30 min. This time of rinsing was chosen in order to avoid cellulose film swelling by water.

Solution retention value (SRV)

The volumes of liquor retained in the pulp (SRV) were determined at 20 °C, as described in literature.[23] Pulp samples, 0.5 g in weight, were immersed in solution for 24 hours at 20 °C. The pulp samples were then centrifuged at 4000 g for 10 minutes and weighed (W_w). The samples were dried in an oven at 105 °C for 4 h and the weight was measured (W_d). Solvent retention values were calculated using Equation 1.

$$SRV = (W_w - W_d) / W_d \bullet \rho \quad (1)$$

where ρ is density of the measured solutions. The measurement was performed 3 times for each sample to obtain a mean value.

NMR studies of cellulose/IL/swelling agent dopes

Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded at 27 °C, using an Avance II Plus spectrometer (Bruker, Germany) at

700 and 175 MHz, respectively. DMSO-d_6 (at 2.50 ppm {^{1}H}) and CD_3NO_2 (at 60.5 ppm {^{13}C}) were used as the chemical shift standards in these experiments. It is well known that the dilution of a sample with an NMR standard affects the IL and cellulose chemical shifts,[24-28] and therefore DMSO-d_6 and CD_3NO_2 were used as external standards.

Table 1
Selected properties of the used swelling agents [19-22]

	Molar volume V, cm^3/mol	DN (donor number)	AN (acceptor number)	π* (polarity)	β (basicity)	α (acidity)	Boiling point, ^oC
DEE	103.9	19.2	9.3	0.27	0.47	0.00	35
DMF	77.1	26.6	16.0	0.88	0.69	0.00	153
DMSO	71	29.8	19.3	1.00	0.76	0.00	189
EAc	98.2	17.1	3.9	0.55	0.45	0.00	77
FA	39.7	24.0	39.8	0.97	0.48	0.71	210

GPC (Gel Permeation Chromatography) of cellulose films

Cellulose degree of polymerization (DP) was determined with GPC, which was provided with a set of three PLgel Mixed A columns (300 x 7.5 mm) with a guard column (Polymer Laboratories Ltd.). A DMAC/0.5% LiCl solution was used as an eluent system.

RESULTS AND DISCUSSION

The chemical affinity between the swelling agent and cellulose is proportional to SRV (solution retention values) for all of the swelling agents tested and shows how easily the swelling agent accepts cellulose active centers, increasing the cellulose pulp surface area and loosening the cellulose supramolecular structure. Empirical data demonstrating the effectiveness of cellulose swelling within the studied swelling agents are presented in Table 2.

In general, the obtained data correlate with previous studies.[16-19] It is clear that the reduction of absorption in the order DMSO > DMF > FA > EAc > DEE is in line with the solvents' basicity values, β, (the ability to accept hydrogen atoms).

Table 2
SRVs of the studied swelling agents toward cellulose

Swelling agent	SRV, ml/g
DMSO	18.4
DMF	16.1
FA	14.0
EAc	6.2
DEE	5.8

Table 3
Dissolution times of 2 wt% preswollen cellulose in BMIMAc at 110 °C

Used swelling agent	Dissolution time, min
EAc	18
DMSO	22
DEE	25
DMF	30
FA	40
-	40

Table 4
Degree of polymerization of cellulose regenerated from its 2 wt% solutions in BMIMAc

System used for film preparation	Swelling agent	DP_w
Native cellulose	-	600
Cellulose coagulated from BMIMAc solutions	-	525
-«-	DMSO	600
-«-	DMF	580
-«-	FA	550
-«-	DEE	600
-«-	EAc	600

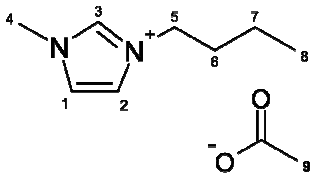

Figure 1: BMIMAc structure with hydrogen atoms marked as observed in ^{1}H NMR spectra

Despite the basicity of DEE being slightly higher than that of EAc (0.47 c.f. 0.45), DEE shows the lowest SRV due to its large molar volume and high volatility. It is fair to say that cellulose (with weak acid properties[25]) is interacting strongly with basic molecules.

