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Short communication

Preparation of chitin nanofiber-reinforced carboxymethyl cellulose films

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ABSTRACT

In this study, we investigated the preparation of chitin nanofiber (CNF)-reinforced carboxymethyl cellulose (CMC) films by their electrostatic interaction. First, CMC films and self-assembled CNF dispersions with methanol were prepared by casting technique and regeneration from chitin ion gels with an ionic liquid, respectively. Then, the CMC films were immersed in the dispersions with the different CNF contents, followed by centrifugation to obtain the desired composite films. The amounts of the absorbed CNFs on the films were calculated by the weight increases after the above compatibilization procedure. The presence of CNFs on the films was also confirmed by the SEM and IR measurements. The mechanical properties of the composite films were evaluated by tensile testing, which suggested the reinforcing effect of CNFs present on the CMC films.

1. Introduction

Naturally occurring polysaccharides such as cellulose and chitin are the representative biomass resources on the earth [1,2] and have widely been studied for their potential to become environmentally benign substitutes for petroleum-based materials because of their eco-friendly and biodegradable properties [3,4]. Cellulose is the most abundant natural polysaccharide, which consists of a chain of β-(1 → 4)-linked D-glucose residues and is a very important renewable resource used in a number of traditional applications, such as in furniture, clothing, and medical products [5,6]. Various derivatives of cellulose have also been synthesized and used in practical applications [7]. Carboxymethyl cellulose (CMC) is one of the most widely applied cellulose derivatives and shows good processabilities such as the film formation, which has practically been used in detergent, food, paper, and textile industries [8]. Because CMC has a number of carboxylic acid groups, it is an acidic polysaccharide (Fig. 1). The commercially available CMC is generally composed of its sodium salt form, which exhibits water solubility.

Chitin is a structurally similar polysaccharide as cellulose, but which has acetamido groups at C-2 position in place of hydroxy groups in cellulose [9–11]. Thus, it is an aminopolysaccharide composed of a chain of β-(1 → 4)-linked *N*-acetyl-D-glucosamine residues (Fig. 1). Because the acetyl groups in the isolated chitin samples from natural sources are partially cleaved (generally several %), it can be considered as a basic polysaccharide having free amino groups.

In this study, we have performed to prepare composite materials from the aforementioned acidic and basic polysaccharides by their electrostatic interaction. Specifically, we used self-assembled nanofibers as a chitin moiety for compatibilization with CMC. In the previous study, we found that such self-assembled chitin nanofibers with ca. 20–60 nm in width and several hundred nm in length were facilely obtained by regeneration from chitin ion gels with an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr, Fig. 1), using methanol, followed by sonication [12,13], which had been based on our investigation on the gelation of chitin with the ionic liquid [14]. In this paper, accordingly, we report the preparation of self-assembled chitin nanofiber (CNF)-reinforced CMC films by the electrostatic interaction on surface of the film according to the procedure in Fig. 2. The morphology and mechanical property of the resulting films were evaluated by the SEM measurement and tensile testing, respectively. The present approach facilely provides new bio-based composite materials from two abundant natural polysaccharides.

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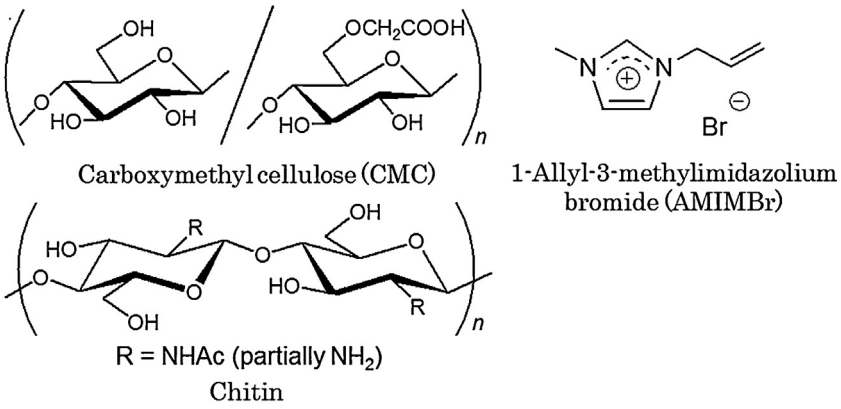

Fig. 1. Chemical structures of carboxymethyl cellulose (CMC), chitin, and 1-allyl-3-methylimidazolium bromide (AMIMBr).

