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Note

A facile preparation of gel materials from a solution of cellulose in ionic liquid

Jun-ichi Kadokawa,* Masa-aki Murakami and Yoshiro Kaneko

Department of Nanostructured and Advanced Materials, Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

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Abstract—This paper reports a facile preparation of a flexible gel material from a solution of cellulose (15% w/w) in an ionic liquid of 1-butyl-3-methylimidazolium chloride by keeping it at room temperature for 7 days. Elemental analysis data indicated that the obtained gel material was composed of cellulose, the ionic liquid, and water. Both XRD and TGA results suggested that crystalline structure of cellulose was largely disrupted in the material. However, the existence of non-crystalline aggregates was assumed by the XRD data of the material. The gel material was probably obtained by the formation of cellulose aggregates in the solution, attributed to the gradual absorption of water. When the material was heated at 120 °C, it became soft, and converted into a fluid at 150 °C. By keeping the soft material at room temperature for 2 days, a gel material was regenerated, which was more transparent compared with the original material.

Keywords: Cellulose; Gel; Ionic liquid

Cellulose is a representative natural polysaccharide and the most abundant organic substance on earth, the structure of which consists of a chain of β-(1→4)-linked glucose residues.[1] It is a very important renewable resource that has a number of traditional applications including its use in furniture, clothing, and medical products. For over a century, researchers have been attracted by this fascinating and sustainable natural substance and have carried out fundamental and practical studies of this material. Because it has been difficult to extend other novel applications to cellulose, which has been attributed to strong inter- and intra-molecular hydrogen bonding, considerable efforts are still being devoted to improve the processability of cellulose.[2] However, due to the stiff molecules and close chain packing via the numerous hydrogen bonds as described above, it is hard to dissolve cellulose in water and in most common organic solvents. This property causes difficulties in improving the processability, fusibility, and functionality of cellulose. To date, only a limited number of solvent systems for cellulose has been found, such as the LiCl–*N*,*N*-dimethylacetamide (DMAc) system.[3]

It has been reported that at room temperature ionic liquids having the imidazolium structure can be used to dissolve cellulose.[4–8] For example, it was found that 1-butyl-3-methylimidazolium chloride (BMIMCl) dissolved cellulose in high concentrations.[4] On the basis of the above points, we have recently studied the preparation of composite materials based on cellulose using BMIMCl as well as other ionic liquids.[9,10] In the course of this work, we found that when a highly concentrated solution of cellulose in BMIMCl was kept at room temperature, a gel material formed with the exclusion of excess BMIMCl. Regarding cellulose gels, it is well-known that cellulose is produced in bacteria, that is, bacterial cellulose forms a gel because of its ultra-fine structural network.[11] Although some gelations of cellulose from plant origin in alkaline aqueous or LiCl–DMAc solutions have been reported via thermal, deionization, and other processes,[12–15] a variety of methods for the

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* Corresponding author. Tel.: +81 99 285 7743; fax: +81 99 285 3253; e-mail: kadokawa@eng.kagoshima-u.ac.jp

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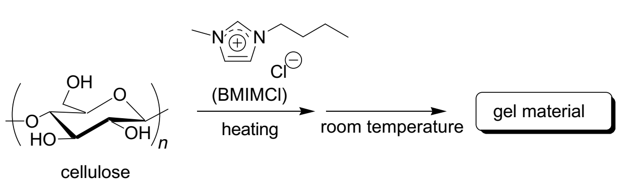
gelation of plant cellulose without derivatization has not been achieved to date.

In this paper, we report a facile preparation of gel materials from a solution of cellulose in BMIMCl (Scheme 1), which are composed of cellulose, BMIMCl, and water. In relation to the present work, Rogers and co-workers have already prepared blended cellulose or composite films from a solution of cellulose in BMIMCl.[16,17] The films were obtained by casting the solution onto a glass plate, followed by reconstitution by the addition of water. In comparison with the previous studies, the materials described in this paper are not films, but are gels, which can be obtained by a simple procedure without the need for a reconstitution or regeneration process. Moreover, it should be noted that the materials obtained in this study can be handled and are thermally softened, which further become fluids. Therefore, we are convinced of a possibility for improving the processability and fusibility of cellulose by the generation of gel materials, leading to new applications.

When the solution of cellulose (15% w/w) in BMIMCl (molar ratio of glucose unit to BMIMCl = 1:6.19) was kept between glass plates at room temperature for 7 days (Fig. 1a), it gradually became turbid with the formation of gel material. During the process, the excess BMIMCl was excluded from the material. Thus, the material was purified by washing with ethanol to remove the excluded excess BMIMCl and dried under reduced pressure. The isolated material had a flexible nature as shown in Figure 1b and it was characterized by elemental analysis, X-ray diffraction (XRD), and thermal gravimetric analysis (TGA).

