



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.

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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 \rightarrow 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 10¹⁰ to 10¹¹ 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, Prabakaran, 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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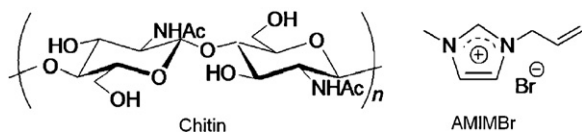


Fig. 1. Structures of chitin and 1-allyl-3-methylimidazolium bromide (AMIMBr).

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

A typical example for the preparation of composites composed of chitin nanowhiskers with PVA (1:0.3) was as follows (Run 1,

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.

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 K α 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,

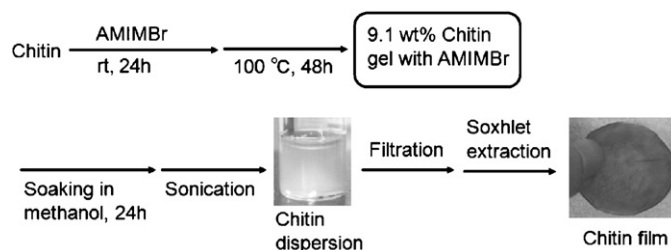


Fig. 2. Procedures for the preparation of chitin dispersion and film.

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