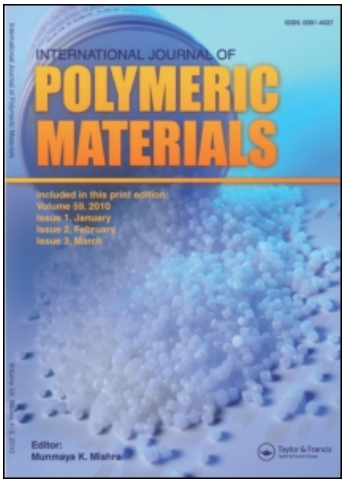

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Manasvi Dixit,[1] Deepika,[1] Mahesh Baboo,[1] Kananbala Sharma,[1] N. S. Saxena,[1] D. K. Avasthi,[2] and Pawan K. Kulriya[2]

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This paper reports the effect of the irradiation of 50 MeV Li^{+3} ions on the thermomechanical properties of PMMA/PC blends. The radiation has been carried out at fluences of 10^{10} to 10^{12} ions/cm^2 to observe any kind of chain scissoring/crosslinking occurring in the sample. The irradiated as well as the pristine samples have been characterized using X-ray diffraction (XRD), Fourier transform spectroscopy (FTIR), scanning electron microscopy (SEM) and dynamic mechanical analyzer (DMA) to study the induced changes in the structural, morphological and mechanical properties in blend films. The XRD results show an increase in the degree of crystallinity upon ion irradiation at low fluences ($\leq 10^{11}$ ions/cm^2) and a decrease in crystallinity at high fluences ($>10^{11}$ ions/cm^2), while the FTIR spectra show no appreciable change after irradiation. The mechanical characterization reveals that radiation significantly modifies the mechanical properties and the glass transition temperature of these polymeric blends.

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Keywords glass transition temperature, irradiation, mechanical properties, PMMA/PC blends, structural characterization

INTRODUCTION

Ion beam treatment of polymers has inspired much interest in scientists and engineers in recent years due to induced improvement in their mechanical, optical and electrical properties. Ion irradiation in polymers destroys the initial structure by crosslinking, scissioning and emission of atoms, molecules and molecular fragments which lead to a change in properties such as density (1), hardness and strength (2), electrical conductivity (3), optical transmission (4), molecular weight distribution (5) and solubility (6). Crystallinity is also affected by ion irradiation (7) and a decrease in crystallinity is observed at high fluence irradiation. The crystallinity plays a crucial role in almost all polymer properties such as mechanical, optical, electrical and even thermal properties. The effectiveness of these changes produced in the polymers depends on the structure of the polymer and the experimental conditions of the ion irradiation like ion energy, fluence, mass, charge and the nature of the targeted material itself.

When an energetic ion transverses through a polymer, it loses its energy by interacting with target nuclei (nuclear stopping) and by interacting with target electron (electron stopping). Nuclear stopping arises from collisions between the energetic ions and target nuclei, which cause atomic displacement and chain scissioning. Electronic stopping is mainly determined by the charge state of the ion and its velocity as the orbital electrons of the moving ion are stripped off to a varying degree depending upon the ion velocity (8). A wide variety of material modifications in polymers have been studied by using the ion irradiation technique (9–11). The interaction of heavy ions with polymer induces irreversible changes in their micromolecular structure. Therefore, a study of the influence of radiation on the morphology, mechanical properties and glass transition temperature of the polymer blend is essential for an understanding of how to optimize processing condition and properties. The mechanism responsible for these improvements should also be understood well.

In the present work efforts have been made to study the effect of ion beam treatment on the glass transition temperature and mechanical properties of PMMA/PC blends of different composition. PMMA/PC blends are a material of interest due to their good compatibility and mechanical properties. The blends have been irradiated with Li^{+3} ion beam of 50 MeV energy at different fluences. A variety of techniques such as FTIR, SEM, XRD, and DMA have been used to identify and quantify the behavior of blends versus the blend ratio and for irradiation fluence.

EXPERIMENTAL

Sample Preparation

Poly (methyl methacrylate) (PMMA, Alfa Essar) and polycarbonate (PC, Goodfellow) in powder form were used as received. Tetrahydrofurane (THF) was used as a solvent. Films of poly methyl methacrylate (PMMA) and polycarbonate (PC) blends were prepared by solution casting technique. The blend of PMMA/PC had compositions of 100/0, 75/25, 50/50, 25/75, and 0/100 by weight. Solutions of PMMA and PC in THF were first prepared at various polymer compositions at 50°C temperature. The polymer solutions were then mixed with continuous stirring and subsequently cast onto glass petri dishes to form transparent films with a thickness of $\sim$100 μm. The cast films were dried under ambient conditions for 24 h and then placed in a vacuum oven to remove residual solvent for 24 h (12). The films were then peeled off from the petri dishes for further characterization and studies.

Li^{+3} Ion Irradiation

The prepared samples were mounted on a vertical shielding ladder and irradiated in a scattering chamber of material science beam line by 50 MeV Li^{+3} ions available from the 15UD Pelletron Accelerator at IUAC, New Delhi, India. All irradiations were performed in vacuum (10^{-6} Torr) at ambient temperature. The beam current was kept below 1 pnA to suppress thermal decomposition. The ion beam fluence was varied in the range 10^{10} to 10^{12} ions/cm^2. In order to expose the target 1.5 cm × 1.5 cm areas, the beam was scanned in the x-y plane. Energy of 50 MeV has been chosen for ensuring uniform irradiation of about 100 μm thick samples.

