
Thermal Sampling and Compensation Phenomena of PVVH/ZnO Nanocomposite Polymer Using TSDC Technique

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Abstract: Thermo-electrets of poly (vinyl chloride-co-vinyl acetate-co-2 hydroxy propyl acrylate) PVVH and its nanocomposite PVVH/ZnO were prepared using the thermal poling method. Thermally stimulated depolarization current TSDC technique used to study the alpha relaxation of the samples. The global spectra of the nanocomposites revealed that ZnO nanoparticles are completely compatible with the polymer matrix. The activation energy was calculated and found to be in the range of 0.69-1.25 eV. TS technique was used to resolve the complex TSDC behavior and thermodynamic parameters were obtained from Eyring relationship which verified the linear relation between the activation enthalpy ΔH and the activation entropy ΔS . The compensation phenomena had been studied and the degree of disorder DOD of all samples has been calculated and results values in the range 15 to 35.24 Cal degree⁻¹.

Keywords: Nanocomposites, TSDC, Thermal Sampling, Enthalpy, Entropy, Activation Free Energy, Compensation, DOD

1. Introduction

Polymer nanocomposites have gained a great attention in recent years due to their mechanical and barrier properties, especially at very low filler content, it has a wide field of applications such as super capacitors, solar cells, sensors and lithium ion batteries [1]. One of the most useful and very high sensitive techniques which used to study the dielectric relaxation of materials is thermal stimulated depolarization current TSDC technique. TSDC was used to study and quantify the defects (trap charges, dipoles or oxygen vacancies) which exist in the dielectric materials [2], the accumulations of charges in polycrystalline [3], also to evaluate the influence of dipole content on the relaxation strength and the thermal stability of the system [4]. Generally, TSDC technique is a dielectric technique in which the dynamic of the system is observed through the trend of the previously aligned structural dipoles to orientate at random as the mobility of the system increase during the continuous heating from temperatures far below T_g [5]. Poly

(vinyl chloride-co- vinyl acetate-co-2-hydroxypropyl acrylate) PVVH is a linear terpolymer which is characterized by its flexibility and the structure is highly sensitive to the variation of temperature [6] is selected for this study. Thermal sampling technique (TS) has been applied to polymers, showing the ability to isolate quasi-elementary process of the complex spectra, enabling a complete characterization of the corresponding distribution of characteristic times [7]. By using Arrhenius equation, it is very easy to study the activation energy and relaxation time of the polymer [8]. Also by using Eyring relation, it is easy to study thermodynamic parameters such as Gibb's free energy, enthalpy and entropy which show a linear relationship between the enthalpy and entropy [9-10], it also allows to study the compensation phenomena which characterized by compensation point (is indicative of cooperative molecular movements and that T_c is the temperature at which all the relaxations involved in the process occur with the same relaxation time) [11], which is correlated to the physical properties of the material.

The aim of this paper is to study the TSDC spectra of PVVH with doping ZnO nanoparticles, also the TS behavior of the nanocomposite with different concentrations. The

thermodynamic parameters, compensation phenomena, the degree of disorder and thermal expansion of samples were calculated. The activation energy and relaxation time were calculated from TSDC and TS spectra.

2. Experimental

2.1. Materials

Poly (vinyl chloride – co vinyl acetate – co 2-hydroxypropyl acrylate) (PVVH) (Aldrich chemical company, USA), Dimethyl formamide (El Nasr pharmaceutical chemical co. Egypt) and Acetic Acid 96% (El Nasr pharmaceutical chemical co. Egypt), Zinc sulphate hepta-hydrate (Alfa Aesar, Germany), Sodium Hydroxide (El Nasr pharmaceutical chemical co. Egypt) and Deionized water is used for preparing ZnO nanoparticles.

2.2. Methods

2.2.1. Preparation of PVVH/ZnO Nanocomposites Polymer Films

PVVH was dissolved in 20 ml DMF under continuous stir at 323 K until completely dissolved. ZnO nanoparticles powder (with different concentrations) is dissolved in 10 ml DMF with 0.5 ml acetic acid as an initiator, stir until completely dissolved, then it sonicated for 20 minutes. The ZnO solution was added to PVVH solution drop by drop, then stir and sonicated for 1 hour. The resultant solution of PVVH/ZnO is poured into a glass petri dish in the oven at 333 K for two days. Films are ready with thickness ranged from 30 to 60 μm, which measured by digital micrometer Mitutoyo no 293-521-30 Japan. Carbon paste Kontakt-Chemie, Germany was used as a conducting electrode.

2.2.2. TSDC Instrument

A home-made cell was used to investigate the global TSDC spectra through temperature range 300-400 K. Parallel plate electrodes were used, with the upper plate spring-loaded to maintain electrical contact during thermal cycling. To obtain a global TSDC spectrum, the samples were polarized by a static electric field of 3×10^6 V/m at the polarizing temperature T_p down to the freezing temperature, with cooling to freeze in dipole orientation. When samples are short-circuited, the depolarization current due to segmental orientation was measured as the temperature increased. The current was measured with a Keithley electrometer 610C at a constant heating rate 3 K/min. The temperature was measured with a temperature controller unit Digi-sence, 2186-25A, Cole-Parmer instrument Co, USA.

