Effect of sodium hydroxide on properties of shrimp-shells-extracted chitin nanofibers

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Abstract. Shrimp shells from seafood wastes were used as a raw material to prepare chitin nanofibers (ChNFs) by combined chemical and mechanical treatments. The extraction of chitin from shrimp shells involved multistep procedures of deproteinization, demineralization, and deacetylation. The deacetylation refers to the replacement process of acetyl groups by reactive amino groups (-NH₂). After that, treated chitin were fibrillated by high-speed blending to disintegrate ChNFs. In this work, we studied the effect of sodium hydroxide (NaOH) concentrations (0 - 30 %wt) on properties of ChNFs. Fourier transform infrared (FT-IR) spectra showed with increasing concentrations of NaOH, the intensity of the peak located at ~1550 cm⁻¹, corresponding to the presence of amide groups (-NH) on chitin molecules decreased. This was an indication of the removal of acetyl groups. The thermal stability of ChNFs was subsequently analyzed by thermogravimetric analysis (TGA). With increasing the concentrations of NaOH, the lower thermal stability of ChNFs was obtained. In addition, the morphologies of ChNFs with widths of a few nanometers were observed by a field emission scanning electron microscope (FE-SEM). The prepared ChNFs in this work could be possibly used as a reinforcing agent for composite applications.

1. Introduction

According to environmentally sustainable concerns, the use of renewable natural resources such as shrimp or crab shells from seafood processing industries has become attractive for the production of alternative materials to replace petroleum-based materials. Chitin is a natural material that can be extracted from crustacean shells, and has a similar structure to cellulose. At the second carbon position, chitin has an acetamido group (-NHCOCH₃) while cellulose has a hydroxyl group (-OH). Attempts have been made to prepare chitin nanofibers (ChNFs) due to their promising properties such as high strength, stiffness, and thermal stability, which can be used to improve mechanical properties of polymers [1-3]. The preparation of ChNFs requires a complex tool and high energy consumption. Therefore, several approaches have been introduced to easily obtain ChNFs with less energy consumption [4, 5]. The introduction of the deacetylation process, the transformation of the acetyl groups to amino groups in the chitin structure, results in a decrease of the induced adhesion between chitin molarcular chains. This allows the efficient disintegration of ChNFs with less energy consumption. When the degree of deacetylation is more than 50%, deacteylated chitin would be converted to chitosan as shown in Figure 1 [6].

Here, various concentrations of NaOH (0 - 30 %wt) were introduced in the deacetylation process, associated with a high-speed blender to obtain ChNFs extracted from shrimp shells [5-9]. Effects of NaOH concentrations on properties of the prepared ChNFs were further investigated.
Figure 1. Reaction of the deacetylation process transforming acetyl groups to amino groups.

2. Experimental

2.1 Materials
Shrimp shells were obtained from Mahachai, Samut Sakhon, Thailand. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) (37%) were purchased from QREC Chemical Co. (Chonburi, Thailand) while acetic acid was purchased from RCI LABSCAN company. All materials were used as received without further purification.

2.2 Preparation of Chitin nanofibers
Initially, shrimp shells were deproteinized using 4 wt% NaOH for 24 h at room temperature. Then, the treated chitin was neutralized with distilled water, and dried at 65 °C. Secondly, the demineralization was introduced by treating chitin with 4 wt% HCl for 24 h at room temperature, and the neutralization with distilled water was further applied. The deacetylation to remove acetyl groups from chitin structure was the third-step method. During this step, various concentrations of NaOH between 0 and 30 % were used to treat chitin for 2 h at 100 °C, and the deacetylated chitin was washed with deionized water for several times until neutral. The solid concentration of the chitin suspension was adjusted to be ~ 1 w/v% with distilled water. Finally, the chitin suspension was disintegrated using a high-speed blender (Stromix 3500 watt, 40000 rpm) for 30 min. During fibrillation, a few drops of acetic acid were added into the suspension to adjust pH to be 3 - 4 in order to facilitate fibrillation by electrostatic repulsive force. Chitin nanofibers (ChNFs) were coded as NaOH X where X was a NaOH concentration used to treat chitin. For example, NaOH 10 was the ChNF sample treated with 10% of NaOH.

2.3 Characterization of Chitin nanofibers
ChNF samples were analyzed using a Fourier transform infrared spectrometer (FT-IR, Thermo-Nicolet 6700). FT-IR spectra were collected between the wavenumber range of 4,000 to 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) and accumulation of 64 scans.

Thermal properties of ChNFs prepared with various NaOH concentrations were measured using a thermogravimetric analyzer (TGA/SDTA, Mettler Toledo). The ChNF samples were heated to 700 °C at a heating rate of 10 °C min\(^{-1}\) under nitrogen atmosphere.

Morphology of ChNFs deacetylated with various NaOH concentrations were investigated using a field emission scanning electron microscope (FE-SEM JSM-7610F) with an acceleration voltage of 5 kV and a magnification of 20000 times. Before each observation, a sample was sputter-coated with a thin layer of gold to avoid electrical charge during the operation.
3. Result and discussion