Characterization

Fourier transform infrared (FTIR) spectra of the pristine and all of the irradiated samples were recorded in the wave number range 400–4000 cm^{-1} (Thermo-Nicolet Nexus 670 FTIR spectrophotometer) with a resolution of 4 cm^{-1}. The X-ray diffraction patterns were recorded using CuKα ($\lambda = 1.54$ Å) radiation from the Brukar AXS D8 diffractometer with a scan speed of 1° min^{-1}. The diffraction angle (2θ) has been varied from 10° to 40° with a step size of 0.02°.

The surface morphology of pristine and irradiated surfaces was obtained using scanning electron microscopy (SEM) (Model: Quanta Fe-200). For SEM analysis all the samples were fractured in liquid nitrogen and coated with gold.

The glass transition temperature and the mechanical properties of the polymer blends were measured by a Tritec 2000 dynamic mechanical

analyzer (DMA) before and after irradiation through temperature and stress-strain scan, respectively. The details about DMA have been discussed elsewhere (13, 14). The temperature scan was performed from 30 to 180°C temperatures at a heating rate/ramp rate of 2°C/min at constant load, and the stress-strain scan was performed at 30°C temperature with load rate 0.1 N/min in tension mode. Frequency of oscillation was fixed at 1 Hz and the strain amplitude was kept at 0.01 mm, which lies within the linear viscoelastic region.

RESULTS AND DISCUSSION

The projected range of 50 MeV Li^{+3} ion beams in the PMMA/PC blends was calculated to be ~ 400 μm, using the SRIM-97 code (Ziegler 1997), which is four times more than the thickness of polymer films used. The SRIM-97 indicates that 95–99% of energy lost by 50 MeV Li^{+3} ions in a 100 μm thick PMMA/PC blend is electronic in nature. The electronic energy loss is dominant for ions with high energy and involves the energy transfer to atoms in the target due to inelastic electron–electron interaction. Collisional processes produce lattice vibration and the displacement of the target atoms. Displacement damage is usually considered to be the most important cause of material modification in solids.

Structural Properties

XRD Analysis

Figures 1–3 show the XRD patterns for pristine and irradiated PMMA, PC and 50 PMMA/50PC blend films irradiated with Li^{+3} ions to various fluences, respectively. The diffraction pattern of all the samples emphasize the amorphous nature of these samples. All the XRD patterns show a broad halo in the 2θ range 10–20°. This broadening is a signature of the polymeric nature of the samples and is also indicative of the fact that the material possesses only short-range order.

Another feature to be noticed from the XRD patterns of these samples is that upon swift heavy ion (SHI) irradiation, the intensity of the peaks increases up to 10^{11} ions/cm^2 fluence, and beyond this fluence, a decrease in intensity has been observed. The increase in the degree of crystallinity with the increase in ion fluence up to 10^{11} ions/cm^2 is due to the systematic alignment of polymer chains by chain folding, while the decrease at a fluence of 10^{12} ions/cm^2 is due to chain scissioning of polymeric structure.

Although the intensity of the diffraction peak varies (increase and decrease) during irradiation, no significant shift of the peak position is observed, implying no significant change in lattice parameter.

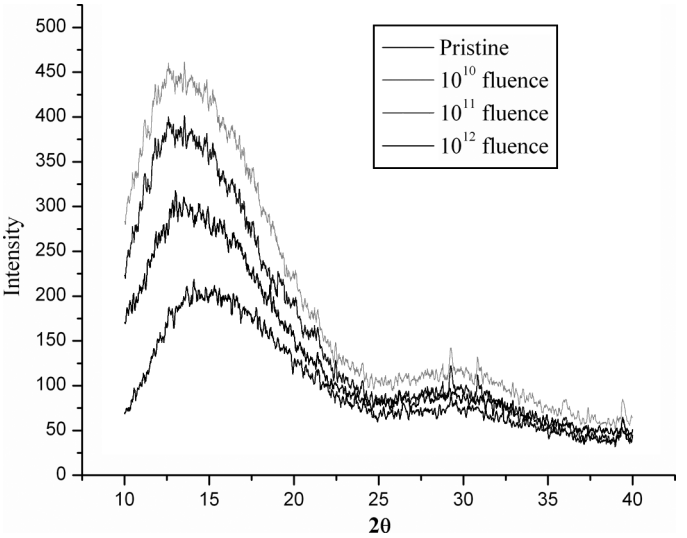

Figure 1: XRD pattern of pristine and irradiated PMMA polymer films.

FTIR Analysis

FTIR spectra of pristine and irradiated polymer films of 50 PMMA/50PC blend are presented in Fig. 4 as a representative case. The FTIR spectra of 50 PMMA/50PC blends show the attribution of both PMMA and PC bonding which was observed individually in pure PMMA and pure PC samples. The attributions of the observed bands in PMMA/PC blends are indicated in Table 1.

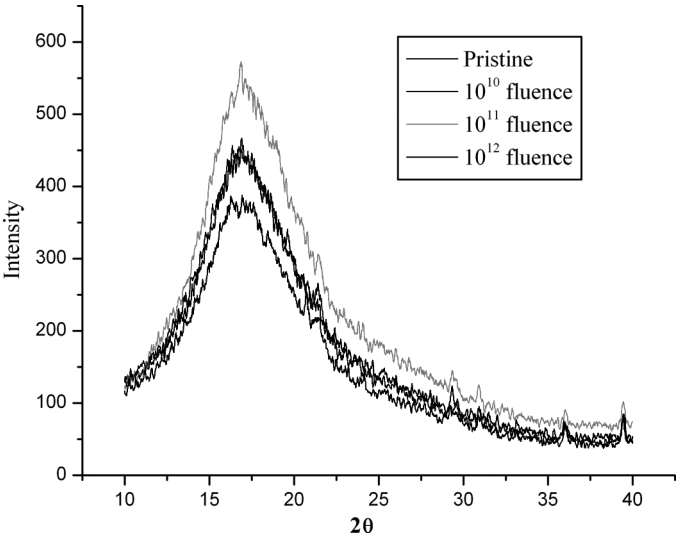

Figure 2: XRD pattern of pristine and irradiated PC polymer films.

