

Preparation of chitin nanofibers by surface esterification of chitin with maleic anhydride and mechanical treatment



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ABSTRACT

Esterification with maleic anhydride significantly improved the mechanical disintegration of chitin into uniform 10-nm nanofibers. Nanofibers with 0.25° of esterification were homogeneously dispersed in basic water due to the carboxylate salt on the surface. Esterification proceeded on the surface and did not affect the relative crystallinity. A cast film of the esterified chitin nanofibers was highly transparent, since the film was free from light scattering.

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1. Introduction

A nanofiber is defined as a fiber with a diameter of less than 100 nm. Due to their unique morphology, nanofibers are quite different from micron-sized fibers in their dimensional, optical, and mechanical properties. Chitin is the second most abundant biopolymer on earth that has *N*-acetyl glucosamine repeating units, and is the main component of exoskeletons of crustaceans such as crab and prawn. An exoskeleton has a hierarchical structure consisting of fine chitin nanofibers (Raabe et al., 2006; Chen, Lin, McKittrick, & Meyers, 2008). Recently, chitin nanofibers were obtained by the mechanical disintegration of commercial chitin powder extracted from the shell of red snow crab (Ifuku et al., 2010). The nanofibers were highly uniform, with widths of approximately 10 nm. Since commercial chitin powder consists of aggregates of nanofiber, chitin was transformed into nanofibers by mechanical processing (e.g., high-pressure fluidizing (Kose and Kondo, 2011; Dutta et al., 2013; Ifuku, Yamada, Morimoto, & Saimoto, 2012)), disk milling (Ifuku et al., 2009; Ifuku, Miwa, Morimoto, & Saimoto, 2011; Ifuku, Nogi et al., 2011), and ultrasonic breaking (Fan, Saito, & Isogai, 2008b; Fan, Fukuzumi, Saito, & Isogai, 2012; Lu et al., 2013), powerful blender (Mushi, Butchosa, Salajkova, Zhou, & Berglund, 2014; Mushi, Kochumalayil, Cervin, Zhou, & Berglund, 2016). However,

strong mechanical stress was required to disintegrate chitin into nanofibers due to the strong hydrogen bonding generated between nanofibers. A lot of energy was consumed to obtain nanofibers, raising their production cost. Thus, the development of an efficient disintegration process is indispensable to the commercial application of chitin nanofibers.

Chemical treatment can improve disintegration efficiency. For instance, Isogai et al. reported chitin nanocrystals prepared by TEMPO-mediated oxidation of α -chitin (Fan, Saito, & Isogai, 2008a). Carboxylate groups were formed by the oxidation of chitin at the C-6 primary hydroxyl group on the nanofiber surface, facilitating mechanical disintegration with the assistance of the osmotic pressure effect. Iwamoto et al. prepared lignocellulose nanofibers by the esterification of wood flour with maleic anhydride (Iwamoto & Endo, 2015). Carboxylate groups were generated by the esterification of hydroxyl groups at the C2, 3, and 6 positions of cellulose. The carboxylate group significantly reduced the energy required to produce lignocellulose nanofibers. Inspired by these previous works, we here studied the facile mechanical disintegration of commercially available chitin powder into nanofibers by chemical treatment with maleic anhydride. Since chitin also has hydroxyl groups at the C3 and C6 positions, it would be esterified also by maleic anhydride. And generating a carboxylate group on chitin enables the facile conversion of chitin into nanofibers by the subsequent mechanical treatment.

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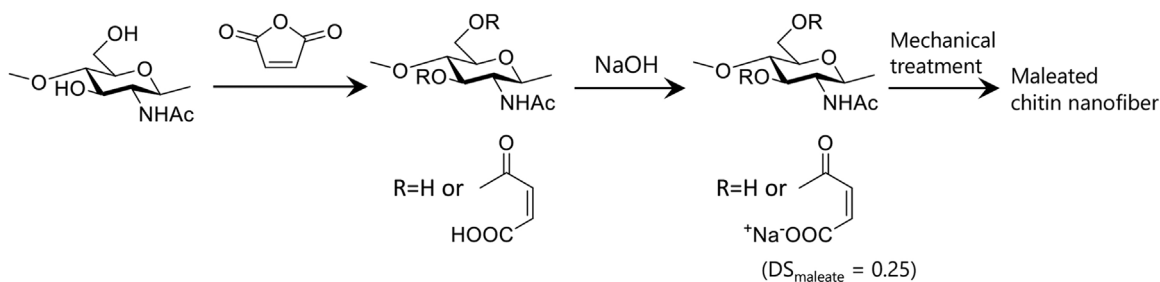


Fig. 1. Preparation scheme for the surface-maleated chitin nanofiber.

2. Experimental

2.1. Materials

Chitin powder from crab shell with a 6.4% degree of deacetylation (DDA) was purchased from Koyo Chemical Industry (Hyogo, Japan) and used without further purification. Maleic anhydride was purchased from Nacalai Tesque (Kyoto, Japan) and used as received.

