

# Thermally stimulated depolarization currents and thermal sampling technique of $\gamma$ -irradiated gelatin and PVA homopolymers and 50/50 (wt/wt %) blend sample

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## To cite this article:

F. H. Abd El-kader, S. A. Gaffar, A. F. Basha, S. I. Bannan, M. F. H. Abd El-kader. Thermally Stimulated Depolarization Currents and Thermal Sampling Technique of  $\gamma$ -Irradiated Gelatin and PVA Homopolymers and 50/50 (wt/wt %) Blend Sample. *European Journal of Biophysics*. Vol. 2, No. 5, 2014, pp. 61-71. doi: 10.11648/j.ejb.20140205.12

**Abstract:** Thermally stimulated depolarization current (TSDC) and thermal sampling (TS) method were used to systematically characterize the  $\alpha$ -relaxation process in gelatin and PVA homopolymers and their blend sample of 50/50 (wt/wt %) composition. In addition,  $\gamma$ -irradiation effect on TSDC spectra of samples under investigation was studied. Measurements of TSDC at different polarizing field strengths, polarization temperatures and times made it possible to obtain a complete picture of kinetic transitions, local modes of motion and space charge polarization in one heating cycle. On  $\gamma$ -irradiation, the change in shape, position and area of the  $\alpha$ -relaxation peak of the samples were attributed to the variation of distribution function of associated relaxation times. The thermal sampling procedure was applied to decompose the complex relaxations into their narrowly distributed components. The molecular parameters such as activation energy ( $E_a$ ) and pre-exponential factor ( $\tau_0$ ) for TS processes have been estimated. A linear relationship between the activation energy and logarithm of pre-exponential factor confirms the existence of a compensation behavior. The compensation temperature  $T_c$  and compensation time  $\tau_c$  for the present samples have been determined.

**Keywords:** Gelatin/PVA, Thermal Stimulated Depolarization Current, Thermal Sampling Process, Relaxation Processes

## 1. Introduction

Blending one polymer with another is an effective way of achieving a suitable combination of physical and chemical properties and better processing characteristics and sometimes making its cost lower and its application wider. The usefulness of TSDC in terms of both high sensitivity and high temperature resolution when using the TS method has been recognized for some time. The low equivalent frequency (ca.  $10^{-4} - 10^{-2}$  Hz) of the TSDC measurement is also useful in separating overlapping relaxations or a continuous distribution of relaxations<sup>1-8</sup>.

Gelatin is a protein of animal origin, which can be obtained from collagen by acidic or alkaline hydrolysis. Gelatin is widely utilized in food industry, medical application and daily life<sup>9-11</sup>. PVA is a very important bioequivalent material used in medicine and surgery<sup>12,13</sup>.

Detailed literature survey suggests that little information is available on gelatin/PVA blends. Therefore, we have attempted systematic studies on TSDC combined with TS to explore the charge transport in the samples under investigation. Also, the induced effect of  $\gamma$ -irradiation via TSDC for such samples is examined. Also, the induced effect of  $\gamma$ -irradiation on TSDC for such samples was examined.

## 2. Experimental methods

The gelatin used was a food-grade supplied by E. Merck; (Darmstadt, Germany). Its maximum limit of ash impurity was 2.0 % and its grain size was less than 800  $\mu\text{m}$ . The polyvinyl alcohol (PVA) granules were supplied by El-Nasr Company; (Cairo, Egypt). Approximate molecular weight was 125,000, residual polyvinyl acetate was 0 - 3 % and maximum ash contents was 0.75 %.

Weighed amounts of gelatin were dissolved in distilled

water at room temperature. Also, weighed amounts of PVA granules were dissolved in a mixture of distilled water and ethanol at a 4:1 ratio. A solution of gelatin and PVA was prepared by mixing them together at 50/50 (wt/wt %) using a magnetic stirrer at 333 K. Films of appropriate thickness ( $\approx 0.01$  mm) were cast onto stainless steel Petri- dishes and then dried in an oven at 323 K for about 2 days until the solvent completely evaporated. Several samples were subjected to  $\gamma$ -doses in the range 5 – 100 kGy using a  $^{60}\text{Co}$  source with a dose rate of 8.6 Gy/hr at room temperature.

The samples were inserted between the plates of a capacitor and polarized by the application of an electric field  $E_p$  at temperature  $T_p$  for a large time  $t_p$ , compared to the dielectric relaxation time. With the electric field still applied, the sample was cooled to room temperature and then the field was reduced to zero. TSDC recordings were performed while varying the temperature, in the range from 303 to 423 K, at a fixed heating rate of 1 K/min. The current was measured using a Keithley 617 electrometer.

Thermal sampling consists of polarization of the sample at temperature  $T_p$  and subsequently depolarization at a temperature  $T_d$  a few degrees (5 K) lower, thus ensuring that only the dipoles corresponding to this temperature window remain polarized. The sample was then cooled down and the depolarization current measured during linear heating as in normal TSDC.

Statistical significance was assessed using t-test for independent samples, at a critical level of  $p = 0.05$ .

### 3. Results and Discussion

#### 3.1. Thermally Stimulated Depolarization Currents

The experimental measurements of TSDC were repeated on several virgin samples, and only reproducible data were reported. In order to determine the suitable starting conditions of measurements and to identify the origin of TSDC peaks<sup>14,15</sup>, the mutual polarization effects of different conditions of field intensity, temperature and time on TSDC were studied on individual polymers and 50/50 (wt/wt %) blend samples.

##### 3.1.1. Effect of Poling Field ( $E_p$ )

Figure 1 shows the effect of field strengths from 0.5 to 4 kV/cm on TSDC spectra of gelatin and PVA homopolymers and their blend sample of 50/50 (wt/wt %) composition under the same other polarizing conditions ( $T_p = 333$  K and  $t_p = 45$  min.). It can be seen from Fig. 1a that for pure gelatin each spectrum consists of a single broad peak which appears near its glass transition temperature  $T_g$  ( $\alpha$ -relaxation). This result is generally consistent with that previously reported in the literature<sup>16</sup>. The temperature ( $T_{max}$ ) of the relaxation peak is nearly constant at about  $345 \pm 2$  K independent of  $E_p$ . On the other hand, the width of the relaxation peak increases with increasing  $E_p$ , which may result from a change in the distribution function of the associated relaxation times. An additional peak is also observed around 393 K for 0.5 kV/cm, which may be masked completely with the broad one at

higher polarizing field strengths. Under the influence of electric field, the irregularly distributed dipoles and/or ionic charge polarization are mobilized/oriented in a certain direction. Thermal activation at constant rate causes the release of charges due to their mobilization, giving a peak at the site of maximum release of charge<sup>17</sup>. The occurrence of a maximum does not necessarily mean that a single thermally activated process is involved, competing thermally activated processes or a temperature-dependent structure may be advocated as well. The insert of Fig. 1a shows a linear dependence of peak current ( $I_{max}$ ) on field intensity ( $E_p$ ) suggesting that it does correspond to a dipolar relaxation mechanism<sup>18</sup>.

