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Short communication

Control of mechanical properties of chitin nanofiber film using glycerol without losing its characteristics

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ABSTRACT

Surface-deacetylated chitin nanofiber films plasticized with glycerol were prepared to control mechanical properties. Nanofiber networks were able to retain excessive glycerol content up to 70% to obtain self-standing film. All films were flexible and highly transparent independent of glycerol content. Glycerol significantly decreased the Young's moduli and tensile strengths, and increased the fracture strain due to its plasticizing effect. At the same time, glycerol did not change the high transparency or the low thermal expansion of the nanofiber film.

1. Introduction

Chitin is the main component of exoskeletons of crustaceans such as crab and shrimp. Chitin is known as the second most abundant biopolymer after cellulose (Muzzarelli, 2012). Chitosan is a polysaccharide obtained by the deacetylation of chitin. Chitosan has many attractive properties (Dutta, Tripathi, Mehrotra, & Dutta, 2009): it is film-forming, biocompatible, biodegradable, non-toxic, anti-bacterial, and anti-fungal properties. Thus, chitosan film is available as edible films, coatings, and packaging materials for the quality preservation of a variety of food and agricultural products (Ziani, Fernández-Pan, Royo, & Maté, 2009).

We have prepared chitin nanofibers (CNFs) from crab and prawn shells, and from the cell walls of mushrooms by removal of matrix substances followed by mechanical treatment (Ifuku and Saimoto, 2012; Ifuku et al., 2009). The CNFs have a fine nanofiber network with a width of approximately 10 nm. Since the CNFs are dispersed homogeneously in water, they are easy to handle and are shaped into the desired forms. This characteristic will likely expand the applications of chitin. Moreover, CNFs have excellent mechanical properties thanks to the α-type extended crystalline structure. Recently, surface-deacetylated CNF film has been reported (Fan, Saito, & Isogai, 2010; Ifuku et al., 2013). Although the nanofiber surface was transformed into chitosan, the core part was maintained as extended chitin crystal. Due to its high dispersibility in water, its characteristic nano-morphology, and mechanical properties, the cast film has high transparency, high mechanical properties, and low thermal expansion. Moreover, due to the surface properties of chitosan on the CNFs, the film showed antifungal activity. For food packaging, especially edible film and coatings, controlling the mechanical properties of the surface-deacetylated CNF film is necessary depending on the intended use.

The addition of plasticizing agents is an effective method for controlling the mechanical properties and overcoming the brittleness of the CNF film. Plasticizers effectively reduce the intermolecular forces, soften the rigidity of the film structure, and increase the mobility of the polymeric chains, resulted in an adjustment of the mechanical properties. Glycerol has been shown to be a suitable plasticizer to obtain flexible chitosan films, taking into account the plasticization efficiency and high biocompatibility (Suyatma, Tighzert, & Copinet, 2005; Srinivasa, Ramesh, & Tharanathan, 2007).

In this study we evaluated the influence of the presence of glycerol on the optical, mechanical, and thermal expansion properties of surface-deacetylated CNF film. Adjusting these parameters will increase the application of chitin nanofibers as a novel, environmentally friendly, multi-performance material.

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2. Experimental

2.1. Materials

Chitin powder from crab shells was purchased from Nacalai Tesque, Inc. The degree of deacetylation of the chitin was 3.9%. Glycerol was purchased from Wako Pure Chemical Industries, Ltd. and used as received.

2.2. Preparation of surface-deacetylated CNF

Surface-deacetylated chitin nanofibers were prepared by reference to a previously reported procedure and modified especially for the alkaline concentration (Fan, Saito, & Isogai, 2010). Briefly, chitin powder (40 g) was stirred in 20% (w/w) NaOH (3.0 L) for 6 h at 160 °C under an inert atmosphere. After deacetylation, the supernatant was removed by decantation. The precipitate was washed with distilled water by centrifuge. For nano-fibrillation, the deacetylated chitin was dispersed in 2.0 L of aqueous acetic acid (1.0% (w/w)). The sample was passed through a grinder (MKCA6-3; Masuko Sangyo Co., Ltd.) at 1500 rpm and repeated three times. The concentration and degree of deacetylation of the thus obtained deacetylated chitin nanofibers were 1.2 wt.% and 8%, respectively.

