International Journal of Engineering Research and Technology.
ISSN 0974-3154 Volume 11, Number 9 (2018), pp. 1371-1382

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Relaxation Map analysis of Poly (Vinyl Chloride-co-Vinyl Acetate-co-2-Hydroxypropyl Acrylate) / Poly (Acrylonitrile-Butadiene-Styrene) Polymer Blend

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ABSTRACT

Thermally stimulated depolarization current (TSDC) and thermal sampling techniques (TS) are carried out to study the relaxation behavior of PVVH, ABS and its polyblend samples. It is found that, PVVH and ABS are characterized by a dipolar relaxation peak and detected at 347 and 389 K, respectively. Relaxation map analysis (RMA) has been discussed for all samples. It is observed that, pure samples are chractaerized by one compensation point and some of polyblend materials are characterized by two compensation points. The coordinates of the compensation point are used to calculate the density of disorder (DOD) of the samples.

Keywords: Relaxation, Compensation, RMA, Eyring transform, Entropy, Enthalpy, DOD.

INTRODUCTION

The polymer blends have been attracted much attention in the area of research and development in polymer science in the past three decades, because of their potential usage in many applications, such as, sensors, shielding and membranes [1-4]. The commercial advantage is that polymer blends provide a method to give materials with new property profiles, which reduces development costs. Blending of polymers is an interesting subject to investigate the phase separation and polymer interaction at microsopic levels [5].

As alleady well known, the physical properties of polymers are attributed to molecular motions which are very complicated. This motion is evident by relaxations which are detected during mechanical and dielectric investigationss. One favorable method to investigate the physical properties of polymers is thermally stimulated depolarization current, (TSDC). TSDC technique is used to study molecular structure of polymeric materials because of its high sensitivity to detect the transitions which depend on mobility changes of molecular scale structural units [6-10]. In TSDC, the resultant current as a result of the depolarization process of polarized quenched sample is recorded during the heating cycle, giving global TSDC spectrum. Moreover, the advantage of TSDC technique is its ability to decompose TSDC spectra into its elementary processes, i.e, thermal sampling response.

This work is focused to investigate relaxation map analysis (RMA) of PVVH/ABS polymer blend. The composition of the polyblend samples studied was varied in a wide range from pure PVVH to pure ABS.

EXPERIMENTAL

Poly (vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) (PVVH) is supplied fom Aldrich Chemicals. Poly (acrylonitrile-butadiene-styrene) (ABS) is supplied from Poly Sci., USA. The films of samples are prepared using casting method. Tetrahydrofuran (THF) is used a common solvent for PVVH and ABS. The solvent was eleminated in an oven, at temparture of ~ 323 K for two days.

TSDC technique is described in more detail elsewhere [11]. The resultant global TSDC spectrum contains many peaks whose shape and position are fingerptint of the relaxation process of the material under investigation. Thermal sampling (TS) technique is used to investigate and analyse specific regions in global TSDC spectrum. TS technique allows the decomposition of TSDC spectrum into its elementary relaxation processes, i.e., relaxation map analysis (RMA). Hence, TS experiment is carried out to investigate the fine structure of PVVH/ABS polyblends.

RESULTS and DISCUSSION

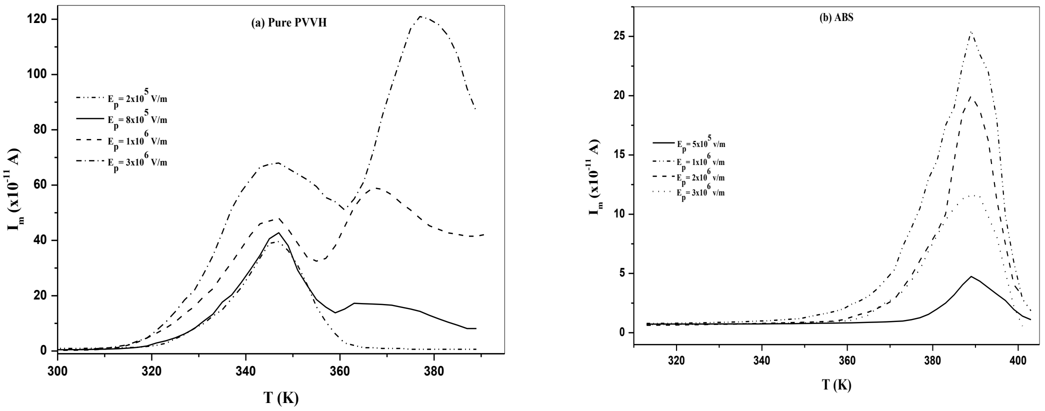


Figure 1: TSDC spectrum for (a) PVVH at T_p= 343 K and (b) ABS at T_p= 383 K, and t_p= 15 min.