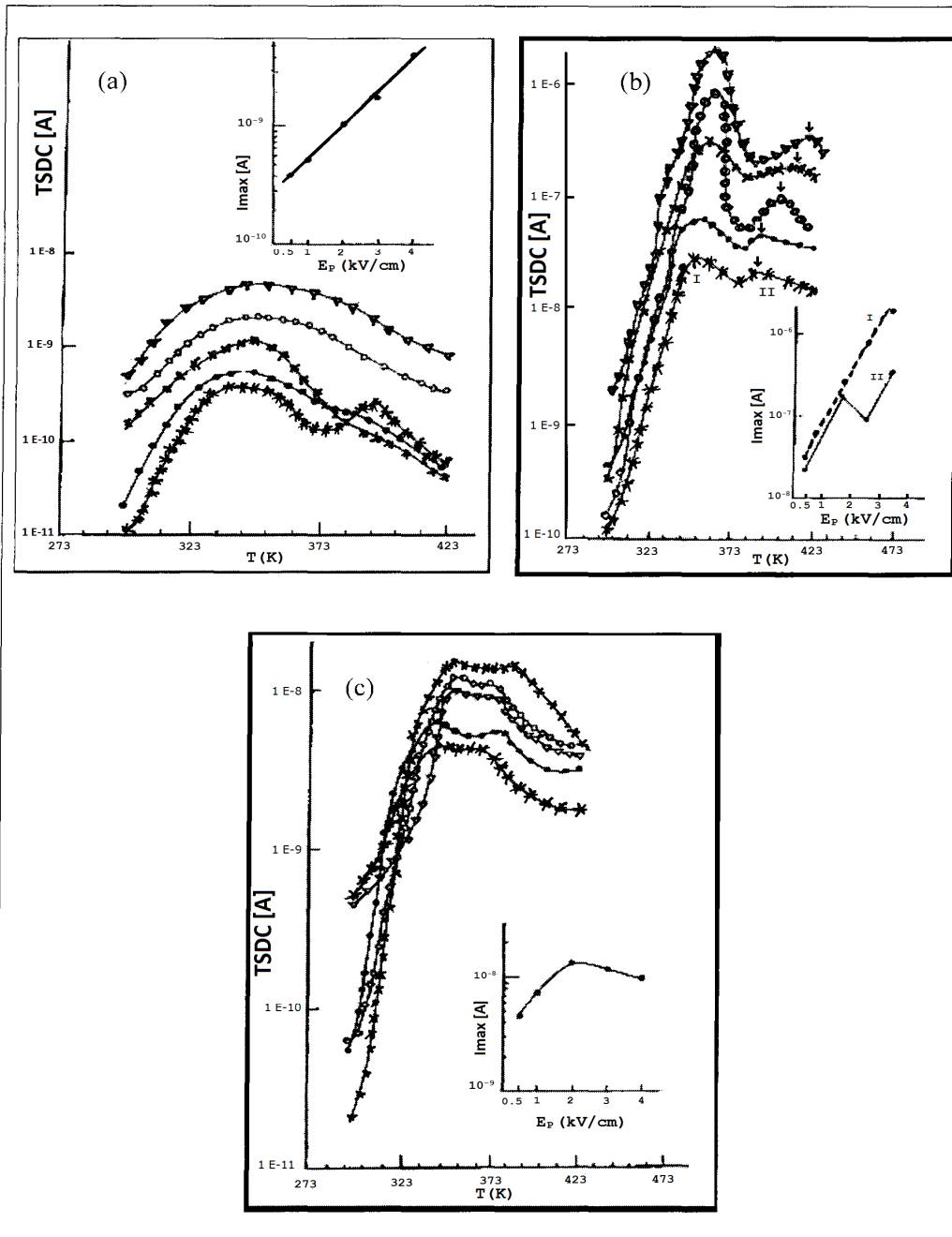
Two separate broad current peaks are observed for pure PVA samples at various polarizing field strengths consistent with those reported in the literature<sup>19-21</sup>, see Fig. 1b. The low-temperature peak ( $\alpha$ -relaxation) which appears near the  $T_g = 356 \pm 2$  K of PVA, can be attributed to the relaxation of permanent dipoles associated with the micro-Brownian motions of large chain segments. However, the high-temperature peak ( $\rho$ -relaxation) may be a result of the diffusion of the space charge either at the electrode or due to motion of the excess charge arising from the increased chain mobility<sup>22,23</sup>. Furthermore, a close examination of Fig. 1b shows that the temperature of the  $\alpha$ -relaxation peak is independent of  $E_p$ , while the  $\rho$ -relaxation peak is shifted towards higher temperatures with increasing  $E_p$ . Also, it is evident from the insert of Fig. 1b that the variation of  $I_{max}$  is linear for  $\alpha$ -relaxation peak (I), while it is irregular for  $\rho$ -relaxation peak (II) with increasing  $E_p$ . These observations lead us to believe that the low temperature relaxation peak does correspond to a dipolar relaxation mechanism, while the high-temperature relaxation peak is related to space charge effect.

In the gelatin/PVA blend sample of 50/50 (wt/wt %) composition there is only one composite peak which has two maxima due to overlapping of two different relaxation processes, see Fig. 1c. The maximum at low-temperature is nearly that of the glass transition of the blend system. Thus, the lower temperature relaxation process is due to the superposition of dipolar groups with a continuum distribution of the relaxation time<sup>24</sup>. The later one appearing on the higher-temperature side of the composite peak has been associated with the upper component of the glass transition involving the amorphous phase constrained by crystallite<sup>25</sup>.

The insert of Fig. 1c shows that  $I_{max}$  of the  $\alpha$ -relaxation peak for the polyblend system increases with increasing  $E_p$  up to 2 kV/cm, followed by a slight decrease with an increasing poling field strength. In the mixture of the two polymers, the friction coefficient of gelatin may be affected by the presence of PVA, and hence a deviation from linearity is present as seen in the insert of Fig. 1c. Thus, the deviation indicates the miscibility of the gelatin/PVA system, contributing to the formation of hydrogen bonding interactions between  $-\text{NH}_2$  and  $-\text{COOH}$  groups in gelatin and  $-\text{OH}$  groups in PVA. In addition, the deviation from linearity at higher fields, above 2 kV/cm may arise from the strong

susceptibility to blend-forming conditions and is ascribed to the trapping of charge carriers generated in the bulk as well

as injected from the electrodes.



