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Dielectric properties and surface morphology of swift heavy ion beam irradiated polycarbonate films

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Abstract Swift heavy ion beam irradiation induces modification in the dielectric properties and surface morphologies of polycarbonate (PC) films. The PC films were irradiated by 55 MeV energy of C⁵⁺ beam at various ions fluences ranging from 1×10^{11} to 1×10^{13} ions cm⁻². The dielectric properties (i.e., dielectric constant, dielectric loss, and AC conductivity) and surface morphologies of pristine and SHI beam irradiated PC films were investigated by dielectric measurements, atomic force microscopy (AFM), and optical microscopy. The dielectric measurements show that the dielectric constant, dielectric loss, and AC conductivity increase with ion fluences and temperature, however, the dielectric constant and AC conductivity decrease while dielectric loss increases with frequency. AFM shows the increase in average roughness values with ion fluences. The change of color in PC films has been observed from colorless to yellowish and then dark brown with increases of ion fluence by using optical microscopy.

Keywords SHI · Polycarbonate · Dielectric properties · Optical micrographs · AFM

Introduction

Polycarbonate (PC) is a very important polymeric material, due to its properties for electronic and optoelectronic applications. It is of excellent transparency, light weight,

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high stability, and wide bandgap materials. Energetic ion interaction with PC plays a crucial role in significantly modifying their physiochemical properties [1–6].

Swift heavy ion (SHI) beam plays a very important role in the field of polymeric material for improvements of its properties [7, 8]. The technological significance of SHI irradiation of polymeric material is in several industrial applications such as microelectronic, solar cells, biosensors, medical sterilization, biomedical, and other high-technology applications [9–16]. It established the fact of interaction of SHI beam radiation with polymeric material to several changes in the polymer properties due to induced chain scissions and crosslinks. In general, cross-linking improves physical properties of the polymer material and chain scissoning to make the opposite behavior of the polymer material.

Numerous investigations have been reported with the effect of X-ray, electron, proton, gamma, and laser radiations-induced changes in the optical, electrical, and thermal properties of PC [17–23]. It was found that PC is affected generally by high X-ray, electron, proton, gamma, and laser irradiation doses. Several studies were performed on the effect of SHI beam irradiation-induced changes in the optical, electrical, and thermal properties of PC [24–30].

In this study, we investigate the dielectric and surface morphology of PC films by using 55 MeV Carbon (C^{5+}) beam at different ion fluences ranges from 1×10^{11} to 1×10^{13} ions cm⁻². The dielectric and surface morphology were investigated by using dielectric measurement, atomic force microscopy (AFM), and optical microscopy, respectively.

Experimental procedure

PC pallets were procured from Redox, India and the density of PC was 1.2 g cm^{-3} . The PC films were prepared by solvent



casting method with the chemical composition of $C_{16}H_{14}O_3$. The details of PC film preparation technique can be found in the literature [2, 28-30]. The thickness of the PC films was typically $\sim 25 \, \mu \text{m}$. PC films of the size of $1 \times 1 \, \text{cm}^2$ were irradiated with 55 MeV Carbon ion beam at different ions fluences ranges from 1×10^{11} to 1×10^{13} ions cm⁻² by using in general purpose scattering chamber (GPSC) under ambient temperature and pressure of 10⁻⁶ torr at Inter University Accelerator Center (IUAC), New Delhi India. 101.96 μm was the range of the ion beam in polymer (PC). The projected range was calculated by using SRIM-2008 (software). So the range of the ions is greater than the thickness of the PC films. For dielectric measurement, PC films were coated by using the silver paste over the central circular area of 0.8 cm diameter both surfaces (electrodes preparation) of pristine and SHI beam irradiated PC films. The dielectric properties were investigated in the temperature ranging from 300 to 450 K with wide frequency ranges from 1 kHz to 1 MHz by measuring the capacitance (C_p) and dielectric loss as a function of frequency of applied voltage using LCR meter (Agilent Precision 4285).

