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Characterization of grafted chitosan films

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Abstract

Chitosan was prepared from chitin using a deacetylation process. The molecular weight and degree of deacetylation of chitosan were determined by viscosity and infrared spectroscopy respectively. Chitosan films were grafted by 2-hydroxyethylmethacrylate (HEMA) using a ^{60}Co gamma-irradiation technique. The change in physico-chemical properties of modified films due to graft level of HEMA onto chitosan were estimated. The tensile properties of modified films decreased on increasing graft level. The grafted films showed improved thermal stability. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Chitosan films; Chitin; Grafting

1. Introduction

Recently, there has been a growing interest in grafting of vinly monomers onto chitosan for biomedical and industrial applications. This chemical combination of natural and synthetic polymers yields new materials which could have desirable properties including biodegradabilities. Graft copolymerization of methylmethacrylate (MMA) onto chitosan is carried out using Fenton's reagent as a redox initiator in an aqueous medium, in the presence of atmospheric oxygen. The extent of grafting and homopolymer formation were found to depend on chitosan, amount of initiator, monomer concentration, reaction temperature and reaction time (Lagos and Reyes, 1988). The grafting of MMA onto chitosan is studied by photo-induced and initiator method, and the polymerization proceeded mainly by the photolysis of amino groups. The degree of grafting and number of grafted chains generally decreased in the following order: the initiator method > photo-induced > without catalyst > the photo-induced method with photosensitizer (Takahashi et al., 1987). Chitosan is grafted with acrylonitrile, MMA, methylacrylate and vinyl acetate using azobisisobutyronitrile as an initiator under both homogeneous and heterogeneous conditions (Blair et al., 1987). Grafting of acrylamide and HEMA onto chitosan was studied using ceric (IV) salt as redox initiator (Kim et al., 1987; Cho et al., 1990). Graft copolymerization of styrene, vinyl acetate, acrylamide and MMA onto chitosan using ^{60}Co gamma-irradiation method has been reported in the literature (Shigeno et al., 1982).

The present study describes physico-chemical behavior of 2-hydroxyethylmethacrylate grafted chitosan films at different grafting levels.

2. Experimental

2.1. Materials

The degree of deacetylation and molecular weight of chitosan prepared from chitin, was found to be 83% and 250 kDa, respectively. HEMA monomer (E. Merck, Germany) was purified by distillation at 70 °C/20 mmHg and stored at 4 °C (Grant and Grassie, 1976).

2.2. Preparation of modified chitosan films

The details of preparation of original and modified chitosan films have been reported elsewhere (Singh and Ray, 1994). In brief, modified films were prepared by graft copolymerization of HEMA onto chitosan using ^{60}Co gamma-ray irradiation in a water–methanol (1:1) solvent system. The homopolymer formed during reaction was removed by extracting films in methanol for 24 h.

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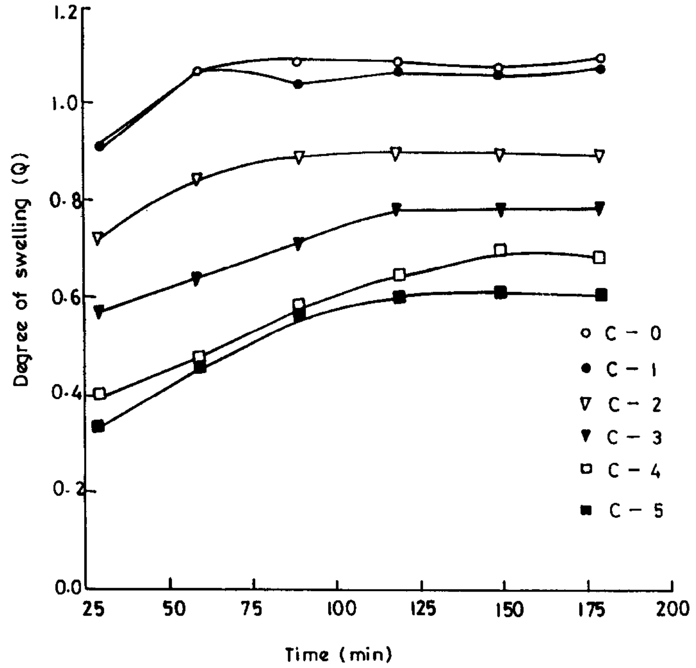

Fig. 1. The swelling kinetics of grafted chitosan films.

