



TSDC of Irradiated and Non-Irradiated Cellulose Acetate

T. Fahmy^{1,2*}, E. O. Abdelmutlib³, M. I. Abdelhamid², W. B. Elsharkawy¹, Z. M. Elqahtani⁴, M. T. Ahmed^{1,2}



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¹Dept. of Physics, College of Science and Humanities in Al-Kharj, Prince Sattam bin Abdulaziz University, Al-Kharj 11942, Kingdom of Saudi Arabia.

²Polymer Research Group, Physics Dept., Faculty of Science, Mansoura University, 35516 Mansoura, Egypt.

³Al-Mnsoura Specialist Hospital, 35511 Mansoura, Ministry of Health, Egypt.

⁴Dept. of Physics, College of Science, Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

Abstract

Films of cellulose acetate (CA) have been prepared by casting method using tetrahydrofuran (THF). CA films are γ -irradiated with varying radiation doses of 10, 20, 30, 40, 50 and 60 kGy using cobalt-60 (⁶⁰Co) source. Global thermally stimulated depolarization current (TSDC) of non-irradiated and irradiated CA samples has been investigated under the effect of various poling electric field (E_p) in a temperature range from 300 K to 440 K. It is observed that, global TSDC spectra of non-irradiated and irradiated CA samples are characterized by two relaxation peaks. One in the low temperature range ~ 321 K and the other in the high temperature range ~ 376 - 383 K are observed for non-irradiated sample. On the other hand, these temperatures are shifted towards lower temperature for irradiated samples to be located at 317 K and ~ 371 K. These relaxations are assigned as β and ρ -relaxation and attributed to molecular motion of the polar acetate groups, $C_2H_3O_2$ and polarization of the space charges, respectively. TS-technique has been carried out to decompose global TSDC spectra of all samples into its elementary peaks and the molecular parameters such as, activation energy and pre-exponential factor are calculated for each TS peak. Relaxation map (RM) of all samples has been analyzed using Eyring transformation and thermodynamic parameters such as, enthalpy activation (ΔH), entropy activation (ΔS) and Gibbs free energy (ΔG) are estimated. The compensation phenomenon was verified by the linear relationship between both enthalpy and entropy.

Keywords: Cellulose Acetate, Irradiation, TSDC, Relaxation Map, Enthalpy, Entropy, Compensation.

1. Introduction

Cellulose is a symmetric linear polymer consists of D-glucopyranose. Cellulose is the most abundant natural polysaccharide and due to its ability to regenerate and biodegrade it has been considered the greenest material available. Due to the hydroxyl groups on the surface of cellulose, the formation of a hydrogen bond is preferred, and the cellulose chains are grouped into highly ordered structures. Cellulose as a polymer matrix is the subject of increasing interest due to its wide potential in various applications.

Cellulose acetate as a derivative of cellulose has gained special interest during the past decades due to its application in food, textiles, pharmaceutical industries, paper, packaging, in the processes of separation such as dialysis, gas separation, hemodialysis and thin films for electronic applications [1-5]. In addition, cellulose acetate is used in the medical applications field, such as membrane for desalination, whereas, other derivatives of cellulose such as cellulose acetatebutyrate (CAB) are used in capsule form to release drugs [6].

*Corresponding author e-mail: tfahmy_5@yahoo.com; <https://orcid.org/0000-0002-5078-2245>

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Irradiation in polymers leads to the destruction of the initial structure by way of formation of free radicals, crosslinking, irreversible bond cleavages, etc., which leads to the formation of saturated and unsaturated groups and fragmentation of molecules. These processes create defects within the polymer that are clearly responsible for altering the chemical and physical properties of the material [7]. γ -irradiation process is used in the biological sterilization of many materials used in the manufacture of biomedical products.

The decomposition of polysaccharides such as cellulose, pectin, and starch by cleavage of glycosidic bonds is carried out by ionizing radiation. It is known that after irradiation, molecules of cellulose are altered by breaking the glycoside bonds and introducing the carbonyl and carboxyl groups [8]. The advantages of polymer decomposition by irradiation include the ability to enhance quantitative and repeated changes, without chemical reagents and special devices for controlling the environment, additives and temperature.

Thermally stimulated depolarization current (TSDC) is a dielectric technique in the temperature domain to characterize the dielectric response of the polymeric materials under study. TSDC conforms to the measurement of dielectric loss at low constant frequencies in the range 10^{-2} to 10^{-4} Hz versus temperature [9-11]. The distinguishing feature of the TSDC method is the low equivalent frequency, which is often used to extend dielectric measurements to the low frequency. The resulting global TSDC spectrum contains many peaks whose location, shape, and size provide valuable information on the timescale and dielectric strength of the different relaxation mechanisms that distinguish one material from another [12-19]. The result of the TSDC experiment is a global spectrum containing all the dielectric active relaxation processes excited by the electric field (E_p) between initial temperature (T_0) and poling temperature (T_p).

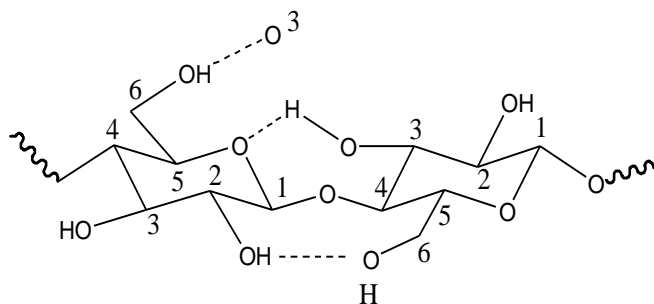
One of the advantages of TSDC over other techniques is that the thermal sampling (TSDC-TS) is a powerful technique used for resolving the global TSDC spectrum to obtain

its elementary peaks that have a single relaxation time. TS technique allows the polarization of narrow segments of the complex thermal current and, thus, enables the analysis of the global spectrum into their "individual" components. TS technique advantage increases effectively when used in the fractional analytical mode, i.e., analysis of relaxation map, (RM) [20-24]. In this technique, only a small portion of the entire spectrum will be polarized to obtain a single relaxation. By changing the values of the polarization and depolarization temperature ($T_p - T_d = 5K$) and repeating the process over the entire scale, some of elementary modes are obtained one by one. The set of TS curves obtained can be independently analyzed and provide further insights into the general features of the complex spectrum that was recorded during global TSDC experiments.

The main purpose of this manuscript is to highlight the effect of γ -irradiation with different doses on the molecular dynamics of irradiated cellulose acetate using TSDC-TS technique. RMA of non-irradiated and irradiated CA will be constructed to calculate the thermodynamic parameters such activation of enthalpy, entropy and Gibbs free energy.

2. Experimental Work

Films of cellulose acetate with average molecular weight $\sim 30,000$ and (39.8 wt. % acetyl content) (Aldrich polymers) were prepared by casting method. 0.5 gm of cellulose acetate was dissolved in 50 ml of Tetrahydrofuran (THF) solvent at room temperature (~ 300 K) with stirring for approximately 30 minutes. The solution was stirred for another 30 minutes at 323 K, then the polymer solution was casted onto well cleaned glass substrate in the laboratory oven for one day, to be sure that the solvent was completely evaporated. The films thickness ranged from 15-50 μm as measured using a digital micrometer (Mitutoyo No: 293-521-30, Japan). The produced films were then kept in an isolated environment to avoid the effect of temperature and humidity on the samples. Scheme 1 displays the chemical structure of cellulose acetate.



Scheme 1. The chemical structure of cellulose acetate.

CA films were exposed to γ -ray irradiation using a cobalt-60 (^{60}Co) source with a dose rate of 5×10^4 rad/min. Films of CA were placed in the direction of beam at 5 cm from the source and irradiated with varying radiation doses of 10, 20, 30, 40, 50 and 60 kGy.