**Figure 1.** Effect of polarizing field ( $E_p$ ) on TSDC of (a) pure gelatin, (b) pure PVA and (c) 50/50 (wt/wt %) gelatin/PVA blend sample at polarization temperature  $T_p = 333$  K and polarization time  $\tau_p = 45$  min.  $E_p = 0.5$  kV/cm ( $\ast$ ), 1 kV/cm ( $\bullet$ ), 2 kV/cm ( $\times$ ), 3 kV/cm ( $\circ$ ) and 4 kV/cm ( $\blacktriangledown$ ).

### 3.1.2. Effect of Polarization Temperature ( $T_p$ )

Figure 2 depicts the TSDC obtained for both gelatin and PVA homopolymers and 50/50 (wt/wt %) blend sample, after 45 min. of 2 kV/cm poling at different polarization temperatures (313, 333, 353 and 373 K). It can be seen from the insert of Fig. 2 that with the increase of  $T_p$  the  $T_{max}$  of PVA  $\alpha$ -relaxation peak is linearly shifted towards higher temperatures, while its curvature is increased for both pure gelatin and the 50/50 (wt/wt %) blend sample. The shift in peak temperature with  $T_p$  is indicative of distribution of

relaxation time<sup>26</sup>. At low polarization temperatures all the dipoles are not activated. As  $T_p$  is increased, more and more slow dipoles are activated, and the peak temperature shifts towards higher values<sup>27</sup>.

The magnitude of the  $\alpha$ -relaxation peak for both homopolymers increases with increasing  $T_p$  reaching a saturation value at 333 and 353 K for PVA and gelatin, respectively. However, the peak current for the 50/50 (wt/wt %) blend sample increases with increasing  $T_p$ , evidencing two different rates of decreasing order at higher

temperatures. Saturation of peak current for homopolymers probably occurs because of the accumulation of carriers near the sample electrodes, which decreases the applied field. On the other hand, the reduction in growth rate of peak current at higher polarization temperatures (353 and 373 K) for blend

samples may be explained assuming that under these conditions more subpolarizations of inverse polarity are activated<sup>28,29</sup>. At lower  $T_p$ , the conduction is slow so that fewer carriers are available to accumulate and this reduces the height of the peak.

