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Rate Theory and Relaxation Map Analysis of Iodine-Doped Poly(Ethyl Methacrylate) composite films using Thermally Stimulated Depolarization Current-Thermal Sampling (TSDC-TS) Technique

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Abstract

Iodine-doped Poly (Ethyl Methacrylate) composites have been prepared using casting method. Global TSDC of the composite samples has been investigated using TSDC-TS technique. It is found that, global TSDC spectra of pure PEMA are characterized by two relaxations. The first relaxation which is observed as a shoulder in the temperature range 324-333 K is attributed to the motion of side group and named β-relaxation. Whereas, the second relaxation is observed in the glass temperature range of PEMA at $T_m = 347$ K and named as dipolar relaxation, i.e., α-relaxation. On doping with iodine, a new relaxation peak has been obtained at high temperatures ~ 397-409 K, and named as space charge relaxation, i.e., ρ-relaxation. Complex TSDC spectra of PEMA-Iodine composites have been resolved into its elementary peaks using TS technique. These elementary peaks have been used to construct relaxation map (RM) of all samples using Eyring transformation. The existence of compensation phenomenon for all samples is also verified and the coordinates of each compensation point have been estimated. These coordinates are used to calculate the density of disorder (DOD) and thermal expansion coefficient of the samples. The thermodynamic parameters of the samples, such as, enthalpy, entropy and Gibbs free energy have been calculated at different poling temperatures.

Keywords: PEMA - Iodine - Composite, TSDC-TS - Relaxation map – Rate Theory - Compensation temperature.

1. Introduction

Poly (ethyl methacrylate), PEMA is a methacrylic ester polymer. PEMA has high surface resistance, high optical transparency and excellent chemical resistance. Doping of polymers with halogen dopants (I, Br, Cl) for electronic devices fabrication is currently attracted more attention in the research area. Iodine doping is more promising because it does not induce any polymer degradation. Iodine is an attractive dopant because it can be diffused into a polymer chain and reacts reversibly to form I_3^- or I_5^-, donating a hole to the material forming charge transfer complexes [1].

Thermally stimulated depolarization currents technique is applied to investigate the electrical properties of polymeric materials and their changes when are exposed to treatments that lead to formative changes. TSDC method is highly sensitive to probe the motions of polar groups or space charges in polymers [2-7]. TSDC is useful in the investigation of polymers to supply us valuable information about extent of mixing between the two individual components and the molecular reaction. It is a powerful technique because of its low equivalent frequency ~ 10^{-3} Hz and its ability to decompose complicated dielectric relaxation behaviour. Relaxation behaviour in polymeric materials is usually interpreted in terms of relaxation time distribution, so that TSDC global spectrum analysis is carried out by fitting the parameter associated to symmetry and shape of relaxation times distribution that characterize these patterns [8-10]. To decompose complex TSDC spectra experimentally and hence, relaxation times distribution, thermal sampling (TS) method has been used, demonstrating the ability of decomposing complex TSDC spectrum into elementary peaks with narrow range of distribution of relaxations [11-15]. The parameters of the elementary peaks such as, relaxation time and activation energy values enable the construction of the so-called

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relaxation map (RM) and calculate the coordinates of the compensation point, i.e., compensation temperature and relaxation time, (T_c and τ_c) [16-17].

Many researchers have studied the relaxation behaviour of polymer blends and polymer composites using different techniques such as, dielectric relaxation spectroscopy (DRS) or TSDC techniques [18-22]. Relaxation map of polymer blends such as, PVC/NBR and PVC/PEMA polyblends has been investigated previously using TSDC technique [23-25]. This investigation revealed that, PVC/PEMA polyblend samples are partially compatible to each other and characterizing by two compensation temperatures, whereas, PVC/NBR polyblend samples are compatible to each other and characterizing by one compensation temperature. Analysis of relaxation map of dye-doped polymer such as, Azodye/ABS doped samples has been studied revealing that these doped samples are characterized by one compensation temperature in the vicinity of ABS glass transition temperature [10].

It is worth noting that not many studies have examined the phenomenon of relaxation of PEMA polymer in the literature. Studying the relaxation phenomenon of PEMA doped with iodine will provide new addition and information in this field. So, the main purpose of this manuscript is to investigate the dependence of TSDC behavior of PEMA on the doping ratio of iodine in a wide range of temperature from 300 to ~ 410 K and to construct relaxation map (RM) of PEMA-Iodine composite using TSDC-TS method. We will take the advantage of TSDC-RMA approach throughout this work to estimate all the molecular parameters of PEMA-Iodine composites.

2. Experimental Work

Poly (ethyl methacylate) (PEMA) with a molecular weight, M_w= 340,000 and Iodine with molecular weight, M_w= 253 have been supplied from Merck. PEMA-Iodine doped samples have been prepared using casting method in chloroform as a common solvent. TSDC technique is already published elsewhere and is carried out using a built in setup in the author's laboratory [23]. The samples are placed between two metal discs used as condenser plates, made of copper. Measurements of TSDC are performed by applying an electric field, E_p, on the samples for certain polarizing time, t_p at 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, β=3K/min and Keithley Electrometer, Model 610C is used to record the current during the heating process. To decompose complex TSDC spectrum into its elementary peaks, thermal sampling technique will be used, because only a small part of relaxation will be detected. Measurements of TS are performed as shown in Figure 1.
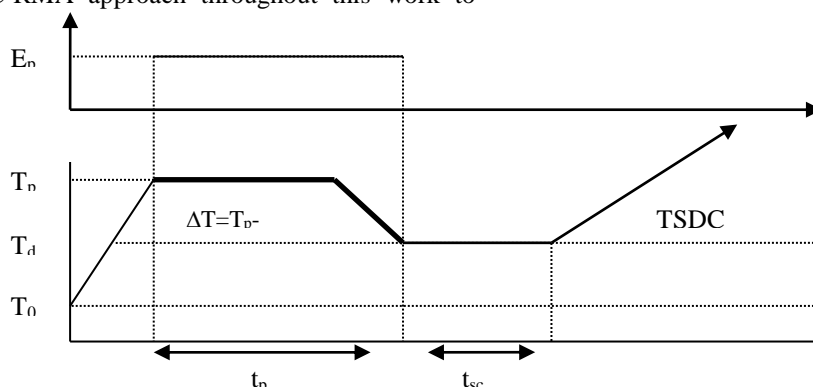

Fig. 1: Schematic diagram of TS technique.

