

Kinetics involved in TSDC spectra of pristine and irradiated PVDF thin film

Dr. Devendra Prasad, Assistant Professor, U P Textile Technology Institute, 11/208, Souterganj, Kanpur (U.P.) INDIA. dev07.2007@rediffmail.com

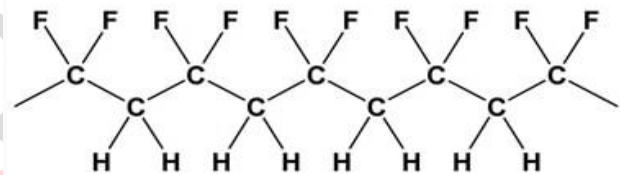
Abstract Dielectric relaxation studies have been made by thermally stimulated depolarization current (TSDC) technique. In the present study an attempt has been made to review the experimentally reported TSDC data of pristine and Ag-ion irradiated Polyvinylidene fluoride (PVDF) thin film in accordance with a different method of analysis as proposed by Prakash. In this method order of kinetics parameter has been reasonably incorporated in mechanism involved in TSDC process. Considered parameter is evaluated from the experimentally reported data. It has been found that the included parameter depends on the experimental conditions whereas activation energy and fundamental relaxation time are the characteristic parameters of the specimen under consideration.

Keywords — Thermally stimulated depolarization, Dielectric relaxation, Order of kinetics, Activation energy and Fundamental relaxation time, Irradiation.

I. INTRODUCTION

Materials which have impurity vacancy dipoles (IV) get polarized in electric field. With the electric field still there, the material gets cool down very speedily to a considerably low temperature the material gets in frozen-in condition. Relaxation time of dipoles is very large or practically infinite when they are in frozen-in condition and remain polarized even after the electric field gets switched off. Frozen-in dipoles are depolarizing at the stage when specimen gets heated at linear constant heating rate. As a result thermally stimulated depolarization current (TSDC) or ionic thermocurrent (ITC) makes its appearance. If TSDC is plotted as a function of temperature is known as TSDC or ITC spectrum. With the help of TSDC or ITC technique one can ascertain the characteristic dielectric relaxation parameters viz activation energy (E_a) and fundamental relaxation time (τ_0) of the specimen. There are number of methods suggested by different peoples who are involved in the same work. Most of the methods which are in use focus on evaluation of dielectric relaxation parameters barring a few methods which are based on order of kinetics parameter [1,2]. There are some anomalies in the methods used like a few of them are fit only for monomolecular or first order kinetics. Some of them have suggested different methods for different order of kinetics without minding the point that whether the evaluated values of dielectric relaxation parameters are holding good with the established equation of peak temperature. Starting from the basic idea that TSDC curve corresponding to monomolecular kinetics is very much similar to a thermoluminescence (TL) glow curve involving monomolecular kinetics[3], and TL glow curves involving second and higher order kinetics [4-8] have already been reported in the literature. It was hence thought proper by Prakash [9] to assess the involvement of

second and higher order kinetics in TSDC spectra. TSDC technique has emerged as an effective and very useful tool [3] for studying the reorientational behavior of dipoles because of its sensitivity, accuracy and convenience.



II. METHOD OF ANALYSIS

A. Review Stage

TSDC data experimentally reported [10] are reanalyzed following the method suggested by Prakash [9]. As per this method of analysis thermally stimulated depolarization current (I) is given by

$$I = \frac{Q_0}{\ell \tau_0} \exp \left[-\frac{E_a}{kT} - \frac{1}{b \ell \tau_0} \int_{T_0}^T \exp \left(-\frac{E_a}{kT'} \right) dT' \right] \quad \dots(1)$$

where Q_0 is the total charge released during TSDC run, ℓ is order of kinetics involved, k is the Boltzmann's constant, T is the absolute temperature, b is linear heating rate, T_0 is the temperature wherefrom TSDC spectrum starts to appear and T' is any temperature between T_0 and T . Equations for TSDC spectra involving first, second or higher order can be obtained from above equation after substituting the corresponding value of ℓ into it. Expression for peak temperature T_m is given by the relation

$$T_m^2 = \frac{\ell b E_a \tau_m}{k} \quad \dots(2)$$

where τ_m is the relaxation temperature at peak temperature T_m and is given by the Arrhenius relation[11] as

$$\tau_m = \tau_0 \exp\left(\frac{E_a}{k T_m}\right)$$

Knowing the values of dielectric relaxation parameters E_a and τ_0 , one can evaluate order of kinetics ℓ parameter using eq.(2).

