Preparation of partially acetylated chitin nanofiber/polyethylene composite film

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Abstract

Chitin is widely distributed in nature and an important renewable resource. However, it has been difficult to provide a wide variety of material applications from chitin, due to poor solubility and processability. In this study, we performed surface modification of self-assembled chitin nanofibers (CNFs) by acetylation and their composite fabrication with a commodity plastic, low density polyethylene (LDPE). The self-assembled CNF dispersion with DMF was first prepared by regeneration from a chitin ion gel with an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr), using methanol, followed by exchange of a dispersion medium according to the previously reported method by us. Surface acetylation of the product was then performed by reaction of acetic anhydride in the dispersion to obtain partially acetylated CNFs, which formed a film by isolation. The composites of the film with LDPE with the different weight ratios were fabricated by pressing at 170 ºC at 0.1 MPa. The SEM measurements of the products observed the morphologies that LDPE interpenetrated from surfaces into cross-sections of the partially acetylated CNF films with increasing the LDPE ratios. The tensile testing of the composite films indicated reinforcing effect of LDPE present in the composites.

Keywords: Chitin; composite, low density polyethylene, nanofiber, surface modification.

Introduction

Polysaccharides are widely distributed in nature and act as vital roles in biological system such as structural materials and energy suppliers [**1**]. Chitin, which is composed of β(1→4)-linked *N*-acetyl-D-glucosamine units (**Fig. 1**), is one of the most abundant structural polysaccharides mainly present in the exoskeletons of crustaceans, shellfishes, and insects [**2-4**]. Although natural polysaccharides have been expected to be used as components in functional materials alternative to petroleum-based components [**5**, **6**], chitin still remains mostly as an unutilized organic resource because of its intractable bulk structure and the presence of numerous intra- and intermolecular hydrogen bonds, leading to poor solubility in water and common organic solvents and poor proccessability [**7**]. Accordingly, the researches concerning the efficient use of chitin as material components have increasingly attracted much attention. Nanofibrillation of chitin has been regarded in recent years as one of the efficient approaches to fabricate chitin-based functional materials [**8-14**]. The resulting chitin nanofibers (CNFs), for example, have been used to produce composite materials with other polymeric components by chemical (covalent linking such as grafting) [**15-20**] and physical (non-covalent interaction) approaches [**21-25**]. As highly polar property of nanofiber surface owing to the presence of numerous hydroxy groups, however, there have not been many examples on the composite preparation of CNFs with hydrophobic plastics and resins. To overcome this drawback of CNFs, chemical modification of hydroxy groups on CNFs, such as acetylation, was conducted [**26**]. The resulting acetylated CNFs were then used to fabricate composite materials with acrylic resin [**27**]. To the best of our knowledge, however, the composite preparation of CNFs with commodity hydrophobic plastics, such as polyethylene, has hardly been reported so far.

Over the past decade, on the other hand, ionic liquids have been regarded as good solvents for polysaccharides [**28-33**] since the dissolution of cellulose with an ionic liquid, 1-butyl-3-methylimidazolium chloride, was reported in 2002 [**34**]. The dissolution of chitin with some ionic liquids has also been reported [**33**, **35**, **36**]. For example, we found that an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr), dissolved chitin from crab shells in concentrations up to ~4.8 wt% [**37**, **38**]. The formation of ion gels of chitin with AMIMBr from the higher content mixtures was also found. In the following study, we achieved the self-assembly of chitin into nanofibers by regeneration from the ion gels using methanol (**Fig. 1**) [**8**, **11**]. The isolation of the self-assembled CNFs from the resulting methanol dispersions by filtration resulted in highly fiber entanglement to obtain CNF films. Surface-initiated graft polymerization approaches from the self-assembled CNFs have been conducted further to produce composite materials with some synthetic polymers linked through covalent linkages [**16**, **17**, **19**, **20**]. Co-regeneration approach from the chitin ion gel coexisting of a highly polar polymer, poly(vinyl

alcohol) (PVA), with AMIMBr using methanol was also performed to fabricate a CNF/PVA composite material by physical interaction [**8**].

