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6

Preparation of Polysaccharide-based Materials Compatibilized with Ionic Liquids

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1. Introduction

Ionic liquids (ILs) are low-melting-point molten salts, defined as which form liquids at room temperature or even at temperatures lower than a boiling point of water. The property is owing to that the liquid state is thermodynamically favorable due to the large size and conformational flexibility of the ions, in which these behaviors lead to small lattice enthalpies and large entropy changes that favor the liquid state (Welton, 1999). In the past more than a decade, ILs have attracted much attention due to their specific characteristics such as a negligible vapor pressure, excellent thermal stabilities, and controllable physical and chemical properties (Plechkova & Seddon, 2008). Beyond these traditional properties of ILs, recently, interests and applications on ILs have been extended to the researches related to biomolecules such as naturally occurring polysaccharides, because of specific good affinities of ILs for them (Seoud et al., 2007).

Polysaccharides are widely distributed in nature and have been regarded as structural materials and as suppliers of water and energy (Schuerch, 1986). Natural polysaccharides such as cellulose, starch, chitin, and other many kinds of them have recently received much attention for use as resources of new green and sustainable materials because of their eco-friendly properties. However, the natural polysaccharides have often exhibited solubility, processability, and feasibility problems due to numerous hydrogen bonds in their polymeric chains, causing difficulty in employing them in a wide variety of materials.

In 1934, Graenacher had already discovered that a molten *N*-ethylpyridinium chloride, in the presence of nitrogen-containing bases, dissolved cellulose (Graenacher, 1934). This was probably the first example of the cellulose dissolution using IL-type solvents. However, this was thought to be of little practical value at the time because the concept of ILs had not been put forward. In 2002, Rogers et al. comprehensively reported that an IL, 1-butyl-3-methylimidazolium chloride (BMIMCl) dissolved cellulose in relatively high concentrations and this research opened up a new way for the development of a class of cellulose solvent systems (Swatloski et al., 2002). Since this publication, ILs have began to be used in the processing of cellulose and other polysaccharides, which mainly concern with the dissolution, homogeneous derivatization and modification, and regeneration (Zhu et al., 2006, Liebert & Heinze, 2008, Feng & Cheng, 2008, Pinkert et al., 2009).

In recent years, ILs have been extensively used as functional components in the polysaccharides-based materials besides the above traditional uses as solvents and media. The concept in these researches is based on the properties of ILs that exhibit good affinities

for the polysaccharides, which are suitably lead to showing well-compatibilization. In this chapter, on the basis of these backgrounds and viewpoints, the preparation of polysaccharides-based materials compatibilized with ILs is described, which is divided by the following two sections. A first topic is the preparation of polysaccharide-polymeric IL composite materials by means of in-situ polymerization of polymerizable ILs. As a second topic, the preparation of IL-gel materials from various natural polysaccharides is disclosed.

2. Preparation of polysaccharide-polymeric ionic liquid composites by in-situ polymerization of polymerizable Ionic Liquids

2.1 Polymeric ionic liquids

Polymeric ILs are defined as the polymers obtained by polymerization of ILs having polymerizable groups (polymerizable ILs) (Green et al., 2009). Thus, 'polymeric ILs' are termed just the polymeric forms of ILs, but they are not necessary to show liquid form at room temperature or even at some ambient temperatures. The polymeric ILs, therefore, are often called 'polymerized ILs' too. The major advantages for providing the polymeric ILs are to be enhanced stability, and improved processability and feasibility in application as practical materials. Polymerizable ILs as a source of the polymeric ILs can be available by incorporating the polymerizable groups at both anionic and cationic sites in the IL structures (Fig. 1). In the former case, polymerizable anions are ionically exchanged to some anions of general ILs (Fig. 1(a)), giving the polymerizable ILs. In the latter case, vinyl, meth(acryloyl), and vinyl benzyl groups have typically been appeared as the polymerizable group (Fig. 1(b)). 1-Vinylimidazole is a commercially available reagent. Therefore, the vinylimidazolium-type polymerizable ILs are prepared by quaternization of 1-vinylimidazole with a variety of alkyl halides. The reaction of haloalkyl (meth)acrylates or vinylbenzyl halides with 1-alkylimidazoles gives the corresponding imidazolium-type polymerizable ILs having the (meth)acryloyl or vinyl benzyl polymerizable groups (Fig. 2). Furthermore, when haloalkyl (meth)acrylates or vinylbenzyl halides are reacted with 1-vinylimidazole, the polymerizable ILs having two polymerizable groups are produced. Because these ILs can be converted into insoluble and stable polymeric ILs with the cross-linked structure by the radical polymerization (Fig. 3), they have a highly potential as the source of the components in the practical materials. On the basis of the above viewpoints, the polymerizable ILs having the acrylate or vinylbenzyl group have been employed for the preparation of polysaccharide-polymeric IL composite materials.

2.2 Preparation of cellulose-polymeric IL composites

Cellulose is the most abundant organic substance on the earth, which consists of β-(1→4)-linked glucose repeating units. Cellulose has limited applications because of the strong inter- and intramolecular hydrogen bonds between the hydroxy groups of the glucose residues. Therefore, considerable efforts have been still devoted to the compatibilization of cellulose with synthetic polymers for improvement of the processability of cellulose. In-situ polymerization method, for example, those giving interpenetrating polymer network (IPN) system has been useful for formation of composites from cellulose (Fig. 4). The IPNs are a special class of polymer blends or composites based on two or more polymers, with each polymer chemically cross-linked or at least one network being prepared in the presence of the others. If all polymers are cross-linked, the blend is called a full-IPN. Semi-IPN differs

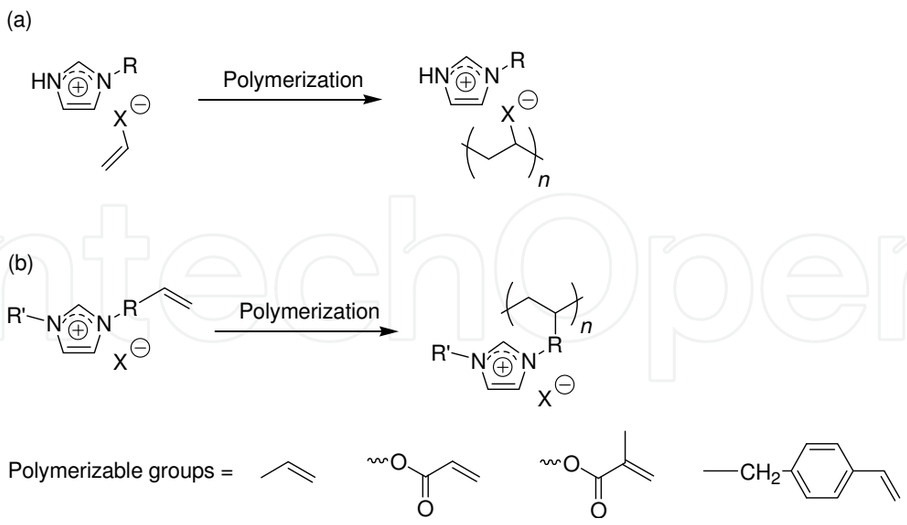


Fig. 1. Polymerization of polymerizable ILs having a polymerizable group at anionic site (a) and cationic site (b).