2. Experimental part

2.1. Materials

Carboxymethyl cellulose (sodium salt, $M_w = 7 \times 10^5$, degree of carboxymethylation = 90%) was purchased from Sigma–Aldrich Co. Chitin powder from crab shells was purchased from Wako Pure Chemical Industries, Ltd., Japan. The weight–average molecular weight and degree of deacetylation values of the chitin sample were estimated by viscometric and IR analyses to be 7×10^5 and 4%, respectively [15,16]. 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 [17]. Other reagents and solvents were available commercially and used without further purification.

2.2. Preparation of CMC film

A commercially available CMC sodium salt (0.50 g, 0.24 mmol) was dissolved with water (200 mL) and treated with cation-exchange resin (Amberlite IR 120B NA) at room temperature for 5 h. After the resin was removed by filtration, the filtrate was concentrated and thinly casted on a paraffin film. Then, it was dried subsequently under ambient conditions and reduced pressure to give a CMC film.

2.3. Preparation of self-assembled CNF dispersion

A procedure was conducted according to our previous publication [12]. A mixture of chitin (0.12 g, 0.59 mmol) with AMIMBr (1.00 g, 4.92 mmol) was left standing at room temperature for 24 h, followed by heating at 100 °C for 24 h with stirring to give a chitin ion gel with AMIMBr. 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 (CNF content; 3.0 mg/mL). The dispersion was diluted two and three folds with methanol to give dispersions with 1.5 and 0.75 mg/mL CNF contents, respectively.

2.4. Preparation of chitin nanofiber-reinforced CMC film

A typical experimental procedure was as follows. The CMC film (20.2 mg, 2.1 cm × 1.2 cm) was immersed in 0.75 mg/mL CNF dispersion (5.0 mL, the amount of chitin; 0.019 mmol) and the system was subjected to centrifugation (2000 rpm) for 30 min twice. Then, the film was washed with methanol and dried under reduced pressure to give a CNF-reinforced CMC film.

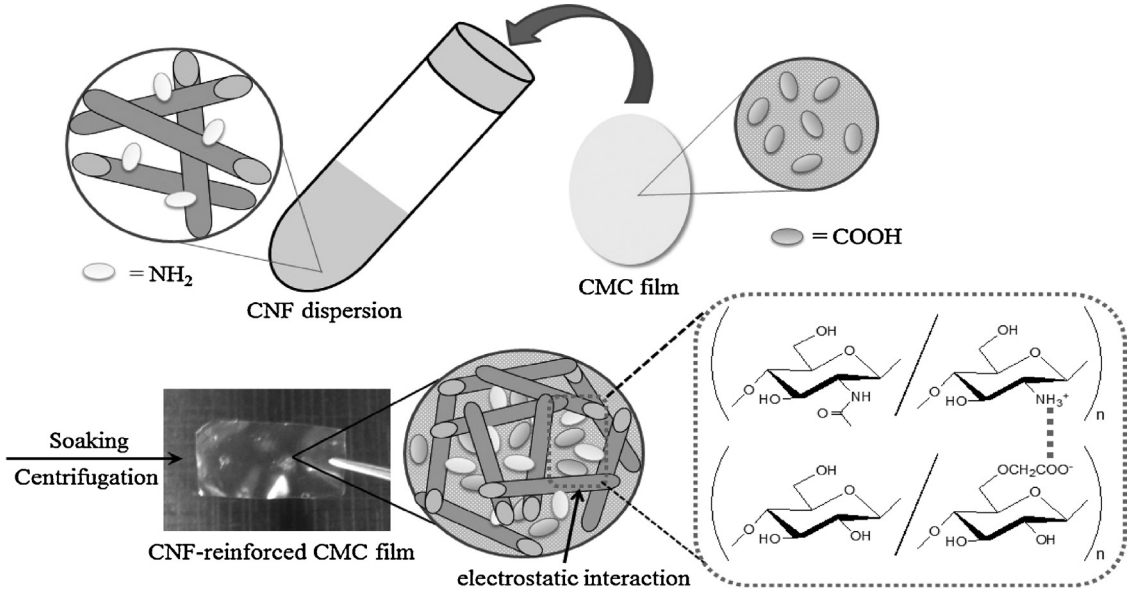

Fig. 2. Schematic image for preparation procedure of self-assembled CNF-reinforced CMC film.