Spectra were obtained by applying the polarizing field for 10 min over a narrow range of temperature from T_p to T_p-5 K and then depolarizing for 10 min at temperature $T_d=T_p-5$ K with the field off. The samples were quenched to the lower desired temperature with the field off. The depolarization spectrum due to a narrow distribution of relaxations was then measured upon reheating at 3 K/min. By applying the TS technique at different polarizing temperature windows T_p-T_d

= 5 K, sets of depolarization curves were obtained for every polarization temperature which are subsets of that obtained from the global TSDC spectra. The signal for this TS spectrum is the result of the reorientation of the narrow packet relaxations which were excited over the 5 K temperature window around T_p . Details of the experimental arrangement and measuring techniques.

3. Results and Discussion

Figure 1, shows the global TSDC spectra of pure PVVH and PVVH/ZnO nanocomposite with different concentrations under the same conditions $T_p=353$ K, $E_p=3 \times 10^6$ V/m, $t_p=10$ min with constant heating rate 3 K/min. The T_p of 353 K was selected near to the glass transition temperature to avoid space charge mechanism or degradation effects. The TSDC for all samples show the same behavior with a single characteristic peak, which covering the glass transition temperature range (333-349) K, is assigned to the α -relaxation of PVVH chains in an interfacial layer close to ZnO nanoparticles [12]. From TSDC spectra, it is clear that the glass transition temperature increases with increasing the concentration of nanoparticle in the polymeric matrix which is corresponding to the increase of the amorphous region of PVVH matrix [13]. The current of TSDC for PVVH/ZnO nanocomposites increases with increasing ZnO concentration up to 1% which can indicate the increase of dipole-dipole interaction [14].

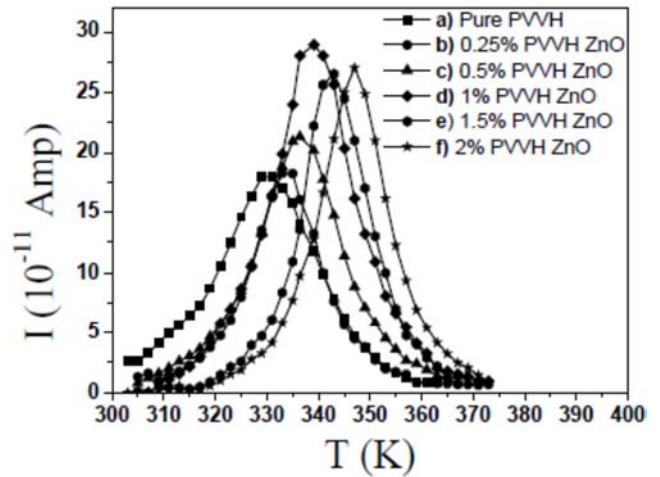


Figure 1. Global TSDC spectra of pure PVVH and PVVH/ZnO nanocomposite with different ZnO nanoparticle concentrations under constant conditions $E_p = 3 \times 10^6$ V/m, $T_p = 353$ K, $t_p=10$ min using carbon paste as an electrode.

The activation energy and relaxation time were calculated from the initial rise part of the spectra by using the Arrhenius equation [8]:

$$I = I_0 \exp(E_a/kT) \tag{1}$$

Where T is the absolute temperature, E_a is the activation energy and k is Boltzmann constant.

$$\tau(T) = \tau_0 \exp(E_a/kT) \quad (2)$$

Where, τ_0 is the pre-exponential factor.

The calculated activation energies were found to be in the range of 0.69-1.25 eV results from the degree of cooperative

nature in the molecular motion at the glass transition temperature [5]. The relaxation times of all samples with different concentrations were found to be in the range of 10^{-17} to 10^{-9} for dipole segmental motion, the molecular parameters are tabulated in table 1.

