

Relaxation Phenomenon of Poly(vinyl alcohol)/Sodium Carboxy Methyl Cellulose Blend by Thermally Stimulated Depolarization Currents and Thermal Sample Technique

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ABSTRACT: The dipolar relaxation in poly(vinyl alcohol) (PVA), sodium carboxy methyl cellulose (NaCMC_s), and their blends were studied using a thermally stimulated depolarization current (TSDC) technique. The mutual effects of polarization conditions such as heating rate, poling temperature, time, and field on the properties of TSDC were investigated. Quantitative analysis of the experimental data is given in terms of dipolar and space charge polarization. A thermal sampling (TS) technique was applied to decompose the complex relaxations in individual polymers and their blend of 0.5/0.5 wt/wt into its normal distribution components. The activation energy of TS-formed electrets was

determined by fitting the experimental curve to Bucci and Fieschi equations. Peak parameters such as activation energy and preexponential factor τ_0 were obtained. A linear relationship between the activation energy and logarithm of the preexponential factor was found, thus confirming operation of the compensation law. In addition, by using the Eyring equation of the rate theory, the activation enthalpy ΔH^\ddagger and the activation entropy ΔS^\ddagger were calculated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1342–1353, 2005

Key words: thermally stimulated currents; thermal sampling; activation energy; dielectric properties; blends

INTRODUCTION

The study of relaxation processes in semicrystalline polymers is a subject of continuing technological interest. Great numbers of investigations have been undertaken with the purpose of characterizing the relaxations in these materials and the detailed description of their molecular processes.

The thermally stimulated depolarization current (TSDC) is a basic tool for identification and evaluation of the dipole reorientation process and of charge carrier trapping (space charge) and recombination levels. The usefulness and sensitivity of TSDC measurements lie in the fact that polarization attributed to individual molecular processes is associated with their low equivalent frequencies (10^{-3} – 10^{-5} Hz), making it especially suitable for studying systems having long relaxation times. Accordingly, TSDC can be used to study the low-frequency dielectric relaxation in solids^{1,2} and polymers.³ To investigate the origin of a peak in the TSDC spectrum, the peak parameters such as polarization parameter^{4,5} and the nature of the electrode⁶ are taken in consideration. To resolve the structure of a distributed relaxation, the thermal sampling (TS) method can be applied.^{7–12}

The TS technique allows one to decompose the broad TSDC spectrum of a relaxation into its elementary (nondestructive) components. The TS peak is characterized by its location in the TSDC spectrum (temperature of maximum intensity T_m) and a series of TS experiments, with different polarization temperatures T_p , give a scanning of the distributed relaxations of the whole spectra. From the analysis of each TS peak the activation parameters (ΔH^\ddagger and ΔS^\ddagger) of the corresponding elementary relaxation mechanisms can be calculated. There are many different methods to perform such calculations, such as initial method,¹³ Bucci's method,¹⁴ Marcum's method,^{15,16} Prölich's method,¹⁷ and temperature displacement TS peak as a function of heating rate.¹ It was shown that the Bucci and initial rise method give the same values for the activation parameters.^{1,18} However, both initial rise and Bucci's methods are mostly used to obtain the activation parameters of the TS peak.

The discharge current $J(T)$ at absolute temperature T is given by¹⁹

$$J(T) = \frac{N\mu_0^2 E_p}{3kT_p \tau_0} \exp\left[-\frac{E_a}{kT} - \frac{1}{\beta\tau_0} \int_{T_0}^T \exp\left(-\frac{E_a}{kT}\right) dT\right] \quad (1)$$

where N is the number of dipoles per unit volume of dipole moment μ_0 , E_p is the poling field, T_p is the polarizing temperature, E_a is the activation energy to

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disorient the dipole, β is the uniform heating rate, k is Boltzmann's constant, T_0 is the initial temperature of the TSDC, and τ_0 is the preexponential factor of time constant for the process. The value of τ_0 is determined by differentiation eq. (1), to obtain the temperature T_m at which maximum current occurs, and equating $dJ/dT = 0$, then

$$\tau_0 = \frac{kT_m^2}{\left[\beta E_a \exp\left(\frac{E_a}{kT_m}\right) \right]} \quad (2)$$

Initial rise method

According to Garlick and Gibson¹³ the low-temperature tail of eq. (1) is given by

$$\log J(T) = \text{constant} - \frac{E_a}{kT} \quad (3)$$

The value of E_a may be determined from the slope of the straight line plot of $\log J(T)$ versus $1/T$ in the range where the current rise initially. The relaxation time could be calculated using the following equation:

$$\tau = \tau_0 \exp(E_a/kT) \quad (4)$$

Bucci method¹⁴

In the derivation of eq. (1)

$$\tau = \frac{\int_{i(T)}^{\infty} J(t) dt}{J(T)} \quad (5)$$

The numerator can be obtained with fairly good accuracy by graphical integration of the TSDC curve. From eq. (4)

$$\ln(\tau) = \ln(\tau_0) + \frac{E_a}{kT} \quad (6)$$

A plot of $\ln \tau$ versus $1/T$ should be a straight line if a uniform process is operative. The slope and intercept of this line determine E_a and τ_0 .

The aim of this article was to show the high-resolution possibilities of TSDC combined with TS to study their kinetic parameters of the relaxation phenomena in both poly(vinyl alcohol) (PVA) and sodium carboxy methyl cellulose (NaCMC_s) homopolymers and their blends, and to study the influence of polarization conditions of TSDC spectra to determine the origin of these relaxation phenomena. The relaxation time data will be analyzed using the rate theory to confirm the existence of the compensation effect.

EXPERIMENTAL

Both PVA and NaCMC_s of molecular weights 14,000 and 4500 were supplied by BDH Chemical Ltd. (Poole, UK). Weighed amounts of natural granules of PVA were dissolved in a mixture of distilled water and ethanol at a ratio of 4 : 1. Also, weighed amounts of NaCMC_s were dissolved in distilled water at room temperature. Solutions of PVA and NaCMC_s were mixed together with different weight percentages (1.0/0.0, 0.7/0.3, 0.5/0.5, 0.3/0.7, and 0.0/1.0 wt/wt (PVA/NaCMC_s)). Thin films of appropriate thickness (~ 0.05 mm) were cast onto stainless steel petri dishes, and then dried in air at room temperature for about 6 days until the solvent was completely evaporated. The sample was sandwiched between two copper electrodes. Polarization of samples was carried out by first heating them to a specified polarizing temperature T_p , and then applying an electric polarizing field E_p for a known polarizing time t_p . Subsequently, the samples were cooled to room temperature under the applied field. The field was reduced to zero, and then TSDCs were recorded while scanning the temperature, in the range from 303 to 423 K at a fixed heating rate of 1 K/min. The current was measured using a Keithley 617 electrometer (Keithley Metrabyte, Taunton, MA).

