Studies of phase separated copolymer blends using thermally stimulated currents and dielectric spectroscopy

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Thermally stimulated currents (t.s.c.s) and a.c. dielectric spectroscopy were used to study poly(butylene terephthalate) (PBT) and blends of PBT with segmented copoly(ester-ether) elastomers. The high sensitivity of t.s.c. and a.c. dielectric techniques as compared to d.s.c. was useful for the study of these blends where the elastomer phase was present at only 20%. The techniques together cover a frequency range of $\sim 5 \times 10^{-3}$–10^5 Hz allowing detailed characterization of amorphous relaxations in these phase separated blends. Two separate glass transitions for the PBT/copoly(ester-ether) blends were observed, unchanged from the original pure components, indicating that they are immiscible and that ester exchange during processing was minimal. Peak assignments are made using a new analysis scheme by comparing activation energies (E_a) determined by the t.s.c. thermal sampling technique with predicted values using the activated states equation. With this method all values of E_a agree with the zero activation entropy prediction except those measured in the vicinity of glass transitions.

(Keywords: copolymer blends; thermally stimulated currents; dielectric spectroscopy)

INTRODUCTION

Blends of semicrystalline plastics with elastomers are of commercial and scientific interest. In phase separated blends of poly(butylene terephthalate) (PBT) the resulting material properties depend strongly on the morphology of the dispersed elastomeric phase and the purity of each phase. A high modulus semi-crystalline polymer such as PBT can be significantly toughened by addition of a low glass transition temperature (T_g), semicrystalline copoly(ester-ether) as a minor component. It is advantageous to have a high degree of toughness imparted to the blend at low levels of elastomer. In polyester(PBT)/copoly(ester-ether) blends there also exists the possibility of ester interchange between polymers[1], which can alter the composition of both components and adversely affect properties. It is important to determine if a compositional change or a partial loss of phase separation has occurred. It is well known that sensitive thermal analysis techniques such as dielectric relaxation are very useful in probing miscibility behaviour. For the blends studied here it is known that thermal analysis techniques such as d.s.c. are rather insensitive to the glass transition of the copoly(ester-ether) phase, and other techniques such as dielectric[2–4] or dynamic mechanical methods are preferred.

The elastomers studied here are poly(ester-ether) copolymers consisting of 'hard segments' derived from butanediol (B) and terephthalic acid (T) copolymerized with 'soft segments' of poly(tetramethylene ether glycol) (PTMEG). It has been shown that the length of the soft segment (PTMEG) is important in determining the degree of miscibility in PBT blends[5] as is the fraction of soft segments (PTMEG) relative to hard segments in the copoly(ester-ethers)[3]. We have chosen to study two copoly(ester-ethers) with relatively high soft segment content (45 and 77 wt% soft segment, *Table 1*). Runt *et al.*[3] have shown that for similar copoly(ester-ethers), e.g. 56 and 42 wt% soft segment, macroscopic phase separation occurs while a.c. dielectric studies showed that PBT and a 16 wt% soft segment copoly(ester-ether) are miscible over a wide concentration range. In the latter case it is presumed that miscibility occurs because of the presence of long sequences of hard segment units in the copoly(ester-ether), which are identical to those in the PBT homopolymer.

Due to the rather complicated spectra obtained in these multiphase blends, interpretation of relaxation spectra is

Table 1 Blend compositions and glass transitions measured by t.s.c.

	PTMEG[a] (wt%)	T_g (PBT phase)[b] (°C)	T_g (elastomer phase)[b] (°C)
PBT	0	42	–[c]
Copolymer-1000	45	–[c]	−62
PBT/copolymer-1000 blend	9	42	−63
Copolymer-2000	77	–[c]	−78
PBT/copolymer-2000 blend	15	40	−76

[a] The blend compositions studied were 20% copolymer and 80% plastic (PBT) resulting in the overall PTMEG value given here
[b] The glass transitions were measured at a scan rate of 7°C min^{-1}. They are roughly equivalent to glass transitions measured by d.s.c.
[c] Only one glass transition is observed with a single amorphous phase

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sometimes difficult[3]. We apply two dielectric techniques here, low frequency thermally stimulated current (t.s.c.) depolarization (10^{-3}–10^{-2} Hz) and conventional a.c. dielectric spectroscopy (10^{2}–10^{5} Hz), both of which are extremely sensitive in the case of moderately polar polymers. The wide frequency range generally leads to additional understanding of the nature of the relaxations. Both dielectric techniques are sensitive to localized segmental relaxations (β relaxation) and co-operative or larger scale segmental relaxations (α or glass transition). For the phase separated blends there are at least four relaxations, one β relaxation and one α relaxation for each phase. Besides its high sensitivity, t.s.c. is also useful because of its flexibility in accommodating a variety of sample shapes and sizes.