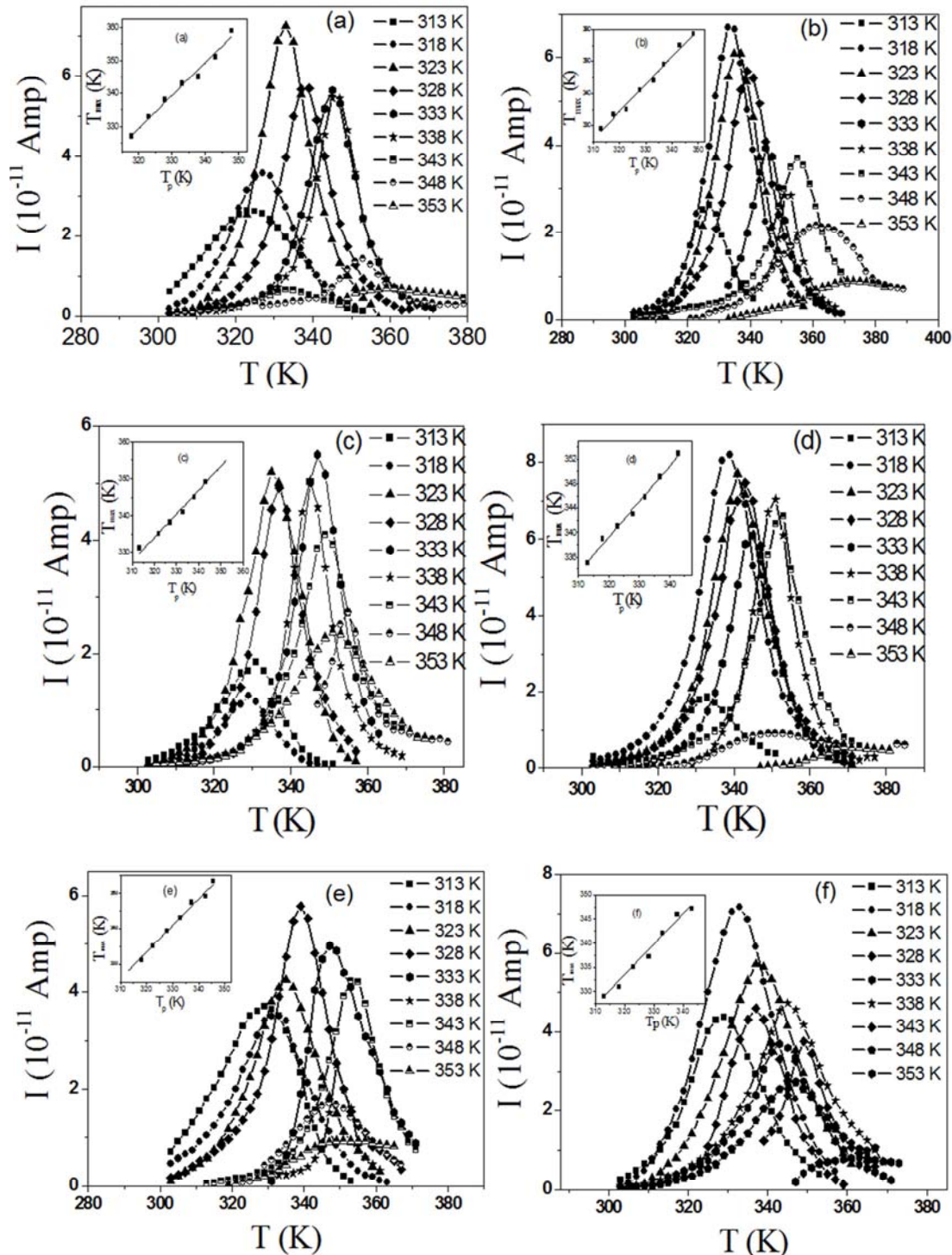


Figure 2. Typical TS spectra of (a) pure PVVH and PVVH/ZnO nanocomposites with different ZnO nanoparticle concentrations (b: 0.25%, c: 0.5%, d: 1%, e: 1.5% and f: 2%).

In order to study the resolving of the complex spectrum of TSDC to its elementary process, TS technique has been studied for pure PVVH and its nanocomposite with different

concentrations at constant poling field $E_p = 3 \times 10^6$ V/m, poling time $t_p = 10$ min and different poling temperatures ranged 313-353 K with polar window $T_p - T_d = 5$ K, as shown

in figure 2. Each TS spectrum results as a set of peaks, which is characterized by a single peak at different maximum positions depending on the poling temperature. The maximum temperature increases linearly with the poling field, the inset figure 2, the slope of this line is unity, which agrees with the theoretical prediction of continuous distribution [15]. The molecular parameters associated with the dipolar relaxation process of all samples, such as

activation energy and pre-exponential factor have been calculated by using the initial rise method as listed in table 2.

It is clear that the distribution of the activation energy and relaxation time are reversely and can be corresponding to the different relaxation modes in polymeric materials, the high values of the activation energy correspond to the strong intermolecular interaction at the glass transition temperature [16].

Table 1. The molecular parameters of PVVH/ZnO nanocomposite.

Samples	Maximum current (10^{-11} Amber)	Maximum temperature (K)	Activation energy (eV)	Relaxation time (sec)
Pure PVVH	18	331	0.697394	6.52E-09
0.25% PVVH/ZnO	19	333	1.196031	1.27E-16
0.5% PVVH/ZnO	21	335	0.850167	3.69E-11
1% PVVH/ZnO	28	339	0.897312	1.01E-11
1.5% PVVH/ZnO	26	343	1.250054	6.96E-17
2% PVVH/ZnO	26	349	1.234329	2.55E-16

Table 2. The molecular parameters of TS spectra for all samples.