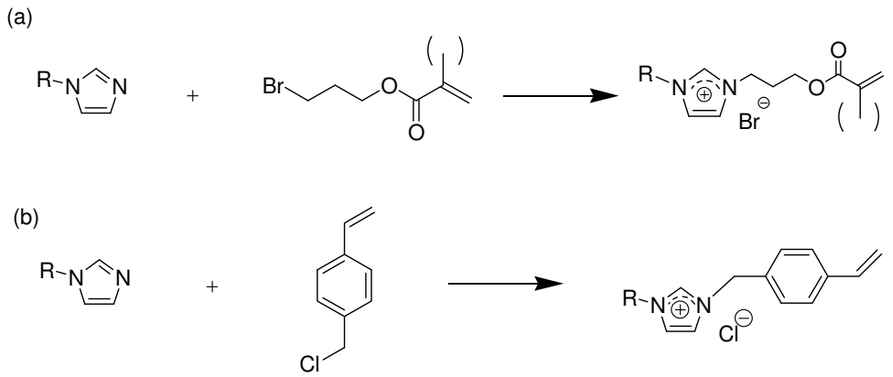


Fig. 2. Typical synthetic schemes for polymerizable ILs having (meth)acrylate (a) and vinylbenzyl (b) groups.

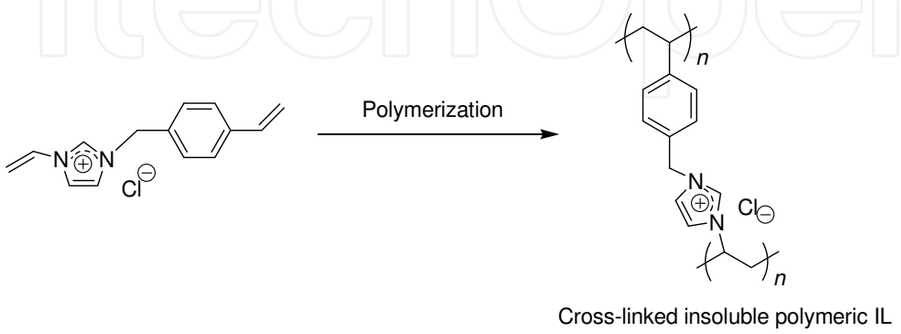


Fig. 3. Polymerization of a polymerizable IL having two polymerizable groups to produce a cross-linked insoluble polymeric IL.

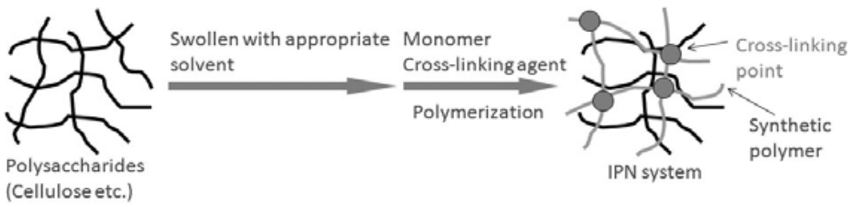


Fig. 4. Schematic image of interpenetrating polymer network (IPN) system.

from the full-IPN, in which it is composed of a non-cross-linked polymer entrapped in another polymer networks. Since the imidazolium-type ILs such as BMIMCl are good solvents for cellulose, it has been interesting to employing the imidazolium-type polymeric ILs as one component for good compatibilization with cellulose. To obtain the IPN-composite of cellulose with the polymeric IL by the in-situ polymerization method, in the first study, a polymerizable IL, 1-(4-acryloyloxybutyl)-3-methylimidazolium bromide (AcMIMBr) was used (Fig. 5) (Murakami et al., 2007).

First, cellulose was dissolved in BMIMCl (9.1 wt%) by heating at 100 °C for 24 h. Then, AcMIMBr (an equimolar amount of the glucose units in cellulose) and a radical initiator, AIBN, were added to the solution and the radical polymerization of the mixture was carried out at 80 °C for 5 h. After the polymerization mixture was washed with acetone and treated further with refluxed acetone, the residue was subjected to Soxhlet extraction with methanol to give the composite. The unit ratio of cellulose to AcMIMBr was calculated by the elemental analysis to be 1.0 : 0.63 and the ^{1}H NMR spectrum of the Soxhlet extract indicated that a part of poly(AcMIMBr) was washed out by the extraction. The IR spectrum of the resulting material suggested the structure composed of cellulose and poly(AcMIMBr). Furthermore, the thermal gravimetric analysis (TGA) and the X-ray diffraction (XRD) data supported the efficient compatibilization of cellulose with poly(AcMIMBr) in the composite. When cellulose and poly(AcMIMBr) were simply mixed in BMIMCl and the obtained mixture was subjected to the same isolation procedure as that for the aforementioned composite, almost of poly(AcMIMBr) was removed out. This result indicated that the simple mixing method of cellulose with poly(AcMIMBr) in BMIMCl was not useful for the efficient compatibilization.

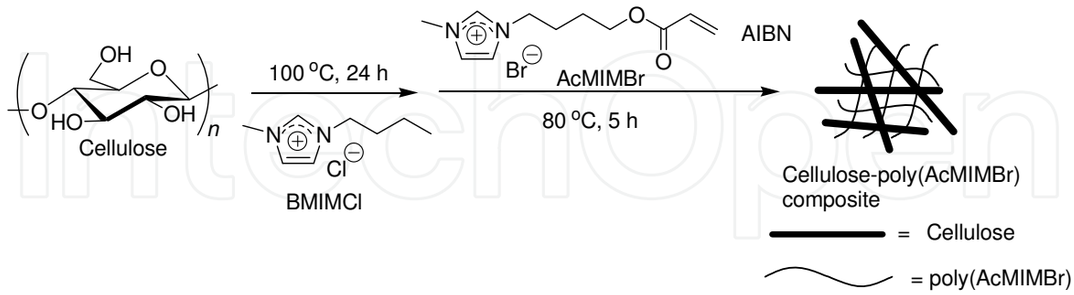


Fig. 5. Preparation of cellulose-polymeric IL composite using two ILs, BMIMCl and AcMIMBr.

Although the aforementioned approach was the efficient for the preparation of the cellulose-polymeric IL composites, the procedure should be improved due to the following disadvantageous points; (1) the necessity of two kinds of ILs and (2) the instability of the obtained composites toward solvents. To solve the second problem, the polymerizable IL having two polymerizable groups was employed, which was polymerized by a radical initiator to give the insoluble and stable cross-linked polymeric IL. Thus, in the improved

procedure for the preparation of cellulose-polymeric IL composites in the next paper, a combined use of a polymerizable IL having acryl and vinyl groups (1-(3-acryloyloxypropyl)-3-vinylimidazolium bromide, AcVIMBr) with AcMIMBr (an alkyl group = propyl) was conceived (Fig. 6) (Takegawa et al., 2009). The former acted as a cross-linker in the produced polymeric ILs by the radical copolymerization of these two ILs. Therefore, the property of the polymeric IL can be changed by the feed ratio of the two ILs in the polymerization. Furthermore, it was found that a mixture of these polymerizable ILs mostly disrupted the crystalline structure of cellulose by pre-treatment, indicating the preparation of the composites to exclusion of use of the solvent IL such as BMIMCl unlike the case in the first study.

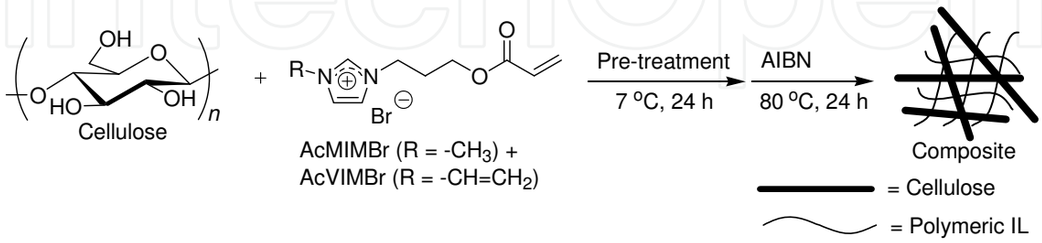


Fig. 6. Preparation of cellulose-polymeric IL composite using acrylate-type polymerizable ILs.