T.s.c. studies of blends and other phase separated systems before 1987 have been reviewed by Bernes *et al.*[6]. Other studies of blends and phase separated copolymers by t.s.c.[7–9] and by the thermostimulated creep technique[10] have been reported and illustrate the high resolving power of these low frequency techniques. The phase separated blends studied here serve to illustrate some of the features of the t.s.c. thermal peak cleaning method[6–9,10–14]. With this method one can access relaxation dynamics directly by determining a spectrum of relaxation times for each polarization temperature (T_p), resulting in a more extensive characterization of the t.s.c. spectra in terms of the values of the apparent activation energy (E_a) at any given temperature. The analysis scheme has been applied to t.s.c. data[15] and is based on Starkweather's[16,17] original application of the activated states equation to characterize polymer relaxations studied by a.c. dielectric spectroscopy and dynamic mechanical methods. The glass transitions are generally the only ones exemplifying a significant degree of co-operativity as is illustrated by a high activation energy, and for the other transitions, the values of E_a are consistent with a zero entropy prediction[15–17]. The absolute accuracy of the values of E_a determined by t.s.c. were verified by a comparison with those determined from the conventional Arrhenius relaxation maps of the a.c. dielectric frequency *versus* the reciprocal temperature of the loss peak[15]. In this paper we examine the trend in the measured values of E_a for the case of phase separated materials, in order to characterize the various transitions.

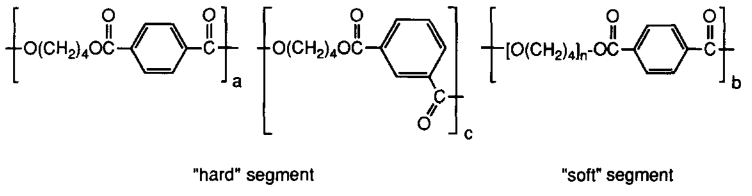
The low equivalent frequency of t.s.c. also leads to additional peak separation for these phase separated systems with overlapping primary and secondary relaxations. In addition, high resolving power is afforded by the t.s.c. thermal sampling technique where it will be shown that high and low activation energy processes can be readily separated even in the case of overlapping transitions.

EXPERIMENTAL

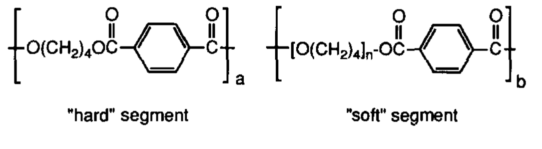
Materials

PBT is toughened, as is measured by the notched Izod test, by blending with elastomeric copolymers. The copoly(ester-ethers) studied here consist of hard segments of butanediol (B) and terephthalic acid (T) and, optionally, isophthalic acid (I) derived units. These hard segments are copolymerized with soft segments consisting of PTMEG and equimolar terephthalate (and optionally isophthalate). The first polymer is designated copolymer-1000 (*Figure 1*). The composition is PTMEG-1000-B-T/I, where PTMEG-1000 refers to 1000 g mol^{-1} PTMEG and B-T/I indicates the presence of residues of copolymerized B, with both T (repeat unit a in the copolymer-1000 structure in *Figure 1*) and I (repeat unit c in the copolymer-1000 structure in *Figure 1*). The structure of copolymer-2000 is also given in *Figure 1* and has a composition referred to as PTMEG-2000-B-T with 2000 g mol^{-1} PTMEG-derived segments and residues from B and T but not I. The blend compositions studied here were 20% copoly(ester-ether) and 80% plastic (PBT) resulting in the overall weight fractions of PTMEG given in *Table 1*.