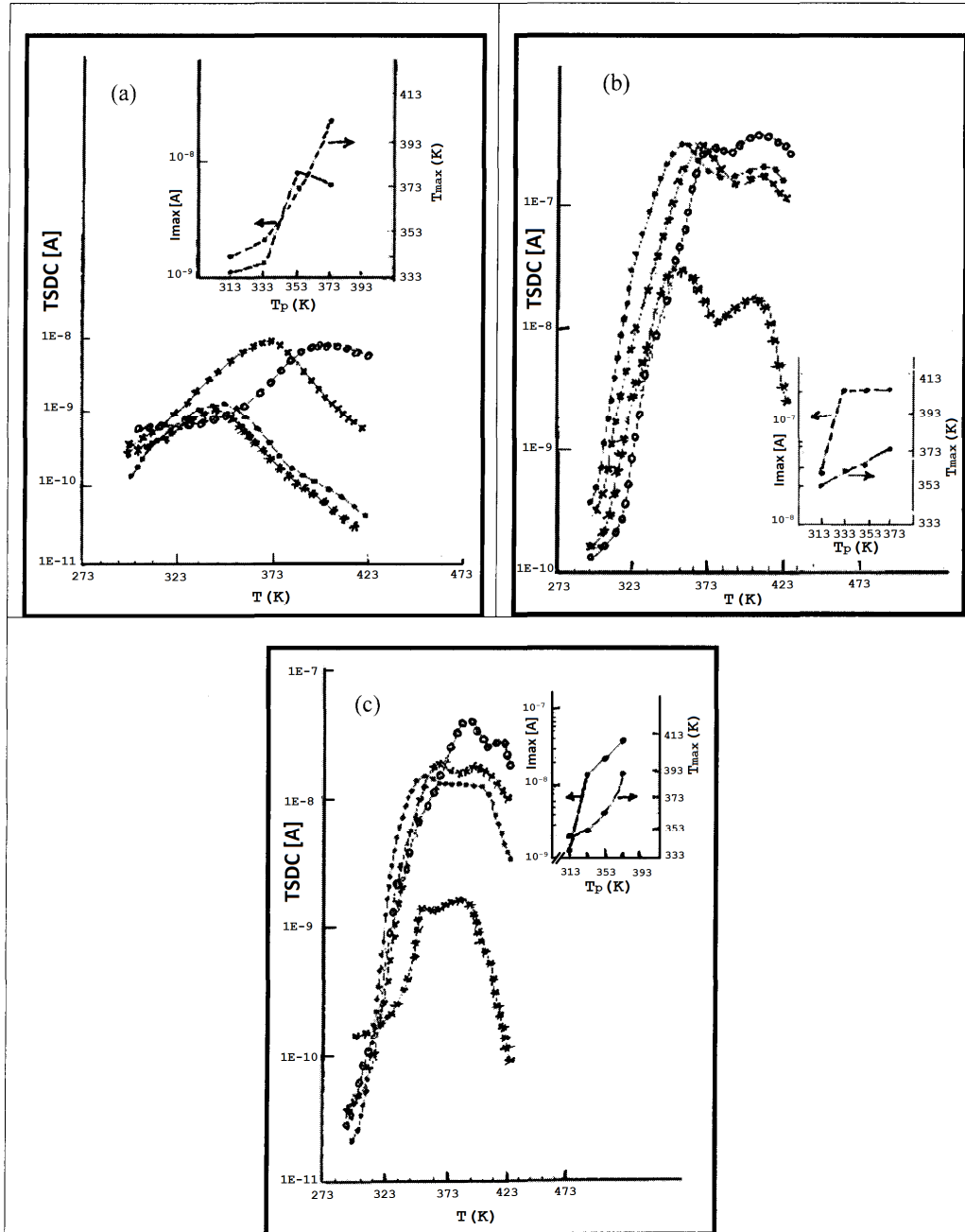


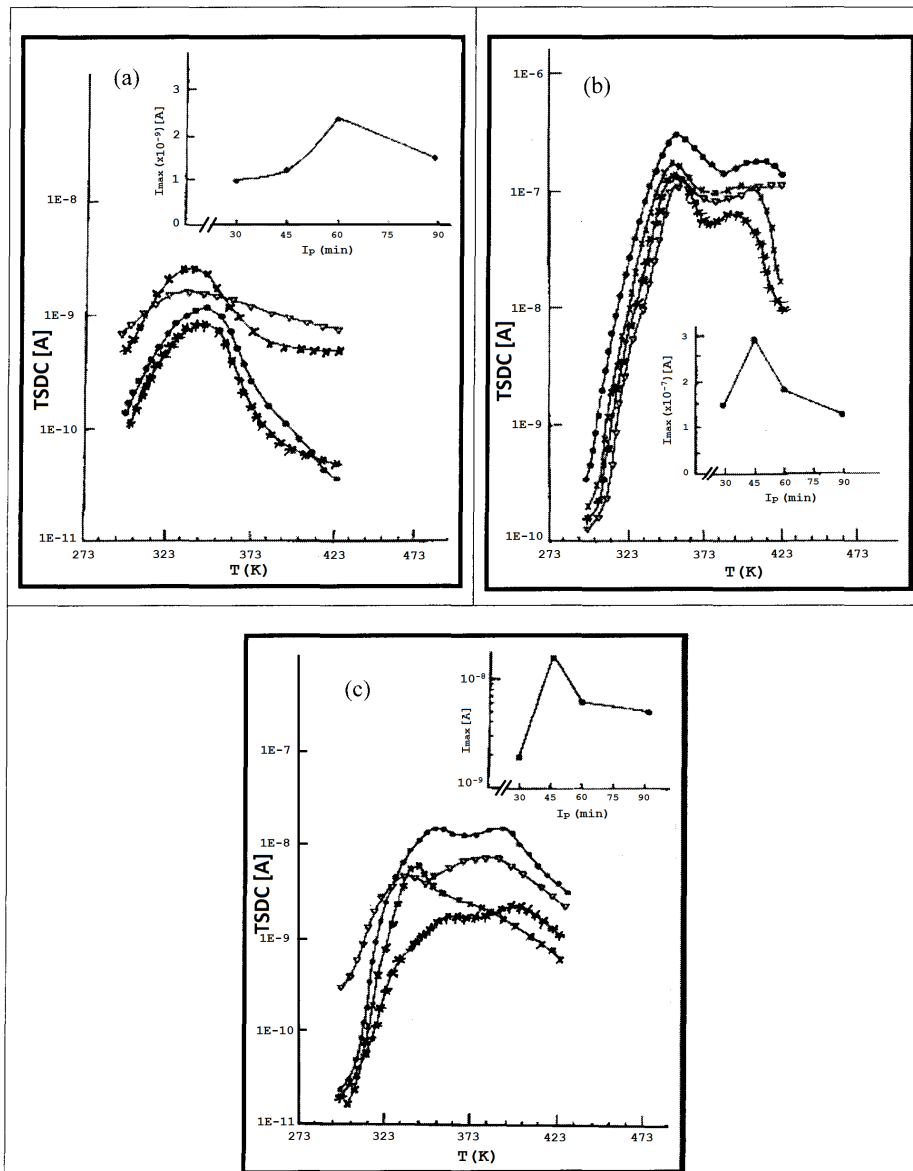
Figure (2). Effect of polarization temperature ( $T_p$ ) on TSDC of (a) pure gelatin, (b) pure PVA and (c) 50/50 (wt/wt %) gelatin/PVA blend sample at polarization field  $E_p = 2$  kV/cm and polarization time  $\tau_p = 45$  min.  $T_p = 313$  K ( $\circ$ ), 333 K ( $\bullet$ ), 353 K ( $\times$ ) and 373 K ( $\circ$ ).

### 3.1.3. Effect of Polarization Time ( $t_p$ )

Figure 3 illustrates the TSDC spectra obtained for homopolymers and 50/50 (wt/wt %) blend samples, after 2 kV/cm poling at a temperature of 333 K for various times (30, 45, 60 and 90 min). It is clear from the figure that the longer the polarization time the smaller the polarization. The height of  $\alpha$ -relaxation peak in TSDC spectra for both pure PVA and

the blend sample are reduced for polarization times above 45 min., while for pure gelatin at polarization times over 60 min., see the inserts of Fig. 3. However, the positions of the relaxation peaks in all samples are irregularly changed with increasing polarization time. On the other hand, the shapes of the relaxation peaks are not significantly affected, except for the blend sample at 60 min. polarization time, where a broad

relaxation peak appears with shoulder at high-temperatures.



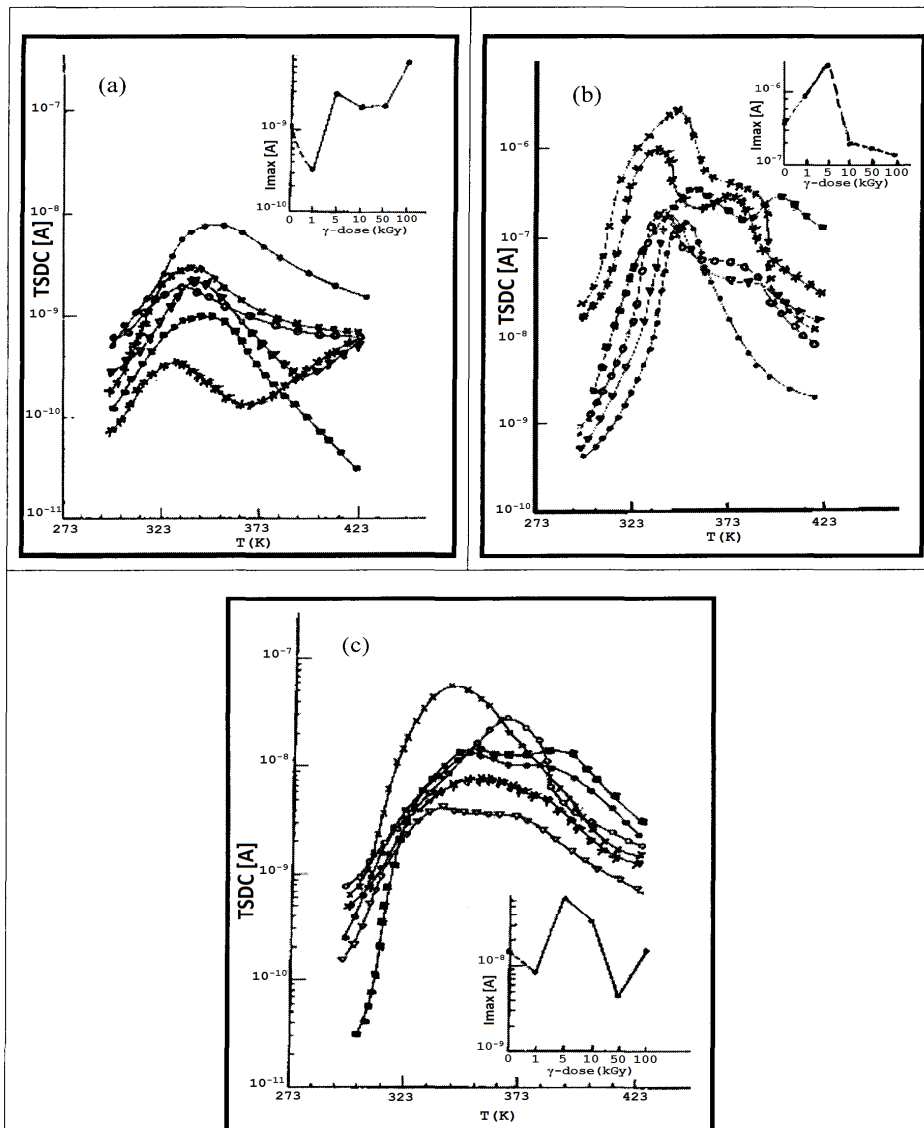
**Figure (3).** Effect of polarizing time ( $\tau_p$ ) on TSDC of (a) pure gelatin, (b) pure PVA and (c) 50/50 (wt/wt %) gelatin/PVA blend sample at polarization field  $E_p = 2$  kV/cm and polarization temperature  $T_p = 333$  K,  $\tau_p = 30$  min. (+), 45 min. (●), 60 min. (x) and 90 min. (▼).

