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ORIGINAL PAPER

Preparation of cellulose-based ionic porous material compatibilized with polymeric ionic liquid

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Abstract Cellulose-based ionic porous material compatibilized with polymeric ionic liquid was prepared by means of templating technique using oil/ionic liquid emulsion in the presence of sorbitane monooleate. In situ polymerization of a mixture of polymerizable ionic liquids, 1-(3-acryloyloxypropyl)-3-methylimidazolium and 1-(3-acryloyloxypropyl)-3-vinylimidazolium bromides was first performed in a solution of cellulose in a solvent of an ionic liquid, 1-butyl-3-methylimidazolium chloride. The sonication of the mixture coexisting with corn oil and sorbitan monooleate, followed by the successive treatment with methanol, acetone, and hexane gave the porous material. The material thus obtained was characterized by the FT-IR, TGA, XRD, and SEM measurements. The SEM images of the material showed the morphology of the porosity with the pore sizes of around 0.15–1.3 μm accompanied with the smaller sizes of 30–70 nm.

Keywords Cellulose · Porous material · Ionic liquid · In situ polymerization · Templating technique · Composite

Introduction

Cellulose is a representative natural polysaccharide and the most abundant organic substance on the earth, which consists of a chain of β-(1 → 4)-linked

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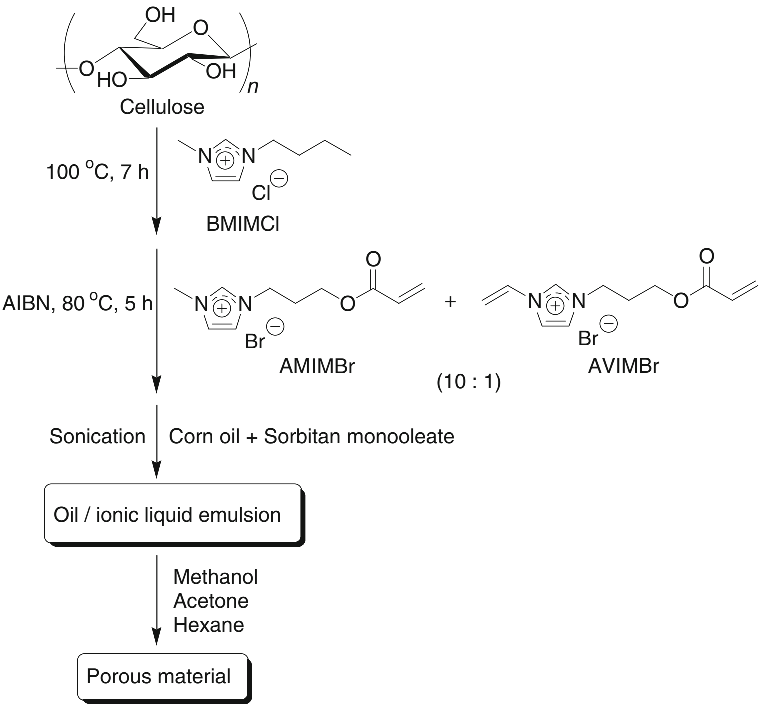
glucose residues [1]. The abundance, low cost, and renewability of cellulose have made it the attractive candidate for the preparation of various bio-based materials. For example, cellulose derivatives have been used to prepare porous materials such as the porous membranes [2]. Templating technique, which is a method popularly employed to provide a definite or a special arranged pattern in materials during its process, is well-known to prepare porous materials [3]. In one of the templating methods, an oil/water system forms an emulsion coexisting with a surfactant as an emulsifier, where oil is used as the template to construct porosity. The templating technique was already used for the preparation of porous nanofibrous cellulose membranes from bacterial cellulose for the application to tissue engineering [4].

On the other hand, room temperature ionic liquids have been popularly used in carbohydrate chemistry including dissolution of polysaccharides [5–11]. For example, it was found that 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride dissolved cellulose in high concentrations [5–7]. Recently, Tsioptsias et al. [12] reported development of micro- and nano-porous composite materials by processing cellulose with the latter ionic liquid and supercritical CO_2. By dissolving cellulose in the ionic liquid and regenerating with water or methanol, in the study, the cellulose hydrogels and methanogels were first obtained. Then, the gels were processed by supercritical CO_2 to give the porous materials.

