Dielectric relaxation processes studies in oxygen- swift heavy ion irradiated Polyvinylidene fluoride (PVDF) thin film using TSDC measurement technique

DINESH SINGH RANA
Department of Instrumentation, Kurukshetra University, Kurukshetra

Thermally stimulated depolarization current (TSDC) measurement technique have been used to investigate the dielectric relaxation processes in 75 MeV Oxygen swift heavy ion (SHI) irradiated Polyvinylidene fluoride (PVDF). The films of 20 μm thickness were irradiated with 75 MeV Oxygen-ion at different fluence: 1.0×10^{10} (1.0E+10), 1.0×10^{11} (1.0E+11), 5.63×10^{11} (5.63E+11), and 5.68×10^{12} (5.68E+12) ions/cm^2. Thermally stimulated depolarization (TSD) current measurements were carried out in the temperature range 30 –165 ^{0}C at different polarization temperature (T_p) and polarization field (E_p). The heating rate (2 ^{o}C/min) and polarization time (1 h.) have been kept constant in all TSDC measurements. TSDC characteristics of 75 MeV Oxygen-ion irradiated PVDF show a well defined current maxima (termed as β-peak) around the polarization temperature (T_p) in the temperature region 70-118 ^{0}C. The TSDC spectra of high T_p poled samples also show a current maximum around 120 ^{0}C (termed as α-peak). The β-peak is attributed to the dipolar relaxation process. The α-peak has been ascribed to the space charge polarization process **due** to the formation of new deep traps and in some cases notably those corresponding to low values of E_p and T_p, The number of peaks actually appearing in these spectra and their location, height and sharpness are governed by depolarization parameters (T_p, E_p). The activation energy and pre-exponential factors corresponding to β-peak and α-peak were also estimated at different polarization temperature (T_p) and polarization field (E_p).

1. Introduction

PVDF piezoelectric polymer not only possesses excellent piezoelectric and electret (electrically polarized polymeric materials) properties, but also good compliance, high mechanical impedance, low acoustic impedance, relatively low dielectric dissipation fraction, low density, capability of being made into large area films and thin films, and low cost etc. Because of these properties, PVDF is widely used in the development of different type of sensors and actuators. The exceptional biocompatibility of PVDF film is used in the development of skin transducer, implantable medical devices and micro actuators [1]. However, the performance of sensors and actuators based on PVDF may be affected due to the strong interaction of various kinds of radiations such as ultraviolet, γ-rays, X-rays, low energetic ions and swift heavy ion with the sensor material. The interaction of these radiations with medium may change the various dielectric relaxation processes in PVDF. The interaction of energetic ion with polymeric materials not only disturbs its molecular-dynamics thereby affecting significantly the various relaxation processes in polymers but also results in certain morphological changes. The behavior of PVDF under exposure **to** different kinds of radiation [2-7] has been reported before. These studies reveal the enhancement in electrical conductivity and change in crystallinity of PVDF

[2]. The crystallinity plays a crucial role in piezoelectric, mechanical, optical, electrical and even thermal properties of polymers [2]. However, little studies related to the change in dielectric relaxation processes, such as orientation of permanent dipoles (orientation polarization), interfacial polarization and space charge polarization, of PVDF polymer following swift heavy ion (SHI) irradiation have been carried out.

The swift heavy ions beam when traverse through the material medium losses its energy in displacing atoms of the material target by elastic collisions called nuclear stopping mechanism or in exciting the atoms by inelastic collisions called electronic mechanism. The elastic collision is the dominate process for low energy ions whereas the inelastic collision dominate process for high energetic ions (SHI). The energy thus deposited in later process (inelastic collision) causes the various modifications in the material. This provides an opportunity to tailor the properties of the material to achieve the desired structural, electrical, chemical and optical properties.