In general, the mutual influence of  $E_p$ ,  $T_p$  and  $t_p$  on the TSDC spectra obtained for individual polymers and their blend sample, as shown in Figs. 1-3, indicates that higher  $T_p$  up to 333 K are enough to enhance time of permanent dipoles and internal free charges to applied electric fields of strength up to 2 kV/cm and allow the equilibrium polarization to be reached in a reasonably short time of 45 min. Longer time, higher temperature and higher polarization field are found to entail a deviation from the trend expected for uniform polarization according to dipolar theory<sup>30,31</sup>.

### 3.1.4. Effect of $\gamma$ -Irradiation on TSDC

Figure 4 shows TSDC thermogram of homopolymers and their blend sample of composition 50/50 (wt/wt %) before and after irradiation with various  $\gamma$ -ray doses (1, 5, 10, 50 and 100 kGy). The irradiated gelatin samples in Fig. 4a are

characterized by the occurrence of one broad  $\alpha$ -relaxation peak. The observed upswing in TSDC curves for  $\gamma$ -ray doses of 1 and 50 kGy was attributed to thermal release of charges at high temperatures due to increased chain mobility<sup>32,33</sup>. The temperature of peak was found to be associated with a remarkable shift toward lower temperatures, except for the dose of 100 kGy, where a small shift toward higher temperatures was noticed. The shift towards lower temperatures was probably due to generation of low-molecular weight species and free chain ends on irradiation<sup>34,35</sup>. On the other hand, the shift towards the higher temperatures at 100 kGy reflects the predominance of crosslinking process. Both crosslinking and degradation processes induced by  $\gamma$ -irradiation occurred simultaneously, one or the other being dominant.



**Figure (4).** TSDC spectra of (a) pure gelatin, (b) pure PVA and (c) 50/50 (wt/wt %) gelatin/PVA blend sample before and after  $\gamma$ -irradiation with different doses, at  $E_p = 2\text{ kV/cm}$ ,  $T_p = 333\text{ K}$  and  $\tau_p = 30\text{ min.}$ , pristine (■), 1 kGy (○), 5 kGy (x), 10 kGy (○), 50 kGy (▼) and 100 kGy (●).

The magnitude of the maximum current  $I_{\max}$  for  $\alpha$ -relaxation peak was decreased at 1 kGy and increased at other doses compared to the pristine samples, following an irregular trend, as shown in the insert of Fig. 4a. Peptide chains of proteins are folded so as to minimize the vector sum of their dipole moment<sup>36</sup>. Conversely,  $\gamma$ -irradiation perturbed the structure of gelatin, increasing the dissymmetry of the charge distribution, which causes a large dipole moment<sup>36</sup>. Also, the random recombination of free radicals together with continued thermal degradation produced by  $\gamma$ -irradiation reduced the TSDC at 1 kGy. However, the increase of  $I_{\max}$  at  $\gamma$ -doses higher than 1 kGy is mainly due to carriers generated by  $\gamma$ -rays which escape recombination and trapping. So, denaturated protein has much larger dielectric increment than the native protein<sup>36</sup>.

TSDC spectra of PVA samples irradiated at relatively low  $\gamma$ -ray doses (1 kGy) follow the general pattern of pristine

samples, see Fig. 4b. At higher  $\gamma$ -ray doses up to 50 kGy, TSDC spectra contain only one broad  $\alpha$ -relaxation peak with a shoulder at higher temperatures. Further,  $\gamma$ -ray doses of 100 kGy lead to the disappearance of the  $\rho$ -relaxation peak, which may be due to the slowly decaying space charge. But, the position of  $\alpha$ -relaxation peak within the exposure range of  $\gamma$ -ray doses is shifted irregularly towards lower temperatures. In addition, the magnitude of the  $\alpha$ -relaxation peak increases with an increasing  $\gamma$ -ray dose up to 5 kGy, followed by a decrease until 100 kGy, as shown in the insert of Fig. 4b.

From the pronounced effect of  $\gamma$ -irradiation on  $T_{\max}$  and  $I_{\max}$  as well as the shape of  $T_g$  relaxation peak, we might assume that the thermally stimulated current is not related to intrinsic properties of PVA, but is indicative of the existence of trapped carriers in the material. These carriers might have been generated by the irradiation process via thermal activation.

In case of 50/50 (wt/wt %) blends, as shown in Fig. 4c, TSDC spectra for samples irradiated with 1, 50 and 100 kGy  $\gamma$ -doses look similar to pristine ones, while TSDC spectra for samples irradiated at 5 and 10 kGy entail only the appearance of one broad Gaussian relaxation peak. The insert of Fig. 4c shows that the peak current at  $\gamma$ -ray doses of 5 and 10 kGy is higher than for pristine samples, and decreases less for other doses. The change in shape, position and area of relaxation peak on irradiation may result from a variation in the distribution function of the associated relaxation times. This suggests that the average relaxation time changed irregularly due to structural modification.