Therefore, for the preparation of the composites, first, cellulose (30 wt% for AcMIMBr + AcVIMBr) was pre-treated in mixtures of AcMIMBr and AcVIMBr with various weight ratios (100 : 0 – 50 : 50) at 7 °C for 24 h. The ability of the ILs that disrupted the crystalline structure of cellulose was evaluated by the XRD and TGA measurements of the pre-treated mixtures. Consequently, the analytical data indicated that the crystalline structure of cellulose was largely disrupted by the pre-treatment. Then, the formation of the composites was performed by the in-situ polymerization of the polymerizable ILs in the pre-treated mixtures. After AIBN was added to the pre-treated mixtures, the mixtures were heated at 80 °C for 24 h, resulting in the composites without any further isolation and purification procedures. The XRD and TGA results of the resulting composites indicated good compatibility of cellulose and the polymeric ILs in the composites in all cases. The compatibility between cellulose and the polymeric ILs in the composites was also evaluated by the SEM observation. The SEM images of the surface and inside area in the composite showed the completely different morphology from those of the standard cellulose, supporting the good compatibility of two components in the composite (Fig. 7). The stability of the composites was examined by washing with methanol by the Soxhlet extraction manner. After washing the composites obtained by using the mixtures of AcMIMBr and AcVIMBr, the unit ratios of cellulose to the polymeric ILs were hardly changed from those before washing. On the other hand, the content of the polymeric IL in the composite resulted by using AcMIMBr alone decreased by washing. The results indicated that the composites from the mixtures of AcMIMBr and AcVIMBr were very stable because of consisting of the cross-linked polymeric IL components formed by the copolymerization of the two polymerizable ILs. In contrast, the component of the polymeric IL in the composite from AcMIMBr alone was washed out, due to its linear structure, which was soluble in methanol. The mechanical property of the composites obtained from the mixtures of AcMIMBr and AcVIMBr with the various weight ratios was evaluated by the stress-strain curves under tensile mode. The composite from AcMIMBr alone showed the more elastic property compared with other composites containing cross-linked poly(AcMIMBr/AcVIMBr). The higher contents of the units from AcVIMBr in the composites affected to sustain the higher stresses until 30 wt% of AcVIMBr in the mixture of the two polymerizable ILs was used.

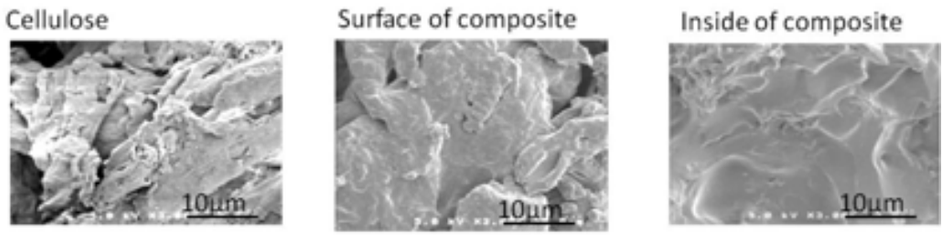


Fig. 7. SEM images of cellulose and composite.

The above in-situ polymerization method was extended to use another polymerizable IL, which was an IL having vinylbenzyl and vinyl polymerizable groups (1-vinyl-3-(4-vinylbenzyl)imidazolium chloride, VVBnIMCl) (Fig. 8) (Kadokawa et al., 2008a). This IL gives the polymeric IL composed of the polystyrene main-chain by radical polymerization. The preparation of the composites composed of cellulose and poly(VVBnIMCl) was carried out by the same procedure as that using AcMIMBr/AcVIMBr. Thus, cellulose (9.1 – 50.0 wt%) was first pre-treated with VVBnIMCl at 7 °C for 24 h. The XRD profile of the pre-treated mixture (33.3 wt%) showed only the slight diminution of the crystalline peaks. This result in comparison with that using AcMIMBr/AcVIMBr indicated that the ability of AcMIMBr/AcVIMBr disrupting the crystalline structure of cellulose was much higher than that of VVBnIMCl. However, the TGA result of the pre-treated mixture (33.3 wt%) using VVBnIMCl exhibited the similar curve as that using AcMIMBr/AcVIMBr, where an onset weight loss at around 250 °C due to the thermal degradation of cellulose was observed, which was ca. 50 °C lower than that of a standard cellulose. The TGA data indicated that the cellulose chains were partially swollen in the pre-treated mixture using VVBnIMCl.

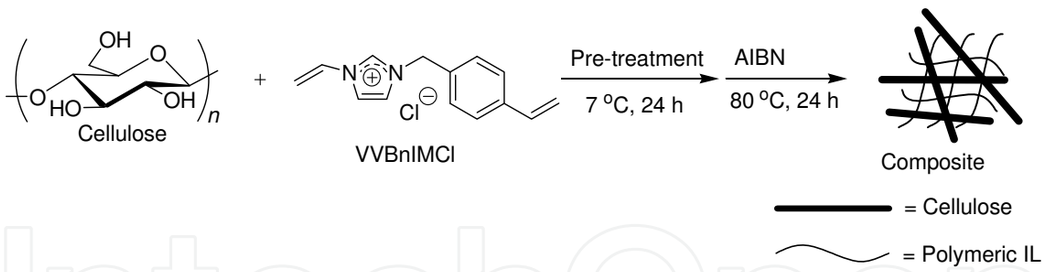


Fig. 8. Preparation of cellulose-polymeric IL composite using vinylbenzyl-type polymerizable IL.

After AIBN was added to the pre-treated mixtures, the mixtures were heated at 80 °C for 24 h to occur the radical polymerization. The composites were thus obtained without any isolation and purification procedures. The XRD and TGA results of all the composites indicated the partial disruption of the crystalline structure of cellulose. The SEM images of the composite supported good compatibility between cellulose and poly(VVBnIMCl) in the composite. The mechanical properties of the composites with 9.1, 33.3, and 50.0 wt% cellulose contents were evaluated by the tensile testing. The composites sustained the stresses in the range 2.5 – 6.5 MPa and the strains at break were 1.3 – 2.0 %. The higher content of cellulose in the composite (50 wt%) caused a brittle property. However, the appropriate content of cellulose affected to sustain higher stress. Consequently, the composite containing cellulose of 33.3 wt% indicated good mechanical property. Because of

the presence of poly(VVBnIMCl) with the cross-linked structure in the composite, it showed the good stability toward washing with methanol.

This in-situ polymerization method was applied to the preparation of cellulose-based ionic porous material compatibilized with the polymeric IL (Fig. 9) (Prasad et al., 2010). This was achieved by combining the in-situ polymerization method with the templating technique using the oil/IL emulsion system. The in-situ polymerization of a mixture of AcMIMBr and AcVIMBr was first performed in a solution of cellulose in a solvent of 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 materials ascertained from the SEM images were found to be around 0.15 – 1.3 μm accompanied with the smaller sizes of 30 – 70 nm (Fig. 10).

