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TSDC behaviour of pristine and irradiated PET/0.8 PHB polymer liquid crystal samples

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Polymers exhibiting liquid crystal behavior, known as polymer liquid crystals (plcs), have captured the attention of engineers and scientists because of their technological potentials and scientific challenges [1–6]. Polymer liquid crystals show clear superiority in connection with chemical resistance, low inflammability, outstanding mechanical properties, applicability at elevated temperatures, high modulus, low isobaric expansivity and often unusual ease of processing [7, 8]. An extensive exploration of dielectric relaxations in pristine as well as high energy ion irradiated polymer liquid crystals is essential for their use in the presence of ionizing radiation, and to understand the configurational changes due to ion irradiation taking place in plcs. The effect of high energy heavy ion irradiation on polymer liquid crystals is not much known. The various dielectric relaxation processes of the polymer liquid crystal samples will be investigated by using thermally stimulated discharge current (TSDC) technique, the most suitable tool [9]. The technique involves mainly two steps. The first step is to form a thermo electret state (frozen in polarization) in the plc sample and the second step is to obtain the discharge current spectrum at a desired heating rate. The different maxima appearing in the TSDC spectrum provide deep insight into the molecular origin of dipolar, space charge and other relaxations. In the present paper we report the TSDC spectra of pristine as well as 100 MeV Ni^{58}-ion irradiated PET/0.8 PHB polymer liquid crystals.

The material used in the present investigation is one of the first known thermoplastic polymer liquid crystals, poly(p-hydroxybenzoic acid-co-ethylene terephthalate) usually written as PET/x.PHB where x represents the molar concentration of liquid crystalline PHB sequences in the copolymer. The pristine samples procured from Eastman Kodak (USA) were of 130 μm thickness. The samples were irradiated with 100 MeV Ni^{58}-ion beam at Nuclear Science Center (PELLETRON Facility), New Delhi. The electrical contacts were made by vacuum evaporation of aluminium on to both the surfaces. The samples were polarized by subjecting them to a desired dc field (polarizing field; E_p) and at a desired temperature (polarizing temperature; T_p) for 1 h. The samples were then cooled to room temperature (within 30 min) in the presence of applied dc field (E_p). The electrodes were short circuited for 10 min to eliminate the fractional stray surface charges accumulated during polarization

The TSD currents were obtained by heating the polarized samples, at a constant heating rate (2 K/min) from room temperature (293 K) to 523 K with the help of Keithley's high precision electrometer (610C). For the study of storage time effects the samples, after being polarized, were stored under non-shorted condition for a pre-determined period.

Thermally stimulated depolarization current spectra of PET/0.8 PHB polymer liquid crystal samples in the temperature range 293–523K are reported in Figs 1 to 3. Fig. 1 represents the variation of TSD currents for the samples polarized at different polarizing fields (E_p: 4×10^6 to 2.0×10^7 V/m) for polarizing temperature of (T_p) 453 K. It is observed that the extremely fast reacting dipoles of both PET and PHB relaxation peak (β'-peak) appearing at lower temperature (i.e., in the range of 308 K) is very pronounced for the samples which are polarized at higher polarizing fields, and the space charge relaxation peak (α-peak) which is appearing at higher temperature (i.e., in the range of 453 K) is missing in the samples polarized at lower polarizing temperature ($T_\mathrm{p} = 353$ K, figure not shown). The peak magnitude is observed to increase with increasing polarizing fields for all the peaks. The β-peak is observed to shift towards a lower temperature as the polarizing field increases. Fig. 2 illustrates the effect of T_p on the TSD current spectra of PET/0.8 PHB polymer liquid crystals at E_p of 1.2×10^7 V/m. With lowering T_p the entire TSDC spectrum is observed to be suppressed and both β' and α-peaks go astray. The β-peak sharpens with increasing T_p. A high temperature maximum around 483 K is observed in the samples which are polarized at high T_p (483 K). Fig. 3 represents the effect of 100 MeV Ni^{58}-ion (Fluence: 3.1×10^{15} ions/m^2) irradiation on TSDC spectra of PET/0.8 PHB polymer liquid crystals electrets ($T_\mathrm{p} = 453$ K & $E_\mathrm{p} = 2.0 \times 10^7$ V/m). The peak intensity (I_m) for β and α-peaks is observed to increase drastically in the irradiated samples whereas for the β'-peak a decrease in the magnitude is observed. The β-peak is found to be shift towards higher temperature region. The shape and initial slope for β-peak is unaltered. Sharpness of the α-peak is increased due to irradiation.

