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Dissolution of cellulose in phosphate-based ionic liquids

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ABSTRACT

Two kinds of alkylimidazolium salts containing dimethyl phosphate or diethyl phosphate were obtained as room temperature ionic liquids synthesized by one step, and both of them have the ability to dissolve untreated cellulose. Especially, 1-ethyl-3-methylimidazolium diethylphosphonate ([EMIM]DEP) could obtain 4 wt% cellulose solution within 10 min under 90. The effects of dissolution temperature on cellulose dissolution time and degree of polymerization were investigated. As dissolution temperature increased, dissolution time was greatly reduced. Both the original and regenerated cellulose samples were characterized with wide-angle X-ray diffraction, thermogravimetric analysis and scanning electron micrograph. The results showed that the crystalline structure of cellulose was converted to cellulose II from cellulose I in native cellulose. It was also found that the regenerated cellulose had good thermal stability with [EMIM]DEP ionic liquid.

1. Introduction

In recent years, non-renewable energy resources are facing economic challenges such as decreasing reserves, increasing prices and energy security issues. However, cellulose, as the most abundant biorenewable and biodegradable organic polymer on the earth, has been concerning for a long time (Dogan & Hilmioglu, 2009). Products derived from cellulose have many important applications in the fiber, paper, film, polymer, and paints industries. Cellulose is a polydispersed linear polyglucan which forms hydrogen-bonded supramolecular structures. Because of its numerous inter- and intra-molecular hydrogen bonds, cellulose is insoluble in most conventional solvents, but it can be dissolved in strong acidic and alkali solutions. Although varied approaches were developed to produce regenerated cellulose, such as viscose rayon, cuprammonium cellulose, lyocell fibers, these solvent systems currently used for cellulose suffered drawbacks such as volatility, unstable or generation of poisonous gas, which lead to a shrinking market. To date, a number of solvent systems, such as N-methylmorpholine-N-oxide (NMMO) (Rosenau, Hofinger, Potthast, & Kosma, 2003), LiCl/DMAc (Potthast et al., 2002a, DMSO/TBAF (Ramos, Frollini, & Heinze, 2005) and NaOH/urea (Wang, Zhao, & Deng, 2008), have been found efficiently for dissolving cellulose. But there remain limitations like high energy consumption, toxicity, cost, difficulty in solvent recovery, or instability in processing. Thus, the discovery of novel solvents with advantageous properties has always been of interest to the field.

Ionic liquid (IL), as a new type of green solvent, has been regarded as the potential solvent for cellulose considering its excellent dissolubility, low toxicity, thermal stability, almost non-volatile and recyclability (Chaumont & Wipff, 2007). ILs are molten salts with a melting temperature below 100 °C. Some of them are liquids at room temperature, which allows them to act as solvents. However, not all ILs has the ability to dissolve cellulose and their dissolution efficiency can vary considerably (Pinkert, Marsh, Pang, & Staiger, 2009). Early in 1934, Graenacher first suggested that molten N-ethylpyridinium chloride, in the presence of nitrogen-containing bases, could be used to dissolve cellulose; however, this seemed to have been treated as a novelty with little practical value since the molten salt system was, at the time, somewhat esoteric and had a relatively high melting point (Graenacher, U.S. Patent, 1934). In 2002, Swatloski et al. reported ILs could be used as nonderivatizing solvents for cellulose and ILs incorporating anions, which were strong hydrogen bond acceptors, were most effective (Swatloski, Spear, Holbrey, & Rogers, 2002). Based on this, more kinds of ionic liquids were found to be the novel solvent for cellulose or other biopolymers dissolution. The main anion of reported ionic liquids are: chloride (Heinze, Schwikal, & Barthel, 2005; Zhao et al., 2008), acetate (Kosan, Michels, & Meister, 2008; Zhang, Zhang, Wu, He, & Xiang, 2010; Maria & Martinsson, 2009) and alkylphosphate (Fukaya, Hayashi, Wada, & Ohno, 2008; Vitz, Erdmenger, Haensch, & Schubert, 2009; Mazza, Catana, Vaca-Garcia, & Cecutti, 2009). Because of their lower viscosity, alkyphosphate-based and acetate-based but not chloride type ILs could dissolve cellulose under mild