The sample is polarized by applying an electric field, E_p, for certain time, t_p at polarizing temperature, T_p. Then, the sample temperature is quickly dropped to a depolarization temperature, T_d lower than T_p by 5K. The electric field will be turned off at this temperature, and the sample will be short-circuited for 15 min, and is quickly cooled back in ice-water to a temperature lower than T_p by 30 K. Hence, by warming the sample again, TS current is recorded with almost constant heating rate, β=3K/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 single relaxation process is obtained in each polarization window, T_p-T_d= 5K. Corona triode method has been used in the atmospheric air for poling the samples of PEMA-Iodine doped. The corona voltage is applied at ~ -6 kV with variable grid voltage. During the poling process, the grid is fixed at a distance from the sample surface ~ 4mm.

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3. Results and Discussion
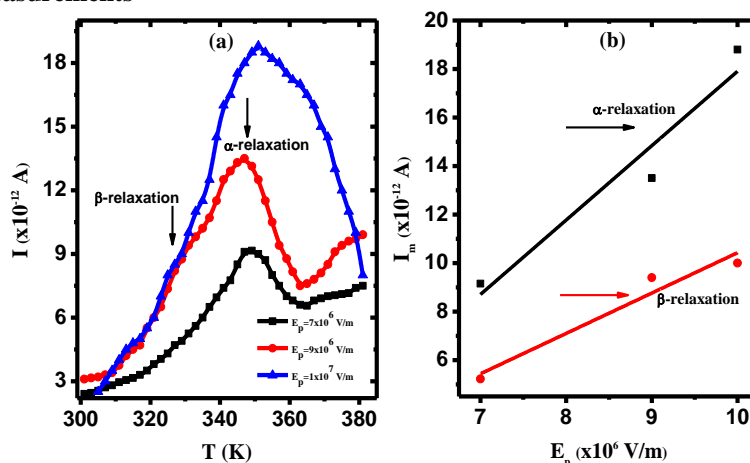### 3.1 Global TSDC measurements

Fig. 2: a) TSDC of pure PEMA at different electric fields, T_p= 345 K, t_p= 15 min and carbon paste is used as conducting electrodes.   b) I_m versus E_p for α and β-relaxations.

TSDC spectrum depends mainly on the investigated material, so one peak or broad peak containing several overlapped peaks can be obtained. Global TSDC spectrum of pure PEMA in temperature range from 300 to 385 K with different polarizing fields is shown in Fig. 2a. It is found that, each TSDC spectrum of PEMA consists of two different transitions. The first transition is detected as a shoulder in a narrow temperature range from 324 to 333 K. On the other hand, the second transition is obtained at T_m~ 349 K.

In general, the amorphous polymer is characterized by at least two different types of relaxation, such as, β-and α-relaxation processes. β-relaxation process is known as a local relaxation due to the motion of the side groups at low temperature [26], whereas, α-relaxation process corresponds to the cooperative relaxation related to the glass transition. These relaxations are of great importance in dissipating the energy and thus the mechanical properties of the material will change. β-relaxation process in PEMA can be observed below 343 K. So, the relaxation which is observed as a shoulder in Fig. 2a can be named as β-relaxation. This relaxation is resulted from rotation of the asymmetric side group – $OCOC_2H_5$ along C-C bond connecting it to the backbone of the polymer and probably, includes coordinated main-chain rearrangement [27]. Motion of the side chain relaxation is mainly controlled by the intra-chain interaction, unlike the Brownian motion of the main chain. The rearrangement of PEMA main-chain is a swing motion about the axis of local chain with ±20° amplitude in the glassy state [28]. Cooperative rocking of the main-chain can be achieved through fluctuations of free volume, i.e., there is enough free volume in the micro-domains even well below glass transition temperature, T_g.

On the other side, the second transition which is observed at T_m~ 349 K, in the glass transition region, where T_g of PEMA ~ 344 K, can be assigned as α-relaxation or dipolar relaxation. This relaxation is attributed to the free rotation motion of ethyl ester group attached to PEMA main-chain [28]. It is observed that, the maximum current, I_m of each relaxation process is increased linearly with the applied electric field, E_p, as shown in Fig. 2b. Initial rise method has been used to determine activation energy values for each relaxation process. The variation in the energies of the polymeric material can be attributed to the slope of the peaks of relaxation, temperature and current density [29,30]. Values of activation energy of α-relaxation are found to be higher than those of β-relaxation, as summarized in Table 1.