The thermally stimulated depolarization current spectra are capable to provide significant analysis of dielectric relaxation processes [8-12]. The Thermally stimulated discharge current (TSDC) investigations in PVDF have been done by several groups [13-17]. Most of the researchers observed a low temperature relaxation

processes α_a, near its glass transition temperature (-40 °C), associated to the dipolar relaxation in the amorphous region owing to the micro-brownian motion in the main chain [14-16]. In addition a relaxation process termed as α_c has also been reported by certain groups [16, 17] above glass transition temperature. The α_c has been associated to the crystalline phase of PVDF. Eliassion [16] have reported two current maxima around 70 °C and 95 °C in her TSDC spectra. Mizutani et al [17] have also reported two TSDC peak above the room temperature associated with interfacial polarization formed by trapped carriers in the surface region of non-polar and polar α- phase PVDF.

In this paper, the dielectric relaxation behavior of 75 MeV Oxygen- swift heavy ion irradiated Polyvinylidene fluoride (PVDF) thin film samples of 20 µm thickness using TSDC technique have been presented.

2. Theoretical considerations on TSDC

When a polymer **is** heated at constant heating rate, decay of polarization P may be described as [12]:

$$P(t) = P_e \left[\exp\left(-\int_0^t \frac{dt}{\tau} \right) \right]$$

(1)

where τ is the dipolar relaxation time and P_e is the equilibrium or steady-state polarization which has been shown by Langevin to be

$$P_e = \frac{S N_d p_\mu^2 E_p}{k T_p}$$

(2)

In this expression S is a geometrical factor depending on possible dipolar orientation (for free rotating dipoles, $S = 1/3$), N_d is the concentration of dipoles, k is Boltzmann's constant, p_μ is the electrical dipole moment and E_p is applied electrical field operating on the dipoles. The temperature variation of τ is given by Arrhenius type equation [12] as**:**

$$\tau(T) = \tau_0 \exp\left(\frac{U}{kT} \right)$$

(3)

where τ_0 is the relaxation time at infinite temperature (the inverse of which is known as the characteristic frequency factor and usually related to the vibrational frequency of the material) and U is the activation energy needed to orient or disorient molecular dipoles. The TSD current density is the rate of change of polarization given as**:**

$$J_D(t) = \frac{-dP(t)}{dt} = \frac{P(t)}{\tau}$$

(4)

In order to obtain the current density produced by the progressive decrease in polarization in the course of a TSDC experiment, where time and temperature are simultaneously varied, the differentiation must be performed in terms of the new variable T. This parameter can be introduced by assuming a simple temperature program, most generally a linearly increasing temperature from a temperature T_0 (initial), so that

$$T = T_0 + qt$$

(5)

where $q = \dfrac{dT}{dt}$ is the heating rate.

Using equation (1), (2), (4) and (5), the current density J_D during a TSDC experiment can be written as:

$$J_D(T) = \frac{P_e(T_p)}{\tau_0} \exp\left(-\frac{U}{kT} \right) \exp\left[-\frac{1}{q\tau_0} \int_{T_0}^T \exp\left(-\frac{U}{kT'} \right) dT' \right]$$

(6)

The first exponential which dominates in the low temperature range, is responsible for the initial increase of the current with temperature (increase of mobility of the rotating dipoles), while the second exponential which dominates at high temperature, gradually slows down the current rise and then depresses it very rapidly, especially for high activation energies (progressive exhaustion of the induced polarization). Differentiation of equation (6) leads to an expression for peak temperature (T_m)

$$T_m = \left[\frac{U}{k} q\tau_0 \exp\left(\frac{U}{kT_m} \right) \right]^{1/2}$$

(7)

It is clear from the above equation that the position of a dipolar TSDC peak is a function of the parameters q, τ_0 and U. In the low temperature tail region $(T \ll Tm)$ of the TSDC spectrum since the integral term in the $J_D(T)$ function [equation (6)] is negligible, the first exponential dominates the temperature rise of the initial current so that

$$J_D(T) = A \exp\left(-\frac{U}{kT} \right)$$

Or

(8)

$$\ln J_D(T) = \ln A - \left(\frac{U}{kT} \right)$$

where A is a constant.

