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Modifications of polycarbonate induced by swift heavy ions

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Abstract

The effects of 80 MeV O^{6+} ions irradiation on polycarbonate (makrofol-DE) have been studied by different characterization techniques, viz. Fourier transform IR spectroscopy, Vickers' microhardness tester, LCR meter, thermogravimetric analysis and differential scanning calorimetry. It is observed that the hardness of the film increases as fluence increases. This may be attributed to the cross-linking effects as corroborated with FTIR spectra. There is an exponential increase in conductivity with log frequency and the effect of irradiation is significant at higher fluences. The dielectric constant/loss is observed to change with the fluence. From the analysis of frequency dependence of dielectric constant it has been observed that the dielectric response in both pristine and irradiated samples obey Jonscher's power law. The results are also explained on the basis of structural modification of polymer due to heavy ion irradiation. TGA/DSC thermograms indicate that there is no significant change in the stability of polymer and glass transition temperature up to the fluence of 2.4×10^{13} ions/cm^2.

Keywords: Polycarbonate (MDE); 80 MeV O^{6+} ions; Microhardness; Dielectric properties; FTIR; TGA; DSC

1. Introduction

Polycarbonate (makrofol-DE) is an amorphous engineering thermoplastic notable for its high impact resistance. It has reasonably good temperature resistance, good dimensional stability and low creep but some what limited chemical resistance and is prone to environmental stress cracking. It is widely used today to prepare track-etched membranes. PC particle track etched membranes are used as templates in nano-tubes and nano-wires manufacturing [1]. There are numerous reports on PC using energetic ions, but mechanical (hardness) and electrical properties induced by swift heavy ion (SHI) irradiation did not receive much attention. Ferain and Legras [2] studied the chemical modifications induced by SHI irradiations (Ar ion 4.5 MeV/amu) in a model compound of PC, i.e. diphenyl carbonate. Steckenreiter et al. [3] studied the degradation processes in PC induced by SHI irradiations with electronic stopping power $(dE/dx)_e$ higher than 4.0 MeV mg^{-1} cm^2. They have reported the alkyne formation in all irradiated polymer using insitu FTIR spectroscopy. Chipara and Reyes-Romero [4] reported electron spin resonance investigations of SHI irradiated PC. They have discussed the nature of free radicals as well as exchange interactions among them on the basis of track structure. Zhu et al. [5] and Wang et al. [6] investigated chemical changes in PC induced by very high energetic ions (>GeV) using ex situ FTIR spectroscopy. They also reported alkyne formation in irradiated PC with electronic stopping power $(dE/dx)_e$ values higher than 3.5 MeV mg^{-1} cm^2. Dehaye et al. [7] investigated the chemical modification induced in bisphenol A polycarbonate by SHI using in situ FTIR spectroscopy. They observed new vibrational bonds in the irradiated samples. Studies on thermal and structural properties of 62 MeV protons irradiated PC were carried out by Mishra et al. [8] at different doses and it was reported that thermal stability decreases as dose increases. The aim of the present work is to investigate the radiation induced changes in electrical, mechanical, thermal and structural properties of 80 MeV O^{6+} ions irradiated polycarbonate (makrofol-DE) at different fluences.

2. Experimental

Three pieces of polycarbonate (makrofol-DE) of composition $(C_{16}H_{14}O_3)_n$; density 1.2 g/cm^3 and each of thickness 413 μm and size 1.5 cm × 1.5 cm were cut from the sheet available from Good Fellow Corporation, UK. These samples were mounted

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on a vertical shielding ladder and irradiated in scattering chamber of material science beam line by 80 MeV O^{6+} ions at IUAC, New Delhi, India. All irradiations were performed in vacuum (10^{-6} Torr) at ambient temperature. The beam current density of the ions was of the order of 12 nA/cm^2. The ion beam fluence was varied in the range 7.4×10^{12} to 2.4×10^{13} ions/cm^2. In order to expose the target 1 cm × 1 cm areas, beam was scanned in the *x*–*y* plane. To study the structural changes including the alteration in position and intensity of the characteristic bands, the FTIR spectra of all samples were recorded in the wave number range 4000–500 cm^{-1}(Bomem Canada, model 104) with a resolution of 4 cm^{-1}. For microhardness test, the indenter employed was the Vickers' pyramidal diamond indenter supplied with the microhardness testing accessory of a Carl Zeiss optical microscope. The electrical properties of all samples were studied using an LCR meter (General Radio, USA, model 1689/Hewlett-Packard, 4284 A). The resistance, dielectric loss and capacitance measurements were carried over the frequency range of 50 Hz–10 MHz at ambient temperature. The AC conductivity was calculated using the relation t/RA (Ω^{-1} cm^{-1}). The dielectric constant was calculated using the relation $\varepsilon = Cp/C_0$, where Cp is capacitance measured using LCR meter, $C_0 = \varepsilon_0 A/t$, where ε_0 is the permittivity of vacuum and A and t are the cross-sectional area of electrode and thickness of the sample, respectively. Thermogravimetric analysis (TGA) was recorded by using a Universal V1.12 TA Instrument in the presence of air from ambient temperature to 800 °C at a predetermined heating rate of 20 °C/min with air as the flushing gas. DSC measurement was carried out by a Universal V1.12 TA Instrument, calibrated through the melting points of indium and tin. About 6 mg of pristine and irradiated samples were heated in the calorimetric furnace in the temperature range of 40–350 °C at a predetermined heating rate of 10 °C/min.