We have been interested in employing the polymeric derivatives of the ionic liquids, so-called polymeric ionic liquids, as the components of the composite materials with the polysaccharides. We already reported the preparation of the composite materials consisting of cellulose and the polymeric ionic liquids by in situ polymerization method [13–15]. As one example for the preparation of the composites [13], cellulose was first dissolved in BMIMCl and the polymerizable ionic liquid such as 1-(3-acryloyloxypropyl)-3-methylimidazolium bromide (AMIMBr) and AIBN as a radical initiator were added to the solution. Then, the radical polymerization of AMIMBr was performed by heating the mixture. The obtained composite was isolated by washing the resulting mixture with a poor solvent for both components, i.e., acetone. This method has inspired us to combine with the aforementioned templating technique to prepare the cellulose-based porous materials compatibilized with the polymeric ionic liquids. For the preparation of this type of the porous material in the present study, we performed our original templating technique, which was based on an oil/ionic liquid emulsion system coexisting with a surfactant.

In this paper, we report that cellulose-based ionic porous material compatibilized with polymeric ionic liquid was successfully prepared by in situ polymerization technique using a mixture of two polymerizable ionic liquids, AMMBr and 1-(3-acryloyloxypropyl)-3-vinylimidazolium bromide (AVIMBr) in BMIMCl, followed by emulsification using the oil/ionic liquid system, according to the procedure shown in Scheme 1. We used the mixture of two ionic liquids as the polymerizable substrates, because the insoluble and stable cross-linking polymeric ionic liquid is obtained by the radical polymerization of these monomers due to the role of AVIMBr as the cross-linking agent, as already discussed in our previous



Scheme 1 Preparation procedure of cellulose-based ionic porous material compatibilized with polymeric ionic liquid

paper [15]. Corn oil was used as the template for the formation of the porous structures via an oil emulsion with an emulsifier of sorbitan monooleate in BMIMCl.

Experimental

Materials

Microcrystalline cellulose was procured from Merck and corn oil and sorbitan monooleate (span 80) were procured from WAKO pure chemical company. The polymerizable ionic liquids, AVIMBr and AMIMBr were synthesized by following the methods as previously described [16] and the structure of each ionic liquid was confirmed by ^{1}H NMR spectrum.

Preparation of porous material

Cellulose (0.0212 g; 0.123 mmol) was dissolved in BMIMCl (1.5012 g; 9.253 mmol) by heating at 100 °C for 7 h. The obtained viscous solution was transferred to a test tube and cooled to room temperature, followed by addition of

AMIMBr (0.034 g; 0.123 mmol) and AVIMBr (0.0034 g; 0.0117 mmol) (molar ratio of AMIMBr to AVIMBr was 10.51:1). Then, AIBN (0.0030 g, 0.0182 mmol) was added prior to the polymerization. The mixture was blended well and heated at 80 °C for 5 h. Corn oil (0.50 mL) and sorbitan monooleate (0.50 mL; 1.15 mmol) was added into the mixture, followed by sonication for 20 min to form a stable oil/ionic liquid emulsion. The washing out of ionic liquids with methanol followed by refluxing with acetone and the removal of oil with *n*-hexane resulted the macroporous materials. The poly[AMIMBr + AVIMBr] was also prepared by the polymerization of the mixture of AMIMBr (0.034 g; 0.123 mmol) and AVIMBr (0.0034 g; 0.0117 mmol) by heating at 90 °C for 5 h in the presence of AIBN.