The activation energy can be determined from *ln J_D vs 1/T* curves. In first approximation, a straight line is obtained, the slope of which gives *–U/k*. Once the

activation energy is known, the characteristic time constant can be calculated using equation (7), as

$$\tau_0 = \frac{kT_m^2}{qU \exp\left(\dfrac{U}{kT_m}\right)}$$

(9)

3. Experimental details

The PVDF polymer was procured from the firm DuPont (USA) in flat film forms of 20 μm thickness. The samples of size 1 cm^2 were mounted on a ladder for the irradiation in a vacuum chamber. The ladder was loaded in a chamber kept in a high vacuum of the order of 10^{-6} Torr. The films were then irradiated with 75 MeV Oxygen-ion at different fluence: 1.0×10^{10}; 1.0×10^{11}; 5.63×10^{11}; and 5.68×10^{12} ions/cm^2 using the PELLETRON facility at Inter University Accelerator Centre (IUAC), New Delhi. The ion beam fluence was measured by integrating the ion charge on the sample ladder with time. Ion energies were selected in such a manner that they can easily pass through the PVDF films. In present investigation, beam current was kept low (0.2 and 0.5 particle nanoampere (PnA)) to avoid any thermal decomposition. The irradiated samples were metalized on both sides by vacuum evaporation of silver to form the good electrical contacts. The sample holder design for this purpose was suspended in a specially designed temperature controlled furnace (for thermo-electret formation), shielded against stray pickups. The furnace could be capable of heating the sample at some arbitrary uniform rate, from room temperature to 170 ^{0}C. The designed experimental setup is shown schematically in Fig. 1.
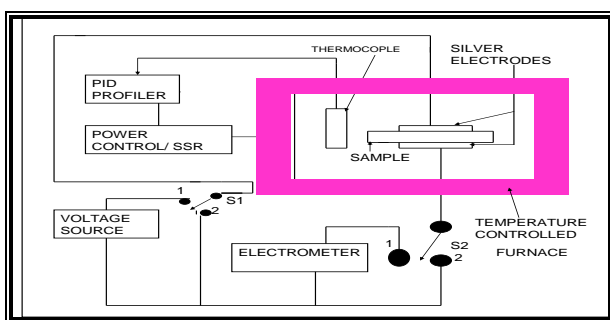

Fig. 1. Schematic diagram of the experimental setup for the TSDC Measurements.

The samples were polarized (Electret formation) by subjecting them to the desire dc bias field (E$_p$) at constant temperature (T$_p$) for 1hour. The sample was then rapidly cooled to the room temperature within fixed time (1/2 h) in the presence of E$_p$. After cooling process the applied electric field E$_p$ was switch off and electrodes were short-circuited for about 10 minutes in order to eliminate the frictional stray surface charges accumulated during

polarization. The Fig. 2 shows the TSDC procedure as a plot of temperature versus time. The TSD current obtained by heating the polarized samples at constant heating rate (2 ^{0}C/minute) from room temperature to 165 ^{0}C were measured with the help of Keithley electrometer (Model 6517A). The corresponding activation energy has been calculated through the above presented method.
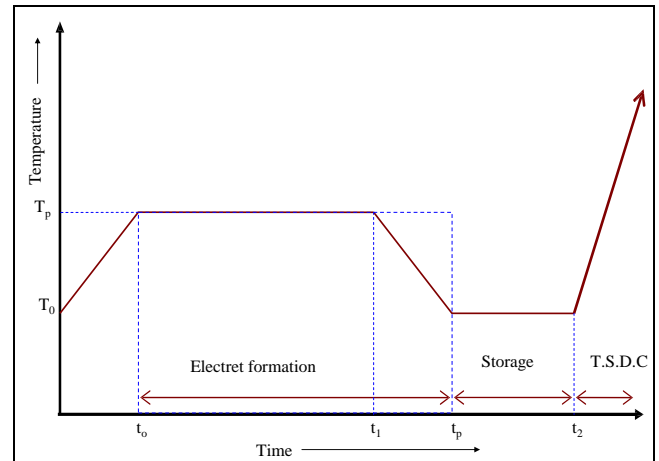

Fig. 2. Experimental schematic representation of TSDC procedure: T$_0$, initial temperature; T$_p$, polarization temperature; t$_0$, start of polarization; t$_1$, start of cooling; t$_p$, switching off the field E$_p$; t$_2$, start of heating the sample and recording the current as the function of temperature.