For the composite preparation of the self-assembled CNFs with commodity hydrophobic plastics, such as polyethylene, in this study, we conducted surface acetylation on the self-assembled CNFs, leading to hydrophobization for providing compatibility with polyethylene (**Fig. 1**). Composite materials of the acetylated CNF film with low density polyethylene (LDPE) were then fabricated by pressing approach. Recently, (acetylated) chitin nanocrystals were used as fillers for reinforcing ultra-high molecular weight PE [**39**]. In this study, a little chitin nanocrystal (0.5 - 1.0 wt%) was filled with PE to fabricate PE-based material. To the best of our knowledge, there has not been the study on the preparation of CNF-based composite material using PE as the reinforcing agent so far.

Experimental

Materials

Chitin powder from crab shells was purchased from Wako Pure Chemicals, Tokyo, Japan. LDPE beads (density; 0.925 g/cm) were purchased from Sigma-Aldrich Co. LLC., USA. 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 [**40**]. Other reagents and solvents were available commercially and used without further purification.

Preparation of partially acetylated CNF film

A mixture of chitin (0.120 g, 0.59 mmol) with AMIMBr (1.00 g, 4.92 mmol) was allowed to stand at room temperature for 24 h and subsequently heated with stirring at 100 °C for 24 h to obtain a chitin ion gel (10 wt%). The gel was then soaked in methanol (40 mL) at room temperature for 48 h, followed by sonication for 10 min to give a self-assembled CNF dispersion with methanol [**8**]. After addition of DMF (20 mL) to the dispersion, the mixture was evaporated at 60 °C for 2 h under reduced pressure to give a CNF dispersion with DMF (ca. 20 mL). Acetic anhydride (0.60 g, 5.90 mmol, 10 equiv. with a repeating unit of chitin) and pyridine (0.70 g, 8.85 mmol, 15 equiv. with a repeating unit of chitin) were then mixed into the CNF dispersion with stirring at room temperature. The mixture was stirred at 60 °C for 12 h to give a partially acetylated CNF dispersion with DMF. The resulting dispersion was subjected to filtration to isolate the product, which was dried at 60 °C for 3 h under reduced pressure to obtain a partially acetylated CNF film.

Preparation of partially acetylated CNF/LDPE composite films

A typical experimental procedure for the preparation of partially acetylated CNF/LDPE composite film was as follows (CNF/LDPE = 1/0.25 (w/w)). The LEPE beads (25.32 mg) were first melted by heating 140 °C for 5 h and molded at that temperature to a flat shape. The partially acetylated CNF film (101.8 mg) was then sandwiched with the resulting flat LDPE, pressed at 140 °C at 0.1 MPa for 5 h, and cooled to room temperature to give the composite film.

Measurements

IR spectra were recorded on a PerkinElmer Spectrum Two spectrometer. For scanning electron, microscopic (SEM) measurement, platinum films were deposited on each sample by magnetron sputtering (sample thickness; ca. 1-5 mm) and images were recorded on a Hitachi SU-70 electron microscope applying a 5 kV accelerating voltage. The powder X-ray diffraction (XRD) measurements were conducted using a PANalytical X'Pert Pro MPD with Ni-filtered CuKα radiation (λ = 0.15418 nm). Differential scanning calorimetric (DSC) measurements were performed on SII TG/DTA 6200 and

