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Investigation of Iodine-Doped Poly(Ethyl Methacrylate) Relaxation by TSDC Technique in the Vicinity of the Glass Transition Temperature

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Corona poling and thermally stimulated depolarization current (TSDC) techniques have been used to study the relaxation behavior of pure and iodine-doped poly(ethyl methacrylate) (PEMA) in the vicinity of the glass transition temperature (T_g). Different parameters, such as corona field and corona temperature, have been used. The global TSDC spectrum of pure PEMA with varying poling field and poling temperature revealed that pure PEMA is characterized by only a single relaxation peak located at $T = 349\text{ K}$. On the other hand, iodine-doped PEMA samples are characterized by two distinguished relaxation peaks. The first one has been observed in the temperature range from 347 K to 363 K , whereas, the second one has been detected at a higher temperature, $T \sim 395\text{ K}$. The origin of the TSDC peaks is attributed to a superposition of dipolar relaxation and space-charge build up. Thermal sampling (TS) technique was used to get more information about the fine structure of pure and iodine-doped PEMA samples.

Keywords: glass transition temperature, iodine doping, poly(ethyl methacrylate), TSDC

INTRODUCTION

In recent years there has been considerable interest in the study of doped polymers for their possible use in microelectronics [1–2]. Iodine is known to form polymer-halogen complexes when doped into polymers, and to affect their electrical and dielectric properties, that is, conductivity, dielectric loss, and relaxation behavior.

Corona discharge provides a good means of treating polymer surfaces, changing their physical and chemical properties. These

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modifications are mainly due to the action of activated neutral species generated by the corona discharge and carried to the sample surface by the corona wind. By their action, the polymer surface may change its conductivity and charge injection may occur into the sample bulk, and hence the relaxation processes change [3–4].

Thermally stimulated depolarization current (TSDC) has proved to be most useful in studying relaxations of polymeric materials [5–8]. In the case of TSDC bound and free charges in the material are activated by a polarizing field above room temperature, and then are frozen by cooling down the sample. The sample is then depolarized at a constant heating rate while the resulting current intensity is recorded as a function of temperature. These measurements reveal the existence of different relaxation processes, such as the dipolar α -relaxation related to the glass transition (T_g) of the material. This relaxation originates from the cooperative motion of the main polymer chain segments when they regain full mobility at T_g .

The aim of this article is to investigate the relaxation behavior of iodine-doped poly(ethyl methacrylate) (PEMA) in the vicinity of the glass transition temperature (T_g).

EXPERIMENTAL WORK

A commercial poly(ethyl methacrylate) (PEMA) obtained from Polyscience, Inc. (USA) was doped with iodine in chloroform as a common solvent and grown into films of thickness ~ 60 – $90 \mu\text{m}$ measured by a digital micrometer (Mitutoyo No: 293-521-30 Japan). The iodine concentration was varied from 0.5 wt% to 30 wt%. The solvent was eliminated in an oven, keeping the temperature at $\sim 323 \text{ K}$ for several days. Carbon paste (Kontakt-chemie, Germany) was used as a conducting electrode with a cross-sectional area of 1 cm^2 .

The method of measuring the thermally stimulated discharge current (TSDC) was already published elsewhere [5–7]. The experimental set-up was designed and built in the authors' laboratory. The sample is placed between two metallic disks used as the plates of a capacitor, made of brass. For TSDC measurements, an electric polarized field, E_p , is applied to the sample at a constant temperature, T_p , during a polarizing time, t_p . With the electric field still applied the sample is cooled down to a temperature, T_0 , sufficiently low to prevent depolarization by thermal agitation. The field is then switched off and the electrodes short-circuited for a certain time to remove stray charges. The TSDC spectra was obtained by reheating the sample at a constant heating rate, $\beta = 3 \text{ K/min}$. The current was measured by using a Keithley Electrometer Model 610.

Thermal sampling (TS) technique consists of “sampling” the relaxation processes within a narrow temperature range by polarizing at a temperature, T_p , and depolarizing at T_d , a few degrees lower than T_p . TS measurements were carried out as follows. An electric field, E_p , is applied to the sample at polarizing temperature, T_p , for certain time, t_p . After that, the sample is cooled rapidly to a temperature that was 5 K lower than T_p . At this temperature, T_d , the field is removed and the sample is short-circuited for certain time, and rapidly cooled again to a temperature that is 30 K lower than T_p . Finally, The TS current was recorded by reheating the sample at a constant heating rate, $\beta = 3$ K/min. In each TS scan only a fraction of the dipoles were polarized, characterized by values of τ_0 and E_α giving relaxation times of the order of the time scale of the experiment for temperatures in the polarization window $T_p - T_d = 5$ K. Thus, for each TS scan the TSDC peak obtained can be assumed to be a single relaxation process characterized by single values of activation energy (E_a) and pre-exponential factor τ_0 .

Pure PEMA and iodine-doped PEMA samples were poled with a corona triode method in atmospheric air. The corona voltage (V_{co}) was kept at -6 kV and the grid voltage (V_g) was variable. The grid was kept about 4 mm from the film. The corona charging process was carried with different conditions such as grid voltage and corona temperature (T_{co}).