TSDC is a very sensitive method to study transport mechanism of charge carriers of the polymeric materials and the behavior of glass transition temperature (T_g) and dieletric relaxation. Figure 1(a&b) displays global TSDC spectra of both PVVH and ABS. It is found that, TSDC spectrum of PVVH is characterized by two relaxation peaks. The first relaxation peak is detected in the vicinity of its glass transition temperature, T_g ~ 347 K, and the second peak is observed in the range of temperature ~ 353-383 K. On the other hand, global TSDC spectrum of ABS is characterized by a relaxation peak and is decteced at T_m~ 389 K, as shown in Figure 1b. To differentiate between the dominant mechanisms of polarization, we should analyse the data of TSDC in terms of poling electric field strength, E_p, as shown in Figure 2.

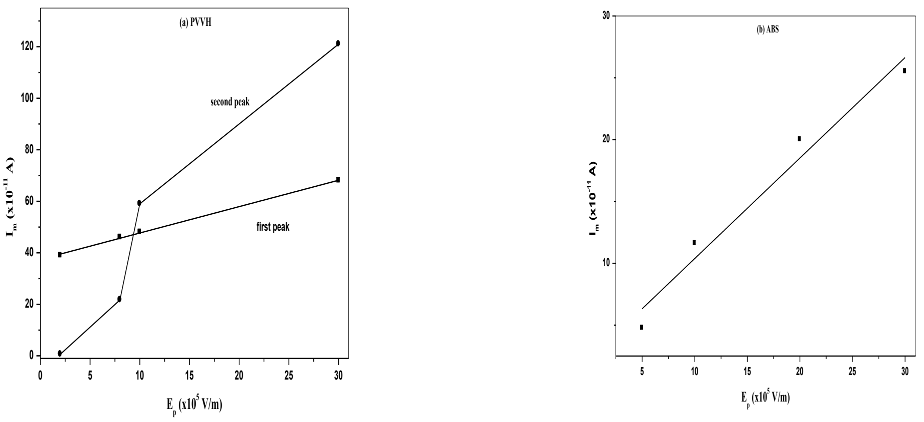


Figure 2: Maximum current (I_m) of relaxation peaks against the polarizing electric field (E_p).

Hence, the first relaxation peak of PVVH is a dipolar peak and named, α-relaxation peak, and can be attributed to the relaxation of permanent dipoles of the main chain, such as C-Cl. On the other hand, the second peak of PVVH is attributed to space charge relaxation, i.e., ρ-relaxation. This relaxtion peak is due to the relaxation of trapped charges at the boundaries of different media with different permitivities and conductivities, i.e., Maxwell-Wagner-Sillar polarization (MWS), due to the heterogeneity of the PVVH system [13]. Also, the relaxation peak of ABS is referred as dipolar peak, i.e, α-relaxation and is attributed to relaxation of the permanent dipoles (C≡N).

Thermal sampling (TS) technique is carried out with a temperature window, T_p-T_d= 5 K to get the fine strurure of complicated TSDC spectrum of pure and polyblend samples, as shown in Figure 3.