3. Result and discussion

When an energetic charged ion strikes a polymeric target, it loses its energy by two mechanisms known as electronic and nuclear stopping. The electronic stopping power of the beam $(dE/dx)_e$ is 5.528×10^1 eV/Å and nuclear stopping power of the beam $(dE/dx)_n$ is 3.148×10^{-2} eV/Å. The projected range of 80 MeV O^{6+} ions in polymer was calculated to be 98.2 μm using SRIM-2003 code [9]. The thickness of the polymer is four times larger than the projected range of the ions in the polymer. Hence, the beam was stopped in the polymer and maximum dissipation of heat took place at the end.

3.1. FTIR analysis

The FTIR spectra of pristine and irradiated PC films are shown in Fig. 1. The absorption bands as obtained from the pristine spectrum are identified as (A) 765 cm^{-1}: out of phase skeletal vibration of C–H deformation; (B) 1030 cm^{-1}: C–O stretching vibration; (C) 1645 cm^{-1}: C=C phenyl ring stretching vibration; (D) 1770 cm^{-1}: C=O stretching vibration; (E) 2484 cm^{-1}: hydroxyl stretching bond; (F) 2928 cm^{-1}: CH_3 stretching vibrations; (G) 3080 cm^{-1}: C–H stretching vibration

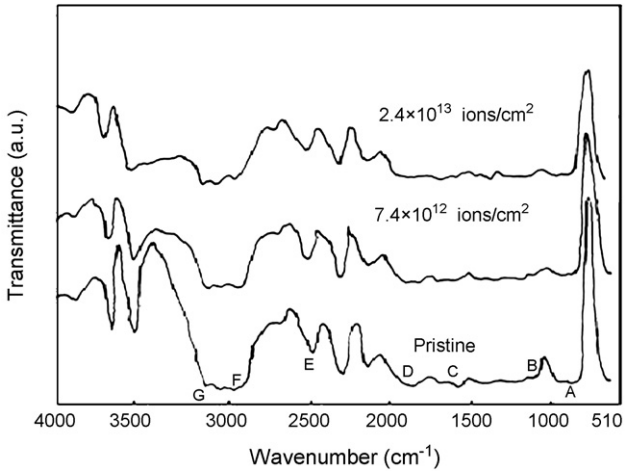

Fig. 1. FTIR spectra of pristine and irradiated PC films.

of aromatic compounds. There is only a slight change in the intensity of the irradiated sample as compared to the pristine sample. The minor changes in the peak-intensities of irradiated samples may be due to the breakage of few bonds in the polymer structure [10].

3.2. Microhardness

The Vickers' hardness value (H_v) was determined with microhardness tester with a Vickers' diamond pyramidal indenter of a Carl Zeiss optical microscope. The indentation diagonals were measured to an accuracy of 0.19 μm using a micrometer eyepiece.

The load dependence hardness was measured in the load range 100–1000 mN for a constant loading time of 30 s. The hardness was calculated using the standard formula

$$H_v = 1.854 \times \frac{P}{d^2}$$

where P is the applied load in mN obtained as the product of the load in g and $g = 9.8$ m s^{-1}, d the average of the two indentation mark diagonal length in μm and H_v is the Vickers' hardness in MPa.

Fig. 2 shows the plot of the Vickers' microhardness (H_v) versus applied load (P) at different fluences. It is evident that H_v value increases with the load up to 300 mN and then saturates beyond the load of 400 mN. The value obtained from the saturation region, therefore, represents the true hardness of the bulk material, since at high loads the indenter penetration depth is also high and surface effects become insignificant. It is also observed that the hardness increases as fluence increases, which can presumably be due to the cross-linking of some of the degraded molecules by irradiation.

3.3. AC electrical frequency response

Fig. 3 shows the variation of conductivity with log frequency (f in Hz) for pristine and irradiated polycarbonate films. A sharp increase in conductivity at 20 kHz has been observed