Measurements of TSDC are carried out by applying a DC electric field, E_p , on the samples for certain polarizing time, t_p at a specific polarization temperature, T_p . As the electric field continues to be applied, the samples are then cooled to a temperature, low enough in order to prevent the depolarization process by the thermal excitation. Then, the electric field is turned off as well as the electrodes are short-circuited by means of the electrometer to remove the stray charges. Global TSDC spectrum is then measured by reheating the samples again with an almost constant heating rate, $\beta=3\text{K}/\text{min}$. This heating rate ensures good spectrum resolution and gives measurable current values high enough to make the background current negligible.

Keithley Electrometer, Model 610C is used to record the current during the heating process.

To decompose global TSDC spectrum into its elementary peaks, thermal sampling technique (TS) will be applied, because only a small part of relaxation will be detected. Measurements of TS are carried out as shown in Fig. 1. The sample is polarized by applying DC polarizing electric field, E_p , at polarizing temperature, T_p for certain time, t_p . The sample temperature was then quickly dropped to a depolarization temperature, T_d lower than T_p by 5K, polarization window, $T_p - T_d = 5\text{K}$. The electric field at this temperature will be turned off and the sample will be short-circuited for 15 min, and was quickly quenched back in ice-water to a temperature lower than T_p by 30 K. Hence, TS current was recorded by warming the sample again with almost constant heating rate of $\beta=3\text{K}/\text{min}$. Therefore, in every TS run, small portion of dipoles will be polarized characterizing by single values of both E_a and τ_0 , assuming that a single relaxation process will be obtained in each polarization window, $T_p - T_d = 5\text{K}$.

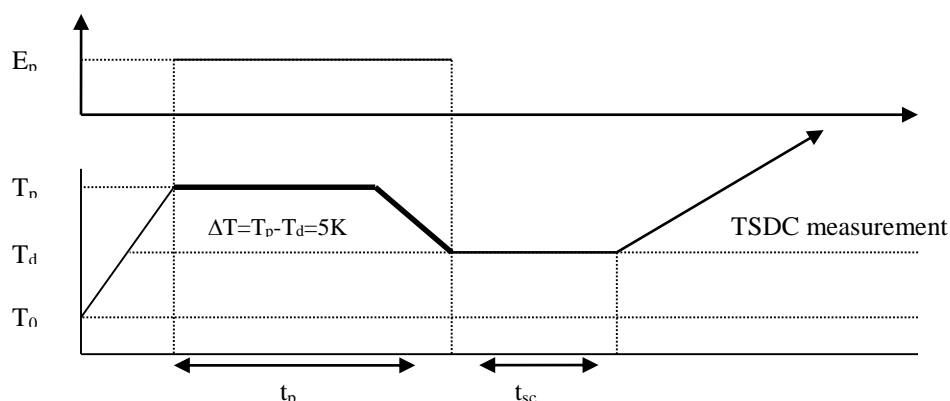


Fig. 1.: Schematic diagram of TS technique.

3. Results and Discussion

Effect of poling electric field (E_p) on Global TSDC of CA

Fig. 2a displays TSDC global spectra of non-irradiated CA samples polarized at $T_p=343$ K. Two different relaxation peaks, one in the low temperature range ~ 321 K and the other in the high temperature range ~ 376 - 383 K are observed. With increasing field strength it was observed that the first relaxation peak was obtained at the same temperature while the second relaxation peak was shifted to a higher temperature. The total released charge is found to increase with increasing field strength, and thus the current magnitude of both peaks increases when the polarized electric field (E_p) increases. The activation energy (E_a) values of each peak have been

estimated using initial rice method by plotting $\log I$ against $1/T$, as shown in Fig. 2(c&d).

Generally TSDC spectrum may results from dipole reorientation (β or α -relaxation), the ionic conductors and impurities migration in the polymeric material (space charge, ρ -relaxation). We can differentiate between different relaxation processes by examining the variation of current intensity (I_m) against the electric field strength (E_p). Thus, it was observed that the current intensity (I_m) for the first relaxation peak increased with the increase in the electric field, while for the second peak, the current intensity increased until it saturated at the high electric fields (E_p) as shown in Fig. 1b. In addition, it was observed that the position of the first peak was a constant that did not shift with the change in the electric field strength, indicating that the main contribution to the first relaxation peak was due to the molecular motion of the polar acetate groups, $C_2H_3O_2$ [25].

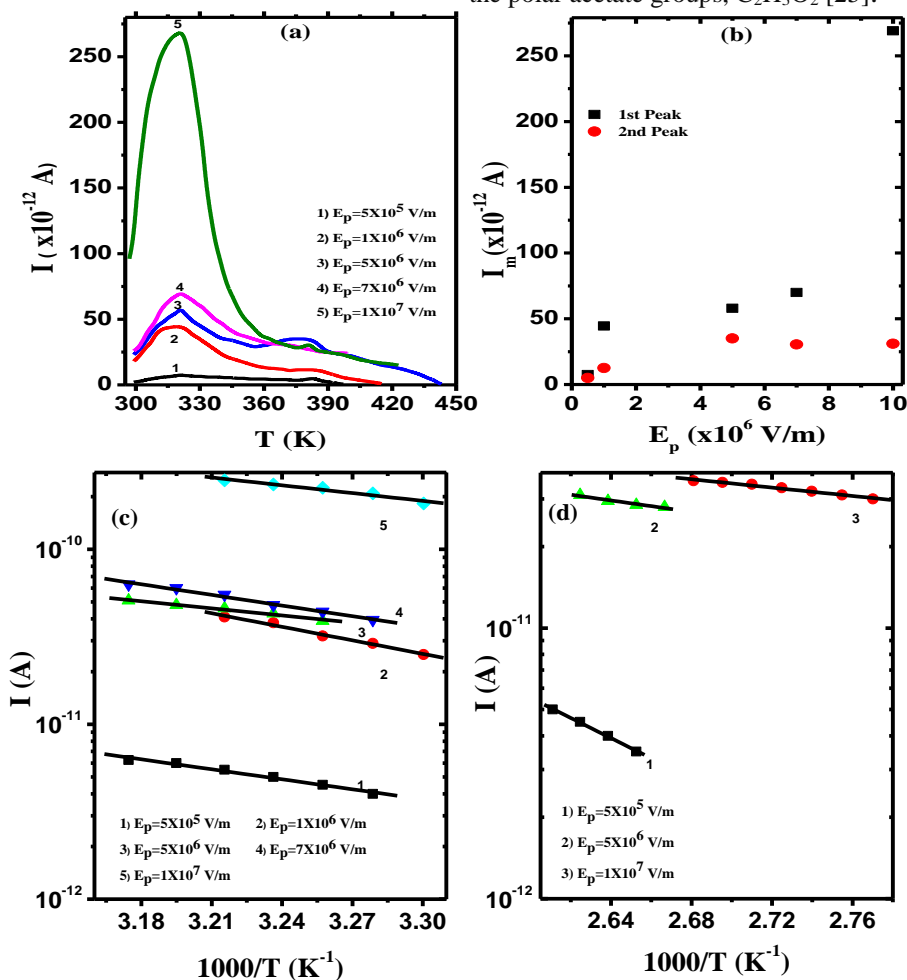


Fig. 2: a) Global TSDC spectra of non-irradiated CA polarized at $T_p=343$ K for $t_p=30$ min., b) Maximum current (I_m) of 1st peak versus applied electric (E_p) and (c&d) current (I) versus $1000/T$ of 1st and 2nd peak according to initial rice method.

Cellulose acetate (CA) structure with polar main-chain and polar side groups

enhances the free carrier formation, which accumulate at the electrode during formation. On the other side, the second relaxation peak obtained at a higher temperature can be attributed to the polarization of the space charge due to trapping of the injected electrons from the metallic electrode close to the surface of polymer. This process is characterized by an increase in the released charge with the applied field strength and a shift in the peak temperature. Since both of these observations were obtained in the current study, it can be assumed that the polarization of the space

charge is the origin of the second TSDC relaxation peak.