As has been found from cellulose swelling kinetics studies, the cellulose swelling rate changes negligibly after one hour of swelling. Therefore, the time of 2 wt% cellulose dissolution (Table 3) was estimated for cellulose, with equal swelling agents content (5 wt%), after the same preswelling time (1 hour). Cellulose preswelling activates the cellulose and consequently reduces the time of its dissolution into the IL (Table 3).

The data in Table 3 show the replacement rate of the swelling agent with the IL, being absorbed, by the cellulose. The data show the increase rate of dissolution when aprotic swelling solvents are used, compared with the protic FA. Protic FA is characterized by its basic and acidic nature. FA is able to interact with the cellulose and the IL, which leads to complications of the cellulose dissolution process. Volatile EAc appears to be the most efficient swelling agent, with the rate of preswollen cellulose dissolution being doubled. The faster dissolution process can minimize the degradation of cellulose macrochain, as shown in Table 4.

From the obtained data (Tables 3 and 4), it may be noted that cellulose activation by preswelling increases the efficiency of the dissolution process and inhibits cellulose degradation. As polymer degraded less when dissolution time was shorter the preswelling of cellulose with DEE, EAc or DMSO allowed polymer degradation to be avoided and cellulose DP to be maintained at the initial, native cellulose, level.

NMR spectroscopy was used to explain the role of swelling agent in the cellulose dissolution process in BMIMAc. The structure of BMIMAc is presented in Figure 1 and the shift of the chemical resonances of the IL protons in Table 5.

Table 5 shows that the resonances of the majority of the IL protons are shielded ($\Delta\ \delta < 0$) in the presence of cellulose, when the polymer is dissolved without preswelling. The observed shift of the NMR signals upfield can be explained by the increasing distance between the imidazolium cation and the anion in the presence of cellulose. The anion itself interacts with cellulose, and as a result, the distance between the anion and the cation is increased and the cation resonances are reduced. Quantum-chemical calculations show that hydrogen in position three (H3) possesses the greatest positive charge and the anion is therefore placed next to it. For example, it was calculated that the distance between the cation's H3 atom and the anion increases from 2.145 Å in BMIMCl to 2.348 Å in the solvated complex cellulose–BMIMCl.[29] The shifting of the H3 resonance downfield may indicate a distancing of the anion from the cation due to the direct interaction of cellulose with the anion, in agreement with the scheme proposed by computer modelling.[29]

Table 5
^{1}H NMR resonances of BMIMAc and BMIMAc in cellulose solutions (700 MHz, 27 °C)

	Proton NMR shifts in BMIMAc								
Swelling agent	1	2	3	4	5	6	7	8	9
DMSO	7.75(-0.04)*	7.88(-0.05)	9.94(-0.04)	3.62(0.02)	3.91(0.03)	1.36(0.07)	0.76(0.06)	0.38(0.09)	1.31(0.07)
DMF	7.81(0.02)	7.95(0.02)	10.07(0.09)	3.65(0.05)	3.94(0.06)	1.37(0.08)	0.78(0.08)	0.38(0.09)	1.32(0.08)
FA	7.60(-0.19)	7.72(-0.21)	9.68(-0.30)	3.59(-0.01)	3.88(0.00)	1.33(0.04)	0.77(0.07)	0.36(0.07)	1.33(0.09)
EAc	7.53(-0.26)	7.63(-0.30)	9.49(-0.49)	3.54(-0.06)	3.84(-0.04)	1.27(-0.02)	0.72(0.02)	0.29(0.00)	1.27(0.03)
DEE	7.78(-0.01)	7.92(-0.01)	9.97(-0.01)	3.59(-0.01)	3.88(0.00)	1.29(0.00)	0.70(0.00)	0.29(0.00)	1.24(0.00)
-	7.79	7.93	9.98	3.60	3.88	1.29	0.70	0.29	1.24
Pure IL	7.89	8.03	10.15	3.64	3.92	1.33	0.73	0.32	1.27

*Values in brackets show the shift of IL's protons for the solution of preswollen cellulose in comparison with a solution of cellulose without swelling

