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Preparation of chitin/cellulose composite gels and films with ionic liquids

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ABSTRACT

In this study, we performed preparation and characterizations of the chitin/cellulose composite gels and films using the two ionic liquids, 1-allyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride. 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 for 4 days. On the other hand, the films were obtained by casting the mixtures on glass plates, followed by soaking in water and drying. The obtained gels and films were characterized by XRD and TGA measurements. The mechanical properties of the gels and films were evaluated under compressive and tensile modes, respectively.

1. Introduction

Polysaccharides are widely distributed in nature and have been regarded as structural materials and as suppliers of water and energy (Stryer, 1995). They have increasingly been important because they possess unique structures and properties being recently better understood, which are much different from those of typical synthetic polymers. Of the many kinds of polysaccharides, cellulose and chitin are the most important biomass resources; cellulose is the most abundant organic substance on earth and chitin is the second most one.

Cellulose consists of a chain of β-(1→4)-linked glucose residues (Fig. 1) (Klemm, Heublein, Fink, & Bohn, 2005). So far, the fundamental and practical studies on cellulose have been carried out, which concern its structure, chemical and physical properties, biosynthesis, and morphology. Chitin is structurally similar to cellulose, but it is an amino polysaccharide having acetamide groups at the C-2 positions in place of hydroxy groups in cellulose (Fig. 1) (Muzzarelli, 1977). Despite its huge annual production and easy accessibility, chitin still remains as an unutilized biomass resource primary because of its intractable bulk structure, and thus, only limited attention has been paid to chitin, principally from its biological properties (Muzzarelli, Jeuniaux, & Gooday, 1986). Although considerable efforts are still being devoted to extend other novel applications to cellulose and chitin on the basis of the viewpoint for efficient use as the biomass resources, the lack of solubility of these polysaccharides in water and common organic solvents causes difficulties in improving their processability, fusibility, and functionality. The solubility problem is due to the stiff molecules and close chain packing via the numerous inter- and intra-molecular hydrogen bonds caused by the hydroxy groups as well as the acetamide groups in the sugar residues. To date, only a limited number of solvent systems for cellulose and chitin had been found, for example, LiCl/*N*,*N*-dimethylacetamide system (Terbojevich, Cosani, Conio, Ciferr, & Bianchi, 1985; Uragami, Ohsumi, & Sugihara, 1981) and NaOH/(thio)urea aqueous solution (Cai & Zhang, 2005; Hirano & Midorikawa, 1998; Zhang, Guo, & Du, 2002) are well-known as the solvents for these polysaccharides. In the previous publications, cellulose/chitin composite beads, films, and membranes have been prepared using these solvent systems (Kondo, Kasai, & Brown, 2004; Liang, Zhang, & Xu, 2007; Zhang et al., 2002; Zheng, Zhou, Du, & Zhang, 2002; Zhou, Zhang, & Guo, 2005).

It has been reported that a variety of room temperature ionic liquids can be used to dissolve cellulose (Feng & Chen, 2008; Liebert & Heinze, 2008). For example, it was found that 1-butyl-3-methylimidazolium chloride (BMIMCl, Fig. 1) dissolved cellulose in relatively high concentrations (Swatloski, Spear, Holbrey, & Rogers, 2002). In the following papers by the same research group, the cellulose films were further obtained by casting the solutions of cellulose in BMIMCl onto a glass plate, followed by reconstitution by the addition of water (Turner, Spear, Holbrey, Daly, & Rogers, 2005; Turner, Spear, Holbrey, & Rogers, 2004). We have also studied preparation of new materials using cellulose and ionic liquids (Kadokawa, Murakami, & Kaneko, 2008a; Murakami, Kaneko, &

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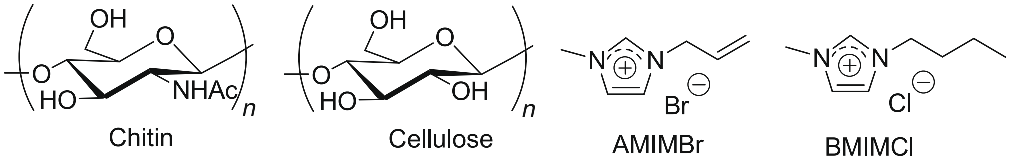

Fig. 1. Structures of chitin, cellulose, AMIMBr, and BMIMCl.

