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I-SEEC 2012

Proceeding - Science and Engineering (2013) 530–535

Proceeding
Science and Engineering

www.iseec2012.com

Science and Engineering Symposium
4th International Science, Social Science, Engineering and Energy Conference 2012

Preparation and structure of chitosan from waste sources

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Abstract

This work presents the preparation of chitosan powders from waste sources including shrimp, crab shells and squid pens. Firstly, all raw materials were washed in distilled water and then they were finely grounded using agate mortar and sieved in the range of 212-250 μm to obtain fine powders. Next, the powdered samples were immersed into solution of chloroform and methanol (with 2:1 ratio) at room temperature to remove fat. To process of deprotienation and decarbonation, the samples were immersed in 5 wt% of NaOH solution for 24 h and in 4 wt% of HCl solution for 1 h, respectively. Finally chitin powders were obtained. To obtain chitosan powders, the chitin powders were firstly immersed in 50 wt% NaOH solution before freezing at 4 ^{o}C for 24 h. Then they were immersed in 10 wt% NaOH solution and heated at 230 ^{o}C for 5 min to remove acetyl group. The XRD results confirm the chitosan from shrimp and crab shells are more crystalline than that from squid pens. Moreover, FT-IR results could full filly assigned to the difference of chitosan from α-chitin and β-chitin. The TGA results showed the chitosan extracted from the crab and shrimp shells exhibited more weight loss than that extracted from the squid pen.

Selection and/or peer-review under responsibility of Faculty of Science and Technology, Kasem Bundit University, Bangkok.

Keywords: Characterization, Chitosan Extracted, Waste sources, FTIR Techniques

1. Introduction

Massive amounts of crab shells, shrimp shells and squid pens have been abandoned as wastes from worldwide seafood companies [1]. The processing of human food production causes shells and residual meat about 50-70% of the total shrimp, crab and squid. Thus this has led to interest for using these wastes [2]. They contain main components such as protein and chitin. A large portion of the waste is chitin, which is not readily digestible and thus the waste cannot be used commercially as animal feed either [3]. Because chitin has a compact structure, it

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is insoluble in most solvents. Therefore, the chemical modifications of chitin are performed. Its most common derivative is chitosan, derived by partial deacetylation of chitin.

Chitosan has several distinctive properties, including biocompatibility and biodegradability, cellular binding capability, acceleration of wound healing, hemostatic properties, and antibacterial properties. Therefore, they have been widely appliedas materials for many applications, such as heavy metal absorption, pulp and paper production, cosmetics, biomedical materials and devices, food additives and a component in drug delivery formulations [3, 4].

In present study, characteristics of chitosan extracted from different sources such as squid pen, shrimp shell and crab shell were quantitatively compared. The crystal structure, chemical structure and thermal behaviour of chitosan powders were evaluated via powder X-ray diffraction (XRD), Fourier transform infrared analysis (FT-IR) and thermogravimetric analysis (TGA) techniques, respectively.

2. Material and Method

2.1 Sample Preparation

Fresh samples of squid pen, shrimp shell and crab shell from food production were collected from a local source in Thailand.This work presents the preparation of chitosan powders from waste sources including shrimp, crab shells and squid pens. Firstly, all raw materials were washed in distilled water and then they were finely grounded using agate mortar and sieved in the range of 212-250 μm to obtain fine powders. Next, the powdered samples were immersed into solution of chloroform and methanol (with 2:1 ratio) at room temperature for 1 h to remove fat. To process of deprotienation and decarbonation, the samples were immersed in 5 wt% of NaOH solution for 24 h and in 4 wt% of HCl solution for 1 h, respectively. Finally chitin powders were obtained. To obtain chitosan powders, the chitin powders were firstly immersed in 50 wt% NaOH solution before freezing at 4 ^{o}C for 24 h. Then they were immersed in 10 wt% NaOH solution and heated at 230^{o}Cfor 5 min to remove acetyl group.