sample	Polar Window (K)	Maximum temperature (K)	Activation energy (eV)	Relaxation time (sec)
Pure PVVH	313-308	324	0.457	3.076E-05
	318-313	327	0.848	1.882E-11
	323-318	333	1.200	1.080E-16
	328-323	338	1.443	4.170E-20
	333-328	343	1.925	5.473E-27
	338-333	345	1.607	4.321E-22
	343-338	351	0.653	1.357E-07
	348-343	359	1.413	2.275E-18
0.25% PVVH/ZnO	313-308	329	0.536	2.159E-06
	318-313	333	1.347	5.805E-19
	323-318	335	1.366	4.014E-19
	328-323	341	0.632	1.469E-07
	333-328	344	2.071	4.498E-29
	338-333	349	3.317	7.926E-47
	343-338	355	0.548	6.614E-06
	348-343	359	0.740	1.226E-08
0.5% PVVH/ZnO	313-308	331	0.710	4.043E-09
	318-313	329	2.273	1.241E-33
	323-318	335	0.951	9.934E-13
	328-323	335	0.971	4.934E-13
	333-328	341	1.559	1.164E-21
	338-333	345	1.697	1.976E-23
	343-338	349	1.206	6.789E-16
	313-308	335	0.273	5.470E-02
1% PVVH/ZnO	318-313	339	1.177	5.367E-16
	323-318	341	1.173	7.777E-16
	328-323	343	1.200	3.977E-16
	333-328	345	1.260	6.461E-17
	338-333	349	1.396	1.047E-18
	343-338	353	1.225	5.710E-16
	313-308	329	0.547	1.409E-06
	318-313	331	0.773	4.166E-10
1.5% PVVH/ZnO	323-318	335	0.738	2.090E-09
	328-323	339	1.077	1.770E-14
	333-328	343	2.426	1.877E-34
	338-333	347	3.116	3.744E-44
	343-338	349	1.464	1.049E-19
	348-343	353	1.891	1.150E-25
	313-308	329	1.276	4.123E-18
	318-313	331	1.046	2.109E-14
2% PVVH/ZnO	323-318	335	0.886	1.028E-11
	328-323	337	1.639	3.685E-23
	333-328	343	1.249	7.214E-17
	338-333	345	0.856	7.417E-11
	343-338	347	2.750	8.788E-39

TS spectrum can be used to study the compensation phenomena which is the linear relationship between the activation energy and $\ln(\tau_0)$ [17]. The thermodynamic parameters such as the activation enthalpy ΔH , the activation entropy ΔS , and Gibb's free energy ΔG can be calculated by Eyring theory [9]. According to Eyring rate theory, the relaxation time $\tau(T)$ can be expressed in terms of entropy (ΔS), then (2) becomes

$$\tau(T) = (h/kT) \exp(\Delta G/kT) \quad (3)$$

Where ΔG is given by

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

$$\ln(\tau T k/h) = \Delta H/kT - \Delta S/k \quad (5)$$

From (5), ΔH could be calculated from the slope of plot $\ln(\tau T k/h)$ versus $1000/T$ and ΔS from the intercept of the line.

The variation of $\ln(\tau T k/h)$ against $1/T$ for pure PVVH and PVVH/ZnO nanocomposites with different concentrations are shown in figure 3. The figure confirms linear relationship and the extrapolated lines are collected at three different compensation points. At the compensation point, all the discrete processes that constitute the broad relaxation near the glass transition temperature have the same relaxation time. The present of three different compensation points may be attributed to that PVVH is terpolymer incompatible and originated from specific inter- and intra-molecular interaction [18]. ΔG was calculated using (4) and considered the temperature $T=T_p$. The thermodynamic parameters of all samples are estimated and listed in table 3. The positive values of ΔS , imply that the macromolecules are in a more disorder state. In addition, the positive value of ΔG means that this system is thermodynamically unstable [19].