The pre-exponential factor (τ_0) of each relaxation peak is estimated using the following formula

$$\tau_0 = \frac{k_B T_{max}^2}{\beta E_a} \exp\left(-\frac{E_a}{k_B T_{max}}\right) \quad (1)$$

Where k_B , T_{max} and β are defined as the Boltzmann's constant, the temperature of peak position and rate of heating, respectively. The molecular parameters of first and second peaks are calculated and listed in Table 1.

Table 1: The molecular parameters of 1st and 2nd peak of non-irradiated CA.

E_p (V/m)	1 st Peak				2 nd Peak			
	T_{m1} (K)	$I_{m1} \times 10^{-12}$ (A)	E_{a1} (eV)	τ_{01} (sec)	T_{m2} (K)	$I_{m2} \times 10^{-12}$ (A)	E_{a2} (eV)	τ_{02} (sec)
5×10^5	321	7.5	0.16	4.27×10^{-2}	383	5	0.32	6×10^{-4}
1×10^6	319	44.5	0.22	0.33×10^{-2}	365	12.5	----	----
5×10^6	321	58	0.29	0.02×10^{-2}	373	35	0.07	2.2
7×10^6	321	70	0.18	1.84×10^{-2}	371	30.5	----	----
1×10^7	321	269	0.17	2.80×10^{-2}	381	31	0.09	5.30

Effect of Polarizing Electric Field (E_p) of Irradiated CA

Radiation treatment on a large commercial scale has proven to be a very effective method for improving the end-use properties of various polymers. The grafting, degradation and crosslinking reactions of radiation-initiated polymers have found

many beneficial applications in elastomers and plastics. The important properties of polymer materials such as mechanical and thermal stability and electrical properties can be greatly improved by radiation treatment. Hence, global TSDC of irradiated CA has been investigated under the effect of various doses.

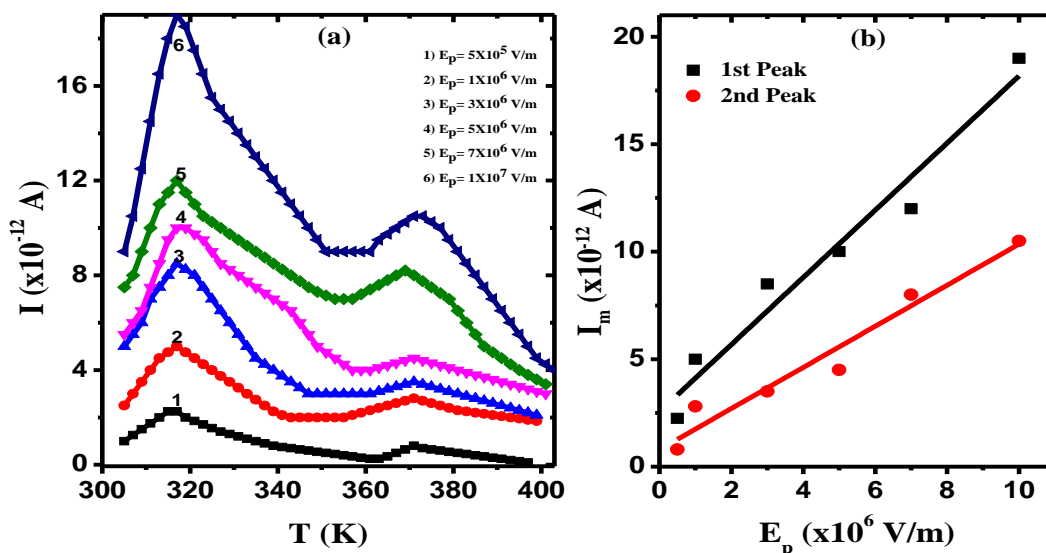


Fig. 3: (a) Global TSDC spectrum of irradiated CA sample with 20 kGy polarized with various poling electric fields (E_p) at $T_p= 343$ K and $t_p= 30$ min. Carbon paste was used as conducting electrode and $\beta= 3$ K/min. (b): Variation of I_m versus E_p of 1st and 2nd peaks.

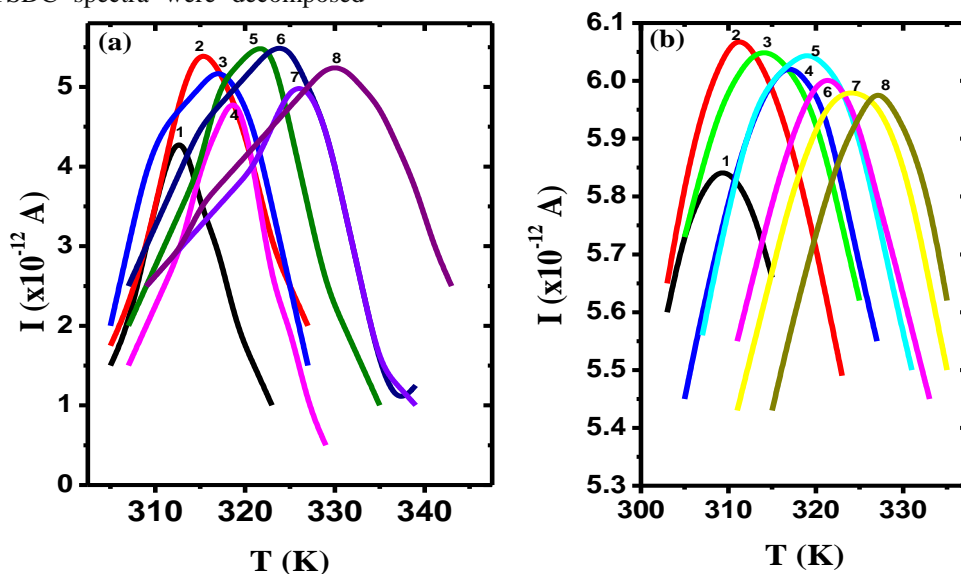
Fig. 3a shows global TSDC spectra of CA irradiated with 20 kGy as a representative sample of irradiated samples. It is observed that irradiated CA sample is characterized by two relaxation peaks with lower current for each peak in comparison with non-irradiated CA. The maximum current (I_m) values of both peaks are found to be poling field dependent, as shown in Fig. 3b. High-energy radiation reactions with polysaccharides lead to dehydrogenation, depolymerization reactions, destruction of basic monomer units and oxidative degradation. It is known that, after irradiation, the scission of the cellulose acetate chain occurs to form carbonyl and carboxyl groups due to the breaking of the glycoside bonds. So, the position of both peaks is shifted towards lower temperature to be located at 317 K and \sim 371 K.

Thermal sampling

The distribution of relaxation times is usually used to describe the phenomenon of relaxation in the polymer, and then analysis of complex TSDC spectra is performed using the appropriate parameter related to the symmetry and the shape of the distribution of relaxation times that characterize these modes [26-28]. Hence, thermal sampling (TS) technique has been carried out [29-31] to resolve complex TSDC modes experimentally and therefore, the dielectric relaxation times distribution. To obtain a more accurate and deeper insight into the relaxation behavior of the non-irradiated and irradiated cellulose acetate (CA) samples, the global TSDC spectra were decomposed

into their elementary spectrum with TS technique in the poling temperature range from 318 to 353 K, with a temperature window, $T_p - T_d = 5$ K for each spectrum. Thus, elementary relaxation processes of non-irradiated and irradiated samples are obtained as shown in Fig. 4. Overall, it was observed that the intensity of the partial depolarization peaks did not exhibit a strong dependence on the poling temperature (T_p) for all samples. When applying the TS to form polymer electrets, only the portion corresponding to the trapping depth (E_a) is filled with the charge carriers, which are not in thermal equilibrium due to the influence of the poling electric field (E_p) during the polarization process. This portion depends on both temperature window and polarization temperature. Also, these charge carriers, not in equilibrium, give rise to the depolarization current when they are thermally stimulated to relax to the equilibrium state.

It was found that, TS peaks are somewhat broader than those for a Debye relaxation. This broadness is observed in the polymers due to the interaction of different relaxation modes and may be explained as a result of the coupling between relaxation times. TS peaks correspond to different relaxation modes and it appears that the relaxation time of each peak is distributed fairly widely. The pre-exponential factor τ_0 is calculated using Eq. 1, suggesting that each peak of TS spectrum resulted from a dipole has a single relaxation time [32-34].



