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Preparation of cellulose–starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid

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A B S T R A C T

This paper reports the preparation of a cellulose–starch composite gel from an ionic liquid solution. The gel was obtained by keeping the homogeneous mixture of cellulose (10% w/w) and starch (5% w/w) in 1-butyl-3-methylimidazolium chloride (BMIMCl) for several days at room temperature and characterized by elemental analysis, X-ray diffraction, and thermal gravimetric analysis. Furthermore, the production of the fibrous material composed of cellulose and starch by reconstitution from the homogeneous mixture (10% w/w each) in BMIMCl is demonstrated.

1. Introduction

Natural polysaccharides provide two important functions. They act as an energy source and as a structural material (Stryer, 1995). Two representative polysaccharides, cellulose, and starch, are composed of the same unit structure, i.e., glucose unit, but linked through the different β-(1 → 4)- and α-(1 → 4)-glycosidic bonds, respectively. Starch contains both amylose with a linear structure and amylopectin with a branched structure with α-(1 → 6)-linked branching points. The roles of cellulose and starch in nature are completely different; a former is the structural material and latter is an energy storage one.

Cellulose is the most abundant organic substance on earth, and thus, a very important renewable resource that has a number of traditional applications including its use in furniture, clothing, and medical products (Klemm, Heublein, Fink, & Bohn, 2005). Because it has been difficult to extend other novel applications to cellulose, which has been attributed to strong inter- and intramolecular hydrogen bonding, considerable efforts are still being devoted to improve the processability of cellulose (Nishio, 1994, chap. 5). Starch is also abundant and inexpensive polysaccharides, which is biodegradable and nontoxic (Lenz, 1993). Therefore, it can be used as biocompatible applications such as implant materials and drug carriers. However, because of the numerous hydrogen bonds, the polysaccharides have a basic solubility problem in most common organic solvents, causing difficulties in extending the processability, fusibility, and functionality of cellulose and starch.

It has been reported that room temperature ionic liquids having the imidazolium structure can be used as solvents for cellulose and starch (Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). For example, it was found that 1-butyl-3-methylimidazolium chloride (BMIMCl) dissolved cellulose in high concentrations (Swatloski, Spear, Holbrey, & Rogers, 2002), and recently an other study reported the dispersion of starch in BMIMCl (Stevenson, Biswas, Jane, & Inglett, 2007). Recently, we reported the formation of the cellulose gel with BMIMCl from a solution of cellulose in BMIMCl (Kadokawa, Murakami, & Kaneko, 2008a), in the course of our studies on the preparation of cellulose materials using ionic liquids (Kadokawa et al., 2008a; Kadokawa, Murakami, & Kaneko, 2008b; Murakami, Kaneko, & Kadokawa, 2007). Gelation proceeded with the exclusion of the excess BMIMCl by keeping the solution (15% w/w) at room temperature for 7 days. The analytical results suggested that the gel was composed of cellulose, BMIMCl, and water, and accordingly obtained by the formation of cellulose aggregates in the solution of cellulose, attributed to gradually absorbing water. The aggregates probably acted as cross-linking points for gel formation. To obtain the new gelling system with the ionic liquid by means of this method, in this paper, we would like to report the preparation of the cellulose–starch composite gel with BMIMCl from the highly concentrated mixture of the two polysaccharids in BMIMCl. Moreover, the preparation of cellulose–starch composite fibrous material by reconstitution from the mixture is demonstrated.

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2. Experimental part

2.1. Materials

Microcrystalline cellulose and potato starch of commercial reagents from Merck and Wako were used, respectively. The ionic liquid, BMIMCl and other reagents were used as received.

2.2. Preparation of gel

The mixture of cellulose (0.1207 g, 0.745 mmol) and starch (0.0603 g, 0.372 mmol) in BMIMCl (1.207 g, 6.92 mmol) was heated at 100 °C for 24 h under argon to obtain a homogeneous viscous material. After the obtained mixture was cooled to room temperature, it was sandwiched between glass plates. The material was kept at that temperature for 5 days to form the gel. The excluded BMIMCl was removed by washing with methanol and the residual gel was dried under reduced pressure.