The projected range of 75MeV Oxygen-ion beams in the PVDF was calculated to be 105. 35 μm using the SRIM-08 code (Ziegler 2008), which **is** larger than the thickness of PVDF samples.

4. Results: oxygen-ion irradiated PVDF samples

The representative TSDC spectra of 75 MeV Oxygen-ion (fluence: 1.0×10^{11} ions/cm^2) irradiated PVDF samples in the temperature range 30-165 ^{0}C have been illustrated in Figs. 3 and 4. The characteristics spectra of Oxygen-ion irradiated samples are almost similar to the TSDC spectra of pristine PVDF samples. The β- peak (β relaxation) appears in temperature region 68 -118 ^{0}C. The TSDC spectra of high T$_p$ poled samples show a current maximum around 120 ^{0}C (α-peak). A δ- peak also shows **its** presence at 164 ^{0}C.

(i) Poling temperature (T$_p$) dependence TSDC

The effect of T$_p$ on TSDC spectra of 75 MeV Oxygen-ion irradiated PVDF samples (fluence; 1×10^{11} ion/cm^2) at E$_p$ = 125 kV/cm field have been illustrated in Fig. 3. The β- peak intensity increases with increasing T$_p$ and shifts toward the higher polarization temperature. The irradiated

samples show an enhancement in I_β as compared to pristine samples. The position of α-peak is unaffected by increase in T_p and shows **an** increase in magnitude with T_p.

(ii) Poling field (Ep) dependence

The effect **of** polarization field E_p on the TSD current spectra of Oxygen-ion (75 MeV at the fluence; 1×10^{11}ions/cm^2) irradiated PVDF samples polarized at T_p=80 ^{0}C has been illustrated in Fig. 4. In each case a well defined current maxima (β-peak) is observed around polarization temperature (T_p=80 ^{0}C). The β-peak intensity increases with E_p. Interestingly in case of irradiated samples at high E_p the β-peak resolves into two current maxima one at polarizing temperature (T_p=80 ^{0}C) and other one at 90 - 95 ^{0}C. The α-peak appears around 120 - 122 ^{0}C. The α-peak intensity increases with E_p while the peak position is almost independent of E_p. The variation of β-peak intensity with E_p, the variation of α-peak intensity with $E_p^{1/2}$ has been shown in Fig. 5 (a) and (b) respectively. The activation energies and pre-exponential factors associated with β-peak and α-peak were calculated and are presented in Table 1.
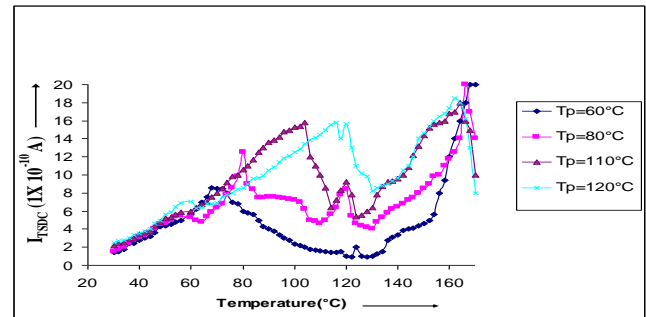

Fig. 3. TSD current spectra of 75 MeV Oxygen-ion irradiated 20μm PVDF thin films at polarization field E_p = 125kV/cm for different polarization temperature (T_p) at fluence; 1×10^{11}ions/cm^2.

Table 1. The activation energy and pre exponential factor for β- and α-peaks at different polarization temperature, T_p and polarization field, E_p for 75 MeV Oxygen-ion irradiated 20 μm PVDF thin film at fluence; 1×10^{11}ions/cm^2.