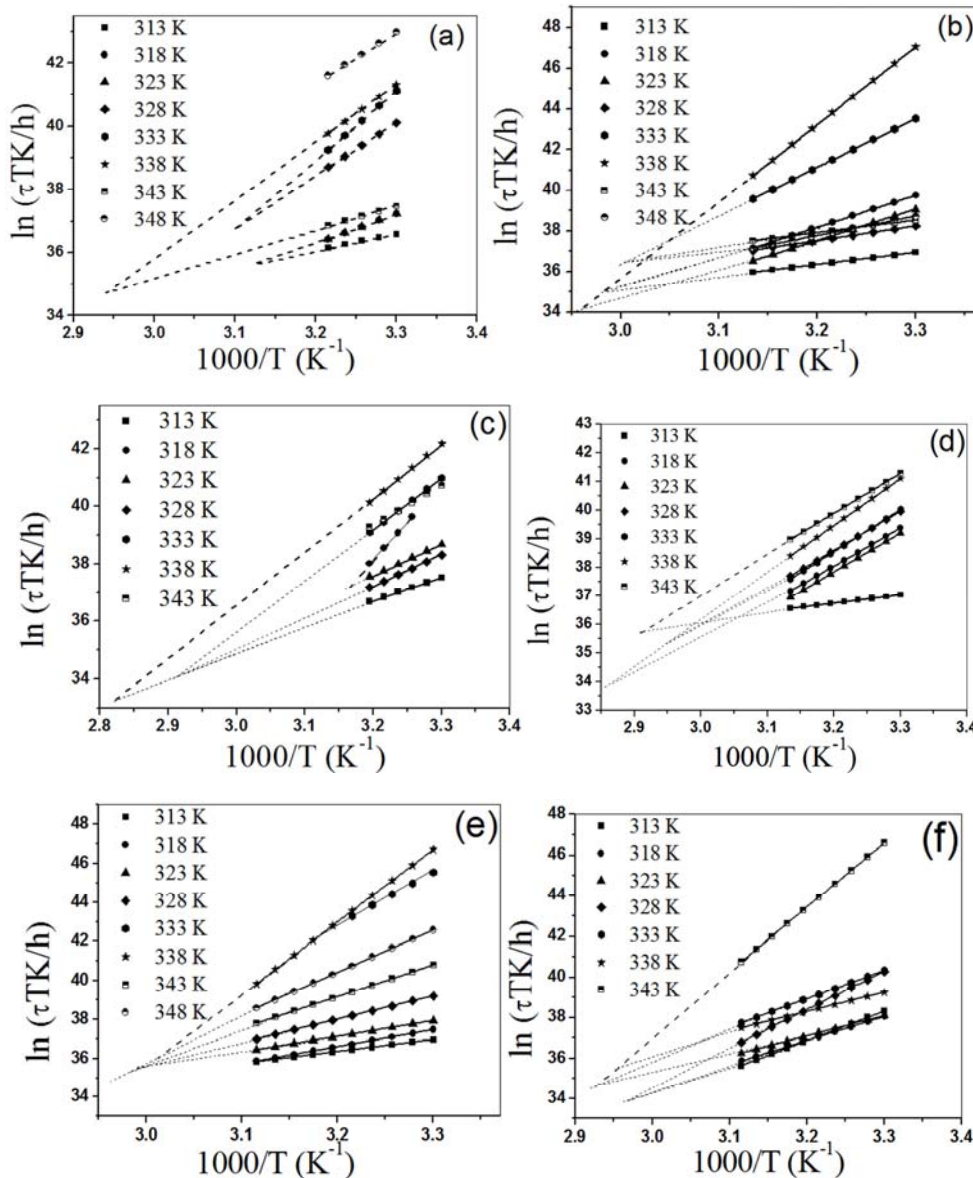


Figure 3. Relation between $\ln(\tau T k/h)$ versus $1000/T$ for (a) pure PVVH and PVVH/ZnO nanocomposites with different ZnO nanoparticle concentrations (b: 0.25%, c: 0.5%, d: 1%, e: 1.5% and f: 2%).

Table 3. Kinetic parameters calculated at polarization temperature T_p for each sample.

Sample	Poling temperature (K)	Activation enthalpy (eV)	Activation entropy (eVK ⁻¹)	Gibb's free energy (eV)
Pure PVVH	313	0.430	-1.733	542.932
	318	0.819	-0.506	161.573
	323	0.819	-0.506	164.100
	328	1.414	1.212	-396.036
	333	1.896	2.715	-902.312
	338	1.578	1.648	-555.398
	343	0.625	-1.168	401.152
	348	1.385	0.867	-300.373
0.25% PVVH/ZnO	313	0.507	-1.511	473.410
	318	1.318	0.933	-295.469
	323	1.337	1.041	-334.802
	328	0.603	-1.303	427.901
	333	2.042	2.990	-993.478
	338	3.288	6.798	-2294.334
	343	0.519	-1.607	551.840
	348	0.711	-0.961	335.238
0.5% PVVH/ZnO	313	0.682	-0.984	308.546
	318	2.246	3.901	-1238.203
	323	0.922	-0.289	94.270
	328	0.942	-0.193	64.294
	333	1.530	1.519	-504.198
	338	1.668	1.870	-630.368
	343	1.177	0.375	-127.315
	313	0.244	-2.385	746.643
1% PVVH/ZnO	318	1.148	0.395	-124.419
	323	1.144	0.406	-129.922
	328	1.171	0.421	-136.815
	333	1.231	0.622	-205.941
	338	1.367	0.981	-330.165
	343	1.196	0.390	-132.411
	313	0.518	-1.474	461.909
	318	0.744	-0.774	246.824
1.5% PVVH/ZnO	323	0.709	-0.934	302.362
	328	1.048	0.074	-23.211
	333	2.397	3.953	-1313.902
	338	3.087	6.198	-2091.696
	343	1.435	1.207	-412.613
	348	1.862	2.475	-859.275
	313	1.247	0.814	-253.671
	318	1.017	0.079	-23.946
2% PVVH/ZnO	323	0.857	-0.455	147.752
	328	1.610	1.846	-603.966
	333	1.220	0.546	-180.495
	338	0.827	-0.656	222.404
	343	2.721	4.963	-1699.579

The activation enthalpy and activation free energy have been plotted against polarization temperature for different nanocomposite concentrations, are shown in figure 4 and 5. It shows that both ΔG and ΔH depend on T_p . It is clear that, in the explored temperature range, the distribution of the activation energy can be attributed to the different relaxation modes in polymeric materials [16]. Table 4 presents the

compensation parameters, such as compensation temperature and the compensation relaxation time for all samples. The compensation effect is described in terms of the activation enthalpy-entropy relationship, where the variation in the activation enthalpy is compensated with the variation in the activation energy.

