



Microwave technique for efficient deacetylation of chitin nanowhiskers to a chitosan nanoscaffold

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ARTICLE INFO

Article history:

Received 17 September 2008

Received in revised form 20 October 2008

Accepted 21 October 2008

Available online 26 October 2008

Keywords:

Chitin-chitosan

Whisker

Microwave technique

Nanoscaffold

ABSTRACT

A chitosan nanoscaffold in the form of a colloidal solution was obtained from the deacetylation of chitin whiskers under alkaline conditions by using a microwave technique in only 1/7 of the treatment time of the conventional method. Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (¹H NMR) techniques confirm the degree of deacetylation to be above 90% within 3 h. The wide-angle X-ray diffraction (WAXD) pattern clearly shows that the highly crystalline chitin whiskers are changed to amorphous chitosan. SEM micrographs show the aggregation of branched nanofibers, whereas the TEM micrographs reveal the scaffold morphology.

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1. Introduction

Chitin is the second most abundant natural polysaccharide next to cellulose, and is obtained from the cell walls of fungi and yeast and from the shells of crustaceans, such as crabs and shrimps.¹ In general, chitin consists of copolymer repeat units of β -(1 \rightarrow 4)-linked 2-acetamido-2-deoxy- β -D-glucose and β -(1 \rightarrow 4)-linked 2-amino-2-deoxy- β -D-glucose. As chitin dissolves only in specific solvents—such as *N,N*-dimethylacetamide (DMAC)–LiCl,^{2,3} hexafluoroacetone, and hexafluoro-2-propanol⁴—its practical uses are limited.⁵ Deacetylating chitin to chitosan, which increases the units of β -(1 \rightarrow 4)-linked 2-amino-2-deoxy- β -D-glucose, is one way to develop a chitin–chitosan-based material because of its good solubility in carboxylic acids.⁶ Up to now, most reports on chitosan have been about potential materials with biocompatibility, biodegradability, bioactivity, and non-toxicity.^{7–10} Despite the many unique properties for utilization, chitosan acid solutions are, sometimes, not ideal for the preparation of the practical materials. However, chitosan derivatives (especially water-soluble chitosans and organo-soluble chitosans) have been reported for novel applications.

Advances in characterization techniques have allowed us to observe materials at the nano-scale level, and the development of

material from the molecular level has become a challenging theme. Currently, the changing of chitin and chitosan from flakes or powder to the nano scale, along with possible novel applications, is being variously reported. For example, Nair and Dufresne reported chitin whiskers by the acid hydrolysis of chitin from crab shells, and their use as nanofibers reinforcing material for natural rubber.¹¹ For chitosan, chemical modification to obtain nanoparticles¹² and electrospinning to obtain nanofibers^{13,14} are some reported cases.

For the past few years, our group has been focusing on various approaches to achieve chitosan nanomaterials, including studies on their unique properties and feasible applications. We succeeded in preparing chitosan nanospheres by conjugating hydrophilic and hydrophobic groups on chitosan.¹⁰ We also found that, by extending the deacetylation after obtaining chitin whiskers, we could obtain nano-sized chitosan.¹⁵ At that time, we found that the uniqueness of deacetylating chitin whiskers to chitosan is that the chitosan so obtained had a fibrous network with a nanoporous structure.

Although obtaining chitosan with nanopores via a simple treatment is attractive (where many advanced applications related to the high surface area and high absorptivity are the goal), we accept the fact that treatment in a concentrated alkaline solution at almost reflux temperature for more than 20 h is quite severe, and may not be practical for large-scale production. As the microwave technique is known to be an effective system for either synthesis^{16–18} or

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depolymerization¹⁹ due to its instantaneous heating and vibrational energy at the molecular level,^{20,21} we herein consider this technique for the efficient deacetylation of chitin whiskers.

2. Experimental

2.1. Materials

Chitin in flake form from shrimp shells was provided by Seafresh (Lab) Company Limited, Thailand. Sodium hydroxide (NaOH) was purchased from Fluka Chemicals, Switzerland, and hexafluoroisopropyl alcohol (HFIP) was obtained from Central Glass Co., Ltd, Japan. Hydrochloric acid (HCl) was purchased from Labskan, Ireland, and the deuterated acetic acid (CD₃CO₂D) and deuterium oxide (D₂O) were purchased from Sigma–Aldrich, the Netherlands. All chemicals were of AR grade, and were used without further purification.

2.2. Instruments and equipment

A Milestone Ethos microwave solvent extraction labstation, at a frequency of 2.45 GHz, was used to treat the chitin whiskers in N₂ at 150 °C. Qualitative and quantitative Fourier-transform infrared spectra were obtained with a Nicolet NEXUS 670 with 32 scans at a resolution of 2 cm⁻¹ in a frequency range of 4000–400 cm⁻¹. ¹H NMR spectra were collected from a Bruker Avance 400 spectrometer with 512 scans by using CD₃CO₂D/D₂O (2% v/v) as a solvent. Wide-angle X-ray diffraction (WAXD) patterns were obtained over a 2–60° 2θ range by a RIGAKU RINT 2000 instrument, using Cu Kα as an X-ray source, which is equipped with a Ni filter and operating at 40 kV and 30 mA. A Perkin–Elmer thermogravimetric differential thermal analyzer was applied using a N₂ flow rate of 20 mL/min with a heating rate of 10 °C/min starting from 50 to 550 °C. The morphology was analyzed by a JEOL JSM-5410LV scanning electron microscope (SEM) at 15 kV and by a H-7650 Hitachi transmission electron microscope (TEM) at 100 kV. A Tohsco HLC-8220 gel-permeation chromatograph (TSK gel Super HM-N and Super H-RC columns; Tohsco Co., Japan) was used to evaluate the molecular weight of the chitosan. The conditions were an operating temperature of 40 °C, using hexafluoroisopropyl alcohol (HFIP) as the eluent, and an eluent flow of 0.2 mL/min.