The blends were prepared from 50 g charges mixed for 10 min at 250°C and 75 rev min^{-1} in a Brabender Plastic-Corder® torque rheometer with an exchangeable blade mixing head equipped with roller blades. All films of the elastomers and respective blends were pressed at 250°C and then cooled at rates varying from 30 to 100°C min^{-1}. This type of thermal history gives a high degree of crystallinity which did not seem to vary during the measurements. The melting temperatures (T_ms) of PBT and the blends (80% PBT) were 223°C as measured by d.s.c. at 10°C min^{-1}. The T_m values for copolymer-1000 and copolymer-2000 were 150°C. The d.s.c. melting endotherm was extremely broad for copolymer-2000 and



Copolymer-1000 (n≈14)



Copolymer-2000 (n≈28)

Figure 1 Repeat units of copolymer-1000 and copolymer-2000. See text for further details the integrated d.s.c. heats of fusion for PBT, copolymer-1000 and copolymer-2000 were 46, 25 and 10 J g^{-1}, respectively.

Background

The complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the dielectric constant and $\varepsilon'' = \varepsilon' \tan \delta$ is the dielectric loss) was measured using a Hewlett Packard LCR meter (model 4274A). The measurements were made at 11 frequencies in the range 10^2–10^5 Hz from −190 to 200°C at a heating rate of 1.5°C min^{-1}. The dielectric loss ε'' is emphasized in this paper.

The t.s.c. instrument was obtained from Solomat Instruments (Stamford, USA). Two different methods of polarizing the sample were used giving either 'global' t.s.c. spectra[18] or thermally cleaned t.s.c. spectra, the latter were obtained using the thermal sampling technique[11]. The global t.s.c. spectra are analogous to low frequency dielectric loss spectra[18]:

$$\varepsilon''(f) = J(t)/(A 2\pi \varepsilon_0 f E) \qquad (1)$$

where $J(t)$ is the measured depolarization current, A is the area of the sample, E is the polarizing field strength (in V m^{-1}), $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1} is the vacuum permittivity, and f is the equivalent frequency of the t.s.c. experiment which is on the order of 10^{-3} Hz for a scan rate of 7°C min^{-1}. The integrated current for a given transition is related to the dielectric increment determined from a.c. dielectric measurements[18].

Global t.s.c. spectra are obtained by first polarizing a film using a static electric field ($E \sim 2000$ kV m^{-1}) over a temperature range from T_p down to the 'freezing temperature' T_0, with cooling during polarization at ~20°C min^{-1} to freeze in the dipolar orientation. With the sample short circuited and $E = 0$, the depolarizing current due to dipolar reorientation was measured as the temperature was increased from T_0 at 7°C min^{-1} to the final temperature $T_f (\geqslant T_p)$. The glass transitions measured by t.s.c. and d.s.c. are identical if measured at the same scan rate.

Thermal sampling was performed by applying the excitation field ($E \sim 2000$ kV m^{-1}) for 2 min over a narrow (1–5°C) temperature window, turning the field off, and then quenching at 30°C min^{-1} to 40°C below T_p. A heating scan is then performed at 7°C min^{-1} to temperatures about 30°C above T_p, thus one thermal sampling spectrum is obtained in ~30 min. By this method only a narrow distribution of relaxations are excited[11,12]. Some improvement in interpretation of complicated relaxation spectra is possible with this method as compared to a.c. dielectric or the standard global t.s.c. experiment. The E_a which characterizes the thermal scan of the thermal sampling spectra is obtained by fractional integration of the individual peaks using the method applied by Bucci *et al.*[19], which gives a spectrum of relaxation times $\tau(T)$:

$$\ln \tau(T) = \ln\left[\int_{T_0}^{T} J(T)\,dT\right] - \ln J(T) \qquad (2)$$

Here T_0 is the initial temperature of the depolarization scan and $J(T)$ is the measured current. The integral of J is evaluated numerically and the values of $\tau(T)$, typically spanning the range 10^1 s $< \tau < 10^4$ s, are plotted *versus* reciprocal temperature in a Bucci plot[19]. They assumed an Arrhenius process where the relaxation time constant τ is related to the barrier height or E_a by:

$$\tau(T) = \tau_0 \exp(E_a/RT) \qquad (3)$$

where τ_0 is the pre-exponential factor. In many cases a linear dependence of $\ln(\tau)$ on $1/T$ is found with the slope equal to $E_a/1.987$ if E_a is in cal mol^{-1}.