RESULTS AND DISCUSSION

TSDC Study

Figure (1a) represents a family of TSDC thermograms for temperatures above room temperature of conventionally polarized PEMA electrets. The polarization conditions such as grid voltage (V_g) and corona temperatures (T_{co}) have been chosen to investigate the α -relaxation. As shown in the figure, global spectrum of pure PEMA is characterized by only a single relaxation peak located at $T = 349$ K, in the vicinity of the glass transition temperature of pure PEMA, which is $T_g \sim 344$ K [6,9]. This peak is often seen as a result of disorientation of polar groups in a polymer. This disorientation results from the molecular motion at the α -relaxation peak, corresponding to the glass-rubber transition temperature (T_g), and is the most intense relaxation due to the amorphous character of the polymer. The dipoles reorientation starts as soon as the cooperative motions create enough freedom. The activation energy (E_a) associated with this relaxation peak has been calculated using the initial rise method [10], namely by plotting $\log I$

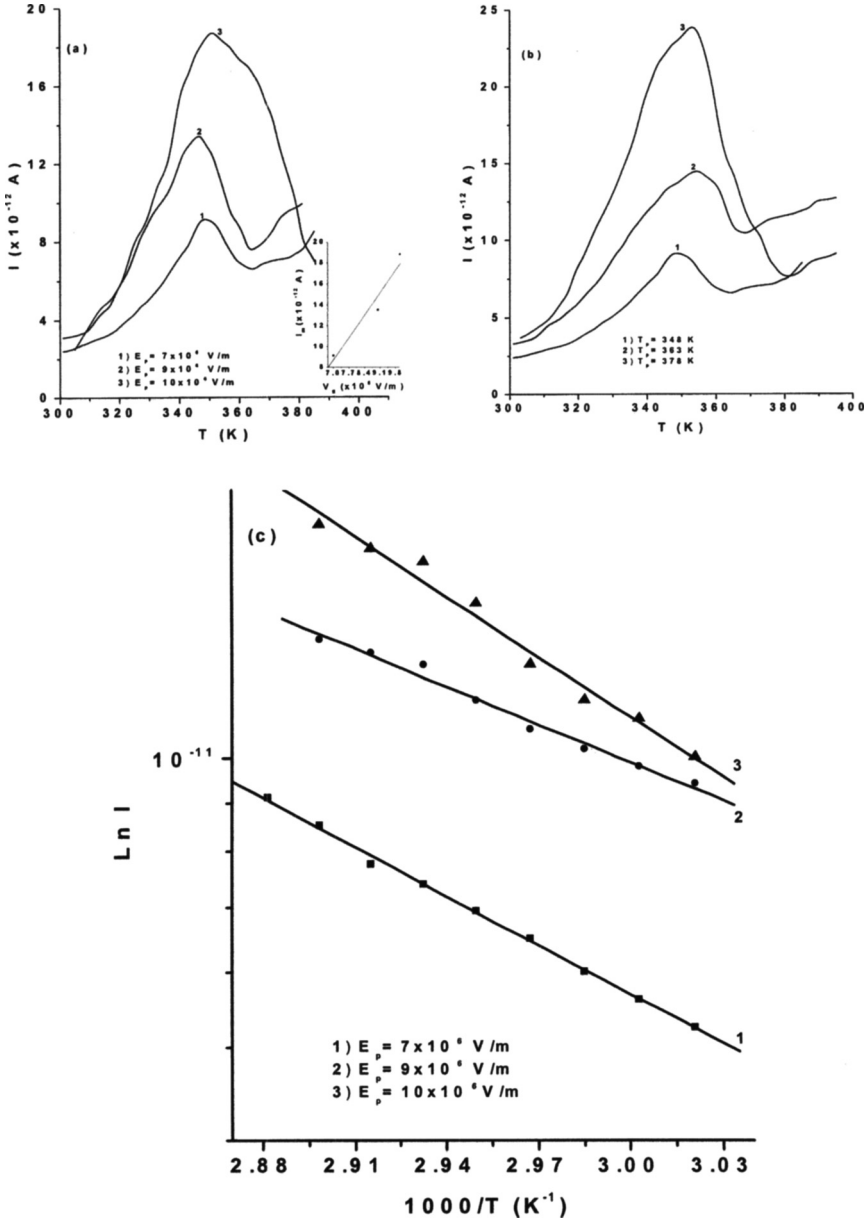


FIGURE 1 (a) TSDC spectra from a negatively corona-changed PEMA sample, $V_{co} = -6$ kV, $T_{co} = 345$ K and $t_{co} = 15$ min. Heating rate $\beta = 3$ K/min, carbon paste was used as a conducting electrode, (b) TSDC of a negatively corona-charged PEMA sample at different corona temperatures. (c) $\ln I$ versus $1000/T$ for pure PEMA at different poling fields.

TABLE 1 Peak Parameters Characterizing PEMA and Iodine-Doped PEMA Samples from TSDC Measurements

| Sample | 1st peak | | | | 2nd peak | | |
|--------|------------------|-----------|------------|-----------------------|-----------|------------|-----------------------|
| | E_p (V/m) | T_m (K) | E_a (eV) | τ_o (sec) | T_m (K) | E_a (eV) | τ_o (sec) |
| Pure | 7×10^6 | 349 | 0.14 | 2.59×10^{-1} | — | — | — |
| PEMA | 9×10^6 | 353 | 0.14 | 1.98×10^{-1} | — | — | — |
| | 10×10^6 | 353 | 0.18 | 5.33×10^{-2} | — | — | — |
| 5 wt% | 1×10^6 | 359 | 0.13 | 5.04×10^{-1} | 389 | 0.24 | 1.23×10^{-2} |
| | 7×10^6 | 359 | 0.17 | 7.41×10^{-2} | 381 | 0.12 | 9.06×10^{-1} |
| | 10×10^6 | 357 | 0.21 | 1.40×10^{-1} | 401 | 0.23 | 3.02×10^{-2} |
| 15 wt% | 1×10^6 | 363 | 0.21 | 1.63×10^{-2} | 399 | 0.36 | 2.95×10^{-4} |
| | 3×10^6 | 359 | 0.11 | 9.16×10^{-1} | 405 | 0.37 | 3.11×10^{-4} |
| | 5×10^6 | 359 | 0.17 | 9.64×10^{-2} | 399 | 0.49 | 4.69×10^{-6} |
| | 10×10^6 | 363 | 0.22 | 1.08×10^{-2} | 409 | 0.32 | 1.64×10^{-3} |

versus $1/T$ from the initial rising portion of the curve, as shown in the Figure 1(c). The activation energy values from the slopes of these curves were calculated and are listed in Table 1. Figure 1(b) indicates that with the rise of the charging temperature the relaxation peak shifted to the higher temperature side. This is because carriers in donor-like states are already activated by thermal energy while the charging temperature is increased and are then retrapped at an energetically deeper level [11].