Table 6
Shifts of BMIMAc ^{13}C resonances in the presence of cellulose, FA and in the solution of cellulose preswollen in FA ($\Delta\delta = \delta - \delta_0$)

C-atom*	BMIMAc–cellulose solution	BMIMAc–FA mixture	BMIMAc with cellulose preswollen in FA
1	-0.02	0.43	0.73
2	0.01	0.45	0.77
3	-0.34	0.12	0.19
4	0.11	0.50	0.88
5	0.09	0.52	0.88
6	-0.02	0.41	0.71
7	0.02	0.44	0.76
8	0.04	0.44	0.78
9 (CH3)	-0.27	0.28	0.28
10 (COO-)	0.10	0.67	-0.06

*Numbered according to Figure 1

In the presence of cellulose, strong upfield shifts ($\Delta \delta < 0$) were also observed for C3 of imidazolium cation and the methyl carbon in the acetate anion (Table 6). Similar results were obtained by Zhang for a cellulose solution in 1-butyl-3-methylimidazolium acetate.[26-28] Zhang referred the shielding of the imidazolium ring resonances to the cation–cellulose interaction, as the interaction of the cation with cellulose hydroxyls is weaker than that with the acetate anion. However, from our point of view, such shielding is caused by the distancing of the anion, bonded with cellulose, from its cation.

There are almost no additional changes of the IL protons in the solution of preswollen cellulose, except for the solutions preswollen in FA and EAc. The upshifting of proton resonance for the samples with these swelling agents is approximately 0.3-0.49 ppm, in comparison with the NMR spectra of the IL solution with unpreswollen cellulose. The imidazolium ring resonances are shielded and even more reduced, as the anion resonances are simultaneously deshielded and increased. Therefore, the cation–anion interaction became weaker in the presence of cellulose swollen in FA and EAc.

However, the nature of this phenomenon for both swelling agents is different. When EAc is used, the interaction of activated cellulose with the anion of IL is more efficient. It is important that no resonance for EAc is found in the spectra. EAc is evaporated from the solution due to its volatility, resulting in loosening of the intra- and intermolecular hydrogen bond system in the polymer and the possible polarization (activation) of these bonds facilitating the dissolution process. It should be noted that volatile DEE does not have the same effect on cellulose. Perhaps DEE does not polarize the hydroxyl groups of cellulose and therefore has a less significant effect on cellulose activation due to its non-polarity.

On the other hand, the shielding of the IL proton resonances, when FA is used, is not caused by a stronger cellulose–IL anion interaction (preswelling of cellulose in FA does not help its dissolution in the IL). The increased distancing of the anion from the cation and the shift of IL protons in this case is caused by direct FA–IL interactions, which was confirmed by the ^{13}C NMR study (Table 6).

The possibility of interaction between FA and IL is confirmed by the deshielding of C10 resonance (acetic carbon of anion resonance). The same resonance deshielding is observed for cellulose/BMIMAc solution, however the presence of preswollen cellulose (in FA) affects the IL in the opposite way. Perhaps cellulose preswollen in FA is not able to build strong hydrogen bonds with the IL. This phenomenon when two solvents are "competing" for the interaction with one substrate is called a "competition effect".[30] Such a "competition effect" complicates cellulose dissolution.

CONCLUSION

The effect of the swelling agent on cellulose dissolution in ionic liquids and cellulose degradation depends on the nature of the solvent being used. The most effective are volatile, aprotic, organic solvents, due to cellulose activation by its preswelling. These swelling agents penetrate the cellulose structure loosening its hydrogen bond net and they can then easily be replaced by the main solvent, the ionic liquid, by evaporation upon heating. The more polar EAc was found to be the most efficient swelling agent for cellulose dissolution. NMR data confirmed that preswelling of cellulose with EAc facilitated and enhanced the interaction between the IL and the polymer. The protic FA was a stronger swelling agent, however its "competition effect" complicated the interaction of the IL with cellulose hydroxyl groups, therefore the application of FA did not facilitate the dissolution process, contrary to other aprotic swelling agents.

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