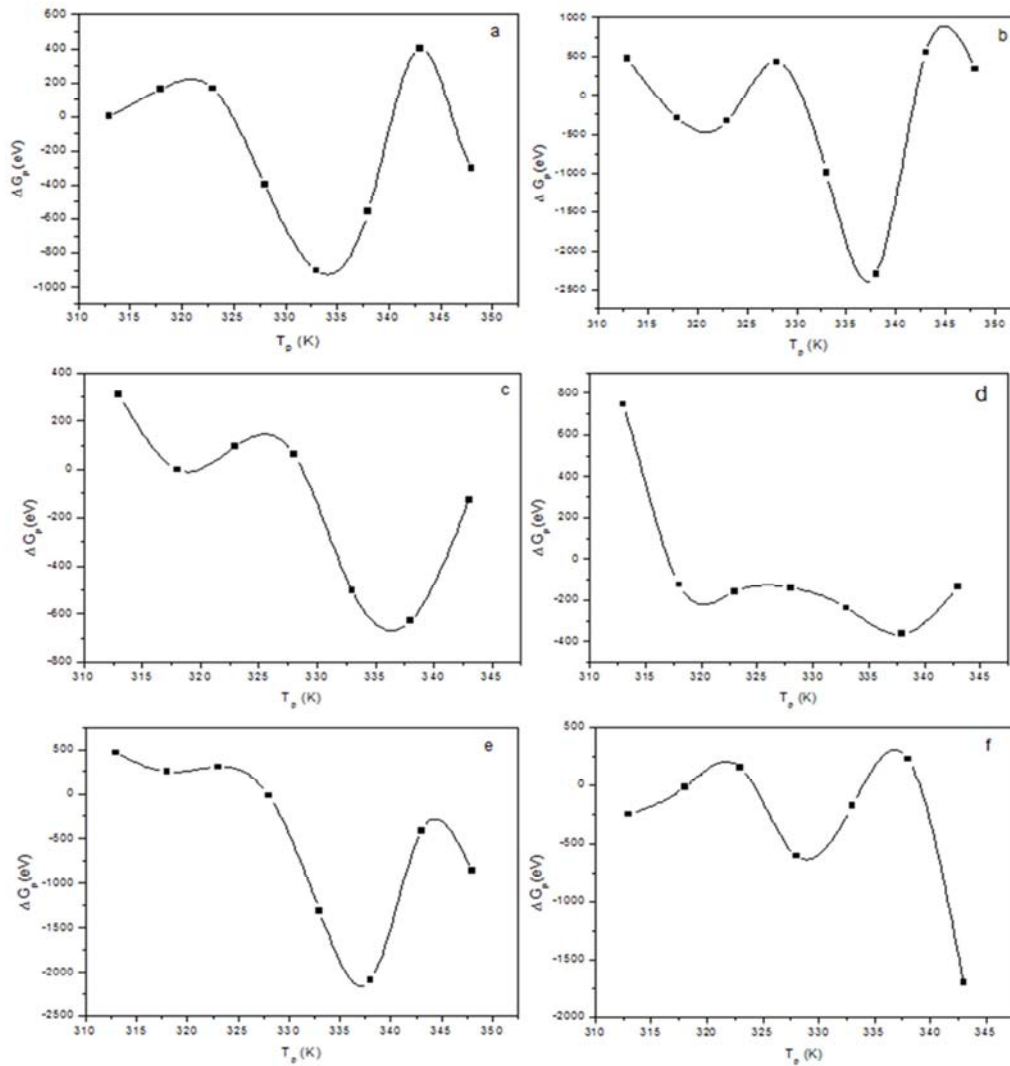


Figure 4. Dependence of Gibbs free energy ΔG on the polarization temperature T_p for (a) pure PVVH and PVVH/ZnO nanocomposites with different ZnO nanoparticle concentrations (b: 0.25%, c: 0.5%, d: 1%, e: 1.5% and f: 2%).

Table 4. Presents the compensation parameters, the degree of disorder DOD, thermal volume expansion β and thermal expansion coefficient $\Delta\beta$.

Sample	Compensation temperature (K)	Compensation relaxation time (sec)	Degree of disorder (Cal deg ⁻¹)	Thermal volume expansion (K ⁻¹)	Thermal expansion coefficient (K ⁻¹)
Pure PVVH	320.97	1922.87	25.75	0.000779	0.000346
	360.06	41.45	33.20	0.000694	0.000309
	362.66	14.83	35.24	0.000689	0.000306
	332.57	994.03	27.00	0.000752	0.000334
0.25% PVVH/ZnO	335.02	233.46	29.89	0.000746	0.000332
	337.95	95.89	31.65	0.00074	0.000329
	315.76	2310.08	25.42	0.000792	0.000352
0.5% PVVH/ZnO	343.64	90.23	31.74	0.000728	0.000323
	354.61	36.49	33.48	0.000705	0.000313
	338.98	319.18	29.24	0.000738	0.000328
1% PVVH/ZnO	343.16	477.09	28.41	0.000729	0.000324
	349.14	72.02	32.16	0.000716	0.000318
	313.66	425793.98	15.00	0.000797	0.000354
1.5% PVVH/ZnO	320.65	592.10	28.11	0.00078	0.000347
	334.22	393.55	28.85	0.000748	0.000332
	337.86	56.80	32.70	0.00074	0.000329
2% PVVH/ZnO	338.58	376.32	28.91	0.000738	0.000328
	340.97	157.88	30.63	0.000733	0.000326