On the basis of the elemental analysis data, the molar ratio of the glucose units to BMIMCl in the materials (obtained from several experiments) was calculated to be in the range of 1:2.48–4.68. Furthermore, the data indicated that the materials contained 8.69–16.0 equiv of water relative to the glucose units. In comparison with the XRD profile of microcrystalline cellulose (Fig. 2a), the diffraction peaks due to crystalline structure of cellulose nearly disappeared in the XRD profile of the material (Fig. 2c). However, some diffraction peaks, probably attributed to crystalline regions of cellulose, are still observed at around 23°. The XRD results shown in Figure 2c indicate that the crystalline structure of cellulose in the gel is mostly disrupted. Moreover, the existence of non-crystalline structures in the material can be assumed by the appearance of the broad diffraction peaks at around 19° as indicated by asterisk in Figure 2c,[18] whereas the diffraction peaks at around 19° are less visible in the XRD profile of the cellulose solution in BMIMCl (Fig. 2b). The crystalline index or the conversion ratio of crystalline into non-crystalline cellulose in the material is not yet clear because the XRD profile of BMIMCl shows broad diffraction peaks as shown in Figure 2d (the intensities are not high), which overlapped with the diffraction peaks of cellulose (Fig. 2c).



Scheme 1. Procedure for the preparation of gel material from a solution of cellulose in BMIMCl.

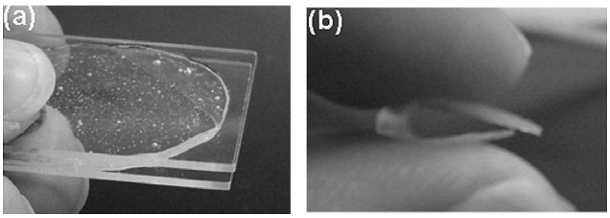


Figure 1. Photographs of gelation process (a) and the obtained gel material (b).

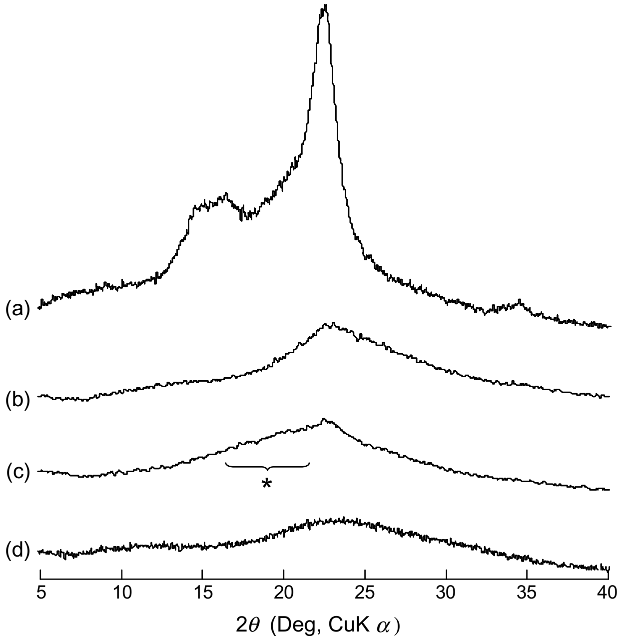


Figure 2. XRD profiles of cellulose (a), a solution of cellulose in BMIMCl (b), the primary formed gel material (c), and BMIMCl (d).

The TGA curve of the material (Fig. 3c) exhibits an onset of weight loss at around 230 °C, which can be reasonably attributed to thermal degradation of cellulose, whereas that of original cellulose shows weight losses starting at 300 °C (Fig. 3a). The difference in the thermal degradation temperatures also indicates disruption of most of the crystalline regions of cellulose in the material.