2.3. Preparation of surface-deacetylated CNF/glycerol composite film

Neat glycerol was blended with the surface-deacetylated CNF suspension with 1.2 wt.% concentration, and treated with super stirrer (Awatori-rentaro, ARE-301, THINKY Ltd.) to mix homogeneously and remove air small bubbles. The mixtures were prepared in the dry weight ratio of surface-deacetylated CNF/glycerol = 10/0, 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, and 3/7. The mixtures were poured into glass Petri dishes coated with release agent and dried ambient condition (40 °C, 3 days). Thus, eight different types of composite films were prepared with approximately 18 μm thick.

2.4. Measurements

The regular light transmittances of surface-deacetylated CNF/glycerol composite films were measured by a UV–Vis spectrophotometer (JASCO-V550) in the wavelength range of 200–800 nm. The tensile strengths and Young's moduli were measured by a universal testing instrument (AG-X, Shimadzu) for samples 50 mm long and 10 mm wide at a cross head speed of 1 mm min^{-1} with a gage length of 30 mm. For data accuracy, at least three specimens were used for testing. The coefficients of thermal expansion (CTE) were evaluated with a thermomechanical analyzer (Q400, TA instruments). Specimens for CTE measurement were 30 mm long and 3 mm wide with a 20 mm span. The measurements were carried out from 30 to 165 °C by raising the temperature at a rate of 5 °C min^{-1} in a N_2 atmosphere in tensile mode under a load of 0.05 N. The CTE values were determined in the second run. At least three specimens were used for testing. The degree of deacetylation was calculated from the C and N contents in the elemental analysis data by using an elemental analyzer (Elementar Vario EL III, Elementar).

3. Results and discussion

Surface-deacetylated chitosan nanofiber films were prepared from the aqueous mixture of glycerol in several proportions by casting and drying at 40 °C for 3 days. Surprisingly, self-standing nanocomposite films were obtained even with a high plasticizer content of 70% because the fine nanofiber network had much space to retain excessive plasticizer.

Fig. 1. The appearance of surface deacetylated chitin nanofiber film plasticized by glycerol.

3.1. Transparency of surface-deacetylated CNF/glycerol composite films

All films with and without glycerol had the same appearance and were transparent (Fig. 1). Fig. 2 shows the regular light transmittance spectra of a series of nanocomposite films. The transmittance of surface-deacetylated CNF film without glycerol was 88.4% at 600 nm. Surface-deacetylated CNF/glycerol films also had a high transparency of approximately 89%, independent of the glycerol content. This result suggests that glycerol was blended homogeneously with the CNFs and fully embedded in the CNF networks since the inter-fibriller aggregation of CNFs or the air cavity in the film causes a loss of transparency.

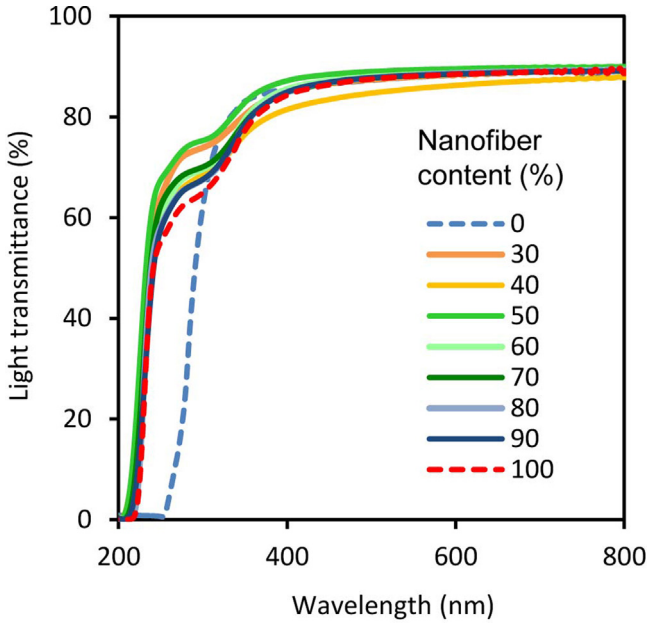

Fig. 2. Regular light transmittance spectra of nano-composite films with a different nanofiber content.