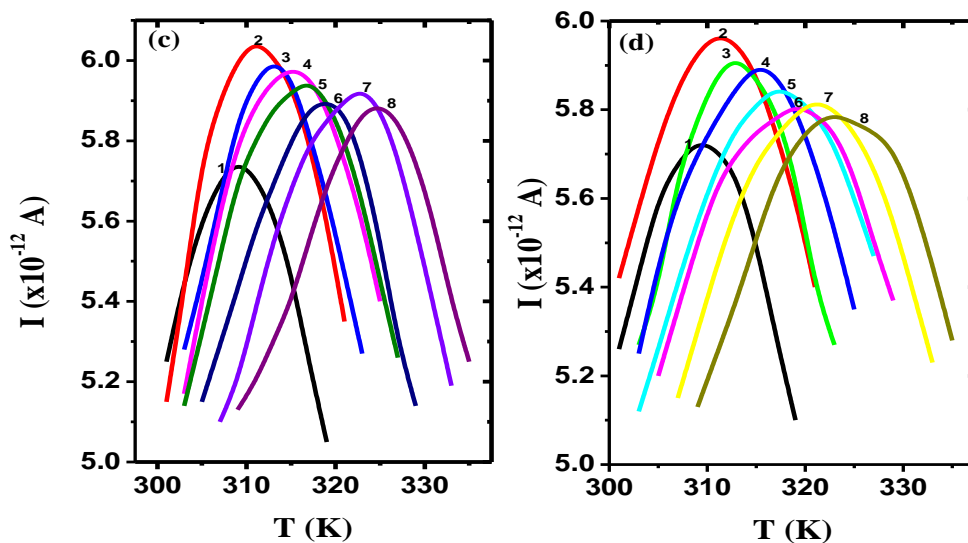


Fig. 4: TS spectra of a) non-irradiated CA, b) irradiated CA with 40 kGy, c) 50 kGy and d) 60 kGy. Poling temperatures (T_p) are: 1) 318 K, 2) 323 K, 3) 328 K, 4) 333 K, 5) 338 K, 6) 343 K, 7) 348 K and 8) 353 K. The samples are polarized with $E_p = 3 \times 10^5$ V/m.

The molecular parameters that characterize non-irradiated and irradiated CA samples, such as the activation energy (E_a) and pre-exponential factor (τ_0) have been estimated and summarized in Table 2. It was observed that, the pre-exponential factor values did not correspond to the classical Debye relaxation time (10^{-13} – 10^{-14} sec). These results are in good agreement with what was previously published elsewhere for dipolar relaxation of polymers [24].

The temperature dependence of relaxation time (τ) obeys Arrhenius equation as follows:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (2)$$

This equation governs either the localized hopping among potential wells or the rotation of permanent dipoles, which may be associated with defects within the polymer matrix [35]. One has to address the issue of compensation phenomenon in the discussion of TSDC-TS data. The compensation is a correlation between pre-exponential factor (τ_0) and the

apparent activation energy (E_a), as obtained in Fig. 5. Empirically, the values $\ln \tau_0$ and E_a are explained in terms of the compensation law and it obeys the following equation [36]:

$$\tau_0 = \tau_c \exp\left(\frac{E_a}{k_B T_c}\right) \quad (3)$$

Substitution of equation (3) into equation (2) gives the compensation equation as follows:

$$\tau(T) = \tau_c \exp\left[\frac{E_a}{k_B} \left(\frac{1}{T} - \frac{1}{T_c}\right)\right] \quad (4)$$

Where τ_c and T_c are adjustable parameters and defined as compensation time and compensation temperature, respectively. One of the most popular assumption of the compensation phenomenon in a polymer is based on the possibility of a process in which chain segments of increasing length contribute to an increase in temperature until reaching a maximum size at the compensation temperature [37].

Table 2: Molecular parameters of non-irradiated and irradiated CA samples.

Sample	TS No.	Polarization window (T_p-T_d)	T_p (K)	T_m (K)	E_a (eV)	τ_0 (sec)
Non-irradiated CA	1	318-313	318	313	0.52	2.30×10^{-8}
	2	323-318	323	315	0.48	1.24×10^{-7}
	3	328-323	328	317	0.48	1.41×10^{-7}
	4	333-328	333	319	0.38	7.64×10^{-6}
	5	338-333	338	322	0.31	1.35×10^{-4}
	6	343-338	343	324	0.26	1.04×10^{-3}
	7	348-343	348	326	0.14	1.49×10^{-1}
	8	353-348	353	330	0.16	7.00×10^{-2}
Irradiated CA (10 kGy)	1	318-313	318	309	0.20	7.51×10^{-3}
	2	323-318	323	313	0.26	7.05×10^{-4}
	3	328-323	328	317	0.13	1.90×10^{-1}
	4	333-328	333	319	0.13	1.98×10^{-1}
	5	338-333	338	321	0.10	7.97×10^{-1}
	6	343-338	343	323	0.21	7.55×10^{-3}
	7	348-343	348	325	0.10	8.54×10^{-1}
	8	353-348	353	327	0.18	2.87×10^{-2}
Irradiated CA (20 kGy)	1	318-313	318	315	0.22	3.91×10^{-3}
	2	323-318	323	315	0.29	2.26×10^{-4}
	3	328-323	328	317	0.42	1.45×10^{-6}
	4	333-328	333	319	0.34	3.66×10^{-5}
	5	338-333	338	321	0.20	7.32×10^{-4}
	6	343-338	343	323	0.02	73.125
	7	348-343	348	323	0.017	95.820
	8	353-348	353	321	0.015	114.85
Irradiated CA (30 kGy)	1	318-313	318	307	0.031	25.470
	2	323-318	323	309	0.130	1.79×10^{-1}
	3	328-323	328	311	0.193	7.30×10^{-4}
	4	333-328	333	313	0.183	7.00×10^{-4}
	5	338-333	338	315	0.114	3.65×10^{-1}
	6	343-338	343	317	0.047	10.755
	7	348-343	348	319	0.028	36.574
	8	353-348	353	323	0.036	22.585
Irradiated CA (40 kGy)	1	318-313	318	309	0.031	26.005
	2	323-318	323	311	0.038	17.629
	3	328-323	328	313	0.028	34.520
	4	333-328	333	317	0.038	18.314
	5	338-333	338	319	0.040	16.470
	6	343-338	343	321	0.036	21.410
	7	348-343	348	323	0.037	20.929
	8	353-348	353	327	0.038	21.005
Irradiated CA (50 kGy)	1	318-313	318	309	0.048	9.290
	2	323-318	323	311	0.080	1.744
	3	328-323	328	313	0.058	5.475
	4	333-328	333	315	0.066	3.731
	5	338-333	338	317	0.054	7.295
	6	343-338	343	319	0.044	12.795
	7	348-343	348	323	0.048	10.981
	8	353-348	353	325	0.037	20.688
Irradiated CA (60 kGy)	1	318-313	318	309	0.044	11.387
	2	323-318	323	311	0.039	15.987
	3	328-323	328	313	0.050	8.413
	4	333-328	333	315	0.042	14.263
	5	338-333	338	317	0.045	11.888
	6	343-338	343	319	0.047	11.010
	7	348-343	348	321	0.044	13.087
	8	353-348	353	323	0.041	16.411

