Structural relaxation around the glass transition temperature in amorphous polymer blends: temperature and composition dependence

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The thermally stimulated depolarization current technique has been used to study the relaxation behaviour in solvent-cast blends of poly(vinyl chloride) (PVC) and acrylonitrile–butadiene–styrene (ABS). The effects of the forming conditions (field, temperature and time) on depolarization have been investigated. The data on blends with components in various weight ratios indicate that the blends are not compatible enough to show one relaxation peak and the 40:60 PVC/ABS blend shows the greatest depolarization current. The blends show two relaxation processes corresponding respectively to the glass transitions of PVC and ABS. Partial polarization and peak-cleaning techniques have been used to obtain both α peaks as a function of blend composition. Curve fitting was carried out and the activation energy E_a and the pre-exponential factor τ_0 were calculated. The data have been used for investigations of relaxations that obey an Arrhenius-like law. Analysis of the data shows that it is possible to study the relaxation behaviour in this system, which was found to be controlled by the free-volume mechanism described by the Williams–Landel–Ferry equation.

(Keywords: structural relaxation; glass transition temperature; amorphous polymer blends)

INTRODUCTION

A large number of physical and physicochemical properties of polymers are connected with relaxation phenomena. Structural relaxation is the kinetically impeded rearrangement of the temperature-dependent structure and is accompanied by changes in different macroscopic properties. The timescale for structural relaxation is highly dependent both on temperature and on the instantaneous structure itself. Dramatic changes in the properties of the polymer, which occur near the glass transition[1,2], are due to micro-Brownian motion. These changes include the equalization of a non-uniformly distributed concentration of structural elements by orientation of dielectric molecules in an electric field, or the return of oriented dipoles to a random arrangement after removal of the external electric field. Molecular motions in solid polymers can be studied with a variety of techniques, among which the thermally stimulated depolarization current (t.s.d.c.) technique is practically useful for polar polymers. The usefulness and sensitivity of the t.s.d.c. technique lie in the fact that polarization due to individual molecular processes is associated with low frequencies. Essentially, the technique provides information on a molecular level. Another advantage of the t.s.d.c. technique is the possibility of using peak-cleaning techniques such as partial heating[3] or fractional polarization[4] to resolve multicomponent or broad peaks, and hence closely spaced relaxations can be separately observed.

The strongly polar character of both poly(vinyl chloride) (PVC) and acrylonitrile–butadiene–styrene (ABS) terpolymer makes the study of the dielectric relaxation processes easy. Relaxation phenomena in PVC[5] and in ABS[6–8] have already been studied. The change of state of the polymer from glassy to rubbery is marked by a pronounced relaxation at the glass transition temperature T_g, indicating the initiation of conformal arrangements of the main chains arising from the coperative movement of the backbone with its side chains. The most marked relaxation in PVC and ABS takes place around the glass-transition region (termed the dipolar relaxation or α peak) owing to the amorphous character of these materials.

The relaxation behaviour in polymer blends with different component ratios has not been systematically investigated before now, although the compensation law has been shown to be obeyed approximately in the majority of the systems investigated[9–12]. Therefore, the object of the present work was to perform a study of the depolarization thermocurrents in PVC/ABS polyblends, aiming to explore the effect of the blending on the discharge currents in the t.s.d.c. spectra and outline the effect of blending on the relaxation processes. Attention has been paid to the study of the motions involved in the α relaxations of the components of the blends. The results of the short-circuit measurements for the polyblends with PVC weight fractions from 0.1 to 0.9 are

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presented. The investigations revealed that the free-volume concept is applicable.

THEORETICAL BACKGROUND

Usually, the temperature dependence of the relaxation time τ can be adequately approximated by the Arrhenius equation

$$\tau(T)=\tau_0 \exp(E_a/kT) \quad (1)$$

where τ_0 is the pre-exponential factor, k is Boltzmann's constant and E_a is the activation energy for the process.