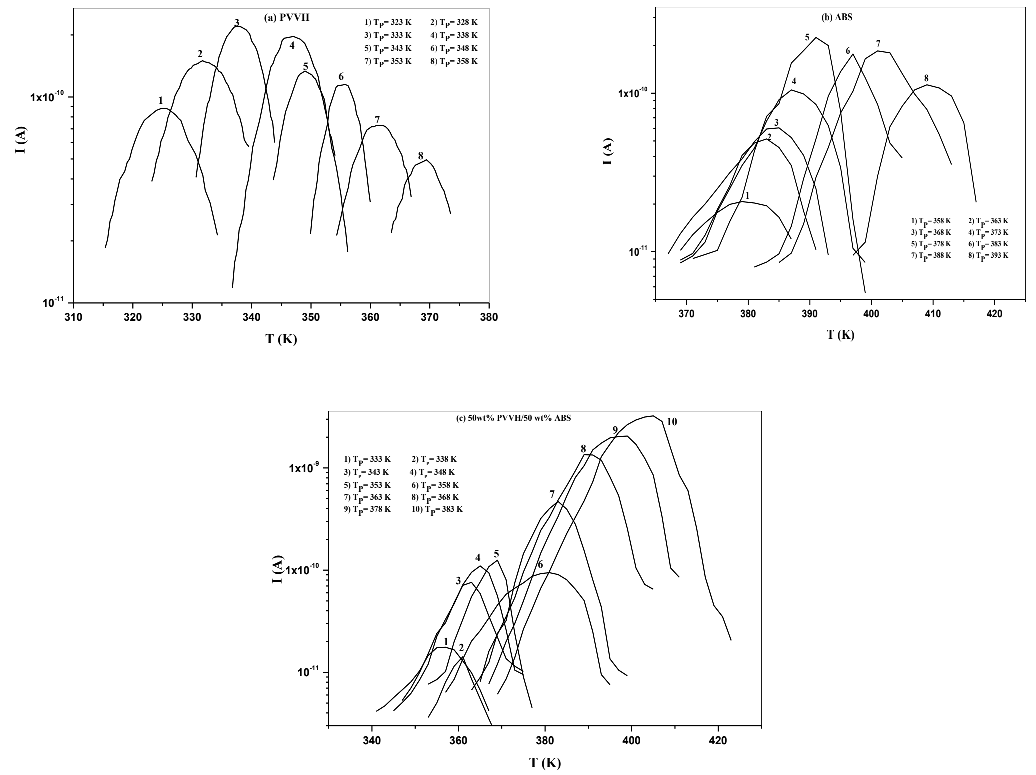


Figure 3: TS spectrum for a) PVVH, b) ABS and c) 50 wt% PVVH polyblend sample.

The relaxation time of each elementary process can be expressed using Arrhenius equation, as follow:

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{k_B T} \right) \qquad (1)$$

It is observed that, peaks of TS spectrum are broader than Debye relaxation type. This broadness can be related to either interaction between different modes of relaxation. The existence of interfaces between different phases in the partially miscible polymers leads to interface polarization effects. Therefore, it makes the explanation of relaxation processes using single Debye curve is very complicated. Arrhenius relaxation can be analyzed using the Eyring transformation [14] to get some kinetic parameters such as enthalpy of activation ΔH, entropy of activation ΔS, and the Gibbs free energy ΔG. Based on Eyring transformation, the relaxation time τ(T) can rewrite in terms of enthalpy (ΔH) and entropy (ΔS), as follows:

$$\tau(T)=\frac{h}{k_B T}\ \exp\left(\frac{\Delta G}{k_B T}\right) \tag{2}$$

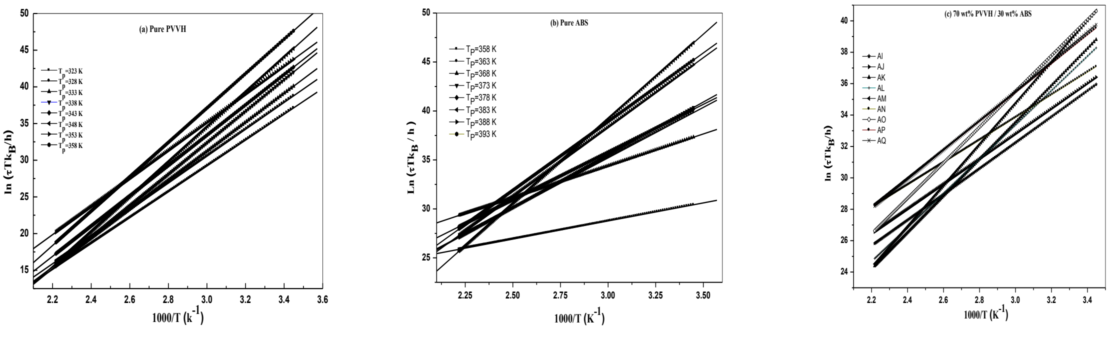
where ΔG is given by

$$\Delta G=\Delta H-T\,\Delta S \tag{3}$$

Hence, Eq. (1) takes the form

$$\ln\left(\frac{\tau T k_B}{h}\right)=\frac{\Delta H}{k_B T}-\frac{\Delta S}{k_B} \tag{4}$$