Kadokawa, 2007). As the recent result in the course of the work, we reported formation of a gel from a solution of cellulose in BMIMCl (Kadokawa, Murakami, & Kaneko, 2008b; Kadokawa, Murakami, Takegawa, & Kaneko, 2009), which was obtained by keeping the solution at room temperature for several days. This method for the preparation of the gel materials with ionic liquids has been extended to other polysaccharides such as carrageenan and guar gum (Prasad, Izawa, Kaneko, & Kadokawa, 2009; Prasad, Kaneko, & Kadokawa, 2009). On the other hand, only a few examples have been reported regarding the dissolution of chitin with ionic liquids (Mantz et al., 2007; Wu, Sasaki, Irie, & Sakurai, 2008; Xie, Zhang, & Li, 2006). For the development of studies on chitin using the ionic liquids, therefore, we have considered to find other ionic liquids which can dissolve chitin. Then, the dissolution of chitin with the ionic liquids can be extended to the further work, e.g., the production of new materials composed of chitin.

On the basis of the above viewpoints, recently, we found that an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr, Fig. 1)) formed a clear liquid with chitin and evaluated its weak gel nature by rheological analysis in a further work (Prasad et al., 2009). In the recent communication, we also reported preparation and electrochemical properties of chitin/cellulose composite gel electrolyte containing binary ionic liquids with aqueous H_2SO_4 for an electric double layer capacitor (Yamazaki et al., 2009). The composite gel was prepared from a homogeneous mixture obtained from a liquid of chitin with AMIMBr and a liquid of cellulose with BMIMCl according to the similar method as that for the aforementioned gel of cellulose with BMIMCl (Kadokawa et al., 2008b).

In this paper, we report the detailed study on the chitin/cellulose composite gels with the ionic liquids, AMIMBr and BMIMCl, including characterization and mechanical property. Moreover, we also describe preparation, characterization, and mechanical property of the chitin/cellulose composite films with the ionic liquids. The films were simply obtained by soaking the homogeneous mixtures of chitin/cellulose with AMIMBr/BMIMCl into water.

2. Experimental

2.1. Materials

Microcrystalline cellulose from Merck was used. Chitin powder from crab shells was purchased from Nakalai Tesque, Inc. The degree of acetylation of the chitin sample was estimated by elemental analysis data to be 94.6%, which was in good agreement with that of a standard chitin (Kurita, 2001)). An ionic liquid, BMIMCl, was purchased from Sigma–Aldrich Co. An ionic liquid, AMIMBr was prepared by reaction of 1-methylimidazole with 3-bromo-1-propene according to the method modified from the literature procedure (Zhao et al., 2005).

2.2. Preparation of chitin/cellulose composite gel with ionic liquids

A typical experimental procedure for preparation of chitin/cellulose composite gel with ionic liquids was as follows (chitin:cellulose = 1:3, mol/mol). Mixtures of chitin (0.0420 g, 0.206 mmol) with AMIMBr (0.860 g, 4.24 mmol) and of cellulose (0.100 g, 0.617 mmol) with BMIMCl (1.00 g, 5.73 mmol) were independently heated at 100 °C for 24 h with stirring to give clear liquids of chitin (5% w/w) and cellulose (10% w/w) in each ionic liquid, respectively. The two liquids were mixed and heated at 100 °C for 1 h with stirring to form a homogeneous mixture. The resulting mixture was transferred to an appropriate mold and it was kept standing at room temperature for 4 days to be a gel form. The gel was taken out from a mold, soaked in acetone for 10 min, and dried under ambient conditions to give a composite gel.

2.3. Preparation of chitin/cellulose composite film with ionic liquids

A typical experimental procedure for preparation of chitin/cellulose composite film was as follows. The homogeneous mixture of chitin and cellulose in the ionic liquids prepared as described above was thinly cast on a glass plate. It was soaked in water and dried under reduced pressure to give a composite film.