At a temperature above the T_g of an amorphous polymer, when the volume is in thermal equilibrium, the α-relaxation time has always been observed to follow the Williams–Landel–Ferry (WLF) equation[13,14]. According to the WLF equation, the ith relaxation times at temperatures T and T_0 take the values τ^i and τ_0^i, so that

$$\tau^i=a_T\tau_0^i \quad (2)$$

$$\log a_T=-\frac{C_1(T-T_0)}{C_2+(T-T_0)} \quad (3)$$

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

The Kovacs–Hutchinson–Aklons (KHA) equation[15] is very useful for studying the kinetics of the α-relaxation processes for $T<T_g+10$ K. The temperature and structure dependence of the ith process is given by

$$\tau^i=A\exp\left(\frac{\Delta H^i}{RT}+\frac{b}{f_T}\right) \quad (4)$$

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

$$f_T=f_g+\Delta\alpha(T-T_g) \quad (5)$$

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

$$\ln a_T=\frac{\Delta H^i}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)+b\left(\frac{1}{f_T}-\frac{1}{f_{T_0}}\right) \quad (6)$$

In this case T affects $\ln a_T$ directly through the first term on the right-hand side and indirectly through its control of the structure, as represented by the free volume f_T in the second term[15].

EXPERIMENTAL

Blend preparation

PVC ($M_w=100\,000$) was supplied by BDH, UK, and ABS was supplied by Polysci, USA. The latter consists of a copolymer of acrylonitrile (A) and styrene (S) grafted on to polybutadiene (B). The relative concentrations of A, B and S were 29.9, 9.39 and 60.8 mol%, respectively. Films of the PVC/ABS blends were prepared by dissolving each component separately in the required weight proportion (the PVC weight fraction in the blend ranged from 0.1 to 0.9) in cyclohexanone, mixing the solutions with continuous stirring and then casting the mixture on to a glass substrate. The solvent was evaporated at 343 K for 1 week. Film thicknesses ranging from 30 to 40 μm, as measured by a travelling microscope, were obtained.

Measurements

Conducting surfaces of film with a 5 mm radius were prepared using conducting carbon paste. Details of the experimental arrangements, measuring techniques and poling procedures have been described in other papers[7,12,16]. T.s.d.c spectra were recorded using a Keithly electrometer 610C. All measurements were performed with a three-terminal electrode system in order to prevent surface leakage currents. The samples were held freely in the home-fabricated conductivity cell, with no pressure exerted on them during the measurements.

The low temperature α_1 relaxation (of PVC) has its maximum temperature at about 358 K, while the high temperature α_2 relaxation (of ABS) corresponds to a peak temperature around 378 K. In order to obtain a separation of the two t.s.d.c. peaks α_1 and α_2, the peak-cleaning method[3,17–20] was used. The following procedure was adopted. The film was polarized at $T_p=358$ K for an interval time $t_p=15$ min at a polarizing field $E_p=3$ V μm^{-1}; the PVC component was polarized practically to saturation, while the ABS component remained nearly unpolarized. After cooling, with the field on, the sample was first discharged by short circuiting at a temperature $T_d=343$ K (15 K lower than the T_g of PVC) for 15 min. After cooling, the sample was reheated at a heating rate $\beta=3$ K min^{-1}. The t.s.d.c. spectrum showing only the α_1 relaxation was then obtained. The α_2 relaxation was obtained by following the same procedure, but the blend was polarized at $T_p=393$ K and discharged at $T_d=363$ K (15 K lower than the T_g of ABS) to remove the α_1 peak. The sample was cooled, reheated and the α_2 relaxation was obtained. The α_1 and α_2 peaks can be considered at a first approximation to be activated Debye-like peaks[21,22]. The peak parameters τ_0 and E_a were measured by curve fitting[8].

RESULTS AND DISCUSSION

Global t.s.d.c. spectra

The global t.s.d.c. spectra of pure PVC ($T_p=363$ K), pure ABS ($T_p=393$ K) and the blends ($T_p=393$ K) polarized for 1 h with an electric field $E_p=4\times10^6$ V m^{-1} are shown in *Figure 1*. Maxima are present, in the case of the blends, at two temperatures assigned to the α relaxations of both PVC and ABS. These peaks are always observed at the same positions, independent of the polarizing field, if the heating rate is kept constant. At temperatures higher than the glass transition of ABS ($T_g=378$ K), pure ABS shows another maximum in the complete t.s.d.c. spectrum. This maximum has been attributed to the motion of the free charge in ABS and is known as the ρ peak[7]. This peak can be attributed to the Maxwell–Wagner–Sillars (MWS) polarization resulting from the accumulation of a virtual charge at the interface of media having different permittivities and conductivities[23]. The MWS polarization is directly related to the heterogeneity of the ABS system. On blending ABS with PVC this peak disappears, and hence the heterogeneity of the system decreases, i.e. the blend