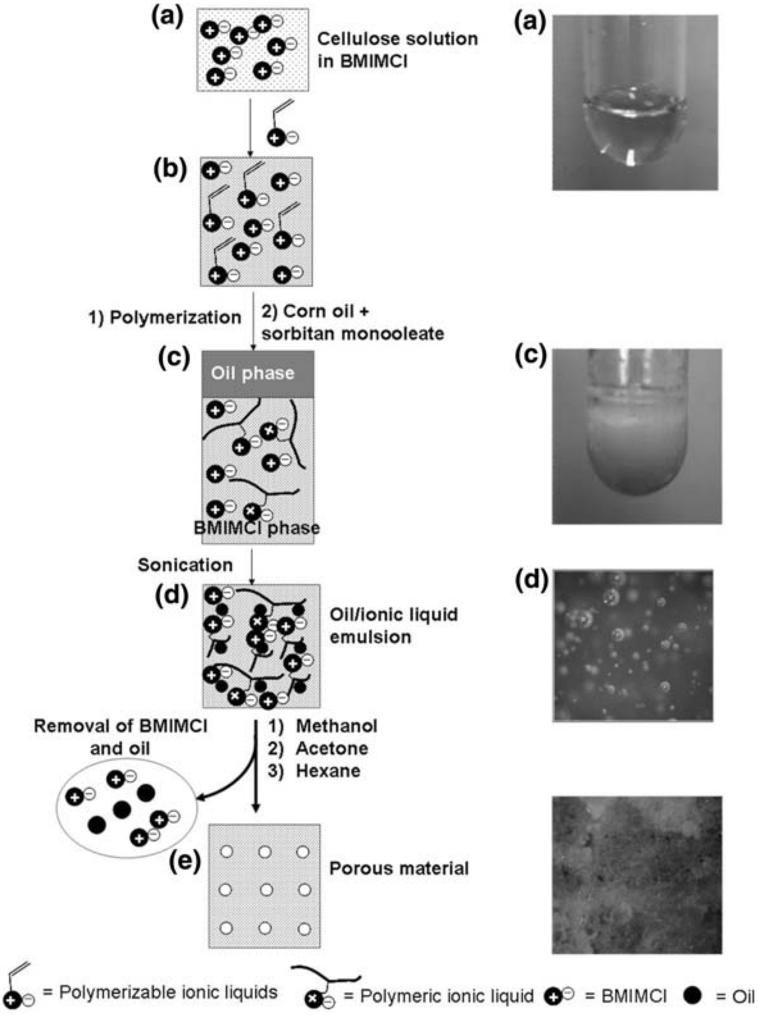
Measurements

IR spectra were recorded on a SHIMADZU FTIR-8400 spectrometer by the KBr pellet method. XRD measurements were conducted using a PANalytical X’ Pert Pro diffractometer with Ni-filtered CuK$_\alpha$ radiation ($\lambda = 0.15418$ nm). Thermal gravimetric analysis (TGA) was performed on SII TG/DTA 6200 in the temperature range of 30–500 °C at a heating rate of 10 °C/min. For scanning electron micrographs (SEM), platinum films were deposited on each of samples by magnetron sputtering and images were recorded on a Hitachi S-4100 scanning electron microscope applying 5 kV accelerating voltage. CCD camera used was a Dino-Lite digital microscope using 200 times magnification.

Results and discussion

The preparation of the ionic porous material based on the composites of cellulose with the polymeric ionic liquid was carried out as schematically shown in Scheme 1. Cellulose was first dissolved in BMIMCl by heating at 100 °C for 7 h. Then, a mixture of AMIMBr and AVIMBr in the molar ratio of ca. 10:1 was added to the above solution and polymerized by heating at 80 °C for 5 h in the presence of AIBN. To the polymerized mixture, corn oil and sorbitan monooleate were added and sonicated for emulsification. Then, methanol was added to the mixture to wash out BMIMCl and the unreacted polymerizable ionic liquids, giving a solid material. To make the material completely free from any ionic liquids, it was further treated with acetone at a refluxing temperature. Finally, the oil existed in the material was removed by washing four times with hexane. Scheme 2 shows the schematic image for the formation of the porous material and the photographs of each step. The clear solution of cellulose in BMIMCl turned into the turbid liquid after the polymerization of AMIMBr and AVIMBr, caused by dispersing the polymeric ionic liquid due to its insoluble property in BMIMCl (Scheme 2a → a lower phase of Scheme 2c). The sonication of the two phase system (Scheme 2c) gave the oil droplets covered with some white colored materials, which are observed in the CCD camera image of the emulsion (Scheme 2d). The covertures are probably the dispersing polymeric ionic liquid coexisting with sorbitane monooleate, which probably work as interface between the oil and the outer liquid because of their amphiphilic natures in this system (a lipophilic nature of the polyacrylate main chain and an ionic liquid-philic nature of the imidazolium substituent in the polymeric ionic liquid). Finally, the removal of BMIMCl (with the unreacted polymerizable ionic liquids) and the oil gave the imprint of the pores in the structure created by the oil droplets (Scheme 2e). It was further observed during emulsification that some small oil droplets moved and coalesced each other, resulting in the larger globules, which caused the formation of materials with non-uniform pore sizes.