Table 1. The molecular parameters of β- and α-relaxation of pure PEMA

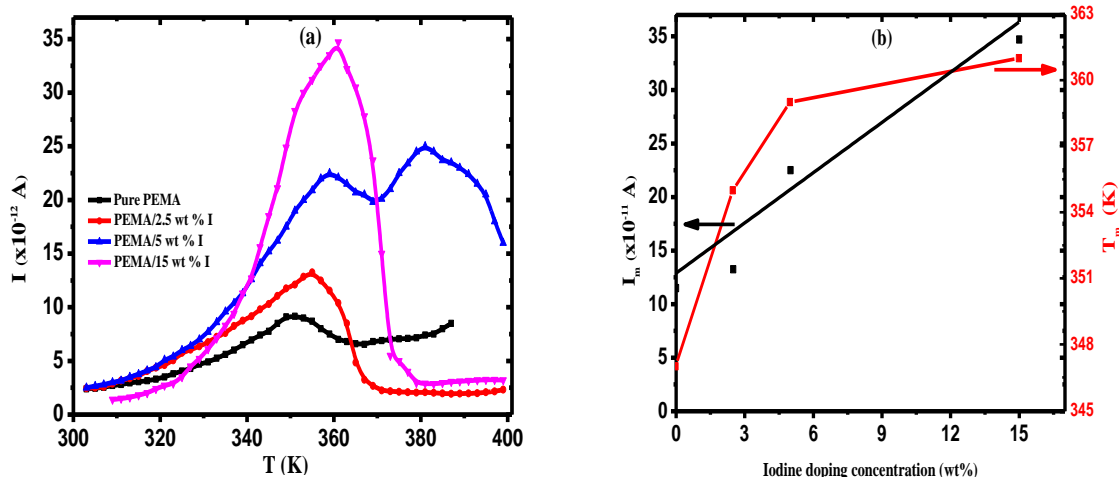| Sample	β-relaxation				α-relaxation		
	E_p (V/m)	T_m (K)	E_a (eV)	τ_0 (sec)	T_m (K)	E_a (eV)	τ_0 (sec)
Pure	7×10^6	324-333	0.13	3.60×10^{-2}	349	0.15	1.40×10^{-2}
PEMA	9×10^6	324-333	0.17	1.00×10^{-3}	347	0.12	1.68×10^{-2}
	1×10^7	324-333	0.12	8.80×10^{-2}	351	0.17	3.00×10^{-3}

Fig. 3: a) TSDC spectra of PEMA and doped samples polarized with negatively corona, T_{co}= 345 K, V_{co}= -6 kV and t_{co}= 15 min, and carbon paste is used as conducting electrodes. b) Maximum current (I_m) versus iodine concentration.

Fig. 3 shows TSDC spectra of PEMA and doped samples polarized with negatively corona. Polarization of the polymeric material may arise due to multiple mechanisms, the most important of which are dipolar orientation, space charge polarization, displacement of the charges and ions displacement with subsequent trapping, etc. In PEMA polymer, lone pair of electrons in the oxygen atoms of C–O–C_2H_5 and C=O can coordinate easily with the salt forming polymer salt complexes. Moreover, iodine may alternatively be transported to polymer chain or reside within crystalline/amorphous boundary and propagate preferentially through the amorphous parts to form charge transfer complexes (CTC), or may be present as molecular complexes between polymer chains. Iodine may form a strong bond with carbonyl carbon of PEMA-$COOCH_3$ ester group, so, the addition of iodine to PEMA will enhance the polar character of PEMA [31].   Hence, the behaviour of TSDC of PEMA has been significantly affected due to the doping with iodine. One can see that, the intensity of TSDC spectrum (I_m) has been increased with increasing doping ratio and the peak position of α-relaxation is found to be shifted to higher

temperature side, as shown in Fig. 3. These changes are indicative to the iodine–PEMA interaction. It is known that donor-acceptor type complexes can be formed when the polymer is doped with halogens, which change in its dielectric and electrical behaviour. The increase in I_m values with increasing iodine concentration reveals that on increasing the doping ratio, the dipoles density participating in the orientation process has been increased as well as the effective polarization has been changed.   This behaviour is well consistent with what has been observed in PMMA-iodine composites [32]. Moreover, an additional relaxation peak has been observed for PEMA/5 wt% I sample at higher temperature, $\sim T_m$= 381 K.   This peak can be assigned as space charge relaxation, i.e., MWS-relaxation or ρ-relaxation due to accumulation of the charges at the interfaces of the heterogeneous PEMA-Iodine sample.   The motion of the space charges at high temperatures is accompanied by the formation of charge carriers resulting from breaking of chemical bonds as well as the ionization of impurities.
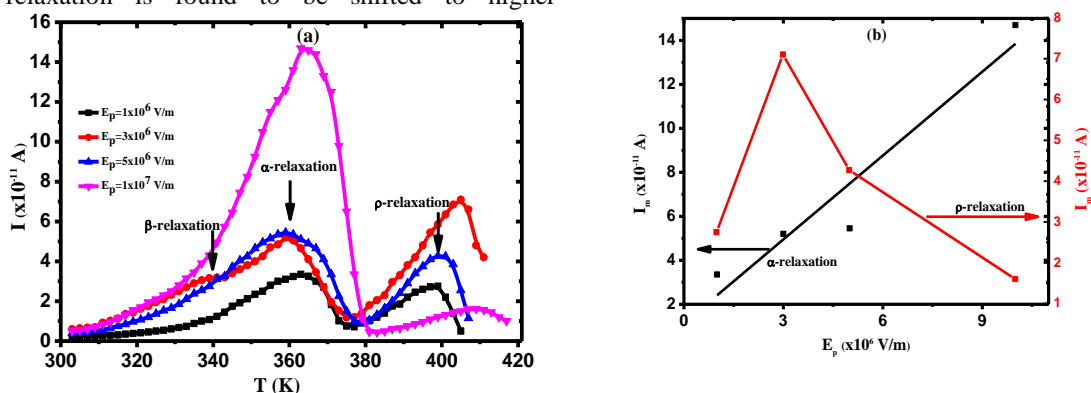

Fig. 4: a) Global TSDC spectra of PEMA/15 wt% I negatively corona-charged, V_{co}= -6 kV, t_{co}=15 min and T_{co}= 348 K. (b) Maximum current, I_m of □ and □-relaxations versus poling electric field, E_p.