III. RESULT AND DISCUSSION

TSDC data as reported for pristine and 100 MeV Ag- swift heavy ion irradiated Polyvinylidene fluoride (PVDF) thin film by Rana [10] has been reanalyzed following the method suggested by Prakash [9]. Prior to suggested method of analysis [9], TSDC spectra were widely used to be analyzed following the procedure of Bucci et. al. [3]. However in the latter method of analysis, evaluated and experimental parameters do not satisfy the then established TSDC peak equation [3]

$$T_m^2 = \frac{b E_a \tau_m}{k} \quad \dots (3)$$

Also, the difference in left hand side and right hand side of eq.(3) was found to be different in different runs recorded on the same specimen. It is particularly because of the fact that different order of kinetics ℓ is involved in different experimental runs as established by Prakash [9] through eq.(2). In fact eq.(2) is a modified form of eq.(3). Rate of rapid cooling for getting frozen-in polarized dipoles happens to be different in different experimental runs although being recorded on the same specimen and by the same worker. This experimental process results in the involvement of different order of kinetics. Consequently, eq.(1) has been developed [9] to meet out this discrepancy. Thus, TSDC spectra is properly and completely expressed with the help of the parameters T_m , $b E_a$, τ_0 and ℓ evaluated following the methodology suggested by Prakash [9]. It would be justified to mention that all the equations considered by Prakash and Bucci et.al. are same except the inclusion of order of kinetics. Thus Prakash method essentially happens to be a modified and versatile version of Bucci et. al. method.

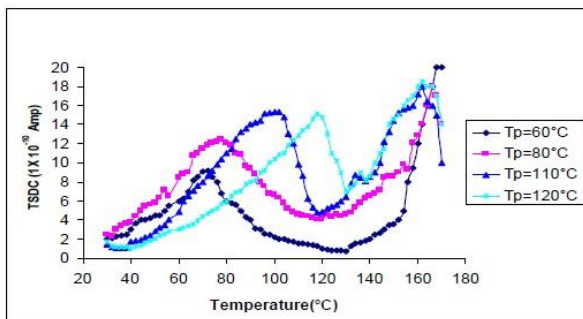


Fig.1 TSDC spectra of Pristine PVDF at constant polarization field $E_p = 125$ kV/cm for different polarization temperature (T_p) [10].

Rana [10] has used PVDF polymer with cross sectional area one sq. cm and of thickness 20 μ m. The specimen mounted on a ladder which was loaded in a chamber kept in a high

vacuum of the order of 10^{-6} Torr. They have used irradiation unit is 100 MeV Ag- ion at fluence rate 1.8×10^{11} ions/cm² with the help of PELLETRON facility. The heating rate (2 °C/min) and polarization time (1 hrs.) have been kept constant in all TSDC measurement. The samples were polarized (Electret formation) by subjecting them to the desired dc bias polarizing field (E_p) at constant polarizing temperature (T_p) for 1hour. The sample was then rapidly cooled to the room temperature within fixed time (1/2h) in the presence of E_p . After cooling process the applied electric field E_p was terminated/ switch off and electrodes were short-circuited for about 10 minutes in order to eliminate the frictional stray surface charges accumulated during polarization. The TSD current obtained by heating the polarized samples at constant heating rate (2⁰ C/minute) from room temperature to 443⁰K were measured with the help of Keithley electrometer (Model 6517A) by Rana [10] in his experiment. The corresponding activation energy and fundamental relaxation time has been calculated through the initial rise method.