Thermal sampling polarization was performed by applying an electric field of 4 kV/cm at a polarization temperature T_p for 45 min to polarize the dipolar entities. Next the temperature was quenched to 5° less than T_p , as fast as possible, held for 15 min, after which time the electric field was shut off. The sample was then cooled to room temperature at a cooling rate of 20°/min. Finally, the depolarization relaxation was measured at a heating rate 1 K/min. X-ray diffraction patterns were obtained using an advanced refractions system (Scintag/USA, Inc., Sunnyvale, CA). The used tube was copper radiation and the filter was nickel. X-ray diffraction was performed to investigate whether the crystalline portion of PVA might be influenced or altered by mixing it with NaCMC_s compound. The scanning of the samples was carried with an X-ray diffractometer at room temperature ($6^\circ \leq 2\theta \leq 70^\circ$). The typical X-ray diffraction patterns of PVA as well as NaCMC_s and 0.5/0.5 (wt/wt) blend sample are shown in Figure 1. It is clear that the samples under investigation are not completely amorphous, but have a relatively higher degree of crystallinity. The observed crystalline peaks in both PVA and NaCMC_s are in good agreement with that reported previously.^{20,21}

RESULTS AND DISCUSSION

Global TSDC spectra

The TSDC global spectra for both PVA and NaCMC_s homopolymers, and their blends of different compo-

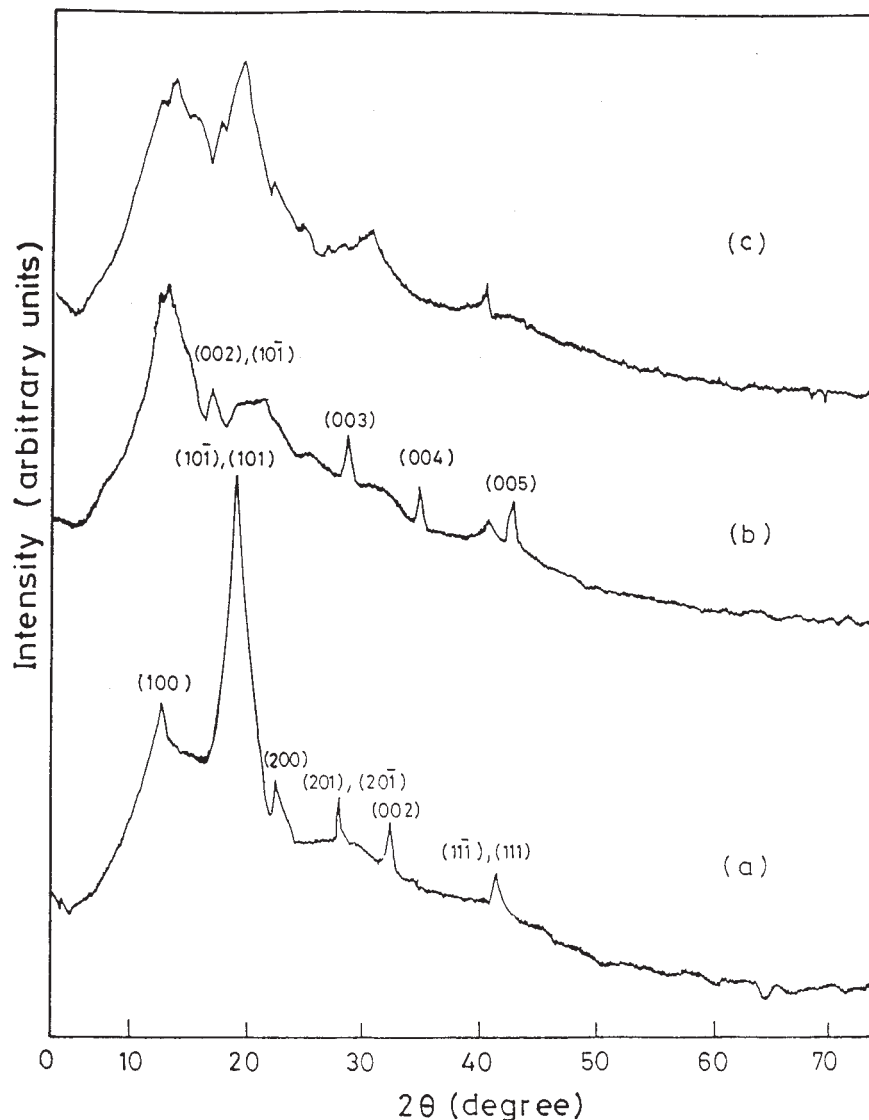


Figure 1 X-ray diffraction patterns of (a) pure PVA, (b) pure NaCMC_s, and (c) 0.5/0.5 PVA/NaCMC_s blend.

sitions at polarizing temperature $T_p = 343$ K, polarizing field $E_p = 4$ kV/cm, polarizing time $t_p = 45$ min, and heating rate $\beta = 1^\circ/\text{min}$, are shown in Figure 2. It must be mentioned that the selected polarizing conditions are the best for obtaining appreciable TSDC for samples under investigation, and this will be discussed later. It can be seen that the PVA spectrum consists of a single pronounced broad peak corresponding to a peak temperature T_m around 353 K, whereas the NaCMC_s spectrum consists of two current peaks: one is composite at T_m around 338 K and the other is a sharp peak (which can be satisfactorily described by Debye relaxation) at $T_m = 355$ K, with a shoulder in the high-temperature side. The hump at the lower-temperature side of the composite peak might be attributable to the relaxation of side chains or small polar groups from the polarized to the equilibrium nonpolarized state.²²

In fact, dielectric materials like polymers show many current peaks for depolarization, characterizing TSD transitions of various kinds.²³ Several distinct dielectric and space charge relaxations are usually present in polarized semicrystalline polymer material. The multiplicity is seen most easily in a scan of depolarization current as a function of temperature. Because of the increase in temperature, the molecular mobilities of various types become successively energized and are available for dipolar orientation.

For blend samples, the positions and magnitudes of TSDC spectra are substantially different from those observed in the individual polymers. A small additional relaxation peak is also observed at the higher-temperature region at about 403, 398, and 395 K for PVA/NaCMC_s blends of compositions 0.7/0.3, 0.5/0.5, and 0.3/0.7, respectively. Apparently, one can thus expect that this peak appearing in the heteroge-