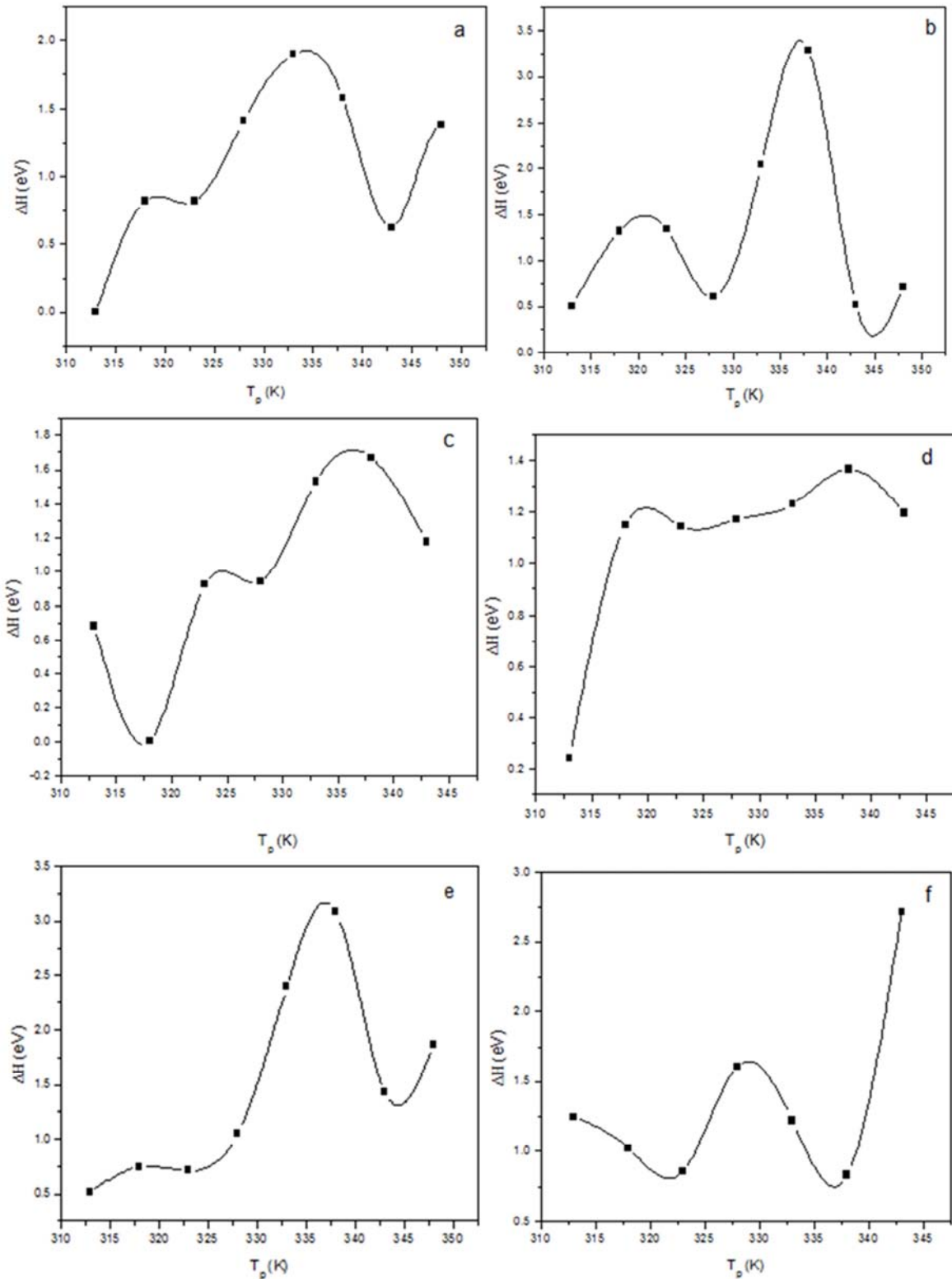


Figure 5. Dependence of enthalpy ΔH on the polarization temperature T_p for (a) pure PVVH and PVVH/ZnO nanocomposites with different ZnO nanoparticle concentrations (b: 0.25%, c: 0.5%, d: 1%, e: 1.5% and f: 2%).

Figure 6, represented the variation of enthalpy ΔH against entropy ΔS of PVVH/ZnO nanocomposite with different concentrations. A linear relationship has been observed for all samples which is a consequence of the structure changes towards equilibrium with increasing the temperature [15].

The energy of the blend relaxation process comprises not only the energy required to displace the segments along the reaction path, but also the energy required to create these segments, which confirms the validity of the compensation law [20].