The obtained material was characterized by the IR, TGA, XRD, and SEM measurements. The IR spectrum of the product in Fig. 1b exhibited the characteristic absorptions due to cellulose and the polymeric ionic liquid. For example, the



Scheme 2 Schematic layout for the formation of porous material and photographs of each step

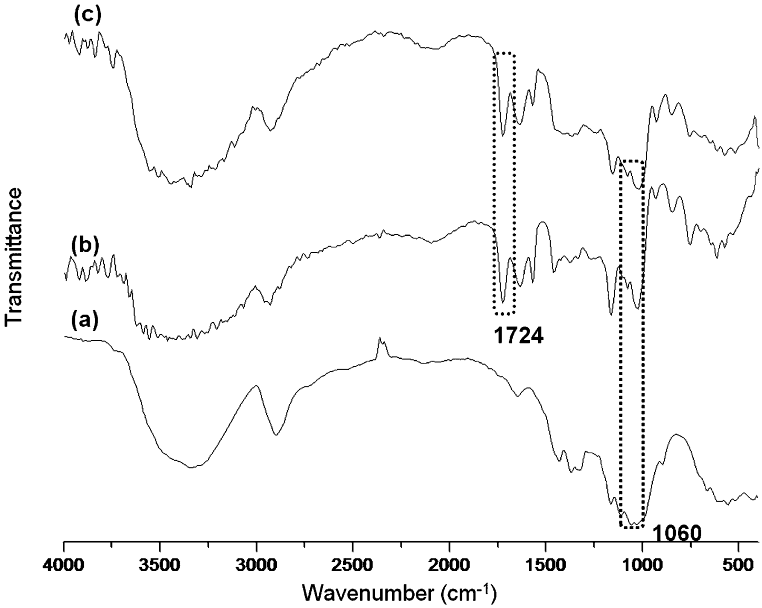


Fig. 1 FT-IR spectra of **a** cellulose, **b** porous material, and **c** porous material obtained after soaking in hot methanol for 4 h

absorptions at 1,060 cm^{-1} due to C–O of cellulose (Fig. 1a) and at 1,724 cm^{-1} due to C = O of the polymeric ionic liquid appeared in the IR spectrum of the porous material. This IR data suggested that the porous material was the composite consisting of cellulose and the polymeric ionic liquid. The porous material was soaked in hot methanol (ca. 40 °C) for 4 h to evaluate its stability in such polar liquid. When the treated material was again subjected to the IR analysis (Fig. 1c), the spectroscopic pattern was quite similar as Fig. 1b, indicating the good stability of the porous material.

The TGA curve of the porous material (Fig. 2c) exhibited an onset of weight loss at around 250 °C, whereas that of cellulose and the poly[AMIMBr + AVIMBr] (Fig. 2a, b) appeared weight losses starting at around 290 and 245 °C, respectively. The different degradation temperature of the porous material from that of the individual component materials was probably caused by the disruption of the crystalline structure of cellulose in the porous material, which was also observed in the XRD measurement (vide infra). It has already been discussed in our previous papers that the lower degradation temperatures, which are observed in the TGA analysis of the composite materials composed of cellulose and the polymeric ionic liquids compared with the original materials, are due to the disruption of the crystalline structures of cellulose [13–15]. The above TGA results indicated the efficient compatibilization of cellulose with the polymeric ionic liquid in the porous material. The TGA curves in Fig. 2 also show small weight losses at the temperature

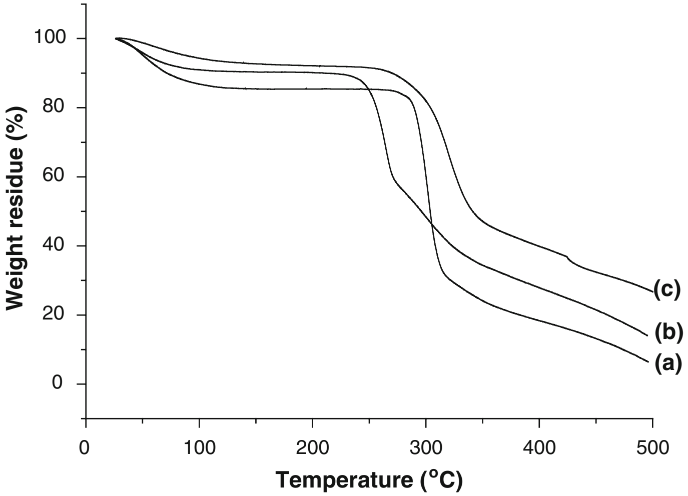


Fig. 2 TGA curves of **a** cellulose, **b** poly[AMIMBr + AVIMBr], and **c** porous material