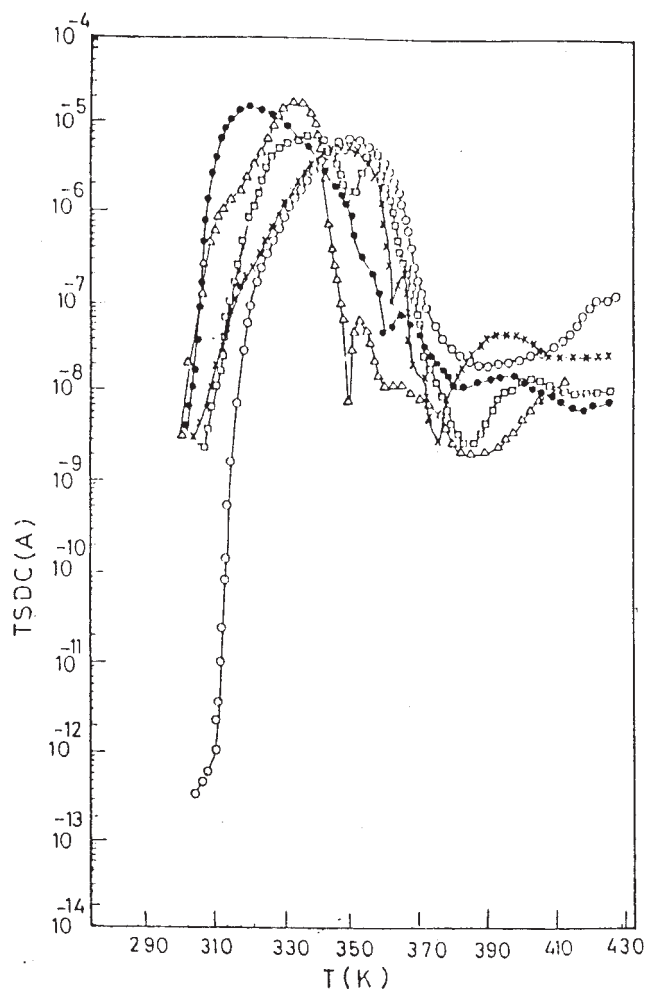


Figure 2 TSDC thermograms at polarization field $E_p = 4$ kV/cm, polarization temperature $T_p = 343$ K, polarization time 45 min for PVA/NaCMC_s blends: (○) 1.0/0.0, (□) 0.7/0.3, (×) 0.5/0.5, (●) 0.3/0.7, and (△) 0.0/1.0 (wt/wt).

neous blends is clearly a consequence of interfacial polarization because its position and magnitude are dependent on the composition of blend, and result from the accumulation of a virtual charge at the interface of media having different permittivities and conductivities.²⁴

Using the initial rise method the activation energy and relaxation time at T_m of the Debye relaxation peak were evaluated and are presented in Table I for pure

NaCMC_s and the blends of different compositions. A close look at Table I shows that the experimentally determined polarization time of 45 min is really much greater than the relaxation time $\tau(T_m)$. This allows the polarized sample²⁵ to achieve a nearly filled state. It can be seen that the addition of NaCMC_s to PVA leads to a remarkable increase in the value of activation energy, suggesting that factors other than single relaxations must contribute to kinetics associated with such peak.

To explain the origin of the relaxation process and to determine the suitable starting conditions for TSDC measurements the mutual effects of different polarization conditions—field intensity, polarizing temperature, and polarizing time—were investigated in addition to the rate of heating on pure polymers and only the 0.5/0.5 blend sample.

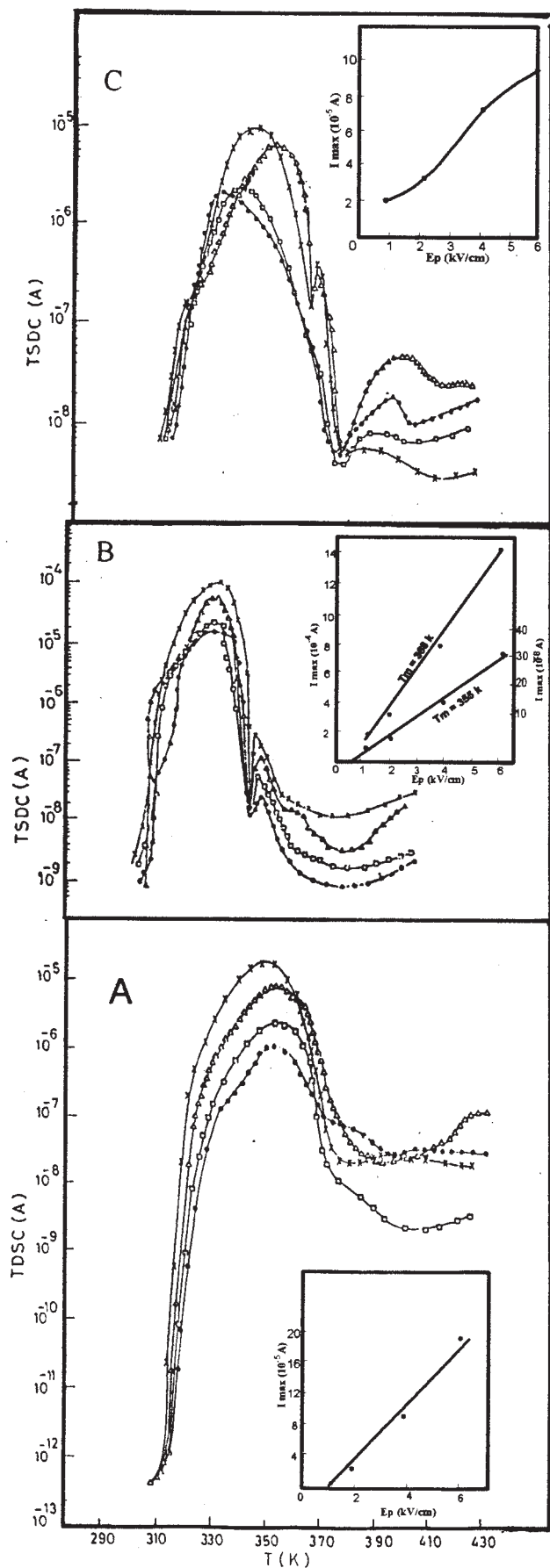
Effect of polarizing field

Figure 3 shows the effect of variation of polarizing field on TSDC spectra of homopolymers and 0.5/0.5 blend samples for constant $T_p = 343$ K and $t_p = 45$ min. Under the influence of electric field the irregularly distributed dipoles of side chains are mobilized/oriented in a certain direction but the peak temperature remains unaffected. Thermal activation at a constant rate causes the release of charges attributed to their mobilization, giving a peak at the site of maximum release of charge.¹ In the case of homopolymers [Fig. 3(A) and (B)], the peak positions are found to be independent of the polarizing field strength. The slight shift in the position of the peaks may be the result of small variations in the heating rate. The insets of Figure 3(A) and (B) show that I_m for the peaks appear at glass transitions, increasing linearly with E_p and indicating that the polarization in such compounds are uniform. Similar behavior is also observed for the sharp peak at 355 K in NaCMC_s. A uniform polarization is generally understood to be attributed to the dipole alignment and/or migration of charge over microscopic distance with trapping.

The most plausible mechanism responsible for the heterocharge is alignment of dipoles; even the complete alignment of dipoles may not be sufficient to produce the observed charge. Therefore it is suggested

TABLE I
Values of the Activation Energies and Relaxation Times for Debye-Like Peaks for PVA/NaCMC_s Samples

Blend composition PVA/NaCMC _s (wt/wt)	Activation energy, E_a (eV)	Relaxation time, $\tau(T_m)$ (s)
1.0/0.0	—	—
0.7/0.3	1.24	9.47
0.5/0.5	1.69	5.21
0.3/0.7	2.66	4.11
0.0/1.0	3.45	3.12



