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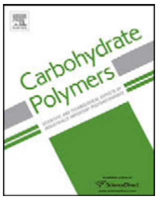

Preparation of chitin nanowhiskers using an ionic liquid and their composite materials with poly(vinyl alcohol)

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ABSTRACT

The preparation of chitin nanowhiskers using an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr) was performed. First, chitin was swollen with AMIMBr by soaking at room temperature, followed by heating at 100 °C. Soaking the resulting gel in methanol and subsequent sonication gave a chitin dispersion. The SEM image of the dispersion showed the formation of chitin nanowhiskers. Then, filtration of the dispersion was carried out to give a chitin film. Composite films of the chitin nanowhiskers with poly(vinyl alcohol) were prepared by a similar procedure to the chitin film. They were characterized by SEM and DSC measurements and their mechanical properties were evaluated by tensile testing.

1. Introduction

Natural polysaccharides provide two important functions, which are as an energy source and a structural material (Berg, Tymoczko, & Stryer, 2006). Cellulose and chitin are well-known structural materials (Schuerch, 1986), and are considered to be the most important biomass resources. Chitin is an aminopolysaccharide consisting of a chain of β-(1 → 4)-linked 2-acetamido-2-deoxy-D-glucopyranose (*N*-acetyl-D-glucosamine) residues (Fig. 1), which occurs mainly in the exoskeletons of shellfish and insects (Muzzarelli, 1977). Despite its huge production in nature (a rate of 10^{10} to 10^{11} tons per year) and easy accessibility, chitin still remains as an unutilized biomass resource primary because of its intractable bulk structure and insolubility in water and common organic solvents, and thus, only limited attention has been paid to chitin, principally from its biological properties (Muzzarelli, Jeuniaux, & Gooday, 1986). Because chitin is the second abundant biomass resource after cellulose, there is major interest in conversion into various useful materials after proper dissolution in suitable solvents. Native chitin in crustacean shells is arranged as microfibrils embedded in a protein matrix. The microfibril consists of nanofibers with 2–5 nm diameters (Chen, Lin, McKittrick, & Meyers, 2008; Raabe et al., 2006). Preparation of nanofibers or nanowhiskers, as observed in the case of cellulose (Abe, Iwamoto, & Yano, 2007; Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009), is one of the most useful methods to practically utilize polymeric materials. For example, cellulose nanowhiskers were used as reinforcing fillers for natural polymeric matrices (Anglès & Dufresne, 2000). Various methods have previously been found for the preparation of chitin nanofibers or nanowhiskers (nanocrystals), such as acid hydrolysis (Goodrich & Winter, 2007; Lu, Weng, & Zhang, 2004; Morin & Dufresne, 2002; Nair & Dufresne, 2003; Paillet & Dufresne, 2001; Revol & Marchessault, 1993), TEMPO-mediated oxidation (Fan, Saito, & Isogai, 2008a, 2008b), ultrasonication (Zhao, Feng, & Gao, 2007), electrospinning (Jayakumar, Prabaharan, Nair, & Tamura, 2010; Min et al., 2004), and mechanical treatment (Ifuku et al., 2009, 2010).

Ionic liquids, low-melting point salts that form liquids at temperatures below a boiling point of water, have been found to be used as good solvents for cellulose (Feng and Chen, 2008; Liebert & Heinze, 2008; Murugesan & Linhardt, 2005; Pinkert, Marsh, Pang, & Staiger, 2009; Seoud, Koschella, Fidale, Dorn, & Heinze, 2007) since it was reported in 2002 that an ionic liquid, 1-butyl-3-methylimidazolium chloride dissolved cellulose in relatively high concentrations (Swatloski, Spear, Holbrey, & Rogers, 2002). However little has been reported regarding the dissolution of chitin with the ionic liquids (Qin, Lu, Sun, & Rogers, 2010; Wu, Sasaki, Irie, & Sakurai, 2008). Recently, we found that an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr, Fig. 1) dissolved or swelled chitin to form weak gel-like materials (Prasad et al., 2009).