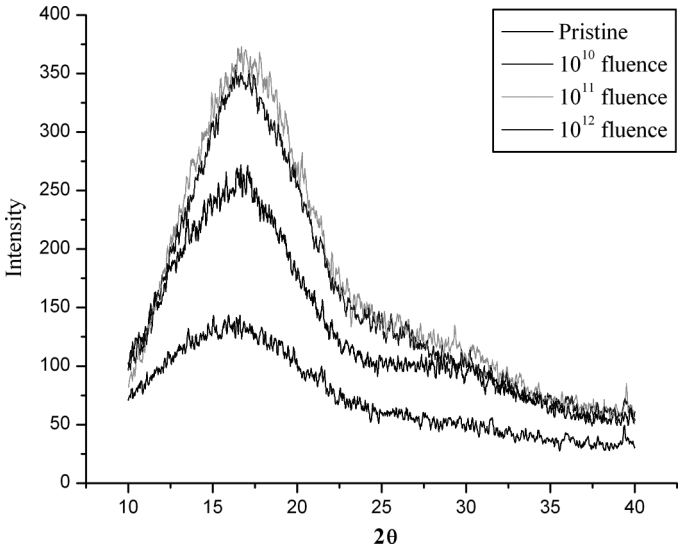

Figure 3: XRD pattern of pristine and irradiated 50 PMMA/50PC blend films.

The results of FTIR analysis 50 PMMA/50PC blend polymer indicates the chemical degradation of the irradiated polymers by the SHI ions. The intensity of the infrared bands, characteristics of the different chemical functional groups decrease with the increase in fluence. However, peak position does not changes which indicate the structural stability of polymer films of PMMA/PC blends towards the ion irradiation upto the ion fluence 10^{12} ions/cm^2.

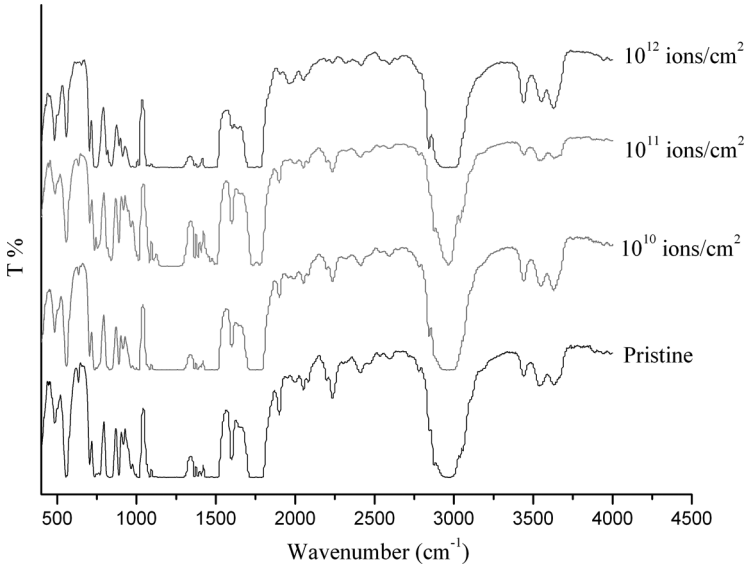

Figure 4: FTIR spectra of pristine and irradiated 50 PMMA/50PC blend films.

Table 1: IR vibrational modes of 50 PMMA/50PC blend

Wave number (cm^{-1})	Attribution
~750	CH_2 rocking vibration
620–970	C-H bending vibration
800–1500	C-O stretching vibration
1350–1450	C-H bending vibration
~1594	C = C phenyl ring stretching vibration
~1730	C = O stretching vibrations in the pendent group (-$COOCH_3$)
1900–2000	C = C stretching vibration
~2414	Hydroxyl stretching bond
2880–3020	C-H stretching vibration of aromatic compounds
3300–3600	C = O stretching vibrations

Surface Morphology Study

The surface morphological studies of the pristine and irradiated (at fluence 1×10^{12} ions/cm^2) polymer films of pure PMMA, pure PC and 50 PMMA/50PC blend are shown in Figs. 5–7, respectively. The SEM micrographs show that the fractured surfaces of the PMMA/PC blends possess very fine phase morphology. The boundary between the PMMA and PC phase is not clearly observed. This suggests a fine dispersion and homogeneous incorporation of PC into the PMMA (15). The results also reveal that the PC is compatible with PMMA in morphological sense.

It is also observed that the surface of these samples becomes rough with increase in ion fluence. This is due to the fact that on irradiating the sample with 50 MeV Li^{+3} ion beams, the ion beam interacts with the matrix of the