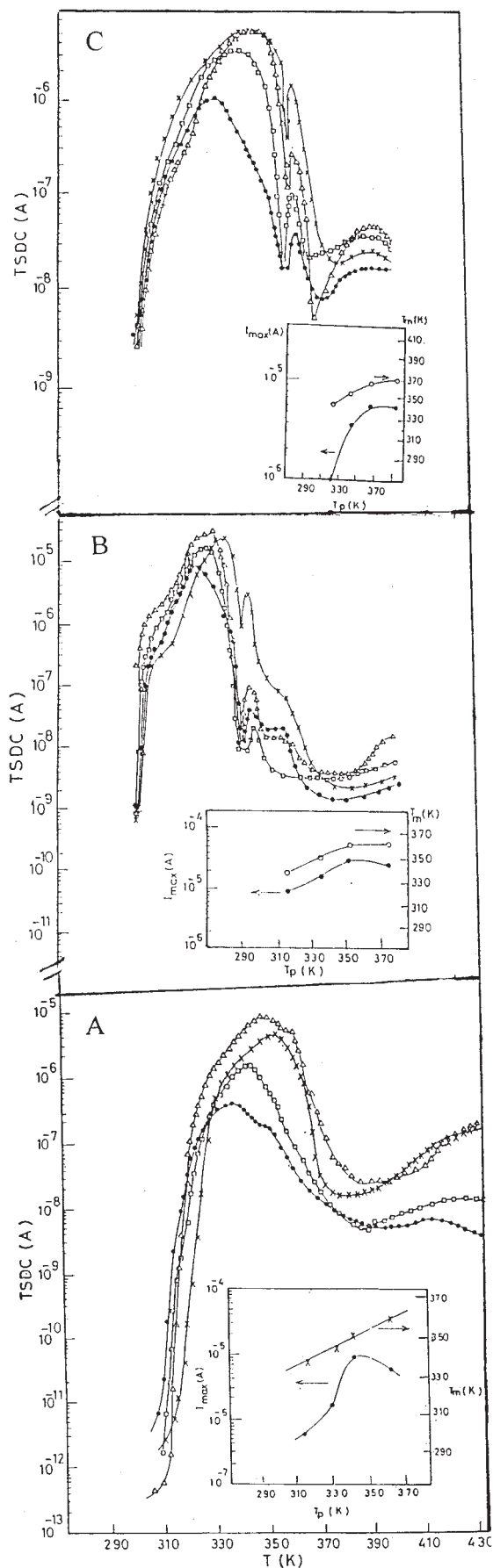
that, in addition to the dipole alignment, the heterocharges may be the result of the thermal excitation of the trapped charge carriers.²⁶ A distribution of localized energy levels or charge traps exists in polymers. The trapped carriers are excited thermally and contribute to electrical conduction. Under the effect of local fields, these charge carriers migrate over microscopic distances and are recaptured. If the capture time is small in comparison to lifetime in the traps, the rate of decay of depolarization or current density depends on the rate of release from the traps.

For the 0.5/0.5 (wt/wt) blend sample, the position of relaxation peaks irregularly changed with increasing polarizing field. At a polarizing field of more than 2 kV/cm a hump and a sharp relaxation peak appeared at lower- and higher-temperature sides of the pronounced broad peak, respectively. The hump is probably related to the so-called sub- T_g intermediate relaxation, which has been reported to appear in a number of polymers.²⁷⁻²⁹ Also, it must be noted that the appearance of a sharp peak at relatively high fields may be explained by the fact that interatomic restraints are reduced sufficiently to permit a nonelastic displacement of neighboring molecules. Poly(vinyl alcohol) ($T_g \approx 350$ K) and NaCMC_s ($T_g \approx 340$ K) have different T_g values and thus a large difference in relaxation time. So if PVA and NaCMC_s independently relax without any interaction, the I_m of the relaxation peaks should be linearly field dependent in the blend sample. In the real mixture of the two polymers, the friction coefficient of PVA may be affected by the presence of NaCMC_s, and thus a deviation from linearity is present, as seen in the inset of Figure 3(C). Thus, the deviation from linearity may be a measure of mutual coupling or intermolecular interaction.³⁰ This seems to be consistent with a suggestion of partial miscibility for PVA/NaCMC_s blend samples. In addition, the deviation from linearity at higher fields, already set in above 4 kV/cm, may suggest that a free-charge-type mechanism also operated.³¹

Effect of polarizing temperature

Figure 4 shows the effect of variation of polarizing temperature on TSDC spectra of homopolymers and 0.5/0.5 blend sample at a constant polarizing field of 4 kV/cm and poling time of 45 min. It can be seen from the insets of Figure 4(A)–(C) that with the increase of T_p the peak position T_m of a T_g relaxation peak is linearly shifted toward the higher-temperature side of

Figure 3 Effect of polarization field $E_p = 1$ kV/cm (●), 2 kV/cm (□), 4 kV/cm (△), and 6 kV/cm (×) for pure PVA [A], pure NaCMC_s [B], and the blend 0.5/0.5 (wt/wt) [C] at polarization temperature $T_p = 343$ K and polarization time 45 min.



PVA, whereas it increases in curved shape for both pure NaCMC_s and 0.5/0.5 blend sample. The shift in peak temperature with T_p is indicative of distribution of relaxation time.³¹ At low polarizing temperatures all the dipoles are not activated. As T_p is increased, an increasing number of slow dipoles are activated, and the peak temperature shifts toward the higher-temperature side.

However, the peak current in all samples increases with increasing T_p up to 343 K, with the rate of order PVA > PVA/NaCMC_s > NaCMC_s and then decreases at 363 K [see the insets of Fig. 4(A)–(C)]. By heating the polarized sample up to or well above the polarization temperature T_p , the release of charges is gradually sped up, and when the half-life of this process become comparable with the timescale of the experiment, discharge becomes measurable and gives rise in the external circuit to a current that first increases with increasing temperature, and then decays when the supply of charges is depleted.²⁵ The decrease of I_m at T_p higher than 343 K can be explained on the basis that, under these conditions, more polarization is activated and/or space charge polarization attributed to charge generation at the electrode–sample interface. These charges are neutralized by conduction current in opposite directions, which means that the observed charge release will be less than the initially stored charge.³² In addition, partial compensation of heterocharge by charge injected from electrode (homocharge) seems a more probable mechanism for the decrease of the charge released in the discharge. Such behavior is characteristic of a heterogeneous phase system with high concentrations of trapping sites at a sample electrode interface.

Effect of polarizing time

Figure 5 depicts the TSDC spectra obtained on homopolymers and 0.5/0.5 (wt/wt) blend samples polarized at a constant E_p and T_p but with varying polarizing times of 30, 45, 60, and 90 min. It is clear from the figures that the longer the polarization times t_p , the smaller the polarization. The height and the area of TSDC peak in both homopolymers and blend sample are reduced for polarizing times more than 45 and 60 min, respectively [see the insets of Fig. 5(A)–(C)]. However, positions of the relaxation peaks in all samples are irregularly changed with increasing polarization time. On the other hand, the shapes of the relaxation peaks are not significantly affected, except for

Figure 4 Effect of polarization temperature $T_p = 313$ K (●), 328 K (□), 343 K (△), and 363 K (×) on TSDC for pure PVA [A], pure NaCMC_s [B], and the blend 0.5/0.5 (wt/wt) [C] at polarization field $E_p = 4$ kV/cm and polarization time 45 min.