Iodine may go substitutionally into the polymer chains or reside at the amorphous/crystalline boundaries and diffuse preferentially through the amorphous regions forming charge transfer complexes (CTC), or it may exist in the form of molecular aggregates between the polymer chains [12]. Figure 2(a & b) depicts the global TSDC of pure and iodine-doped PEMA samples, which were polarized under identical conditions, in case of corona poling and TSDC. The spectrum of pure PEMA is significantly affected by the presence of iodine. The position, intensity, and slope of this peak all changed on doping with iodine. The change in the α -peak position can be attributed to the iodine-polymer interaction. The activation energy values for all samples were estimated and found to be in the range of 0.09, 0.12, 0.20, and 0.22 eV in the case of conventional TSDC, whereas 0.14, 0.14, 0.17, and 0.34 eV in the case of corona poling, for the pure PEMA, 2.5, 5, and 15 wt% doped samples, respectively. This behavior indicates that iodine may form aggregates in PEMA at higher concentrations. Hence, the observed effects of iodine may be explained on the basis of formation of charge transfer complexes. It is known that doping of polymers with halogen results in the formation of donor-acceptor type

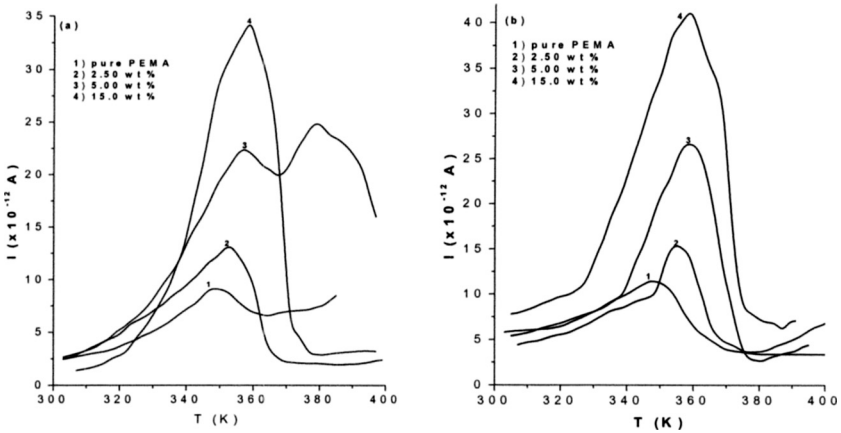


FIGURE 2 (a) TSDC spectra from a negatively corona-charged PEMA and different iodine-doped PEMA samples, $V_{co} = -6$ kV, $T_{co} = 345$ K and $t_{co} = 15$ min. Heating rate $\beta = 3$ K/min, carbon paste was used as a conducting electrode. (b) Conventional TSDC of PEMA and different iodine-doped PEMA samples.

complexes, which bring about change in their electrical and dielectric behavior [13].

Two different doped samples (5 wt% and 15 wt%) were chosen to investigate the global TSDC spectra in detail. Figure 3(a & b) represents a family of TSDC thermograms studied at a fixed corona polarization temperature of $T_{co} = 348$ K for a polarization time of 15 min with different polarization fields. All samples exhibit more or less the same behavior. The asymmetry of global TSDC spectra may be attributed to the distribution function of relaxation times because of the various processes involved. Each sample is characterized by two distinguished relaxation peaks. From the point of view of surface modification, it has been proposed that the corona irradiation of a polymer film has the effect of producing bond breaking and the creation of polar groups. Therefore, the discharge currents could be attributed to the presence of a dipolar relaxation and space-charge build-up during polarization. The first peak, which was detected in the low temperature region, can be attributed to dipolar relaxation, that is, α -relaxation. On the other hand, the second peak located at higher temperatures, can be attributed to space-charge polarization, that is, ρ -relaxation. Further, it was found that the peak position is iodine concentration dependent. The activation energy E_a associated with these relaxation peaks has been calculated as shown in Figure 3 (c-f). All

the molecular parameters characterizing these samples such as E_a and τ_0 are estimated and listed in Table 1.