2.4. Determination of molar ratios among chitin, cellulose, AMIMBr, and BMIMCl in gels and films

A weight of the gel or film sample was measured and the sample was subjected to Soxhlet extraction with methanol for 5 h. A residual part was dried under reduced pressure and the molar amounts of chitin and cellulose in the sample was calculated on the basis of a weight of the dried material and a feed ratio of the two polysaccharides used for preparation of gel or film. The methanol extract was evaporated and dried under reduced pressure. Hydroquinone dimethyl ether as an internal standard was added to the residue and the ^{1}H NMR spectrum of the mixture was measured in $CDCl_3$. The molar amounts of AMIMBr and BMIMCl in the sample was calculated on the basis of a weight of the residue and an integrated ratio of the signals due to $CH_2{=}$ of AMIMBr, $CH_2{-}N$ of BMIMCl, and aromatic protons of the internal standard.

2.5. Measurements

XRD measurements were conducted using a Rigaku Geigerflex RADIIB diffractometer with Ni-filtered CuKα radiation ($\lambda = 0.15418$ nm). TGA measurements were performed on a SII TG/DTA 6200 at a heating rate of 10 °C/min. The stress–strain curves were measured using a tensile tester (Little Senstar LSC-1/30, Tokyo Testing Machine Co.). NMR spectra were recorded on a JEOL ECX 400 spectrometer.

3. Results and discussion

The chitin/cellulose composite gels with ionic liquids were prepared according to the similar experimental manner as that for preparation of the gel of cellulose with BMIMCl (Fig. 2), described in our previous publication (Kadokawa et al., 2008b). Since we had not found any ionic liquids which had ability to dissolve both chitin and cellulose in sufficient concentrations for the present study, two kinds of the ionic liquids, i.e., AMIMBr and BMIMCl were used as follows. The clear liquids of chitin in AMIMBr (5% w/w) and of

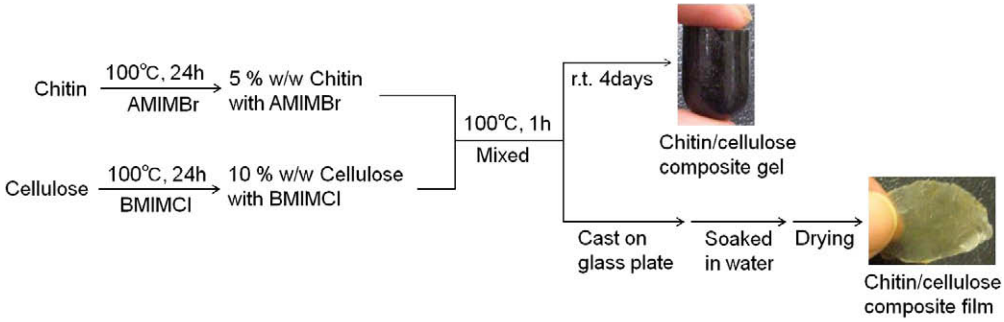

Fig. 2. Preparation procedures for chitin/cellulose composite gels and films with ionic liquids.

cellulose in BMIMCl (10% w/w) were independently prepared by heating each mixture at 100 °C for 24 h. We already confirmed in the previous literature that deacetylation, degradation, and decreasing the molecular weight of chitin did not frequently occur during the experiment for the formation of the 5% w/w clear liquid with AMIMBr (Prasad et al., 2009). Then, the two liquids in desired ratios were mixed at 100 °C to form a homogeneous mixture. The homogeneity of the mixture was confirmed by observation using a charge coupled device camera with 200 times magnification scale. After the mixture was transferred to an appropriate mold and kept standing at room temperature for 4 days, the formed gel was taken out from the mold, soaked in acetone for 10 min, and dried under ambient conditions to give a composite gel. When the feed molar ratios of chitin to cellulose were 1:3 to 1:1, the gels were facilely formed. Increasing the molar ratio of chitin to cellulose than 1:1 did not give the gel formation.

The molar ratios of each material in the gels were estimated as follows. First, the gel was subjected to Soxhlet extraction with methanol to extract the ionic liquids. The molar amounts of chitin and cellulose in the gel were calculated on the basis of a weight of the residual material and the feed ratio of the two polysaccharides used for preparation of the gel. On the other hand, the methanol extract was concentrated and analyzed by the ^{1}H NMR measurement. The molar amounts of the two ionic liquids were calculated by the integrated ratios of the ^{1}H NMR spectrum using hydroquinone dimethyl ether as an internal standard. On the basis of the above two calculations, the molar ratios of chitin, cellulose, AMIMBr, and BMIMCl in the gels were estimated, which were shown in Table 1. By comparing the ratio of each material in the gel of run 1 in Table 1 (chitin:cellulose:AMIMBr:BMIMCl = 1:1:19.5:9.7) with the corresponding feed ratio (chitin:cellulose:AMIMBr:BMIMCl = 1:1:20.0:9.3) for the gel preparation, it was suggested that little ionic liquids were leached out during the gelation process. The data in Table 1 also indicated that the larger amounts of AMIMBr were leached out during the gelation process when the higher feed ratios of the chitin liquid with AMIMBr to the cellulose liquid with BMIMCl were used for the gel preparation (run 2 and 3 in Table 1).