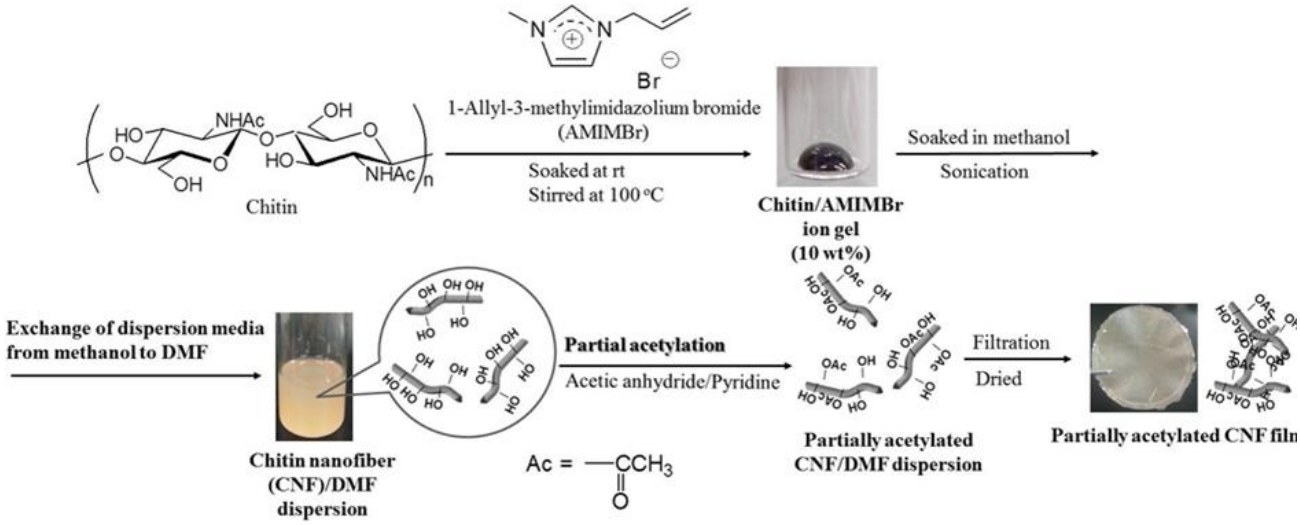

Fig. 1. Procedures for preparation of self-assembled chitin nanofiber (CNF) in dispersion with DMF and surface acetylation under dispersion conditions, followed by film formation.

SII DSC 6220 at a heating rate of 10 ºC/min. The stress–strain curves were measured using a tensile tester (Little Senstar LSC-1/30, Tokyo Testing Machine).

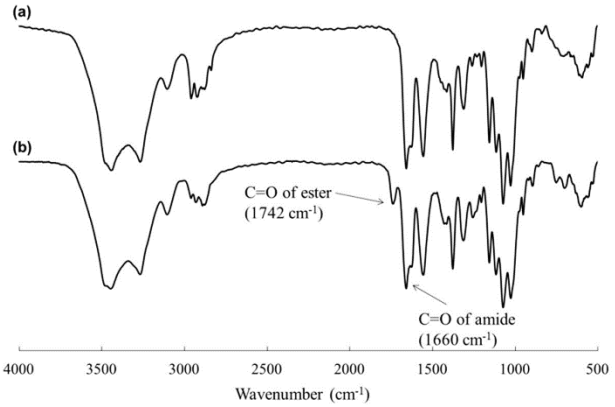

Fig. 2. IR spectra of (a) self-assembled CNF film and (b) partially acetylated CNF film.

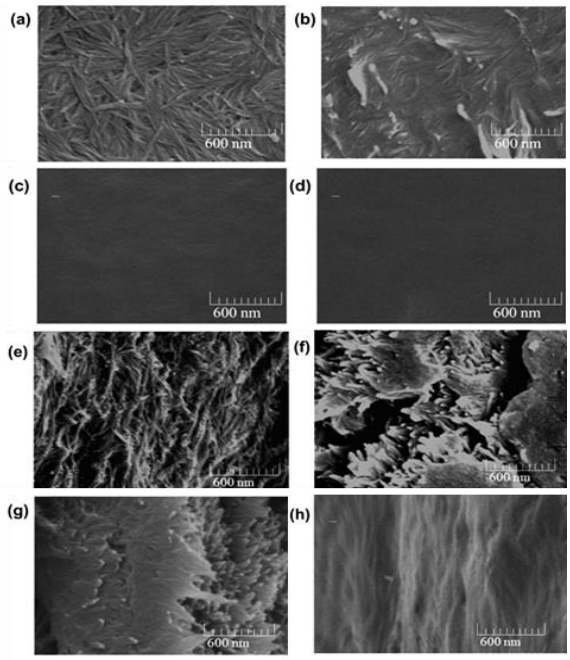

Fig. 3. SEM images of partially acetylated CNF film and composite films (CNF/LDPE ratios = 1/0.25, 1/0.5, 1/1 (w/w)); (a-d) surfaces and (e-h) cross-sections.

Results and discussion

As previously reported, the CNF dispersion with methanol was prepared via gelation with AMIMBr, followed by regeneration using methanol [**8**]. As it is obvious that an acetylation agent, acetic anhydride, would react with methanol present in the dispersion, resulting in inhibition of the reaction with hydroxy groups on CNFs, we have found that exchange of a dispersion medium from methanol to DMF, which is an inert solvent for acetylation, can be performed with remaining the dispersed state [**20**]. In the present study, therefore, the CNF dispersion with DMF was prepared according to the previously reported exchange procedure of the dispersion medium (**Fig. 1**) [**20**].