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The highly doped sample, PEMA/15 wt% I sample is selected to examine the effect of iodine on the behaviour of TSDC spectra of PEMA-iodine composite samples. Fig. 4a depicts global TSDC spectra of PEMA/15 wt% I sample under different electric fields with negatively corona charging in temperature range from RT to ~420 K. The observed asymmetry of TSDC spectrum may be resulted from the relaxation times distribution due to the different processes involved. It is found that, the position of β and α-relaxations of pure PEMA has been shifted towards high temperature side and a third peak at high temperatures has been obtained. To differentiate between different modes of relaxation, data of TSDC peak such as maximum current or peak position should be analysed in terms of polarizing parameters, as shown in Fig. 4b. One can see that, the maximum current of second relaxation, i.e., α-relaxation, has a linear dependence on the electric field, while, maximum current of third relaxation peak varies nonlinearly with E_p. On the other hand, the peak position, T_m of second peak is nearly electric field independent, whereas, the peak position of third peak is shifted towards high temperature with increasing electric field. These features are characterizing different relaxation process, such as, dipolar and space charge relaxation, respectively [33,34]. Hence, the third peak can be attributed to space charge relaxation and named as ρ-relaxation. The peak position shift of ρ-relaxation with different electric field is due to the thermal release of trapped charges in PEMA/Iodine composites during the measurements of TSDC. Initial rise method has been used to calculate the activation energy values of different relaxation processes in PEMA-iodine doped samples, as shown in Fig. 5, (the plots of PEMA/5 wt% I are not shown). The molecular parameters characterizing both α- and ρ-relaxation are estimated and listed in Table 2. It is found that, the values of activation energy for ρ-relaxation are higher than α-relaxation. The higher values of activation energy for ρ-relaxation can be attributed to the deep traps in the composite samples [35].
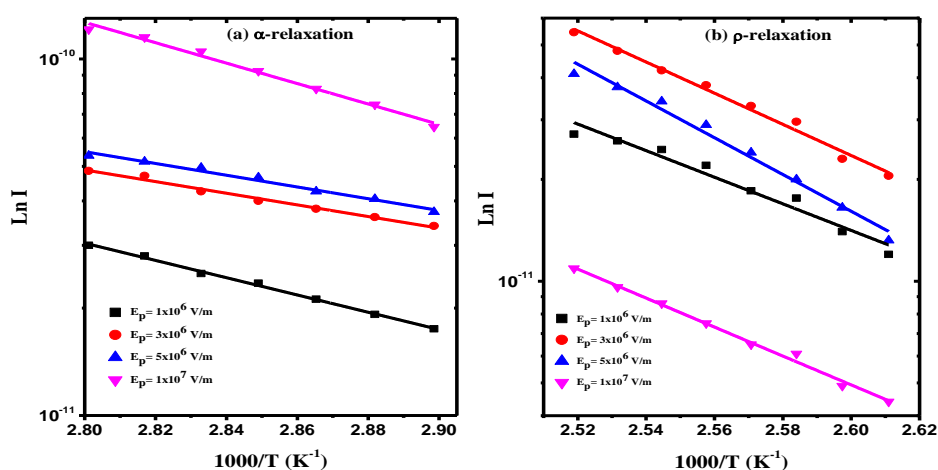

Fig. 5: Ln I versus 1000/T for: a) α-relaxations and b) for ρ-relaxations

Table 2. The molecular parameters of α- and ρ-relaxations of PEMA-Iodine doped samples.

Sample	E_p (V/m)	T_m (K)	E_a (eV)	τ_0 (sec)	T_m (K)	E_a (eV)	τ_0 (sec)
		α-relaxation			ρ-relaxation		
PEMA/5 wt% I	1×10^6	359	0.12	1.31×10^{-1}	389	0.19	3.00×10^{-3}
	7×10^6	359	0.20	2.00×10^{-4}	381	0.11	5.37×10^{-1}
	1×10^7	357	0.12	2.52×10^{-1}	401	0.23	2.00×10^{-4}
PEMA/15 wt% I	1×10^6	363	0.21	2.00×10^{-4}	397	0.34	1.00×10^{-7}
	3×10^6	359	0.14	4.56×10^{-2}	405	0.40	3.00×10^{-9}
	5×10^6	359	0.14	3.96×10^{-2}	399	0.47	1.00×10^{-11}
	1×10^7	363	0.25	1.00×10^{-5}	409	0.37	3.00×10^{-8}

3.2 TS-RMA

Global TSDC spectrum of all samples has been decomposed into their elementary peaks using thermal sampling, TS method. TS polarization procedure is applied with a polarization window, T_p-T_d= 5K. Figure 6 displays the elementary TS spectra for pure PEMA and PEMA/15 wt % I as a representative sample of doped samples.
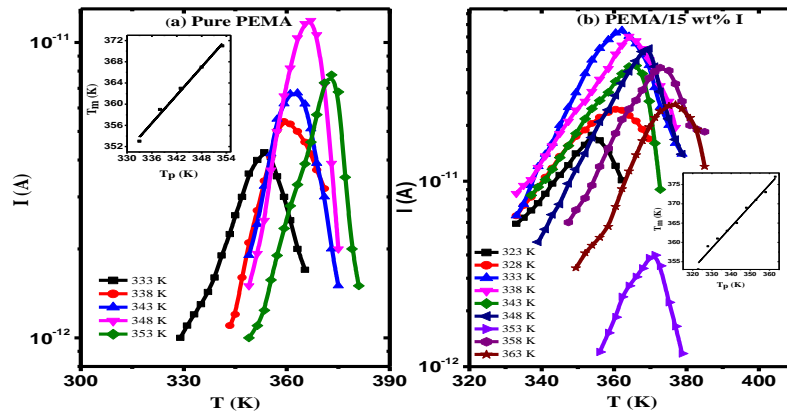
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Fig. 6: TS spectrum of a) Pure PEMA and b) PEMA/15 wt% I at different poling temperatures.