The surface morphology of pristine and SHI beam irradiated films were studied by using AFM (Digital Nanoscope IIIa Instrument, Inc.) in tapping mode. Topographical images were taken for $5\times 5~\mu m^2$ surface area and then average surface roughness was determined. Optical microscopy has also been used to investigate the surface morphology of pristine and SHI beam irradiated PC films. Optical micrographs were taken by using Nikon-Ecilpse (TE-2000) with Nikon Digital camera (DXM 1200F) for surface morphology.

Fig. 1 Dielectric constant as a function of temperature for pristine and SHI beam irradiated PC films at various ion fluences and frequency

Theory of the dielectric measurements

The measured value of capacitance and dissipation factor has been converted into the dielectric constant and AC conductivity. The dielectric constant was calculated using the following relations;

$$\varepsilon' = \frac{C_{\rm p}}{C_{\rm o}} \tag{1}$$

and
$$C_0 = \frac{\varepsilon_0 A}{d}$$
 (2)

where C_p is the capacitance of the polymeric film measured using an LCR meter, A is the area of the electrode (m²), d is the thickness of the polymeric film, and ε_0 is the permittivity of free space (i.e., 8.85×10^{-12} F m⁻¹).

The AC conductivity (σ_{ac}) of the polymeric film was calculated by the following relation;

$$\sigma_{\rm ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta \tag{3}$$

where f is the frequency of the polymeric film.

Results and discussions

Dielectric constant

Figures 1a-d and 2a-d illustrate the temperature and frequency dependence of the dielectric constant at various ion fluences, respectively. Figure 1 shows that the value of dielectric constant slightly increases up to 418 K, then decreases on increasing temperature up to 428 K. Above

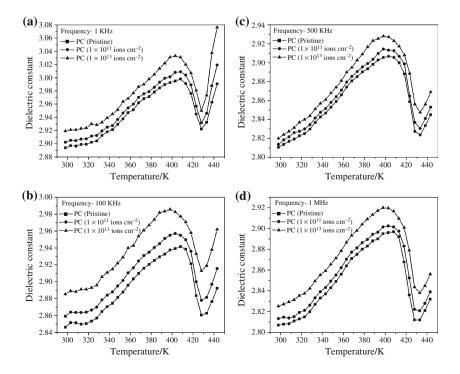
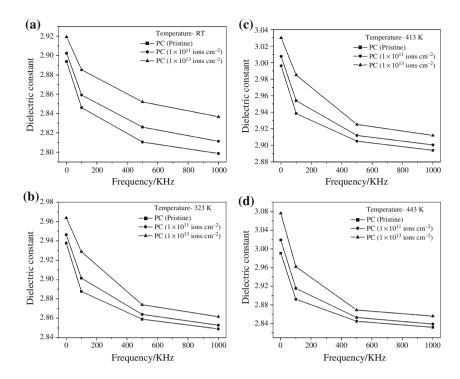




Fig. 2 Dielectric constant as a function of frequency for pristine and SHI beam irradiated PC films at various ion fluences and temperature



428 K, it increases again [31]. So it has been observed that the PC and SHI irradiated films show only single peak or relaxation (i.e. α -relaxation at glass transition temperature region) at different fluences. The α -relaxation occurs due to space charge polarization followed by trapping of charge carriers in deeper traps. The position of the maximum value of dielectric constant is shifted toward the lower temperatures side with increasing fluences due to the crosslinking and degradation of the polymeric material. On the other hand, Fig. 2 shows that the value of dielectric constant of pristine and SHI beam irradiated PC films decreases with frequency [32, 33] due to ion beam irradiation.

Dielectric loss

Figures 3a-d and 4a-d illustrate the temperature and frequency dependence of the dielectric loss at various fluences, respectively. From Figs. 3a-d and 4a-d, it is observed that the value of dielectric loss increases with increasing temperature as well as frequency [31]. The dielectric loss is slightly increased with temperature, but it is highly increased near the glass transition temperature, since the rise of temperature facilitates segmental motion and dipole orientation. So pristine is more useful as compare to irradiated PC films (Fig. 4).