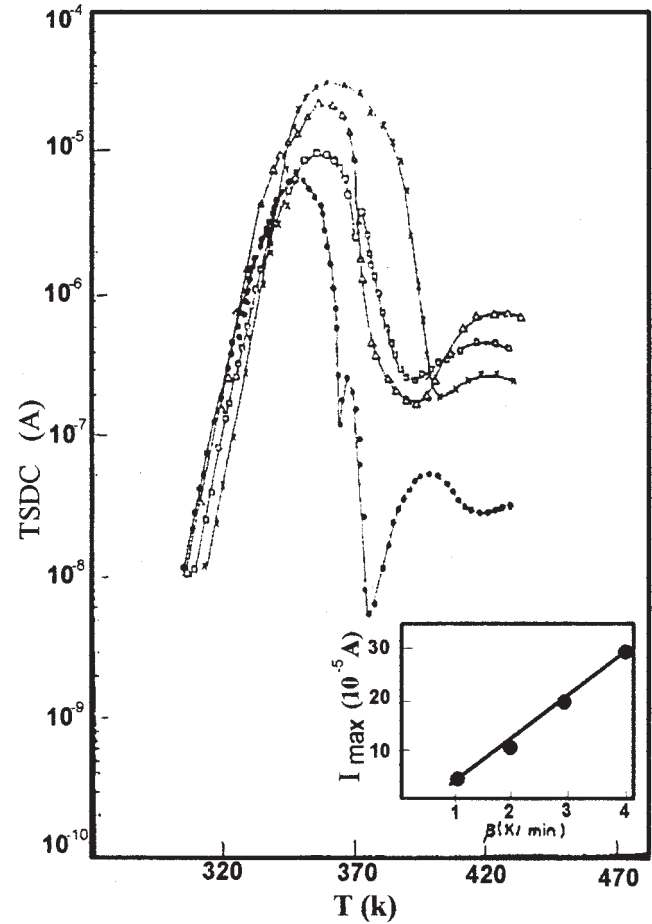
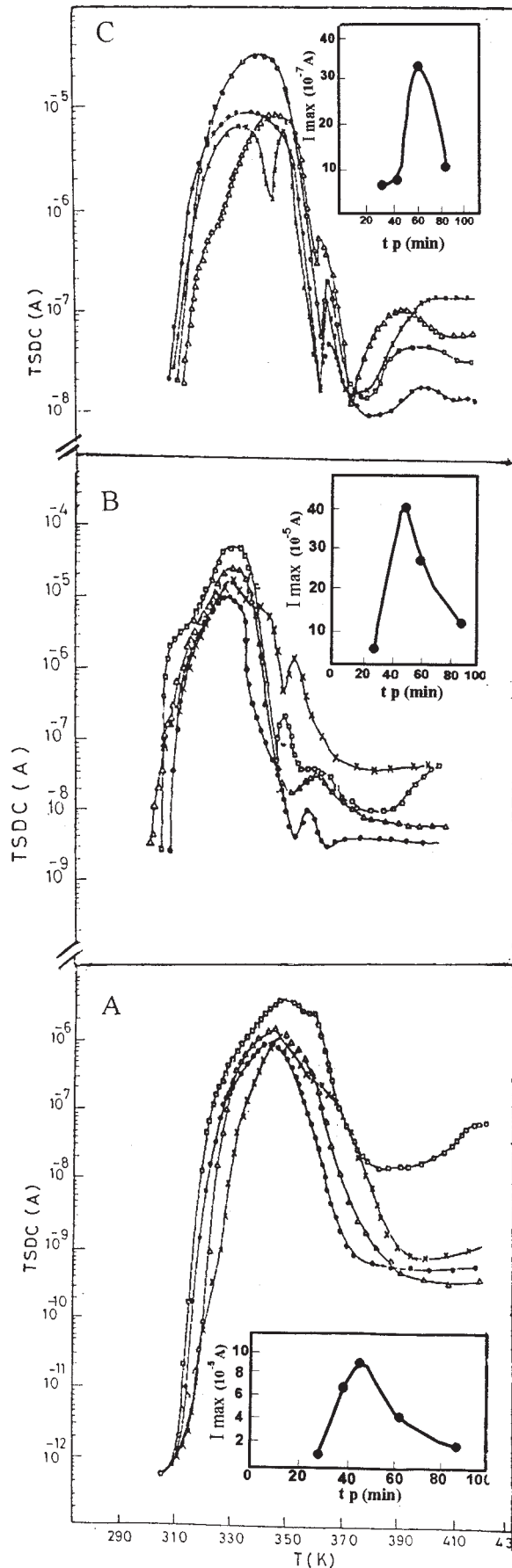


Figure 6 Effect of rate of heating 1 K/min (●), 2 K/min (□), 3 K/min (△), and 4 K/min (×) on TSDC for PVA/NaCMCs blend 50/50 (wt/wt) at polarizing field $E_p = 4$ kV/cm, polarizing temperature $T_p = 343$ K, and polarizing time $t_p = 45$ min.

the blend sample at polarizing time of 90 min; the low-temperature relaxation peak is resolved into two nearly relaxation processes.

Effect of heating rate

The TSDC thermograms of the homopolymers and their 0.5/0.5 (wt/wt) blend samples at various heating rates generally describe a nearly similar behavior for the T_g relaxation peak. Figure 6 illustrates, as a representation, the variation of TSDC of blend samples using various linear heating rates of 1, 2, 3, and 4°/min. Three peaks were observed with heating rates of

Figure 5 Effect of polarization time $t_p = 30$ min (●), 45 min (□), 60 min (△), and 90 min (×) on TSDC for pure PVA [A], pure NaCMCs [B], and the blend 0.5/0.5 (wt/wt) [C] at polarization field $E_p = 4$ kV/cm and polarization temperature $T_p = 343$ K.

1 and 2°/min, whereas at heating rates of 3 and 4°/min, the intermediate sharp relaxation disappeared.

The most straightforward information we can obtain from these spectra is the temperature T_m , at the maximum of depolarization peak. First of all, it is apparent that T_m for the T_g relaxation peak is not strongly affected by the heating rate used, which, in the usual interpretation, is attributed to the fact that the responsible process has a high apparent activation energy. From the inset of Figure 6, it is observed that the peak magnitude increases linearly with increasing heating rate. This is because the same charge is to be released in less time with increasing heating rate. This may be a case of dipolar relaxation.³³

The mutual influence of E_p , T_p , t_p , and β on TSDC spectra obtained for pure polymers and their blend sample, as shown in Figures 3–6, indicates that higher T_p values up to 343 K are enough to enhance the response time of permanent dipoles and internal free charges to applied electric fields of strength up to 4 kV/cm and allow the equilibrium polarization to be reached in a reasonably short time of 45 min. Longer time, higher temperature, and higher field polarization are found to entail a general decrease in TSDC, which, together with the variation of peak temperature T_m with polarizing temperature T_p , may be suggestive of dipolar relaxation masked with space charge³³ in the blend sample.

The results explained above may become useful to differentiate between various processes leading to buildup of polarization polymer dielectric. The process of polarization may be explained by different mechanisms, the importance of which are dipole orientation, ion displacement, and charge injection from electrodes with subsequent trapping in the polymer matrix.