So, the values of ΔH and ΔS of activation could be estimated by knowing the slope and the intercept of the graph of ln (*τTk_B/h*) against 1/T. Figure 4 displays the variation of ln(*τTk_B/h*) versus 1/T, i.e., relaxation map analysis (RMA), for all samples under investigation. Relaxation map analysis is used to correlate the modes of single relaxation to 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, thermal history, crosslinking and processing conditions, its fingerprint will change. As observed in Figure 4, the Eyring plots are normally more linear. By knowing the slope and intercept of these plots at each polarizing temperature T_p, the values of ΔS and ΔH are estimated. Hence, values of ΔG are determined using Eq. (3) at T $=T_p$. Thermodynamic parameters for the samples are calculated and summarized in Table 1. Positive values of ΔG indicate that PVVH/ABS polyblend system is thermodynamically unstable [15].



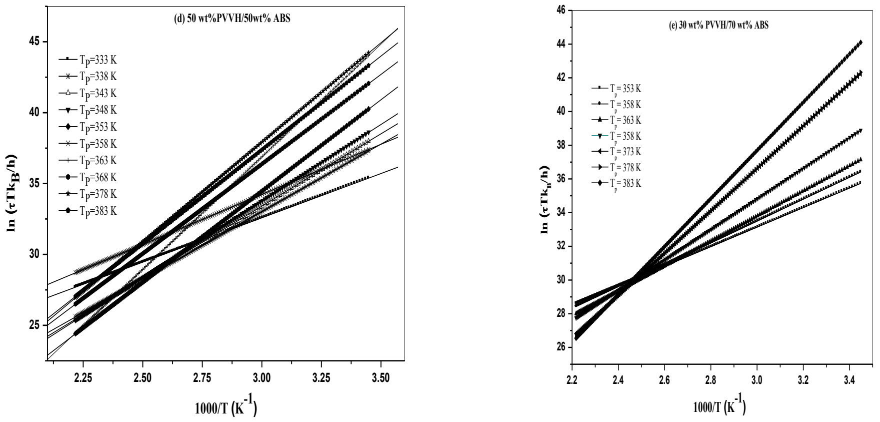


Figure 4: ln ($\tau T k_B/h$) versus 1000/T of (a) PVVH, (b) ABS, (c) 70 wt% PVVH, (d) 50wt% PVVH and (e) 30 wt% PVVH.

The extrapolation of individual lines in Figure 4 for each TS step results in a single point called compensation point. This point is characterized by two coordinates, the compensation temperature, T_C and compensation relaxation time, τ_C. Generally, behavior of amorphous polymers is characterized by at least one compensation point at glass transition temperature [16]. At this compensation point, the elementary or discrete processes that form broad relaxation near T_g have the same relaxation time. Assumption of compensation phenomenon in polymeric materials is due to the possibility of a process where segments of the chain of increasing length contribute at increasing temperatures until to reach a maximum volume at temperature of the compensation, T_c [17]. It is found that, the behavior of both PVVH and ABS is characterized by one compensation point, meaning that a specific set of the molecules of pure materials has the same free energy change at the compensation point [18]. On the other hand, two compensation points are observed in the behavior of some polyblend samples. The coordinates of compensation point (T_c and τ_c) for all investigated materials are estimated and summarized in Table 2.

Table 1: The molecular parameters of PVVH, ABS and its polyblends.

Sample	*TS No:*	*$T_p – T_d$ (K)*	*T_P (K)*	*T_m (K)*	*E_a (eV)*	*τ_0 (sec)*	*ΔH (kJ/mol)*	*ΔS (kJ/mol. Deg)*	*ΔG (kJ/mol)*
Pure PVVH	1	323 –318	323	327	1.55	2.55×10^{-24}	146.43	196.63	82.920
	2	328 – 323	328	335	1.61	1.20×10^{-24}	152.22	202.89	85.670
	3	333 – 328	333	339	1.73	3.63×10^{-26}	163.79	231.95	86.550
	4	338 –333	338	345	1.88	6.24×10^{-28}	178.25	265.71	88.440
	5	343 – 338	343	351	1.81	2.00×10^{-26}	171.50	236.91	90.240
	6	348 – 343	348	355	2.08	5.14×10^{-30}	197.53	305.58	91.190