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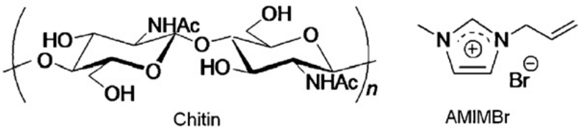

Fig. 1. Structures of chitin and 1-allyl-3-methylimidazolium bromide (AMIMBr).

It was confirmed in the study that degradation and decrease in the molecular weight of chitin did not frequently occur during the procedures for dissolution and gelation. In following papers, we also reported to use AMIMBr as the solvent for modification of chitin and the component of composite gels of chitin with cellulose (Mine, Izawa, Kaneko, & Kadokawa, 2009; Takegawa, Murakami, Kaneko, & Kadokawa, 2010). Thus, we have continued the study on chitin using AMIMBr for the preparation of new chitin-based materials. In this paper, we report that chitin nanowhiskers were easily formed by the gelation of a commercially available chitin powder with AMIMBr, followed by the regeneration with methanol. Furthermore, composite materials of chitin nanowhiskers with poly(vinyl alcohol) (PVA) were prepared by a similar procedure. The present study for the preparation of the chitin nanowhiskers is considered to have great advantages compared to previous methods (Fan et al., 2008a, 2008b; Goodrich & Winter, 2007; Ifuku et al., 2009, 2010; Jayakumar et al., 2010; Lu et al., 2004; Min et al., 2004; Morin & Dufresne, 2002; Nair & Dufresne, 2003; Paillet & Dufresne, 2001; Revol & Marchessault, 1993; Zhao et al., 2007) because of no necessity of any special equipments and chemical modifications. Furthermore, utilizing nanowhiskers from natural polymers contributes to not only the practical use as biomass resources, but also the preparation of high performance bio-based materials.

2. Experimental

2.1. Materials

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). A commercially available PVA with average degree of polymerization (DP) = ca. 4300 and degree of saponification = 98.0–98.8 mol% from Sigma–Aldrich was used. An ionic liquid, AMIMBr was prepared by reaction of 1-methylimidazole with 3-bromo-1-propene according to the method from the literature procedure (Zhao et al., 2005). Other reagents and solvents were used as received.

2.2. Preparation of chitin nanowhiskers

Chitin powder (1.23 mmol, 0.250 g) was soaked in AMIMBr (12.3 mmol, 2.50 g) at room temperature for 24 h, followed by heating at 100 °C for 48 h to give a chitin gel (9.1 wt%) with AMIMBr. After methanol (40 mL) was slowly added to the resulting mixture and the system was left standing at room temperature for 24 h, the mixture was sonicated for 5 min to give a chitin dispersion. The dispersion was filtered and a residue was dried under reduced pressure at 60 °C for 12 h. Then, the resulting material was subjected to Soxhlet extraction with methanol (70 mL) for 5 h and dried under reduced pressure at 60 °C for 12 h to give a film of chitin nanowhiskers.

2.3. Preparation of composites composed of chitin nanowhiskers with PVA

Table 1
Ratios of chitin, PVA, to AMIMBr in feeds and composites.

Run	Weight ratio in feed[a]	Molar ratio in feed[a]	Molar ratio in composite[a,b]
1	1:0.30:10	1:1.02:10	1:0.95:0.063
2	1:0.20:10	1:0.68:10	1:0.64:0.064
3	1:0.10:10	1:0.34:10	1:0.32:0.041
4	1:0.05:10	1:0.17:10	1:0.16:0.061
5	1:0.01:10	1:0.034:10	1:0.033:0.044

[a] Chitin:PVA:AMIMBr.
[b] Determined based on the weights of composites.