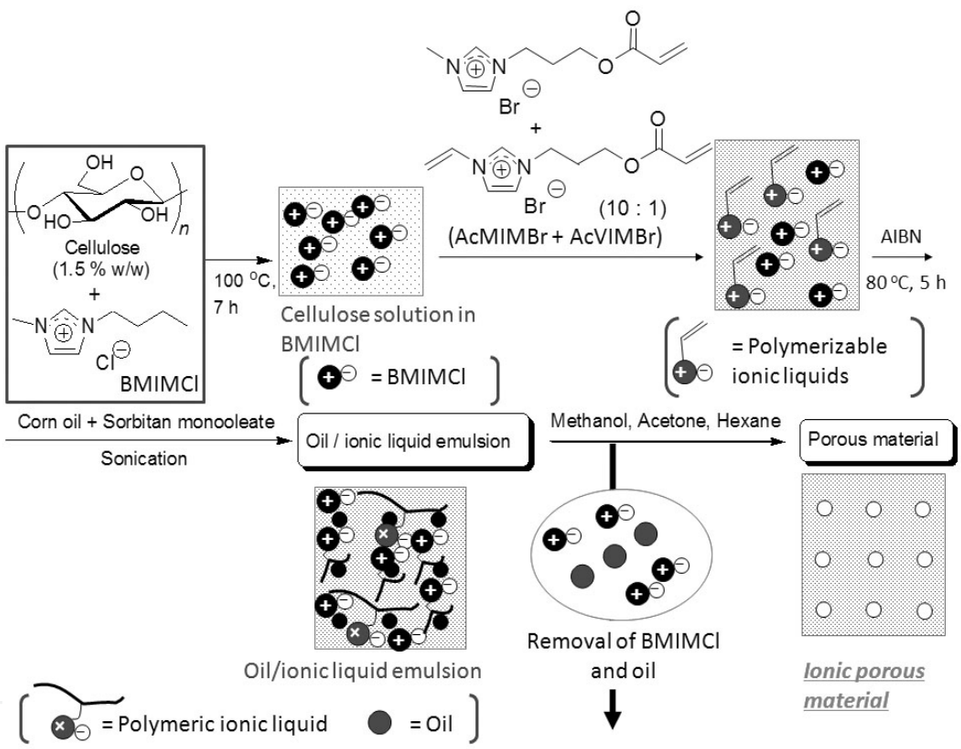


Fig. 9. Schematic image for formation of cellulose-based ionic porous material compatibilized with polymeric IL.

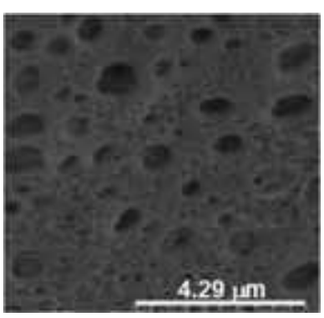


Fig. 10. SEM image of porous material.

2.3 Preparation of carrageenan-polymeric IL composites

Seaweed-originated polysaccharides like agarose and carrageenan have been used to prepare some functional materials such as electrical conductive materials by incorporating salts into their gel matrices as well as by doping with conducting polymers such as polyaniline and polypyrrole. Following the preparation of the aforementioned cellulose composites with the polymeric ILs, the new composite materials using *ι*-carrageenan of a seaweed polysaccharide was also prepared by compatibilizing with the polymeric ILs by means of in-situ polymerization technique (Fig. 11) (Prasad & Kadokawa, 2010). *ι*-Carrageenan is a water-soluble phycocolloid extracted from red algae consisting of alternating 1,3-linked α-D-galactopyranose unit and 1,4-linked β-3,6-anhydro-D-galactopyranose unit with sulfates on C-4 of the galactopyranose unit and C-2 of the anhydro-D-galactopyranose unit (Section 3.2). Due to the presence of the charges, it is expected to form well-miscible composites with the polymeric ILs through cross-linking via ionic exchange, which possibly contributes to improving the mechanical properties of the materials. It has also been considered that the material may exhibit the electrical conductivity due to the ionic nature. Therefore, the preparation of the composite materials composed of *ι*-carrageenan and the polymeric ILs by the in-situ polymerization of the polymerizable ILs was performed. The polymerizable ILs used were AcVIMBr and VVBnIMCl. For the preparation of the composite using AcVIMBr, BMIMCl was used for the dissolution of *ι*-carrageenan because its direct soak in AcVIMBr was not possible due to the high viscosity of AcVIMBr. Thus, *ι*-carrageenan was first dissolved in BMIMCl by heating at 100 °C for 7 h. Then, the radical polymerization of AcVIMBr with AIBN in the solution was performed, followed by the work-up procedure, to give the composite. Because unlike AcVIMBr, VVBnIMCl was no viscous, on the other hand, the composite using VVBnIMCl was prepared without use of any solvent for dissolution of *ι*-carrageenan. The CP-MS ^{13}C NMR and IR spectra of the resulting composites fully supported which were composed of *ι*-carrageenan and the corresponding polymeric ILs.

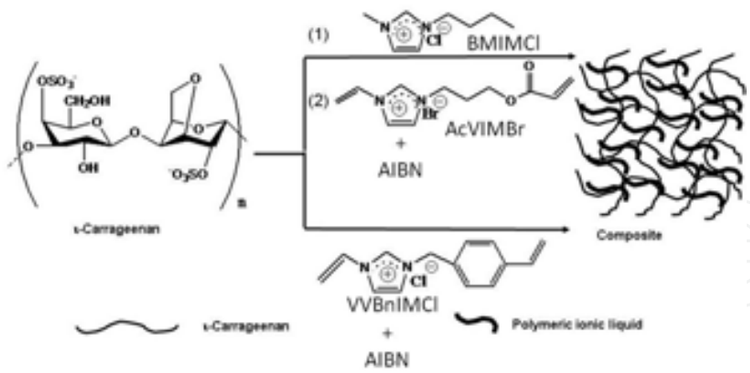


Fig. 11. Preparation of *ι*-carrageenan-polyIL composites.

Immiscible components were not seen in the charge coupled device (CCD) camera views (mm scale) of the surfaces of the composites. However, the SEM images with the nm scale of the two composites exhibited the different phase structures. The SEM image of the composite with poly(AcVIMBr) showed loose structures with nano scale distributions, whereas closer packed nano structures were observed in the SEM image of the composite with poly(VVBnIMCl). The morphology for the former material was probably caused by the removal of the solvent, BMIMCl, during the work-up procedure.

The mechanical properties of the composites of *ι*-carrageenan with poly(AcVIMBr) and poly(VVBnIMCl), which were evaluated under compressive mode, showed the fracture stresses of 108.07 and 102.0 MPa with the fracture strains of 25.0 and 10.7 %, respectively. These values were larger than those of the respective cellulose composite with each polymeric IL. The good mechanical properties of the present composites were reasonably explained by the formation of the good miscibility as observed in the SEM images, which were owing to the cross-linking through the ionic exchange between *ι*-carrageenan and the polymeric ILs. The electrical conductivities of the composites with poly(AcVIMBr) and poly(VVBnIMCl) were measured to be 6.2×10^{-4} and 1.6×10^{-4} S cm^{-1}, respectively, which were comparable to the conductance of semiconductor. On the other hand, cellulose composites with poly(AcVIMBr) and poly(VVBnIMCl) showed the electrical conductivity values of ca. 1.3×10^{-5} and 2.8×10^{-5} S cm^{-1}, respectively. The higher electrical conductivity of the present composites indicated the role of the effective ionic exchange during the formation of the composites, due to the presence of charges in *ι*-carrageenan.

3. Preparation of ionic liquid-gels of polysaccharides

3.1 Preparation of ionic liquid-gels of cellulose

When a solution of cellulose in BMIMCl (13.0 wt%) was left standing at room temperature for 7 days, it was found that the formation of a gel gradually took place with exclusion of excess BMIMCl from the gel matrix (Fig. 12) (Kadokawa et al., 2008b). Thus, the gel was purified by washing with ethanol to remove the excluded BMIMCl and dried under reduced pressure. The resulting gel had flexible and manipulatable natures and was characterized by the elemental analysis, XRD, and TGA. The XRD result of the gel indicated that the crystalline structure of cellulose was mostly disrupted in the gel. The elemental analysis and TGA data suggested that gel was composed not only of cellulose and BMIMCl, but also of water. On the basis of the above analytical results, it was considered that the gel was produced by the formation of non-crystalline aggregates of cellulose in the solution during gradually absorbing water owing to the strong hygroscopic nature of BMIMCl (Fig. 13). The aggregates probably acted as cross-linking points for the gelation.