RESULTS AND DISCUSSION

A.c. dielectric spectra

The a.c. dielectric spectra for the pure materials and their blends are given in *Figures 2–4*. The compositions of these materials are given in *Table 1*. D.s.c. was not useful for determining the copolymer T_g in the blends. The comparison plots of the dissipation factor ($\tan \delta = \varepsilon''/\varepsilon'$) at 1000 Hz in *Figures 2* and *3* indicate that the blends essentially follow a rule of mixtures. The PBT glass transition at 64°C for the copolymer-2000 blend in *Figure 2* is not shifted from the T_g of pure PBT but is slightly lower in magnitude. In *Figure 3* the onset of conductivity occurs at a lower temperature in the blend but is evident that T_g is unchanged at 64°C.

The glass transitions for the pure copolymer-2000 and copolymer-1000 are very prominent and occur at −63°C and −29°C in *Figures 2* and *3*, respectively. The strong

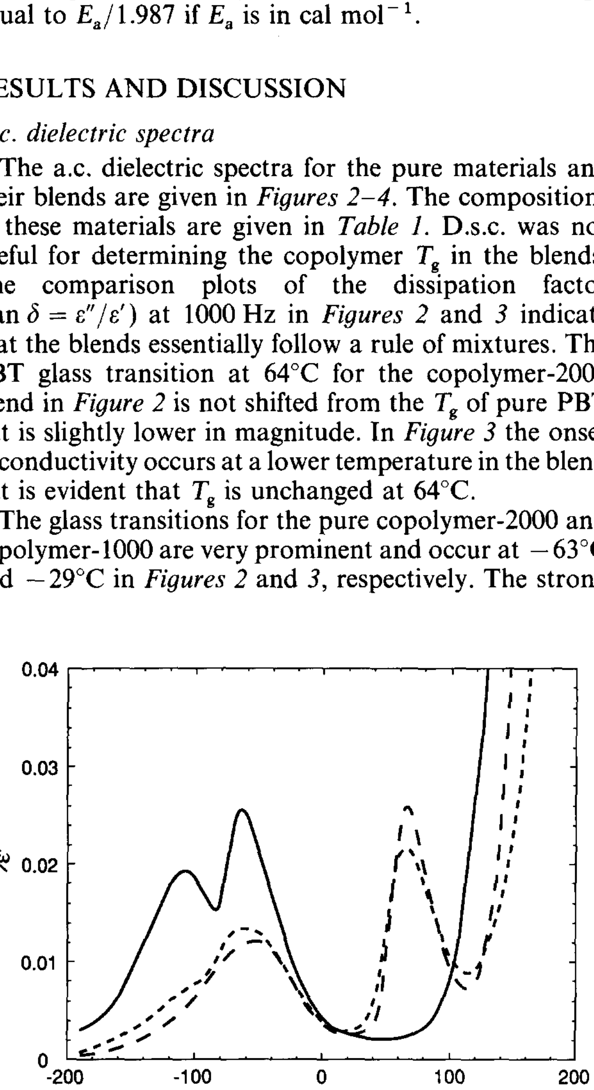


Figure 2 A.c. dielectric measurements of $\tan \delta = \varepsilon''/\varepsilon'$ at 1000 Hz for PBT homopolymer (——), copolymer-2000 (——) and a 20% blend of copolymer-2000 in PBT (– –)

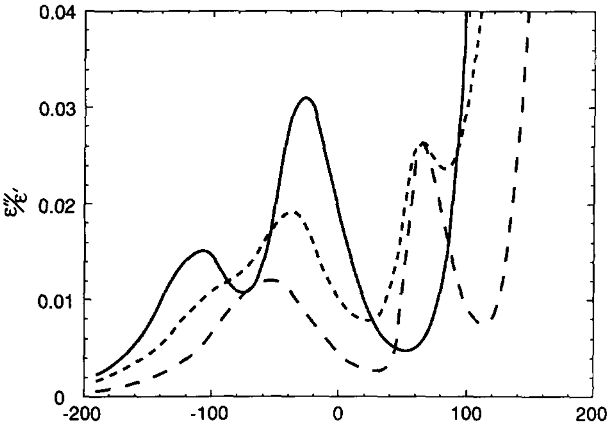


Figure 3 A.c. dielectric measurements of $\varepsilon''/\varepsilon'$ at 1000 Hz for PBT homopolymer (——), copolymer-1000 (——) and a 20% blend of copolymer-1000 in PBT (– –)

