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Effect of deacetylation time on the preparation, properties and swelling behavior of chitosan films

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ABSTRACT

The effect of time during the deacetylation of chitin by hot alkali was studied to ascertain the film forming ability of chitosan. Five types of chitosan films were prepared in a single step deacetylation process by varying the alkaline treatment time from 2 to 10 h. The degree of deacetylation (DD) of chitosan and chitosan films were characterized using Fourier transform infrared spectroscopy (FT-IR) and elemental (CHN) analysis methods. The DD was found not to vary significantly beyond 2 h of deacetylation and the DD values by CHN analysis was higher than by FT-IR method. The degree of crystallinity (crystallinity index, CrI) of the chitosan films was also evaluated by X-ray powder diffraction method and the film prepared with 2 h deacetylation showed lower CrI. The morphology of this film by scanning electron microscopy (SEM) shows homogeneous and continuous structure. Swelling index of the films was measured in phosphate buffer solution at physiological conditions and film prepared with 2 h deacetylation showed maximum swelling index. However, the film formed with 6 h deacetylation process has the highest DD with higher CrI and low contact angle values. This film seems to be more suitable for biomedical applications.

1. Introduction

Chitosan is a natural polysaccharide comprising copolymers of glucosamine with *N*-acetylglucosamine and can be obtained by alkaline *N*-deacetylation of chitin, the second most abundant natural polymer after cellulose (Lisbeth Illum, 1998). Basically, the process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin leaving behind a complete amino group (NH_2) and chitosan versatility depends mainly on this high degree chemically reactive amino group (Khan, Peh, & Ch'ng, 2002). However, in order to exploit the utility of this biopolymer, it is imperative to determine its degree of deacetylation (DD), i.e. the average number of D-glucosamine units per 100 monomers expressed as a percentage (Sabnis & Block, 1997). The DD is one of the most important chemical characteristics as it influences the performance of chitosan in many of its applications (Pankaj & Lawrence, 1999). In addition, the DD which determines the content of free amino groups in the polysaccharides can be employed to differentiate between chitin and chitosan (Li, Revol, & Marchessault, 1997). For example, the increase either in temperature or strength of sodium hydroxide solution could enhance the removal of acetyl groups from chitin, resulting in a range of chitosan molecules with different properties and hence its applications. It is therefore essential to characterize chitosan by determining its DD prior to its utilization at the developmental stage of film forming systems (Khan et al., 2002). Various analytical techniques have been used in the determination of chitosan's *N*-deacetylation (DD) and the most popular techniques being the infrared spectroscopy because, it is a convenient technique for determining deacetylation easily in solid state (Sabnis & Block, 1997). The chitosan films can be prepared from the commercially available chitosan powders (Arvanitoyannis, Nakayama, & Aiba, 1998; Mingyu et al., 2003; Tanabe, Okitsu, Tachibana, & Yamauchi, 2002; Zhang, Li, Gong, Zhao, & Zhang, 2002). However, the film forming properties were not studied in detail in terms of its crystallinity, morphology etc. (Lopes & Carla, 2007; Rong & Hurng-Dar, 1996; Mima, Miya, Iwamoto, & Yoshikawa, 1983). Hence, the present work was planned to prepare the chitosan films from deacetylated chitosan powders with different DD levels and to study the effect of time during the alkaline treatments mainly on the stability of the film by measuring its swelling index.

2. Materials and methods

2.1. Materials

Chitin (S.D. Fine chemicals Mumbai, India) with 6–8% nitrogen content and other high purity chemicals such as sodium hydroxide

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(Sisco research laboratories Pvt. Ltd., Mumbai), acetic acid (Thomas Baker chemicals Pvt. Ltd., Mumbai) etc., were procured from the local suppliers.

2.2. Experimental

Chitosan powder was prepared by deacetylating chitin by dissolving 0.5 g in 100 ml of alkaline solution with 50 Wt.% sodium hydroxide for 2 h at a constant temperature of 107 °C using a magnetic stirrer (Ilauro Lima & Claudio Airoldi, 2004). The powder were then filtered from alkaline solution and washed thoroughly with distilled water until neutral pH is obtained. The powders were dried subsequently using an oven. The different percentages of deacetylated chitosan samples were obtained by varying the deacetylation time from 2 to 10 h.