When the gel was heated at 120 °C, it was gradually softened, and converted into a fluid at 150 °C. The soft material, which was obtained by heating the gel at 120 °C for 2 h, could be transferred to the gel form again by standing it at room temperature for 2 days. The regenerated gel was still flexible and was more transparent than the primary formed gel. Because the aggregates of cellulose as the cross-linking points in the regenerated gel were probably dispersed well by the heating-cooling process compared with those in the primary gel, the gel after regeneration was more transparent than before.

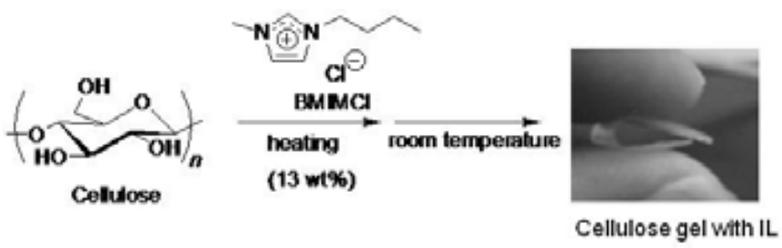


Fig. 12. Procedure for preparation of cellulose gel with IL.

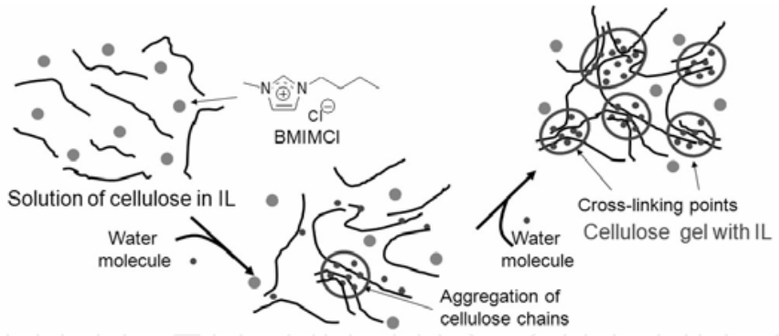


Fig. 13. Schematic image for procedure of formation of cellulose gel with IL.

This gelation technique was extended to the preparation of cellulose/starch composite gel with BMIMCl (Kadokawa et al., 2009). When the mixture of cellulose (9.1 wt%) and starch (4.8 wt%) in BMIMCl was heated at 100 °C for 24 h, a homogeneous liquid was formed, which was left standing at room temperature for 4 – 6 days. Consequently, the excess BMIMCl was excluded from the liquid to take place the gelation. Thus, the resulting gel was purified by washing with methanol to remove the excluded excess BMIMCl and dried under reduced pressure. In the XRD profile of the gel, the diffraction peaks due to the crystalline structures of the standard cellulose and starch were not obviously exhibited, indicating that the crystalline structures of the polysaccharides were largely disrupted in the gel. The results of the elemental analysis and TGA indicated that the gel was composed of the polysaccharides, BMIMCl, and water, as same as the aforementioned gel from cellulose and BMIMCl. From the data, the similar gelation process was conceived as that for the gel of cellulose with BMIMCl.

The homogeneous mixture of cellulose and starch (9.1 wt% each) in BMIMCl, obtained by heating as same as above, had a very viscous nature, and thus, could be raised from the surface. The resulting fine linear material was subjected to the formation of the composite fibrous material by soaking into acetone. The SEM picture of the obtained material showed the fiber form with ca. 100 – 200 μm diameters, but the crystalline and particle images, which were observed in the SEM pictures of the standard cellulose and starch, were not seen. The XRD result of the material indicated that the crystalline structures of cellulose and starch chains were not regenerated well, suggesting the good compatibilization of the two polysaccharides in the fibrous material.

It was found that a clear liquid of chitin (4.8 wt%) with ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr) was obtained by heating a mixture of chitin with AMIMBr at 100 °C for 48 h (Prasad, Murakami et al., 2009). The disappearance of the chitin powder in the liquid was confirmed by the CCD camera view and the SEM observation. The IR spectrum, TGA curve, and XRD profile of the regenerated chitin from the liquid as well as the analytical data of its hexanoyl derivative supported that the degradation and decreasing the molecular weight of chitin did not frequently occur during the dissolution process. On the other hand, when a mixture of 6.5 wt% chitin was soaked in AMIMBr at room temperature for 24 h, heated at 100 °C, and then cooled to room temperature, it turned into the gel-like form. The dynamic rheological measurements showed that both 4.8 wt% and 6.5 wt% chitins with AMIMBr behaved as the weak gels. However, it was seen that the obtained 6.5 wt% chitin with AMIMBr did not flow upon leaning a test tube, while the 4.8 wt% chitin with AMIMBr started to flow upon leaning (Fig. 14). The much lower yield stress

of 4.8 wt% chitin with AMIMBr than that of 6.5 wt% chitin with AMIMBr supported that 4.8 wt% chitin with AMIMBr can flow under gravitation.

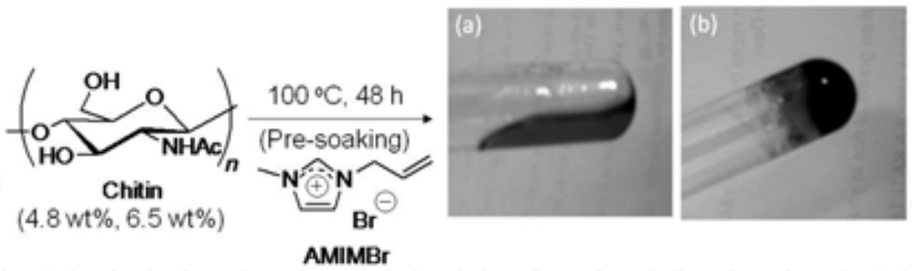


Fig. 14. Dissolution and gelation of chitin with IL; 4.8 wt% (a) and 6.5 wt% (b).

Thus, the preparation of the chitin/cellulose composite gel and film using the two ionic liquids, AMIMBr and BMIMCl, was performed (Fig. 15) (Takegawa et al., 2010). First, chitin and cellulose were dissolved in each appropriate ionic liquid. Then, the two liquids were mixed in the desired ratios at 100 °C to give the homogeneous mixtures. The gels were obtained by standing the mixtures at room temperature for 4 days and the films were obtained by casting the mixtures on a glass plate, followed by soaking in water and drying. The resulting gels and films were characterized by the XRD and TGA measurements, which showed relatively good miscibility among the polysaccharides and the ionic liquids in the materials. The mechanical properties of the gels and films were changed depending on the ratios of chitin to cellulose in the materials.

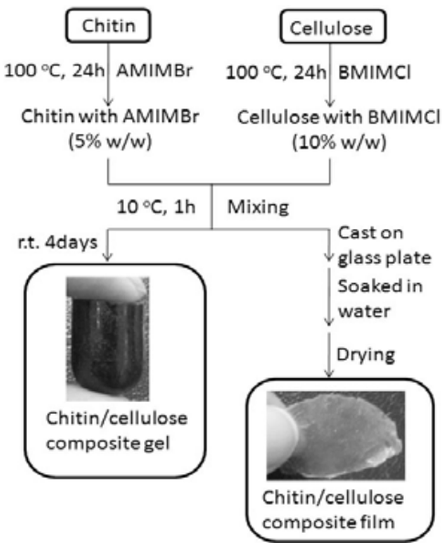


Fig. 15. Preparation procedure for chitin / cellulose composite gel and film with ILs.