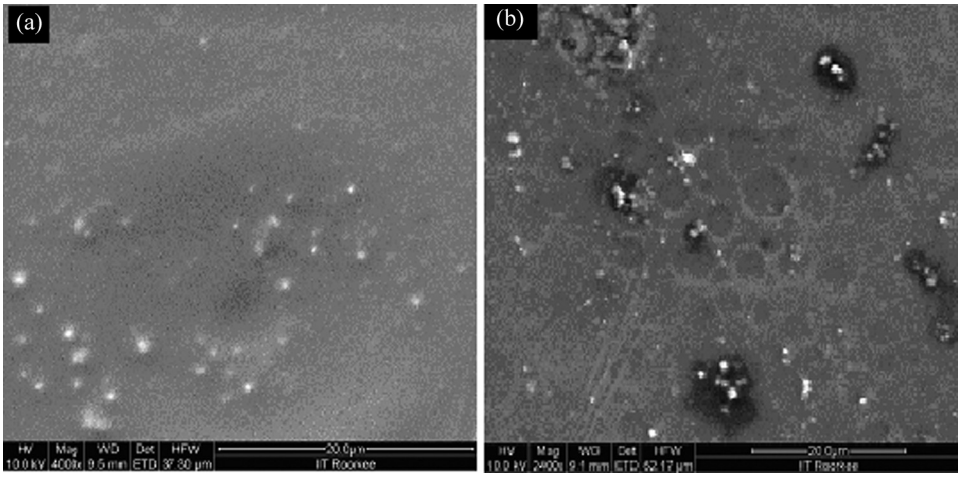

Figure 5: SEM images of (a) pristine PMMA and (b) irradiated PMMA at 10^{12} ions/cm^2 fluence.

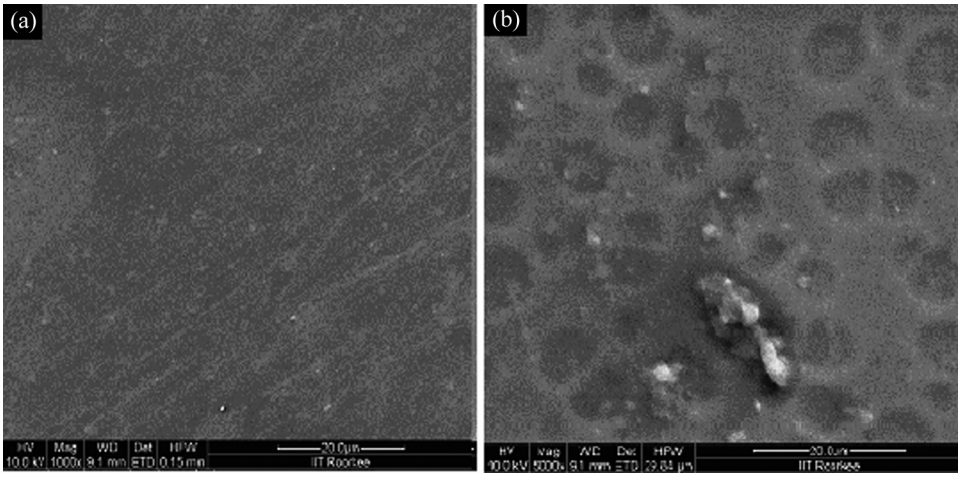

Figure 6: SEM images of (a) pristine PC and (b) irradiated PC at 10^{12} ions/cm^2 fluence.

polymer chains and induces irregularities in the samples by creating small pores. These small pores lead to an increase in the roughness of the sample.

Mechanical Characterization

Ion irradiation has been performed on the pristine samples of PMMA/PC blends in order to see any chain scissioning and crosslinking and consequently their effect on the glass transition temperature and mechanical properties such as tensile strength, stiffness, toughness, Young's modulus and elongation at break. The pristine samples were irradiated with 50 MeV lithium ion beam

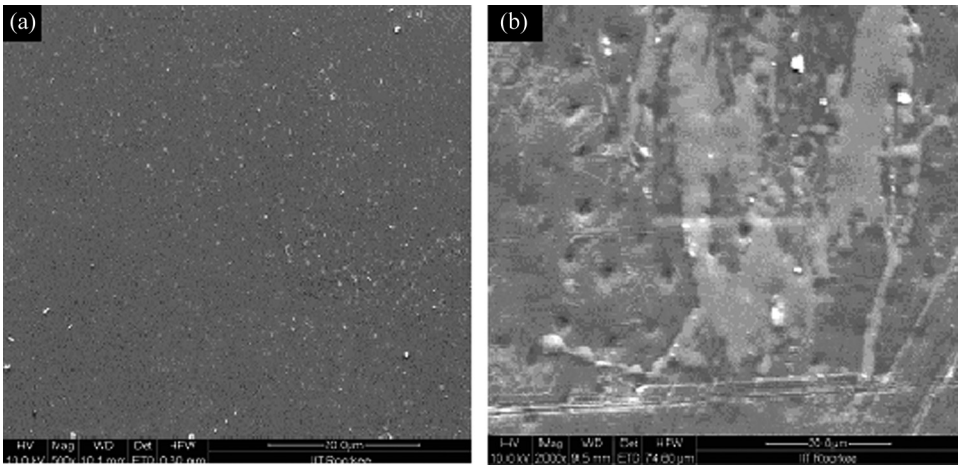

Figure 7: SEM images of (a) pristine 50 PMMA/50PC and (b) irradiated 50 PMMA/50PC at 10^{12} ions/cm^2 fluence.

with three different fluences (10^{10}, 10^{11} and 10^{12} ions/cm^2). The effect of ion irradiation on the above mentioned properties has been mentioned below.