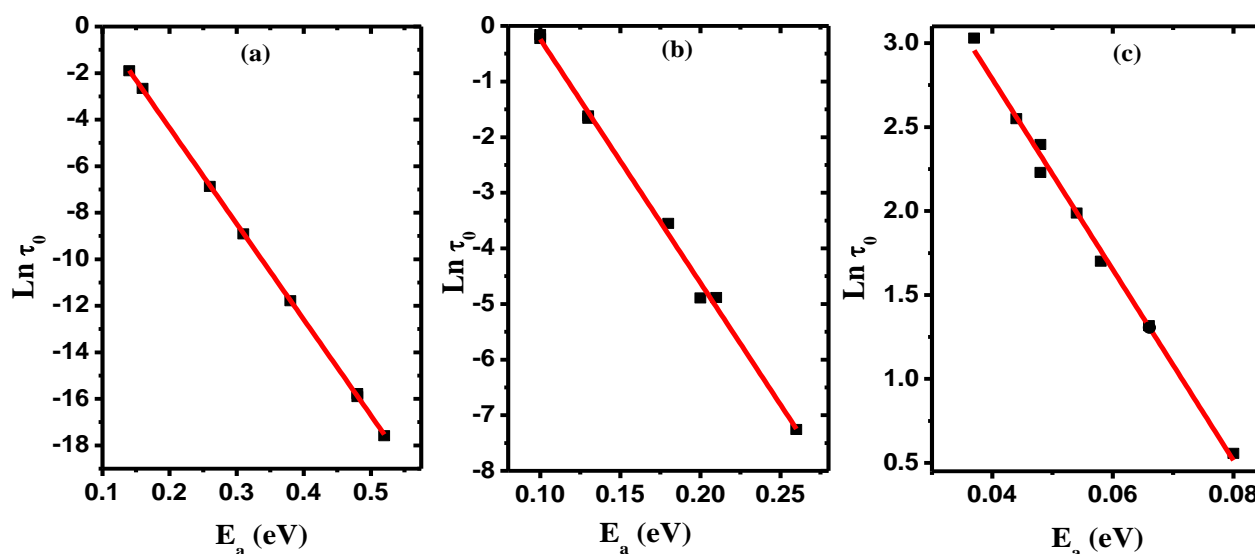


Fig. 5: The variation of pre-exponential factor (τ_0) against activation energy (E_a) for the elementary process (TS-peaks) for a) non-irradiated CA, b) irradiated CA with 10 kGy and c) irradiated CA with 10 kGy.

Arrhenius relaxation can be analyzed using the Eyring transformation to get many thermodynamic parameters such as, activation enthalpy (ΔH), activation entropy (ΔS) and Gibbs energy (ΔG). The relaxation time $\tau(T)$ can be expressed based on Eyring rate theory in terms of entropy as follows [38]:

$$\tau(T) = \frac{h}{k_B T} \exp\left(\frac{\Delta G}{k_B T}\right) \quad (5)$$

Where

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

In terms of thermodynamic, the activation enthalpy defines the heat change associated with binding, whereas, and the activation entropy defines the disorder change of the overall system

Hence,

$$\tau(T) = \frac{h}{k_B T} \exp\left(\frac{\Delta H}{k_B T}\right) \exp\left(-\frac{\Delta S}{k_B}\right) \quad (7)$$

Hence, the values of ΔH and ΔS at each polarizing temperature are estimated from the slope ($\Delta H/k_B$) and intercept ($-\Delta S/k_B$) of the plot of $\ln(\tau T k_B/h)$ against $1/T$, as shown in Fig. 6. An appropriate regression over the full range of individual relaxation lines gives the activation enthalpy and entropy values and listed in Table 3. So, by knowing the values of ΔH and ΔS , the values of ΔG are calculated and summarized in Table 3.

Compensation evidence in the literature is often presented in the form of a plot between ΔS and ΔH and proportional to linear regression with a slope called compensation temperature (T_c), as shown in Fig. 7 according to the following equation.

$$\Delta S = M_c \beta \Delta H \quad (8)$$

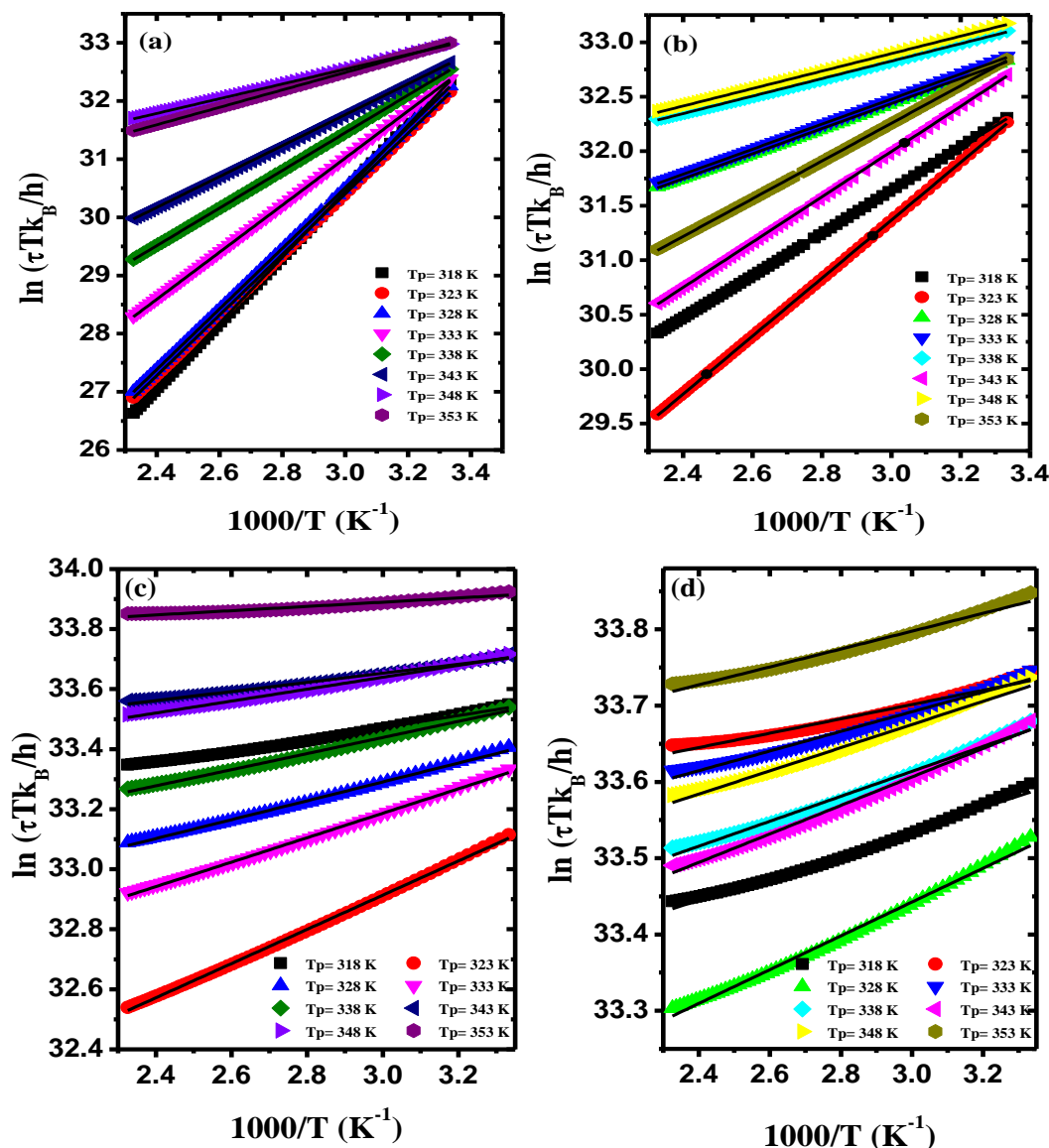


Fig. 6: The variation of $\ln(\tau T k_B/h)$ against $1/T$ for a) non-irradiated CA, b) irradiated CA with 10 kGy, c) irradiated CA with 50 kGy and d) irradiated CA with 60 kGy.