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conditions. Besides, the imidazolium-based phosphoric ILs are easier to be synthesized than acetate-based ILs. It is encouraging that N-ethyl-N′-methylimidazolium methylphosphonate enables the preparation of 10 wt% cellulose solution by keeping it at 45 °C for 30 min with stirring and rendered soluble 2–4 wt% cellulose without pretreatments and heating (Fukaya et al., 2008). In the same year, Kamiya et al. (2008) first reported imidazolium-type ionic liquid-[EMIM][DEP] played a positive role in an enzymatic process for the saccharification of cellulose, which suggested the initial information on the potential of [EMIM][DEP] as suitable solvent for cellulose or other biopolymers. However, there is limited data about the detailed process parameters of dissolution cellulose in phosphate-based ILs.

As is known, the solution temperature has a significant influence on solution time and performance of regenerated cellulose. In our study, two phosphate-based ILs 1-methyl-3-methyl imidazolium dimethyl phosphate ([MMIM][DMP]) and 1-ethyl-3-methyl imidazolium diethyl phosphate ([EMIM][DEP]) were synthesized by the methods reported by other researchers (Kuhlmann, Himmler, Giebelhaus, & Wasserscheid, 2007). A systematic study on dissolution cellulose with different temperatures using synthesized phosphate-based IL was investigated. The morphology of original and regenerated cellulose was observed using a polarized optical microscope and scanning electron microscopy (SEM). The degree of polymerization was evaluated using an Ubbelodhe capillary viscometer.

2. Experiment

2.1. Materials and chemistry

The cellulose material used in this study was cotton–ramie pulp (Shandong Helon Co., Ltd, China). The degree of polymerization (DP) of cotton–ramie pulp was 575.6. All cotton–ramie pulps were cut into small pieces, and dried at 100 °C for 12 h without activation treatment before use. All other reagents and solvents were of analytic grade and were used as received.

ILs ([MMIM][DMP] and [EMIM][DEP]) were synthesized according to established literature procedures (Kuhlmann et al., 2007). The yield of ILs was 91%. Structure of ILs were verified by FT-IR and ^{1}H NMR: FT-IR (3101.15 cm^{-1}, =C–H; 1573.71 cm^{-1} and 1396.03 cm^{-1}, C=N; 756.06 cm^{-1}, Imidazole ring; 1570–1573 cm^{-1}, P=O; 1048–1248 cm^{-1}, P-OR.). ^{1}H NMR [MMIM]DMP: (500 MHz, $CDCl_3$), $\delta \times 10^{-6}$: 10.328 (1H, s, NC*H*N), 7.455 (2H, m, NC*HCH*N), 3.904 (6H, s, H_3CNCHNCH_3), 3.450 (6H, d, P(OCH_3)$_2$); [EMIM]DEP: (500 MHz, $CDCl_3$), $\delta \times 10^{-6}$: 10.617 (1H, s, NC*H*N), 7.378 (2H, m, NC*HCH*N), 4.279 (2H, q, NCH_2CH$_3$), 3.982 (3H, s, NCH_3), 3.857 (4H, m, P(OCH_2CH$_3$)$_2$), 1.480 (3H, t, NCH$_2$CH_3), 1.159 (6H, t, P(OCH$_2$CH_3)$_2$).

2.2. Dissolution and regeneration of cellulose

Dried cotton–ramie pulp was added into a flask containing [MMIM][DMP] or [EMIM][DEP] respectively according to a weight ratio of 4% (cellulose pulp to IL). The cellulose solution was stirred continuously in an oil bath at 70 °C, 80 °C, 90 °C, 100 °C, 110 °C and 120 °C. Dissolution time was not recorded until the cellulose was completely dissolved. The process of direct dissolution of cellulose was observed by a polarized optical microscope because of the high crystallinity of cotton–ramie pulp. When the vision field of microscope appeared black totally, the cotton–ramie pulp was considered to be dissolved completely. Finally, a transparent cellulose solution with about 4 wt% polymer concentration was obtained. After the complete dissolution of cellulose in ILs, the solution was cast onto a horizontal glass plate to give a thickness of about 0.50 mm, and the air bubble was took off by putting an another glass plate, and then both glass plates were immediately immersed in the water in ethanol to wash ILs repeatedly. Then the transparent regenerated cellulose film was obtained and dried at 50 °C in a vacuum oven for 24 h.