E_p (KV/cm)	T_p (°C)	β-relaxation				α-relaxation			
		T_m(°C)	U(eV)	τ_o (1×10^{-5})s	τ_m (s)	T_m(°C)	U(eV)	τ_o (1×10^{-5}) s	τ_m (s)
125	60	68	0.3	23	7.3	-	-	-	-
125	80	80	0.43	0.3	5.45	120	0.75	-	3.87
125	110	104	0.23	878	11.62	120	0.35	0.20	8.29
125	120	116	0.21	1235	13.55	120	-	-	-
150	80	80, 90	0.25	253	9.4	120	0.54	0.06	5.38
175	80	80, 94	0.31	28	7.6	120	0.18	7930	16.2
190	80	80, 96	0.31	28	7.56	122	0.37	14.1	7.85

(iii) Fluence dependence

The effect of fluence on the TSDC spectra of 75 MeV Oxygen-ion irradiated PVDF samples polarized at T_p=80 °C and E_p= 150kV/cm has been illustrated in Fig. (6). The fluence dependence of current maxima of β-peak and α-peak are shown in Fig. 7. At low fluence of irradiance (1.0×10^{10} ions/cm^2), β-peak intensity is initial decreasing as compared to the β-peak intensity of pristine sample. The β-peak intensity of ion irradiated samples at higher fluencies increases compared to the β-peak intensity of pristine sample. In case of β-peak, I_β shows an increase with fluence. In case of α-peak, the I_α shows decreases with fluence initially. Thereafter it shows a sudden increase at higher fluences. The activation energy and pre-exponential factors corresponding to β- and α-peaks, obtained by above presented method are given in Table 2. The intensity of δ- peak is almost independent on the fluence.
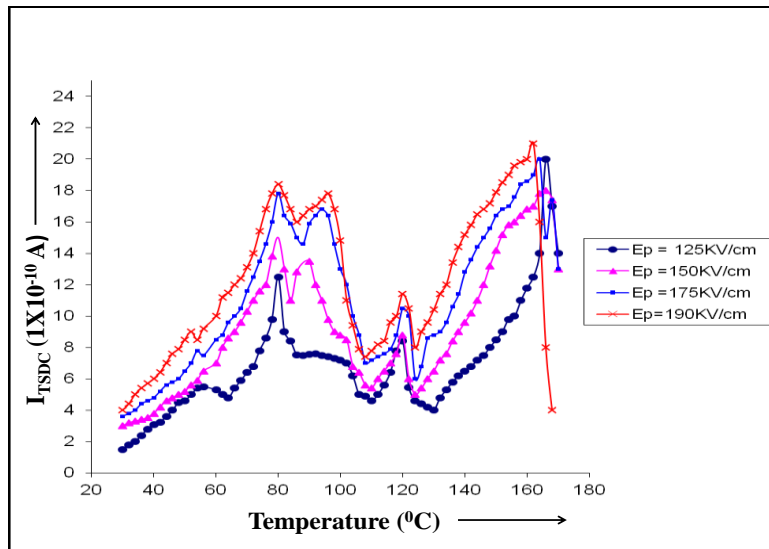
Fig. 4. TSD current spectra of 75 MeV Oxygen-ion irradiated 20μm PVDF at Polarization temperature Tp = 80 °C for different poling fields at fluence of $1×10^{11} ions/cm^2$.
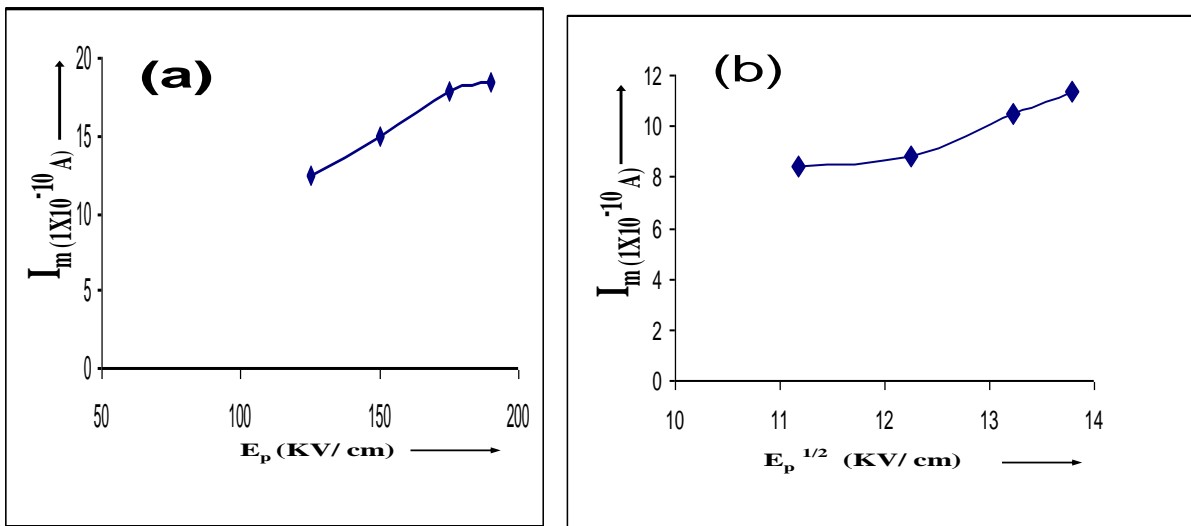

