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Preparation of cellulose-polymerized ionic liquid composite by in-situ polymerization of polymerizable ionic liquid in cellulose-dissolving solution

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Abstract

A cellulose-polymerized ionic liquid composite was prepared by in-situ polymerization method using two kinds of ionic liquids, which dissolved cellulose as a solvent and had a polymerizable acrylate group, respectively. Cellulose was dissolved in the ionic liquid of the solvent, and the radical polymerization of the polymerizable ionic liquid was carried out by 2,2′-azobis (isobutyroniitrile) in the solution. The results of the IR spectrum and elemental analysis indicated that the isolated product was a composite consisting of cellulose and the polymerized ionic liquid. The TG and DSC data of the product were different from those of cellulose, supporting the efficient compatibilization of cellulose with the polymerized ionic liquid in the composite.

Keywords: Cellulose; Ionic liquid; Composite; Compatibilization; In-situ polymerization

1. Introduction

Cellulose is the most abundant organic substance on the earth, which consists of β-(1→4)-linked glucose repeating units (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose has limited applications because of the strong inter- and intra-molecular hydrogen bonding between the hydroxy groups of the glucose residues. Considerable efforts have been devoted to the compatibilization of cellulose with synthetic polymers to improve the processability of cellulose (Nishio, 1994). Because of chain stiffness and close chain packing via the above mentioned hydrogen bonds cellulose, is hard to dissolve in water and most common organic solvents. To date, only a limited number of solvent systems for cellulose have been found, for example, LiCl/*N*,*N*-dimethylacetamide (DMAc) is a well-known as the solvent for cellulose (Terbojevich, Cosani, Conio, Ciferri, & Bianchi, 1985). In-situ polymerization methods, for example, those giving interpenetrating polymer network system have been useful for formation of nanocomposites from cellulose by means of the above solvent systems, in which the appropriate vinyl monomers such as *N*-vinylpyrrolidone and 2-hydroxyethyl metharylate radically polymerize in the presence of cellulose, giving rise to the desired composites (Nishio & Hirose, 1992; Miyashita, Nishio, Kimura, Suzuki, & Iwata, 1996). However, these solvents have some limitations such as volatility, toxicity, cost, difficulty in solvent recovery, and instability in applications. It has been reported that room temperature ionic liquids having the imidazolium structure can be used to dissolve cellulose (Zhang, Wu, Zhang, & He, 2005). For example, it was found that 1-butyl-3-methylimidazolium chloride (1, Scheme 2) dissolved cellulose in relative high concentrations, e.g., ca. 10 wt% by heating (Swatloski, Spear, Holbrey, & Rogers, 2002). In our work this ionic liquid was used as a solvent for efficient compatibilization of cellulose with a

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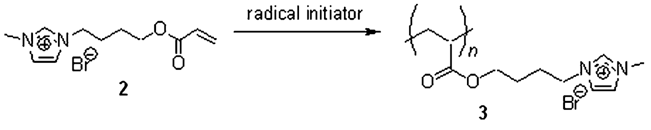
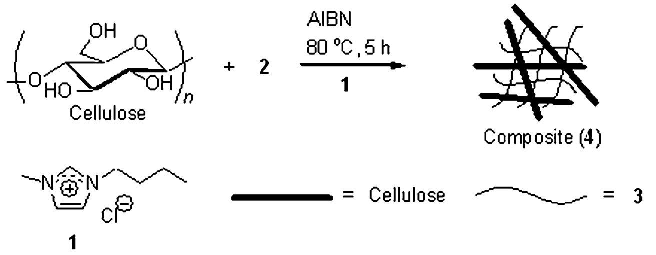


Scheme 1. Free-radical polymerization of polymerizable ionic liquid 2.



Scheme 2. Schematic image for compatibilization of cellulose with polymerized ionic liquid.

synthetic polymer. In this respect, a composite system based on cellulose and 1 by dissolution and constitution procedures has already been reported (Turner, Spear, Holbrey, & Rogers, 2004; Turner, Spear, Holbrey, Daly, & Rogers, 2005). Since we have assumed that the imidazolium structure similar to that in 1 may have good affinity with cellulose, we have been interested in employing the polymeric derivatives of the imidazolium-type ionic liquids as one component for good compatibilization with cellulose by breaking the hydrogen bonding in cellulose (Ohno, Yoshizawa, & Ogihara, 2004). To obtain the composite of cellulose with the polymeric ionic liquid by the in-situ polymerization method, in this study, we have used 1-(4-acryloyloxybutyl)-3-methylimidazolium bromide (2) as the polymerizable ionic liquid, which polymerizes by an radical initiator, giving a polymerized ionic liquid (3) (Scheme 1) (Fukushima et al., 2003). In this paper, we report the good compatibilization of cellulose with 3 by the in-situ polymerization of 2 in cellulose-dissolving solution using 1 to give the composite 4 as shown in Scheme 2. First, cellulose is dissolved in 1 as the solvent. Then, 2 and a radical initiator are added to the solution and the free-radical polymerization starts by heating. Finally, the isolation procedures produce 4 composed of cellulose and 3.