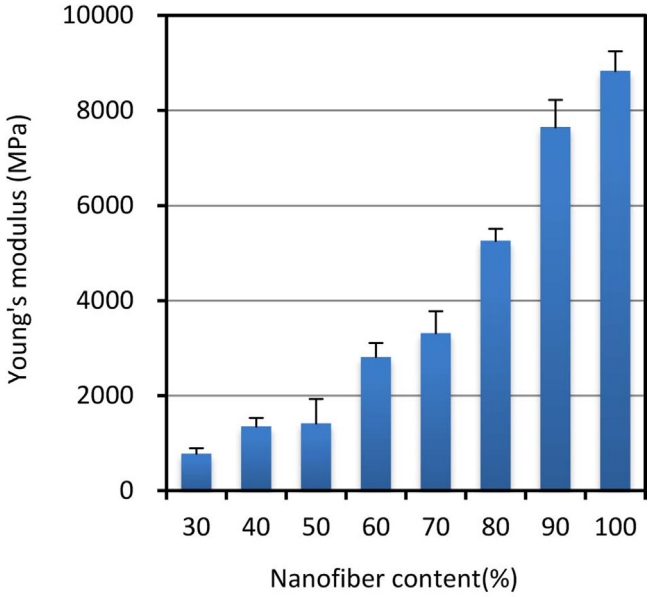

Fig. 3. Young's moduli of nano-composite films with a different nanofiber content.

3.2. Mechanical properties of surface-deacetylated CNF/glycerol composite films

Young's moduli and fracture strengths of the surface-deacetylated CNF films with a series of glycerol contents are shown in Figs. 3 and 4, respectively. CNFs from crab shell has an extended alpha type crystalline structure. Thus, surface-deacetylated CNF also has efficient mechanical properties. The Young's modulus and tensile strength of surface-deacetylated CNF film without glycerol were very high, 8833 MPa and 157 MPa, respectively. These mechanical properties were almost equal to that of cellulose nanofiber cast film (Abe & Yano, 2009; Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009). The Young's modulus and tensile strength decreased drastically and proportionally from 8833 to 776 MPa and from 157 to 22 MPa, respectively, with increasing

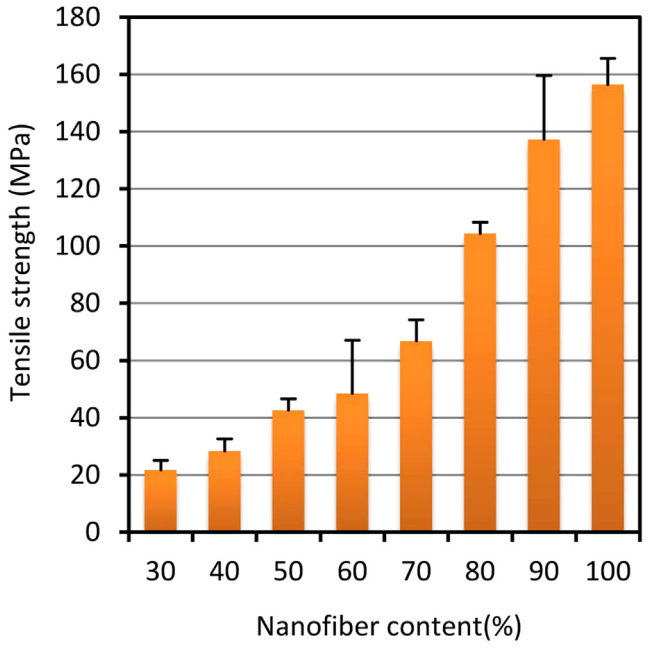

Fig. 4. Tensile strengths of nano-composite films with a different nanofiber content.