Sample	*TS No:*	$T_p - T_d$ *(K)*	T_P *(K)*	T_m *(K)*	E_a *(eV)*	τ_0 *(sec)*	*ΔH (kJ/mol)*	*ΔS (kJ/mol. Deg)*	*ΔG (kJ/mol)*
	7	353 – 348	353	363	1.68	$1.06x10^{-23}$	158.96	184.79	93.740
	8	358 –353	358	369	2.05	$1.91x10^{-28}$	194.64	275.55	95.990
70 wt% PVVH	1	333 – 328	333	353	0.74	$9.36x10^{-11}$	68.3	-62.850	89.270
	2	338 –333	338	357	0.72	$3.30x10^{-10}$	66.42	-73.320	91.200
	3	343 – 338	343	359	1.04	$9.91x10^{-15}$	97.27	13.190	92.740
	4	348 – 343	348	361	0.97	$9.67x10^{-14}$	90.52	-5.7300	92.510
	5	353 – 348	353	369	1.16	$5.13x10^{-16}$	108.84	37.790	95.500
	6	358 –353	358	373	0.65	$1.06x10^{-08}$	59.6	-102.14	96.230
	7	363 – 358	363	383	1.01	$2.03x10^{-13}$	94.37	-11.890	98.690
	8	368 – 363	368	389	0.82	$1.38x10^{-10}$	76.06	-66.080	100.37
	9	373 – 368	373	391	0.84	$7.68x10^{-11}$	77.98	-61.210	100.81
50 wt% PVVH	1	333 – 328	333	357	0.57	$4.87x10^{-08}$	51.92	114.73	13.720
	2	338 –333	338	361	0.85	$4.44x10^{-12}$	78.92	37.470	66.260
	3	343 – 338	343	363	0.91	$8.03x10^{-13}$	84.65	23.260	76.680
	4	348 – 343	348	365	0.96	$2.04x10^{-13}$	89.47	11.880	85.340
	5	353 – 348	353	369	1.14	$7.77x10^{-16}$	106.83	-34.310	118.95
	6	358 –353	358	381	0.64	$2.22x10^{-08}$	58.65	108.25	19.900
	7	363 – 358	363	383	1.40	$1.02x10^{-18}$	131.92	-89.390	164.37
	8	368 – 363	368	389	1.12	$1.05x10^{-14}$	104.92	-12.710	109.60
	9	378 – 373	378	399	1.24	$7.48x10^{-16}$	116.47	-34.640	129.57
	10	383 –378	383	405	1.17	$5.00x10^{-15}$	109.74	-18.860	116.97
30 wt% PVVH	1	358 –353	358	377	0.59	$6.06x10^{-08}$	53.88	-116.63	95.630
	2	363 – 358	363	381	0.67	$5.06x10^{-09}$	61.60	-95.990	96.440
	3	368 – 363	368	387	0.81	$1.07x10^{-10}$	75.09	-63.960	98.630
	4	373 – 368	373	389	1.11	$1.85x10^{-14}$	104.01	8.0050	101.03
	5	378 – 373	378	391	1.12	$1.38x10^{-14}$	104.98	10.440	101.03
	6	383 – 378	383	395	1.26	$2.99x10^{-16}$	118.47	42.280	102.29
Pure ABS	1	358 –353	358	379	0.35	$2.27x10^{-06}$	30.74	-146.73	83.270
	2	363 –358	363	383	0.92	$3.45x10^{-12}$	85.70	-35.430	98.560
	3	368 – 363	368	385	0.59	$1.51x10^{-07}$	53.88	-124.21	99.590
	4	373 – 368	373	387	0.96	$1.17x10^{-12}$	89.55	-26.450	99.420
	5	378 – 373	378	391	0.87	$3.57x10^{-11}$	80.88	-54.840	101.61
	6	383 – 378	383	397	1.52	$1.58x10^{-19}$	143.54	104.96	103.34
	7	388 – 383	385	401	1.25	$8.31x10^{-16}$	117.51	33.780	104.40
	8	393 – 388	393	409	1.24	$2.03x10^{-15}$	116.54	26.360	106.10

In addition, the compensation behavior is observed in the light of the Eyring theory of activated states [14], i.e., in terms of enthalpy-entropy relationship. Fig. 5 shows the behaviour of entropy versus enthalpy of PVVH, ABS and 70 wt% PVVH polymer blend as a representative sample. A linear relationship has been found for the samples under investigation, indicating that the compensation law is verified. This linear relation between ΔH and ΔS is a result of structural changes to equilibrium state with increasing temperature [19]. This behavior has been found for other polymeric materials [20-23].