Where M_c is a dimensionless constant and equals to 4 and β is thermal volume expansion coefficient [39]. It is easy to justify the compensation between ΔH and S when the free energy changes of similar systems are or nearly the same [40]. Enthalpy-entropy compensation (EEC), indicating to any increase in enthalpy during non-covalent bonding of two molecules is often largely canceled out by a simultaneous decrease in entropy [41]. Similar behavior of enthalpy-entropy compensation (EEC) behavior has been published elsewhere in various fields [42-45]. The narrow range of Gibbs free energy

(ΔG) and the interdependence of enthalpy (ΔH) and entropy (ΔS) in the same system strongly indicate the effect of a kinetic compensation effect [46]. Eby assumed that different relaxation phenomena in the polymers were attributed to self-diffusion of chains and stated that the above relation should be appropriate for the activation criteria defined in the relaxation studies [47]. Substituting eqn. (8) to eqn. (7) leads to a new definition of the compensation temperature in the following compensation equation as follows:

$$\tau(T) = \frac{h}{k_B T} \exp\left(\frac{\Delta H}{k_B T}\right) \left[\frac{1}{T} - M_c \beta\right] \quad (9)$$

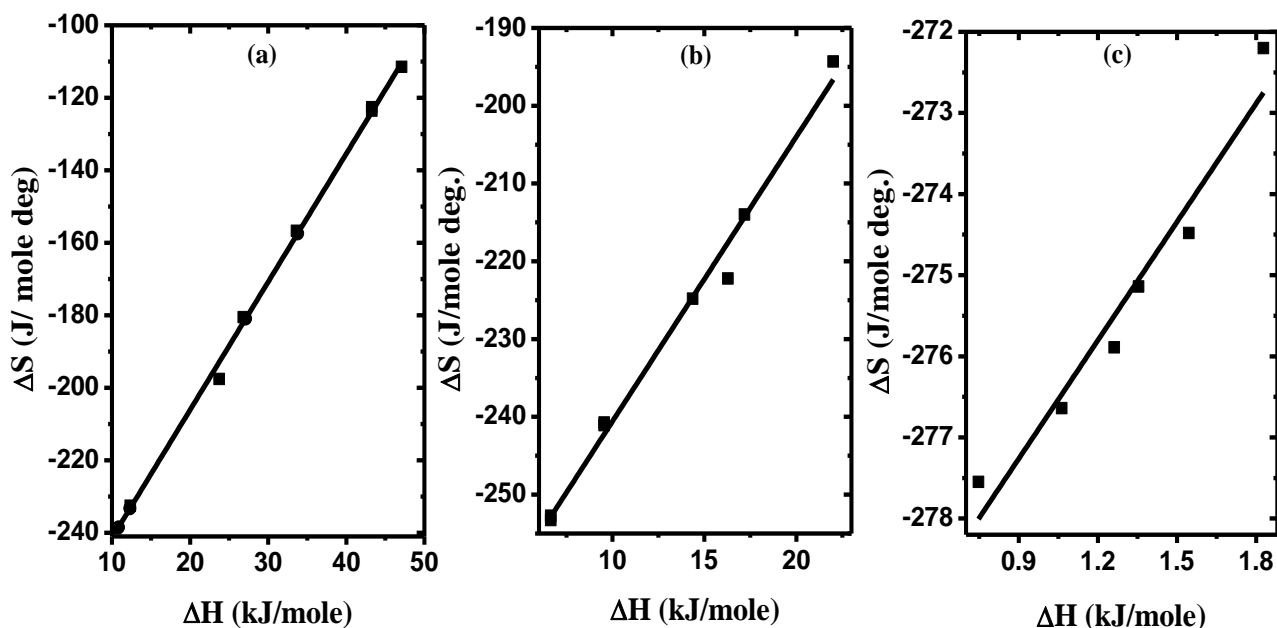


Fig. 7: The variation of ΔS versus ΔH for a) non-irradiated CA, b) irradiated CA with 10 kGy and c) irradiated CA with 60 kGy.

Therefore, the compensation temperature (T_c) based on the eqn. 9 is now defined as, $T_c = 1/M_c \beta$. The compensation temperature can be used to estimate the difference of the thermal volume expansion coefficient ($\Delta\beta$) above and below glass transition

temperature (T_g) of the polymer using the empirical formula, $T_c = 1/9\Delta\beta$ [48]. Hence, the values of β , $\Delta\beta$ and T_c for non-irradiated and irradiated CA samples are calculated and listed in Table 4.

Table 3: Molecular parameters of non-irradiated and irradiated CA samples.

Sample	TS No:	Polarization window	T_p (K)	ΔH (kJ/mole)	ΔS (J/mole deg.)	ΔG (kJ/mole)
Non-irradiated CA	1	318-313	318	47.10	-111.48	82.55
	2	323-318	323	43.28	-122.62	82.88
	3	328-323	328	43.28	-123.53	83.80
	4	333-328	333	33.64	-156.68	85.82
	5	338-333	338	26.83	-180.52	87.85
	6	343-338	343	23.75	-197.55	91.52
	7	348-343	348	10.46	-238.76	93.55
	8	353-348	353	12.37	-232.53	94.46
Irradiated CA (10 kGy)	1	318-313	318	16.28	-222.22	86.95
	2	323-318	323	22.01	-194.31	84.77
	3	328-323	328	9.553	-240.75	88.52
	4	333-328	333	9.553	-241.08	89.83
	5	338-333	338	6.646	-252.71	92.06
	6	343-338	343	17.19	-214.00	90.60
	7	348-343	348	6.646	-253.29	94.79
	8	353-348	353	14.37	-224.80	93.73
Irradiated CA (20 kGy)	1	318-313	318	18.19	-208.52	84.50
	2	323-318	323	24.92	-184.84	84.63
	3	328-323	328	37.38	-142.89	84.25
	4	333-328	333	29.74	-169.72	86.26
	5	338-333	338	16.28	-194.56	82.05
	6	343-338	343	-0.996	-290.18	98.54
	7	348-343	348	-1.329	-292.51	100.46

	8	353-348	353	-1.495	-294.01	102.29
Irradiated CA (30 kGy)	1	318-313	318	0.008	-277.31	88.19
	2	323-318	323	9.553	-240.25	87.16
	3	328-323	328	15.61	-194.56	79.44
	4	333-328	333	14.62	-194.23	79.30
	5	338-333	338	7.975	-246.23	91.20
	6	343-338	343	1.495	-274.31	95.59
	7	348-343	348	-0.249	-284.45	98.74
	8	353-348	353	0.490	-280.46	99.49
Irradiated CA (40 kGy)	1	318-313	318	0.008	-281.62	89.57
	2	323-318	323	0.681	-278.38	90.60
	3	328-323	328	-0.27	-284.03	92.89
	4	333-328	333	0.681	-278.72	93.49
	5	338-333	338	0.872	-277.81	94.77
	6	343-338	343	0.490	-280.05	96.55
	7	348-343	348	0.581	-279.80	97.95
	8	353-348	353	0.681	-279.88	99.48
Irradiated CA (50 kGy)	1	318-313	318	1.644	-273.07	88.48
	2	323-318	323	4.652	-259.19	88.37
	3	328-323	328	2.575	-268.66	90.69
	4	333-328	333	3.323	-265.51	91.74
	5	338-333	338	2.159	-271.07	93.78
	6	343-338	343	1.246	-266.17	92.54
	7	348-343	348	1.578	-274.48	97.09
	8	353-348	353	0.581	-279.71	99.32
Irradiated CA (60 kGy)	1	318-313	318	1.246	-274.81	88.64
	2	323-318	323	0.747	-277.55	90.39
	3	328-323	328	1.827	-272.2	91.12
	4	333-328	333	1.063	-276.64	93.19
	5	338-333	338	1.354	-275.14	94.35
	6	343-338	343	1.545	-274.48	95.69
	7	348-343	348	1.262	-275.89	97.27
	8	353-348	353	0.971	-277.81	99.04

Table 4: The values of β , $\Delta\beta$ and T_c for non-irradiated and irradiated CA samples.