Table.1 Experimentally reported [10] T_p , T_m , E_a , τ_0 and evaluated values of order of kinetics (ℓ) for TSDC spectra of Pristine PVDF sample at constant polarizing field (E_p).

T_p (°K)	T_m (°K)	E_a (eV)	τ_0 (s)	ℓ
333	345	0.33	7.75×10^{-5}	$1.82 \times 10^{+2}$
353	353	0.36	3.9×10^{-5}	$1.66 \times 10^{+2}$
383	375	0.51	0.062×10^{-5}	$1.61 \times 10^{+2}$
393	391	0.33	39×10^{-5}	$1.71 \times 10^{+2}$

The experimentally reported [10] TSDC spectra of pristine PVDF sample is shown in Fig.1. This spectrum has been recorded by Rana at fixed polarizing field (E_p) for different polarizing temperature (T_p). TSDC characteristics show a well defined peak (termed as β -peak) in the temperature region 343⁰K-393⁰K. Another peak is observed around 435⁰K termed as δ -peak. In certain cases a kink is also observed around 408⁰K. The β -peak shifts toward higher temperature with increasing T_p . An increase in β - peak intensity is also observed with T_p . The corresponding activation energies (E_a) and pre exponential factors or fundamental relaxation times (τ_0) associated with β -peak were calculated using initial rise method by Rana [10] are as given in table.1. As per the eq.(2) order of kinetics is evaluated and illustrated in table.1. At fixed polarization temperature ($T_p = 353^\circ$ K) the TSDC spectra of Pristine PVDF sample for different polarizing fields are shown in Fig.2. All TSDC characteristics spectra show the occurrence of β -peak around temperature 353⁰K. Although the peak location is unaffected by E_p , the peak magnitude increases with increase E_p .

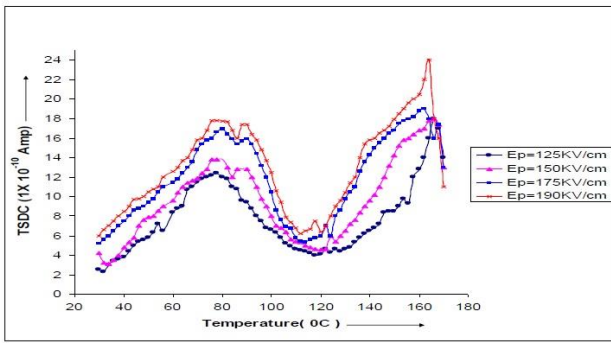


Fig.2 TSDS spectra of Pristine PVDF at constant polarization temperature $T_p = 353^\circ\text{K}$ for different polarization fields [10].

Here the δ - peaks are also observed around 437°K . The experimentally reported [10] and evaluated (ℓ) parameters are presented in table.2.

Table.2 Experimentally reported [10] E_p , T_m , E_a , τ_o and evaluated values of order of kinetics (ℓ) for TSDC spectra of Pristine PVDF sample at constant polarizing temperature (T_p).

E_p (kV/cm)	T_m ($^\circ\text{K}$)	E_a (eV)	τ_o (s)	ℓ
125	353	0.36	3.9×10^{-5}	1.66×10^2
150	353	0.55	0.006×10^{-5}	1.37×10^2
150	361	0.55	0.006×10^{-5}	2.14×10^2
175	353	0.29	0.5×10^{-5}	1.61×10^4
175	363	0.29	0.5×10^{-5}	2.21×10^4
190	353	0.21	1121×10^{-5}	1.34×10^2
190	361	0.21	1121×10^{-5}	1.67×10^2

TSDC spectra of Ag-ion irradiated PVDF sample are illustrated in Figs.3 & 4 as reported by Rana [10]. These characteristics spectra almost have almost the same pattern as in case of pristine PVDF samples.