A typical example for the preparation of composites composed of chitin nanowhiskers with PVA (1:0.3) was as follows (Run 1, Table 1). Chitin powder (1.23 mmol, 0.250 g) was soaked in AMIMBr (12.3 mmol, 2.50 g) at room temperature for 24 h, followed by heating at 100 °C for 48 h to give a chitin gel with AMIMBr. Then, a solution of PVA (1.25 mmol, 0.0750 g) in hot water (temperature slightly below the boiling point, 3.0 mL) was mixed to the gel at 80 °C with stirring. After methanol (40 mL) was slowly added to the resulting mixture, the system was left standing at room temperature for 24 h, followed by sonication to give a dispersion of chitin nanowhiskers and PVA. The dispersion was filtered and a residue was dried under reduced pressure at 60 °C for 12 h. Then, the resulting material was subjected to Soxhlet extraction with methanol (70 mL) for 5 h and dried under reduced pressure at 60 °C for 12 h to give a composite film.

2.4. Measurements

XRD measurements were conducted using a PANalytical X'Pert Pro MPD with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). SEM images were obtained using Hitachi SU-70 electron microscope. DSC measurements were carried out using a heating rate of 10 °C min^{-1} on an SII DSC 6220. NMR spectra were recorded using a JEOL ECX400 spectrometer. Stress–strain curves were measured using a tensile tester (Little Senster LSC-1/30, Tokyo testing Machine Co.).

3. Results and discussion

3.1. Preparation of chitin nanowhiskers

First, chitin was swollen with AMIMBr according to the procedure reported in the previous study (Prasad et al., 2009) to give a chitin gel with AMIMBr (9.1 wt%). We found that a chitin dispersion was obtained when the gel was treated with methanol at room temperature for 24 h to slowly regenerate chitin, followed by sonication (Fig. 2). The resulting dispersion was diluted with methanol, which was subjected to the SEM measurement. Fig. 3b shows the SEM image of a spin-coated sample on a glass plate from the diluted dispersion in comparison with that of a chitin powder (Fig. 3a). It was observed that chitin powder was made up some bundles of fibers. On the other hand, nanowhiskers with ca. 20–60 nm in width and several hundred nanometers in length were seen in the SEM image of the sample from the dispersion,

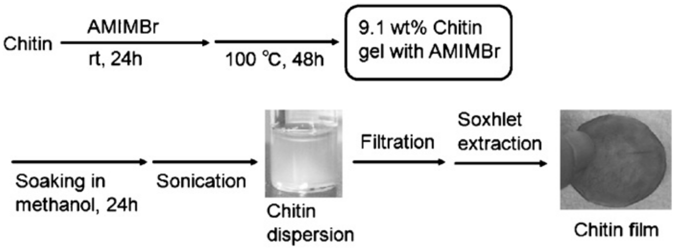

Fig. 2. Procedures for the preparation of chitin dispersion and film.