Sample	β	$\Delta\beta$	T_c (K)
Non-irradiated CA	8.83×10^{-4}	3.92×10^{-4}	283
Irradiated CA (10 kGy)	9.13×10^{-4}	4.06×10^{-4}	274
Irradiated CA (20 kGy)	9.85×10^{-4}	4.38×10^{-4}	254
Irradiated CA (30 kGy)	1.34×10^{-3}	5.96×10^{-4}	187
Irradiated CA (40 kGy)	1.28×10^{-3}	5.69×10^{-4}	195
Irradiated CA (50 kGy)	1.25×10^{-3}	5.53×10^{-4}	201
Irradiated CA (60 kGy)	1.22×10^{-3}	5.40×10^{-4}	206

The isokinetic behavior of Gibbs free energy (ΔG) against the poling temperature (T_p) for non-irradiated CA and some samples of irradiated CA as a representative samples is

shown in Fig. 8. It is observed that, Gibbs free energy varies linearly with the poling temperature, i.e., it always increases monotonically with T_p .

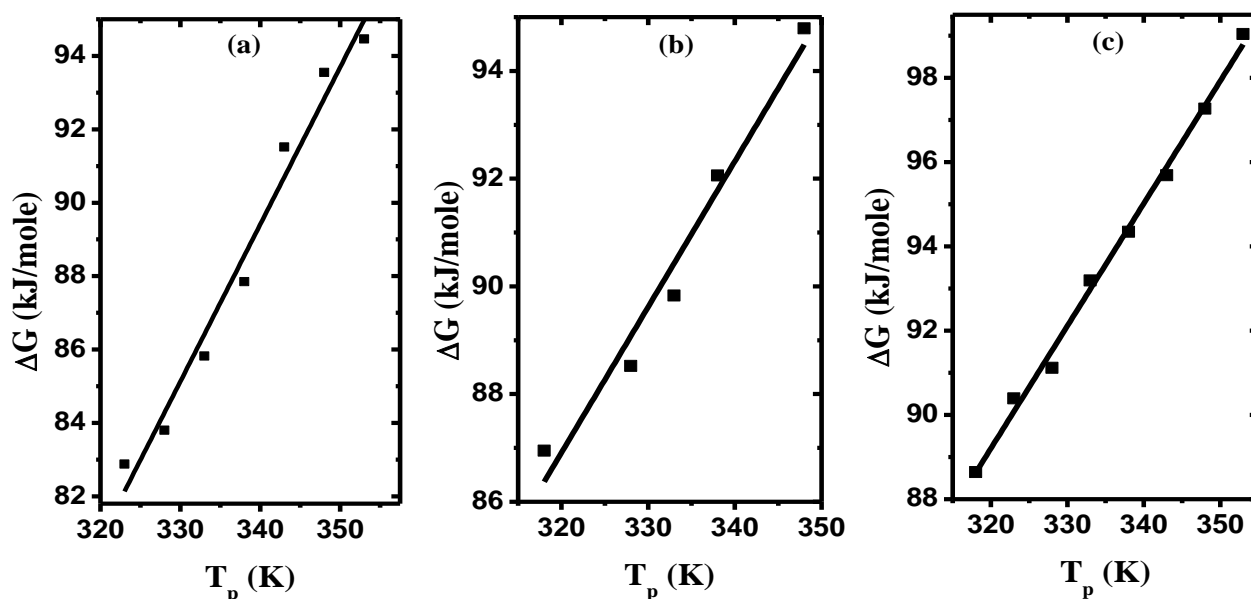


Fig. 8: The isokinetic plot of ΔG against T_p for a) non-irradiated CA, b) irradiated CA with 10 kGy and c) irradiated CA with 60 kGy.

4. Conclusion

Global TSDC of non-irradiated and irradiated CA samples has been investigated in a temperature range from 300 K to 440 K under the effect of various poling electric field (E_p). It is found that global TSDC spectrum of non-irradiated CA is characterized by two relaxation peaks. One in the low temperature range located at $T_m=321$ K and the other in the high temperature range ~ 376 -383 K. These relaxations are assigned as β and ρ -relaxation and associated to molecular motion of the polar acetate groups, $C_2H_3O_2$ and polarization of the space charges, respectively. Moreover, the maximum current (I_m) of these peaks is found to be electric field dependent, i.e., it increases linearly with increasing electric field. On the other hand, the temperature position of these relaxations is shifted towards lower temperature for irradiated samples to be located at 317 K and ~ 371 K. This decreasing in peak position may due to the degradation of CA samples because of the irradiation process. TS-technique has been carried out resolve global TSDC spectra of all samples into its elementary peaks and the molecular parameters such as, activation energy and pre-exponential factor are estimated for each TS peak. Eyring transformation is used to construct relaxation map (RM) of all samples, hence, the thermodynamic parameters such as, enthalpy activation (ΔH), entropy activation (ΔS) and Gibbs free energy (ΔG) are

calculated. The linear relationship between enthalpy activation ΔH and entropy activation ΔS indicates the compensation law of non-irradiated and irradiated CA samples is valid. The compensation temperature (T_c), thermal volume expansion coefficient (β) and $\Delta\beta$ are calculated for non-irradiated and irradiated CA samples.

5. Conflicts of interest

The authors declared that they have no conflicts of interest to this work.

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References

- [1] Y. Cao, J. Wu, T. Meng, J. Zhang, J. He, H. Li, Y. Zhang, Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl), *Carbohydrate Polymers* 69(4) (2007) 665-672.
- [2] D.A. Cerqueira, G.R. Filho, C.d.S. Meireles, Optimization of sugarcane bagasse cellulose acetylation, *Carbohydrate Polymers* 69(3) (2007) 579-582.
- [3] K. Oksman, Y. Aitomäki, A.P. Mathew, G. Siqueira, Q. Zhou, S. Butylina, S. Tanpichai, X. Zhou, S. Hooshmand, Review of the recent developments in cellulose nanocomposite processing, *Composites Part A: Applied Science and Manufacturing* 83 (2016) 2-18.
- [4] M. Sousa, A.R. Brás, H.I.M. Veiga, F.C. Ferreira, M.N. de Pinho, N.T. Correia, M. Dionísio, Dynamical Characterization of a Cellulose Acetate Polysaccharide, *The Journal of Physical Chemistry B* 114(34) (2010) 10939-10953.
- [5] J. Summerscales, N.P.J. Dissanayake, A.S. Virk, W. Hall, A review of bast fibres and their composites. Part 1 – Fibres as reinforcements, *Composites Part A: Applied Science and Manufacturing* 41(10) (2010) 1329-1335.
- [6] N.A.J.B. Hoenich, Cellulose for medical applications: past, present, and future, 1(2) (2006) 270-280.
- [7] T. Sharma, S. Aggarwal, S. Kumar, V.K. Mittal, P.C. Kalsi, V.K. Manchanda, Effect of gamma irradiation on the optical properties of CR-39 polymer, *Journal of Materials Science* 42(4) (2007) 1127-1130.
- [8] K.J.J.I.I.T. Nitzel, The influence of electron beam processing on the degradation of cellulose, 2(1) (1984) 11-30.
- [9] J.J. Moura Ramos, M.F.M. Piedade, H.P. Diogo, M.T. Viciosa, Thermal Behavior and Slow Relaxation Dynamics in Amorphous Efavirenz: A Study by DSC, XRPD, TSDC, and DRS, *Journal of Pharmaceutical Sciences* 108(3) (2019) 1254-1263.
- [10] P. Pissis, A. Anagnostopoulou-Konsta, Dielectric studies of proton transport in hydrated proteins, *Solid State Ionics* 46(1) (1991) 141-145.
- [11] H. Smaoui, M. Arous, H. Guermazi, S. Agnel, A. Toureille, Study of relaxations in epoxy polymer by thermally stimulated depolarization current (TSDC) and dielectric relaxation spectroscopy (DRS), *Journal of Alloys and Compounds* 489(2) (2010) 429-436.
- [12] J.J.E. Van Turnhout, Thermally stimulated discharge of electrets, (1980) 81-215.
- [13] M. Ahmed, T.J.J.o.t.K.P.S. Fahmy, Study of the relaxation phenomenon of Poly (vinyl chloride-co-vinylacetate-co-2-hydroxypropyl acrylate)/Poly (methyl methacrylate) blends using TSDC-TS technique: dipole-dipole interaction approach, 59(1) (2011) 98-104.
- [14] T. Fahmy, M.T. Ahmed, Alpha relaxation study in poly(vinyl chloride)/poly(ethyl methacrylate) blends using thermally stimulated currents, 49(7) (2000) 669-677.
- [15] M. Ahmed, T.J.J.o.P.M. Fahmy, Carrier transport and thermally stimulated depolarization current in iodine-doped poly (vinyl chloride), 17(2) (2000) 133-138.
- [16] M.D. Migahed, T. Fahmy, Structural relaxation around the glass transition temperature in amorphous polymer blends: temperature and composition dependence, *Polymer* 35(8) (1994) 1688-1693.
- [17] A. Sharma, S. Yarramaneni, J.K. Quamara, Evaluation of dielectric relaxation parameters from TSDC analysis of pristine and ion irradiated kapton-H polyimide, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 269(8) (2011) 759-763.
- [18] T. Fahmy, I. Elsayed, H. Abdelwahed, W. Elsharkawy, Relaxation Map analysis of Poly (Vinyl Chloride-co-Vinyl Acetate-co-2-Hydroxypropyl Acrylate)/Poly (Acrylonitrile-Butadiene-Styrene) Polymer Blend.