These analytical data suggest that the gel material is composed of cellulose, BMIMCl, and water and obtained by the formation of non-crystalline aggregates in solution by gradually absorbing water. The

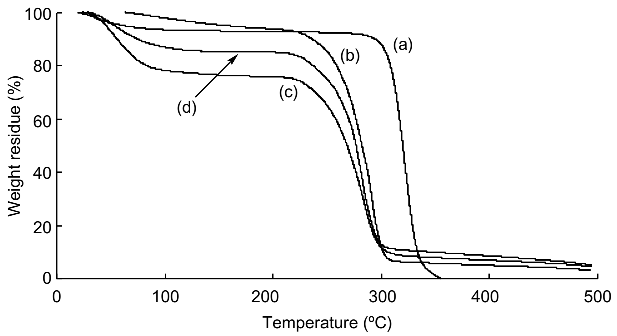


Figure 3. TGA curves of cellulose (a), a solution of cellulose in BMIMCl (b), the primary formed gel material (c), and the regenerated gel material (d).

aggregates probably act as cross-linking points for the gelation process. The absorption of water during the formation of the gel material is supported by more frequent weight losses at around 50–100 °C, which is attributed to water, by comparing its TGA curve with that of the cellulose solution in BMIMCl (Fig. 3b and c).

When the material was heated at 120 °C, it was gradually softened, and converted into a fluid at 150 °C (Fig. 4). The soft material obtained by heating at 120 °C for 2 h could be transferred to the gel form again by keeping it for 2 days at room temperature. The regenerated material was still flexible and was more transparent than the primary formed material as shown in Figure 4. For example, at 500 nm, transmittance of the primary formed gel material was 65.4% and that of the regenerated material was 90.6%. Although the XRD profile of the regenerated gel material was almost the same as that of the primary material, weight losses at 50–100 °C in the TGA curve of the regenerated material (Fig. 3d) are smaller compared with those of the primary material (Fig. 3c) at the temperature ranges in the TGA curve. Because these weight losses are attributed to water in the materials, the content of water in the regenerated material is estimated to be lower than that in the primary material. This is also supported by the comparison of the elemental analysis data between the primary and the regenerated gel materials. For example, when the primary material, having the ratio of glucose unit, BMIMCl, to water of 1:4.35:11.6, was heated and regenerated, the ratio changed to 1:3.13:8.44. These data indicate that a gel with higher content of cellulose was obtained by the regeneration procedure. Furthermore, the non-crystalline aggregates of cellulose as the cross-linking points in the regenerated gel material were probably dispersed well by the heating–cooling process compared with those in the primary gel material. Therefore, the gel material after regeneration was more transparent than before.

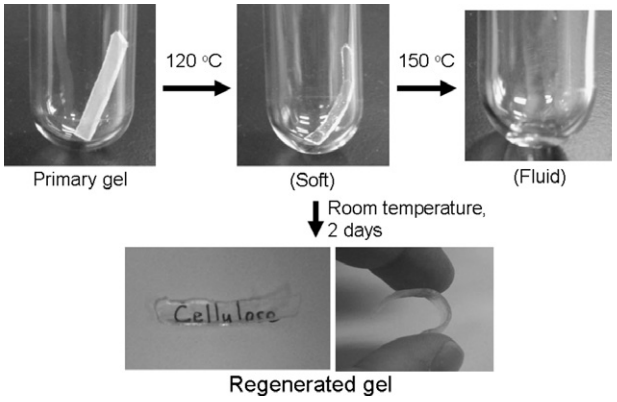


Figure 4. Appearance of the heating procedure of the primary formed gel material and for the regenerated gel material.

In conclusion, we have reported a facile preparation of a flexible gel material from a solution of cellulose (15% w/w) in BMIMCl, which was obtained by keeping the solution at room temperature for 7 days. Elemental analysis data of the materials, obtained by the several experiments, indicated that the ratios of the glucose unit, BMIMCl, to water were the ranges of 1:2.48–4.68:8.69–16.0. Both XRD and TGA results suggested that the crystalline structure of cellulose was mostly disrupted in the material. However, the existence of non-crystalline aggregates was assumed by the XRD data of the material. These analytical data indicated that the material was 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. When the material was heated at 120 °C, it became soft, and converted into a fluid at 150 °C. By keeping the soft material at room temperature for 2 days, a gel material was formed that was more transparent compared with the primary material. Further studies on the detailed physical and mechanical properties as well as the applications of the present gels are now in progress.

1. Experimental

1.1. Materials

Microcrystalline cellulose of a commercial reagent from Merck was used. The ionic liquid, BMIMCl and other reagents were used as received.

1.2. Preparation of gel material

As a typical procedure for the preparation of the gel, cellulose (0.323 g, 15% w/w for BMIMCl) was dissolved in BMIMCl (2.15 g) by heating at 100 °C for 24 h. After the solution was cooled to room temperature, it was sandwiched between glass plates. The material was kept at that temperature for 7 days to form the gel material. The excluded BMIMCl was removed by washing with ethanol and the residual gel was dried under reduced pressure.

1.3. Measurements

X-ray diffraction (XRD) measurements were conducted at a scanning speed of $2\theta = 0.2°$/min 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.

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