



SYNTHESIS AND CHARACTERIZATION OF SEVERAL AMPHIPHILIC CHITOSAN DERIVATIVES

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ABSTRACT

Several kind of amphiphilic derivatives of chitosan namely lauryl chitosan, lauryl succinyl chitosan, and lauryl carboxymethyl chitosan were synthesized by chemical modification of chitosan. These generally involved reactions between chitosan and succinic anhydride, monochloroacetic acid or lauryl aldehyde under acidic or basic condition. These derivatives were developed as dispersant for the removal of oil from sea water. The chemical structures of chitosan derivatives were characterized by FTIR and $^1\text{H-NMR}$. In the $^1\text{H NMR}$ spectra, the peaks at about 0.8-1.7 ppm, assigned for hydrogen of lauryl group. IR studies confirmed the appearance of peak at $1730\text{-}1630\text{ cm}^{-1}$ and $2930\text{-}2860\text{ cm}^{-1}$ were characteristic of -COO^- and lauryl group. These indicate that hydrophobic and hydrophilic group attached to chitosan.

Keywords: *Hydrophilic, hydrophobic, amphiphilic and chitosan.*

INTRODUCTION

Chitosan is a linear polysaccharide of β -(1,4)-2-amino-2-deoxy-D-glucopyranose (GLcN) and 2-acetamido-2-deoxy-D-glucopyranose (GLcNAc) residues. Based on its biological properties, such as antibacterial, non-toxicity, biodegradability, haemocompatible and biocompatibility, it becomes an interesting material (Ma et al. 2008).

Chitosan have been used as hydrophilic backbone to prepare amphiphilic polymers by hydrophobic substitution. The introducing of a long alkyl substituent in chitosan polymer chain results in decreasing in solubility of hydrophobically modified chitosan derivatives. The strategy to increase solubility of

hydrophobically modified chitosan includes an additional synthetic step of N,O-carboxymethylation or N-succinylation of chitosan, which generally enlarge solubility. A presence of carboxylic groups compensates partly a loss of solubility caused by the hydrophobicity of long chain alkyl groups grafted to chitosan (Tikhonov et al. 2008).

The introduction of both hydrophobic and hydrophilic functions into chitosan was expected to explore a novel feature for biopolymer chemistry (Ngimhuang et al. 2004). Chitosan derivatives with both hydrophobic groups and hydrophilic groups could form micelles and solubilize hydrophobic compounds. These properties make it become importance to biological and pharmaceutical or biotechnological applications (Ramos et al. 2003 & Sui et al. 2005).

In this study, several derivatives of chitosan that have amphiphilic properties had been synthesized and had been characterized by Fourier Transform Infra Red (FTIR) and Nuclear Magnetic Resonance spectroscopy (¹H-NMR). These derivatives have the potential to develop as dispersant for the removal of oil from sea water.

EXPERIMENTAL

2.1 Reagents

Chitosan was used as raw material. Dodecyl aldehyde and succinic anhydride were supplied by Aldrich. Monochloroacetic acid and all chemicals were analytic grade reagents.

2.2 Preparation of chitosan derivatives

2.2.1 Preparation of Lauryl Chitosan (LC)

Lauryl chitosan was prepared by the method of Ramos et al. (2003). Chitosan (1 g) was suspended in a water-methanol 1:1 mixture (100 ml), lauryl aldehyde (1.5 g) was added and stirred for 30 min. Reduction was carried out with sodium borohydride solution (0.5 g dissolve in 10 ml of water) for 2h with mechanical stirring. The preparation was left overnight. The reaction mixture was then neutralized with HCl 5M solution and the lauryl chitosan was precipitated with methanol. The precipitate was filtered and washed with 90% methanol/water, methanol, hexane and acetone.

2.2.2 Preparation of Lauryl Carboxymethyl Chitosan (LCC)

Carboxymethyl chitosan (CC) was prepared by the method of Sun et al. (2008). Chitosan (10 g), sodium hydroxide (10 g), isopropanol (50 ml) and water (50 ml) were added into a flask to swell and alkalize at a given temperature for 1 h. The monochloroacetic acid (15 g) was dissolved in isopropanol (20 ml), added

into the reaction mixture drop-wise for 30 min and reacted for 4 h at the same temperature, then stopped by adding 70% ethyl alcohol (200 ml). The solid was filtered and rinsed in 70-90% ethyl alcohol, and vacuum dried at room temperature. The product was Na salt carboxymethyl chitosan (Na-CC). Na-CC (1 g) was suspended in 80% ethyl alcohol aqueous solution (100 ml), hydrochloric acid (10 ml, 37%) was added and stirred for 30 min. The solid was filtered and rinsed in 70-90% ethyl alcohol to neutral, vacuum dried. The products were the H-form carboxymethyl chitosan (H-CC). Addition of lauryl group to CC was done by the method to prepared lauryl chitosan but chitosan had changed with carboxymethyl chitosan.