Glass Transition Temperature (T_g)

Figures 8–9 show plots of Tan δ vs. temperature for pristine and ion-irradiated PMMA and PC polymers, whereas Figure 10 shows the plot of Tan δ vs. temperature for pristine and ion-irradiated 50 PMMA/50PC blend as a representative case. The glass transition temperatures (T_g) for pristine PMMA, 75 PMMA/25PC, 50 PMMA/50PC, 25 PMMA/75PC and PC films have been found at 83.8, 129.5, 133.2, 149.4 and 150.5°C, respectively. The results of PMMA/PC blends show that all blends exhibited a single T_g, which is between the T_g of both blend components. This single glass transition temperature indicates miscibility between two polymers, suggesting that PC is compatible with PMMA. This miscibility is due to the n–p complex formation between the ester group of PMMA and the phenyl ring of PC (16, 17).The similar fact was also observed in SEM micrographs. The figures also show a significant change in the glass transition temperature on irradiation. The glass transition temperatures are shifted to higher temperature as fluence increases up to the 10^{11} ions/cm^2. According to Chipara (18, 19), a change in T_g towards higher values is indicative of the presence of crosslinking reactions in polymers. On irradiation, collective excitations (plasmons) are produced (20), which causes chain folding or crosslinking of the polymer chains. This

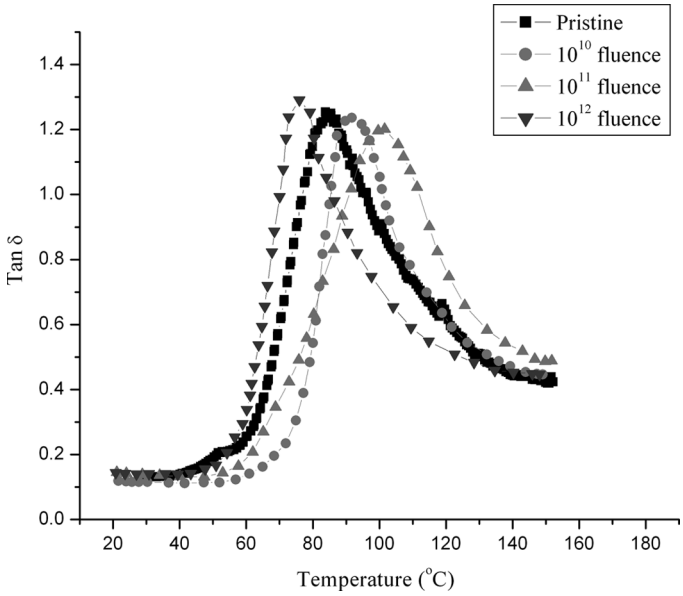

Figure 8: Variation of tan δ with temperature for pristine and irradiated PMMA polymer films.

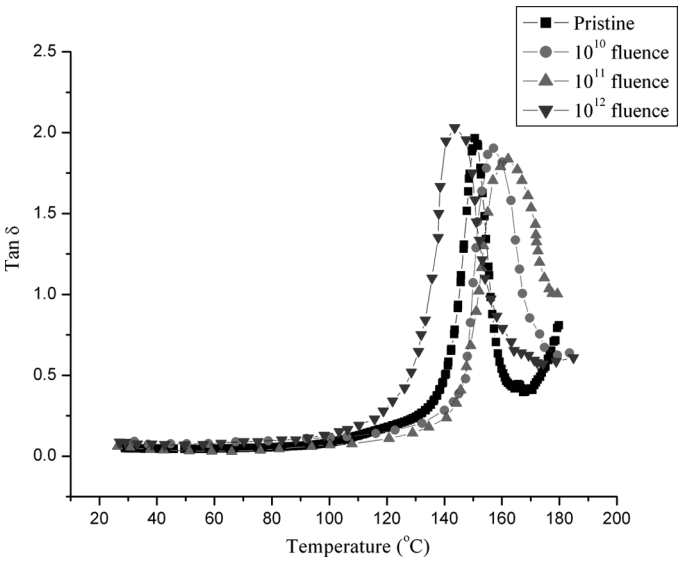

Figure 9: Variation of tan δ with temperature for pristine and irradiated PC polymer films.

crosslinking in turn makes the polymer more compact. When the fluence is low, i.e., 10^{10} ions/cm^2, the frequency of the collective excitations is less and therefore a less compact structure is formed. On increasing the fluence to 10^{11} ions/cm^2, compactness of the structure increases due to increased

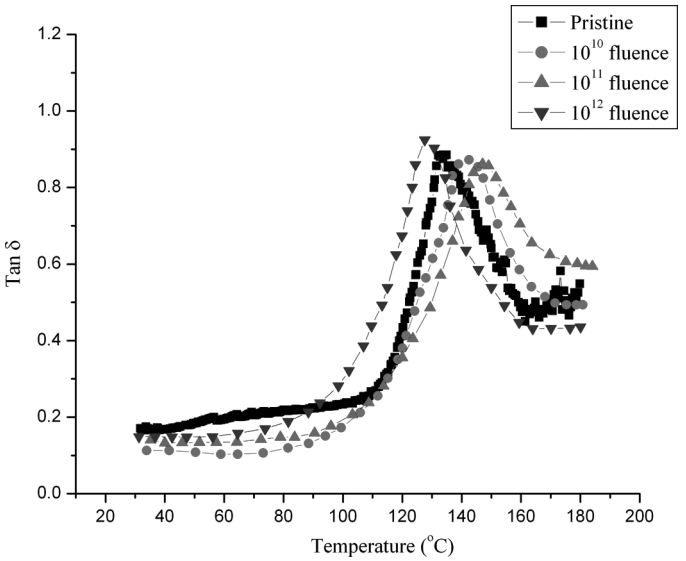

Figure 10: Variation of tan δ with temperature for pristine and irradiated 50 PMMA/50PC blend films.