3.1 Chemical groups of chitin nanofibers

Functional groups of the untreated (NaOH 0) and treated ChNFs (NaOH 10 and NaOH 30) characterized by FT-IR are shown in Figure 2. After the deacetylation process with NaOH treatment, both NaOH 10 and NaOH 30 samples showed similar characteristic peaks to the undeactylated chitin sample (NaOH 0). The FT-IR spectra obtained for all chitin samples exhibit the peaks located at ~3480 and 3269 cm⁻¹, corresponding to -OH absorption and -NH stretching bands, respectively. The peaks related to amide characteristic (1620 and 1650 cm⁻¹ for amide I, 1550 cm⁻¹ for amide II and 1320 cm⁻¹ for amide III) were also found for all samples. With the introduction of the deacetylation process with NaOH, a decrease in the intensity of these amide peaks located at 1550, 1620 and 1650 cm⁻¹ was observed, and NaOH 30 presented the lowest intensity of these amide peaks in comparison with those of NaOH 0 and NaOH 10, resulting from the transformation of the acetyl groups to amino groups. This would be because the NaOH 30 sample might contain the higher degree of deacetylation than the others. It should be noted that the peak at 1590 cm⁻¹, corresponding to amino groups, found in chitosan could not be observed for NaOH 10 and NaOH 30 materials [10]. This might be owing to the predominance of the remained amino groups in the chitin structure in comparison with amounts of amino groups generated by the deacetylation process. It is worth noted that the amino groups on the treated ChNFs backbone were cationized by acetic acid, leading to easily disintegration of nanofibers by acid-induced electrostatic repulsion.

![Figure 2](image)

*Figure 2.* Fourier transform infrared (FT-IR) spectra of the treated chitin nanofibers (ChNFs).

3.2 Morphology of chitin nanofibers

The morphologies of ChNFs measured by FE-SEM are shown in Figure 3. The FE-SEM micrographs could confirm that fibrillation of ChNFs with a diameter range of 14–18 nm prepared with 30% NaOH while aggregated fibrils could be easily observed from NaOH 0 and NaOH 10. The fiber aggregation was fibrillated into homogeneous nanofibers at a high concentration of NaOH by using a house-hold food blender because the cationization of the amino groups on the ChNFs surface could produce the electrostatic repulsion. Therefore, the physicochemical properties of ChNFs would be dependent on a
concentration of NaOH. Similar disintegration of ChNFs from the literatures with widths of 20-30 nm was prepared by a high speed blender at 15,000 rpm [2, 11, 12].

![Micrographs of ChNFs treated with various concentrations of NaOH taken by a field emission scanning electron microscope (FE-SEM). Arrows points to fibrillated nanofibers.](image)

3.3 Thermal properties of chitin nanofibers

Figure 4 presents thermograms of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) of the chitin samples treated with NaOH. There are two main degradation regions found for untreated and treated ChNFs with 10 % NaOH. The first transition occurs at temperature between 50 and 100 °C owing to moisture evaporation. The second mass loss transition is the degradation of chitin, which happens between 345 and 400 °C. This degradation is caused by dehydration of saccharide rings and acetylated and deacetylated chitin units. On the other hand, the NaOH 30 sample showed three distinctive degradation transitions including moisture evaporation, glycosidic bond and chitin degradation. The occurrence of glycosidic bond degradation could be due to the transformation of acetyl groups to amino groups resulting from the deacetylation treatment. Thermal degradation temperature of the NaOH 0, NaOH 10 and NaOH 30 samples at 10% mass loss were 293.9, 289.9 and 243.7 °C, respectively. It can be seen that the thermal degradation temperature of ChNFs treated with NaOH decreased in comparison with that of untreated ChNFs due to a higher number of amino groups in the chitin structure, as confirmed by FT-IR measurements. The char content at 700 °C was also proportionally dominated by the content of amino groups in the chitin backbone [13]. The char content of NaOH 30 at 700 °C was 35.1% while NaOH 0 and NaOH 10 had a char content of 24.1 and 25.7%, respectively.

![Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) thermograms of the treated ChNFs.](image)
4. Conclusion

- ChNFs with diameters in the range of 14 and 18 nm were successfully extracted from shrimp shells by using the combined alkaline treatment with mechanical disintegration.
- The FT-IR spectra showed the reduction of acetyl groups of the chitin structure after the deacetylation treatment.
- With increasing NaOH concentrations, the lower thermal ability of the treated ChNFs associate with a higher content of the residue at high temperature was observed.
- The prepared ChNFs in this work could be possibly used as a reinforcing agent for composite applications.

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Reference

[1] Salaberria A M, Labidi J and Fernandes S C M 2014 Chem. Eng. J. 256 356-364
[2] Hatanaka D, Yamamoto K, and Kadokawa J 2014 Int. J. Biol. Macromol. 69 35-39
[3] Coltelli M, Cinelli P, Gigante V, Aliotta L, Morganti P, Panariello L, and Lazzeri A 2019 Int. J. Mol. Sci. 20(3) 504
[4] Biswas S K, Shams M I, Das A K, Islam M N and Nazhad M M 2015 Fibers Polym. 16(4) 774-781
[5] Wang J, Kasuya K, Koga H, Nogi M and Uetani K 2021 Nanomaterials 11 658
[6] Moura C M D, Moura J M D, Soares N M, and Pinto L A D A 2011 Chem. Eng. Process. 50(4) 351-355
[7] Nawawi W M F W, Lee K Y, Kontturi E, Murphy R J and Bismarck A 2019 ACS Sustain. Chem. Eng. 7 6492-6496
[8] Uetani K and Yano H 2011 Biomacromolecules 12 348-358
[9] Rahimi K S M, Batchelor W, Kosinkova J, Pepper R, Brown R and Rainey T 2019 Cellulose. 26(8) 4799-4814
[10] Li M C, Wu Q, Song K, Cheng H N, Suzuki S and Lei T 2016 ACS Sustain. Chem. Eng. 4 4385-4395
[11] Biswas S K, Das A K, Yano H and Shams M I 2013 Sci. Am. J. Chitin Chitosan Sci. 1 138-143
[12] Shams M I and Yano H 2013 J. Polym. Environ. 21 937-934
[13] Nam Y S, Park W H, Ihm D and Hudson S M 2010 Carbohydr. Polym. 80 291-295