To know the dominant mechanism of polarization one needs to analyze the TSDC peak data in terms of the polarization parameters. For example, it is known that in the case of dipolar polarization, the

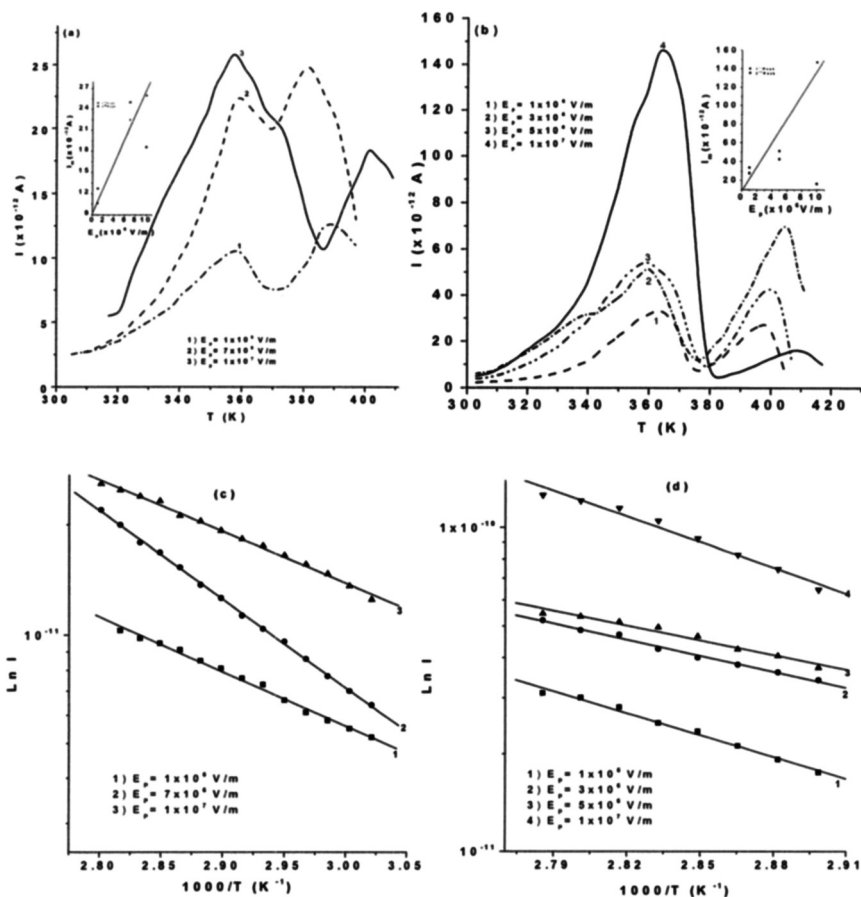


FIGURE 3 TSDC spectra from a negatively corona-charged (a) 5 wt% iodine-doped PEMA, (b) 15 wt% iodine-doped PEMA, $T_{co} = 348$ K, $t = 15$ min. (c–d) $\ln I$ versus $1000/T$ for 5 wt% and 15% wt iodine-doped PEMA for 1st peak at different poling fields. (e–f) $\ln I$ versus $1000/T$ for 5 wt% and 15% wt iodine-doped PEMA for 2nd peak at different poling fields. (g) Effect of corona temperature (T_{co}) on global TSDC of 5 wt% iodine-doped PEMA. $E_p = 7 \times 10^6$ V/m, $t = 15$ min and heating rate $\beta = 3$ K/min, carbon paste was used as a conducting electrode.

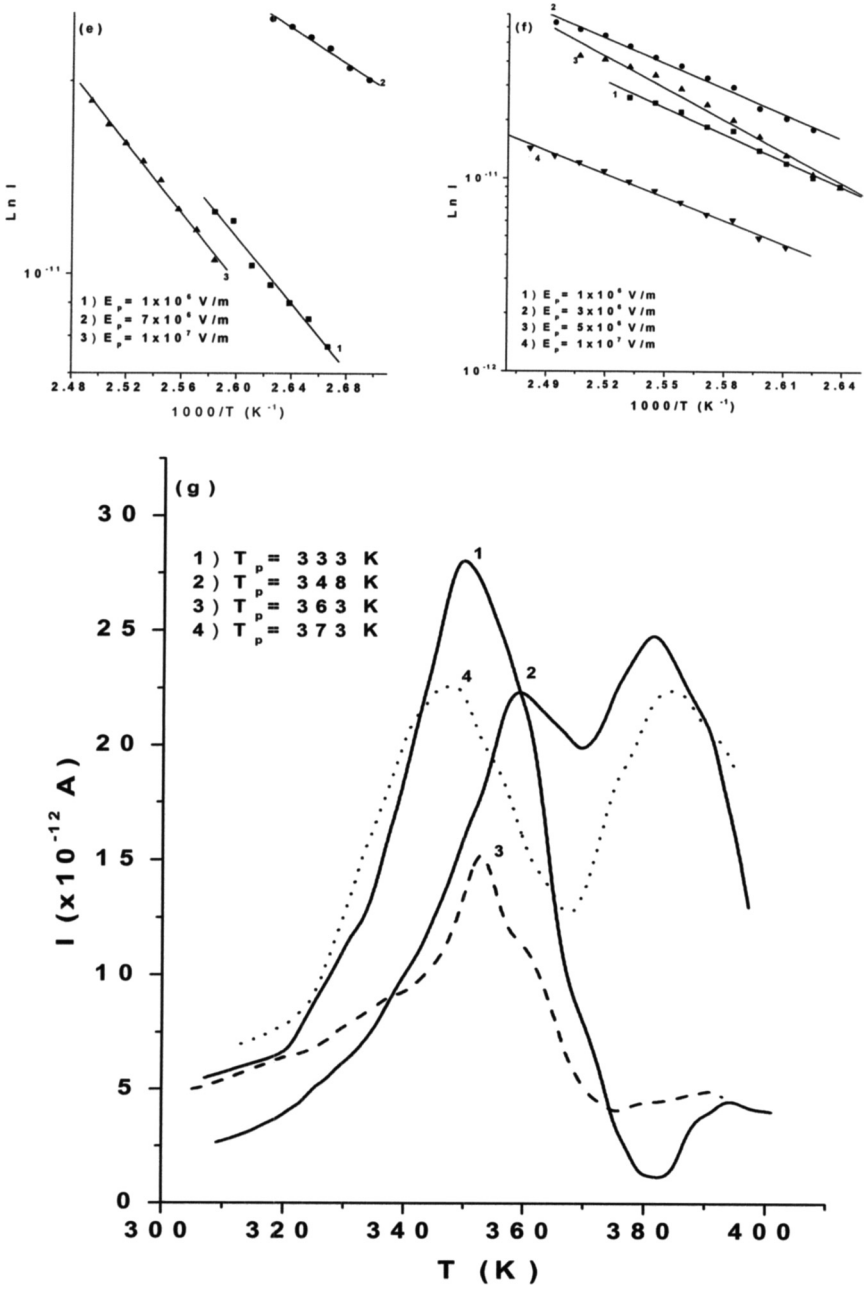


FIGURE 3 Continued.