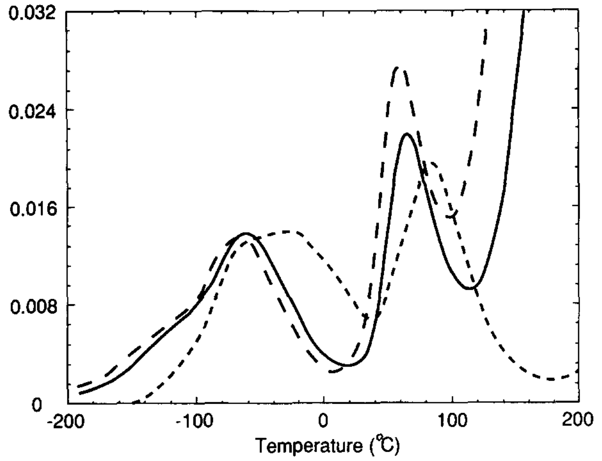


Figure 4 Tan $\delta = \varepsilon''/\varepsilon'$ at frequencies of 200 Hz (— —), 1000 Hz (——) and 100 000 Hz (- -) is plotted for the blend of copolymer-2000 with PBT

Table 2 Comparison of activation energies for glass transitions of PBT phases

	E_a (t.s.c.)[a] (kcal mol^{-1})	E_a (10^3 Hz)[b] (kcal mol^{-1})
PBT	93 ± 15	115 ± 10
Copolymer-2000 blend[c]	46	65
Copolymer-1000 blend[c]	57	60

[a] Values taken from *Figures 5* and *6* at 42°C

[b] Determined by taking the tangent of the Arrhenius relaxation map of a.c. dielectric data at 1000 Hz

[c] Activation energies are for the higher temperature glass transition in the blend

β transition for PBT is merged with the copolymer glass transitions. The copolymer glass transition and the PBT β relaxation are almost equal in magnitude since the blend is 80% PBT. In *Figure 2* at 1000 Hz they occur at the same temperature in the blend giving rise to a single peak at −62°C. In *Figure 3*, because of the higher T_g (−29°C) of copolymer-1000, the glass transition peak of the blend is artificially shifted to lower temperature due to overlap with PBT β peak which was originally at −58°C giving rise to a combination peak at −40°C. The overlap of the two leads to difficulties in determining the peak positions and the variation of peak temperatures with frequency in order to determine the activation energy. In the case of the t.s.c. data presented later, the peaks are well separated because of the low measurement frequency. In *Figures 2* and *3* for copolymer-2000 and copolymer-1000, respectively, β transitions occur at −110°C for both pure copolymers. The copolymer β transitions appear as shoulders in the blends because the copolymers are only present at 20%. The PBT β transition occurs at −58°C as was discussed above.

Tan δ at $f = 200$, 1000 and 100 000 Hz is plotted in *Figure 4* for the blend of copolymer-2000 with PBT. Both T_g peaks shift with frequency and the lower T_g peak is partially merged with the PBT β transition. From the variation of the peak temperature with f, one can estimate E_a. Some results are tabulated for the glass transitions of the PBT phases in *Table 2*; the values are quite large as would be expected for glass transitions. For the glass transition of the copolymer phase in the blend at ~−60°C (*Figure 4*), the overlap with the PBT β peak makes the analysis very qualitative as was discussed earlier. The general feature of a low activation energy process such as a β transition is that the peak shifts much more in temperature for each increment in frequency as compared to a high activation energy process such as a glass transition. Thus, at 100 000 Hz the β peak at −25°C is almost separate from the copolymer glass transition (*Figure 4*). Then at 1000 Hz it shifts to ~−60°C which is directly on top of the glass transition. Over these two decades in frequency the glass transition peak of the pure copolymer-2000 varies by only 19°C because of the higher E_a (~35 kcal mol^{-1}). This is to be compared with $E_a = 12.2 \pm 1$ kcal mol^{-1} for the PBT β relaxation at −55°C, and $E_a = 10 \pm 1$ kcal mol^{-1} for the copolymer-1000 and copolymer-2000 β relaxations at −110°C. Some of the these features are seen more directly with t.s.c. because the low equivalent frequency separates the peaks.