2. Experimental part

2.1. Materials

Microcrystalline cellulose a commercial reagent from Merck was used. Ionic liquids 1 and 2 were prepared according to the literature (Turner et al., 2004; Fukushima et al., 2003). Other reagents and solvents were used as received.

2.2. Preparation of composite 4

Cellulose (0.0522 g, 0.322 mmol) was dissolved in 1 (0.522 g) by heating at 100 °C for 24 h. The obtained viscous solution was cooled to room temperature and 2 (0.0931 g, 0.322 mmol) and AIBN (0.0030 g, 0.0161 mmol) were added. The mixture was blended well and heated at 80 °C for 5 h under argon. After the reaction mixture was cooled to room temperature, acetone was added. The obtained insoluble product was washed several times with acetone and treated further with acetone under the reflux conditions for 6 h. After the acetone-insoluble fraction was dried under the reduced pressure, it was purified further by Soxhlet extraction with methanol for 8 h and dried under the reduced pressure to give 4 (0.1076 g). Elemental analysis data: C, 44.75; H, 6.77; N, 5.11.

2.3. Preparation of mixture of cellulose and 3

First, a polymerized ionic liquid 3 was prepared by free-radical polymerization of 2. Under argon, 2 (0.0500 g, 0.173 mmol) and AIBN (0.0014 g, 0.00870 mmol) was dissolved in 1 (0.2926 g) and the mixture was heated at 80 °C for 5 h. The resulting solution was diluted with methanol (2.0 mL) and the solution was poured into acetone (20 mL) to precipitate the polymeric product. The precipitate was isolated by decantation and dried under the reduced pressure to give 3 (0.0 195 g, 0.0675 mmol) in 39.0% yield. ^{1}H NMR (CD_3OD) $\delta = 1.56$–2.45 (br, $-CH_2CH(C{=}O)-$, 3H), 1.75, 2.04 (br s, $CH_2\mathit{CH_2}\mathit{CH_2}CH_2$, 4H), 4.03 (s, CH_3, 3H), 4.25 (br s, $N-CH_2$, 2H), 4.40 (br s, OCH_2, 2H), 7.70, 7.84 (br s, $CH{=}CH$, 2H), 9.22 (s, $N-CH-N$, 1H). Cellulose (0.0522 g, 0.322 mmol) was dissolved in 1 (0.522 g) by heating at 100 °C for 24 h. The obtained viscous solution was cooled to room temperature and 3 (0.0931 g, 0.322 mmol) was added. The mixture was blended well and heated at 80 °C for 5 h. The isolation procedures same to those for 4 gave the mixture (0.108 g). Elemental analysis data: C, 41.04; H, 6.2; N, 1.92.

2.4. Measurements

NMR spectra were recorded on a JEOL ECA 600 spectrometer. IR spectra were recorded on a SHIMADZU FTIR-8400 spectrometer. TG analyses were performed on a SII TG/DTA6200 at a heating rate of 10 °C/min. DSC measurements were carried out using a heating rate of 10 °C/min from room temperature to 400 °C on a SII DSC 6000. Before analyses, the sample was preheated to 120 °C, kept at that temperature for 5 min, and then cooled to room temperature. XRD measurements were conducted at a scanning speed of $2\theta = 0.2$ °/min using a Rigaku Geigerflex diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). Elemental analyses were performed using a Perkin-Elmer 2004 CHNS/O analyzer.

3. Results and discussion

According to Scheme 2, we attempted to provide the composite 4 consisting of cellulose and 3 by the radical polymerization of 2 (an equimolar amount of the glucose units in cellulose) using AIBN in cellulose-dissolving solution. After the obtained mixture was washed with acetone and treated further with refluxed acetone, the product was purified by Soxhlet extraction with methanol to give the desired composite. The unit ratio of cellulose to 3 in the produced material was calculated by the elemental analysis data to be 1.0:0.63. The ^{1}H NMR spectrum of the Soxhlet extract (methanol-soluble fraction) showed the signals due to 3, in addition to the main signals assigned to 1 and no signals ascribed to 2 were observed. These results indicated that a part of 3 in the reaction mixture was not compatibilized, but washed out during the isolation procedures, in spite of complete consumption of 2 by the polymerization.