Table 1
Dissolution conditions of cellulose in ILs [MMIM][DMP] and [EMIM][DEP].

ILs ([MMIM]DMP)		IL ([EMIM]DEP)	
Dissolution temperature (°C)	Dissolution time (min)	Dissolution temperature (°C)	Dissolution time (min)
70	400	70	100
80	320	80	20
90	300	90	11
100	270	100	6
110	243	110	4
120	188	120	2

2.3. Recycling of ionic liquid

The liquids containing ILs and ethanol, obtained from cellulose regeneration, were first concentrated under vacuum. Then the concentrated solution was freeze-dried over 48 h to obtain the recycled ILs.

2.4. Characterization

The degree of polymerization (DP) of regenerated cellulose film was measured by the following procedures: Dried regenerated cellulose film was cut into small pieces and dissolved in cupriethylenediamine hydroxide solution. The intrinsic viscosity of the regenerated cellulose in cupriethylenediamine hydroxide solution was measured using an Ubbelodhe viscometer, and then the DP of the regenerated cellulose films was calculated.

Original and regenerated cellulose films were characterized by wide-angle X-ray diffraction (E-1020, Hitachi, Ltd., Japan) and thermogravimetric analysis (TG209, NETZSCH Co. Ltd, Germany). The dissolution process of cellulose was monitored by the polarizing microscope (XP-203, Shanghai Changfang Optical Instrument Co., Ltd., China). The surface and fractured surfaces of regenerated cellulose film were photographed by scanning electron microscopy (S-4800-I, Hitachi, Ltd., Japan).

3. Results and discussion

3.1. Dissolution and regeneration of cellulose

The dissolution of cellulose in ionic liquids [MMIM][DMP] and [EMIM][DEP] at different temperatures was studied in a 4 wt% cellulose solution. The dissolution process of cellulose in [EMIM][DEP] under the polarizing microscope was shown in Fig. 1. It could be seen that at the beginning of dissolution, there were plenty of bright cellulose fibrils. As time went on, the cellulose became swollen and shortened. The pulp left the vision of the polarizing microscope only in 11 min in [EMIM][DEP] while in 300 min in [MMIM][DMP]. Table 1 listed the solubility of cotton–ramie pulp in ILs. In Table 1, as the dissolution temperature increased, the dissolution time of both ILs was greatly reduced. There were two possible reasons for this: one reason was that the interaction between anions and cations was weakened due to high temperature so as to form the hydrogen bonds between the hydroxyl protons of cellulose and the alkyl-phosphate anion of the IL. The other one was that from cellulose itself. At higher temperature, cellulose molecules motion intensified, which could promote molecular chains to fracture. So the inter- and intramolecular hydrogen bonds

