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Effect of gamma radiation on the Physico-mechanical properties of Chitosan Ethylene glycol (EG) films

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ABSTRACT

Thin chitosan films were prepared by casting method and their mechanical properties like tensile strength, elongation at break were studied .Cross linking agent ethylene glycol (EG) was incorporated with chitosan in various ratios (where chitosan: EG 70:30,80:20and 90:10).Both chitosan and chitosan EG films were treated with gamma radiation. Films of 10% EG with chitosan treated with100 krad of gamma radiation showed the highest mechanical and thermal properties. The TS of 100 krad gamma treated chitosan EG film was 26.7 MPa and Eb is14.0%. Water uptake of the films was carried out at room temperature (25°C) in an aqueous medium. Thermal properties such as DSC and TGA studies were performed to understand the behavior of the irradiated chitosan EG films on application of thermal energy. Results of X-ray (XRD) analysis indicate the crystallinity and amorphous condition of the different intensity of diffraction peak.

Keywords: Crystallinity, amorphous, cross linking agent, diffraction peak, thermal properties.

1. Introduction

Chitin, a naturally mucopolysaccharide and is well known to consist of 2-acetamido-2-deoxy-β-d-glucose through a β (1-4) linkage. Chitosan is the *N*-deacetylated derivative of chitin, although this *N*-deacetylation is almost never complete. As most of the present day polymers are synthetic materials, their biocompatibility and biodegradability are much more limited than those of natural polymers such as cellulose, chitin, chitosan and their derivatives. However, these naturally abundant materials also exhibit a limitation in their reactivity and process ability [1-2]. In this respect, chitin and chitosan are recommended as suitable functional materials because these natural polymers have excellent properties such as biocompatibility, biodegradability, non-toxicity, adsorption properties etc. Ethylene glycol is a colorless, viscous and hydrophilic liquid capable of forming polymer. Some approaches for the graft copolymerization of hydrophilic polymer onto chitosan and chitosan were reported as a technique to improve the affinity to water or organic solvents. Grafting polyethylene glycol onto chitosan is a convenient approach to water soluble chitosan derivatives [3-6].Use of multifunctional monomers in radiation cross linking is very common. A multifunctional vinyl monomer promotes rapid free-radical propagation reaction leading to network (cross linking) polymer structures through grafting via their double bonds [7]. Hydrophilic monomer (EG) was selected to improve the mechanical properties of the hydrophilic chitosan films by keeping its inherent biodegradable behavior to some extent Here, gamma radiations was used to observe the difference in performance of mechanical and thermo mechanical properties for chitosan ethylene glycol (EG) films [8, 9]. Photo curing provides some advantages like low energy consumption, ambient temperature, reduce reaction time, enhanced product quality etc [10, 11] **.**The extent of grafting and homopolymer formation was found to depend on chitosan, amount of initiator, reaction temperature and reaction time [12].

In the present work, chitosan EG films of different ratios (70:30, 80:20; 90:10) were taken to make an attempt to discuss the effects of gamma radiation on chitosan EG films for uplifting the properties.

2. Materials and Methods

Chitosan was extracted from dried prawn shell waste. Ethylene glycol (EG), sodium hydroxide, hydrochloric acid, acetone, acetic acid ; purity 99.9% was supplied by Marck , Germany.Photo initiator (Derocur-1173) was supplied from Ciba-Geigy, Switzerland. Chitosan was extracted from dried prawn shell. 2% chitosan solution was prepared in 2% acetic acid aqueous solution. The films were prepared by casting on glass plate at room temperature. Chitosan ethylene glycol (EG) bioblend films of different ratios (70:30, 80:20, and 90:10) were prepared. For the preparation of chitosan EG blend (chitosan and EG ratio were70:30, 80:20, and 90:10 w/w), chitosan solution was prepared and mixed with EG solution with continuous stirring for about half an hour [10]**.** The solution was cast onto the silicon cloth frames mounted

on flat glass plate for film formation and dried in an oven at 70^0C for 12 hours. The dried films (about 0.20 mm thickness) thus prepared were peeled off and cut into small pieces for further tests.