2.3. Characterization

2.3.1. Swelling studies

The swelling studies of original and modified samples were carried out in phosphate buffer solution (pH 7.4, 0.1 M) at 37 °C as a function of time. The degree of swelling of these samples was calculated using the following equation:

$$\text{Degree of swelling } (Q) = \frac{W_s - W_d}{W_d}$$

where W_s and W_d are the weights of swollen and dry samples respectively.

2.4. Thermal properties

Thermal properties of original and modified samples were studied using a DuPont differential scanning calorimeter (DSC-2000) at a heating rate of 10 °C min^{-1} from 50 to 400 °C. The DSC unit was precalibrated with indium for the entire working range and the base fine was obtained using an empty aluminium pan.

Thermogravimetric analysis (Dupont, TGA-980) was performed in the temperature range from 50 to 600 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere (60 cm^3 min^{-1}).

2.5. Mechanical properties

The tensile properties of original and modified samples were measured using an Instron tensile tester (UTM, 1112) under the following conditions:

Cross head speed	2.5 cm min^{-1}
Gauge length	3.0 cm
Temperature	25 °C
Relative humidity	65%

The ultimate tensile strength and percent elongation at break were calculated.

2.6. X-ray diffraction studies

The wide angle X-ray diffraction (WAXD) patterns were obtained on Rigaku diffractometer using nickel filtered Cuk_α radiation at a scanning speed of 2° min^{-1} over the 2θ range from 10 to 35°.

The diffraction patterns were resolved into two parts, corresponding to scattering by amorphosous (A_a) and crystalline phase (A_c). The ratio of area corresponding to crystalline phase (i.e. area under sharp peaks) to the total area $\{A_c/(A_c + A_a)\}$ was taken as the degree of crystallinity. Percentage crystallinity was calculated as follows:

$$\% \text{ Relative crystallinity} = \frac{A_c}{(A_c + A_a)} \times 100$$

3. Results and discussion

Chitosan films were found to be transparent and flexible. No change in appearance of films was observed upon

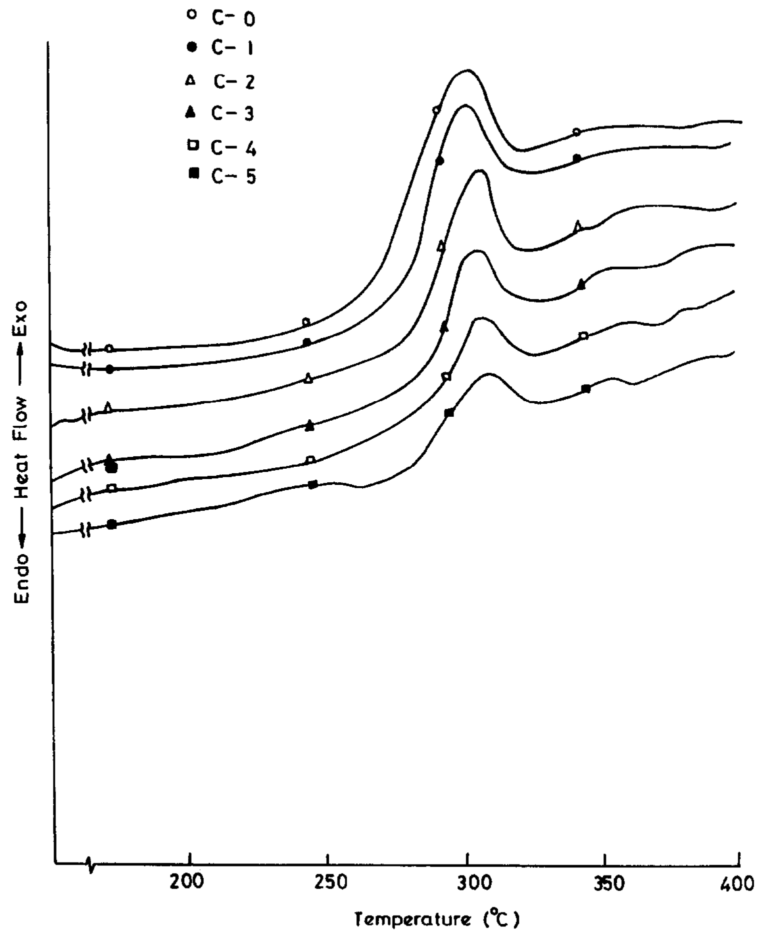

Fig. 2. DSC thermograms of original and grafted chitosan films.

storage in the dry state. However, on increasing grafting level of HEMA, the modified films became brittle when dry.