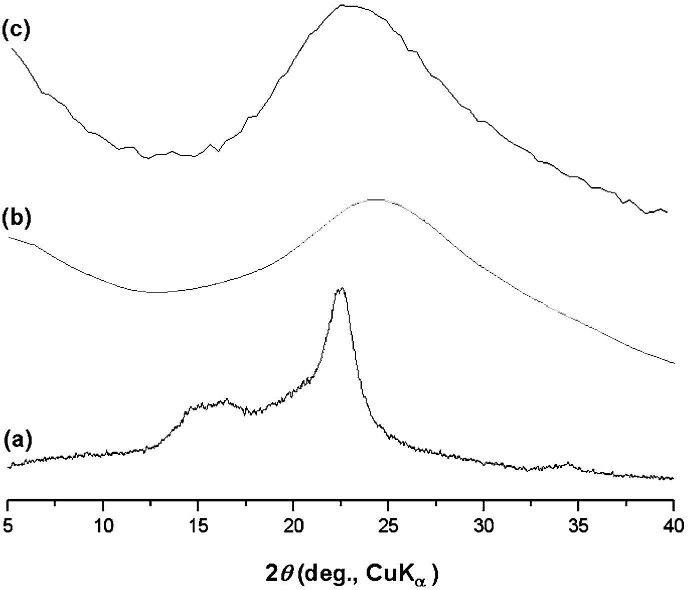


Fig. 3 XRD profiles of **a** cellulose, **b** poly[AMIMBr + AVIMBr], and **c** porous material

below 100 °C, which are reasonably explained as due to evaporation of water present in the materials.

The efficient compatibilization was also supported by the XRD measurement, in which the XRD profile of the porous material in Fig. 3c did not show any diffraction peak due to the crystalline structure of cellulose (Fig. 3a). The XRD result indicated that the crystalline structure of cellulose was not maintained in the porous material

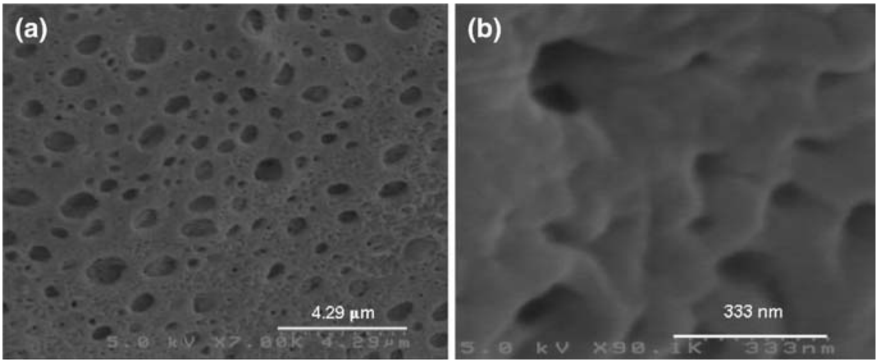


Fig. 4 SEM images of porous material

by the efficient compatibilization with the polymeric ionic liquid using the in situ polymerization method.

The morphology of the porous material was investigated by using the SEM imaging. Fig. 4a shows the typical SEM image of the porous material. The pore sizes observed are mainly around 0.15–1.3 µm, but some smaller pores with the scales of several tens of nanometer seem to be existed. Indeed, the magnified image (Fig. 4b) shows the pores with the diameters of around 30–70 nm besides the larger pores with an order of a hundred nanometer scale. The formation of the larger globules formed by coalescence of the primary-formed oil droplets during emulsification probably caused the formation of non-uniform pores in the structure.

Conclusion

By combining the in situ polymerization method with the templating technique using oil/ionic liquid emulsion system, we have demonstrated that the preparation of the cellulose-based ionic porous material compatibilized with the polymeric ionic liquid is prepared. In situ polymerization of the polymerizable ionic liquids was first performed in a solution of cellulose in a solvent of an ionic liquid, BMIMCl. Then, the sonication of the mixture coexisting with corn oil and sorbitan monooleate, followed by the treatment with the appropriate solvents gave the porous material. The pore sizes in the material ascertained from SEM images were found to be around 0.15–1.3 µm accompanied with the smaller sizes of 30–70 nm The further work in order to obtain the better porous materials with the more uniform pores is presently going on in our research group. This will possibly be achieved by optimizing the quantitative factors in each substrates used in the present system. Furthermore, the application by using the ionic porosity of the present material is also in progress, which will be reported in the future.

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