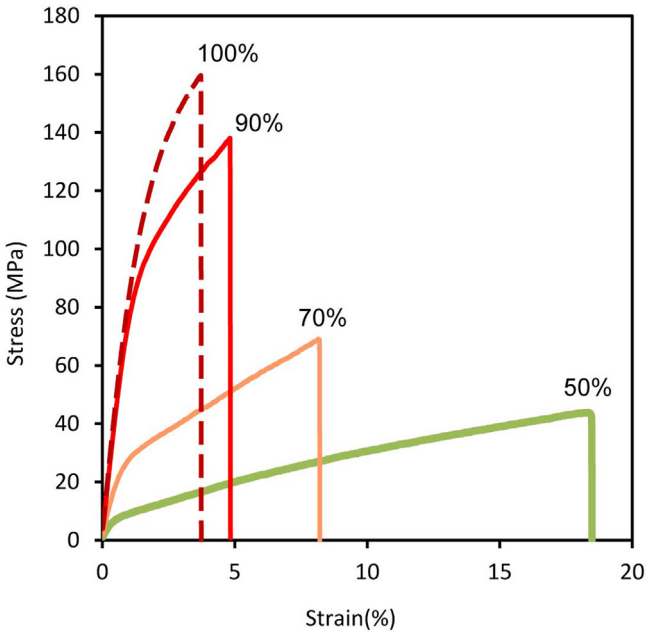

Fig. 5. Stress-strain curves of nano-composite films with a different nanofiber content.

glycerol content from 0 to 70%. These values corresponded to a 91 and 86% decrease, respectively. Fig. 5 shows typical stress–strain curves of surface-deacetylated CNF films with and without glycerol. Glycerol can make a fragile CNF film ductile. The fracture strain of the nanocomposite film increased from 5.4 to 16.3% with increasing glycerol content in the film from 0 to 50%, respectively. These results indicate that glycerol works effectively as a plasticizer to control the mechanical properties of the CNF film.

3.3. Thermal expansion of surface-deacetylated CNF/glycerol composite film

Thermal expansion is generally associated with the depth of the atomic bond energy function and has an inverse relationship with Young's modulus. Since CNFs have a high Young's modulus, surface-deacetylated CNFs also have low thermal expansion. Coefficient of thermal expansion (CTE) of surface-deacetylated CNF

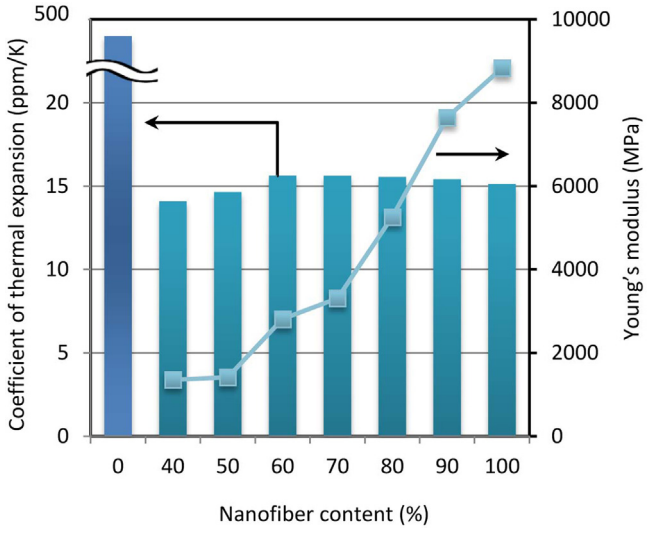

Fig. 6. Coefficients of thermal expansion and Young's moduli of nano-composite films with a different nanofiber content.

film without glycerol is only 14.9 ppm K^{-1} (Fig. 6). On the other hand, neat glycerol had a much higher CTE (490 ppm K^{-1}). However, the nanocomposite films surprisingly had an almost constant CTE, independent of the glycerol content and kept initial CTE values of approximately 15 ppm K^{-1}, although the Young's modulus of the nanocomposite film drastically decreased from 8833 to 1352 MPa, while increasing the glycerol content from 0 to 60%, respectively. The explanation for this contradictory trend is that since the glycerol was fluid at room temperature, the glycerol could not expand the rigid chitin nanofibers network. Thus, glycerol could control the mechanical properties without increasing the CTE of the CNF film.

4. Conclusion

Surface-deacetylated chitin nanofiber films with glycerol were prepared by casting and were characterized in detail. Due to the plasticizing effect of glycerol, the Young's modulus and tensile strength were decreased and the fracture strain was increased depending on the glycerol content. On the other hand, glycerol did not affect the transparency and thermal expansion of the cast film. Thus, the mechanical properties of the nanofiber film were controlled for many purposes without losing the high transparency and low thermal expansion. This study will increase the application of chitin nanofibers as novel, high-performance films and encourage the use of chitin as a natural and environmentally friendly material, especially for edible films, coatings, and packaging materials

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