3.1. Swelling studies

The rate of swelling of original and modified samples are presented in Fig. 1. All the samples reached an equilibrium state within 3 h. There is no significant change in swelling kinetics of irradiated chitosan films. The degree of swelling of grafted samples decreased from 0.89 to 0.61 as a function of graft level of HEMA from 14 to 58%. The crosslinking of HEMA molecules in the polymer network may be responsible for the decrease in swelling of grafted samples. The hydrophilic nature of chitosan is due to the presence of free amino groups on the C-2 carbon. During the grafting process, a substantial number of free amino groups are blocked by the growing chains of poly(HEMA). These changes are also responsible for the decrease in swelling.

3.2. Thermal properties

DSC thermograms of original and modified chitosan are shown in Fig. 2 and the values of decomposition temperature and enthalpy change are summarized in Table 1. No significant variation is observed in decomposition temperature and enthalpy values upon gamma-irradiation

Table 1
Thermal properties of original and HEMA grafted chitosan

Sample	Grafting of HEMA (%)	Decomposition temperature (°C)	Enthalpy change (J g^{-1})	IDT (°C)	FDT (°C)
C-0*	—	273.5	141.8	270.7	329.4
C-1**	—	273.6	141.7	270.7	329.4
C-2	14	276.6	90.5	274.6	374.9
C-3	29	277.0	70.8	276.9	391.2
C-4	37	277.6	40.3	278.3	401.3
C-5	58	279.7	25.4	285.2	444.7

*Original; **irradiated.

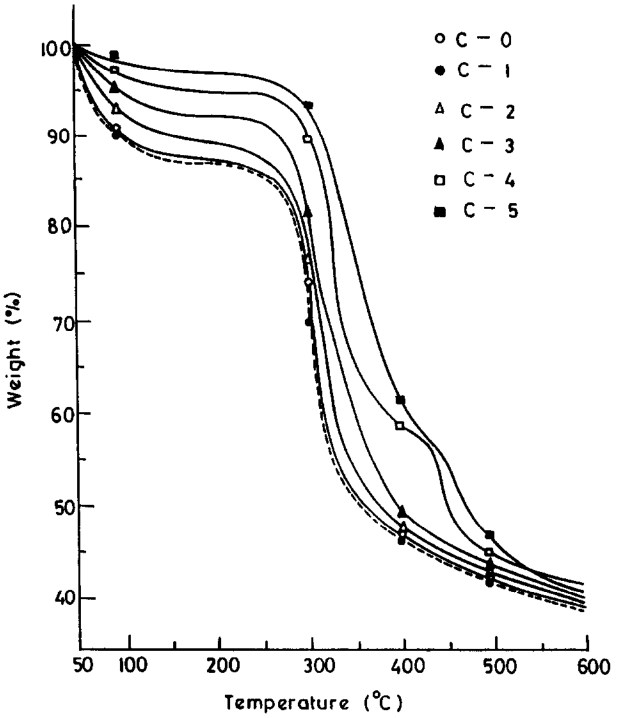

Fig. 3. TGA thermograms of original and grafted chitosan films.

of chitosan up to 0.54 Mrad. However, decomposition temperature increases marginally by 4–5 °C upon grafting with HEMA, whereas a substantial decrease is observed in enthalpy of samples from 90.5 to 25.4 J g^{-1} upon graft level from 14 to 58%. This may be due to two step decomposition of the grafted sample. The formation of a crosslinked network structure in grafted chitosan would also contribute to the above.