current associated with the relaxation peak varies linearly with the polarization field, whereas, in the case of space-charge polarization, the current varies nonlinearly with the polarization field. Thus the TSDC spectra were investigated for various electric fields for the two iodine-doped PEMA samples, as shown in Figure 3(a & b). The peak current associated with the first peak increases linearly with the polarization field, whereas, the peak current associated to the second relaxation peak deviated from this linearity, as shown in the figure. Thus it is concluded that the spectrum is a result of a superposition of dipole orientation and space charge effects.

Figure (3g) shows the global TSDC spectrum of a 5 wt% iodine-doped sample corona poled at different poling temperatures (T_{co}). The position of the first peak was slightly shifted toward the higher temperature side. The shift of the position was from 349 K to 353 K. This behavior is commonly observed in dipolar TSDC, in which the peak shifts when $T_p < T_g$ and does not shift for $T_p > T_g$ [14,4].

TS Study

In summary, the global TSDC spectrum is often too broad to be attributed to a single relaxation frequency. The TSDC study points to a superposition of dipole orientation and space charge effects. The investigation of the complete TSDC spectrum shows the existence of various relaxation modes in the iodine-doped PEMA samples. Hence, this spectrum can be considered as a complex one, and only its resolution can provide information on the various processes. Such a resolution could be performed by the TS technique [15]. The application of TS technique results in quasi-nondistributed peaks, so that interpretation of the resulting spectra is easier than the depolarization discharge, which is obtained from a conventionally polarized electret. It has been used, with a temperature window, $T_w = T_p - T_d = 5K$, to decompose the whole TSDC spectrum into elementary contributions, as shown in Figure 4.

When the TS technique is used to form the electrets, only the fraction corresponding to the range of trapping depth (E_a) is filled with carriers, which are not in thermal equilibrium due to the effect of the electric field during the polarization process. This fraction is dependent on the polarization temperature and on the window width. These carriers, not in equilibrium, are the ones that give rise to the depolarization current when they are thermally stimulated to relax to the equilibrium state, which corresponds to a depolarized sample. The TS peaks are somewhat broader than for a Debye relaxation, as shown in Figure 4. Such broadness is frequently observed in polymeric materials and can be explained as a consequence of the coupling between

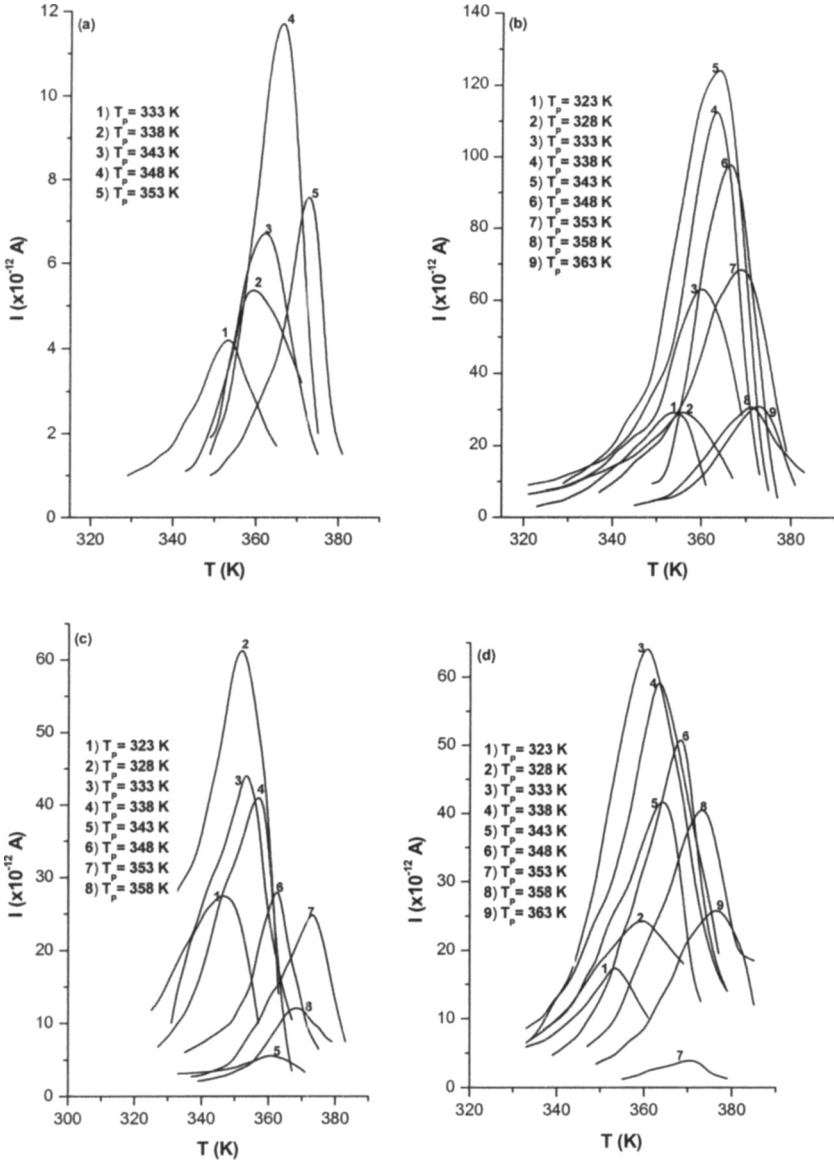


FIGURE 4 Elementary TS spectra: (a) Pure PEMA, (b) 0.5 wt% iodine-doped PEMA, (c) 5 wt% iodine-doped PEMA, and (d) 15 wt% iodine-doped PEMA.