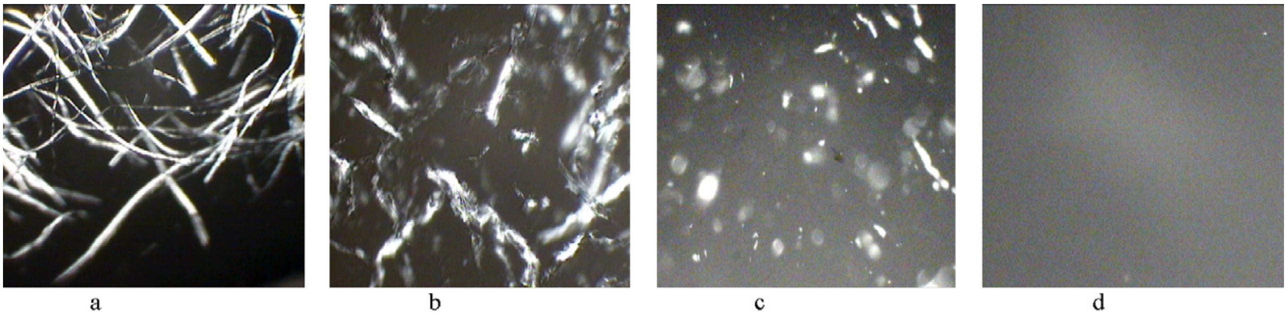

Fig. 1. Optics microscope photos of cellulose dissolution at different time: (a) 0 min; (b) 2 min; (c) 7 min; (d) 11 min. Dissolution condition: 90 °C, cotton–ramie pulp was dissolved in [EMIM]DEP.

of cellulose were disrupted easily. Furthermore, it was obvious that [EMIM][DEP] showed a better dissolution condition compared with [MMIM][DMP]. It could be seen that the anions structure of ILs affected the solubility significantly and the reasons need to be further studied.

3.2. Degree of polymerization

The effect of temperature on the DP of cellulose was studied in Fig. 2. There were two photos of cellulose pulp and the regenerated cellulose film respectively in Fig. 2. In order to obtain the DP values of cellulose, cellulose pulp and the regenerated cellulose film were first dissolved in cupriethylenediamine hydroxide solution as the procedures mentioned before. It could be seen from the chart that in the temperature range from 70 to 90 °C, the DP values (from 474.5 to 447.6) of the cellulose regenerated from [EMIM][DEP] were slightly smaller than that of the original cellulose (DP = 575.6) while the DP values of the cellulose regenerated from [MMIM][DMP] was from 451.2 to 380. The reduction of DP values of regenerated cellulose in [MMIM][DMP] was more obvious because of the longer dissolution time. Besides, the regenerated cellulose from ILs was degraded seriously when the dissolution temperature was above 100 °C. Therefore, in order to stabilize the DP of regenerated cellulose, dissolution temperature should be chosen below 100 °C as much as possible. Obviously, the ionic liquid [EMIM][DEP] was superior to some of the reported systems in which cellulose degradation definitely occurred (Zhang, Wu, Zhang, & He, 2005; Potthast, Rosenau, Sixta, & Kosma, 2002).

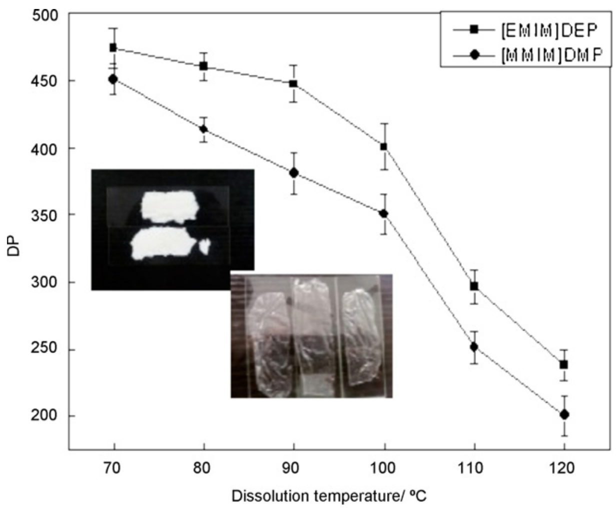

Fig. 2. Effect of dissolution temperature on DP of regenerated cellulose.

3.3. Wide-angle X-ray diffraction

Fig. 3 illustrated the wide-angle X-ray diffraction curves of original cellulose (spectrum a) and regenerated cellulose (spectrum b and c). The diffraction curve of native cellulose was typical cellulose I structure. It had strong crystalline peaks at 14.26°, 16.77° and 22.58° corresponding to the (1 1 0), $(\overline{1\,1\,0})$, and (0 0 2) planes of crystals, and weak crystalline peaks at 34.64° to the (0 0 4) plane (Oh et al., 2005). After dissolution and regeneration, the diffraction curve of regenerated cellulose film were the typical diffraction patterns of cellulose II by the presence of the broad crystalline peak at around 12.5° and 20.0° (Cao & Tan, 2005).