2.3. FT-IR spectroscopy

Fourier transform infrared spectroscopy (Spectrum one, Perkin-Elmer, USA) was used to analyze the functional groups of the various deacetylated chitosans in order to find out the possible interactions between hydroxyl and amide groups, which are the major functional groups in determining degree of deacetylation. The deacetylated chitosan powders are made in the form of pellets using KBr and analyzed between 400 and 4000 cm^{-1}.

2.4. CHN elemental analysis

The CHN analysis of deacetylated chitosans was carried out using CHNS/O analyzer (2400 Series II, Perkin-Elmer, USA) and the DDs were calculated from the following equation (Xuan, Lirong, & Wei, 2003).

$$DD = \left(1 - \frac{C/N - 5.145}{6.861 - 5.145}\right) \times 100 \quad (1)$$

where, C/N is carbon to nitrogen ratio.

2.5. X-ray powder diffraction

X-ray powder diffraction studies were carried out for both chitin and deacetylated chitosans using a X-ray powder diffractometer (XD-D1, Shimadzu, Japan) of Cu Kα radiation ($\lambda = 1.54$ A°) with the scanning rate of 0.05°/step and with 2θ ranging from 5° to 30° in order to study the crystallinity index (CrI) of the polymer before and after the treatments at (0 2 0) and (1 1 0) planes. The crystallinity indices were determined by the following equations.

$$CrI = [I_{020} - I_{am}/I_{020}] \times 100 \quad (2)$$

$$CrI = [I_{110} - I_{am}/I_{110}] \times 100 \quad (3)$$

Where I_{020} and I_{110} are the maximum intensities of diffraction peaks at (0 2 0) and (1 1 0) planes and I_{am} is the intensity of amorphous diffraction region (Zhang, Xue, Xue, Gao, & Zhang, 2005).

2.6. Preparation of films

Chitosan films were prepared by solvent casting method by taking known amount of deacetylated chitosan powder and dissolving in 0.3 M acetic acid. The castings were made by pouring the chitosan solution into teflon coated glass moulds and subsequently kept in an oven at 50 °C in order to dry. The chitosan films were removed from the moulds and neutralized with 1 Wt.% NaOH solution for 30 min and washed thoroughly with distilled water and dried subsequently. The dimensions of the films were measured using a digital micrometer (Digimatic Micrometer, Mitutoyo – Japan).

2.7. Swelling index measurements

The dried films of chitosan were immersed in phosphate buffer solution of pH 7.4 at ambient temperature until swelling equilibrium was attained. The weight of swollen sample (Ws) was measured after removing the surface water with blotting paper. Swelling index (SI) was then calculated on the basis of the weight of swollen and dry films (Wd) using the following equation.

$$SI = [(Ws - Wd/Wd)] \times 100 \quad (4)$$

2.8. Contact angle measurements

Static contact angles of chitosan films were measured using a contact angle goniometry (GBX-Digidrop, France). Five microlitres of distilled water were dropped onto the surface of the films before measuring. The contact angle data was obtained from the images of water droplets on film surface.

2.9. SEM analysis

Surface morphology of all the chitosan films was analyzed using scanning electron microscopy (FEI-Quanta 200, Netherlands).

3. Results and discussion

3.1. Mechanism of deacetylation

The process of deacetylation causes the removal acetamido (CH_3CONH) group during hot alkali treatments leaving more amino (NH_2) groups and this takes place in the amorphous region of chitin, then proceeds from the edge to the inside of the crystalline region (Tolaimatea et al., 2000). The chemical formula of chitin and chitosan is shown in Fig. 1.

3.2. Degree of deacetylation

Fourier transform infrared spectroscopy (FT-IR) spectroscopy studies were carried out to evaluate the DD of deacetylated chitosan samples. From the infrared spectra as shown in the Fig. 2, the large and intense bands located at 3700 and 3000 cm^{-1} can be attributed to axial OH and NH group vibrations, which are more

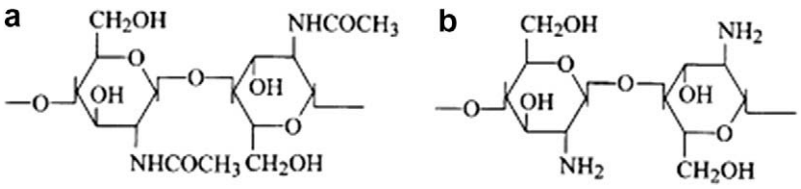

Fig. 1. Structures of chitin (a) and chitosan (b).