Global t.s.c. spectra

Global t.s.c. spectra are plotted in *Figures 5* and *6* on a log scale. (The E_a plots will be discussed later.) T.s.c. spectra were collected at a scan rate of 7°C min^{-1} so the glass transitions are comparable to those determined by d.s.c. The PBT β peak is seen at −115°C in *Figure 5*. For copolymer-2000 and copolymer-1000 the β peaks are shifted off the plot to lower temperatures and should occur at ~−160°C. Because of the low frequency of t.s.c., the β peaks are well separated from the glass transition clearly showing that T_g for the copolymer phase is not shifted in the blends as compared to the pure copolymers. The glass transitions for the copolymer-2000 and copolymer-1000 phases are represented by

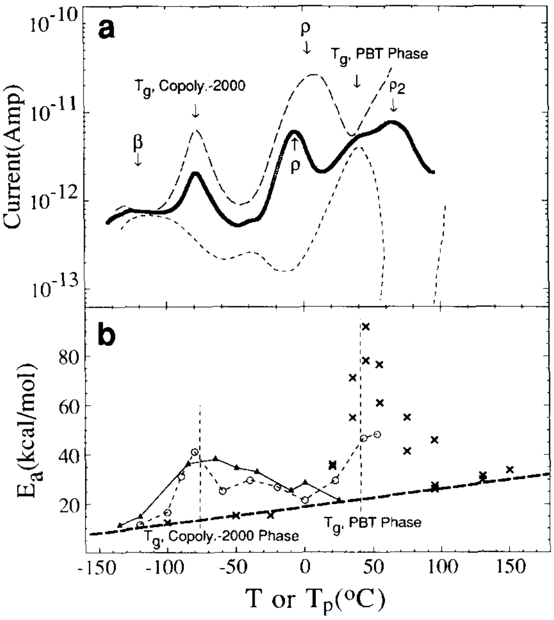


Figure 5 (a) T.s.c. spectra of current *versus* T for PBT (- -) and copolymer-2000 (— —) and a blend of 20% copolymer-2000 in PBT (——). The relaxation assignments are marked on the plot. For copolymer-2000 and PBT the T_p was 55°C, E was 2000 kV m^{-1}, and the films had areas of 50 mm^2. The T_p for the blend was 75°C and the other parameters were the same. (b) Activation energies for PBT (×), copolymer-2000 (▲) and the copolymer-2000 blend (○) determined from the thermal sampling technique plotted *versus* T_p. The thick broken line was calculated using equation (4) assuming zero activation entropy (see text). Each maximum is a signature of a glass transition. The curves were drawn through the data to indicate the trend

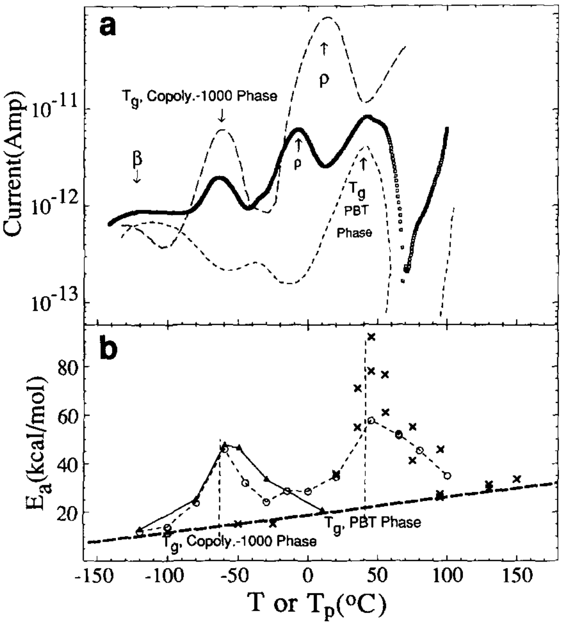


Figure 6 (a) T.s.c. spectra of current *versus* T for PBT (- -) and copolymer-1000 (——) and a blend of 20% copolymer-1000 in PBT (□). The relaxation assignments are marked on the plot. The T_p was 55°C, E was 2000 kV m^{-1} and the films had areas of 50 mm^2. (b) Activation energies for PBT (×), copolymer-1000 (▲) and the copolymer-1000 blend (○) determined from the thermal sampling technique plotted *versus* T_p. The thick broken line was calculated using equation (4) assuming zero activation entropy (see text). Each maximum is a signature of a glass transition. The curves were drawn through the data to indicate the trend

sharp peaks at −78°C and −63°C in *Figures 5* and *6*, respectively. Both of these features are strong indications that the system is highly phase separated without an appreciable degree of ester exchange between the two components, and illustrate the power of combining t.s.c. measurements with a.c. dielectric spectroscopy.