3. Results and discussion

The films were irradiated under different gamma doses (50,100, 250, 500 doses). The relative humidity of the room was around 60-65%.The mechanical properties of the films were investigated after 20-24h of gamma irradiation to ensure the completion of free- radical reactions. Tensile strength (TS) and percent elongation at break (Eb %) were evaluated. It was found that TS and Eb of the gamma treated chitosan EG (90:10) film are higher than that of raw chitosan film. The results of TS values for raw chitosan film

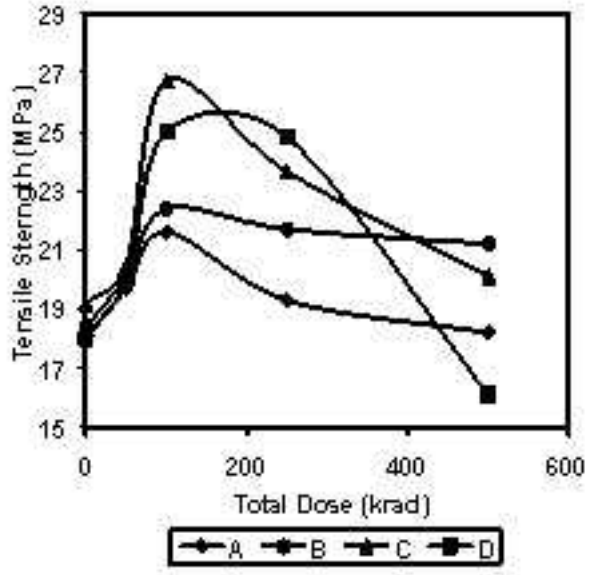

Fig. 1: Tensile strength (TS) of chitosan :EG film of A (70:30), B (80:20), C (90:10), D (raw chitosan film) against the number of gamma dose.

and chitosan: EG films of different ratios (70:30, 80:20, 90:10) are shown in figure.1 where TS values are plotted against gamma radiation at different doses (50, 100, 250, 500 krad). The TS values for raw chitosan: EG films (70:30, 80:20, and 90:10) are 18.3 MPa, 18.8 MPa and 19.2 MPa respectively. 100 krad gamma treated chitosan: EG (90:10) film showed the highest mechanical property and the highest TS value was 26.74 MPa . So, 100 krad gamma treated chitosan: EG film (90:10) film enhanced 49 % TS compared to that of raw chitosan film. From figure 2, a significant change in elongation at break (Eb%) occurred. The Eb values for raw chitosan EG films (70:30, 80:20, and 90:10) were 10.8, 11.5, and 12. From figure. 2, it is clear that Eb values increased (up to 100 Krad) then decreased. The highest Eb value is 13.9 % for 100 krad gamma treated chitosan: EG (90:10) film.

The tensile properties increase with initial gamma radiation dose, attains the maximum value at 100 krad of gamma radiation and then decreases as the radiation dose increases.

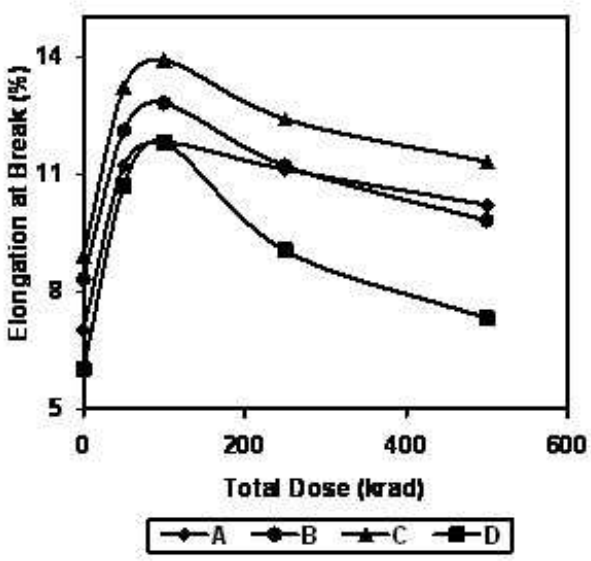

Fig. 2: Elongation at break (Eb) of chitosan EG film of A (70:30), B (80:20), C (90:10), D (raw chitosan film) against the number of gamma dose.