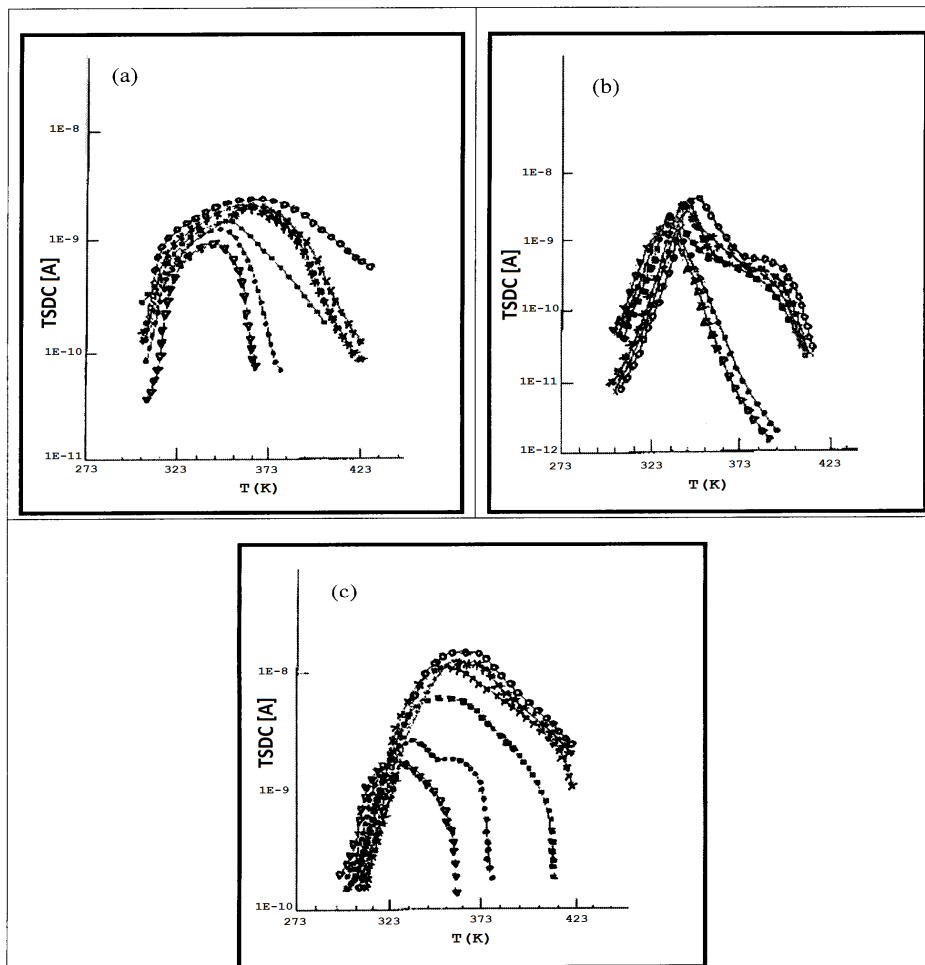
The t-test applied for the experimental data shown in the inserts of Fig. 1 – 4 resulted in statistically significant t and p values, between (2.11 – 3.50) and (0.006 – 0.041), respectively.

TSDC spectra of both homopolymers and their 50/50 (wt/wt %) blend sample upon irradiated with  $\gamma$ -rays in the range 1 – 100 kGy allow one to argue that the structure of these materials is changed. This change evidently is due to the action of  $\gamma$ -irradiation on the samples that results in ion recoils and free radicals via elastic collision with the structural arrangement of the molecules. The ions and free

radicals are not stable but cause further reactions that may result in either degradation or crosslinking. Further, the irradiation was carried out in air and hence, the gaseous ions formed around the samples may produce homocharge on the surface of the specimen<sup>37</sup>.

### 3.2. Thermal Sampling of TSDC Spectra

Different changes in the TSDC spectrum have been studied by the thermal sampling (TS) technique, which allows polarization of narrow segments of the whole thermocurrent spectrum and thus, separation of the complex global peaks into their components<sup>29,38,39</sup>. Thermal sampling polarization procedure was applied at a temperature window equal to 5 °C for  $t_p = 45$  min. and  $E_p = 2$  kV/cm in gelatin and PVA homopolymers and their 50/50 (wt/wt %) blend. Six representative thermal sampling spectra were obtained for each investigated material at  $T_p = 308, 313, 318, 323, 328$  and  $333$  K, as shown in Fig. 5 in order to illustrate some of the features of the TS experiment. It is evident that the peak intensities shown roughly reproduce the shape of the global TSDC spectrum including the glass transition.



**Figure (5).** TSDC of windowing polarized (a) gelatin, (b) PVA and (c) 50/50 (wt/wt %) blend sample at  $E_p = 2$  kV/cm,  $\tau_p = 45$  min. and  $T_p = 308$  K ( $\blacktriangledown$ ), 313 K ( $\bullet$ ), 318 K ( $\blacksquare$ ), 323 K ( $\times$ ), 328 K ( $\ast$ ) and 333 K ( $\circ$ ).

The peaks are broader regardless of intensity, indicating a noncooperative low value of activation energy and/or the existence of interaction between dipolar molecules<sup>40,41</sup>. The maximum current of the peaks increases as  $T_p$  increases and the temperature; at which the maximum appears,  $T_{max}$ , shifts to slightly higher values with  $T_p$ . The TS spectra of pure gelatin shown in Fig. 5a are symmetrical well away from  $T_g$  (at  $T_p = 308$  and 313 K) while they are asymmetric near  $T_g$  as indicated by the broad tails at higher temperatures. The asymmetry is the result of a variation in the activation energy across  $T_g$  and is seen in most homopolymers systems<sup>42,43</sup>. In case of pure PVA Fig. 5b, the TS spectra at  $T_p = 308$  and 313 K show only the  $\alpha$ -relaxation peak while at higher polarization temperatures ( $T_p > 313$  K) the spectra include both the glass transition and space charge relaxation peaks. However, for 50/50 (wt/wt %) blend samples shown in Fig. 5c the TS spectra contain composite relaxation peaks with two maxima as in the case of global TSDC spectrum except for  $T_p = 308$  K where only one relaxation peak was present at

the glass transition.

Bucci *et al.*<sup>44</sup> first applied a method to extract the relaxation dynamics from the TS spectra. The relaxation times  $\tau(T)$  are determined from the measured depolarization current  $J(T)$  by:

$$\tau(T) = \frac{\int_{T_i}^{T_f} J(T) dT}{J(T)} \quad (1)$$

where  $T_i$  and  $T_f$  are the initial and final temperatures. For a process with a single relaxation time the temperature dependence of  $\tau$  can be described by the Arrhenius equation:

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

where  $\tau_0$  is the pre-exponential factor,  $K_B$  is Boltzmann's constant and  $E_a$  the apparent activation energy.