The XRD profiles of the gels in Fig. 3c–e exhibited little diffraction peaks due to the crystalline structures of chitin and cellulose as observed in Fig. 3a and b. Fig. 4 shows the TGA curves of the gels in comparison with those of chitin and cellulose. The TGA curves of the gels in Fig. 4c–e exhibited weight losses starting at around 200 °C, which were almost 100 °C lower than those of chitin and cellulose in Fig. 4a and b. These characterizations indicated that the crystalline structures of the polysaccharides were not maintained in the gels due to good miscibility of the two polysaccharides with the ionic liquids. The TGA curves of the gels also showed weight losses of 12.9–14.5% at temperatures up to 100 °C, which were reasonably explained by evaporation of water. These data suggested that the gels contained relatively large amounts of water, and accordingly the following similar gelation mechanism was considered as that for the gel of cellulose with BMIMCl reported in our previous paper (Kadokawa et al., 2008b). The present gels were gradually formed with absorption of water

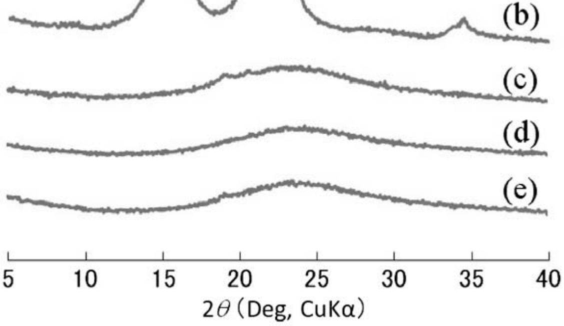

Fig. 3. XRD profiles of chitin (a), cellulose (b), gels prepared in chitin/cellulose feed ratios of 1:1 (c), 1:2 (d), and 1:3 (e).

Table 1
Preparation and characterizations of chitin/cellulose composite gels with ionic liquids.

Run	Chitin:cellulose:AMIMBr:BMIMCl		Compressive mode	
	Molar ratio in feed	Molar ratio in gel	Fracture stress (kPa)	Fracture strain (%)
1	1:1:20.0:9.26	1:1:19.5:9.7	44.6	14.1
2	1:2:20.0:18.5	1:2:15.5:17.8	92.9	13.0
3	1:3:20.2:27.3	1:3:16.3:27.4	130	14.0

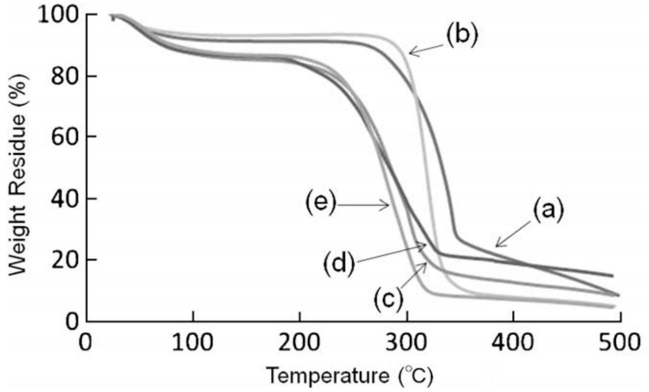

Fig. 4. TGA curves of chitin (a), cellulose (b), gels prepared in chitin/cellulose feed ratios of 1:1 (c), 1:2 (d), and 1:3 (e).