Other detailed evaluations of the product have been made as follows. The IR spectrum of the product in Fig. 1(a) exhibits the characteristic absorptions due to both cellulose and 3. For example, the absorptions at 1060 cm^{-1} due to C—O of cellulose (Fig. 1(b)) and at 1724 cm^{-1} due to C═O of 3 (Fig. 1(c)) appeared in the IR spectrum of the product. This IR data suggests that the product is the composite 4 consisting of cellulose and 3. After 4 was treated with water at 70 °C for 100 min, the unit ratio of cellulose to 3 in the residual material was changed to be 1.0:0.31 based on the elemental analysis data. In addition, the IR spectrum showed that the intensity of the absorption due to C═O groups of 3 definitely decreased in comparison with Fig. 1(a). These analytical data indicated that 3 in the composite 4 was partially washed out by the treatment with water. The signals observed in ^{1}H NMR spectrum of the filtrate were fully assigned to the structure of 3, indicating the progress of the in-situ polymerization in cellulose-dissolving solution. The above experimental results also suggested that 3 was not linked covalently to cellulose in 4. Fig. 2 shows the TG curve of 4 in comparison with that of cellulose and 3. The TG curve of 4 (Fig. 2(a), bold line) exhibits an onset of weight loss at 245 °C, whereas that of cellulose and 3 (Figs. 2(b) and (c)) appear weight losses starting at 300 and 261 °C, respectively. These differences of TG profiles indicate the efficient compatibilization of cellulose with 3 in the composite 4. The thermal property of 4 is also confirmed by means of the DSC measurements. The DSC trace of cellulose exhibits exothermic profiles at the temperatures higher than ca. 300 °C (Fig. 3(b)). On the other hand, a strong exothermic peak at 256 °C is observed in the DSC trace of 4 (Fig. 3(a)), which probably due to the thermal degradation of cellulose. This thermal property of

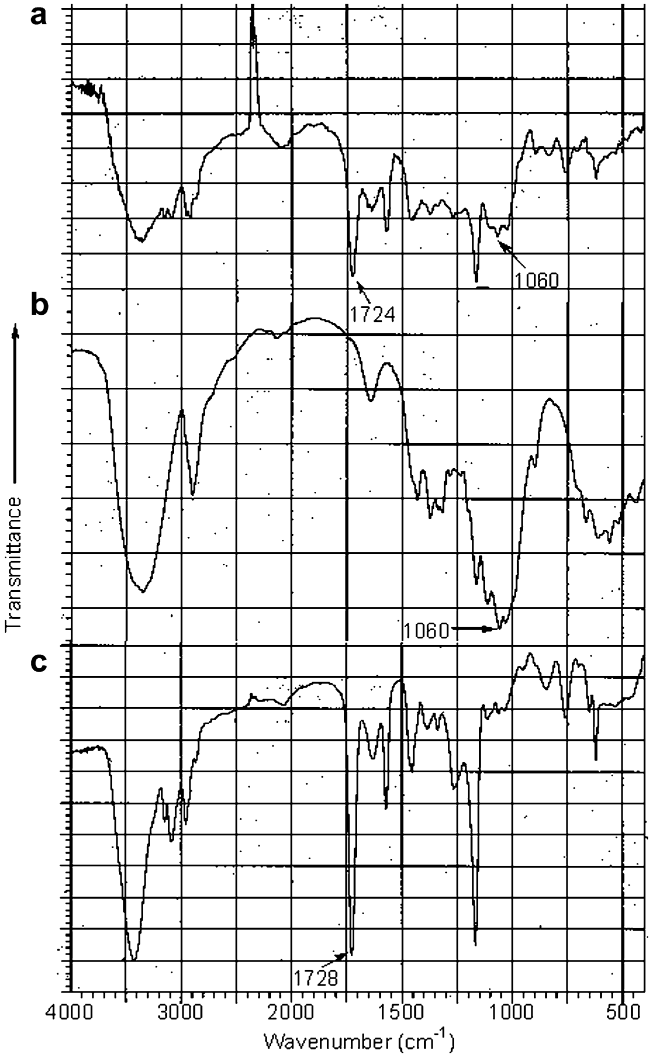


Fig. 1. IR spectra of 4 (a), cellulose (b), and 3 (c).

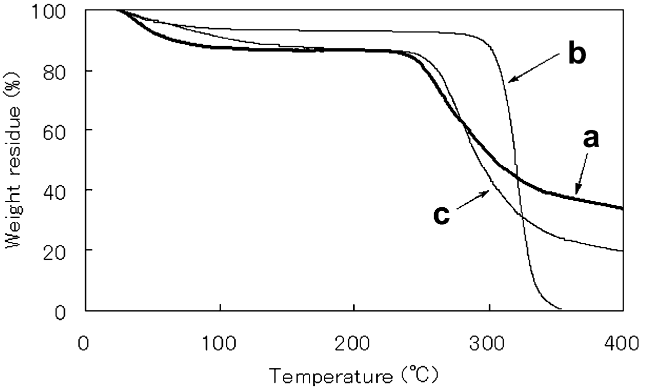


Fig. 2. TG curves of 4 (a), cellulose (b), and 3 (c).