2.3. Preparation of chitin whiskers

Chitin whiskers were prepared by modifying the conditions based on the report from Nair and Dufresne.¹¹ Chitin (**1**, 3 g, 14.8 mmol) was hydrolyzed with 3 N HCl (300 mL) at 105 °C for 3 h. After washing the product thoroughly with deionized water, the alkaline product was further treated in 3 N HCl (300 mL) at 105 °C for 6 h. The product was dialyzed in distilled water until it was neutral (pH 7) to obtain chitin whiskers, **2**. FTIR (KBr, cm⁻¹): 3000–2800 cm⁻¹ (C–H stretching); 1661 and 1624 cm⁻¹ (amide I), and 1557 cm⁻¹ (amide II).

2.4. Preparation of a chitosan nanoscaffold

Chitin whiskers (**2**) in aqueous solution (solid content ~5.91%, 5 mL) were treated in aq NaOH (40% w/v, 25 mL) at 150 °C in the microwave chamber under N₂ atmosphere. The sample was collected and dialyzed in distilled water until it was neutral (pH 7), after treating times of 1, 3, and 6 h, to obtain chitosan **3**. Similarly, treatment using aq NaOH for 50% and 60% w/v was also carried out. FTIR (KBr, cm⁻¹): 3500–3300 cm⁻¹ (OH); 3000–2800 cm⁻¹ (C–H stretching); 1661 cm⁻¹ (amide I); and 1595 cm⁻¹ (–NH₂). ¹H

NMR: δ 1.9 (NH–Ac); 3.15 (H-2 of GLcN unit in chitosan), and 3.5–4.0 (H-3 to H-6 of pyranose ring).

2.5. Evaluation of the degree of deacetylation

The degree of deacetylation (%DD) was determined from the ¹H NMR spectrum. The peak areas of the *N*-acetyl group at 1.9 ppm and of the H-2 at 3.15 ppm were considered for substituting in the following equation to calculate %DD:

$$\%DD = \left\{ 1 - \left[\frac{(I_{\text{CH}_3/3})}{(I_{\text{H2}})} \right] \right\} \times 100$$

The %DD was also quantitatively analyzed by FTIR using OPUS spectroscopic software, version 2.0. The peaks of interest were 1658 cm⁻¹ (–CONH–) and 895 cm⁻¹ (C–O–C).

3. Results and discussion

3.1. Chemical structure analysis

Chitin flakes (**1**) were treated in hydrochloric acid (3 N) (as reported by Nair and Dufresne¹¹) before being further treated with NaOH. Compared to the FTIR spectrum of **1** (Fig. 1(a)), that of **2** shows sharp characteristic peaks in all ranges, as seen from the peaks at 3500–3300 cm⁻¹ (–OH); 2900–2800 cm⁻¹ (C–H stretching); and 1661, 1624, and 1557 cm⁻¹ (amides I and II) (Fig. 1(b)). This implies highly crystalline chitin whiskers.

Phongying et al.¹⁵ demonstrated the preparation of chitosan by treating chitin whiskers in NaOH 40% for 21 h to obtain a degree of deacetylation of 95%. Under these conditions, a colloidal solution was obtained. Here, **2** was deacetylated using a 40–60% alkaline solution to obtain **3** in the form of a colloidal solution. For the 60% alkaline treatment, the FTIR spectrum (Fig. 1(c)) shows a significant decrease in the peak of 1661 cm⁻¹ with a new peak at 1595 cm⁻¹ (–NH₂), as compared to **2** (Fig. 1(b)). This indicates that the acetyl group of chitin was significantly removed.

Figure 2 shows the chemical shift at δ 1.9 (–CH₃– in chitin unit), 3.15 (H-2 of pyranose ring), and 3.5–4.0 (H-3 to H-6 of pyranose ring), which is calculated for the degree of deacetylation of 96%.

3.2. Optimal conditions of the microwave technique for deacetylation

In order to find the optimal conditions for the deacetylation of chitin whisker, the alkaline concentration and the treating time

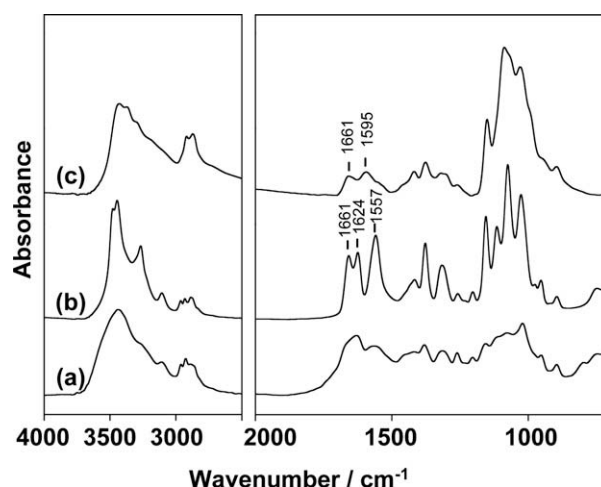


Figure 1. FTIR spectra of (a) **1**, (b) **2**, and (c) **3** in 60% alkaline solution for 6 h treating time.

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