Table 2: The glass transition temperatures of pristine and irradiated PMMA, PC and PMMA/PC blend films

Radiation fluence	T_g of PMMA (°C)	T_g of 75 PMMA/ 25PC (°C)	T_g of 50 PMMA/ 50PC (°C)	T_g of 25 PMMA/ 75PC (°C)	T_g of PC (°C)
Pristine	83.8	129.5	133.2	149.4	150.4
10^{10}	91.5	135	141.8	155.6	157.1
10^{11}	102	138.8	147.1	159.1	162.5
10^{12}	76.2	123	127.7	144.1	144.2

excitations and the value of T_g is higher than that obtained at fluence of 10^{10} ions/cm^2. On further increasing the fluence to 10^{12} ions/cm^2, the collective excitations increases to such an extent that chain scissioning takes place in the sample and therefore the compactness of the polymer decreases. This decrease in compactness is generally due to the increase in molecular mobility as a result of scissioning of the polymer chains. This fact is also corroborated through XRD measurements. At 10^{12} ions/cm^2, the loss of crystallinity of polymers is observed, which is directly related to scission processes at main chains of the polymer.

The effect of ion irradiation on glass transition temperatures of PMMA, 75 PMMA/25PC, 50 PMMA/50PC, 25 PMMA/75PC blends and PC films are given in Table 2. The results reveal that the ion radiation promotes crosslinking simultaneously with scission, which causes the modification in the glass transition temperature.

Storage Modulus and Tensile Properties

Figures 11–12 show the variation of storage modulus with temperature for pristine and ion irradiated PMMA and PC, whereas Figure 13 shows the variation of storage modulus with temperature for pristine and ion-irradiated 50 PMMA/50PC blend as a representative case.

From these figures it is observed that the storage modulus of pristine as well as irradiated PMMA, PC and PMMA/PC blends decreases as the temperature increases due to softening of the films. At first, the storage modulus slowly decreases with increasing temperature and then there is a rapid decrease in the region of glass transition. As the temperature increases to T_g, the polymer chains have sufficient thermal energy to rotate, resulting in a sharp decrement in modulus and then attainment of a constant value at higher temperatures.

It is also observed from these figures that the value of the storage modulus of PMMA, PC and PMMA/PC blends increases as fluence increases up to the 10^{11} ions/cm^2, and beyond 10^{11} ions/cm^2 fluence, the storage modulus shows a lower value as compared to pristine samples. This trend of storage modulus suggests that the stiffness of the samples increases with ion irradiation

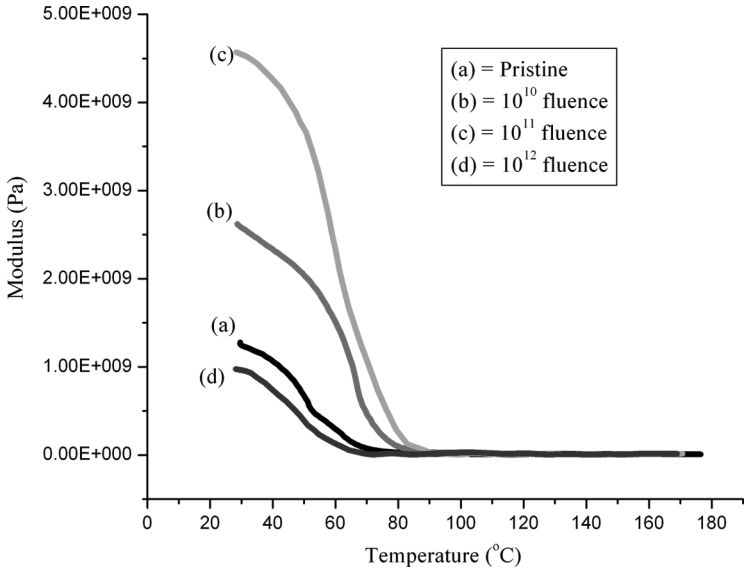

Figure 11: Variation of storage modulus with temperature for pristine and irradiated PMMA polymer films.

($\leq 10^{11}$ ion/cm^{2}fluence) due to induced crosslinking between polymer chains and at a fluence of 10^{12} ion/cm^2, stiffness decreases due to chain scissioning.

Figures 14–15 show the tensile stress strain behavior for pristine and ion-irradiated PMMA and PC at room temperature (30°C), whereas Figure 16

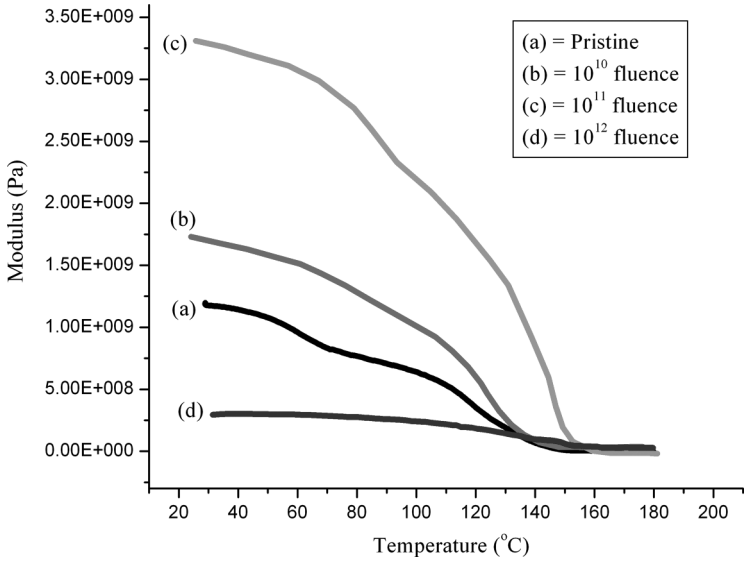

Figure 12: Variation of storage modulus with temperature for pristine and irradiated PC polymer films.

