

Study of graft copolymerization of *N*-maleamic acid-chitosan and butyl acrylate by γ -ray irradiation

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Received 15 November 2004; received in revised form 17 April 2005; accepted 19 April 2005
Available online 9 June 2005

Abstract

N-maleamic acid-chitosan was synthesized and characterized by Fourier transform infrared spectra analysis (FT-IR) and ¹H NMR. The graft copolymerization of *N*-maleamic acid-chitosan and butyl acrylate (BA) in acetic acid aqueous solution was investigated, using the γ -ray of ⁶⁰Co γ -irradiation method. DSC (differential scanning calorimetry) trace of *N*-maleamic acid-chitosan-g-PBA has a glass-transition temperature (T_g) at -42°C . The thermal stabilities of the graft copolymer were studied by the thermal gravimetric analysis (TGA). The effect of synthesis variables in the graft copolymerization have been discussed in the light of grafting efficiency, grafting percentage, and homopolymer percentage. Increasing grafting percentage was observed when the monomer concentration and total dose were increased or when the reaction temperature was decreased.

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Keywords: *N*-maleamic acid-chitosan; Graft copolymerization; ⁶⁰Co γ -rays

1. Introduction

Chitosan is a polycationic polymer with a specific structure and properties. It is insoluble in most solvents but is soluble in dilute organic acids such as acetic acid, formic acid, succinic acid, lactic acid, and malic acid [1]. Many efforts to prepare functional derivatives by chemical modifications to increase the solubility in water have been reported [2–7]. The chemical combination of natural and synthetic polymer is a promising method for the preparation of new materials that could have desirable properties.

Recently, there has been a growing interest in grafting modification of chitosan. Radiation processing has many advantages over other conventional methods. In radiation processing, no catalysts or additives are needed to initiate the reaction. So the product is free from impurities such as chemical residues from initiators. The radiation methods are

relatively simple, and moreover, the degree of crosslinking and grafting can be controlled easily by varying the absorbed dose. In the polymerization for free radicals induced by radiation, the formation of primary radicals does not depend on the temperature, but only on the radiation intensity [8]. This allows that the polymerization is initiated in low temperatures. Therefore, the method is found to be very useful in chemical modification of chitosan. Using the γ -ray of ⁶⁰Co γ -irradiation method, chitosan can be grafted with considerable monomers, which have vinyl group [9–11].

In this paper, we developed a method to connect maleic anhydride with chitosan. The resulting *N*-maleamic acid-chitosan was modified by grafting copolymerization with butyl acrylate. Maleoylation enabled the grafting reaction to be carried out in a homogeneous system. Butyl acrylate was selected because it is hydrophobic and soft monomer, which grafted with the *N*-maleamic acid-chitosan, is expected to increase the hydrophobicity of macromolecule. Hydrophilicity of the films formed from graft copolymer solution was tested.

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2. Experimental section

2.1. Materials and instruments

Chitosan was obtained from San Huan Ocean Biochemical Co. Ltd. (China). Its degree of deacetylation and the apparent viscosity were determined as 91.2% and 30 MPa s. Butyl acrylate (BA) was chemical grade. Maleic anhydride was of reagent grade and used as received. Solvents were purified in usual manners.

IR spectra were recorded on a Bruker Vector-22 FT-IR spectrometer scanning from 4000 to 400 cm^{-1} at room temperature. The samples were ground with KBr crystal and the mixture of them was pressed into a pellet for IR measurement. ^1H NMR spectra was recorded on an AVANCE 300 NMR Spectrometer, using D_2O -containing CF_3COOD as solvent. X-ray powder diffraction diagrams were recorded with a Japan D/Max-rA X-ray diffractometer using graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer Pyris 1 DSC (Perkin-Elmer Cetus Instruments, Norwalk, CT) at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 flow from -60 to 200°C . The thermal gravimetric analysis (TGA) was conducted on a Shimadzu TGA-50H Thermal Analyzer under N_2 flow. The heating rate was $20^\circ\text{C}/\text{min}$.