The low temperature peak (β'-peak) appearing around 308 K is mainly ascribed to the dipolar

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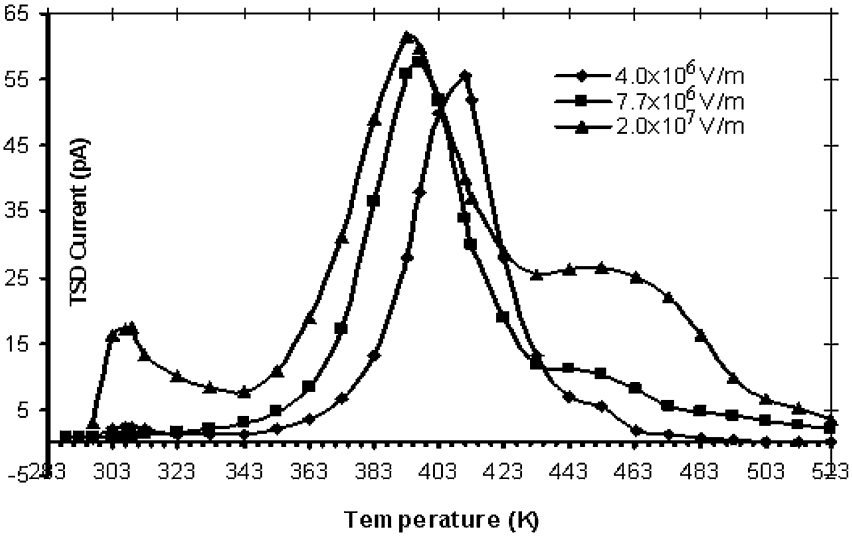


Figure 1 The TSD current spectra of pristine PET/0.8 PHB plc samples polarized at different E_p ($T_p = 453$ K).

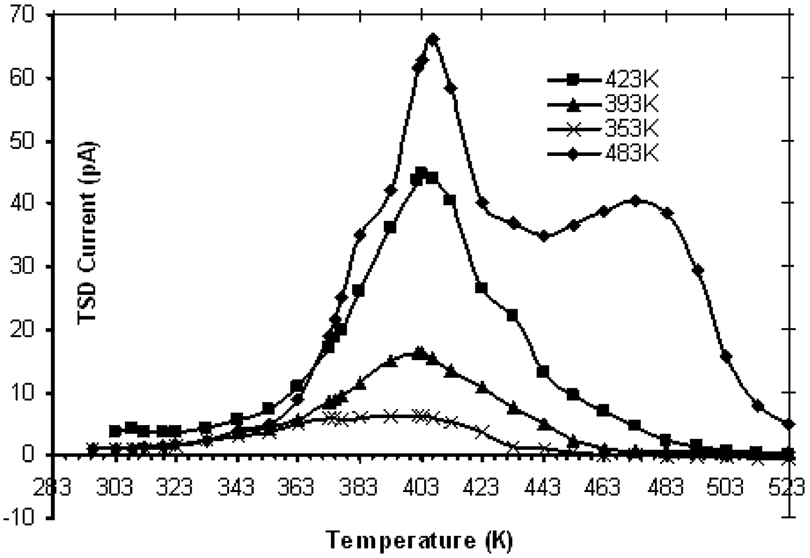


Figure 2 The TSD current spectra of pristine PET/0.8 PHB plc samples polarized at different T_p ($E_p = 1.2 \times 10^7$ V/m).

