



Facile nanofibrillation of chitin derivatives by gas bubbling and ultrasonic treatments in water



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ABSTRACT

In this paper, we report that nanofiber network structures were constructed from chitin derivatives by gas bubbling and ultrasonic treatments in water. When chitin was first subjected to N₂ gas bubbling with ultrasonication in water, the SEM images of the product showed nanofiber network morphology. However, nanofiber network was not re-constructed by the same N₂ gas bubbling and ultrasonic treatments after agglomeration. We then have paid attention to an amidine group to provide the agglomeration–nanofibrillation behavior of chitin derivatives. An amidinated chitin was synthesized by the reaction of the amino groups in a partially deacetylated chitin with *N,N*-dimethylacetamide dimethyl acetal, which was subjected to CO₂ gas bubbling and ultrasonic treatments in water to convert into an amidinium chitin by protonation. The SEM images of the product clearly showed nanofiber network morphology. We further examined re-nanofibrillation of the agglomerated material, which was obtained by mixing the nanofibrillated amidinium chitin with water, followed by drying under reduced pressure. Consequently, the material was re-nanofibrillated by N₂ gas bubbling with ultrasonication in water owing to electrostatic repulsion between the amidinium groups. Furthermore, deprotonation of the amidinium chitin and re-protonation of the resulting amidinated chitin were conducted by alkaline treatment and CO₂ gas bubbling–ultrasonic treatments, respectively. The material showed the agglomeration–nanofibrillation behavior during the processes.

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1. Introduction

Naturally occurring polysaccharides are widely distributed in nature and have been regarded as structural materials and as suppliers of energy.¹ Fabrication of new bio-based and environmentally benign materials from them has been exploited alternative to petroleum-based materials because of their eco-friendly and biodegradable properties.² Chitin is an aminopolysaccharide consisting of a chain of β-(1→4)-linked *N*-acetyl-D-glucosamine (GlcNAc) residues, which is one of the most abundant polysaccharides and occurs mainly in the exoskeletons of crustaceans, shellfishes, and insects.^{3–5} Despite its huge annual production in nature 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 biocompatible properties.⁶ Therefore, the researches concerning

conversion of chitin into functional bio-based materials have attracted much attention even in recent years.⁷ Native chitin in the exoskeleton of crustacean is arranged as microfibrils embedded in a protein matrix. The microfibril consists of nanofibers with 2–5 nm diameters.^{8,9} Accordingly, one of the efficient approaches to produce chitin-based functional materials is nanofibrillation, such as the fabrication of nanofibers and nanowhiskers, from its native sources.^{10–16} Conventional approach to the construction of chitin nanostructures is mainly performed upon top-down procedures that break down the starting bulk fibril materials from natural resources by appropriate treatments in water, such as grinding mechanical technique and electrostatic repulsion by the introduction of carboxylate groups.^{17–20} Because such dispersed chitin nanostructures under wet conditions tend to agglomerate by drying process due to strong hydrogen bonding among numerous hydroxy groups on the chitin chains, there have not been many reports on nanofibrillation from the dried chitin agglomerates.²⁰

In this study, we have found nanofibrillation of chitin derivatives facily took place by gas bubbling and ultrasonic treatments in water. Furthermore, we have noted an amidine group for the

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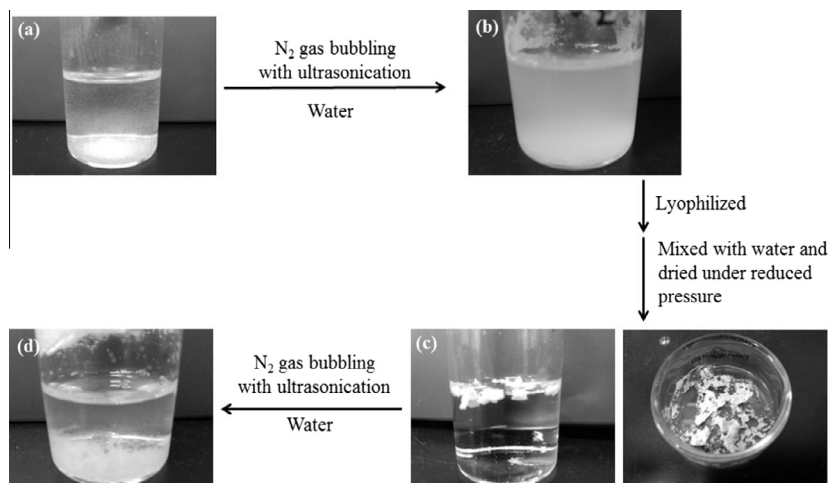


Figure 1. Dispersion of chitin by N₂ gas bubbling with ultrasonication in water (a→b), agglomeration by mixing nanofibrillated chitin with water, followed by drying under reduced pressure (b→c), and treatment of agglomerated chitin by N₂ gas bubbling with ultrasonication in water (c→d).

production of a chitin derivative, which exhibits re-nanofibrillation behavior even after agglomeration by drying. Because the amidine group is reversibly converted into amidinium bicarbonate by protonation under CO₂ gas treatment conditions in water,²¹ and thus has been used as the functional group for the production of reversibly coagulatable and redispersible polymeric materials,^{22–24} we have considered that the introduction of the amidine group into chitin leads to provide its re-nanofibrillation behavior.