2.2 Sample Characterization

The crystalline structures of chitosan extracted from different sources ware identifield powder by X-ray diffractometer (model- PW-1830). These analyses were carried out on powdered samples by a Philips diffractometer using monochromatized CuKα radiation. The X-ray tube was operated at 30 kV and 25 mA. These samples were scanned in the 2θ range of 5-30° with a scanning speed of 5°/min. Their function groups were obtained by FT-IR measured at room temperature cover the range from 400-4000 cm^{-1} using FT-IR spectrometer (Perkin Elmer model 2000) with KBr pellet technique. The obtained FT-IR results were employed to calculate a degree of deacetylation (%DD) of chitosan powders. The thermal properties of these samples were characterized using a thermogravimetric analyzer (Perkin Elmer model TGA7). All of the measurements were performed under an air atmosphere and heated from room temperature to 700 °C with heating rate of 10 °C/min.

3. Results and Discussion

The chitosan extracted from different sources was carried out by X-ray diffraction, as shown in Fig. 1. The XRD patterns of chitosan exhibiting broad diffraction peaks at 9.85^{o} and 20^{o} could be indexed as (020) and (110) planes of chitosan, respectively. These indicate typical fingerprints of semi-crystalline chitosan [5].The obtained XRD results clearly revealed the chitosan prepared from crab shell and shrimp shells had higher intense peaks than that prepared from squid pen because the crystal structure of crab shell and shrimp shell are the orderly arrangement.

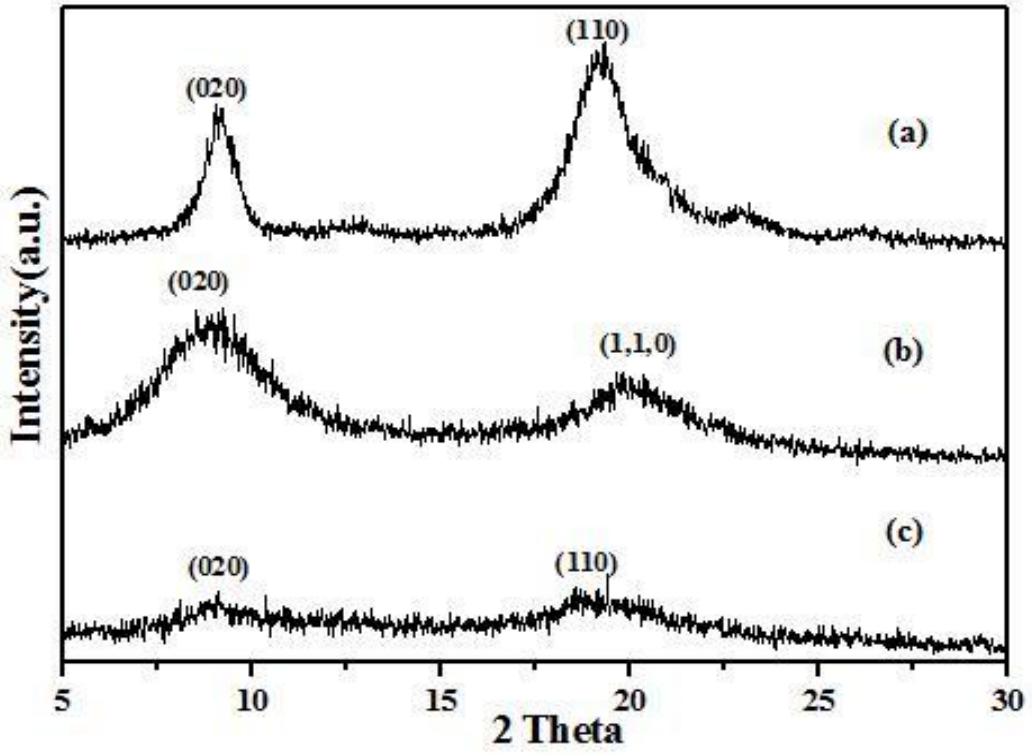

Fig. 1. XRD of chitosan extracted from (a) crab shell (b) shrimp shells and (c) squid pens