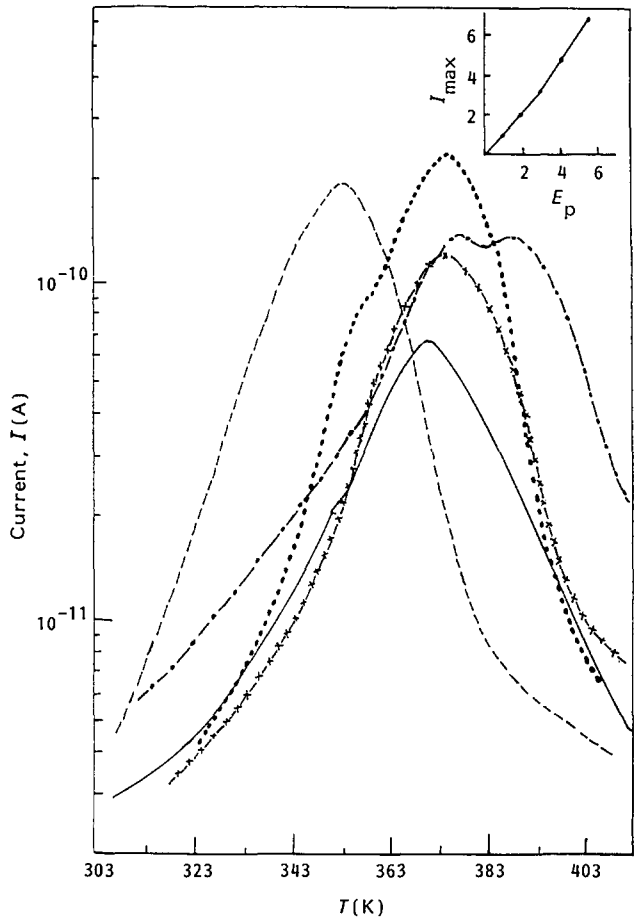

Figure 1 T.s.d.c. spectra of PVA/ABS blends polarized with $E_p = 4 \times 10^6$ V m^{-1} for 1 h at $T_p = 363$ K for pure PVC and $T_p = 393$ K for pure ABS and the polyblends: (– – –) 100:0; (···) 60:40; (– × – × –) 50:50; (——) 30:70; (– · – · –) 0:100

is more homogeneous than ABS homopolymer. This may be attributed to the miscibility or entanglement of PVC in ABS.

The two glass transitions of the pure components are clearly seen in blends containing 0 to 40 wt% ABS. ABS shows a maximum current peak at about 373 K and PVC shows a small hump at about 353 K. Above 40 wt% ABS the α peak of PVC has nearly disappeared.

PVC and ABS have different T_g and hence a large difference in relaxation rate. Furthermore, differential scanning calorimetry studies[24] have shown that PVC and ABS may not be compatible enough for the blend to show a single T_g. So, if PVC and ABS independently relax without any interaction, the I_{max} should be linearly field dependent for each component in the blend. This must be fictive behaviour. In the real mixture of the two polymers, the friction coefficient of PVC may be affected by the presence of ABS, and hence a deviation from linearity is present in the inset of *Figure 1*. The stronger the interaction, the bigger the deviation. Eventually, the relaxation rates of the two polymers approach each other, i.e. the polymers relax cooperatively, and the shift from linearity will minimize. Thus, the deviation from linearity may be a measure of mutual interaction.