Fig. 5. Variation of peak current (I_m) with (a) poling field E_p (kV/cm) for β-peak (b) $E_p^{1/2}$ for α- peak in 75 MeV Oxygen-ion irradiated PVDF (20 μm) samples at fluence; $1×10^{11} ions/cm^2$ ($T_p = 80$ °C).
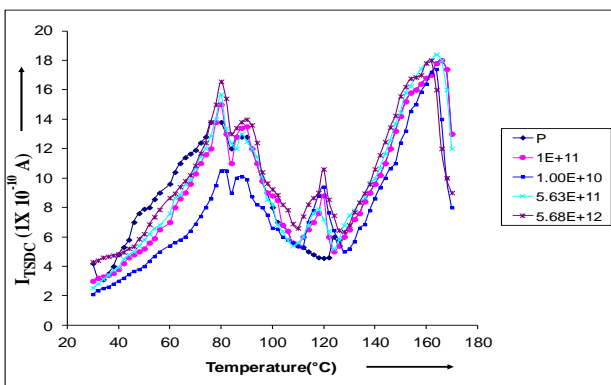

Fig. 6. The effect of fluence on the TSDC spectrum of 75 MeV Oxygen-ion irradiated 20 μm PVDF thin films corresponding to β-peak and α-peak at T_p=80 and E_p=150kV/cm.
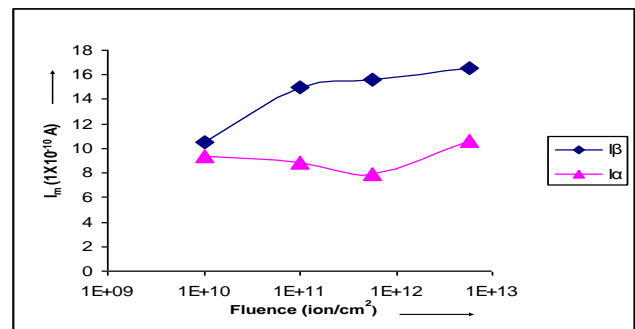

Fig. 7. The effect of fluence on the current maxima of β-peak and α - peak for Oxygen – ion irradiated PVDF samples polarized at T_p=80 and E_p=150kV/cm.

Table 2. The activation energy and pre exponential factor for β- and α- relaxation for different fluencies of 75 MeV Oxygen-ion irradiated 20 μm PVDF thin film at E_p=150 kV/cm and T_p=80 °C.

Fluences Ions/cm^2	β-relaxation				α-relaxation			
	T_m (°C)	U in (eV)	τ_o (1×10^{-5}) s	τ_m (s)	T_m (°C)	U in (eV)	τ_o (1×10^{-5}) s	τ_m (s)
1×10^{10}	78	0.27	107	8.68	120	0.74	0.00007	3.92
1×10^{11}	80	0.25	253	9.4	120	0.5	0.16	5.8
5.625×10^{11}	80	0.27	107	8.68	120	0.61	0.0076	4.71
5.675×10^{12}	80	0.34	8.24	6.89	120	0.3	0.01	9.67