Thermal sampling of TSDC spectra

The thermal sampling polarization procedure was applied with a temperature window of 5° in the cases of PVA, NaCMC_s, and their 0.5/0.5 wt/wt blend sample. Six elementary peaks were obtained for each investigated material at $T_p = 318, 323, 328, 333, 338,$ and 343 K, as shown in Figure 7. It is evident that the peak intensities shown roughly trace out the shape of the glass transition of the global TSDC spectrum. In the case of NaCMC_s the sub- T_g relaxation peak is also observed at most polarizing temperatures. The peaks are broader regardless of intensity, indicating a non-cooperative low value of activation energy and/or the existence of interactions between dipolar molecules.^{4,34,35} It can be seen that for polarization temperatures up to 343 K the mechanism responsible for the T_g peak is activated. The maximum current of the peaks increased as T_p increases and the temperature at which the maximum appears, T_m , shifts to slightly

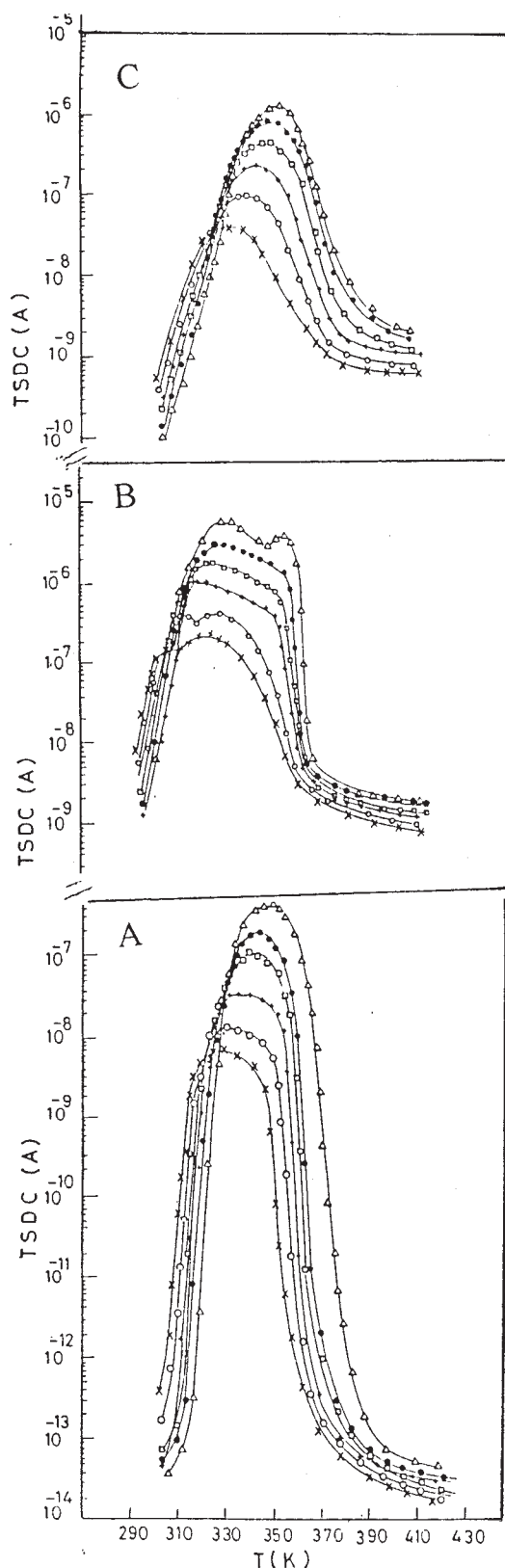
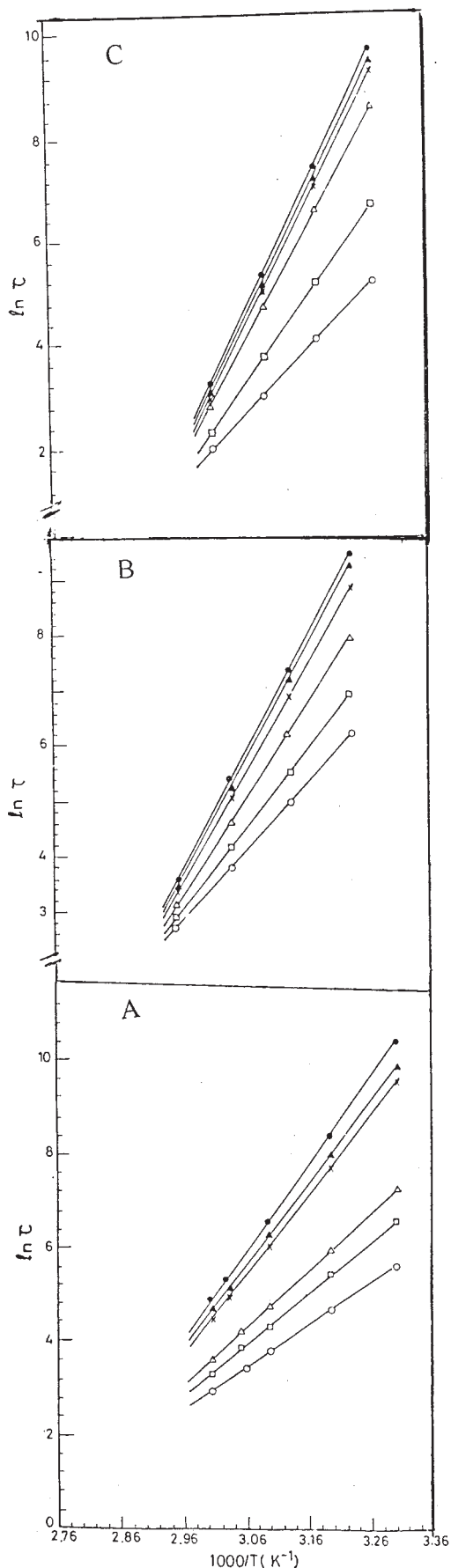


Figure 7 TSDC windowing polarized on TSDC for pure PVA [A], pure NaCMC_s [B], and the blend 0.5/0.5 (wt/wt) [C] at $t_p = 45$ min; $E_p = 4$ kV/cm; $T_p = 343$ K (Δ), 333 K (\square), 328 K ($+$), 323 K (\circ), and 318 K (\times).



higher values with T_p . At $T_p = 343$ K the carriers activated during the TS process, trapped in a trapping level for which there is a maximum number of trapping states available.^{4,36}

Each TS spectrum results in one Arrhenius line of relaxation times after numerical integration using the Bucci method. Several representative Arrhenius lines thus obtained for the samples under investigation are shown in Figure 8(A)–(C). The activation energy (E_a) and the preexponential factor (τ_0) for each TS process were obtained from $\ln \tau$ versus $1/T$ dependency and are presented in Table II. The values of the calculated τ_0 are several orders of magnitude smaller than the Debye relaxation time (10^{-14} – 10^{-12} s). These smaller values have also been found in α -relaxation for many polymers^{37,38} and they have been explained by means of the cooperative character of the molecular motion in this transition. According to Lushcheikin,³⁹ τ_0 ranges from 10^{-13} to 10^{-10} s and from 10^{-25} to 10^{-18} s for dipole groups and dipole segmental relaxation processes, respectively. Thus, the observed relaxations are mainly considered to correspond to a dipole-segmental motion (see Table II). It can be also noted that the activation energy E_a is an increasing function of T_p . This effect is related to the TS process because, to form an electret by TS, the polarizing field is switched off at the beginning of cooling step, while there is still enough thermal energy for the carriers trapped in shallow levels to be released. Because the trapping levels available for the carriers depend on the temperature, in a TS polarization process the charges become trapped in a narrow energy level range.⁴⁰

For a process with single relaxation time the temperature dependency of τ can be described by eq. (4). If a compensation behavior is observed, there is a concomitant increase of τ_0 and E_a so that the Arrhenius lines converge to a single point of coordinates τ_c and T_c such that

$$\tau_0 = \tau_c \exp\left(\frac{-E_a}{kT_c}\right) \quad (7)$$

Accordingly

$$\tau(T) = \tau_c \exp\left[\frac{E_a}{k} \left(\frac{1}{T} - \frac{1}{T_c}\right)\right] \quad (8)$$

which is the well-known compensation equation.