In this paper, we report the fabrication of nanofiber network structure from a commercially available chitin powder by the simple N₂ gas bubbling with ultrasonication in water. Furthermore, an amidinium chitin was synthesized from the nanofibrillated chitin by successive partial deacetylation, amidination, and CO₂ gas treatment. The re-nanofibrillation behavior of the product was investigated by agglomeration of the wetted product by drying under reduced pressure and subsequent N₂ gas bubbling with ultrasonication in water. Agglomeration and re-nanofibrillation of the amidinium chitin were also attempted by successive deprotonation and re-protonation processes. The present study provides the facile fabrication of chitin nanostructures, which have a potential for practical applications as biocompatible nanomaterials in the future.

2. Results and discussion

2.1. Nanofibrillation of commercial chitin

In this study, first, an attempt of direct nanofibrillation of a commercial chitin powder was made in water. Consequently, because chitin was dispersed in water by N₂ gas bubbling with ultrasonication at room temperature (Fig. 1a→b), we assumed the progress of the nanofibrillation. To evaluate the structure of the product in nano-scale, first, small fractions of the dispersion were dried on a scanning electron microscopy (SEM) sample plate under the ambient conditions and the SEM images of the resulting sample showed nanofibers (Fig. 2b), which were completely different from those of an original chitin powder (Fig. 2a). Then, the whole nanofibrillated chitin was isolated by lyophilization of the dispersion and the resulting product was also subjected to the SEM measurement. In the SEM images of the product (Fig. 2c), the nanofiber network morphology with an average width of 93 nm (calculated from widths of 20 fibers) was seen. These SEM results indicated that chitin was efficiently nanofibrillated by the facile N₂ gas bubbling and ultrasonic treatments in water. The nanofibrillation was probably caused by disentanglement of native

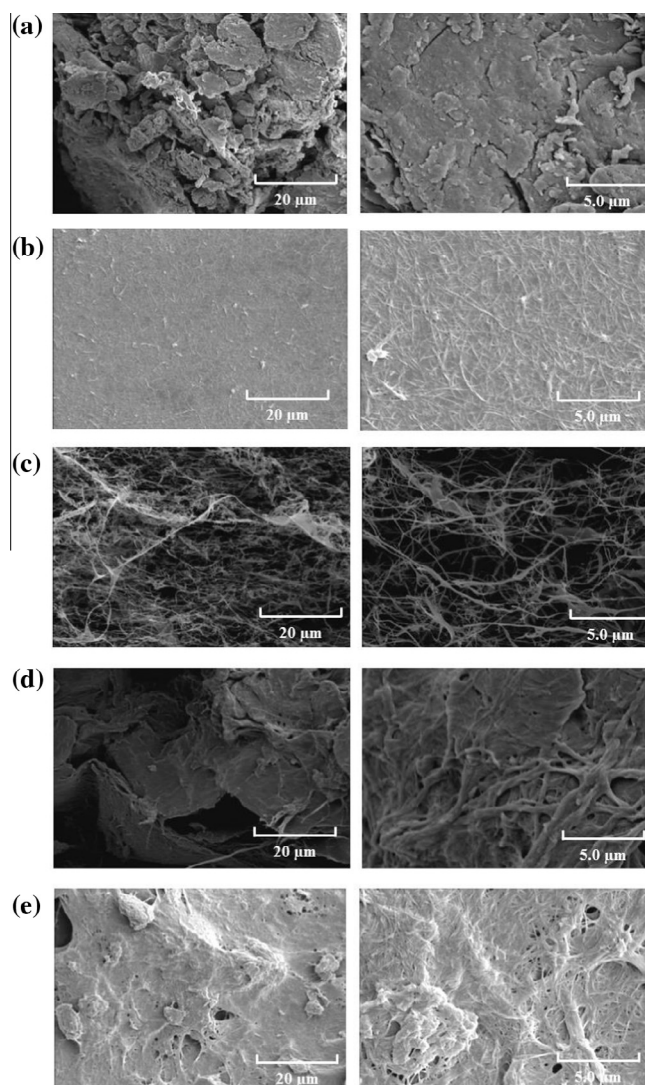


Figure 2. SEM images of commercial chitin powder (a), nanofibrillated chitins by N₂ gas bubbling with ultrasonication in water (b; after drying small fractions of the dispersion under ambient conditions, c; after lyophilization of the dispersion), agglomerated chitin by mixing nanofibrillated chitin with water, followed by drying under reduced pressure (d), and after treatment of agglomerated chitin by N₂ gas bubbling with ultrasonication in water (e).

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