In order to explore the dependence of the t.s.d.c. spectrum on the concentration of ABS in the blend, one may consider the concept of dipole–dipole interactions, i.e. the movement of the electric dipoles of PVC (C–Cl) is affected by the presence of the electric dipoles of ABS (C≡N). As the concentration of ABS increases, the C≡N dipole density increases and hence the t.s.d.c. increases until a certain compatibility limit is reached which is a state of thermodynamic stability for the PVC/ABS blend (60:40 PVC/ABS). If the amount of ABS added exceeds the compatibility limit, the enhancement of the intermolecular interactions in the blend must lead to the suppression of molecular motions[25]. The result is a decrease in the t.s.d.c. levels. The poling field may play an important role in the conformational arrangement. This implies that although it enhances the motion of the mobile dipoles, it increases the probability of formation of a more rigid chain conformation. In general, the relaxation behaviour of PVC is altered by the presence of ABS. One of the two α relaxations may have been hindered by the presence of the other process. However, some short-range compatibility might exist, since the enhancement of depolarization currents was observed in 40:60 PVC/ABS.

The results obtained on the 50:50 sample polarized at a constant E_p but with varying T_p and t_p are shown in *Figures 2* and *3*. As shown in *Figure 2*, the magnitude of the polarization and the positions of the α peaks are strongly influenced by the polarization temperature. It should first be noted that since the polarization temperature T_p is lower than the T_g of ABS, the current peak reflects only the polarization due to PVC. More pronounced effects are observed in the vicinity of 373 K. The

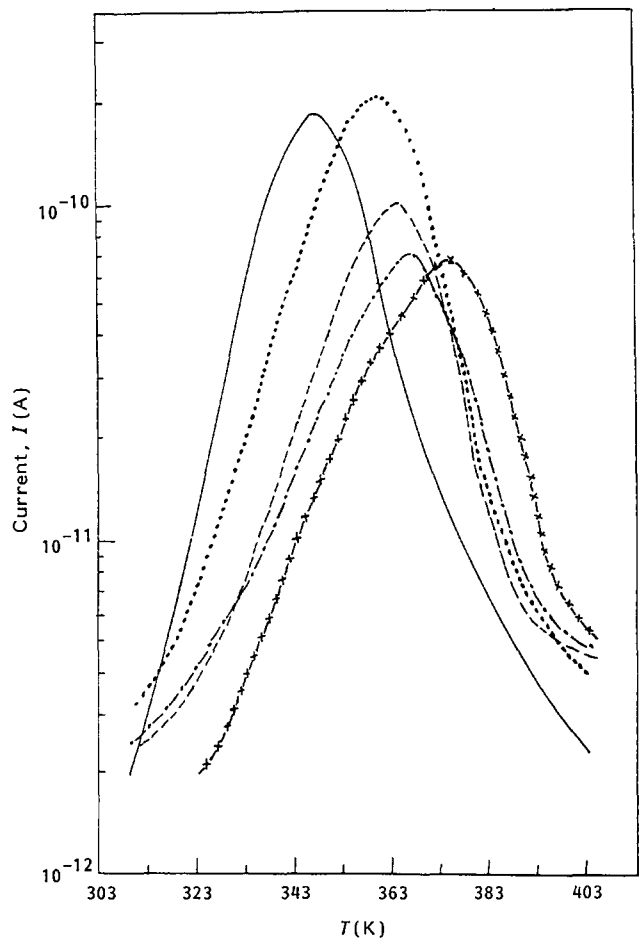

Figure 2 T.s.d.c. spectra of the 50:50 PVC/ABS polarized with $E_p = 4 \times 10^6$ V m^{-1} for 1 h at various polarization temperatures: (——) 353 K; (···) 363 K; (– – – –) 373 K; (– · – · –) 383 K; (– × – × –) 393 K

α relaxation of ABS appears as the temperature increases and the polarization time extends.

A decrease in the magnitude of the PVC α relaxation, together with a shift to a higher temperature and a change in the shape of the current peak, could be observed systematically for polarization temperatures of 373 to 383 K.

Furthermore, one sees clearly in *Figure 3* that the longer the polarization time t_p, the smaller the polarization. For $t_p > 15$ min, the height and the area of the t.s.d.c. peak are reduced. On the other hand, the shapes and the positions of the α peaks are not significantly affected. Hence, it is likely that polarization of PVC is complete in 15 min at ca. 358 K and that of ABS is complete in 15 min at ca. 378 K. The occurrence of only the ABS α relaxation does not necessarily imply a single, thermally activated process due to dipole–dipole interactions – a temperature-dependent structure may also be involved.