- [19] T. Mzir, M.W. Khemici, M. Dahmane, M. Mzir, N. Doulache, Dielectric characterization of polyvinyl chloride/polymethyl methacrylate (PVC/PMMA) blends by TSDC technique, *International Journal of Polymer Analysis and Characterization* 23(8) (2018) 675-683.
- [20] J.J. Moura Ramos, M.T. Viciosa, H.P. Diogo, Thermal behaviour of two anti-inflammatory drugs (celecoxib and rofecoxib) and slow relaxation dynamics in their amorphous solid state. Comparison between the dynamic fragility obtained by dielectric spectroscopy and by thermostimulated currents, *Molecular Physics* 117(5) (2019) 644-660.
- [21] T. Fahmy, M.T. Ahmed, Thermal induced structural change investigations in PVC/PEMA polymer blend, *Polymer Testing* 20(5) (2001) 477-484.
- [22] M.T. Ahmed, T. Fahmy, Distributed relaxations in PVC/PEMA polymer blends as revealed by thermostimulated depolarization current, *Polymer Testing* 18(8) (1999) 589-599.
- [23] M. Migahed, M. Ishra, T.J.J.o.P.D.A.P. Fahmy, Rate theory and cooperative structural relaxation in amorphous polymer blends as revealed by a thermal sampling study, 27(10) (1994) 2216.
- [24] M.D. Migahed, M. Ishra, A. El-Khodary, T. Fahmy, Compatibility of polyacrylonitrile-butadiene with polyvinylchloride as explored by thermally stimulated depolarization current, *Polymer Testing* 12(4) (1993) 335-349.
- [25] P. Khare, P. Jain, R.J.B.o.M.S. Pandey, Effect of doping on TSD relaxation in cellulose acetate films, 23(6) (2000) 529-532.
- [26] M.W. Khemici, A. Gourari, N. Doulache, Dielectric Characterization of Poly Ethylene Naphtalene 2,6 Dicarboxylate (PEN) by Thermally Stimulated Currents Technique (TSC), *International Journal of Polymer Analysis and Characterization* 14(4) (2009) 322-335.
- [27] T. Fahmy, Dielectric Relaxation Spectroscopy of Poly (Vinyl Chloride-co-Vinyl Acetate-co-2-Hydroxypropyl Acrylate)/Poly (Acrylonitrile-Butadiene-Styrene) Polymer Blend, *Polymer-Plastics Technology and Engineering* 46(1) (2007) 7-18.
- [28] T. Fahmy, Investigation of Iodine-Doped Poly(Ethyl Methacrylate) Relaxation by TSDC Technique in the Vicinity of the Glass Transition Temperature, *International Journal of Polymeric Materials and Polymeric Biomaterials* 56(3) (2007) 291-306.
- [29] M.D. Migahed, M. Ishra, A. El-Khodary, T. Fahmy, TSDC and the role of space charge in polyacrylonitrile/methylacrylate copolymer films, 53(10) (1994) 1315-1322.
- [30] N. Alves, J. Gómez Ribelles, J.J.J.o.M.S. Mano, Part C: Polymer Reviews, Study of the molecular mobility in polymers with the thermally stimulated recovery technique—A review, 45(2) (2005) 99-124.
- [31] T. Fahmy, H.R. Hafiz, M.T. Ahmed, Structural and relaxation aspects in azodye-doped abs films: TSDC study, *International Journal of Polymeric Materials and Polymeric Biomaterials* 51(10) (2002) 875-889.
- [32] M. Zieliński, M. Kryszewski, Thermal sampling technique for the thermally stimulated discharge in polymers model calculations, 42(1) (1977) 305-314.
- [33] M. Ahmed, T.J.P.-P.T. Fahmy, Engineering, Alpha relaxation study of poly (vinyl chloride co-vinylacetate-co-2-hydroxypropyl acrylate), 44(8-9) (2005) 1559-1572.
- [34] J.J. del Val, A. Alegria, J. Colmenero, J.M. Barandiarán, Thermally stimulated depolarization current (TSDC) study of molecular motions in the glass-transition region of polyarylate (PAr), *Polymer* 27(11) (1986) 1771-1776.
- [35] M. Sayer, A. Mansingh, J. Webb, J.J.J.o.P.C.S.S.P. Noad, Long-range potential centres in disordered solids, 11(2) (1978) 315.
- [36] J. del Val, J.J.P.B. Colmenero, Compensation laws and β -relaxation in poly (vinyl chloride), 17(5) (1987) 489-495.
- [37] J.D. Hoffman, G. Williams, E. Passaglia, Analysis of the α , β , and γ relaxations in polychlorotrifluoroethylene and

- polyethylene: Dielectric and mechanical properties, 14(1) (1966) 173-235.
- [38] S. Glasstone, K.J. Laidler, H. Eyring, The theory of rate processes; the kinetics of chemical reactions, viscosity, diffusion and electrochemical phenomena, McGraw-Hill Book Company, 1941.
- [39] R.W. Keyes, Volumes of Activation for Diffusion in Solids, 29(3) (1958) 467-475.
- [40] A. Pan, T. Biswas, A.K. Rakshit, S.P.J.T.J.o.P.C.B. Moulik, Enthalpy–entropy compensation (EEC) effect: a revisit, 119(52) (2015) 15876-15884.
- [41] U.J.M. Ryde, A fundamental view of enthalpy–entropy compensation, 5(9) (2014) 1324-1336.
- [42] J.D. Chodera, D.L.J.A.r.o.b. Mobley, Entropy-enthalpy compensation: role and ramifications in biomolecular ligand recognition and design, 42 (2013) 121-142.
- [43] A.I. Dragan, C.M. Read, C.J.E.B.J. Crane-Robinson, Enthalpy–entropy compensation: the role of solvation, 46(4) (2017) 301-308.
- [44] J.M. Fox, M. Zhao, M.J. Fink, K. Kang, G.M.J.A.r.o.b. Whitesides, The molecular origin of enthalpy/entropy compensation in biomolecular recognition, 47 (2018) 223-250.
- [45] T.J.I.J.o.P.M. Fahmy, Corona charging and thermal sampling of stretched poly (vinyl chloride), 54(3) (2005) 183-198.
- [46] J. Guerra, B. Bajwa, P. Kumar, S. Vazquez, V.V. Krishnan, S.J.A.o. Maitra, Validation of Enthalpy–Entropy Compensation Mechanism in Partial Amide Bond Rotation, 5(16) (2020) 9348-9355.
- [47] R.J.T.J.o.C.P. Eby, Empirical Relations of Thermodynamic "Constants" to the Activation Parameters of Polymer Relaxations, 37(12) (1962) 2785-2790.
- [48] B.B. Sauer, P.J.P. Avakian, Cooperative relaxations in amorphous polymers studied by thermally stimulated current depolarization, 33(24) (1992) 5128-5142.