AC conductivity

Figures 5a-d and 6a-d show the variation of AC conductivity with temperature and frequency for pristine and

SHI beam irradiated PC films. It is clear from Figs. 5a-d and 6a-d that the value of AC conductivity of pristine PC is lower compared with irradiated films. This can be seen that the value of AC conductivity increased with fluence, which is attributed to the formation of conjugated double bonds [34]. Figure 5a-d represents the value of AC conductivity increasing linearly with temperature (i.e., from room temperature up to near the glass transition temperature), but near the glass transition temperature AC conductivity highly increasing with temperature. This can be attributed to the temperature-induced relaxation on the rigid structure which was responsible for increase in dipole orientation [21]. Figure 6a-d shows the characteristics of AC conductivity as a function of frequency at various temperatures (i.e., RT, 323, 413, and 443 K). The value of AC conductivity decreasing with frequency due to the free radicals produced due to scissoning of the polymer chains.

It is clear from Figs. 1a-d to 6a-d that the value of dielectric constant, dielectric loss and AC conductivity of pristine PC are lower compared with irradiated films. This can be seen that the value of dielectric constant, dielectric loss and AC conductivity increasing with fluence, which are attributed to the formation of conjugated double bonds [34].

Atomic force microscopy

AFM was performed to investigate the surface morphology and value of surface roughness. AFM images of pristine and SHI beam irradiated PC films were recorded using



Fig. 3 Dielectric loss as a function of temperature for pristine and SHI beam irradiated PC films at various ion fluences and frequency

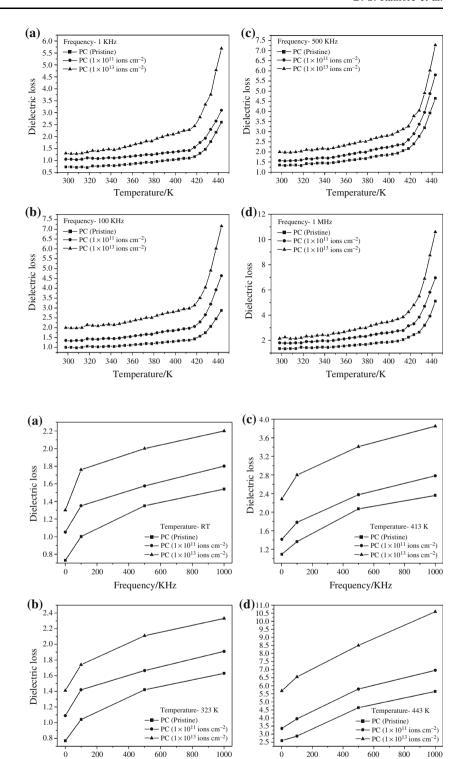


Fig. 4 Dielectric loss as a function of frequency for pristine and SHI beam irradiated PC films at various ion fluences and temperature

Digital Nanoscope IIIa in tapping mode. The 3D AFM images of $5\times 5~\mu\text{m}^2$ surface area of pristine and SHI beam irradiated PC films at fluences of 1×10^{11} and 1×10^{13} ions cm⁻² were shown in Fig. 7a–c. The average surface roughness of 3.12 nm was observed in pristine PC. After ion beam irradiation, average surface roughness was

increased from 3.12 to 6.71 nm with fluences of 1×10^{11} and 1×10^{13} ions cm⁻² [35]. So the value of average surface roughness increased with fluence related to progressive degradation of the polymeric chains due to the cross-linking leading to change in free volume fraction for modified surface of the films.