One can see that, there is a linear dependence between peak position temperatures, T_m and poling temperature, T_p, with a slope approximately equals to the unity, which is well consistent with the theoretical models of continuous distribution of relaxation times [25]. TS technique provides an observation of a narrow peak in the global TSDC spectra. TS spectra of investigated samples are characterized by broadness as published for many polymers. This broadness is an indication to the interaction between different types of relaxation [16,17]. The molecular parameters of each TS spectrum have been estimated and summarized in Table 3.

To get more and valuable information about the thermodynamic parameters of the PEMA-Iodine composite, such as enthalpy activation, ΔH, entropy activation, ΔS, Gibbs free energy, ΔG, and construct relaxation map (RM), Arrhenius relaxation can be analysed using Eyring transformation. Therefore, according to Eyring transformation, the relaxation time $\tau(T)$ can be expressed in terms of ΔH and ΔS as follows [36]

$$\tau(T) = \frac{h}{k_B T} \exp\left(\frac{\Delta G}{k_B T}\right) \qquad (1)$$

Where, ΔG is given by

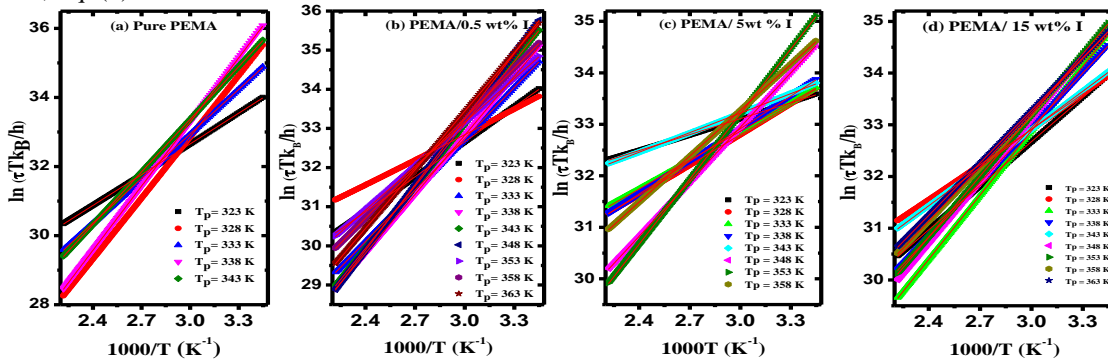$$\Delta G = \Delta H - T \Delta S \qquad (2)$$

Hence, Eq. (1) will become

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

$$\ln\left(\frac{\tau T k_B}{h}\right) = \frac{\Delta H}{k_B T} - \frac{\Delta S}{k_B} \qquad (3)$$

Hence, the values of both ΔH and ΔS can be calculated by knowing values of slope and the intercept of $\ln(\tau T k_B/h)$ versus $1/T$ plot. The relaxation map (RM) of the polymer material can be obtained by transforming the elementary peaks of TS technique which are obtained at different polarization temperatures into their Eyring representation. Fig. 7(a-d) illustrates the variation of $\ln(\tau T k_B/h)$ against $1/T$, i.e., relaxation map analysis (RMA), for all samples. These plots are found be more linear than the direct Arrhenius lines. The values of ΔH, ΔS and ΔG are calculated at each polarization temperature and summarized in Table 3. RMA attempts to associate the modes of single relaxation (relaxation time against temperature) to physical and/or thermo-kinetic parameters. RMA is considered as a fingerprint of the material state. So, if the material state is modified because of many factors such as, processing conditions, crosslinking and thermal history its fingerprint will change.

Fig. 7: The variation of $\ln(\tau T k_B/h)$ against $1/T$ for pure PEMA and doped samples.

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Table 3. The molecular parameters of PEMA-Iodine doped samples.

Sample	TS No:	T_P (K)	T_P–T_d (K)	T_m (K)	E_a (kJ/mol)	τ_0 (sec)	ΔH (kJ/mol)	ΔS (J/mol. Deg)	ΔG (kJ/mol)
	1	333	323-318	353	27.99	9.98×10^{-04}	24.590	-197.22	88.293
	2	338	328-323	359	52.11	1.89×10^{-07}	48.932	-126.03	90.268
	3	343	333-328	363	38.60	2.43×10^{-05}	35.723	-166.4	91.134
Pure PEMA	4	348	338-333	367	55.01	1.18×10^{-07}	51.424	-122.12	92.701
	5	353	343-338	371	45.36	3.61×10^{-06}	42.203	-150.53	93.836
	1	323	323-318	353	27.99	9.67×10^{-04}	24.757	-196.97	88.379
	2	328	328-323	355	21.23	1.42×10^{-02}	17.778	-219.32	89.715
PEMA/0.5 wt% I	3	333	333-328	359	39.57	1.60×10^{-05}	36.304	-162.91	90.554
	4	338	338-333	363	44.39	2.49×10^{-06}	41.704	-147.46	91.546
	5	343	343-338	365	47.29	1.45×10^{-06}	44.030	-142.97	93.070
	6	348	348-343	367	49.22	6.87×10^{-07}	46.439	-136.74	94.026
	7	353	353-348	369	33.78	1.65×10^{-04}	30.987	-182.27	95.328
	8	358	358-353	371	38.60	3.84×10^{-05}	35.307	-170.14	96.217
	9	363	363-358	373	44.39	5.11×10^{-06}	41.372	-153.44	97.071
	1	323	323-318	347	11.58	5.26×10^{-01}	8.557	-249.31	89.084
	2	328	328-323	351	19.30	2.38×10^{-02}	15.784	-223.56	89.111
	3	333	333-328	353	18.34	3.36×10^{-02}	15.452	-226.47	90.865
PEMA/5 wt% I	4	338	338-333	357	20.27	1.70×10^{-02}	17.529	-220.82	92.165
	5	343	343-338	361	13.51	2.92×10^{-01}	10.468	-244.41	94.300
	6	348	348-343	363	32.81	2.50×10^{-04}	29.243	-185.76	93.887
	7	353	353-348	369	37.64	4.15×10^{-05}	34.975	-170.8	95.269
	8	358	358-353	373	27.99	1.85×10^{-03}	24.590	-202.37	97.040
	1	323	323-318	353	27.02	1.49×10^{-03}	23.594	-200.55	88.370
	2	328	328-323	359	22.20	1.04×10^{-02}	18.858	-216.75	89.951
	3	333	333-328	361	37.64	3.72×10^{-05}	34.393	-169.89	90.967
	4	338	338-333	363	32.81	2.50×10^{-04}	29.243	-185.76	92.029
PEMA/15 wt% I	5	343	343-338	365	23.16	5.95×10^{-03}	20.354	-212.09	93.102
	6	348	348-343	369	36.67	7.13×10^{-05}	33.230	-175.29	94.231
	7	353	353-348	371	35.71	9.45×10^{-05}	32.566	-177.70	95.294
	8	358	358-353	373	31.85	3.71×10^{-04}	28.993	-189.00	96.655
	9	363	363-358	377	30.88	5.32×10^{-04}	28.080	-191.99	97.772

