



Short communication

Fabrication of cationic chitin nanofiber/alginate composite materials



Koki Sato, Kohei Tanaka, Yusei Takata, Kazuya Yamamoto, Jun-ichi Kadokawa*

Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

ARTICLE INFO

Article history:

Received 1 April 2016

Received in revised form 28 May 2016

Accepted 7 June 2016

Available online 8 June 2016

Keywords:

Alginate

Chitin nanofiber

Composite material

Ion exchange

Ionic cross-linking

ABSTRACT

We have already found that an amidinated chitin, which was prepared by the reaction of a partially deacetylated chitin with *N,N*-dimethylacetamide dimethyl acetal, was converted into an amidinium chitin bicarbonate with nanofiber morphology by CO₂ gas bubbling and ultrasonic treatments in water. In this study, we performed the fabrication of composite materials of such cationic chitin nanofibers with an anionic polysaccharide, sodium alginate, by ion exchange. When the amidinium chitin bicarbonate nanofiber aqueous dispersion was added to an aqueous solution of sodium alginate, the composite material was agglomerated, which was isolated by centrifugation, filtration, and lyophilization, to form a manipulatable sheet. The morphology of the resulting sheet at nano-scale was evaluated by SEM measurement.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Polysaccharides are widely distributed in nature and act as important *in vivo* substrates, such as structural material and supplier of energy [1,2]. They are also regarded as representative biomass resources and are used as the components in functional bio-based materials alternative to petroleum-based materials because of their biodegradable, low-toxic, and eco-friendly properties [3,4]. Chitin, which is a natural aminopolysaccharide composed of $\beta(1\rightarrow4)$ -linked *N*-acetyl-D-glucosamine repeating units, occurs mainly in the exoskeletons of crustaceans, shellfishes, and insects [5–8]. Although chitin is one of the most abundant polysaccharides, it still remains mostly as an unutilized biomass resource mainly because of its intractable bulk structure and insolubility in water and common organic solvents owing to numerous intra- and intermolecular hydrogen bonds and stiff molecular chain packing [9]. Therefore, the researches concerning the incorporation of chitin into functional bio-based materials have attracted much attention even in recent years. One of the efficient approaches to fabricate chitin-based functional materials is nanofibrillation, such as nanofibers and nanowhiskers [10–16]. Break down the starting bulk fibril materials from native chitin by appropriate treatments in water has mainly been conducted to induce nanofibrillation, such as grinding mechanical technique and electrostatic repulsion by the introduction of carboxylate groups [17–21].

In the previous study, we also reported that the facile nanofibrillation of a commercial chitin powder took place by N₂ gas bubbling and ultrasonic treatments in water (Fig. 1, SEM image) [22]. After the obtained nanofiber networks were agglomerated once drying under reduced pressure, however, re-nanofibrillation of the agglomerate did not occur by the N₂ gas bubbling and ultrasonic treatments. This is because that aggregated chitin nanostructures, resulted by drying, are not facilely re-dispersed due to strong hydrogen bonding among numerous hydroxy and acetamido groups on the chitin chains [20]. To provide the re-nanofibrillation behavior in chitin, the amidine groups were introduced according to the reaction in Fig. 1. The amidine groups are reversibly converted into amidinium bicarbonates by protonation under CO₂ gas treatment conditions in water [23], and have been used as the functional group for the production of reversibly coagulatable and redispersible polymeric materials [24–26]. The amidinium chitin bicarbonate was obtained from the amidinated chitin by CO₂ gas bubbling and ultrasonic treatments in water (Fig. 1), which exhibited the agglomeration-nanofibrillation behavior owing to electrostatic repulsion between the amidinium groups.

We have continuously been studying the fabrication of composite materials of the amidinium chitin nanofibers with anionic polymers by ion exchange. For the production of such composite materials, we have chosen alginic acid (alginate), also a representative natural polysaccharide. Alginate occurs both as a structural component in marine brown algae (*Phaeophyceae*) comprising up to 40% of the dry matter, and as capsular saccharides in soil bacteria [1]. It is a linear heteropolysaccharide consisting of (1→4) linked β -D-mannuronic acid (M) and α -L-guluronic acid (G), which construct

* Corresponding author.

E-mail address: kadokawa@eng.kagoshima-u.ac.jp (J.-i. Kadokawa).