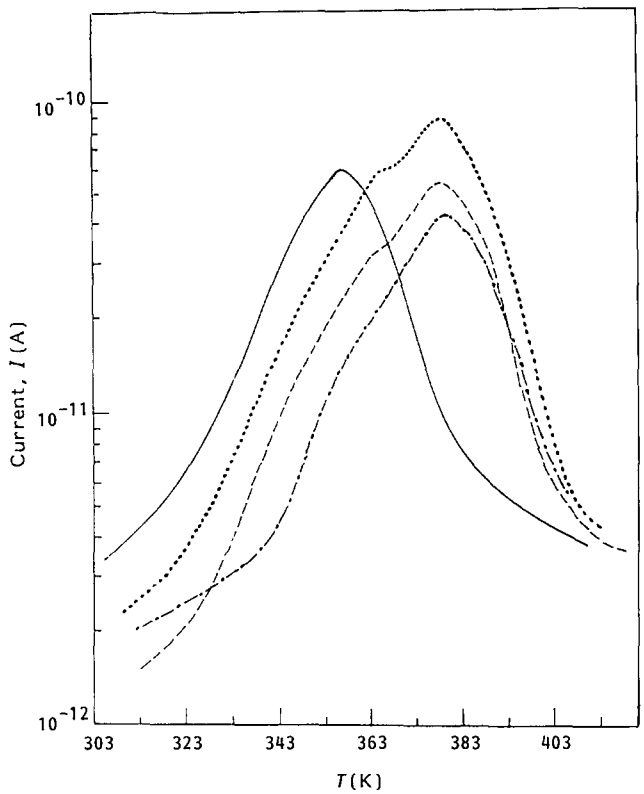

Figure 3 T.s.d.c. spectra of the 50:50 PVC/ABS blend polarized with $E_p = 3 \times 10^6$ V m^{-1} at $T_p = 393$ K for different polarization times: (—) 0 s; (– · – · –) 900 s; (– – –) 1800 s; (· · · ·) 3600 s

Determination of the peak parameters τ_0 and E_a

The rate at which the depolarization current decays with time can be expressed in terms of the polarization P and the relaxation time τ, and hence the monoenergetic t.s.d.c. $I(T)$ is simply the rate of change of polarization[26]

$$I(T) = -(AP_0/\tau_0)\exp\left[-(E_a/kT) - (\beta\tau_0)^{-1} \times \int_{T_0}^{T} \exp(-E_a/kT)\,dT\right] \quad (7)$$

where P_0 is the initial polarization and is given by

$$P_0 = N\mu^2 E_p/3kT \quad (8)$$

where A is the area of the film, N is the dipole concentration and μ is the dipole moment.

In order to obtain the kinetic parameters associated with each relaxation process, fractional polarization and the peak-cleaning technique were used as mentioned before. Evaluation[8] of the experimentally determined t.s.d.c. curves was carried out and good fits were eventually obtained between the theoretical and experimental curves, as shown in *Figure 4*. The peak parameters τ_0 and E_a associated with the dipolar relaxation processes of PVC, ABS and the polyblends were determined and are compiled, together with the peak maximum temperatures T_m, in *Table 1*. It can be seen clearly from *Table 1* that the temperature at which the maximum reorientation