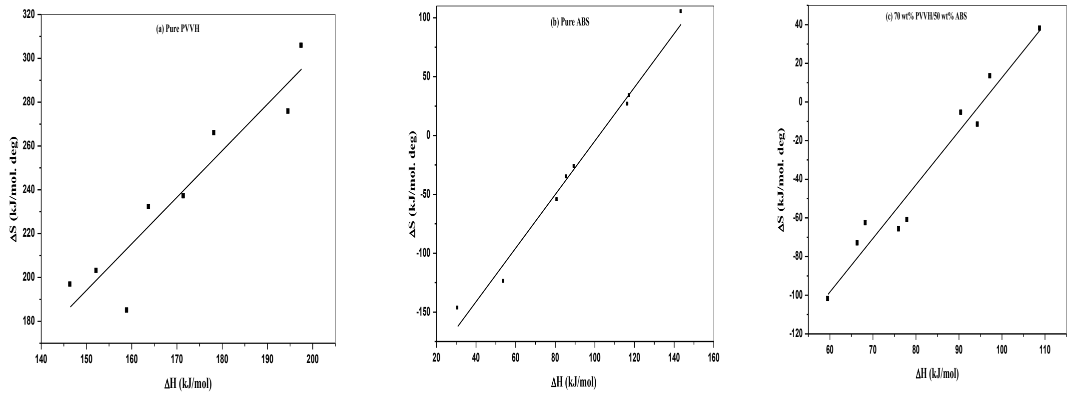


Figure 5: ΔS against ΔH of (a) PVVH, (b) ABS and (c) 70 wt% PVVH/ 30 wt% ABS.

The compensation phenomenon has been verified through the linear relationship between τ_0 of each elementary process (TS spectra) and the activation energy (E_a) of that processes, as shown in Figure 6. The existence of this behavior is strong evidence for PVVH/ABS poly blend system is partially compatibile to each other [21].

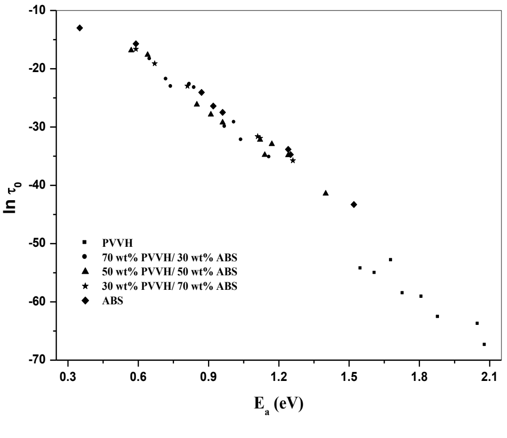


Figure 6: ln τ_0 against activation energy (E_a) of the elementary process of TS spectra.

The dependence of ΔG of pure samles and 70 wt% PVVH as a representative sample of polyblend materials on poling temperature, T_P has been shown in Figure 7. It is observed that, ΔG varies linearly with T_P for pure and polyblend samples, i.e., it increases with increasing T_P, even through the glass transition temperature region.