The chitin/cellulose composite gel with ionic liquids was employed as the novel electrolyte for an electric double layer capacitor (EDLC) (Yamazaki et al., 2009, Yamazaki et al., 2010a, 2010b). First, the gel was treated with an aqueous 2.0 mol/L H_2SO_4 solution for 3 h. Electrochemical characteristics of the obtained acidic chitin/cellulose composite gel electrolyte were investigated by galvanostatic charge-discharge measurements. The test cell with the composite gel electrolyte showed a specific capacitance of 162 F/g at room temperature, which was higher than that for a cell with an H_2SO_4 electrolyte (155 F/g). The

composite gel electrolyte exhibited the excellent high-rate discharge capability in a wide range of current densities as well as an aqueous H_2SO_4 solution. Moreover, the discharge capacitance of the test cell retained over 80 % of its initial value in 10^5 cycles even at a high current density of 5000 mA/g. The temperature dependence of the ionic conductivity for the composite gel electrolyte was the Arrhenius-type and similar to an aqueous H_2SO_4 solution. Furthermore, the self-discharge of the EDLC cell with the composite gel electrolyte was advantageously slow in comparison with the cell containing only the aqueous H_2SO_4 solution. The above results indicated that the acidic chitin/cellulose composite gel electrolyte had a practical applicability to an advanced EDLC with the excellent stability and working performance.

3.2 Preparation of ionic liquid-gels of food hydrocolloids

Besides the abundant polysaccharides like cellulose, starch, and chitin, many kinds of natural polysaccharides from various sources such as plants, animals, seaweeds, and bacteria have been known. For example, some polysaccharides are used as hydrocolloids for a stabilizer, a viscous agent, and a structure provider in food industries (Fig. 16). However, there have not been many reports on the use of these food hydrocolloids as a source of practical materials.

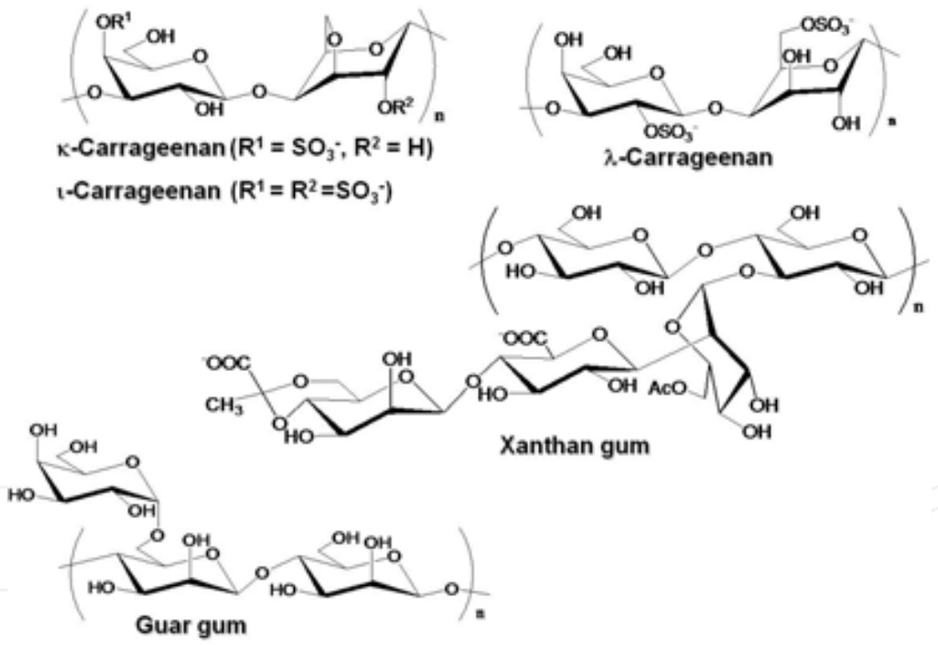


Fig. 16. Structures of typical food hydrocolloids, carrageenans, xanthan gum, and guar gum.

Carrageenan is a water soluble phycocolloid extracted from red algae and is used mostly as a stabilizer and a structure provider in the food and ice cream industries. Three major varieties of carrageenans are known, which are *κ*-, *ι*-, and *λ*-carrageenans. They differ in the number and position of sulfate groups on the repeating garactopyranose units. To efficiently employ the food hydrocolloids as a source of the materials, the gelling system of *κ*-, *ι*-, and *λ*-carrageenans with BMIMCl was reported (Prasad, Kaneko et al., 2009). First, 13.0 wt% carrageenan was dissolved in BMIMCl by heating at 100 °C for 10 h with stirring. After the

solution was cooled to room temperature, a gel was formed, which could suitably be handled after 12 h of standing upon addition of acetone and excess ionic liquid leaching out from the gel was washed out with ethanol. κ-Carrageenan gave the formation of hard gel while other two carrageenans gave the formation of softer gels with BMIMCl (Fig. 17). A schematic representation for the formation of the gels is shown in Fig. 18. At elevated temperatures, carrageenans are soluble in BMIMCl, and thus exist as random coils in the solutions. Upon cooling, three dimensional networks develop, leading to the formation of junction zones in the polysaccharide chains (Phase 1). The subsequent treatment of the mixture with acetone causes further aggregation and stabilization of the junction zones, particularly for the parts close to the surface, resulting in a stronger gelling system with the exclusion of BMIMCl (Phase 2). The excluded excess BMIMCl was washed out with ethanol to give the formation of the compact gels. The composite gels of carrageenans and cellulose with BMIMCl could be obtained by the same procedure as that described above. The mechanical properties of the carrageenan gels, as well as the composite gels with cellulose and BMIMCl, under the compressive mode were better than those of the hydrogels of κ- and ι-carrageenans and the cellulose gel with BMIMCl.

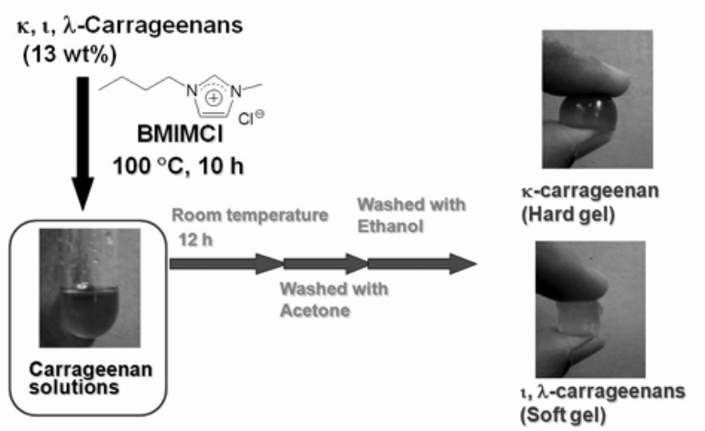


Fig. 17. Preparation of carrageenan gels with IL.

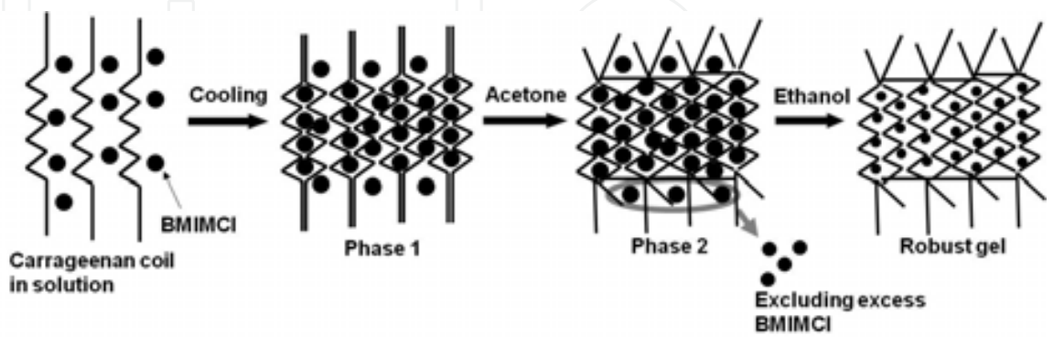


Fig. 18. Schematic representation for formation of carrageenan gels with IL.