2.2. Synthesis of *N*-maleamic acid chitosan

A mixture of chitosan and maleic anhydride in 2% acetic acid solution was stirred under $0\text{--}30^\circ\text{C}$. After 5–8 h, the product was dialyzed by dialysis membrane and dried in vacuum to acquire *N*-maleamic acid-chitosan (*N*-MA-CS), which is soluble in water. The degree of substitution (DS) is about 100%, determined by ^1H NMR.

2.3. Graft copolymerization and treatment of copolymer

The copolymerization of *N*-maleamic acid-chitosan and butyl acrylate were carried out in acetic acid aqueous solution under nitrogen for a specified time in a ^{60}Co γ -ray source chamber. After completion of the reaction, the contents were collected by filtration. It was extracted completely by Soxhlet's extraction method with ethanol, and dried to acquire *N*-maleamic acid-chitosan-g-PBA. The homopolymer of butyl acrylate was removed from the crude graft copolymer films by exhaustive Soxhlet's extraction method with toluene for 48 h. The graft parameters [grafting percentage ($G\%$), grafting efficiency ($E\%$), homopolymer percentage ($H\%$)] used to characterize the nature of the copolymer are defined and calculated as follows:

$$G\% = \frac{W_g - W_0}{W_0} \times 100$$

$$E\% = \frac{W_g - W_0}{W_2} \times 100$$

$$H\% = \frac{W_H}{W_2 + W_3} \times 100$$

where W_g is the weight of graft copolymer, W_0 the weight of *N*-maleamic acid-chitosan, W_2 the weight of reacted monomer (BA), W_3 the weight of unreacted monomer (BA), and W_H is the weight of homopolymer.

2.4. Water absorption measurements

The graft copolymer of known weights was immersed in distilled water at 25°C until equilibrium was reached (almost 24 h). The films were removed, blotted quickly with absorbent paper, and then weighed. The absorption percentage of these samples was calculated using the following equation:

$$X\% = \frac{M_1 - M_0}{M_0} \times 100$$

where M_0 and M_1 are the weight of dry and swollen samples, respectively.

3. Results and discussion

3.1. Fourier transform infrared analysis

The FTIR spectrum of the final grafted product, *N*-maleamic acid-chitosan-g-PBA was shown in Fig. 1. Compared to the spectrum of *N*-maleamic acid-chitosan, the peaks at $2800\text{--}3000 \text{ cm}^{-1}$ (methylene groups) was strengthened and an ester carbonyl stretching band was observed at 1735 cm^{-1} , which belonged to butyl acrylate. It proved that the PBA chains were grafted onto chitosan successfully.

3.2. NMR analysis of *N*-maleamic acid-chitosan

The ^1H NMR spectrum confirmed the formation of *N*-maleamic acid-chitosan. In Fig. 2, the strong signal due

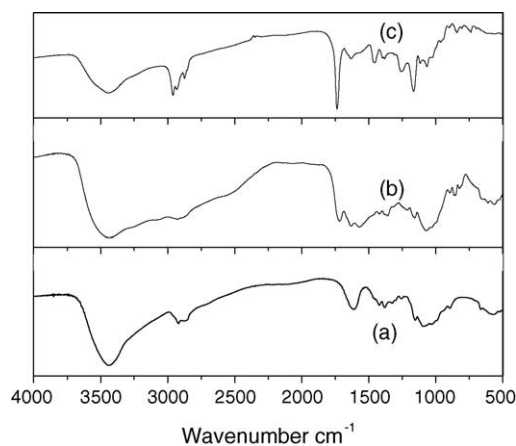


Fig. 1. IR spectra of chitosan (a), *N*-maleamic acid-chitosan (b), *N*-maleamic acid-chitosan-g-PBA (c).

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