This may be caused by the radiation degradation at higher gamma doses.In chitosan EG film, both the methylene and hydroxyl group have the change to go into radical formation in photo curing procedure [13]. This also helps to form more cross linking between chitosan and EG. The ending hydroxyl groups of EG in case of pendent linking also form a hydrogen bond with each other or with chitosan molecule. From the above discussion, this is quite clear that at 100 krad of total dose, TS and Eb increased. Actually gamma radiation can play a significant role for the modification of polymers [14-17]. Gamma radiation is ionizing radiation and has strong effect on natural polymers .Use of gamma radiation attributed higher mechanical properties; gamma radiation produces three types of reactive species in polymer (chitosan). These are ionic, radical, and peroxide. The peroxide species are produced because the polymers were irradiated in presence of oxygen [18-20]. When chitosan is subjected to gamma radiation, some radicals are produced. Gamma radiation also ruptures some carbon-carbon bonds and produces radicals. Chain scission may also take place to form other radicals. Cross-linking and chain scission occurred when polymers are exposed to gamma radiation [21-23]. Polysaccharides and other natural polymers generally degrade by breaking of glycosidic linkage under gamma radiation.

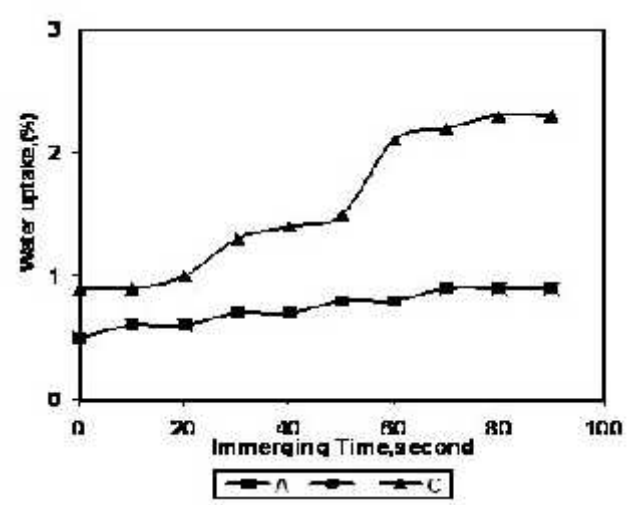

Fig. 3: Water uptake properties of (A) raw chitosan film, (B) gamma treated chitosan: EG (90:10) film.

Percentage of water uptake of 100 krad gamma treated chitosan: EG (90:10) film, raw chitosan film was plotted against Immersion time (second). Water uptake was measured by soaking the chitosan EG films in a static water bath at room temperature (25 ^{o}C) for about 10 to 90 seconds and shown in figure 3. From the figure, it is clear that water uptake values increased with the increase of immersion time and after 70 seconds reached to plateau for all cases. The water uptake percentage is highest for gamma treated chitosan: EG (90:10) film and least for the raw chitosan film.