2.2.3 Preparation of Lauryl Succinyl Chitosan (LSC)

Succinyl chitosan (SC) was prepared by the method of Zhu et al. (2007). 1 g of chitosan was dissolved into 200 ml distilled water and then transferred into a flask. Succinic anhydride (0.2 g) was dissolve in acetone (20 ml) and added into the flask by drop-wise for 30 min at room temperature, and then the reaction was allowed for 4 h at 40°C. The reaction mixture was cooled to room temperature. The mixture precipitated in an excess of ethanol, was filtered to remove the solvent, and then washed with 70-90% ethanol. Finally the product was dried at 40°C under vacuum for 24 h. Addition of lauryl group to succinyl chitosan was done by the method to prepared lauryl chitosan but chitosan had changed with succinyl chitosan.

3. RESULT AND DISCUSSION

3.1 Synthesis of chitosan derivatives

The introduction of a hydrophobic alkyl chain onto chitosan, carboxymethyl chitosan and succinyl chitosan leads to amphiphilic chitosan derivatives. In this case, the introduction of C12 chain gives rise to lauryl chitosan (LC), lauryl carboxymethyl chitosan (LCC) and lauryl succinyl chitosan (LSC). In LC, LCC and LSC derivatives, chitosan, carboxymethyl and succinyl as hydrophilic moities and lauryl groups as hydrophobic one.

3.2 Characterization of derivatives

Structure of chitosan and its derivatives were confirmed by FTIR spectra. The FTIR spectra of chitosan, lauryl chitosan, lauryl-CC and lauryl-SC were given in Fig. 1(a), (b), (c) and (d). The basic characteristics of chitosan were reflected at the peaks at 3439 cm^{-1} (O-H,-NH stretch), 2923 cm^{-1} (C-H stretch), 1642 cm^{-1} (Amide I) and 1377 cm^{-1} (Amide III). The absorption bands at 1148 cm^{-1} (asymmetric stretching of the C-O-C bridge), 1079 and 1026 cm^{-1} (skeletal vibration involving the C-O stretching) are the

characteristics of its saccharine structure (Aiping et al. 2006). The IR spectrum of lauryl chitosan, lauryl-CC and lauryl-SC had the absorption at about $1736-1633\text{ cm}^{-1}$ due to carbonyl stretching (Sun et al. 2008). While the two peaks at 1074 and 1030 cm^{-1} were attributed to the methyl rocking and C-CH₃ stretching vibration respectively of the lauryl group. Besides that, the absorption peaks at 2923 and 2855 cm^{-1} are correspond to the aliphatic chain. These evidences suggest that the hydrophilic group and hydrophobic group were introduced to chitosan (Sui et al. 2008). The ¹H NMR spectra of lauryl chitosan, lauryl-CC and lauryl-SC were given in Fig. 2(a), (b) and (c). In the spectra, the signals at 4.6 ppm (C1), 4.3, 4.4 ppm (C2) and 3.4-3.8 ppm (C3, C4, C5, C6) were corresponding to the ring methenyl protons of chitosan backbones. The signal at 1.9 ppm is due to the survival of the N-acetylglucosamine units of chitin. The signals at 2.2-2.6 ppm were assigned to the methylene protons of the carboxymethyl and succinyl. In the spectra of lauryl chitosan, lauryl-CC and lauryl-SC, signals at 0.7-0.8 ppm were attributed to the methyl protons at the terminal group (-CH₃) and signals at 1.2-1.5 ppm were corresponding to the methene hydrogen of the lauryl group (Sui et al. 2008).

CONCLUSION

Several kind of amphiphilic derivatives of chitosan were prepared by introduced lauryl to chitosan, carboxymethyl chitosan or succinyl chitosan. The chemical structures of lauryl chitosan, lauryl carboxymethyl chitosan and lauryl succinyl chitosan were characterized by FTIR and ¹H NMR. Based on the result, confirmed that hydrophilic group and hydrophobic group were introduced to chitosan. In considerations above, amphiphilic chitosan derivatives will be useful to develop as dispersant for the removal of oil from sea water.