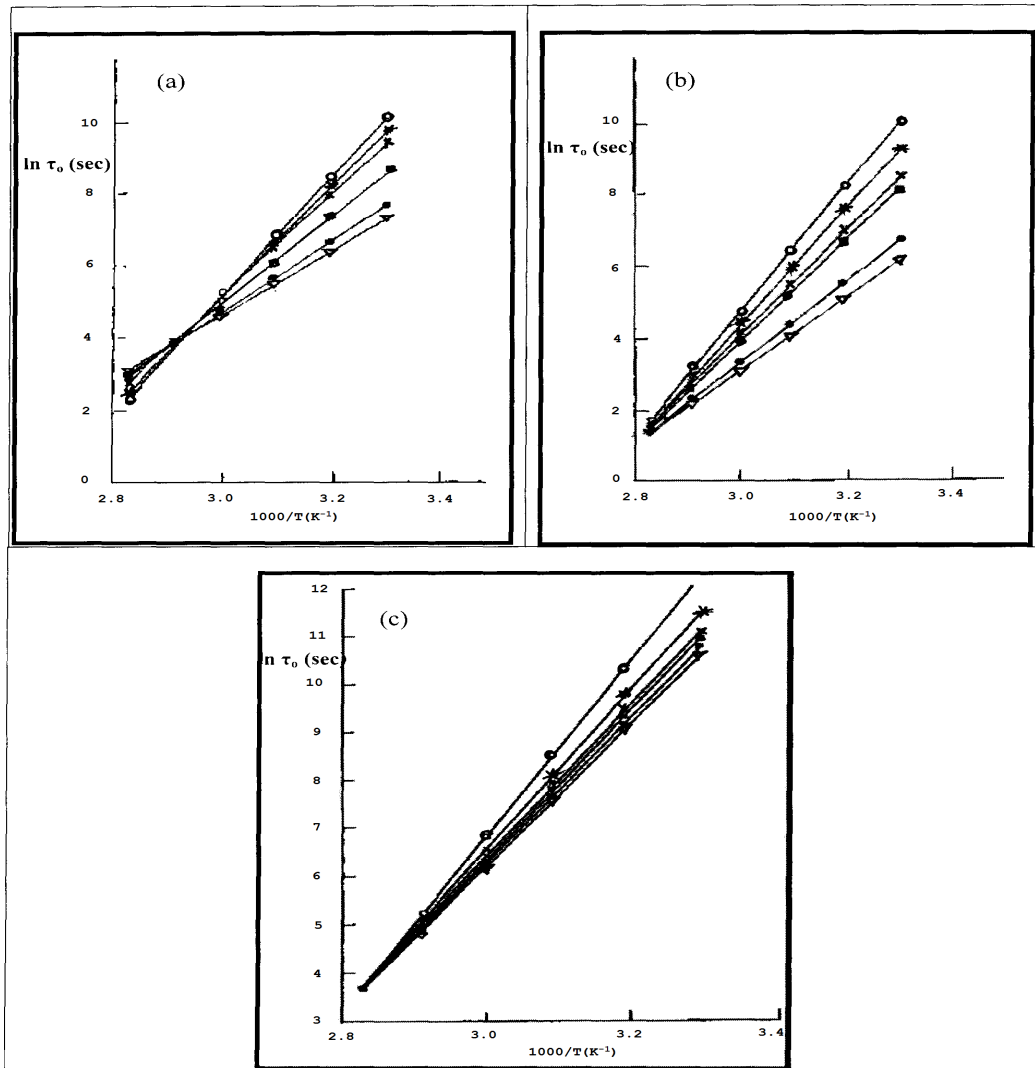


Figure (6). Bucci lines ( $\ln \tau$  vs  $1000/T$ ) for (a) pure gelatin, (b) pure PVA and (c) 50/50 (wt/wt %) gelatin/PVA blend sample, corresponding to the TS processes,  $T_p = 308$  K ( $\blacktriangledown$ ), 313 K ( $\bullet$ ), 318 K ( $\blacksquare$ ), 323 K ( $\times$ ), 328 K ( $*$ ) and 333 K ( $\circ$ ).



Several representative Arrhenius lines thus obtained for both homopolymers and the 50/50 (wt/wt %) gelatin/PVA blend sample are shown in Fig. 6. The activation energy ( $E_a$ ) and the pre-exponential factor ( $\tau_0$ ) for each TS process were obtained from  $\ln \tau$  versus  $1/T$  dependency and are presented in Table (1). The values of calculated  $\tau_0$  in Table (1) are several orders of magnitude smaller than the Debye relaxation time ( $10^{-14}$  -  $10^{-12}$  sec). Two types of dielectric relaxation have been established for all polymers<sup>45</sup>, namely dipole-segmental and dipole group relaxations. Large relaxation times are characteristic of dipole-group losses in polymers, and still higher ones, of dipole-segmental losses<sup>46</sup>. As shown in Table 1, the  $\tau_0$  of the various materials investigated correspond mainly to a dipole segmental motion<sup>47</sup>. In addition, it must be mentioned that the activation energy increases with increasing  $T_p$ . This behavior corresponds to the so-called compensation effect, which is a

feature of the glass transition relaxation in polymeric materials.