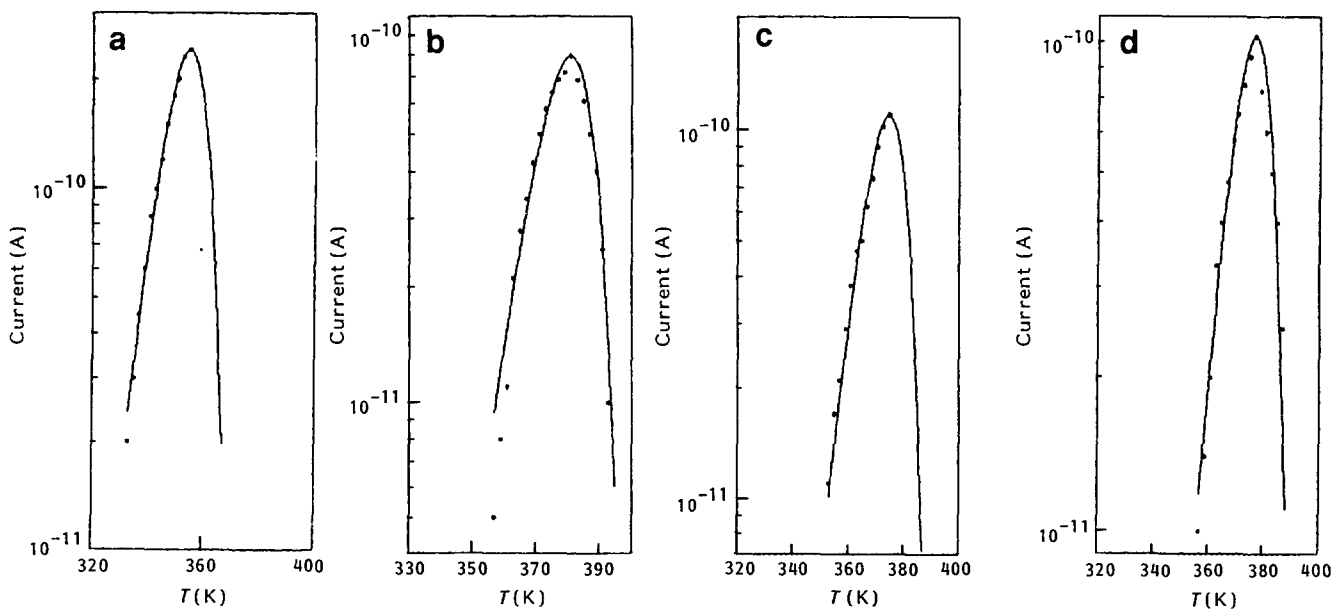

Figure 4 Examples of the results of curve fitting for (a) pure PVC, (b) pure ABS, (c) the α_1 relaxation (PVC) and (d) the α_2 relaxation (ABS) in 50:50 PVC/ABS. The points indicate the experimental results and the solid curves are the best fits to the theoretical curve providing the parameters τ_0 and E_a

current is observed is independent of the dipole concentration. The parameters τ_0 and E_a do not show a specific trend when the composition of the blend is changed, only an irregular fluctuation.

The fluctuation in τ_0 and E_a led us to suggest that at least part of the scatter in the reported values for τ_0 and E_a is due to dipole–dipole interactions. *Figure 5* shows the correlation between E_a and $\log \tau_0$. The figure indicates that there is an exponential relationship between E_a and τ_0 of the form

$$\tau_0 = A \exp(BE_a) \quad (9)$$

where A and B are constants. This relationship is usually obeyed with respect to dipole–dipole interactions, as found by Lenting *et al.*[27] and Van Weperen *et al.*[28]. So, blending of PVC and ABS alters the molecular mechanism of the α relaxation of PVC.