The chitosan powders were initially investigated for their chemical structure and functional groups using FT-IR spectroscopy as shown in Fig. 2.The large and intense bands located at 3700 and 3000 cm^{-1} could be attributed to axial OH and NH group vibrations. The axial O–H bond appeared in the 3435 cm^{-1}[7]. The axial C–H bond that appears in the 3000–2800 cm^{-1} range was intense for the chitin biopolymer [9]. The absorption bands of chitin at about 2920, 2879, 1418, and 1378 cm^{-1} were assigned to the C-H stretching and rocking bands [8]. The absorption bands of chitin at about 1659, 1563 and 1317cm^{-1} were amide I, amide II, and amide III, respectively [8]. The absorptions at 1418 cm^{-1} and 1378 cm^{-1} were assigned as CH_2 and CH bending bands respectively [8]. The absorption band at about 1156 cm^{-1} was assigned to the bridge oxygen stretching [8]. The absorption bands at about 1070-1030 were considered as the contribution of the C-O stretching [10]. CAOAC bridge as well as glucosidic linkage presented at 898-899 cm^{-1} [10]. The obtained FT-IR results confirm the average yield of chitosan production from crab shell, shrimp shell and squid penby degree of deacetylation (%DD) were 79, 80, 80% respectively.

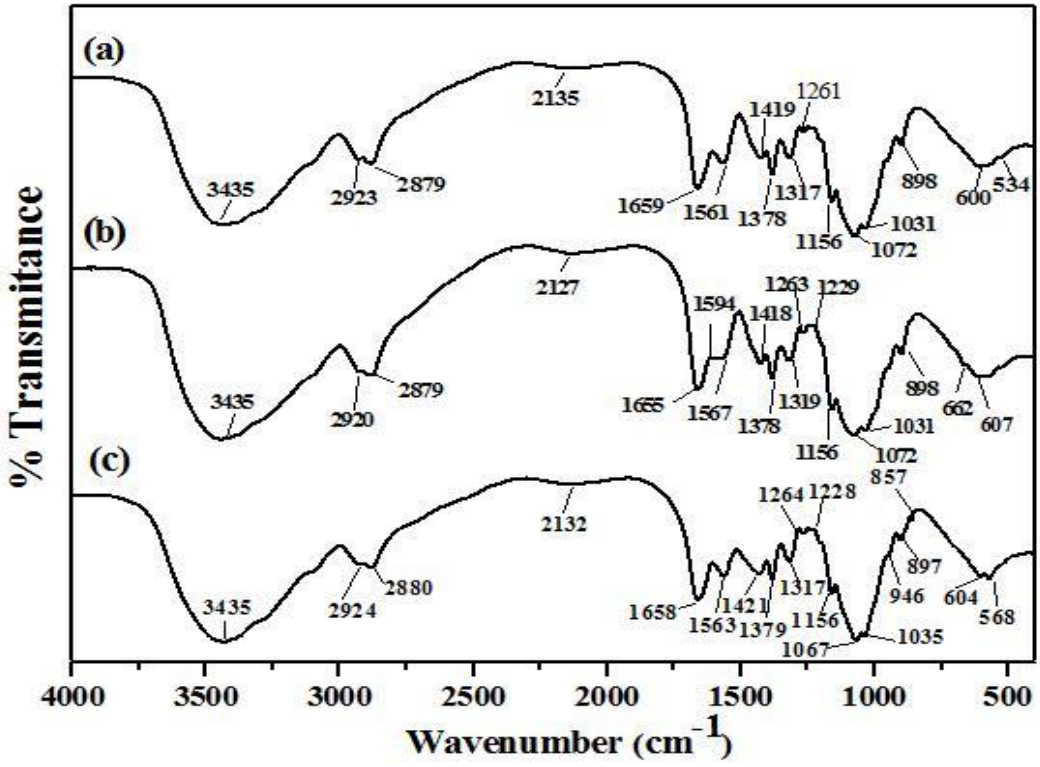

Fig. 2. FT-IR spectra of chitosan extracted from (a) crab shell (b) shrimp shell and (c) squid pen

The TGA curves of all samples were show in Fig.3. The temperature ranges were classified as region I (room temperature-280^{o}C), region II (280-400^{o}C), region III (400-700^{o}C), respectively. In the region I of all samples with weight loss of 8, 8 and 9 % weight for samples of (a), (b) and (c) due to loss of residual or physically absorbed water on membranes surface [11, 12].As increased temperature up to 450 ^{o}C in region II, this loss found to be 32, 37 and 38 % weight for samples of (a), (b) and (c) this region exhibited a rapid for chitosan [12]. Finally the temperature up to 700 ^{o}C (region III), the weight loss was found to be 60, 55 and 53 % weight for samples of (a) (b) and (c).The loss in region III could suggest the presence of minerals that were not extracted in the acidic stage [13].