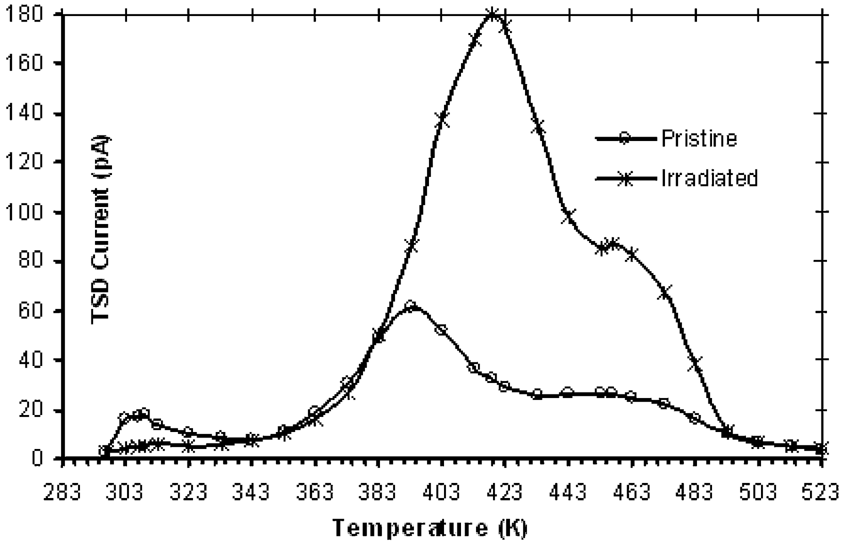
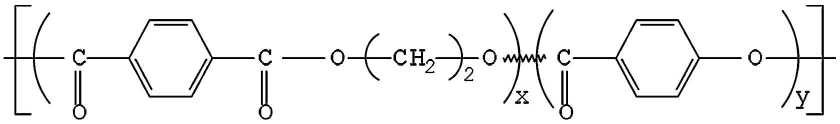


Figure 3 The TSD current spectra of pristine & 100 MeV Ni ion irradiated (Fluence: 3.1×10^{15} ions/m^2) PET/0.8 PHB plc samples polarized at $T_p = 453$ K and $E_p = 2.0 \times 10^7$ V/m.

polarization relaxation as a result of the cooperative molecular motion of the extremely fast reacting polar groups of PET or PHB phase present in the chemical structure of the PET/x. PHB polymer liquid crystals. It is clearly understood by this fact that the current maxima mainly depends on the strength of the polarizing field (Fig. 1). In the earlier studies on PET/0.3PHB plcs authors have observed the same nature for this low temperature peak [9]. The chemical structure of the PET/x. PHB polymer liquid crystal is shown below:



The large number of residual reactive groups (>C=O) present in the main structure provides the polar nature to the PET/0.8PHB polymer liquid crystal. At elevated poling temperatures (T_p) under the influence of a strong field (E_p) this leads to randomization of dipole orientation. The TSDC current maxima (β-peak) in Fig. 1 appearing in the range of 393–408 K has been assigned to electric dipole orientation polarization, which implies the occurrence of uniform bulk polarization i.e., the dipolar origin of β-peak [10, 11]. This peak was confirmed by TSPC, electrical conduction and dielectric constant/loss measurements of PET/x.PHB polymer liquid crystals by authors [4, 9, 12, 13]. The SEM and d. s. c. investigations [6, 14] have shown the biphasic nature of this polymer liquid crystal. The β relaxation appears to be closely associated with PET rich phase. Jackson and Khufuss [3] have shown that PET/0.3 PHB has two T_g values around 358 and 439 K. The hybrid peak which appears around 460 K is due to the dipoles inside the rigid amorphous phase (rigid amorphous phase is a portion of the amorphous phase which remains rigid above T_g in certain semi-crystalline polymers) coexisting with the space charge relaxation. This peak has been attributed to melting of rod-like structures forming smectic-E like phase. A significant decrease in the space charge relaxation peak (α-peak) for a longer duration confirms the hybrid nature of this relaxation. In the case of irradiated samples, the nature of the TSDC spectra is similar to pristine samples. We observed that the three peaks get affected by the irradiation. The increase in the peak magnitude for β and α-peaks shows that ion irradiation results in the dimerization of carbonyl groups and provides the distributive deep shallow energy trap centers.

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