Compensation phenomenon has been found intensively in the area of chemical kinetics and has been published in many TSDC studies [37-40]. It has been assumed that, at the compensation temperature, T_c, all the relaxation process will obtain at a single compensation relaxation time, τ_c. The compensation is generally identified using relaxation spectra observed below glass transition temperature in the polymer glass by TSDC, where the glass is not in equilibrium state due to the incomplete volume relaxation. Compensation behaviour takes place near T_g for a lot of polymers due to the increase in the activation energy, E_a associated with T_g. Compensation point of each sample has been observed in Fig. 7(a-d) when the Eyring lines are converged into a single point. Generally, the amorphous materials are characterized by at least one compensation point in the glass transition temperature region. It is observed that, RM of PEMA is characterized by one compensation point in the range of its dipolar relaxation, i.e., α-relaxation, whereas, doped samples are characterized by two compensation points in the range of α- and ρ-relaxation.

The compensation phenomenon in polymeric materials can be considered as an indicator to the cooperative segmental molecular movements or other different types of cooperative transitions due to the increasing of activation energy around T_g. So, if some activation parameters have been increased with temperature, the processes of local relaxations can also reveal the compensation behaviour feature. It is observed that the value of compensation temperature is slightly greater than the glass transition of PEMA, i.e., $T_c > T_g$, as observed for many polymers [41]. Coordinates of each compensation point (T_c and τ_c) are calculated and summarized in Table 4. The coordinates T_c and τ_c have a great importance in calculation the values of coefficient of thermal expansion, γ and the variation of thermal expansion coefficient $\Delta\gamma$ below and above T_g of the materials under investigation using the following formula [42]

$$\gamma = \frac{1}{4T_c} \qquad\qquad \Delta\gamma = \frac{1}{9T_c} \quad (4)$$

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The values of γ and $\Delta\gamma$ are estimated and summarized in Table 4. These values are found to be in good agreement with the values of many polymers [2,16]. Values of both T_c and τ_c can be used to interpret the basic characteristics of the polymer state when affected by both the bonding environment and polar groups. Values of density of disorder (DOD) of

PEMA-iodine doped samples are determined using T_c and τ_c and listed in Table 4, as follow [43]

$$DOD = 100 - 2\left[\ln(T_c\tau_c) + 23.76\right] \quad (5)$$

DOD values can be used to reflect the degree of compatibility between different phases of copolymers, polymer composites and polymer blends [44].

Table 4. The values of compensation temperature, compensation relaxation time, thermal expansion coefficients and DOD.

Sample	T^*_c (K)	T_{c1} (K)	τ_{c1} (Sec)	T_{c2} (K)	τ_{c2} (Sec)	γ (K^{-1})	$\Delta\gamma$ (K^{-1})	DOD (cal/deg)
Pure PEMA	351.24	354.73	11.764	----	----	7.04x10^{-4}	3.13x10^{-4}	35.81
PEMA/0.5 wt% I	348.43	356.50	15.340	387.14	3.358	7.01x10^{-4}	3.11x10^{-4}	35.27
PEMA/5 wt% I	337.83	350.50	19.434	392.92	8.814	7.31x10^{-4}	3.25x10^{-4}	34.83
PEMA/15 wt% I	348.43	349.40	18.346	386.10	5.851	7.15x10^{-4}	3.18x10^{-4}	34.95

T^*_c values are calculated from ΔS-ΔH relationship.
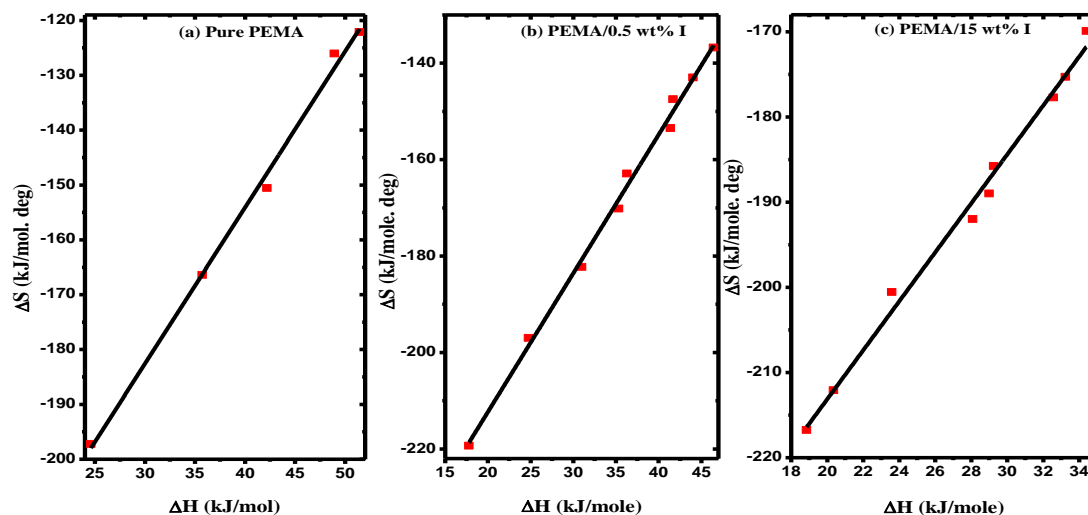

Fig. 8: ΔS versus ΔH for a) PEMA, b) PEMA/0.5 wt% I and c) PEMA/15 wt% I.