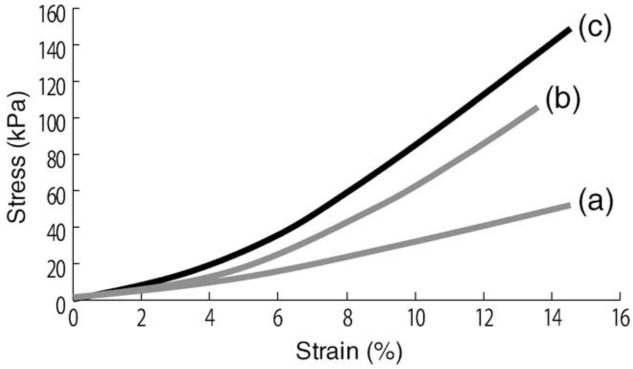

Fig. 5. Stress–strain curves under compressive mode of gels prepared in chitin/cellulose feed ratios of 1:1 (a), 1:2 (b), and 1:3 (c).

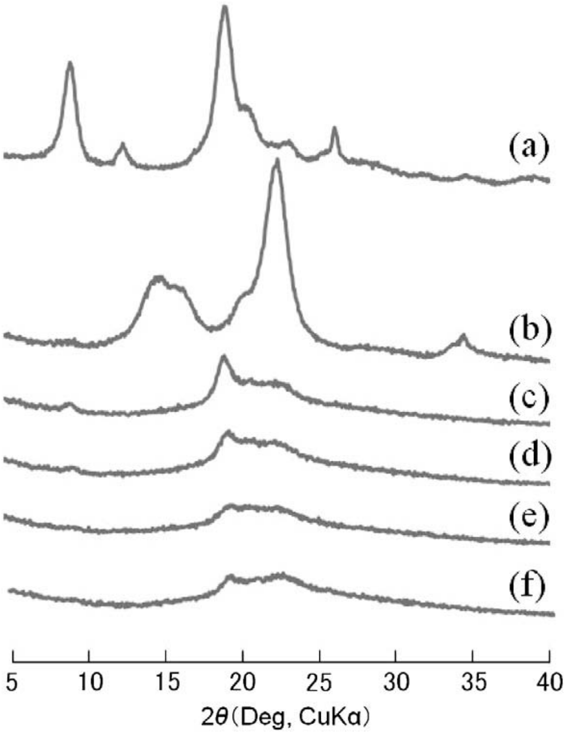

Fig. 6. XRD profiles of chitin (a), cellulose (b), films prepared in chitin/cellulose feed ratios of 1:3 (c), 1:5 (d), 1:7 (e), and 1:9 (f).

and simultaneously exclusion of the excess ionic liquids. Thus, the aggregates of the polysaccharide chains were formed during this process, which probably acted as cross-linking points for the gel formation.

The stress–strain curves of the gels under compressive mode were measured, which are shown in Fig. 5. The fracture stresses and strains were 44.6–130.0 kPa and 13.0–14.1%, respectively. The mechanical properties became more brittle with increasing the ratio of chitin in the gels.

The chitin/cellulose films were further obtained by casting the homogeneous mixtures of chitin/cellulose with AMIMBr/BMIMCl onto a glass plate, followed by reconstitution in water. First, the chitin/cellulose homogeneous mixtures with AMIMBr/BMIMCl were prepared in the feed molar ratios of chitin to cellulose = 1:9 to 1:3 according to the same procedure as that described above for the preparation of the chitin/cellulose composite gels. Then, the homogeneous mixtures were thinly casted on glass plates, which were soaked in water. The resulting gel-like materials were dried under reduced pressure to give the chitin/cellulose composite films. Increasing the molar ratio of chitin to cellulose than 1:3 did not form the stable film. The molar ratios of each material in the films were estimated by the same method as that for the composite gels, which are listed in Table 2. In all the films, the molar ratios of AMIMBr and BMIMCl to a repeating unit of chitin were less than 0.9 and 2.5, respectively. These data indicated that most of the ionic liquids used for the film preparation were removed by the above experimental procedure.