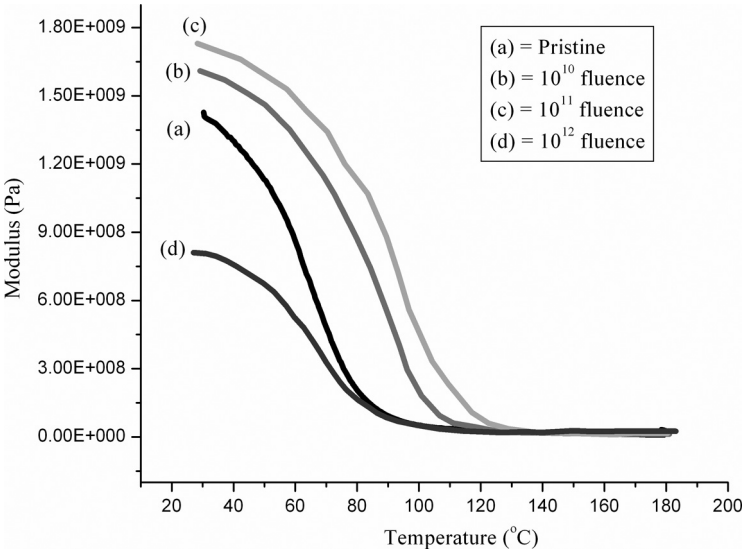

Figure 13: Variation of storage modulus with temperature for pristine and irradiated 50 PMMA/50PC blend films.

shows the tensile stress strain behavior for pristine and ion-irradiated 50 PMMA/50PC blend as a representative case. In all cases, at low strain nearly elastic deformation is observed, where the strain is nearly proportional to the applied stress, whereas for higher levels of strain, the deformation becomes plastic and preferential orientation can be induced in the sample.

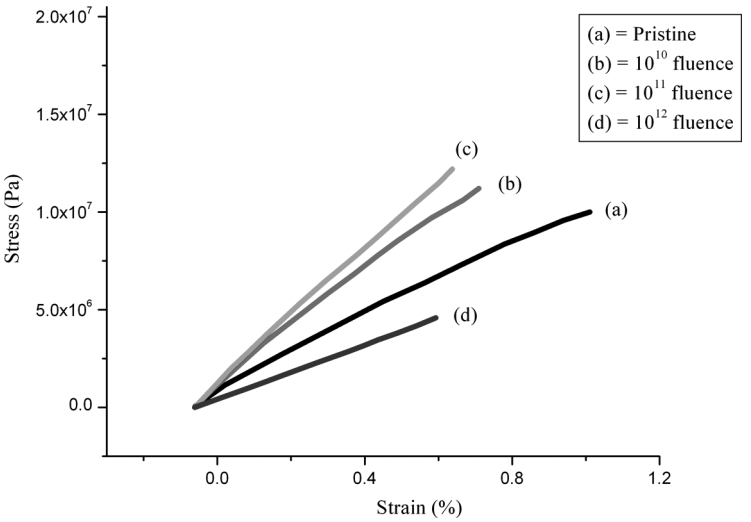

Figure 14: Tensile stress strain-behavior for pristine and irradiated PMMA polymer films.

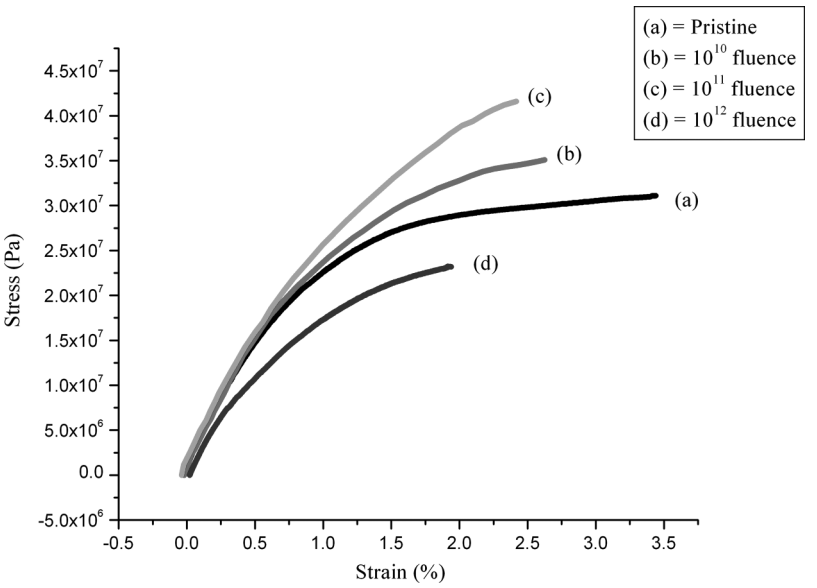

Figure 15: Tensile stress-strain behavior for pristine and irradiated PC polymer films.

The changes in the deformation characteristics of PMMA upon the incorporation of PC under an applied load are clearly evident. A pure pristine PMMA sample shows linear elastic stress strain behavior. In PMMA, there is no yield point and fracture is mainly caused by crazing. Here the stress

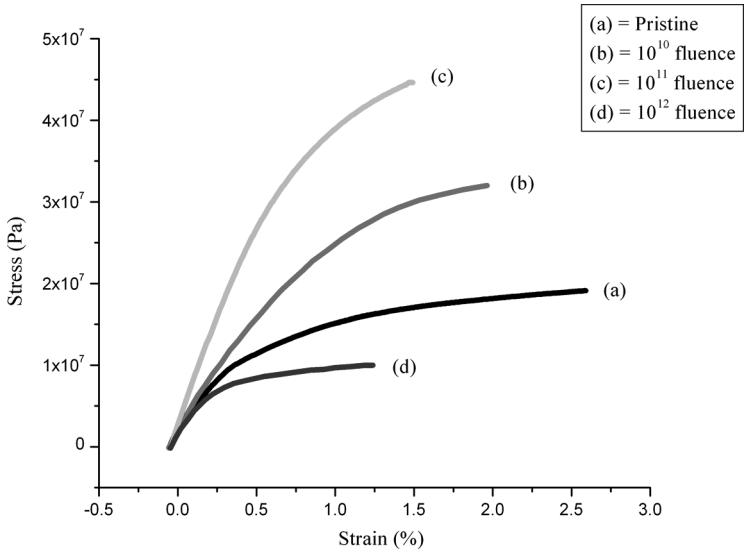

Figure 16: Tensile stress-strain behavior for pristine and irradiated 50 PMMA/50PC blend films.