Frequency/KHz

Frequency/KHz



Fig. 5 AC conductivity as a function of temperature for pristine and SHI beam irradiated PC films at various ion fluences and frequency

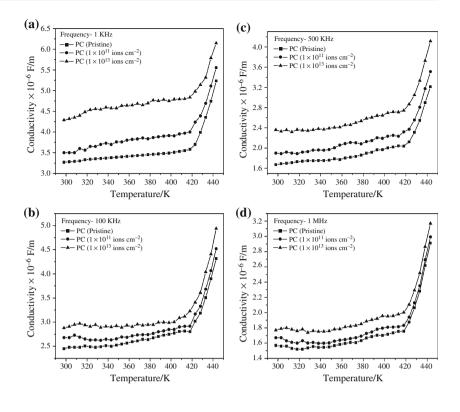
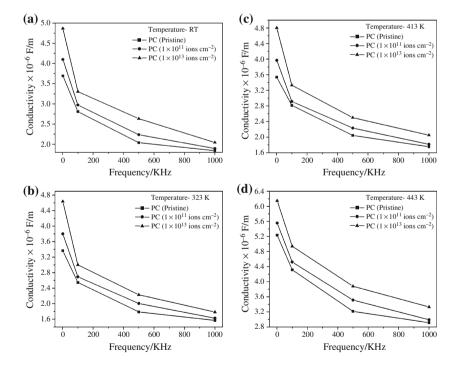


Fig. 6 AC conductivity as a function of frequency for pristine and SHI beam irradiated PC films at various ion fluences and temperatures



Optical microscopy

The surface morphology and colors of PC films of 20 µm area were measured by optical microscopy. The optical micrographs of pristine and SHI beam irradiated films at

various fluences were shown in Fig. 8 (a) pristine, (b) 1×10^{11} ions cm⁻², and (c) 1×10^{13} ions cm⁻². Pristine PC films show the colorless and flake type surface. After irradiation, colors of PC films were observed to change from colorless to yellowish then dark brown and



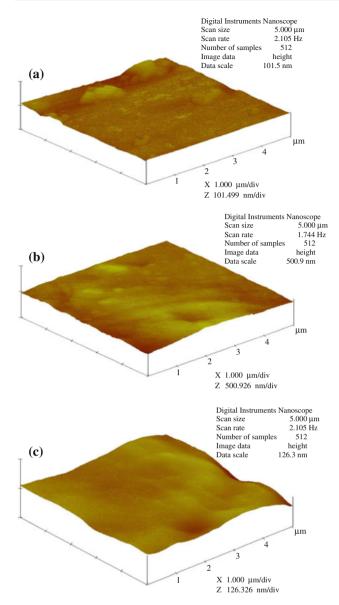


Fig. 7 AFM three-dimension topographic images of a PC pristine b PC (1 \times 10¹¹ ions cm⁻²), and c PC (1 \times 10¹³ ions cm⁻²)

black dark spot (crater) appears in the whole area of films. The size of craters increased with ion fluences due to the degradation of the polymer chain. The change in color of the polymeric films was due to the formation of amorphous hydrogenous carbon clusters and density of the carbon clusters increases with increasing fluences.

Conclusions

It is concluded that the dielectric constant, dielectric loss, and AC conductivity increase with ion fluences and temperature,

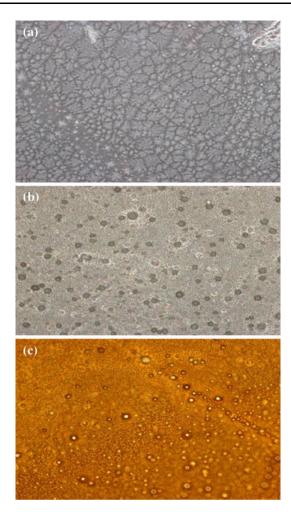


Fig. 8 Optical micrographs of **a** PC pristine **b** PC $(1\times10^{11}~\rm ions~cm^{-2})$, and **c** PC $(1\times10^{13}~\rm ions~cm^{-2})$

however, the dielectric constant and AC conductivity decrease while dielectric loss increase with frequency. The changes in dielectric properties are due to the chain scission and degradation of polymer. AFM shows that the average surface roughness values increase with ion fluences. Optical microscopy shows the change in color from colorless to yellowish and then dark brown. There is no region of change in color but defects are due to the low density because the degradation processes induced by the ion beam irradiation of the polymers are macromolecular chain scission and cross-linking.

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