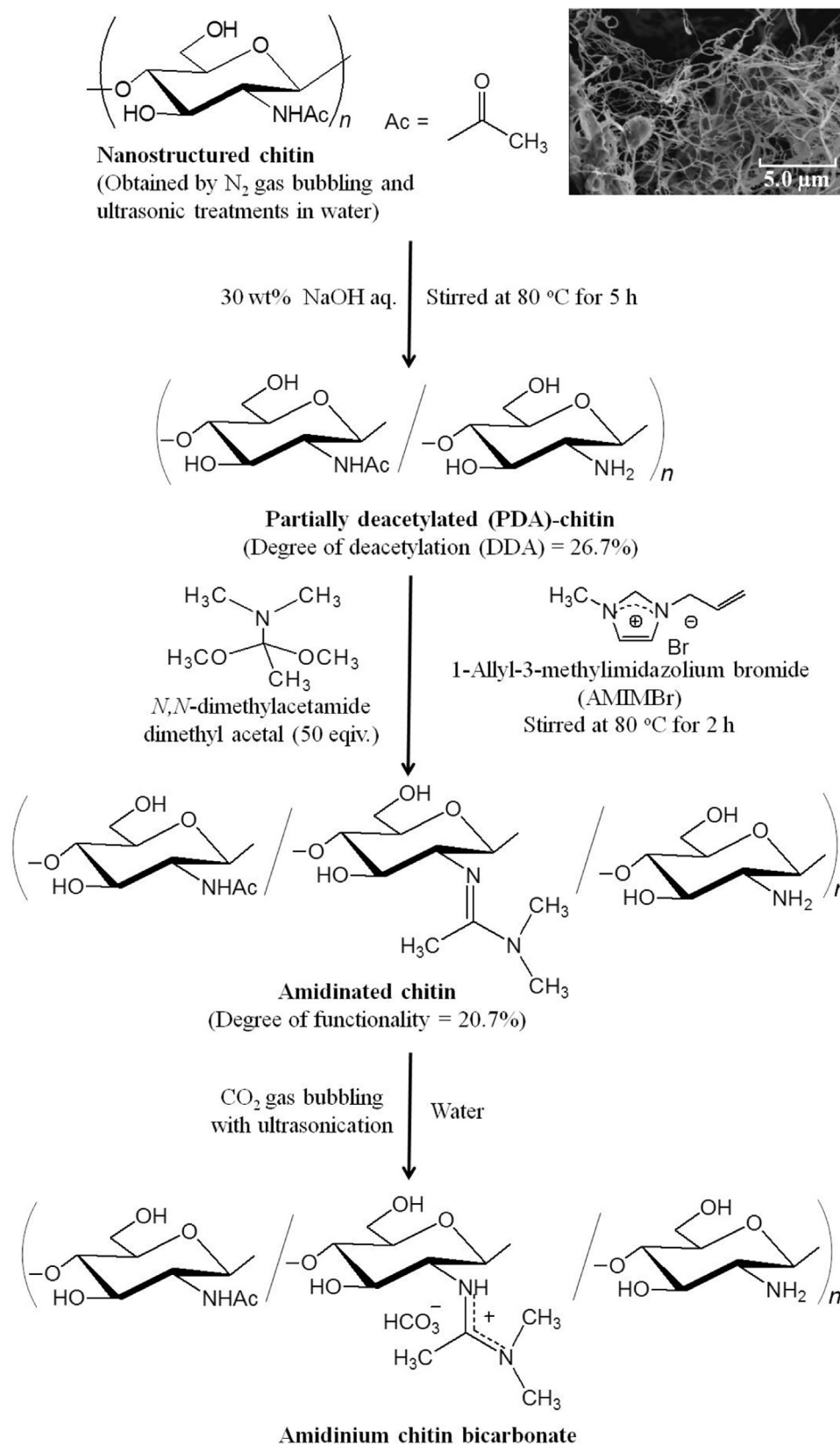


Fig. 1. Synthesis of amidinated chitin via partial *N*-deacetylation of chitin and conversion into amidinium chitin bicarbonate [22].

a block structure of homosequential (MM and GG) blocks and/or heterosequential (MG and GM) blocks. Owing to the presence of the carboxylic acid groups, alginate has an anionic nature (Fig. 2a), forming alginate salts with cationic metals such as Ca²⁺ and Na⁺

[27]. Furthermore, because calcium alginate is insoluble and though swells in water, alginate beads are conventionally prepared by ionic cross-linking of carboxylates with Ca²⁺. Therefore, we expected the facile fabrication of composite materials of the cationic ami-

Download English Version:

<https://daneshyari.com/en/article/1985679>

Download Persian Version:

<https://daneshyari.com/article/1985679>

[Daneshyari.com](https://daneshyari.com)