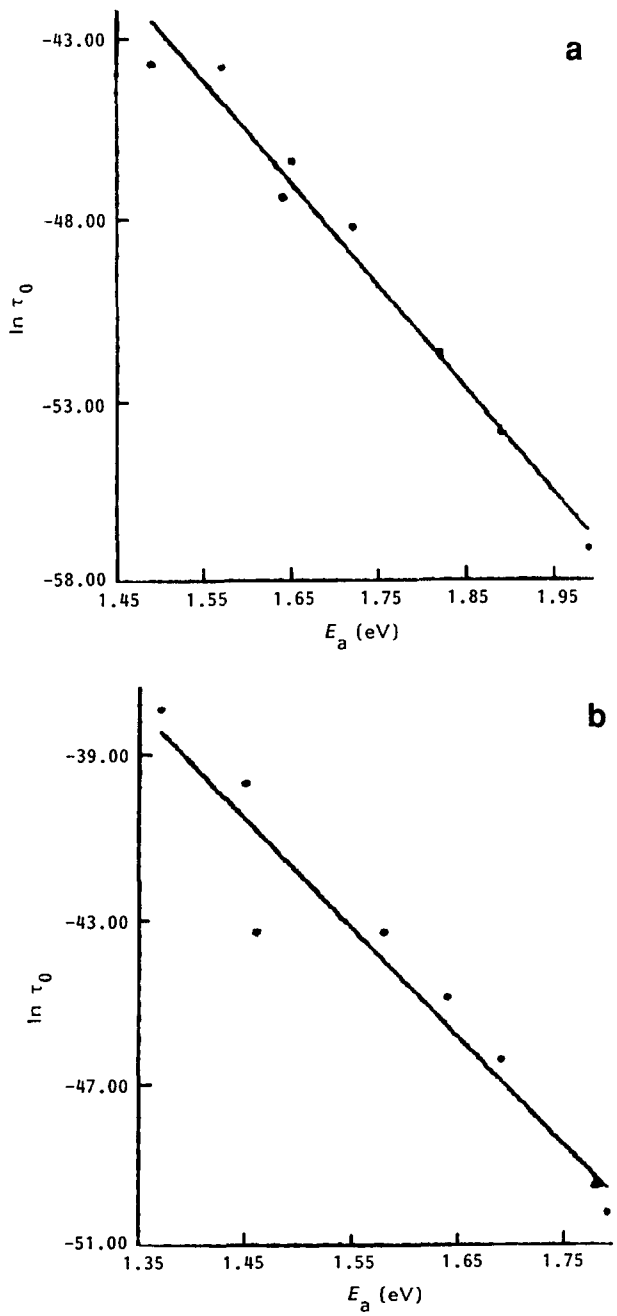

Figure 5 Plots of the experimental results showing the correlation between the characteristic relaxation time τ_0 and the activation energy E_a associated with the dipole relaxations (a) α_1 and (b) α_2 in the investigated materials

Table 1 Relaxation parameters of the α_1 and α_2 peaks for the investigated materials

Material	T_{m1} (K)	τ_{01} (s)	E_{a1} (eV)	T_{m2} (K)	τ_{02} (s)	E_{a2} (eV)
PVC (pure)	353	1.05^{-19}	1.49	–	–	–
10% ABS	363	2.59^{-21}	1.64	369	3.46^{-17}	1.37
30% ABS	363	7.05^{-21}	1.65	373	5.73^{-18}	1.45
40% ABS	363	1.16^{-21}	1.72	379	1.56^{-19}	1.58
50% ABS	363	1.59^{-25}	1.99	377	1.61^{-22}	1.79
60% ABS	363	9.50^{-20}	1.57	381	7.05^{-21}	1.69
70% ABS	363	3.90^{-24}	.189	379	3.17^{-22}	1.78
90% ABS	363	3.52^{-23}	1.82	381	3.16^{-20}	1.64
ABS (pure)	–	–	–	381	8.55^{-18}	1.46

It is clear from *Table 1* that meaningless values of E_a and τ_0 are obtained. The values of E_a and τ_0 are physically unreasonable. The reason, of course, is that this relaxation is expected to exhibit WLF behaviour. Hence, we can use these phenomenological, apparent kinetic parameters τ_0 and E_a as useful tools in order to investigate the relaxation behaviour of each component in the blend.

First of all, it is important to notice that E_a depends on the blend composition and τ_0 has exceptionally low values. These characteristics cannot be merely attributed to the relaxation of a thermally activated molecular site, but can be explained in terms of cooperative motions (dipole–dipole interactions) corresponding to long-range conformational changes characteristic of the α relaxation. Free-volume models are the most adequate approaches to the molecular relaxation in the glass-transition region. They assume that molecular transport around the glass transition is driven by the fractional free volume[29,30]. In this framework E_a and τ_0 are directly related to the characteristic free-volume parameters.

The relaxation times τ were calculated according to equation (1). Then, the ratios a_T of the electrical relaxation times at temperature T to their values at $T_0 = T_m \simeq T_g$ were evaluated. *Figure 6* illustrates the dependence of the shift factor a_T on the temperature for the α-relaxation distribution in the blends according to equation (6). It is clear that all the curves intersect at $T \approx T_m$ but differ greatly in nature. The distribution changes shape so that at the mergence point all the relaxation times τ take the same value τ_g. This leads to the conclusion that all the processes have the same relaxation time at T_g and hence all the molecules of every component have the same configuration.