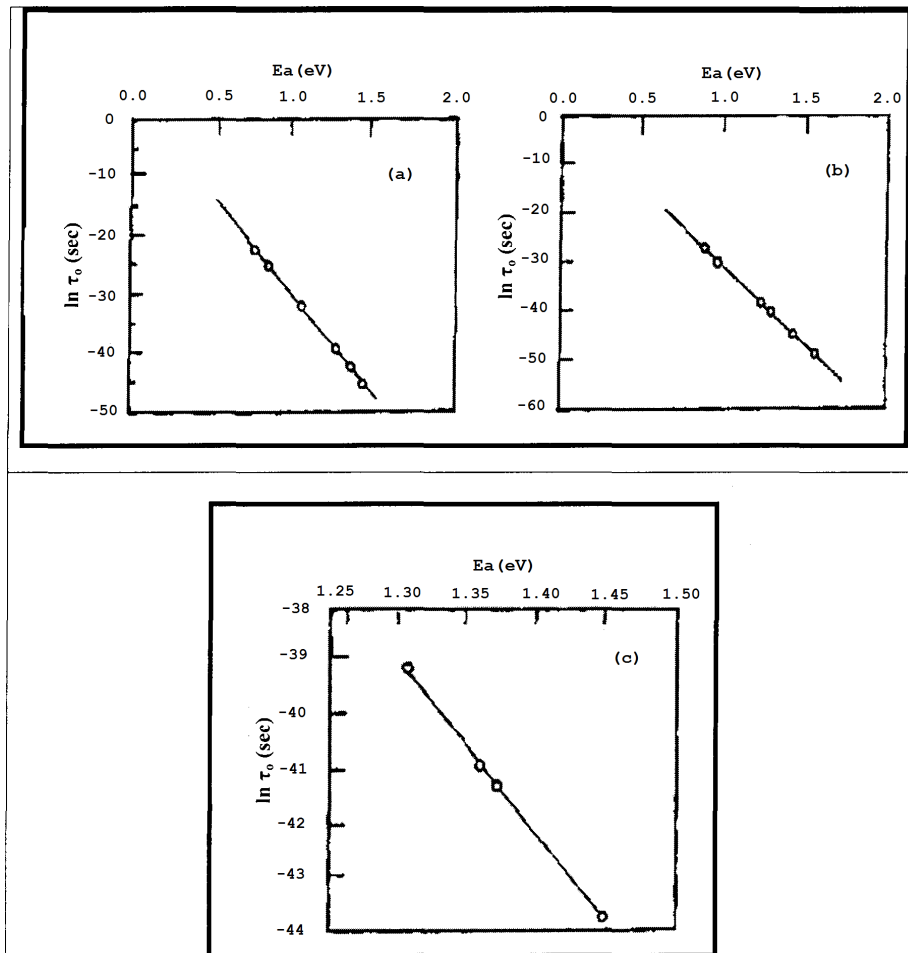
If  $\ln \tau_0 = f(E_a)$  is a linear function, the so-called compensation law is considered valid<sup>40</sup>;

$$\tau_0 = \tau_c \exp\left[-\frac{E_a(\tau)}{K_B T_c}\right] \quad (3)$$

Substitution of eq. (3) into eq. (2) gives the compensation equation:

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

where  $\tau_c$  and  $T_c$  represent compensation time and compensation temperature, respectively.



**Figure (7).** Variation of the pre-exponential factor of relaxation time ( $\tau_0$ ) vs the activation energy ( $E_a$ ) for the TS of (a) pure gelatin, (b) pure PVA and (c) 50/50 (wt/wt %) gelatin/PVA blend sample.

Fig. 7 shows a linear dependence of  $E_a$  versus  $\ln \tau_0$  for individual polymers and their blend sample, which reflects the existence of the compensation law<sup>48,49</sup>. The verification of the compensation law itself, namely the existence of a distribution of relaxation times converging towards a single one, called compensation time ( $\tau_c$ ) at compensation

temperature ( $T_c$ ), seems to be a constant feature in all the materials investigated in the present study. The value of  $\tau_c$  and  $T_c$  for homopolymers and their blend sample are calculated and presented in Table 2. It can be seen that  $T_c$  is generally around the temperature at peak maximum of TSDC (global peak) suggesting a dipolar molecular relaxation for

all samples. Nevertheless, the small difference between  $T_g$  and  $T_c$  seems to be related to the breadth of the glass transition and/or kinetic effects believed to depend on the stiffness of polymeric chains. In general, the parameters  $T_c$ ;

and  $\tau_c$  that transcribe the coupling characteristics between the different modes of relaxation are related to the properties of amorphous polymers or of amorphous regions in semicrystalline polymers<sup>50</sup>.

**Table (1).** Variation of maximum peak position ( $T_{max}$ ), activation energy ( $E_a$ ) and pre-exponential factor ( $\tau_0$ ) with polarization temperature ( $T_p$ ) for pure samples and 50/50 (wt/wt %) gelatin/PVA blend sample.

$T_p$ (K)	Gelatin			PVA			50/50 (wt/wt %)		
	$T_{max}$ (K)	$E_a$ (eV)	$\tau_0$ (sec)	$T_{max}$ (K)	$E_a$ (eV)	$\tau_0$ (sec)	$T_{max}$ (K)	$E_a$ (eV)	$\tau_0$ (sec)
308	340	0.78	$1.83 \times 10^{-10}$	326	0.87	$1.41 \times 10^{-12}$	324	1.30	$1.02 \times 10^{-17}$
313	346	0.86	$1.28 \times 10^{-11}$	332	0.96	$7.32 \times 10^{-14}$	332	1.30	$1.01 \times 10^{-17}$
318	349	1.06	$1.45 \times 10^{-14}$	334	1.21	$2.53 \times 10^{-17}$	349	1.30	$1.01 \times 10^{-17}$
323	356	1.27	$9.95 \times 10^{-18}$	340	1.26	$4.43 \times 10^{-18}$	358	1.36	$1.66 \times 10^{-18}$
328	364	1.36	$5.04 \times 10^{-19}$	342	1.40	$4.77 \times 10^{-20}$	359	1.37	$1.13 \times 10^{-18}$
333	365	1.44	$3.10 \times 10^{-20}$	348	1.54	$5.89 \times 10^{-22}$	361	1.44	$1.00 \times 10^{-19}$

**Table (2).** Compensation temperature  $T_c$  and time  $\tau_c$  for pure homopolymers and 50/50 (wt/wt %) blend sample.

Sample	$T_c$ (K)	$\tau_c$ (sec)
Gelatin	342	53.0
PVA	358	2.7
50/50 (wt/wt %)	352	40.0

## 4. Conclusion

The combined use of TSDC and TS in the study of investigated samples resulted in complementary information on the energetic and spatial distribution of charges. The TSDC studies of irradiated homopolymers and their 50/50 (wt/wt %) blend sample showed that  $\gamma$ -rays affect the shape, position and area of  $\alpha$ -relaxation peak due to dimerization of polar groups, providing new shallow and deep energy traps in the form of conjugated bonds. These allow one to argue that  $\gamma$ -irradiation induced structural changes in these materials. The experimental polarization time (45min.) is really much greater than the relaxation time  $\tau(T_{max})$  which allows the reaching of saturation state of the polarized sample.

The TS method is extremely sensitive to cooperative glass-transition like motions, and in heterogeneously relaxing systems, can resolve cooperative relaxations even; if they are only a small fraction of the overall relaxing species. The  $\alpha$ -relaxation peak, which is usually attributed to the micro-Brownian motions of the polymer backbone and is a feature of amorphous polymers or amorphous regions of semicrystalline polymers is characterized by a distribution of activation energies (compensation behavior).

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