Figure 8 Bucci lines ($\ln \tau$ versus $1000/T$) for pure PVA [A] pure NaCMC_s [B], and the blend 0.5/0.5 (wt/wt) [C], corresponding to TS processes. $T_p = 312$ K (○), 323 K (□), 328 K (Δ), 333 K (×), 338 K (▲), and 843 K (●).

TABLE II
Values of T_m , E_a , τ_0 , ΔH , and ΔS for PVA, NaCMC_s, and 0.5/0.5 (wt/wt) Blend Samples at Different Polarization Temperatures

Sample		T_p (K)					
		318	323	328	333	338	343
PVA	T_m (K)	321	329	337	341	345	349
	E_a (eV)	0.8	0.95	1.07	1.449	1.51	1.6
	τ_0 (s)	1.5×10^{-11}	1.15×10^{-13}	2.36×10^{-15}	1.12×10^{-20}	1.55×10^{-21}	8.45×10^{-23}
	ΔH (kJ/mol)	0.078	0.094	0.106	0.144	0.15	0.16
	ΔS (kJ/mol.K)	0.032	0.012	0.048	0.156	0.17	0.199
0.5/0.5	T_m (K)	330	333	335	338	343	345
	E_a (eV)	0.94	1.25	1.67	1.81	1.85	1.9
	τ_0 (s)	4.64×10^{-14}	1.42×10^{-18}	1.08×10^{-24}	9.95×10^{-24}	2.6×10^{-25}	4.87×10^{-25}
	ΔH (kJ/mol)	0.088	0.118	0.158	0.171	0.175	0.180
	ΔS (kJ mol ⁻¹ K ⁻¹)	0.004	0.092	0.207	0.244	0.257	0.272
NaCMC _s	T_m (K)	305	309	311	313	315	323
	E_a (eV)	1.02	1.18	1.4	1.6	1.7	1.75
	τ_0 (s)	5.74×10^{-15}	2.58×10^{-17}	1.52×10^{-20}	1.76×10^{-23}	6×10^{-25}	1.1×10^{-25}
	ΔH (kJ/mol)	0.095	0.11	0.132	0.151	0.161	0.167
	ΔS (kJ mol ⁻¹ K ⁻¹)	0.02	0.067	0.127	0.184	0.212	0.230

On the other hand, from Eyring's rate theory the relaxation time associated with crossing of barrier ΔG^\ddagger is given by

$$\tau(T) = \frac{h}{kT} \exp\left(\frac{\Delta G^\ddagger}{kT}\right) \quad (9)$$

where h and k are the Plank and Boltzmann constants, respectively. Also ΔG^\ddagger is the activation Gibbs energy, expressed as

$$\Delta G^\ddagger = \Delta H^\ddagger - T_m \Delta S^\ddagger \quad (10)$$

where ΔS^\ddagger and ΔH^\ddagger are, respectively, the entropy and enthalpy of the activation. Thus

$$\tau(T) = \frac{h}{kT} \exp\left(\frac{\Delta H^\ddagger}{kT} - \frac{\Delta S^\ddagger}{k}\right) \quad (11)$$

For a process with single relaxation time, the representation of $\ln[\tau(T)]$ versus $1/T$ (the so-called Eyring plot) gives a straight line whose slope is related to ΔH^\ddagger and whose intercept is related to ΔS^\ddagger . If the compensation behavior is observed, the Eyring lines of the different TS experiments will converge to the compensation point.

A linear relationship between the activation energy E_a and $\ln \tau_0$ has been found in the case of investigated materials, confirming the existence of the compensation law (see Fig. 9). The compensation behavior in polymeric

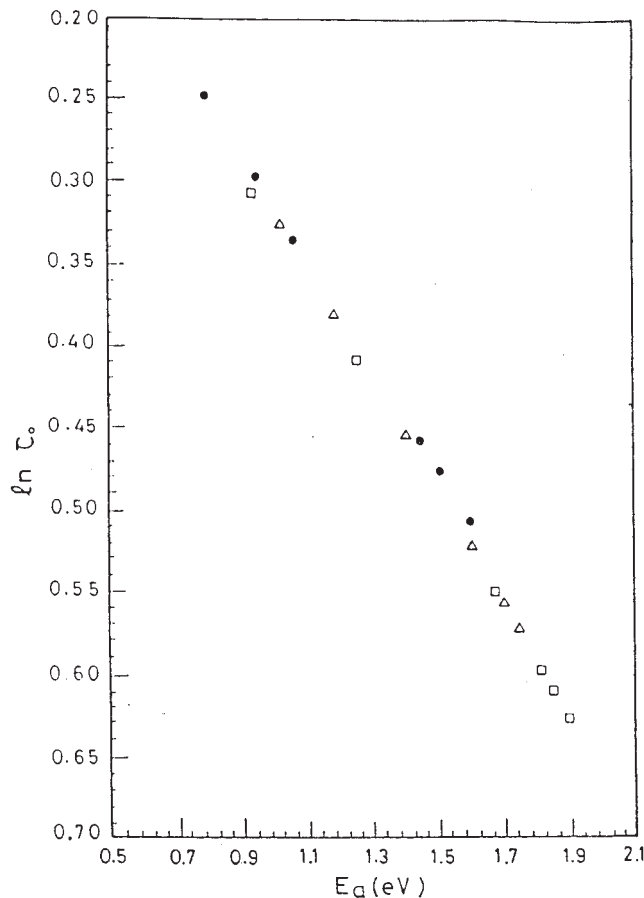
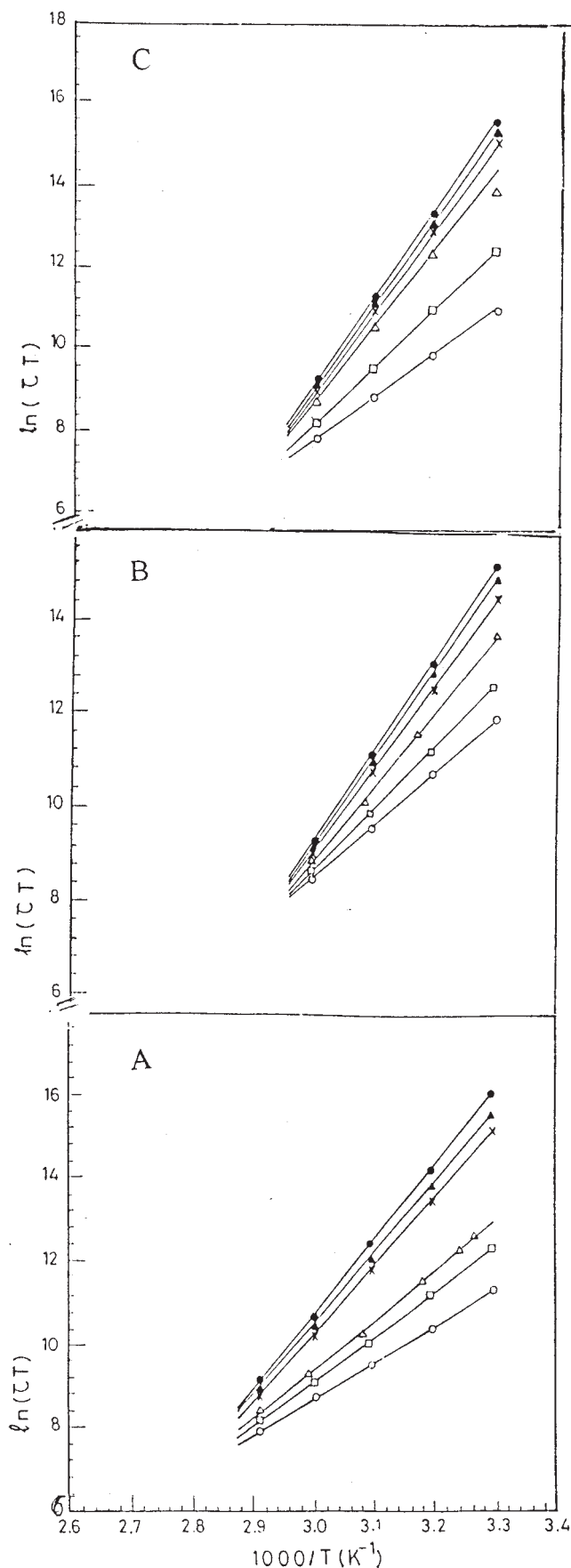