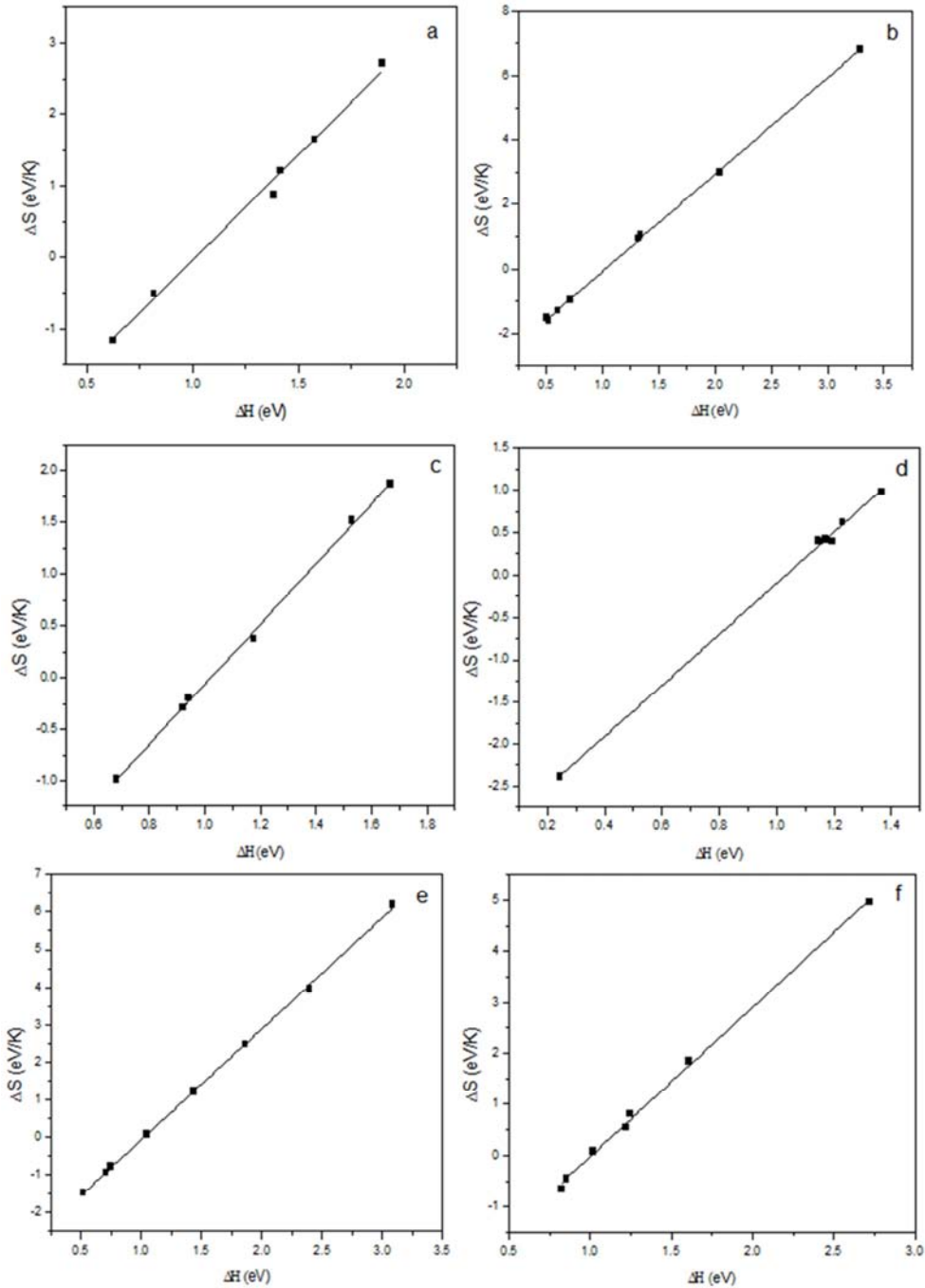


Figure 6. Activated states entropy ΔS plotted versus enthalpy ΔH of (a) pure PVVH and PVVH/ZnO nanocomposites with different ZnO nanoparticle concentrations (b: 0.25%, c: 0.5%, d: 1%, e: 1.5% and f: 2%).

The density of disorder DOD reflects the degree of compatibility of copolymers [15] and can be defined by the relation of entropy against enthalpy when T_p is varied. DOD can be calculated using the coordinating points T_c and τ_c from the equation [21].

$$\text{DOD} = 100 - 2[\ln(T_c \tau_c) + 23.76] \quad (6)$$

The number 100 is arbitrarily added to shift all the values to the positive side. The DOD can be used to measure the degree of disordered and ranged in all investigated samples

from 15 to 35.24 shown in table 4. For amorphous materials, DOD values vary from 30 to 70 [21].

The relation between ΔS and ΔH could be correlated to the coefficient of thermal volume expansion β for the polymer fluid using the empirical relationship [15].

$$\Delta S = M_c \beta \Delta H \quad (7)$$

Where M_c is dimensionless constant and its value is 4. Then, the compensation temperature can be defined as

$$T_c = 1 / \beta M_c \quad (8)$$

The differences in the values of the thermal expansion coefficient $\Delta\beta$ above and below T_g can be determined from the formula $\Delta\beta = 1/9T_c$ for all samples. Values of β and $\Delta\beta$ are calculated and shown in table 4.

4. Conclusions

TSDC global spectra of pure PVVH and PVVH/ZnO nanocomposites exhibit a single relaxation process, with a peak at a maximum temperature near to the glass transition of each concentration. The magnitude of current and its peak position increases with the concentration. Each global spectrum has been resolved into elementary processes characterized by a set of single relaxation peaks. The relaxations can be described by the distribution of relaxation times with different activation energies in each sample. The compensation phenomena revealed the presence of three compensation points and a linear relation between enthalpy and entropy. Also, the degree of disorder and the coefficient of thermal volume expansions were calculated.

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