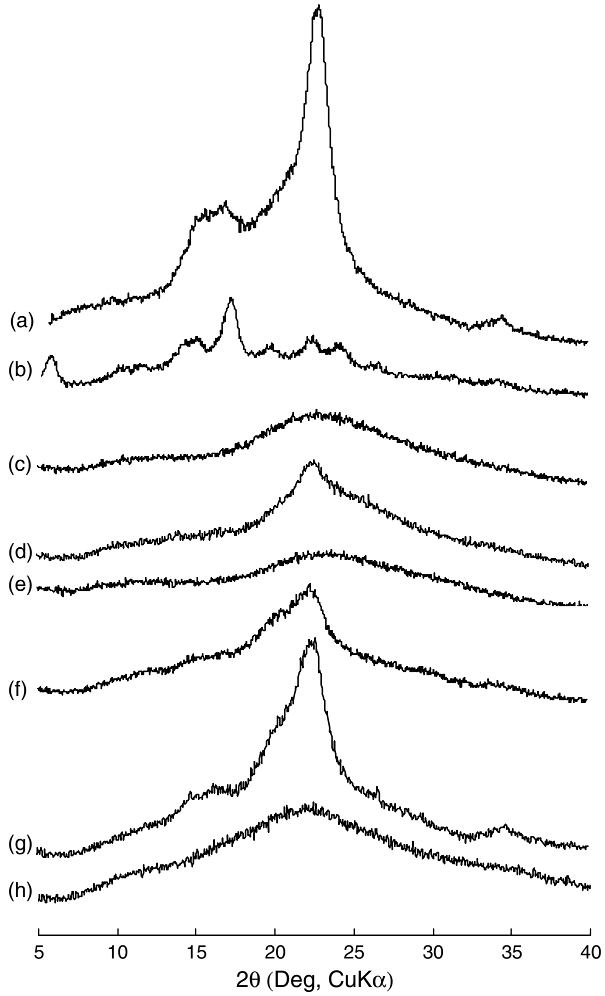


Fig. 1. XRD profiles of cellulose (a), starch (b), gel (c), mixture of cellulose and starch in BMIMCl (d), BMIMCl (e), composite fibrous material (f), regenerated cellulose from BMIMCl solution (g), and regenerated starch from BMIMCl solution (h).

2.3. Preparation of fibrous material

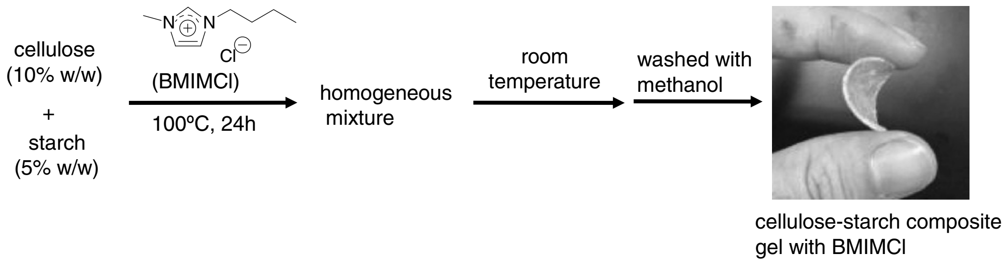
The homogeneous viscous mixture of cellulose and starch (10% w/w each) in BMIMCl was first prepared by the same procedure as that described above. The fine linear material was formed by raising the viscous mixture using a spatula. The material was soaked into acetone for 45 h and dried under reduced pressure to give the composite fibrous material.

2.4. Measurements

X-ray diffraction (XRD) measurements were conducted using a Rigaku Geigerflex RADIIB diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). Thermal gravimetric analysis (TGA) measurements were performed on a SII TG/DTA 6200 at a heating rate of 10 °C/min. Elemental analyses were performed using a Perkin Elmer 2004 CHNS/O analyzer.