Fig. 6 shows the XRD profiles of the composite films with different chitin/cellulose ratios. When the molar ratio of chitin to cellulose was low (1:9), the diffraction peaks due to the crystalline structures of the polysaccharides were hardly observed (Fig. 6f). With increasing the ratios of chitin to cellulose, the small diffraction peaks due to the crystalline structure of chitin were appeared (Fig. 6c–e). These results indicated that cellulose chains were more miscible with the ionic liquids to disrupt the crystalline structure and the chitin chains slightly formed the crystalline structure with increasing their contents in the films. The ratios of AMIMBr to BMMCl in the films were lower than those in feeds when the higher ratios of chitin to cellulose were used (run 1 and 2 in Table 2). This result indicated that AMIMBr was excluded prior to BMIMCl during the gelation under the conditions of run 1 and 2 in Table 2. Therefore, the chitin chains might predominantly form the crystalline structure compared with cellulose in the films with the higher contents of chitin. The TGA curve of the film with the higher chitin ratio to cellulose (1:3) exhibited an onset of weight loss at

Table 2
Preparation and characterizations of chitin/cellulose composite films with ionic liquids.

Run	Chitin:cellulose:AMIMBr:BMIMCl		Tensile mode	
	Molar ratio in feed	Molar ratio in film	Fracture stress (MPa)	Fracture strain (%)
1	1:3:20.0:28.8	1:3:0.90:2.4	8.2	3.7
2	1:5:20.0:48.4	1:5:0.58:2.0	7.5	5.8
3	1:7:20.0:65.7	1:7:0.65:1.7	7.5	7.5
4	1:9:19.7:76.5	1:9:0.43:1.7	9.0	11.0

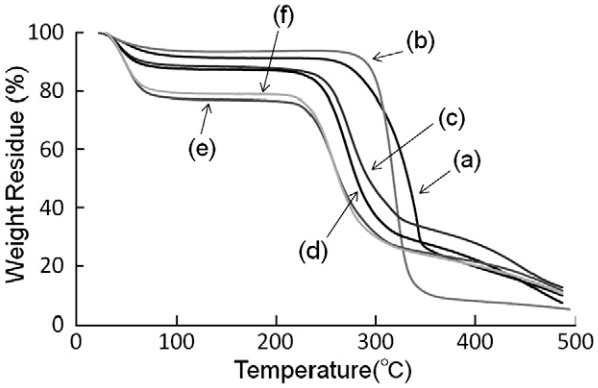

Fig. 7. TGA curves of of chitin (a), cellulose (b), films prepared in chitin/cellulose feed ratios of 1:3 (c), 1:5 (d), 1:7 (e), and 1:9 (f).

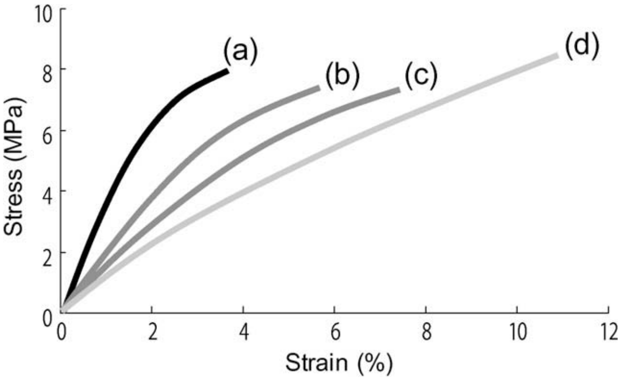

Fig. 8. Stress–strain curves under tensile mode of films prepared in chitin/cellulose feed ratios of 1:3 (a), 1:5 (b), 1:7 (c), and 1:9 (d).

around 250 °C (Fig. 7c), which was ca. 30 °C higher than that appeared in the TGA curve of the film with the lower chitin ratio to cellulose (1:9) (Fig. 7f). This difference is explained by the crystallinity of the chitin chains in the films. The above XRD and TGA results suggested that the two polysaccharides exhibited relatively good miscibility with the ionic liquids in the films although some crystalline structure of chitin was presence in the films with the higher contents of chitin. The presence of the slight amounts of the ionic liquids probably contributed to the miscibility of the two polysaccharides in the films.

The stress–strain curves of the films in Fig. 8 indicated that the mechanical properties became more elastic with decreasing the ratios of chitin to cellulose in the films. The fracture stresses and strains were 7.5–9.0 MPa and 3.7–11.0%, respectively.

4. Conclusions

In this paper, we reported the preparation and characterizations of the chitin/cellulose composite gels and films using the two ionic liquids, AMIMBr and BMIMCl. 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 for 4 days. On the other hand, the films were obtained by casting the mixtures on glass plates, followed by soaking in water and drying. The obtained gels and films were characterized by 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.

Acknowledgments

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