Carbohydrate Polymers 87 (2012) 1490–1494

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Dissolution of cellulose in phosphate-based ionic liquids

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ARTICLE INFO

Article history:
Received 30 July 2011
Received in revised form
10 September 2011
Accepted 12 September 2011
Available online 17 September 2011

Keywords:
Cellulose
Dissolution
Ionic liquid
Regeneration

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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doi:10.1016/j.carbpol.2011.09.045

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, $\mathrm{CDCl_3}$), $\delta \times 10^{-6}$: 10.328 (1H, s, $\mathrm{NC}H\mathrm{N}$), 7.455 (2H, m, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 3.904 (6H, s, $H_3\mathrm{CNCHNC}H_3$), 3.450 (6H, d, $\mathrm{P(OC}H_3)_2$); [EMIM]DEP: (500 MHz, $\mathrm{CDCl_3}$), $\delta \times 10^{-6}$: 10.617 (1H, s, $\mathrm{NC}H\mathrm{N}$), 7.378 (2H, m, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 4.279 (2H, q, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.982 (3H, s, $\mathrm{NC}H_3$), 3.857 (4H, m, $\mathrm{P(OC}H_2\mathrm{CH_3)_2}$), 1.480 (3H, t, $\mathrm{NCH_2C}H_3$), 1.159 (6H, t, $\mathrm{P(OCH_2C}H_3)_2$).

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