These results showed that the cellulose was changed from cellulose I to cellulose II during dissolution and regeneration. Similar results had been reported by Luo, Li, and Zhou (2005).

3.4. Morphology of regenerated cellulose

To observe the detailed morphology of regenerated cellulose film, the images of polarizing microscope and SEM photographs were shown in Fig. 4.

It could be seen that the regenerated cellulose films from [MMIM][DMP]/pulp and [EMIM][DEP]/pulp solution under the polarizing microscope (Fig. 4 A_1, A_2) were both bright for the high degree of crystalization. It indicated the regenerated cellulose films were homogeneous and dense without impurities. The SEM photographs of surface and fractured surfaces of the regenerated films

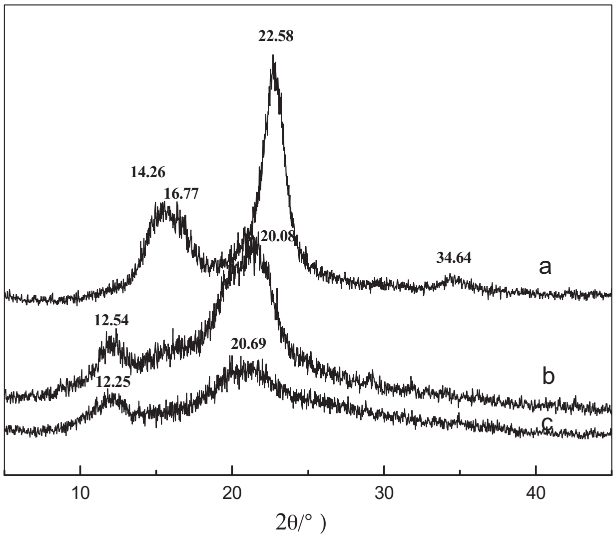

Fig. 3. XRD patterns of original cellulose and regenerated cellulose after dissolution in ILs (a) original cellulose; (b) regenerated cellulose from [EMIM][DEP]; (c) regenerated cellulose from [MMIM][DMP].