Thermograms of the degradation study of original and modified samples by thermogravimetric analysis (TGA) are given in Fig. 3. The results show that the thermogram of irradiated chitosan is similar to that of the original sample. This suggests that irradiation of sample with gamma-rays under experimental total dose (0.54 Mrad) does not produce any detectable change in chitosan structure. The initial decomposition temperature (IDT), and final decomposition temperature (FDT) are presented in Table 1. Grafted samples show an increasing trend in IDT and FDT with increase in percent graft level. This increase in IDT and FDT may be attributed to the formation of cyclic structure of modified chitosan as a result of dehydration of poly(HEMA) owing to its better thermal stability.

Table 2
Mechanical properties and crystallinity of original and HEMA grafted chitosan films

Sample	Grafting of HEMA (%)	Crystallinity (%)	Tensile strength (kg/cm^2)	Elongation (%)
C-0*	—	56.2	281.6	3.1
C-1**	—	56.2	280.3	3.1
C-2	14	51.3	334.5	3.0
C-3	29	46.7	274.8	2.9
C-4	37	42.1	221.7	2.5
C-5	58	39.1	190.9	2.0

*Original; **irradiated.

3.3. Mechanical properties

The tensile properties of original and modified samples were evaluated in the dry state and the results are listed in Table 2. In modified samples, tensile strength first increases up to 14–15% graft level and then decreases with increase in graft level. The percent elongation at break is decreased by 33% on increasing graft level of HEMA from 14 to 58%.

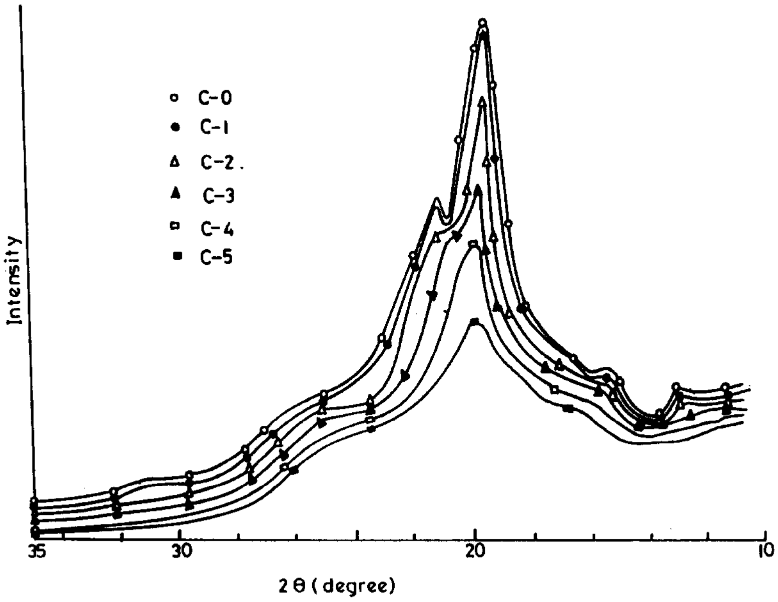

Fig. 4. X-ray diffraction patterns of original and grafted chitosan films.

Increase in tensile strength at 14% graft level may be attributed to the branching effect of poly(HEMA) in the chitosan matrix. The decrease in tensile strength after 14% graft level may be explained on the basis that the grafting is generally followed by compactness of molecular chains in the amorphous region, which increases the brittleness of the polymer backbone. As a result of this, polymer backbone fails to withstand higher load and breaks easily at lower loads, resulting in a decrease in tensile strength.

3.4. X-ray diffraction studies

The X-ray diffraction patterns of original and modified chitosan at various graft level are shown in Fig. 4. The diffractograms show a peak at 20°. No significant change is observed in diffraction pattern of chitosan film upon gamma-irradiation up to 0.54 Mrad. This suggests that crystallinity remains unchanged. The relative intensity of peak decreases substantially on increasing grafting with HEMA. The percent relative crystallinity decreases from 51.3 to 39.1% as a function of graft level of HEMA from 14 to 58% (Table 2). A decrease in crystallinity may be due to introduction of bulky pendant chains of grafted poly(HEMA) in chitosan matrix.

4. Conclusion

A significant variation in physico-chemical properties of chitosan is observed upon grafting with HEMA. The degree of swelling, crystallinity and mechanical properties of modified films are decreased by 45, 30 and 32% respectively at a graft level of 58%, whereas modified films showed improved thermal stability.

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