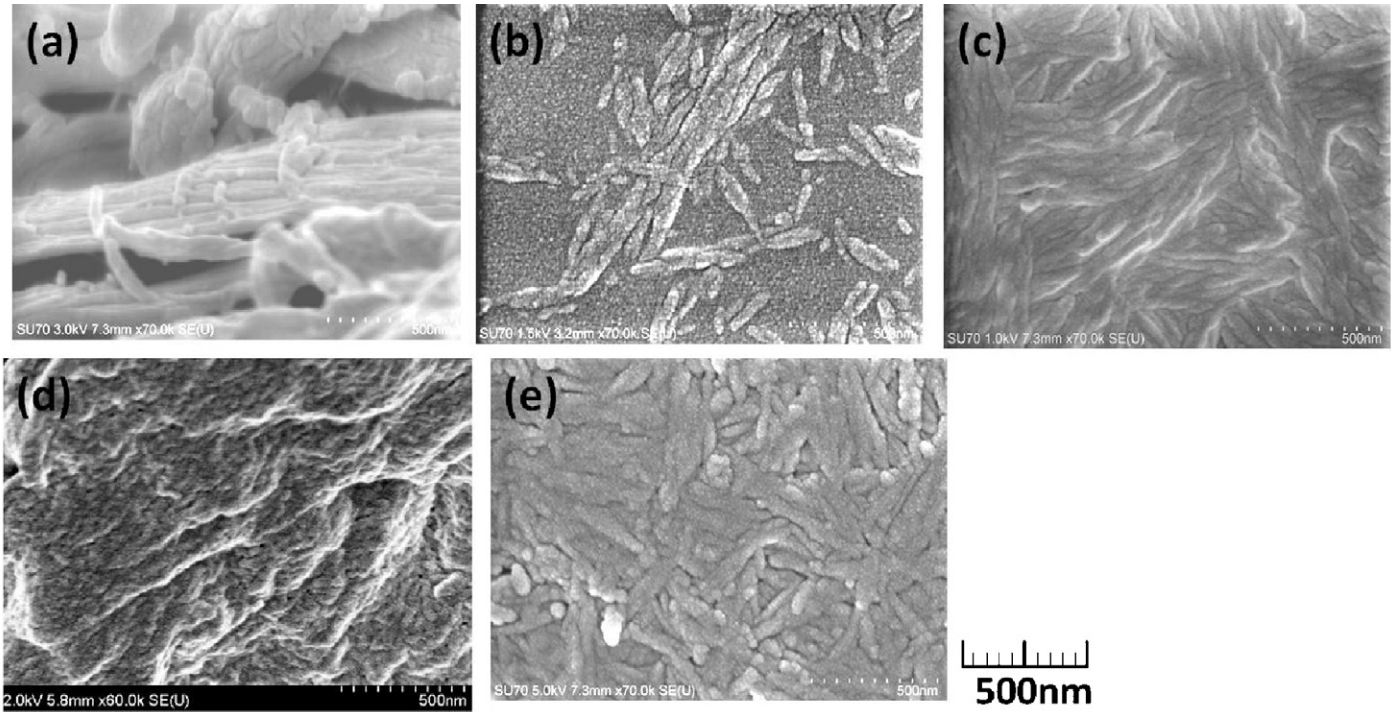

Fig. 3. SEM images of chitin powder (a), chitin dispersion obtained using AMIMBr (b), chitin film obtained using AMIMBr (c), regenerated chitin obtained using BMIMOAc (d), and composite film of chitin nanowhiskers with PVA (e, run 1 in Table 1).

indicating the formation of the chitin nanowhiskers by the above gelation and regeneration procedures of a chitin powder. When the dispersion was filtered, the residue formed a film. The SEM image of the resulting film (Fig. 3c) showed the morphology of highly condensed nanowhiskers. Such condensed structure of the nanowhiskers probably contributed to formability of the film. From the weight of the obtained chitin film, the ratio of chitin to AMIMBr in the film was calculated to be 1:0.046, indicating that AMIMBr used was mostly removed by the above regeneration and Soxhlet extraction procedures with methanol.

The XRD pattern of the chitin nanowhiskers (Fig. 4) mainly showed four diffraction peaks at around 9.5°, 19.5°, 20.9°, and 23.4°, which are assignable to 0 2 0, 1 1 0, 1 2 0, and 1 3 0 planes, respectively. This diffraction pattern typically corresponds to crystalline structure of α-chitin and is in good agreement with that of a chitin powder. These data indicated that the crystalline structure of α-chitin same as that of the original chitin was reconstructed by the above regeneration procedure during the formation of the nanowhiskers.

An attempt was also made to prepare the chitin film using 1-butyl-3-methylimidazolium acetate (BMIMOAc), which was reported as other ionic liquid dissolving chitin and forming a gel (Wu et al., 2008), according to the same procedure using AMIMBr as described above, i.e., gelation with the ionic liquid and regeneration from methanol. However, the regenerated chitin was not dispersed in methanol and was precipitated as aggregates. Indeed, the isolated chitin by filtration of the resulting mixture did not become film form. Moreover, its SEM image (Fig. 3d) exhibited the morphology of aggregates and did not obviously show the nano-scale morphology. These results indicated no formation of the chitin nanowhiskers using BMIMOAc, suggesting that the chitin nanowhiskers were specifically formed using AMIMBr. The specificity of AMIMBr was probably owing to the difference in the dissolution states of chitin in the two ionic liquids.