The compensation behaviour can be interpreted in the light of activation enthalpy-entropy relation, where the change in enthalpy of activation is compensated by the change in entropy of activation. Compensation behaviour of the polymeric materials is observed when the values of ΔS, ΔH and E_a increase in the same time with increasing the temperature. There are usually parallel changes in both enthalpy and entropy for a series of structurally relevant compounds that undergo a specific chemical reaction. That is, the stronger the intermolecular interaction (enthalpy related), the greater the reduced freedom of configurational, hence, the greater the order (entropy related). Such behaviour is called enthalpy-entropy compensation effect. The negative values of activation entropy of PEMA-Iodine composites which are listed in Table 3 reveal that, the polarization process during TSDC measurements improved the local arrangement, i.e., reduced the

disorder in the molecular structure of the materials. Fig. 8 displays the variation of entropy against enthalpy for pure PEMA and doped samples. A linear relationship that characterizes this behaviour between ΔS and ΔH for all samples has been obtained. This linear relation between ΔS and ΔH is result of changes in the structure of the material towards the equilibrium state with increasing the temperature. This behaviour is fully consistent with what has already been published for many polymeric materials [45-46]. The compensation temperature (T_c) has been calculated again by knowing the slope of ΔS-ΔH relationship according to the following empirical formula [43], $T_C = \dfrac{\Delta H}{(-\Delta S)}$ and listed in Table 4. It is noticed that, the values of T_c from Eyring plot (Fig. 7) and ΔS-ΔH plot (Fig. 8) are comparable to each other.
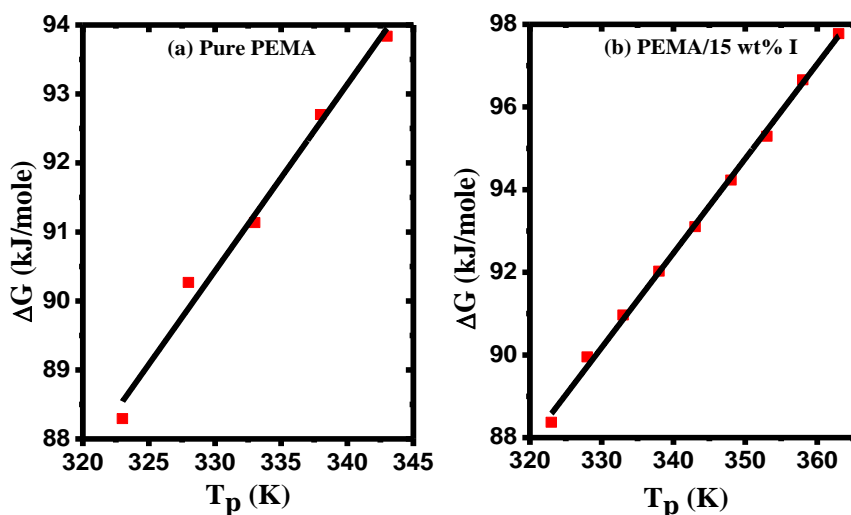
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Fig. 9: Gibbs free energy, ΔG versus poling temperature, T_p for a) pure PEMA and b) PEMA/15 wt% I.

Fig. 9 displays the dependence of Gibbs free energy (ΔG) on the polarization temperature (T_p) for pure and doped PEMA samples. This linear dependence between ΔG and T_p is found to be valid for all different types of relaxation mechanisms including local relaxation process (β-relaxation) and cooperative processes near α-transition of the polymeric material in the glassy state. The increasing of ΔG values with increasing the temperature means that ΔS value is negative.

3.3 Shift factor

The chain relaxation of the polymeric material is a function of the available free volume and chain conformations. The effect of the temperature on the ability of chain relaxation is taken as the basis of time-temperature equation, so, the temperature shift factor can be defined. The shift factor, a_T will be considered as a measure of the mechanical response in the semicrystalline and amorphous polymers, if the viscoelastic response is dominant. In turn, the shift factor will depend on the free volume. The relation between shift factor and free volume, f of the material at different states can be expressed as follows

$$a_T = \exp\left[C\left(\frac{1}{f} - \frac{1}{f_r} \right) \right] \qquad (6)$$

Where: C is a constant, whereas, f and f_r are the fractional free volume at temperature T and at a reference temperature T_r. On the other side, at temperature T, the fractional free volume, f can be written as follow:

$$f = f_r + \alpha(T - T_r) \qquad (7)$$

Where, α is defined as the expansion coefficient of fractional free volume. From the Eq. (6) and Eq. (7), we can obtain [47-48]

$$a_T = \exp\left[-\frac{C}{f_r}\left(\frac{\alpha(T - T_r)}{f_r + \alpha(T - T_r)} \right) \right]$$

$$a_T = \exp\left(\frac{\left[-\dfrac{C}{f_r} \right](T - T_r)}{\left[\dfrac{f_r}{\alpha} \right] + (T - T_r)} \right)$$

$$\log a_T = \frac{\left[-\dfrac{C}{f_r} \right](T - T_r)}{\left[\dfrac{f_r}{\alpha} \right] + (T - T_r)} \qquad (8)$$