Xanthan gum, which is a water soluble polysaccharide produced by *Xanthomonas campestris*, is also a useful food hydrocolloid. It has a cellulose main-chain with anionic trisaccharide side chains attached to alternating glucose units in the main-chain. It was found that

xanthan gum/BMIMCl gels in various contents were obtained from the 9.1 – 50 wt% solutions of xanthan gum in BMIMCl (Izawa et al, 2009, Izawa & Kadokawa, 2010). When the solutions were left standing at room temperature for 30 min, they turned totally into the gel form (Fig. 19). The process of gelation was completely different from that for the aforementioned gels of cellulose and carrageenan with BMIMCl because long duration or treatment with appropriate organic solutions was required to generate the stable gels in their cases. It was considered that the ion-exchange of carboxylate metal cations in the original xanthan gum with BMIMCl took place during the gelation to form imidazolium-carboxylate pair in xanthan gum (Fig. 20). All the gels exhibited good mechanical properties under compressive mode. The 9.1 wt% gel showed elastic nature and the properties gradually changed to harder with increasing the contents of xanthan gum in the gels. It should be additionally noted that these gels did not have apparent fracture points. Interestingly, the gels had the sufficient strength to apply to the tensile test. The 9.1 and 16.7 wt% gels showed good elasticity, in which they were elongated to strain values near by 400%. In contrast, the 50 wt% gel had a hard nature and a fracture stress was 2.1 MPa. Furthermore, the xanthan gum/BMIMCl gels exhibited thermally induced shape-memory effect. First, a desired permanent shape of the gel was prepared by heating-cooling process using an appropriate mold. Subsequently, the gel was softened and deformed by heating at around 50 ^{o}C, and then the intended temporary shape was fixed by cooling the gel at room

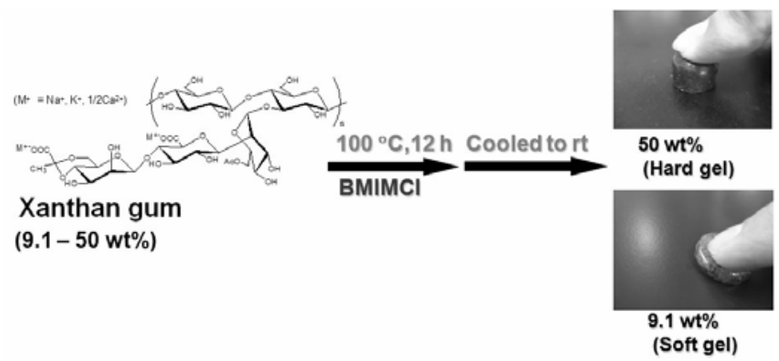


Fig. 19. Preparation of xanthan gum gels with IL.

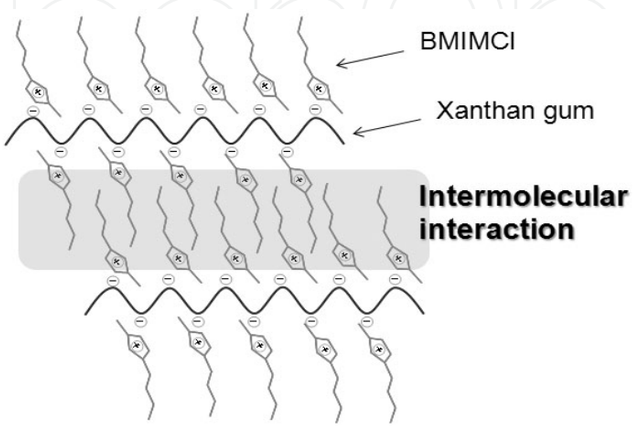


Fig. 20. Ionic exchange between xanthan gum and BMIMCl.

temperature. The temporary shape of the gel gradually returned back to the permanent shape by heating at around 50 °C. Consequently, the gel was almost recovered from temporary shape to permanent shape. It was supposed that the shape memory behavior of the gel was probably generated by the effect of ion-exchange during the gel formation and the rigid nature of the xanthan gum main-chain (Fig. 20).

The 9.1 wt% xanthan gum/BMIMCl gel was converted into a hydrogel of xanthan gum by soaking it (1.15 g) in water (100 mL) (Fig. 21). A water content of the obtained hydrogel (primary form) was estimated to be 94.1 wt%, indicating the formation of the xanthan gum hydrogel with high water content. This material was completely different from the aqueous xanthan gum dispersion because that was thixotropic gel-like paste. The elemental analysis data showed that the gel still contained 2.4 equivalents of the imidazolium groups to a repeating unit of xanthan gum. This is probably due to the presence of ion pair between the imidazolium and carboxylate formed by ion-exchange of carboxylate metal salts in the original xanthan gum with BMIMCl during the formation of the xanthan gum/BMIMCl gel.

Further ion-exchange of the imidazolium groups in the primary formed hydrogel with Ca^{2+} was attempted by soaking it in 0.2 mol/L $CaCl_2$ aqueous solution to obtain an ionically cross-linked xanthan gum hydrogel with divalent cations (Ca^{2+} form) (Fig. 21). The water content of the resulting hydrogel was estimated to be 85.2 wt%, indicating shrinkage of this material compared with the primary hydrogel. In addition, the ionically cross-linked

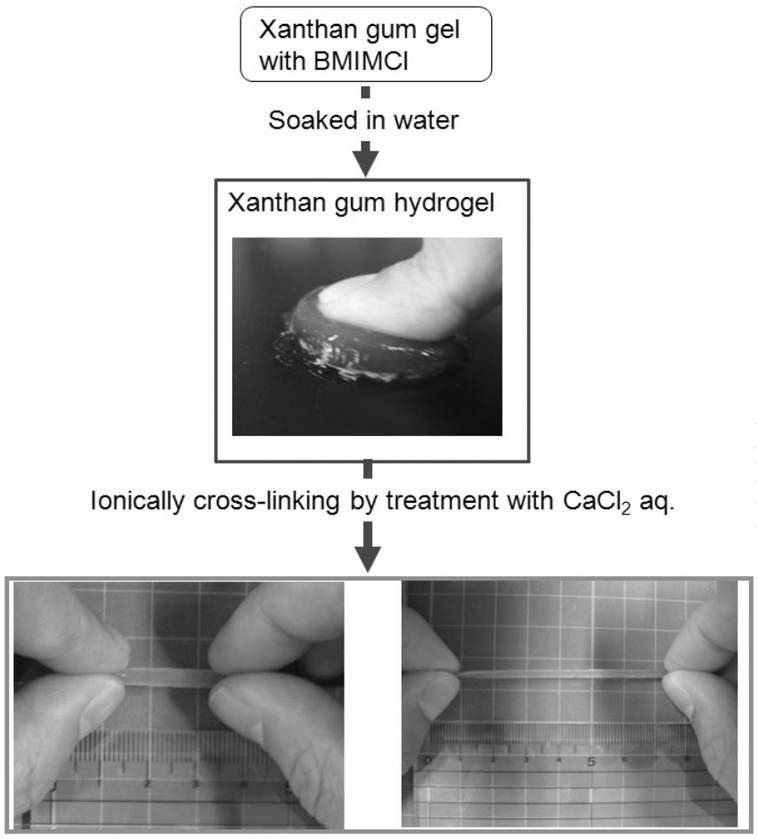


Fig. 21. Preparation of xanthan gum hydrogels from xanthan gum gel with IL.

hydrogel showed a reversible swelling-shrinking behavior. When the ionically cross-linked hydrogel was soaked in water for 1 day, it was gradually swollen to be 134.2% weight, which contained water of 24.4 times weights of xanthan gum. Soaking the swollen hydrogel in 0.2 mol/L $CaCl_2$ aqueous solution for 1 day caused rapid shrinkage to be 7.7% weight. The swelling-shrinking cycle of the hydrogel was repeated further twice. These results indicated that the present hydrogel exhibited salt concentration-induced responsive property. This behavior was probably caused by the conformation change of xanthan gum, which was induced by ionic strength of the aqueous solution. Under compressive mode, the hydrogel in the Ca^{2+} form showed much better mechanical property than the primary formed hydrogel. The primary hydrogel was too weak to be subjected to a tensile test, whereas the hydrogel in the Ca^{2+} form had sufficient strength for tensile testing, which exhibited elongation up to 550%. These results suggested that cross-linking with Ca^{2+} in the hydrogel strongly contributed to enhancement of mechanical properties. The ion-exchanged hydrogels with Na^{+} and Fe^{3+} were also prepared by soaking the primary hydrogel in NaCl and $FeCl_3$ aqueous solutions, respectively.