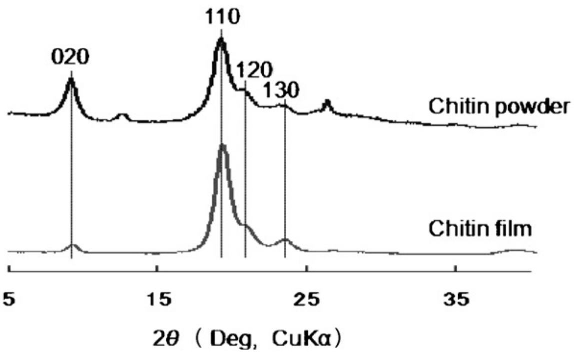

Fig. 4. XRD profiles of chitin powder and chitin film.

3.2. Preparation of composites composed of chitin nanowhiskers with PVA

As one of the possible applications of the chitin nanowhiskers, it was compatibilized with PVA to give corresponding composite materials. Some previous studies have performed the preparation of composites or blends composed of chitin and PVA (Junkasem, Rujjiravanit, Grady, & Supaphol, 2010; Kimura, Sato, Miyashita, Suzuki, & Nishio, 1997; Lee, Kim, & Kim, 1996; Miyashita, Sato, Kimura, Nishio, & Suzuki, 1996; Peesan, Rujiravanit, & Supaphol, 2003; Sriupayo, Supaphol, Blackwell, & Rujiravanit, 2005). However, the present method described as follows was completely different from the previous techniques. Furthermore, although the chitin nanowhiskers, which were prepared by acid hydrolysis, have previously been incorporated in the composites with PVA, the contents of the nanowhiskers were less than 30% (Peesan et al., 2003; Sriupayo et al., 2005). In the present study, thus, the ratios of chitin to PVA in feed for the preparation of the composites were set to be higher than 50 wt%, i.e., 1:0.30, 1:0.20, 1:0.10, 1:0.05, and 1:0.01 (Runs 1–5, Table 1). First, the 9.1 wt% chitin gel with AMIMBr was prepared according to the aforementioned procedure and solutions of the desired amounts of PVA (DP = ca. 4300) in

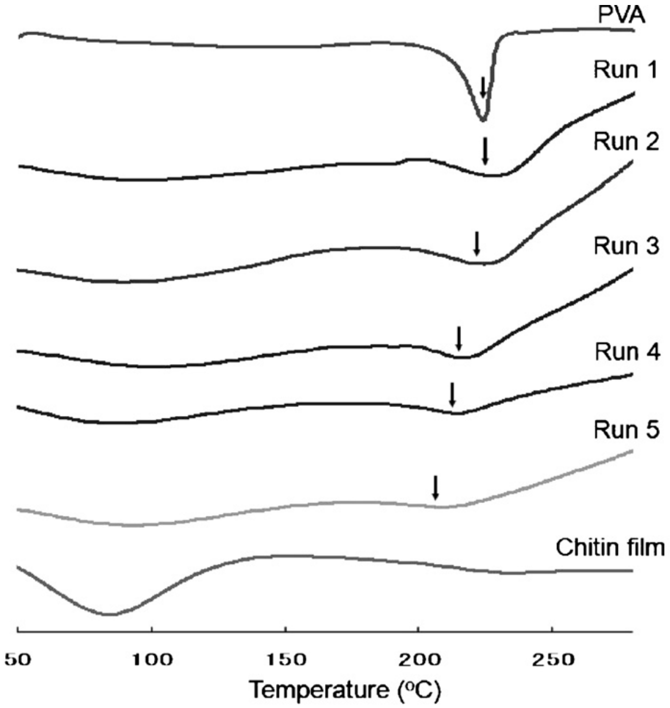

Fig. 5. DSC profiles of composites obtained from various feed weight ratios of chitin to PVA and chitin film.

hot water were added to the gel; PVA with such high DP exhibited less solubility in common solvents and was soluble in a few solvents such as hot water and hot DMSO. Then, the same regeneration, filtration, and Soxhlet extraction procedures gave the chitin nanowhiskers/PVA composite materials, which also became film form. To determine the ratios among chitin, PVA, to AMIMBr in the composites, the following control experiment was conducted, in which the same experiment procedure as aforementioned for the preparation of the composites was carried out without use of chitin and the amount of the regenerated PVA was compared with the feed amount. Accordingly, 94 wt% of PVA used was regenerated by the control experiment. Because of insolubility of chitin with methanol, on the other hand, its quantitative amount was regenerated by the regeneration procedure. Taking into consideration the above findings in addition to the weights of the obtained composite films, thus, the ratios among chitin, PVA, to AMIMBr in the composites were calculated, which are shown in Table 1. In all cases, most of AMIMBr was removed, but a small amount still remained in the composites.