On the other hand, the WLF equation can be expressed in general terms as follow [49]

$$\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \qquad (9)$$

Where $a_T = \dfrac{\tau_T}{\tau_{Tr}}$ (τ_T and τ_{Tr} represent the values of the characteristic relaxation time at temperatures T and T_r), C_1 and C_2 are constants, respectively.
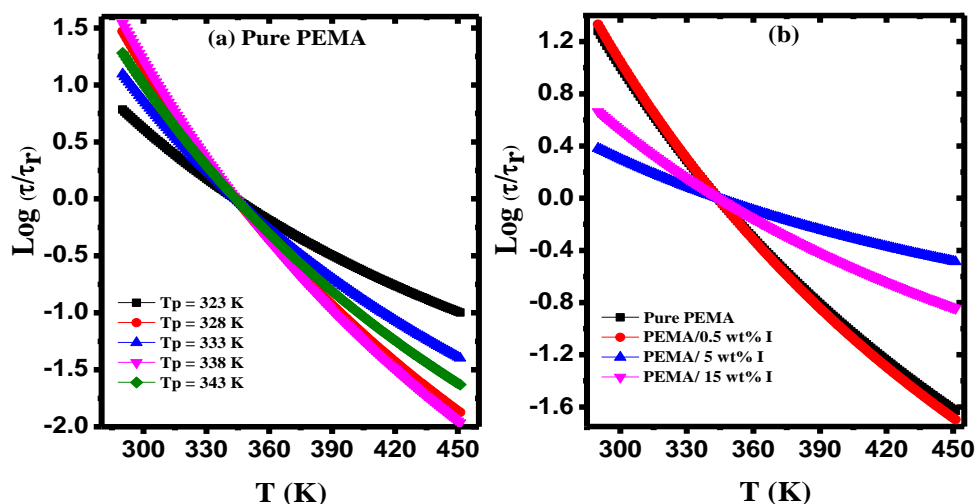
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Fig. 10: Log (τ/τ_r) against temperature for a) PEMA and b) PEMA and doped samples.

Fig. 10 displays the time-temperature shift factor behaviour of PEMA and PEMA-Iodine composite samples. All curves of the samples are found to intersect at $T=T_r$ but differ greatly in nature. Eq. 9 can be rewritten in another form as follow:

$$\frac{-1}{\log a_T} = \frac{C_2 + (T - T_r)}{C_1 (T - T_r)} = \frac{C2}{C_1 (T - T_r)} + \frac{1}{C_1} \qquad (10)$$

To obtain the values of the constants C_1 and C_2, Eq. 10 can be rearranged to get a linear form as follows:

$$\frac{(T - T_r)}{\log a_T} = \frac{-(T - T_r)}{C_1} - \frac{C_2}{C_1} \qquad (11)$$

Eq. 11 is plotted for pure PEMA and doped samples at reference temperature, T_r of 344 K, as shown in Fig. 11. The values of C_1 and C_2 are calculated from the slope and intercept of each line, where the slope and the intercept are equivalent to ($-1/C_1$) and ($-C_2/C_1$), respectively, and listed in Table 5. The obtained data of C_1 and C_2 are well consistent with other polymers [50].
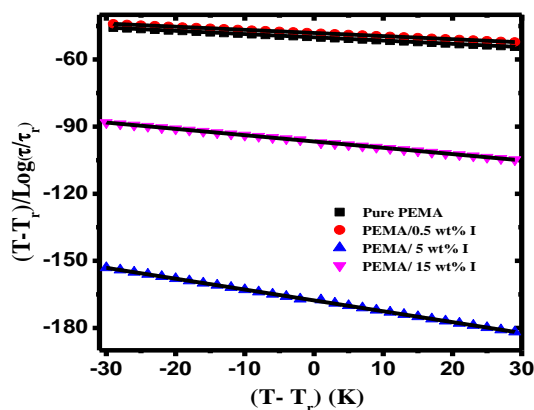
Fig. 11: WLF equation of PEMA and doped samples.

Table 5. The values of C_1 and C_2 of WLF equation.

Sample	C_1 of WLF equation	C_2 of WLF equation
Pure PEMA	6.66	333.73
PEMA/0.5 wt% I	7.14	343.64
PEMA/5 wt% I	2.04	342.22
PEMA/15 wt% I	3.55	343.87

Conclusion

Different modes of relaxation, such as, local relaxation, dipolar relaxation and space charge relaxation have been observed in PEMA-Iodine composites using TSDC-TS technique. It is found

that, global TSDC spectra of pure PEMA are characterized by two relaxations, β and α-relaxations at 324-333 K and T_m= 347 K, respectively. These relaxations are attributed to the motion of side group of –OCOC$_2$H$_5$ along C-C bond and due to free rotation motion of ethyl ester group attached to

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PEMA main-chain, respectively. On the other hand, with iodine doping, a new relaxation peak has been obtained at high temperatures ~ 397-409 K and named as space charge relaxation, i.e., ρ- relaxation. It is found that the activation energy values of ρ-relaxation are higher than for α-relaxation. The higher values of activation energy for ρ-relaxation are attributed to the deep traps in the composite samples. Complex TSDC spectra of PEMA-Iodine composites have been decomposed into its elementary peaks using TS technique. These elementary peaks have been used to construct relaxation map (RM) of all samples. Relaxation map analysis (RMA) has been investigated for all samples and the compensation phenomenon for all samples is also verified in the region of α and ρ- relaxations. The coordinates of each compensation point, i.e., compensation temperature (T_c) and compensation relaxation time (τ_c) have been estimated and are used to calculate the density of disorder (DOD). Moreover, values of enthalpy, entropy and Gibbs free energy have been calculated for all samples at different polarization temperatures. The linear relationship between both enthalpy and entropy once again confirmed the verification of compensation phenomenon.

Acknowledgment

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