5. Discussion

In the present TSDC spectra, the β-peak can be associated to the dipolar relaxation process. The dipolar origin of β-relaxation arises from CF_2 linkage which is strongly polar in nature. The dipolar origin of β-relaxation can be observed from certain characteristics of β-peak such as (i) peak current varies linearly with the polarization field (Fig. 5) indicating an uniform bulk polarization. However a little deviation from the straight line nature of E_p vs I_m occurs at high value of polarization field E_p. (ii) a shift in the β-peak temperature towards higher temperature with increasing T_p (Fig. 3) and (iii) the activation energy, U value (Table 1) for dipolar relaxation process in PVDF polymer as presented by Neagu etal [18]. In certain cases we observed an additional current peak (~90 °C) in the vicinity of β-peak (Fig. 4) particularly at higher E_p. We term this as β'-peak. We associate the β' relaxation process to the dipolar nature of CH_2. The distribution of activation energies for β-relaxation process (Tables 1 and 2) suggests that the relaxation process originates from the crystalline phase as also observed by Neagu etal [18]. The initial decrease in $I_β$ for the samples irradiated with lower fluence as compared to pristine samples can be associated to the loss in polar groups due to demerization. An enhancement in $I_β$ intensity with fluence followed by saturation (Fig. 7) suggests that the Oxygen-ion irradiation has affected this relaxation process in multiple ways. The increase in $I_β$ indicates the formation of some dipolar groups in PVDF upon irradiation enhancing β relaxation process. FTIR spectra of irradiated PVDF samples have also revealed the presence of carbonyl groups (C=O) [19]. The formations of new sub polar groups due to ion irradiation have been reported in Kapton-H polyimide polymer [11].The saturation in $I_β$ value at high fluencies indicates the balancing between the loss in CF_2 groups and the formation of new sub polar groups.

The high temperature peak (α-peak) in ion irradiated samples is ascribed to the space charge polarization process. The α-peak is pronounced at high temperature and fields and this is in agreement to the fact that this relaxation is favorable for high Ep/Tp values [12]. The space charge character of α-peak is confirmed from the fact that its peak current varies linearly with $(E_p)^{1/2}$ [Fig. 5 (b)]. Further the space charge nature of α- relaxation is confirmed by the high values of its activation energies (Tables 1 and 2). The origin of α- relaxation is governed by several factors. One of the major causes for this relaxation is interfacial polarization due to Maxwell Wagner Sillars (MWS) effect [8, 12]. The other cause for α relaxation is the injection of charge carriers from the electrodes at the metal polymer interface. An enhancement in the interfacial polarization and hence α-relaxation is expected in irradiated samples due to the production of a large number of free radicals arising from the scission process of polar groups [20-21].

The α-relaxation in ion irradiated samples significantly depends on the charge trapping mechanism through shallow/deep trapping centers In PVDF the free radical formation resulting from the demerization of polar CF_2 and CH_2 groups, becomes the source of these energy traps [21]. This is also confirmed by our previous study of FTIR spectra of irradiated PVDF samples [19, 23]. The presence of CF_2 and CH_2 in this polymer is revealed by the absorption bands, appearing around 1181 cm^{-1} and 974 cm^{-1} respectively [19, 23]. The decrease in the intensity of these absorption bands in irradiated samples confirms the demerization of CF_2 and CH_2 groups.

Further the radiation induced cross linking and crystallinity will also contribute towards α-relaxation. An enhancement in the crystallinity in low fluence Oxygen-ion irradiated PVDF samples have been already presented [20]. The variation of α-peak intensity with fluence (initial decrease in $I_α$ followed by sudden increase at higher fluence) indicates the occurrence of secondary radiation induced crystallization (SRIC) phase. Previous XRD data have shown an enhancement in crystallinity in low fluence Oxygen-ion irradiated samples [20] whereas a reduction in crystallinity have been observed in the high fluence irradiated samples. This is in conformity with the fact that SRIC disappears at high fluence irradiation [22] and α-relaxation decreases.