The SEM images of the composite (Fig. 3e, feed weight ratio of chitin to PVA = 1:0.3, Run 1) showed that the nanowhisker-like morphology was maintained and PVA components probably filled in spaces among the whiskers, indicating relative immiscibility of chitin and PVA in the composite. Indeed, the DSC profiles of all the composites (Fig. 5) exhibited endothermic peaks due to a melting point of PVA. These results suggested PVA in the composites had some crystallinity, indicating immiscibility toward chitin. However, as shown in Fig. 5, the melting points of PVA were shifted to lower temperatures accompanied with broadening when the contents of chitin in the composites increased. These data indicated that the crystallinities of PVA were decreased in the composites with increasing the contents of chitin. From the DSC results, therefore, we supposed that chitin and PVA might be partially miscible at the interfacial area between the two polymers in the composites by the formation of hydrogen bonding between them or by the presence of a small amount of AMIMBr.

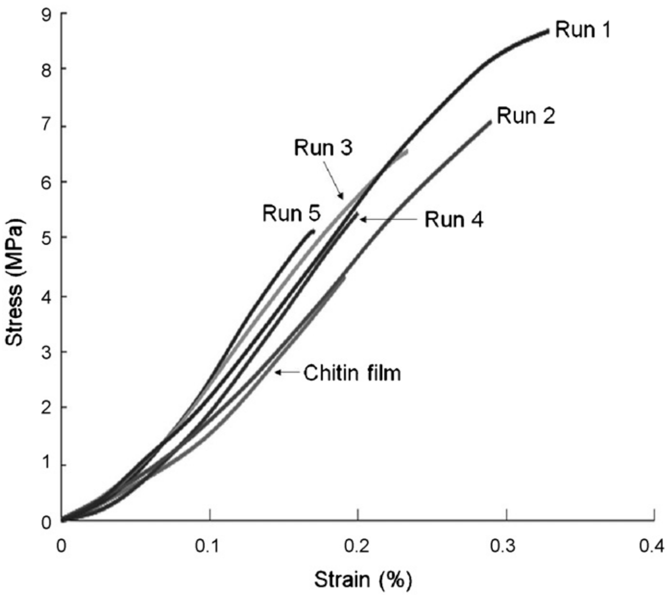

Fig. 6. Stress–strain curves of composite films and chitin film under tensile mode.

The stress–strain curves of the composite films under tensile mode were measured to evaluate their mechanical properties (Fig. 6). Both the values of fracture stresses and strains tended to be increased with increasing the contents of PVA in the composites. These results suggested the enhancement of the mechanical properties with increasing the ratios of PVA to chitin in the composites.

4. Conclusions

In this paper, we reported the preparation of the chitin nanowhiskers using an ionic liquid (AMIMBr). First, 9.1 wt% chitin gel with AMIMBr was prepared by soaking at room temperature and heating at 100 °C. Then, the gel was soaked in methanol to regenerate chitin, followed by sonication, to give a chitin dispersion. The SEM image of the spin-coated sample from the dispersion showed the formation of the chitin nanowhiskers with ca. 20–60 nm in width and several hundred nanometers in length. The filtration of the dispersion gave the chitin film, which had the condensed structure of the nanowhiskers. Furthermore, the composite films composed of the chitin nanowhiskers with PVA were obtained according to the same procedure as that of above. The DSC profiles of the composites indicated a possibility for partial miscibility at the interfacial area between chitin nanowhiskers and PVA, probably due to the formation of hydrogen bonding or the presence of a little amount of AMIMBr. The tensile testing of the composite films indicated the enhancement of the mechanical properties with increasing the ratios of PVA to chitin.

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