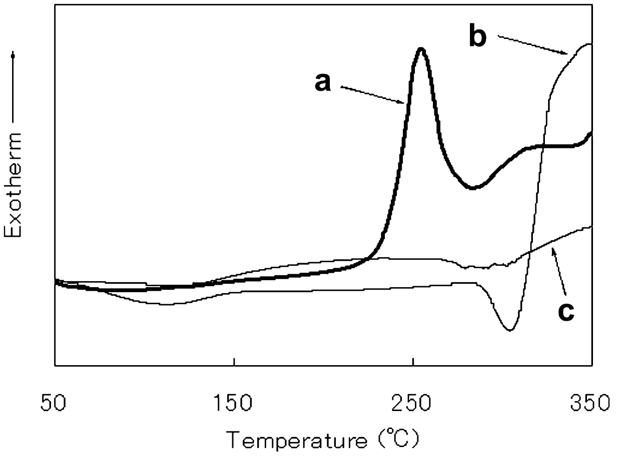


Fig. 3. DSC traces of 4 (a), cellulose (b), and 3 (c).

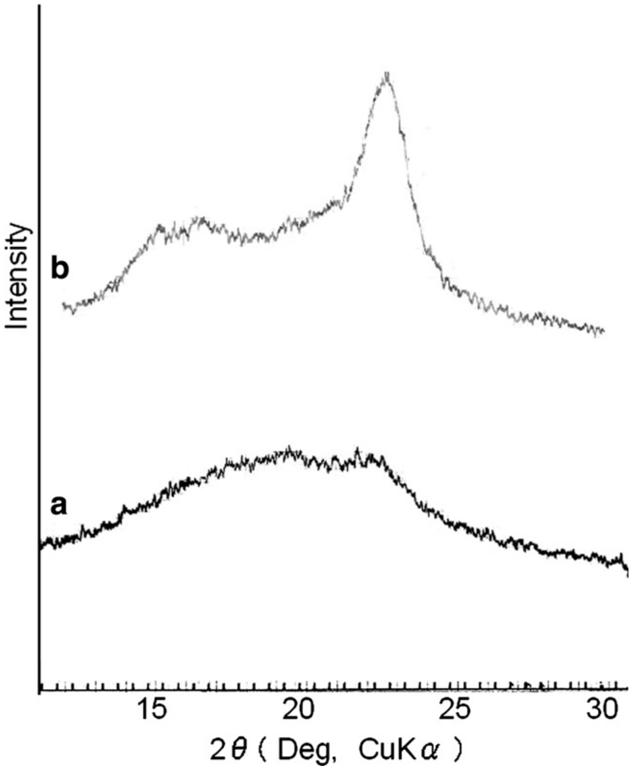


Fig. 4. XRD profiles of 4 (a) and cellulose (b).

4 indicated in the DSC profile is in good agreement with TG result of 4 as described above. The lower degradation temperature of cellulose in 4 compared with that of original cellulose is attributed to the loss of the crystalline structure of cellulose by the compatibilization with 3. Although compatibility in the composite materials can be estimated from the change of glass transition temperature (Tg) of both components, obvious peaks due to Tg are not observed in the DSC traces of 4 as well as 3 at ranges of the temperatures measured. The detailed discussion of the DSC data is now in progress in our research group. The efficient compatibilization is also supported by the X-ray diffraction (XRD) measurement, in which the XRD profile of 4 does not show any diffraction peak (Fig. 4(a)). This result is quite different from that of cellulose; the XRD profile of natural cellulose indicates two diffraction peaks at around $2\theta = 15$ and 23° as the typical diffraction pattern of cellulose type I (Fig. 4(b)). These XRD results indicate that the crystalline structure of cellulose was not maintained in 4 by the efficient compatibilization with 3 using the in-situ polymerization method. When cellulose and 3 were simply mixed in 1 and the obtained mixture was isolated by the procedures same as those for 4, almost of 3 was removed by Soxhlet's extraction with methanol. The unit ratio of cellulose to 3 in the mixture was 1.0 : 0.15 calculated by the elemental analysis data. This result indicated that the simple mixing method of cellulose with 3 in the ionic liquid 1 was not useful for the efficient compatibilization.

4. Conclusion

We have examined the compatibilization of cellulose with the polymerized ionic liquid 3 by the in-situ polymerization of the polymerizable ionic liquid 2 in cellulose-dissolving solution using 1. The analytical data of the isolated product supported the formation of the composite 4 consisting of cellulose and 3. The thermal analyses and XRD measurement of 4 indicated that cellulose and 3 were efficiently compatibilized, probably attributed to the good affinity between these two polymeric chains. This method will possibly be extended to the compatibilization of cellulose with the various polymeric ionic liquids, giving new materials having novel and practical properties.

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