CONCLUSION

The factors affecting the t.s.d.c. spectra of PVC/ABS blends from 0 to 100% have been studied: polarizing field, polarization temperature and polarization time. The qualitative and quantitative studies show that both T_p and t_p play major roles in the features and structure of the complex spectrum. The temperature and time dependences show a shift of the α_1 peak position and the appearance of the α_2 peak as both T_p and t_p increase, with no change at the higher T_p ($T_p < T_{g2}$) of ABS. Conformational change is observed as the wt% of one component changes and this is due to interactions between the two polymers (dipole–dipole interactions).

Separation of the α peaks was carried out by examination of the relaxation processes described by the WLF equation. The results indicate a possible WLF behaviour. However, the use of a single relaxation time can give only an approximate account of the complex relaxation, especially around the T_g in polymer blends.

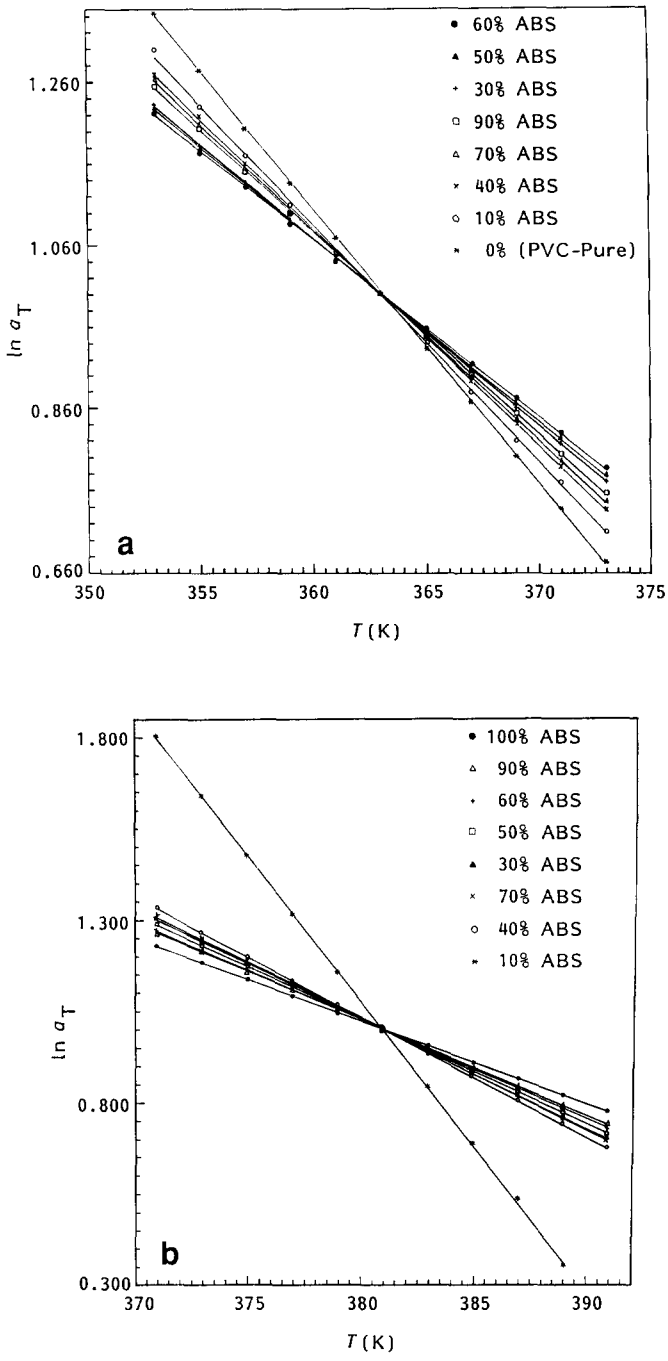

Figure 6 Illustration of the temperature dependence, according to equation (6), of the shift factor a_T for the two relaxations (a) α_1 and (b) α_2 in the blend

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