2.2. Esterification of α -chitin with maleic anhydride

Chitin was esterified as described previously, with partial modification (Iwamoto & Endo, 2015). The scheme for preparing the esterified chitin nanofiber is shown in Fig. 1. Dry chitin powder (6 g) from crab shell reacted with maleic anhydride (30 g) at 120 °C for 3.5 h with occasional stirring. The reactant was collected by filtration and washed with acetone and then with pure water thoroughly until the filtrate became neutral. To neutralize the introduced maleate groups, approximately 10–15 mL of 1.0 M NaOH aqueous solution was added to the esterified chitin water dispersion until the pH of the solution reached 11. The excess NaOH was then removed by washing with pure water until the pH of the suspension became 7.8. The final concentration of the esterified chitin dispersion was 1.29 wt%. The sample was stored in the refrigerator. The experimental yield was estimated by gravimetric analysis.

2.3. Mechanical disintegration

The esterified chitin was diluted with water at 0.5 wt%, and the dilution was treated with a grinder (MKCA6-3; Masuko Sangyo Co., Ltd., Kawaguchi, Japan) twice. The grinder treatment was performed at 1500 rpm with a clearance gauge of -1.5 (corresponding to a 0.15 mm shift) from the zero position, which was determined as the point of slightest contact between the grinding stones. In principle, there is no direct contact between the stones due to the presence of chitin suspension.

2.4. Film preparation

Esterified chitin nanofiber dispersion was diluted with deionized water at 0.1 wt% concentration. After removal of dissolved gases under vacuum, the aqueous dispersion was casted on Teflon plates and dried in the oven at 50 °C until the dried films detached from the plates by themselves.

2.5. Characterization

The zeta potential of aqueous esterified chitin nanofiber dispersion at 0.5 wt% was measured using a laser-Doppler method apparatus (ELSZ-1000ZS, Otsuka Electronics, Hirakata, Japan). At least five samples were measured to know the average value. For field emission scanning electron microscopic (FE-SEM) observation, esterified chitin nanofiber dispersion was diluted with an

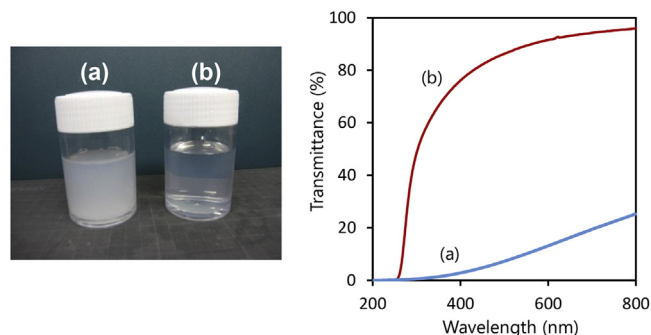


Fig. 2. Photograph and UV-vis spectra of (a) untreated and (b) maleated chitin nanofiber dispersions.

excessive amount of ethanol and dried in an oven. The dried samples were coated with an approximately 2 nm layer of platinum using an ion sputter coater and were observed by FE-SEM (JSM-6700F; JEOL, Tokyo, Japan) operating at 2.0 kV. The light transmittances of 0.1 wt% nanofiber dispersion and the self-standing films were measured using a UV-vis spectrophotometer (V550; JASCO, Tokyo, Japan). The degree of substitution (DS) of the maleate group introduced onto the nanofiber surface was calculated from the C and N weight percentages obtained from an elemental analyzer (Vario, EL III; Elementar, Hanau, Germany) according to:

$$\text{C}/12.01 : \text{N}/14.01 = (8 + 4n) : 1$$

where C and N are the weight percentages of carbon and nitrogen atoms obtained from the elemental analysis and n is the molar ratio of the DS values of the introduced maleate groups against the N-acetyl glucosamine unit of the nanofiber. Electrical conductivity titration method was also applied to determine DS (Fan et al., 2008a).

Infrared spectra of the samples were recorded with an FT-IR spectrophotometer (Spectrum 65, Perkin-Elmer Japan, Tokyo, Japan) equipped with an ATR attachment. The X-ray diffraction profiles were obtained using X-ray goniometer scanning from 5° to 60° with Ni-filtered $\text{CuK}\alpha$ from an X-ray generator (Ultima IV; Rigaku, Tokyo, Japan) operating at 40 kV and 40 mA. The crystallinity indices (CI) of the samples were calculated from the ratio of the area of four crystalline peaks derived from (020), (110), (120), and (130) plane to the total area from $2\theta = 5^\circ$ to 30° (Park, Baker, Himmel, Parilla, & Johnson, 2010). The esterified chitin crystal sizes of the (020) and (110) planes were measured from the widths at half heights of the diffraction peaks, using Scherrer's equation (Alexander, 1979).

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