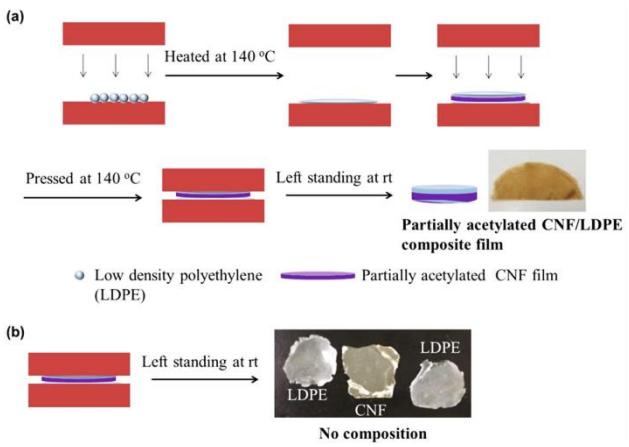

Fig. 4. Preparation of composite films (a) from partially acetylated CNF and LDPE and (b) from CNF and LDPE.

Then, the reaction of acetic anhydride with hydroxy groups on CNFs in the dispersion with DMF was carried out in the presence of pyridine to produce the acetylated CNFs. The produced CNFs were isolated by subjecting the dispersion to filtration, which formed a film. The detection of an ester carbonyl absorption at 1742 cm^{-1} in the IR spectrum of the produced film (**Fig. 2**) suggested the progress of acetylation. From the intensity ratio of the two carbonyl absorptions due to ester and amide I (1742 and 1660 cm^{-1}, respectively) in the IR spectrum, the value of degree of acetylation on CNFs was estimated to be 0.43 with a repeating unit of chitin according to a method described in the literature [**41**]. The SEM images of the resulting film observe the nanofiber morphologies (**Fig. 3(a, e)**), similar as those before the acetylation, indicating the progress of acetylation on surfaces of CNFs.

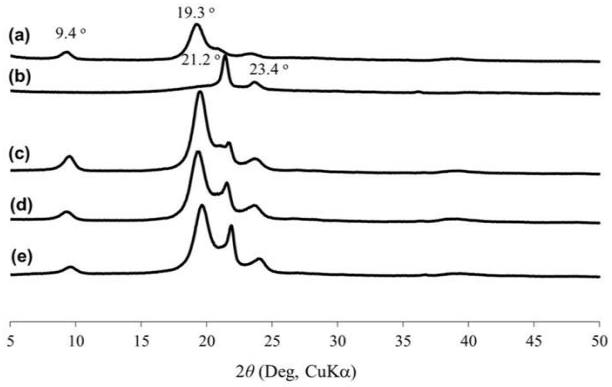

Fig. 5. XRD profiles of (a) partially acetylated CNF film, (b) LDPE, and (c-e) composite films (CNF/LDPE ratios = 1/0.25, 1/0.5, 1/1 (w/w)).

Then, the preparation of partially acetylated CNF/LDPE composite films was attempted (**Fig. 4(a)**). For the composite preparation, LDPE beads were first melted by heating at 140 ºC (above the melting point) and molded to a sheet shape by pressing at that temperature for 5 h. The partially acetylated CNF films were then sandwiched with the melted LDPE sheets (CNF/LDPE = 1/0.25, 1/0.5, 1/1 (w/w)) and pressed at 140 ºC at 0.1 MPa for 5 h, followed by cooling to room temperature, to fabricate the composite films. The same procedure using

the original CNF film without surface modification did not show compatibility with LDPE because two polymers were easily separated after the preparation procedure as shown in **Fig. 4(b).** These results indicated the effect of surface acetylation for exhibiting compatibility of CNFs with the commodity hydrophobic plastics, LDPE, owing to hydrophobization on the CNF surface.

The SEM image of surface of the composite film with the CNF/LDPE ratio = 1/0.25 shows the nanofiber morphology as observed in that of the partially acetylated CNF film, whereas such morphology was not seen in the SEM images of the films with the higher LDPE ratios (**Fig. 3(a)-(d)**). Furthermore, the SEM images of cross-sections of the composite films observe the morphologies that the nanofibers are gradually covered by the LDPE solids with increasing the LDPE ratios (**Fig. 3(e)-(h)**).