relaxation times belonging to a broad distribution of relaxation times or due to the interaction of different modes of relaxation [5,16–17].

As is well known, these peaks correspond to different relaxation modes, and it seems that the relaxation time in each peak is distributed over a fairly wide range. The pre-exponential factor τ_0 was calculated by using Eq. 1, assuming that each TS peak is due to a dipole with a single relaxation time [18]:

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

where T_{\max} is the temperature at the maximum of a TS peak, k_B is the Boltzmann's constant, β is the rate of heating, and E_a is the activation energy. The temperature dependence of τ_0 should then obey the Arrhenius equation as follows

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

This equation governs either the rotation of permanent dipoles or the localized hopping between neighboring potential wells, which may be associated with the presence of defects inside the matrix [19]. All the molecular parameters characterizing these samples, such as the activation energy (E_a) and pre-exponential factor (τ_0), have been calculated and are listed in Table 2. The values of pre-exponential factors do not correspond to the classical Debye relaxation time (10^{-13} – 10^{-14} s). This result has also been published elsewhere [20] in the case of the α -relaxation of PVC. In the case of the α -relaxation in amorphous polymers this fact is interpreted as a result of the cooperative character of the molecular motion associated with the glass transition temperature.

Experimentally, a compensation law between τ_0 and E_a is observed that obeys

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

where τ_c and T_c are adjustable parameters with no clear physical sense [21]. Using this definition the expression for the introduced time factor becomes

$$\tau(T) = \tau_0 \exp\left[\frac{E_a}{k_B} \left(\frac{1}{T} - \frac{1}{T_c}\right)\right] \quad (4)$$

This expression was introduced for kinetic first order [22]. In Figure 5, τ_0 is illustrated as a function of the activation energy E_a for pure

TABLE 2 Peak Parameters Characterizing PEMA and Iodine-Doped PEMA Samples from TS Peaks

| Sample | Polarization | Window | T_m (K) | E_a (eV) | τ_0 (sec) |
|---------|--------------|--------|-----------|------------|-----------------------|
| PEMA | 323 | 318 | 353 | 0.287 | 9.98×10^{-4} |
| | 328 | 323 | 359 | 0.539 | 1.89×10^{-7} |
| | 333 | 328 | 363 | 0.402 | 2.43×10^{-5} |
| | 338 | 333 | 367 | 0.565 | 1.18×10^{-7} |
| | 343 | 338 | 371 | 0.469 | 3.61×10^{-6} |
| 0.5 wt% | 323 | 318 | 353 | 0.288 | 9.67×10^{-4} |
| | 328 | 323 | 355 | 0.216 | 1.42×10^{-2} |
| | 333 | 328 | 359 | 0.408 | 1.6×10^{-5} |
| | 338 | 333 | 363 | 0.464 | 2.49×10^{-6} |
| | 343 | 338 | 365 | 0.488 | 1.45×10^{-6} |
| | 348 | 343 | 367 | 0.513 | 6.87×10^{-7} |
| | 353 | 348 | 369 | 0.353 | 1.65×10^{-4} |
| | 358 | 353 | 371 | 0.398 | 3.84×10^{-5} |
| | 363 | 358 | 373 | 0.461 | 5.11×10^{-6} |
| 5 wt% | 323 | 318 | 347 | 0.120 | 5.26×10^{-1} |
| | 328 | 323 | 351 | 0.200 | 2.38×10^{-2} |
| | 333 | 328 | 353 | 0.192 | 3.36×10^{-2} |
| | 338 | 333 | 357 | 0.213 | 1.70×10^{-2} |
| | 343 | 338 | 361 | 0.140 | 2.92×10^{-1} |
| | 348 | 343 | 363 | 0.335 | 2.50×10^{-4} |
| | 353 | 348 | 369 | 0.394 | 4.15×10^{-5} |
| | 358 | 353 | 373 | 0.287 | 1.85×10^{-3} |
| | 363 | 358 | 373 | 0.332 | 3.71×10^{-4} |
| 15 wt% | 323 | 318 | 353 | 0.276 | 1.49×10^{-3} |
| | 328 | 323 | 359 | 0.227 | 1.04×10^{-2} |
| | 333 | 328 | 361 | 0.388 | 3.72×10^{-5} |
| | 338 | 333 | 363 | 0.335 | 2.50×10^{-4} |
| | 343 | 338 | 365 | 0.243 | 5.95×10^{-3} |
| | 348 | 343 | 369 | 0.376 | 7.13×10^{-5} |
| | 353 | 348 | 371 | 0.370 | 9.45×10^{-5} |
| | 358 | 353 | 373 | 0.332 | 3.71×10^{-4} |
| | 363 | 358 | 377 | 0.323 | 5.32×10^{-4} |