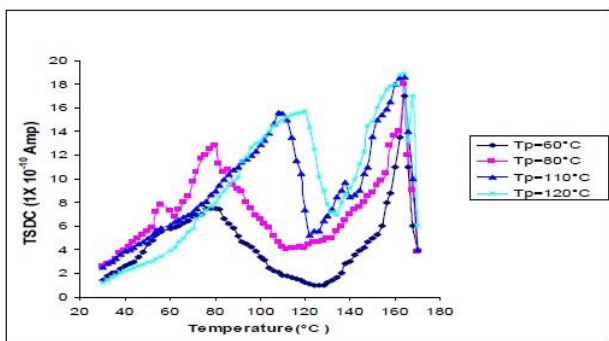


Fig.3 TSDC spectra of Ag-ion irradiated PVDF thin film at constant polarizing field $E_p = 125\text{KV/cm}$ for different polarization temperature (T_p) [10].

The influence of polarizing temperature on TSDC spectrum of 100 MeV Ag-ion irradiated PVDF samples at constant polarizing field is illustrated in Fig. 3. The β -peak (β -relaxation) appears in temperature region $348^\circ\text{K} - 391^\circ\text{K}$. The magnitude of corresponding current also increases

with increasing T_p . The δ - peak is also observed around 437°K .

Table.3 Experimentally reported [10] and evaluated parameters for β -relaxation of TSDC spectra of Ag-ion irradiated PVDF sample at constant polarizing field ($E_p=125\text{kV/cm}$).

T_p ($^\circ\text{K}$)	T_m ($^\circ\text{K}$)	E_a (eV)	τ_o (s)	ℓ
333	351	0.41	0.6×10^{-5}	$1.68 \times 10^{+02}$
353	353	0.29	50×10^{-5}	$1.61 \times 10^{+02}$
383	381	0.21	0.002×10^{-5}	$1.49 \times 10^{+08}$
393	393	0.26	410×10^{-5}	$1.73 \times 10^{+02}$

The corresponding activation energies (E_a) and pre exponential factors or fundamental relaxation times (τ_o) associated with β -relaxation were calculated using initial rise method by Rana [10] are as given in table.3. As per the eq.(2) order of kinetics is evaluated and illustrated in table.3. The influence of polarizing field (E_p) on the TSDC spectra of Ag-ion irradiated PVDF samples at fixed polarizing temperature ($T_p = 353^\circ\text{K}$) has been illustrated in Fig.4 and corresponding reported (E_p , T_p , E_a , τ_o) and evaluated (ℓ) parameters has been given in table.4. Here smoothness of β -peak is less compared to pristine PVDF thin film. In some cases notably those corresponding to low values of E_p and T_p , an additional shoulder designated as γ has also been observed around 328°K .

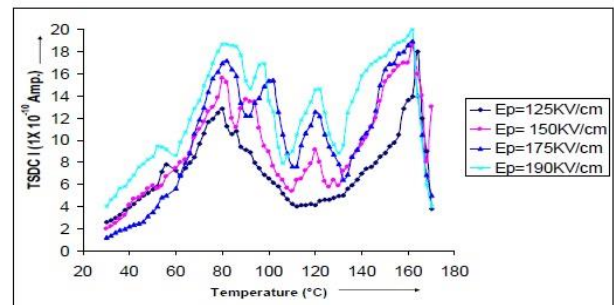


Fig.4 TSDC spectra of Ag-ion irradiated PVDF thin film at constant polarizing temperature $T_p = 353^\circ\text{K}$ for different polarization fields, E_p [10].

In case of TSDC spectra of irradiated PVDF thin film (at constant polarization temperature $T_p = 353^\circ\text{K}$ and for different polarization fields E_p) an additional peak termed as α -peak (α relaxation) around 393°K has also been observed (Fig.4).

Table.4 Experimentally reported [10] and evaluated parameters for TSDC spectra β -relaxation in Ag-ion irradiated PVDF sample at constant polarizing temperature ($T_p=353^\circ\text{K}$).