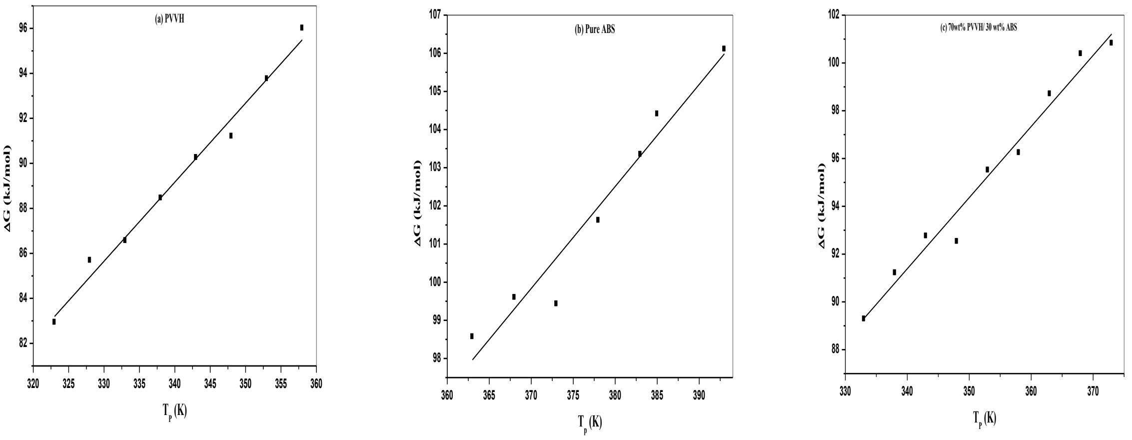


Figure 7: ΔG against poling temperature, T_P of (a) PVVH, (b) ABS and (c) 70 wt% PVVH/ 30 wt% ABS.

The compensation temperature (T_C) is used to calculate the difference of thermal expansion coefficient Δβ above and below T_g using the empirical formula, $\beta = 1/4T_c$ and $\Delta\beta = 1/9\ Tc$ [24]. Values of both β and Δβ for pure and polyblend samples are calculated and summarized in Table 2. The compensation point coordinates can be used to explain properties of the polymer state as the effects of the environment on the bonds and polar groups [20]. When molecular mobility is less inhibited by inter-interamolecular interaction, entropy increases and, conversely, any effect helps to regulate the structure and make the environment more compact, thereby decreasing entropy. Hence, the entropy can be taken as an indicator to the degree of disorder of the polymer structure. Density of disorder (DOD) of the material can be determined using the compensation point coordinates (T_c&τ_c), as follows: [25].

$$DOD = 100 - 2\left[\ln\left(T_C\, \tau_C c\right) + 23.76\right] \qquad (5)$$

Density of disorder can be used to reflect the degree of compatibility of polymer blends or between the different phases of copolymers. The values of DOD for the samples are ranged from 36.32 cal/deg to 51.08 cal/deg.

Table 2: The values of compensation temperature, compensation relaxation time, thermal expansion coefficient and DOD.

Sample	T_{c1} *(K)*	τ_{c1} *(Sec)*	T_{c2} *(K)*	τ_{c2} *(Sec)*	β (K^{-1})	$\Delta\beta$ (K^{-1})	*DOD (ca/deg)*
Pure PVVH	379.21	$5.3\text{x}10^{-3}$	--	--	$6.59\text{x}10^{-4}$	$2.93\text{x}10^{-4}$	51.08
70 wt% PVVH	326.79	127.75	381.67	0.540	$6.5\text{x}10^{-4}$	$2.9\ \text{x}10^{-4}$	41.82
50 wt% PVVH	357.14	7.120	387.59	0.62	--	--	41.51
30 wt% PVVH	401.60	1.540	--	--	$6.2\text{x}10^{-4}$	$2.7\text{x}10^{-4}$	39.62
Pure ABS	389.71	8.28	--	--	$6.41\text{x}10^{-4}$	$2.85\text{x}10^{-4}$	36.32

CONCLUSION

Global TSDC of PVVH and ABS is characterized by a dipolar relaxation peak at 347 and 389 K, respectively. Thermal sampling (TS) technique is carried out to decompose global TSDC spectrum into its elementary process. Relaxation map analysis (RMA) has been discussed and thermodynamics parameters of the samples, such as enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) are estimated. The compensation phenomenon has been examined for pure and polyblend samples. It is observed that, pure samples are chractaerized by one compensation point and some of polyblend samples are characterized by two compensation points. The coordinates of the compensation point are used to calculate the density of disorder (DOD) of the samples. It is found that, DOD is decreased as the PVVH conent is decreased.

ACKNOWLEDGEMENT

We would like to thank Prince Sattam bin Abdulaziz University, KSA and Deanship of Scientific Research for their supporting. The work is supported by the Deanship of Scientific Research in Prince Sattam bin Abdulaziz University, Saudi Arabia under Grant No.2015/01/4353.

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