PEMA and 15 wt% iodine-doped sample as representative curves. There is a strict linear relationship between $\ln \tau_0$ and E_a . Such a linear relationship between the activation energy and the logarithm of the pre-exponential factor of relaxation time is known as the compensation law and has been observed experimentally in many polymers [5–6,23]. The most interesting outcome to be drawn from this figure is that the relaxation results of all investigated materials obey a single relaxation process in the vicinity of the glass transition region, that is, all elementary processes can be ascribed to a dipolar polarization associated with micro-Brownian motion in the amorphous phase. The compensation parameters such as τ_c and T_c are estimated and listed in

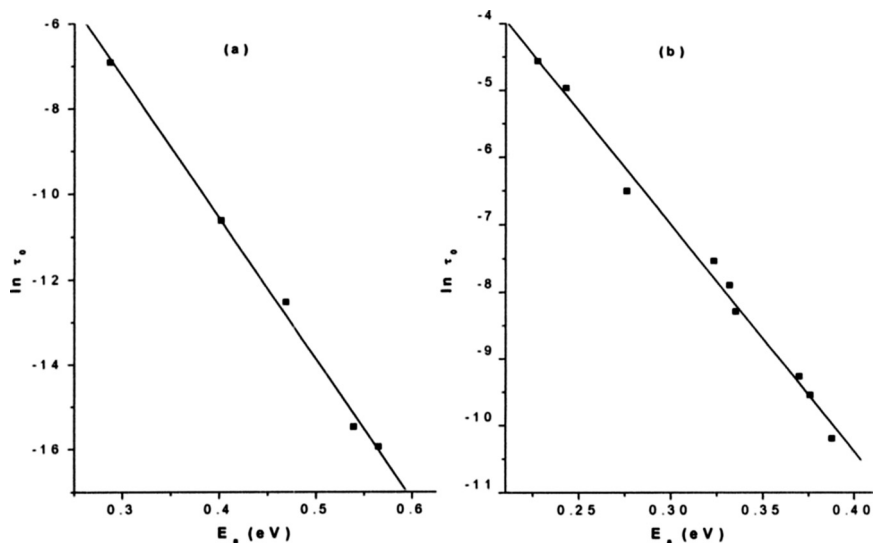


FIGURE 5 Relationship between pre-exponential factor (τ_0) versus activation energy (E_a) of (a) Pure PEMA and (b) 15 wt% iodine-doped PEMA.

Table 3. The compensation temperature can be related to the transfer of heat in agreement with the idea developed by Peacock-Lopez et al. [24], who suggested that T_c is characteristic of the heat transfer between the thermal bath and the polymer chain.

Shift Factor

At a temperature above the T_g of an amorphous material, when the volume is in thermal equilibrium, the α -relaxation time has always been observed to follow the Williams-Landel-Ferry (WLF) equation [25–26]. According to the WLF equation the *ith* relaxation times at

TABLE 3 The Characteristic Values of Compensation Parameters, that is, T_c and τ_c of Pure PEMA and Iodine-Doped PEMA Samples

| Sample | T_c (K) | τ_c (sec) |
|-----------|-----------|----------------|
| Pure PEMA | 349.00 | 14.49 |
| 0.5 wt% | 348.86 | 17.46 |
| 5 wt% | 336.70 | 29.37 |
| 15 wt% | 342.62 | 23.33 |

temperatures T and T_0 take the values τ^i and τ_0^i , so that

$$\tau^i = a_T \tau_0^i \quad (5)$$

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (6)$$

where C_1 and C_2 are constants. The quantity a_T reflects primarily the temperature dependence of the friction coefficient of the chain segments, on which the rate of conformational rearrangement depends. The distribution occurs because the τ_0^i are broad. The shift factor a_T is the same for all relaxation times.

The Kovacs-Hutchinson-Aklonis (KHA) equation [27] is very useful for studying the kinetics of the α -relaxation process for $T < T_g + 10$ K. The temperature and structure dependence of the i th process is given by

$$\tau^i = A \exp\left(\frac{\Delta H^i}{RT} + \frac{b}{f_T}\right) \quad (7)$$

in which ΔH is the activation enthalpy of the i th process, A and b are characteristic material constants and

$$f_T = f_g + \Delta\alpha(T - T_g) \quad (8)$$

where f_T is the fractional free volume, f_g is the fractional free volume at the T_g and $\Delta\alpha$ is the expansion coefficient. For $T < T_g$, it is presumed that the structure does not change, so that f_g the frozen-in free volume. In this case, at temperatures T and T_0 below T_g

$$\ln a_T = \frac{\Delta H^i}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) + b \left(\frac{1}{f_T} - \frac{1}{f_{T_0}}\right) \quad (9)$$

In this case T affects $\ln a_T$ directly by the first term on the right-hand side and by indirect control of the structure, as represented by the free volume f_T in the second term.

The relaxation times τ were calculated according to Eq. 2. Then the ratios a_T of the electrical relaxation times at temperature T to their values at $T_0 = T_m = T_g$ were evaluated. Figure 6 illustrates the dependence of the shift factor a_T on the temperature for the α -relaxation distribution in the investigated materials according to Eq. 9. It is clear that all the curves intersect at $T \sim T_m$ but differ greatly in nature. The distribution changes shape so that at the merge point all the relaxation times τ take the same value τ_g . This leads to the conclusion that all the processes have the same relaxation time at T_g and hence all the chain molecules of each specimen have the same random coil configuration.