The gel formation of food hydrocolloids with BMIMCl was not limited to the anionic polysaccharides, but extended to a neutral polysaccharide, which was guar gum (GG) (Prasad, Izawa et al., 2009). Guar gum (GG) is a galactomannan extracted from the seed of the leguminous shrub *Cyamopsis tetragonoloba* and consists of a (1→4)-linked β-D-mannopyranose main-chain with a branched α-D-garactopyranose unit at 6 position. As a typical procedure for the preparation of the gel of GG with BMIMCl (Fig. 22), first, GG (13.0 wt%) was dissolved in BMIMCl by heating at 100 °C for 5 h. After the solution was cooled to room temperature, it formed a gel, which was suitably handled after 12 h of standing upon addition of acetone and the excess BMIMCl leaching out from the gel was washed out with ethanol. However, the obtained gel started to leach out BMIMCl again after 12 h of preparation unlike other polysaccharide gels with BMIMCl described above. When the gel was further soaked in ethanol for 12 h, a stable hard material of GG with BMIMCl was obtained. The elemental analysis data of the material indicated that during the soaking process, most of BMIMCl was leached out from the gel matrices and subsequent aggregation of the GG chains existing on the surface area of the gel probably took place, causing stabilization of the material, because BMIMCl was soluble, but GG was insoluble in ethanol. The resulting hard material was further applied to the film formation. The hard material with an appropriate size was put on a compression machine and compressed applying gradually variable forces up to a maximum of ca. 10 MPa. Since expulsion of some BMIMCl from the material due to the compression was observed, the film thus obtained was further soaked in ethanol for 2 h to remove the excluded BMIMCl and dried at room temperature (Fig. 20). The film was stable and did not leach out BMIMCl even after long storage under ambient conditions. The tensile testing of the film showed a fracture stress of 17 MPa with a fracture strain of 18.2%. It was observed that the film became hard upon heating and hence it could be arranged to give a shape at higher temperature (Fig. 23). For example, the film was twisted to a desired shape and was heated to a temperature of ca. 70 – 80 °C. The film became hard immediately and retained the shape for a few minutes after the heating was stopped. When the film was then left standing at room temperature, it gradually became soft and returned to the original shape after ca. 15 minutes.

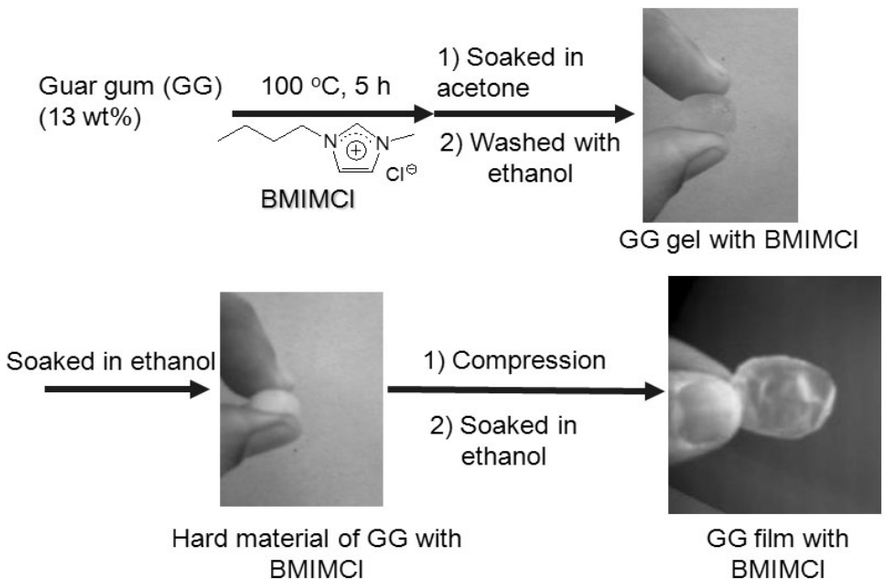


Fig. 22. Preparation of guar gum gel and film with IL.

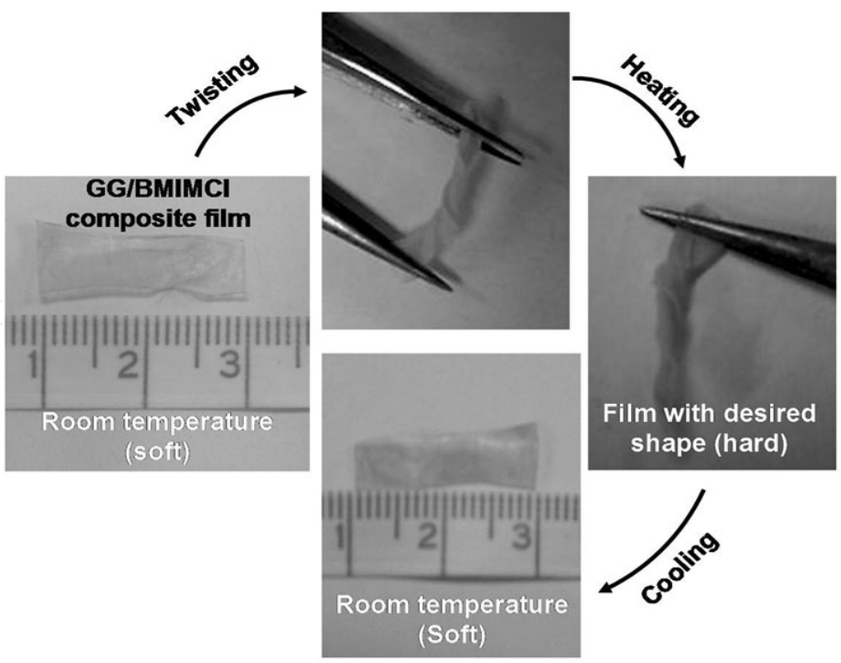


Fig. 23. Temperature-induced shaping ability of guar gum film with BMIMCl.

4. Conclusion

This chapter overviewed the preparation of polysaccharide-based materials compatibilized with ILs. Because of the solubility, processability, and feasibility problems of the polysaccharides due to their numerous hydrogen bonds, they have often showed difficulty in employing in a wide variety of materials. On the basis of the viewpoint that the imidazolium-type ILs have good affinity with the polysaccharides, the well-compatible materials of the polysaccharides with the ILs have been produced from not only abundant polysaccharides but also food hydrocolloids. This type of the research described herein provides new polysaccharide-based functional materials, which leads to efficient usage of the polysaccharides as an organic resource in the practical materials. Therefore, the studies in this research field will increasingly develop with attracting the much attention, which contributes to construction of green and sustainable society in the future.

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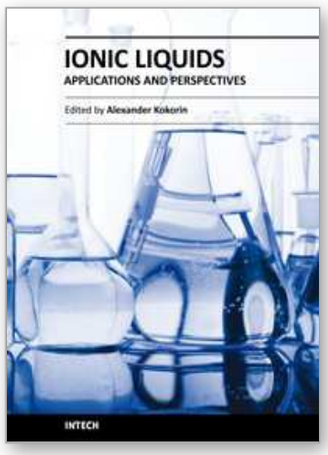
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This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

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