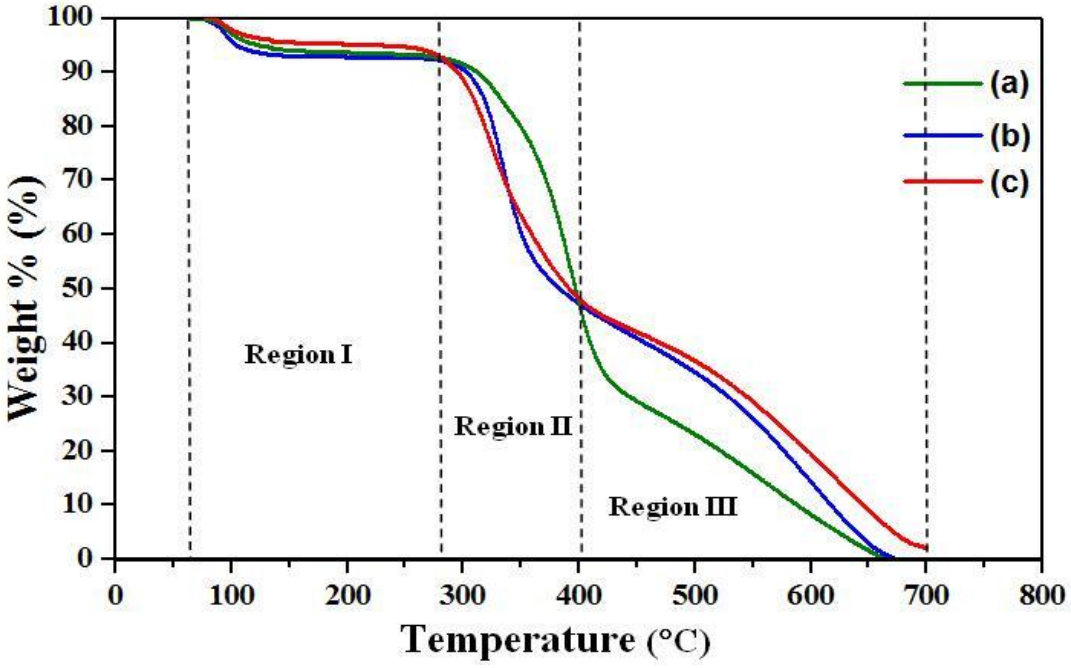

Fig. 3. TGA of chitosan extracted from (a) crab shells (b) shrimp shells and (c) squid pens

4. Conclusion

In the present investigation, chitosan powders were successfully extracted from shrimp shell, crab shell and squid pen for future application. To prepare chitosan powders, all raw materials were washed in distilled water and then they were finely grounded using agate mortar and sieved in the range of 212-250 μm to obtain fine powders. Then, the powdered materials were immersed into solution of chloroform and methanol with 2:1 ratio at room temperature for 1 h to remove fat. For deprotienation and decarbonation, powdered samples were immersed in 50 wt% of NaOH solution for 24 h and in 4 wt% of HCl for 1 h, respectively. To chitin powders were obtained. After that to obtain chitosan powders, the chitin powders were firstly immersed in 50 wt% NaOH solution before freezing at 4 ^{o}C for 24 h. Then they were immersed in 10 wt% NaOH solution and heated at 230^{o}C for 5 min to remove acetyl group.

The chitosan powders extracted from crab shell, shrimp shell and squid pen were employed to investigate by means of XRD, FT-IR and TGA techniques. The XRD results revealed (020) and (110) planes of chitosan were found at 9.85^{o} and 20^{o} and confirmed the different structure crab and shrimp shells. FT-IR techniques confirm the yield of chitosan production from crab shell, shrimp shell and squid pen by degree of deacetylation (DD) was an average 79, 80, 80% respectively. In the TGA results could be attributed to the rapid for chitosan in the range of 250-450^{o}C.

Acknowledgements

The authors wish to thanks the Department of Physics, Faculty of Science, Kasetsart University for providing XRD facilities. This research was financially supported by Faculty of Science, King Mongkut's University of Technology Thonburi.

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