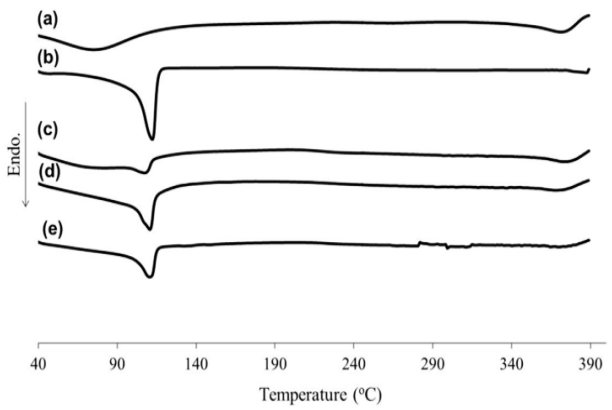

Fig. 6. DSC profiles of (a) partially acetylated CNF film, (b) LDPE, and (c-e) composite films (CNF/LDPE ratios = 1/0.25, 1/0.5, 1/1 (w/w)).

These results suggested that the melted LDPE gradually penetrated from surfaces to cross-sections of the partially acetylated CNF films with increasing the LDPE ratios during the preparation procedure. The XRD profiles of the composite films exhibit diffraction peaks due to crystalline structures of both chitin (9.4 and 19.3°) and LDPE (21.2 and 23.4°) (**Fig. 5**). The data suggested that the composites were fabricated by adhesion at interfacial areas between CNF and LDPE with retaining the respective original crystalline structures. The DSC profiles of the composite films show endothermic peaks assignable to the melting temperature of LDPE at around 110 °C, also supporting to retain its crystalline structure (**Fig. 6**). The stress-strain curves of the composite films by tensile testing show the larger elongation values at break than those of the partially acetylated CNF film, indicating the enhancement of elasticity by the composition with LDPE (**Fig. 7**). Furthermore, the larger tensile strength values were obtained from the composite films with the higher LDPE ratios (**Fig. 7(c), (d)**) compared with the other film with the lower LDPE ratio (**Fig. 7(b)**). These data suggested the reinforcing effect of LDPE on the composition with the partially acetylated CNF film, because of the flexibility of LDPE.

Conclusion

In this study, we investigated the preparation of CNF-based composite materials with LDPE. Surface modification of the self-assembled CNFs, which were prepared by the method developed in our previous study, was first conducted by acetylation using acetic anhydride under the dispersion conditions in DMF.

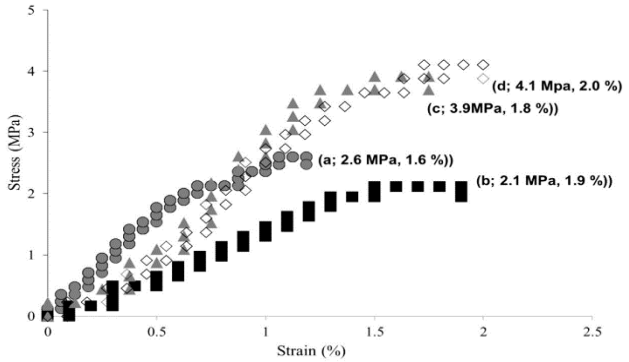

Fig. 7. Stress-strain curves of (a) partially acetylated CNF film and (b-d) composite films (CNF/LDPE ratios = 1/0.25, 1/0.5, 1/1 (w/w)) under tensile mode; values in parentheses are tensile strength (MPa) and elongation at break (%).

After the partially acetylated CNF films, fabricated by filtration from the resulting dispersion, were sandwiched with the melted LDPE with a sheet shape, the materials were pressed at 140°C for 5 h to take place the composition. This approach efficiently gave the desired composite films, whereas the same approach using the original CNF film without surface modification did not induce the composition with LDPE. The analytical results suggested that the composition was progressed by adhesion at interfacial areas between the partially acetylated CNF and LDPE. The tensile testing of the composite films indicated the reinforcing effect of the composition with LDPE on enhancement of mechanical properties. The present approach will be applicable to fabricate new CNF-based composite materials with other commodity hydrophobic plastics in the future.

Author's contributions

Conceived the plan: K.I., R.E.; Performed the expeirments: K.I., R.E., K.Y.; Data analysis: K.Y., J.K.; Wrote the paper. Authors have no competing financial interests.

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