3. Results and discussion

When the mixture of cellulose (10% w/w) and starch (5% w/w) in BMIMCl was heated at 100 °C for 24 h, we obtained a homogeneous material, which was subjected to the following experiments (Scheme 1). For the formation of gel, the homogeneous mixture was kept at room temperature. Consequently, the excess BMIMCl was excluded from the material for 4 to 6 days during the gelation process. Thus, the obtained gel was purified by washing with methanol to remove the excluded excess BMIMCl and dried under reduced pressure, which was characterized by the elemental analysis, XRD, and TGA measurements. On the basis of the elemental analysis data, the molar ratio of the glucose unit (cellulose + starch) to BMIMCl was calculated to be 1:3.59. Furthermore, the data indicated that the gel contained 9.32 equivalents of water relative to the glucose units. These ratios are probably changeable in the case of each sample obtained by the multiple experiments. The result of the above elemental analysis indicates that the gel is composed of the polysaccharides, BMIMCl, and water, as same as the gel from cellulose and BMIMCl previously reported by us (Kadokawa et al., 2008a). In the XRD profile of the obtained gel (Fig. 1c), the diffraction peaks due to the crystalline structures of the standard cellulose and starch (Fig. 1a and b) are not obviously exhibited. Furthermore, the XRD data of the gel should be compared with the XRD profile of a mixture of cellulose and starch (1:0.5) in BMIMCl (Fig. 1d, the molar ratio of the glucose unit to BMIMCl was adjusted to the same as that in the gel (1:3.59)), which exhibits diffraction peaks due to the crystalline structures of the polysaccharides. These XRD results indicate that the crystal-



Scheme 1. Procedure for the preparation of gel from a mixture of cellulose and starch in BMIMCl.

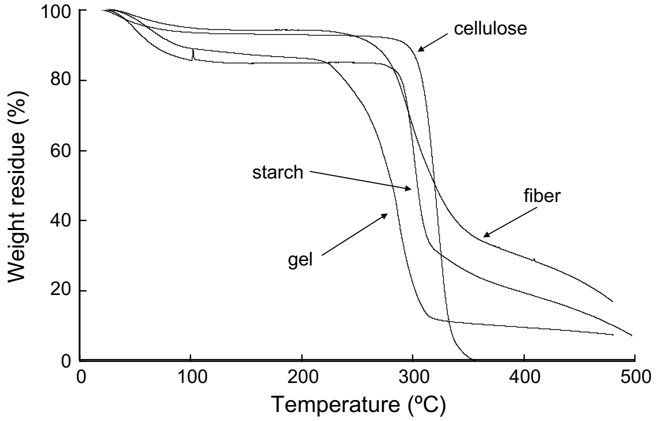
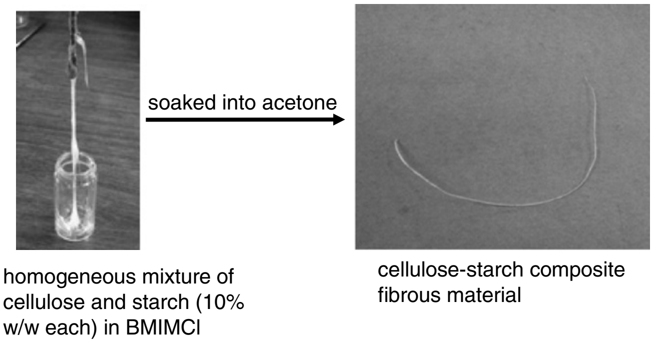


Fig. 2. TGA curves of cellulose, starch, gel, and fibrous material.



Scheme 2. Procedure for the preparation of cellulose-starch composite fibrous material.

line structures of the polysaccharides are largely disrupted in the gel. However, the crystalline index or the conversion ratio of crystalline into non-crystalline in the gel is not yet clear because the XRD profile of BMIMCl shows broad and small diffraction peaks as shown in Fig. 1e, which overlap with the diffraction peaks of cellulose and starch. The TGA curve of the gel (Fig. 2) exhibits an onset of weight loss at around 230 °C, which can be reasonably attributed to thermal degradation of the polysaccharides, whereas that of standard cellulose and starch shows weight losses starting at 300 °C. The difference in the thermal degradation temperatures also indicates disruption of most of the crystalline regions of cellulose and starch in the gel.