Figure 9 Variation of the preexponential factor of relaxation time (τ_0) versus the activation energy (E_a) for the TSDC of (●) PVA, (□) PVA/NaCMC_s, 0.5/0.5 (wt/wt), and (△) NaCMC_s.

TABLE III
Values of T_c and τ_c for PVA, NaCMC_s, and 0.5/0.5 PVA/NaCMC_s (wt/wt) Blend Samples

Sample	T_c (K)	τ_c (s)
PVA	358	2.7
0.5/0.5	346	2.26
NaCMC _s	343	5.43



materials is often considered as indicative of cooperative molecular movements^{41,42} and has been ascribed to the relaxations of entities with variable length.⁴³ The compensation behavior was observed for the glass-transition relaxation of many polymeric materials but it was also claimed that this behavior was characteristic of some sub-glass-transition relaxations.⁴⁴ The values of the compensation temperature T_c and compensation time τ_c for homopolymers and their blend sample, were calculated and are presented in Table III. It is seen that T_c is generally around the glass-transition temperature of maximum intensity of the TSDC global peak, suggesting a dipolar molecular relaxation for all the samples. Nevertheless, it is suggested that the small difference between T_g and T_c is related to the breadth of the glass transition. In general, the parameters T_c and τ_c that transcribe the coupling characteristics between the different modes of relaxation are related to the properties of amorphous polymers or of the amorphous regions in semicrystalline polymer.⁴⁵

In terms of the Eyring equation the representation of the data in the form $\ln[\tau(T)]$ versus $1/T$ for the studied materials gives straight lines, indicating that these relaxations follow a time distribution (see Fig. 10). From this figure, the activation enthalpy ΔH^\ddagger and the entropy ΔS^\ddagger , for each TS process, were calculated and are presented in Table II. One can notice that the values of entropy of homopolymers and their blend are very small, indicating that the dipolar relaxation is mainly predominant. Thus, the reorientation motions of the dipoles take place without significant perturbation of the position order of the macromolecules. Figure 11 shows a linear relationship between ΔH^\ddagger and ΔS^\ddagger for the investigated materials, indicating that the compensation law is operative.

From the above results, it is clear that the glass-transition peak (which is usually attributed to the micro-Brownian motions of the polymer backbone and is a feature of the amorphous regions of semicrystalline polymer) of the material under investigation shows clear composition behavior.

CONCLUSIONS

The presence of crystalline regions in semicrystalline polymers is known to affect the glass transition of the material that is usually broader than that in amorphous materials. The breadth of the glass transition was quantified by TSDC applied in the thermal sampling (TS) mode. The magnitude of the apparent activation energy

Figure 10 Relaxation results of $\ln[\tau(T)]$ versus $1000/T$ for pure PVA [A], pure NaCMC_s [B], and the blend 0.5/0.5 (wt/wt) [C], corresponding to TS processes. $T_p = 312$ K (○), 323 K (□), 328 K (△), 333 K (×), 338 K (▲), and 343 K (●).

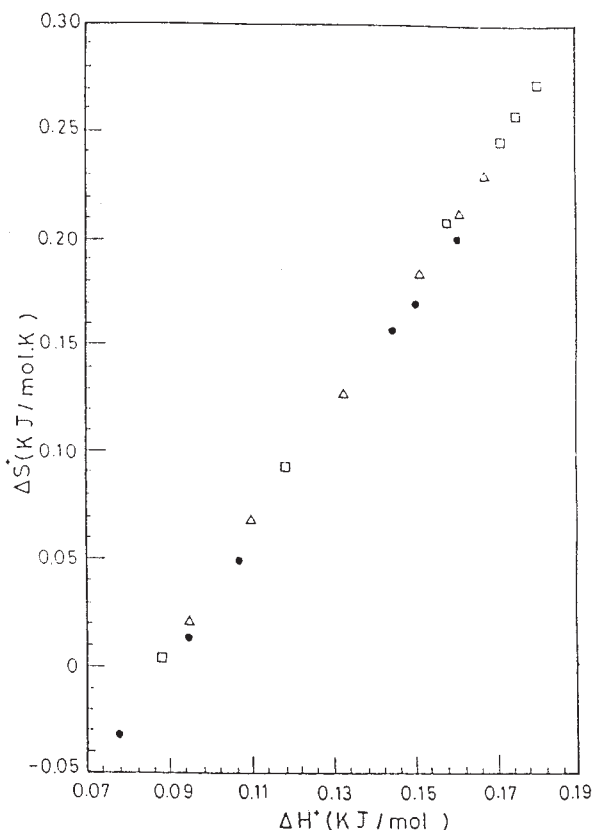


Figure 11 Compensation plot, ΔS^\ddagger versus ΔH^\ddagger for PVA/NaCMC_s blend samples: (●) PVA, (□) 0.5/0.5 (wt/wt), and (△) NaCMC_s.

E_a obtained by the TS method indicates that the relaxation is cooperative (glass-transition-like) or noncooperative. Because PVA and NaCMC_s are polar semicrystalline polymers, their dipoles will become oriented with the applied electric field and polarization resulting from this motion can produce T_g relaxation peak with lower activation energy. The obtained values of the entropy of the dipolar relaxation are very small, probably because the orientation motions take place without perturbation of the position order of the macromolecules. The TS studies indicate that the validity of the compensation law is valid and the values of τ_0 indicate that the observed relaxation processes mainly correspond to a dipole segmental motion.

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