6. Conclusions

SHI irradiation induced changes in PVDF thin films have investigated using TSDC technique. TSD current

spectra are also used to estimate activation energy and pre-exponential factors corresponding to β-relaxation and α-relaxation processes. The α-relaxation processes show higher activation energy compared to β-relaxation processes. The significant conclusions drawn from our present TSD current investigations are**:**

- Dipolar relaxation process has been associated to the dipolar nature of CF_2 group.
- The ion irradiation affects both the β-relaxation as well as α-relaxation process in multiple ways.
- The ion irradiation causes the formation of shallow/deep energy trap centers in form of conjugate bonds.
- The irradiation induced scission process causes formation of free radicals, providing large number of deep energy centre enhancing α-relaxation.
- The nature of the variation of α-peak with fluence shows the occurrence of secondary radiation induced crystallinity (SRIC) phase.

Reference

[1] J. Ryu et al,   **B**iosensors and **B**ioelectronics **21**, 822 (2005).

[2] L. Calcagno, P. Musumeci, R. Percolla, G. Foti, Nuclear Instr. and method In Phys. Res., **B91**, 461(1994).

[3] K. D. Pae, S.K. Bhateja, etal; J. of Polymer Sci part B; Polymer Phys. **25**, 717 (1987).

[4] Z. X. Zhen, Radiat. Phys. Chem, **35**, 194 (1990).

[5] M. A. Said, C. M. Balik, J et al, Polym. Sci, **B26**, 1457 (1988).

[6] Y. Rosenberg, A. Sregmann, M. Narkis, S. Shkolnik, J. Appl. Polym Sci. **45**, 783 (1992).

[7] Youn Mook Lim, Youn Moo Lee etal, J. Ind. Eng. Chem., **12**(4), 589 (2006).

[8] J. Van Turnhout, "in: Electrets, G.M. Sessler (Ed.)," Springer-Verlag, Berlin, 81, (1980).

[9] R. P. Bharadwaj, J. K. Quamara, K. K. Nagpaul, B. L. Sharma, Phys. Stat. Sol. (a), **80**, 559 (1983).

[10] M. Garg, J. K. Quamara, Nucl. Inst. and Meth. in Phys. Res. B, **179**, 83 (2001).

[11] J. K. Quamara, M. Garg, T Prabhavathi, thin solid film, **449**(1-2), 242 (2004).

[12] J. Vanderschueren, J. Gasiot, in: Thermally Stimulated Relaxation in Solids, edited by P. Braunlich, Springer-Verlag, Berlin, p. 135, 1979.

[13] M. Neidhofer, F. Beaume, L. Ilos, A. Bernes, C. Lacabanne, Polymer, **45**, 1679 (2004).

[14] T. Mizutani, J .Phys. D. Appl. Phys. **14**, 1139 (1981).

[15] K. Doughty, J. Phys. D. Appl. Phys. **19**, L29 (1986).

[16] S. Eliasson, J. Phys. D. Appl. Phys. **18**, 275 (1985).

[17] T. Mizutani, T. Nagata, M. Ieda, J. Phys. D. Appl. Phys., **17**, 1883 (1984).

[18] E. R Neagu, J. S Hornsby, D. K. Das Gupta, J. Phys. D. Appl. Phys., **35**, 1229 (2002).

[19] D. S. Rana, D. K. Chaturvedi, J. K. Quamara, Proc. IMechE, Part J: J. Engineering Tribology, **224**(J7), 667 (2010).

[20] D. S. Rana, D. K. Chaturvedi, J. K. Quamara, Journal of Materials engineering and Performance **20**(2), 276 (2011).

[21] Dinesh Singh Rana, J. Optoelectron. Adv. Mater.-Rapid Commun. **6**(5-6), 642 (2012).

[22] D. Fink, V. Hanatowich, P. Y. Apel, in: Fundamentals of Ion Irradiated Polymers, D. Fink (Ed.), Springer-Verlag, Germany, p. 313, 2004.

[23] D. S. Rana, D. K. Chaturvedi, J. K. Quamara, J. Optoelectron. Adv. Mater. **11**(5), 705 (2009).

_____
[*]Corresponding author: dineshsrana24@rediffmail.com, rana.kuk@gmail.com