The homogeneous mixture of cellulose and starch (10% w/w each) in BMIMCl, obtained by heating as same as above, had a very viscous nature, and thus, could be raised from the surface as shown in Scheme 2. The obtained fine linear material was subjected to the formation of the composite fibrous material by soaking into acetone. By keeping the material in acetone for 45 h, BMIMCl was removed out, and the obtained composite was dried under reduced pressure to give the cellulose-starch fibrous material. The ratio of the glucose unit, BMIMCl, to water was determined by the elemental analysis to be 1:0.0365:0.833, indicating that BMIMCl was mostly removed by the above reconstitution process. The SEM picture of the obtained material (Fig. 3c) shows the fiber form with ca. 100–200 μm diameter, but the crystalline and particle images, which are observed in the SEM pictures of the standard cellulose and starch, respectively (Fig. 3a and b), are not seen. The XRD profile of the fibrous material in Fig. 1f shows the diffraction pattern probably due to the crystalline structures of the polysaccharides, which is the similar to that of the regenerated cellulose and starch obtained from the solution of each polysaccharide in BMIMCl (15% w/w) by the same procedure as that for the composite fibrous material (Fig. 1g and h). However, the intensity of the diffraction peaks in the XRD profile of the fibrous material (Fig. 1f) is much lower than that of the regenerated cellulose (Fig. 1g), probably attributed to coexisting with starch. These XRD results

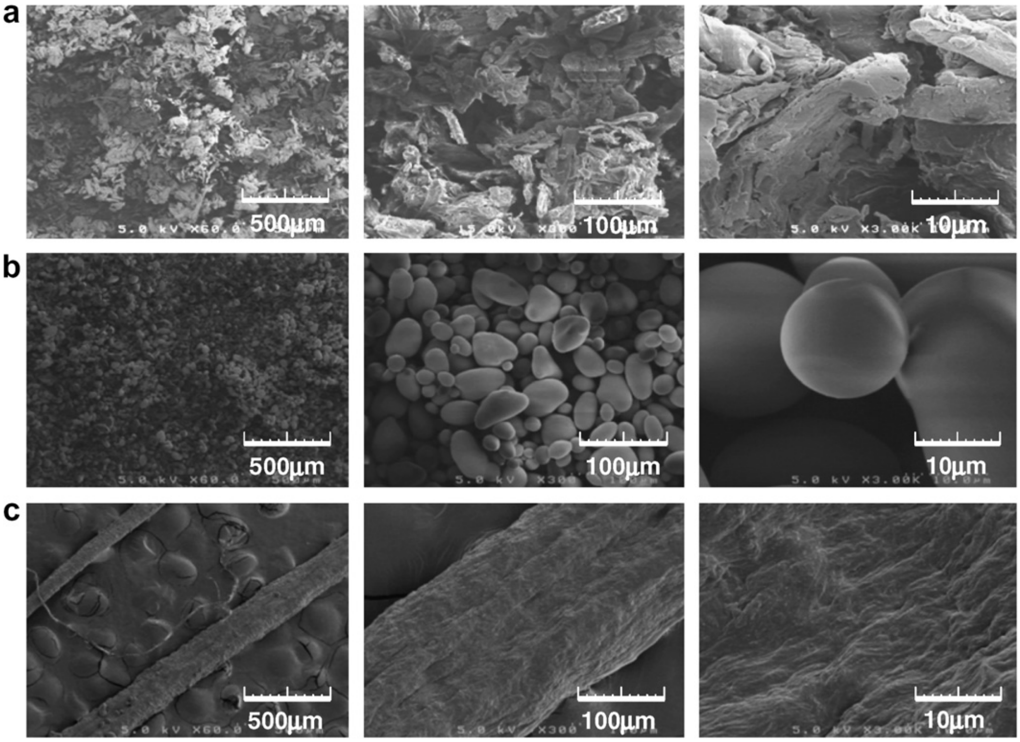


Fig. 3. SEM images of cellulose (a), starch (b), and fibrous material (c).

indicate that the polysaccharide chains are aggregated in the fibrous material by the reconstitution but the crystalline structures of cellulose and starch chains are not regenerated well unlike the regenerated cellulose, probably due to the compatibilization of the two polysaccharides. The TGA result of the material (Fig. 2) exhibits a higher weight loss temperatures than those of the gel, attributed to aggregation of the polysaccharide chains by removing BMIMCl from the viscous mixture.

4. Conclusion

We have reported the preparation of cellulose-starch composite gel with BMIMCl from the homogeneous mixture of the polysaccharides in BMIMCl. The analytical results indicated that the crystalline structures of the cellulose and starch were largely disrupted in the gel. Furthermore, the facile production of the cellulose-starch composite fibrous material was performed by soaking the homogeneous mixture into acetone. The SEM and XRD data of the obtained material showed the compatibilized fibrous structure of ca. 100–200 μm diameter.

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