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Figure

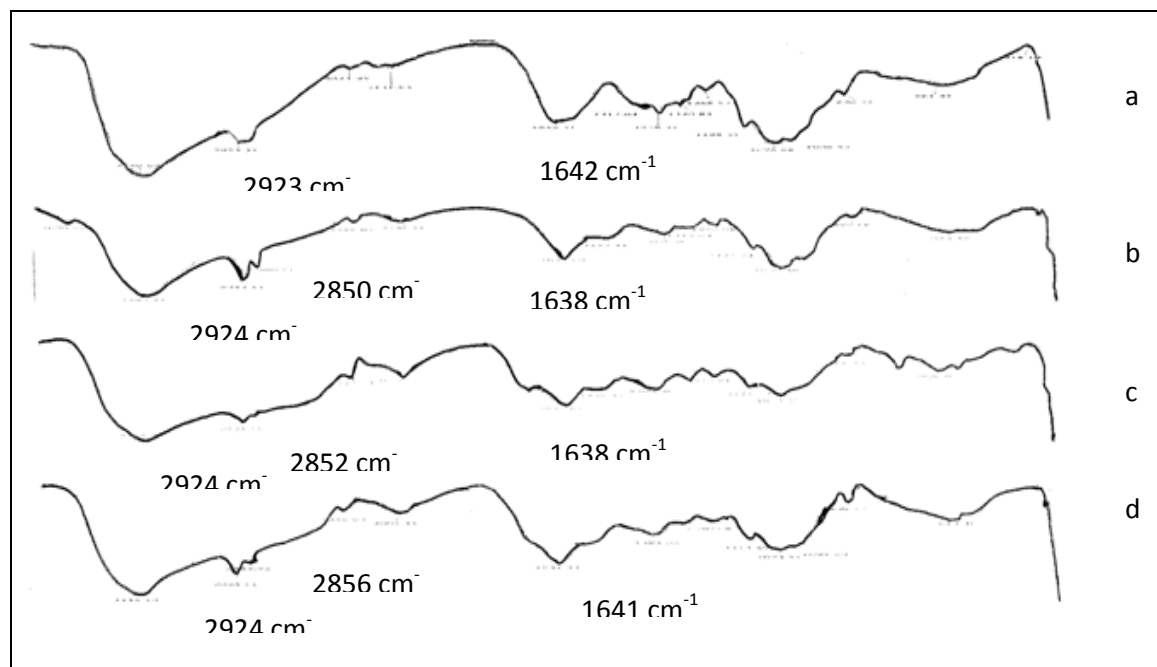


Fig 1 Spectrum FTIR of (a) Chitosan, (b) lauryl chitosan, (c) lauryl carboxymethyl chitosan and (d) lauryl succinyl chitosan

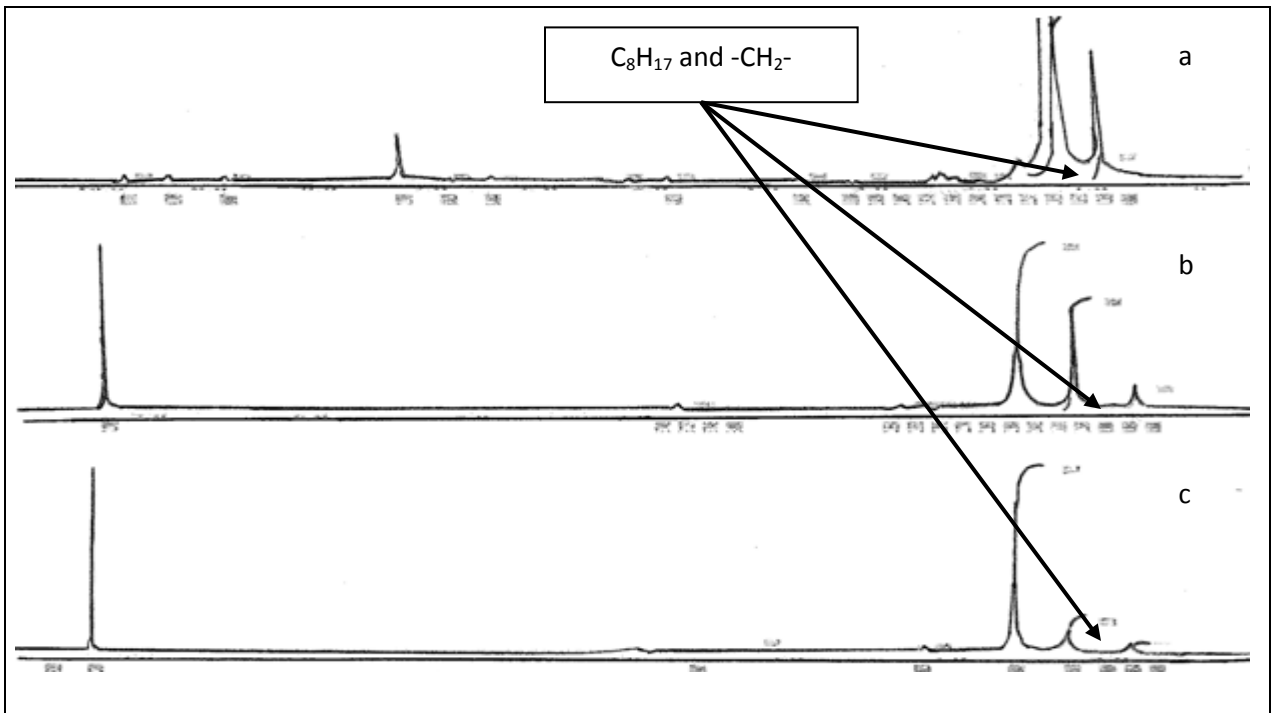


Fig 2 Spectrum NMR of (a) lauryl chitosan, (b) lauryl carboxymethyl chitosan and (c) lauryl succinyl chitosan