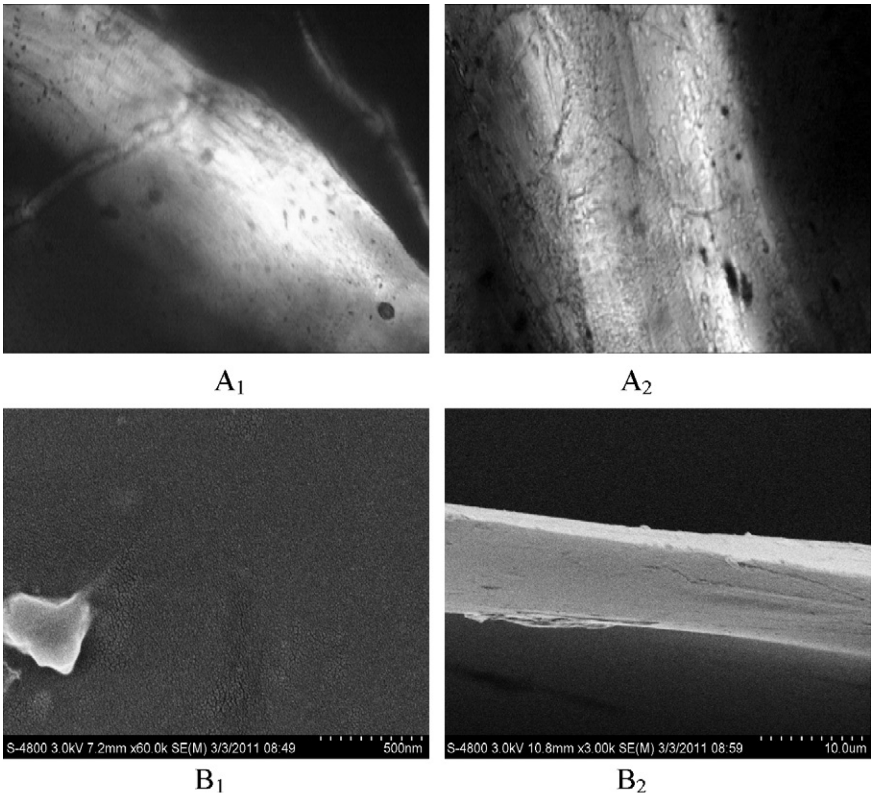

Fig. 4. Morphology of regenerated cellulose film: A1, A2: images of polarizing microscope of regenerated cellulose film from [MMIM][DMP]/pulp and [EMIM][DEP]/pulp solution; B1, B2: SEM photos of surface and fractured surfaces of regenerated cellulose film from [EMIM][DEP]/pulp solution.

were showed in Fig. 4 B$_1$, B$_2$. They displayed uniformity from the interior to the exterior, which indicated the regenerated cellulose had dense texture. Similar structure was observed by Zhang et al. (2005).

3.5. Thermal analysis

Fig. 5 displayed the TGA curves of native cellulose (a) and regenerated cellulose film (b) and (c). As were shown in Fig. 5, the thermal decomposition process of original cellulose and regenerated cellulose had three stages. The small initial dropped occurring near 100 °C in all cases was due to the evaporation of retained moisture. The original cellulose started to decompose at 250 °C, whereas the regenerated cellulose film(a) and film(b) began to decompose at 230 °C and 200 °C respectively. At 50% weight loss, the decomposition temperature was at 355 °C for original cellulose, 350 °C for regenerated cellulose film(a), and 300 °C for regenerated cellulose film(b). These figures implied that the thermal stability of both regenerated cellulose were lower than that of original cellulose. It was noteworthy that thermal stability of the regenerated cellulose film(a) was closer to original cellulose. The partial destruction of crystalline part and hydrolysis were probably the reason for this decrement.

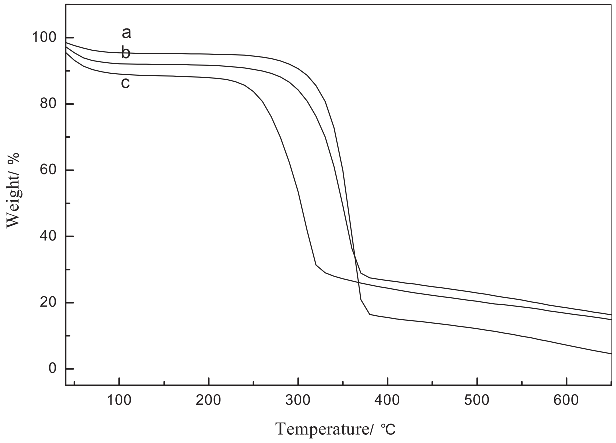

Fig. 5. TGA curves of original cellulose (a) and regenerated cellulose film from [MMIM][DMP]/pulp solution (b) and [EMIM][DEP]/pulp solution (c).

In addition, the residual of regenerated cellulose was higher than native cellulose, and the residual of film(b) was more than film(a). Pyrolysis residues of cellulose were the primarily indecomposable inorganic salts. It demonstrated that more inorganic salts were involved into cellulose in the dissolution and regeneration process. So, thermal stability of film(b) was much better than film(a).

4. Conclusions

In summary, phosphate-based ionic liquids showed the potential abilities to dissolve cellulose and especially [EMIM][DEP] enabled the preparation of 4 wt% cellulose solution within 10 min under 90 °C. Dissolution temperatures would be chosen below 100 °C to stabilize the DP of regenerated cellulose. After dissolution and regeneration in ionic liquid, the crystalline structure of cellulose was converted from cellulose I to cellulose II. Regenerated cellulose films were homogeneous and dense. The thermal stability of cellulose regenerated from [EMIM][DEP] was closer to the original cellulose, but the pyrolysis residues increased after dissolution and regeneration in ionic liquid. Therefore, [EMIM][DEP] was a promising solvent for cellulose with low melting point and low viscosity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2011.09.045.

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