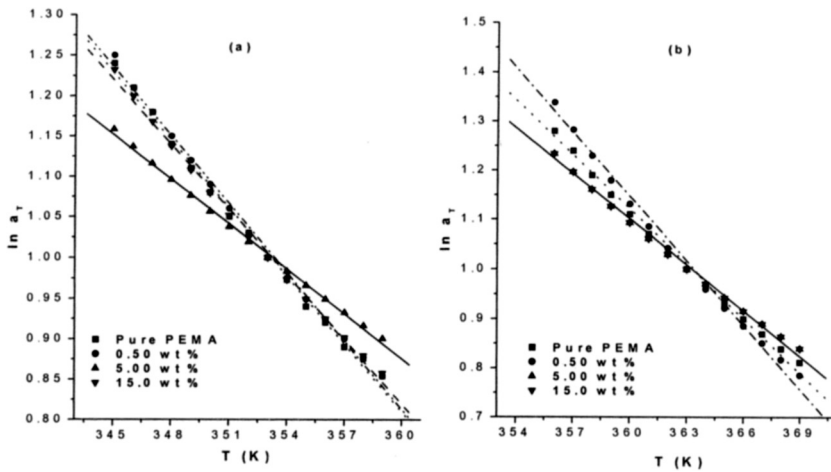


FIGURE 6 Illustration of the temperature dependence according to the Eq. 9 of the shift factor a_T two different temperatures.

CONCLUSION

Corona poling and TSDC techniques have been used to investigate the influence of iodine on the global TSDC spectrum of PEMA at different poling parameters such as poling field and poling temperature. The TSDC manifestation of the glass transition is evidenced by a depolarization current peak. Hence, it was observed that TSDC spectrum of pure PEMA is characterized by a single relaxation peak at $T = 349$ K. This peak is termed as dipolar α -relaxation peak and could be attributed to the mainchain motion. On the other hand, the iodine-doped PEMA samples are characterized by two different relaxation peaks. The first peak is located in the temperature range from 349 K to 363 K, whereas the second one is observed at $T \sim 395$ K. Hence, this global spectrum of iodine-doped samples could be attributed to a superposition of dipolar relaxation and space-charge relaxation processes. TSDC spectrum of PEMA and iodine doped samples in the temperature range that corresponds to α -relaxation can be resolved if the electrets are formed by using thermal sampling techniques.

REFERENCES

- [1] Pai, D. M., *J. Non-Cryst. Solids* **59/60**, 1255 (1983).
- [2] Korzhenko, A. A., Tabellout, M., Wmery, J. R., Pud, A. A., Rogalsky, S., and Shapoval, G. S., *Synth. Metals* **98**, 157 (1998).

- [3] Migahed, M. D., Abdel-Hamid, M. I., and Abo El Wafa, A. M., *Polym. Testing* **20**, 805 (2001).
- [4] Fahmy, T., *Inter. J. Polym. Mater.* **54**, 183 (2005).
- [5] Migahed, M. D. and Fahmy, T., *Polymer* **35**, 1688 (1994).
- [6] Ahmed, M. T. and Fahmy, T., *Polym. Testing* **18**, 589 (1999).
- [7] Fahmy, T. and Ahmed, M. T., *Polym. Inter.* **49**, 669 (2000).
- [8] Fahmy, T. and Ahmed, M. T., *Polym. Testing* **20**, 477 (2000).
- [9] Perrin, P. and Prude' homme, E. R., *Polymer* **32**, 1468 (1991).
- [10] Garlick, B. J. and Gibson, A. F., *Proc. Phys. Soc.* **60**, 574 (1948).
- [11] Chen, R. and Kirsh, Y. (1981). *Analysis of Thermally Stimulated Processes*, Pergamon Press, Oxford.
- [12] Ahmed, M. T. and Fahmy, T., *J. Polym. Mater.* **17**, 138 (2000).
- [13] Chand, S., Radhakrishnan, S., and Mehendru, P. C., *J. Phys. D: Appl. Phys.* **51**, 2499 (1982).
- [14] Hundal, J. S. and Nath, R., *J. Phys. D: Appl. Phys.* **31**, 482 (1998).
- [15] Mudarra, M., Belana, J., Canadas, J. C., Diego, J. A., *J. Polym. Sci. Part B, Polym. Phys.* **36**, 1971 (1998).
- [16] Migahed, M. D., Ishra, M., El-Khodary, A., and Fahmy, T., *Polym. Testing* **12**, 3355 (1993).
- [17] Zienlinski, M. and Kryszewski, M., *Phys. Status Solidi.* **A42**, 305 (1977).
- [18] Perlman, M. M., *J. Appl. Phys.* **24**, 2645 (1971).
- [19] Sayer, M., Mansingh, A., Webb, B., and Noad, J., *J. Phys. C: Solid State Phys.* **11**, 315 (1978).
- [20] del Val, J. J., Algeria, A., Colmenero, J., and Barandiam, J. M., *Polymer* **27**, 1771 (1986).
- [21] Mudarra, M., Belana, J., Canadas, J. C., and Diego, J. A., *J. Polym. Sci. Part B, Polym. Phys.* **36**, 1971 (1998).
- [22] Lacabanne, C., Chatain, D. G., Monpagens, J. C., Hiltner, A., and Baer, E., *Solid State Commun.* **27**, 1055 (1978).
- [23] Mudarra, M. and Belana, J., *Polymer* **38**, 5815 (1997).
- [24] Peacock-Lopez, E. and Suhl, H., *Phys. Rev.* **B26**, 3774 (1982).
- [25] Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M., and Ramos, A. R., *J. Polym. Sci. Polym. Phys. Ed.* **17**, 1097 (1979).
- [26] Williams, M. L., Landel, R. F., and Ferry, J. D., *J. Am. Chem. Soc.* **77**, 3701 (1955).
- [27] Kovacs, A. J., Hutchinson, J. M., and Aklonis, J. J. (1978). *The Structure of Non-Crystalline Materials*, Wiley, New York.