Table 3: Mechanical properties of pristine and irradiated PMMA polymer films

Radiation fluence	Storage modulus (GPa)	Young's modulus (GPa)	Elongation at break (%)	Ultimate Tensile strength (MPa)	Fracture energy (J)
Pristine	1.27	1.29	1.08	10.8	0.037
10^{10}	2.56	1.45	0.71	11.1	0.028
10^{11}	4.56	2.29	0.63	12.4	0.011
10^{12}	0.96	0.65	0.59	4.6	0.005

increases linearly with strain (or very nearly linearly) until ultimate mechanical failure is obtained while pure pristine PC behaves as a ductile polymer undergoing yielding.

The effect of ion irradiation on mechanical properties such as storage modulus, Young's modulus, tensile strength, elongation at break and fracture energy of PMMA, 75PMMA/25PC, 50PMMA/50PC, 25PMMA/75PC blends and PC polymer films blends at room temperature (30°C) are given in Tables 3–7, respectively. From these tables, it is observed that the values of storage modulus, Young's modulus and ultimate tensile strength increase with the increase in radiation at lower fluence ($\leq 10^{11}$ ion/cm^2). On further increase of the fluence to 10^{12} ions/cm^2, a decrease in the value of the above-mentioned properties is observed. The values of elongation at break and fracture energy (toughness) decreases continuously with an increase in irradiation fluence.

The above observations are manifestations of radiation-induced crosslinking as well as chain scissioning occuring in these polymer blends. As mentioned earlier, SHI irradiation increases the crosslinking in the polymer blend samples up to 10^{11} ion/cm^2, which reduces the chain mobility, and the samples become more compact, hard and stiff and therefore a higher value of storage modulus, Young's modulus and ultimate tensile strength is observed. While, on increasing the fluence to 10^{12} ion/cm^2, the chain scissioning takes place and therefore the molecular motion of the scissioned chains is fast enough for viscous flow, which in turn reduces the value of modulus and strength.

Table 4: Mechanical properties of pristine and irradiated 75 PMMA/25PC blend films

Radiation fluence	Storage modulus (GPa)	Young's modulus (GPa)	Elongation at break (%)	Ultimate Tensile strength (MPa)	Fracture energy (J)
Pristine	1.37	1.85	1.99	15.95	0.071
10^{10}	1.87	1.97	1.46	21.2	0.062
10^{11}	4.21	2.46	1.41	24.9	0.045
10^{12}	0.25	1.25	1.13	9.34	0.023

Table 5: Mechanical properties of pristine and irradiated 50 PMMA/50PC blend films

Radiation fluence	Storage modulus (GPa)	Young's modulus (GPa)	Elongation at break (%)	Ultimate tensile strength (MPa)	Fracture energy (J)
Pristine	1.42	2.37	2.61	19.15	0.114
10^{10}	1.60	2.49	1.96	32	0.102
10^{11}	1.71	4.99	1.49	44.6	0.084
10^{12}	0.80	1.95	1.23	10	0.034

Table 6: Mechanical properties of pristine and irradiated 25 PMMA/75PC blend films

Radiation fluence	Storage modulus (GPa)	Young's modulus (GPa)	Elongation at break (%)	Ultimate tensile strength (MPa)	Fracture energy (J)
Pristine	1.82	2.53	2.97	27.55	0.244
10^{10}	2.73	2.81	2.34	41.3	0.181
10^{11}	4.60	3.33	2.03	45.4	0.135
10^{12}	1.28	2.31	1.24	16.5	0.048

Table 7: Mechanical properties of pristine and irradiated PC polymer films

Radiation fluence	Storage modulus (GPa)	Young's modulus (GPa)	Elongation at break (%)	Ultimate tensile strength (MPa)	Fracture energy (J)
Pristine	1.19	1.18	3.41	30.8	0.278
10^{10}	1.71	2.39	2.62	35.1	0.213
10^{11}	3.28	2.50	2.41	41.6	0.143
10^{12}	0.30	1.93	1.94	19.4	0.098

Radiation on one hand increases the hardness but on the other hand it induces rigidity in the samples and makes it more brittle. This fact is observed as lower values of elongation at break and toughness with an increase in radiation fluence.

CONCLUSIONS

A systematic study of structural and mechanical characterization of pristine and ion-irradiated PMMA, PC and PMMA/PC blends leads to the following conclusions.

1. The structural and morphological characterization of PMMA, PC and PMMA/PC blends reveal that irradiation does not cause any significant

structural modification in the samples, and therefore samples are structurally stable.

2. The existence of a single glass transition temperature (T_g) for PMMA/PC blends is suggestive of the fact that the blends are compatible. Also the regular increase with increasing fluence and a sudden decrease of glass transition with a further increase of the fluence is an outcome of chain crosslinking and chain scissioning in the blends.

3. The increase in the mechanical properties like storage modulus, Young's modulus and ultimate tensile strength, with an increase in PC content in the blend as well as with radiation fluence (upto $\leq 10^{11}$), suggests that these blends can be used in industrial applications concerning mechanical strength under a radiation environment.

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