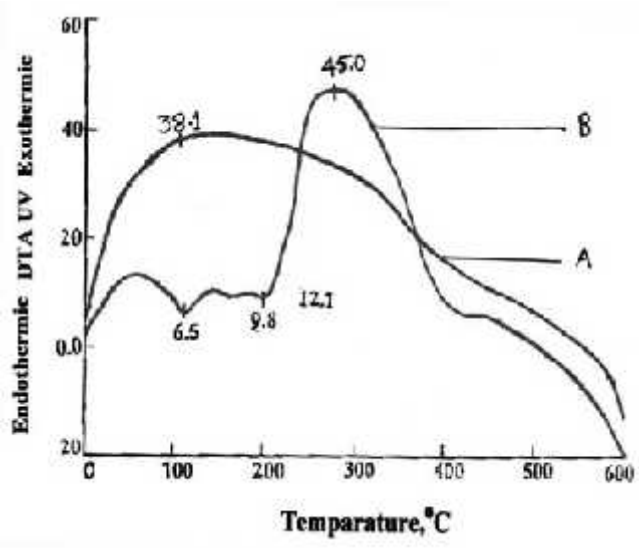

Fig. 4: DTA curve of (A) raw chitosan film (B) irradiated chitosan: EG (90:10) film

DTA curve of raw chitosan film and irradiated chitosan: EG (90:10) films are shown in figure 4. The glass transition temperature, melting temperature and melting enthalpy of the prepared films are measured by using DTA technique. Figure 4 showed the first heating scan programmed from 0 to 600 ^{0}C at a heating rate of 10 ^{0}C/min. The midpoint of the specific heat change associated with the glass transition is taken as the glass- transition temperature (Tg) and the peak temperature of the melting endotherm is taken as the melting temperature (Tm). The area underneath the endotherm divided by the total sample weight (ΔH/ chitosan EG film, j/g) indicated the percentage of structural order in the prepared film. From figure 4, Tm value was 38.1 for raw chitosan film at a temperature range between 90 ^{0}C – 120 ^{0}C and Tm value for irradiated chitosan: EG (90:10) film showed 45.0 between 250 ^{0}C - 300 ^{0}C. Endothermic peak is found for irradiated film at a temperature range between 90 ^{0}C -- 220 ^{0}C but no endothermic peak is found for raw chitosan film.

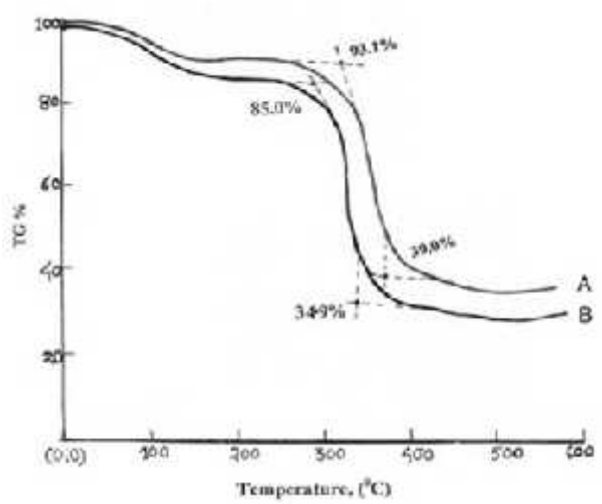

Fig. 5: TGA curve of (A) irradiated chitosan: EG (90:10) film (B) raw chitosan film

Thermographs of raw chitosan film and 100 krad gamma treated chitosan: EG (90**:**10) films are shown in figure.5. For irradiated chitosan: EG (90:10) film**,** the weight loss at 70 ^{0}-180 ^{0}C is due to the moisture vaporization and other weight loss at 220-380 ^{0}C is due to the degradation of chitosan film in figure.5**.** For raw chitosan film, one weight loss at 80- 160 ^{0}C is due to the moisture vaporization. The second weight loss at 270- 370 ^{0}C is due to the thermal degradation of raw chitosan film and residual weight is 34.9 %.So,it is clear that 100 Krad gamma treated chitosan EG(90:10) film was more stable than raw chitosan film.

4. Conclusion

From this investigation, it can be concluded that gamma radiations are effective to improve the mechanical properties of chitosan EG films. TS of gamma treated chitosan EG(9:10) film is 26.74 Krad and Eb is 13.9%.The thermo-mechanical properties have been drastically improved for gamma treated (100 Krad) chitosan EG (90:10) film. Water uptake values reached almost static after 70 sec of immersing in aqueous media.DSC and TGA studies were performed to understand the behavior of both raw and irradiated films on application of thermal energy.

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