E_p (kV/cm)	T_m ($^\circ\text{K}$)	E_a (eV)	τ_o (s)	ℓ
125	353	0.29	50×10^{-5}	$1.6 \times 10^{+2}$
150	353	0.28	84×10^{-5}	$1.38 \times 10^{+2}$
150	363	0.28	84×10^{-5}	$1.88 \times 10^{+2}$

175	353	0.44	0.27×10^{-5}	$1.42 \times 10^{+2}$
175	373	0.44	0.27×10^{-5}	$3.43 \times 10^{+2}$
190	353	0.28	84×10^{-5}	$1.38 \times 10^{+2}$
190	369	0.28	84×10^{-5}	$2.24 \times 10^{+2}$

The peak intensity for all the peaks increases with E_p . The activation energies and fundamental relaxation time associated with α – peak were calculated using initial rise method by Rana[10]. Reported values of these parameters along with evaluated order of kinetics parameter are illustrated in table.5.

Table.5 Experimentally reported [10] and evaluated parameters for TSDC spectra α -relaxation in Ag-ion irradiated PVDF sample.

E_p (kV/cm)	T_p (°K)	T_m (°K)	E_a (eV)	τ_o (s)	ℓ
125	383	411	0.61	0.01×10^{-5}	$2.37 \times 10^{+2}$
150	353	393	0.48	0.29×10^{-5}	$2.0 \times 10^{+2}$
175	353	393	0.57	0.01×10^{-5}	$3.43 \times 10^{+2}$
190	353	395	0.7	0.0004×10^{-5}	$1.69 \times 10^{+3}$

IV. CONCLUSION

In the present study order of kinetics parameter has been evaluated from reported values of experimental and characteristic parameters of TSDC spectra of pristine and Ag-ion irradiated PVDF thin film. This parameter depends on experimental conditions like rate of rapid cooling during polarization. It has been observed that order of kinetics parameter decreases due to irradiation of the considered sample. Considered Prakash method of analysis is in fact Bucci et. al. method in which concept of order of kinetics has been reasonably incorporated.

ACKNOWLEDGMENT

The author is thankful to the Director of his institute for providing the facilities and also thankful to Prof. Jai Prakash, Ex Pro Vice Chancellor, Pt. D D U Gorakhpur University, Gorakhpur for inculcating research temper.

REFERENCES

- [1] R Chen and Y Kirsch, ‘Analysis of Thermally Stimulated Processes’ Pergamon Press, New York, **1981**.
- [2] R Chen and S W S Mckeever, ‘Theory of Thermoluminescence and Related Phenomena’, World Scientific, **1997**.
- [3] C. Bucci, R. Fieschi, and G. Guidi, “Ionic Thermocurrents in Dielectrics”, Phys. Rev., 148,816, **1966**.
- [4] R. Chen, and S.A.A. Winer , “Effects of Various Heating Rates on Glow Curves”, J. Appl. Phys., 41,5277, **1970**.

[5] R. Chen, D J Huntley, G W Berger, “Analysis of thermoluminescence data dominated by second-order of kinetics”, Phys Stat Soli a (Germany) , 79, 251, **1983**.

[6] J. Prakash and D. Prasad, “Mechanisms responsible for the appearance of a thermoluminescence glow curve”, Phys Stat Soli a, 142, 281, **1994**.

[7] J. Prakash, “Thermoluminescence glow curve with second order kinetics”, Solid State Commun, 85, 647, **1993**.

[8] J. Prakash, P K Singh and D K Dwivedi, “Thermally stimulated processes: I- Mechanisms involved in the appearance of a thermoluminescence glow curve”, Indian J. Pure Appl. Phys., 44, 532, **2006**.

[9] J. Prakash, “A model for the occurrence and analysis of ionic thermocurrent spectrum involving different orders of kinetics”, Pramana J of Phys, 80, 2, **2013**.

[10] D. S. Rana, “TSDC measurements and analysis of pristine and 100 MeV Ag- swift heavy ion irradiated Polyvinylidene fluoride (PVDF) thin film”, Optoelectronics and Advanced Materials – Rapid Communications, Vol. 6, No. 5-6, p. 642- 647, **2012**.

[11] S.A. Arrhenius “U ber die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Sa uren”, Z Phys. Chem. 226, **1889**.