An interesting feature of the t.s.c. spectra in *Figures 5* and *6* is that blends all have strong ρ peaks around −5°C. These are absent in the a.c. dielectric spectra and are definitely not glass transitions as will be shown later by the activation energy analysis. In the pure copolymers in *Figures 5* and *6* there are also broader peaks at 10°C (±5°C) which are also labelled ρ and probably arise from a similar origin. The ρ transitions are most likely to be due to space charge injection and trapping at crystal/amorphous boundaries and subsequent release[18] during depolarization. The ρ transition generally occurs at $T > T_g$.

At temperatures around 40°C the glass transition for the PBT phase is detected in the blends. Sometimes it is only a shoulder (e.g. *Figure 5*) because of the strong peak (ρ_2) just above T_g, which is due to the accumulation and release of charges from the crystal/amorphous interface in PBT and possibly other interfaces related to the blend morphology. This assignment is also clarified by the activation energy analysis presented below. The glass transitions for both phases are presented in *Table 1* and indicate that the blends are strongly phase separated and that ester exchange upon mixing is minimal.

One other feature of the t.s.c. spectra is that one can determine the continuous phase by observing the onset of d.c. conductivity. The onset of d.c. conductivity is defined as the temperature ($T \gg T_p$) at which a spontaneous ohmic current is detected. For the pure copolymers the d.c. conductivity onset is indicated by the sharp upturn in the current in *Figures 5* and *6* at ~50°C. This temperature is at a much lower temperature than the d.c. conductivity onset for the blend (>90°C for blends in *Figures 5* and *6*). The onset in the blends is similar to that for pure PBT. All these features are evidence that the PBT is the continuous phase in the blends.

Thermal sampling of global t.s.c. spectra

From the discussion above it is evident that only a rough assignment of the various relaxations can be made in these complicated spectra although comparison with a.c. dielectric results simplifies the assignment considerably. An easily applied experimental strategy is described below which is shown to be useful in cases where the assignment is more difficult.

As was discussed earlier, the global t.s.c. spectra can be experimentally decomposed by the thermal sampling method. A few representative spectra obtained by the thermal sampling method are shown in *Figure 7* for the copolymer-2000/PBT blend. (The broken and solid curves are used for clarity.) Because the sample is only polarized over a narrow 5°C temperature range (the arrows in *Figure 7* indicate the T_p values) the peaks are sharp and can be analysed in terms of a narrow distribution of relaxations generally characterized by a single activation energy. It should also be noted that the peak intensities in the thermal sampling spectra (*Figure 7*) roughly follow the overall shape of the global t.s.c. spectrum for the blend (*Figure 5*) as expected[12].

To determine the exact value of E_a, fractional integration is performed on each thermal sampling spectrum via equation (2). Integration of the six spectra in *Figure 7*, gives the relaxation time (τ) spectra which are plotted in an Arrhenius form in *Figure 8* for the copolymer-2000 blend. The qualitative indication from the limited set of data in this plot is that the slopes, which are directly proportional to E_a, are the steepest around the two glass transitions. From each Arrhenius curve we extract one value of E_a. The results of many separate thermal sampling experiments are summarized in *Figures 5* and *6* for all the materials. It is found that there is a maximum in E_a at each respective glass transition.

To understand the trend of E_a with T and get a qualitative indication of why E_a maximizes at T_g we refer

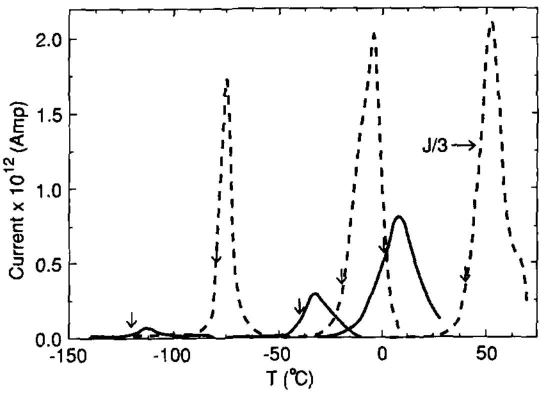


Figure 7 A few representative individual spectra obtained by the thermal sampling technique are shown for the blend of PBT with copolymer-2000. The vertical arrows indicate the T_p values. The intensity of the highest temperature spectrum has been reduced by a factor of three for the plot

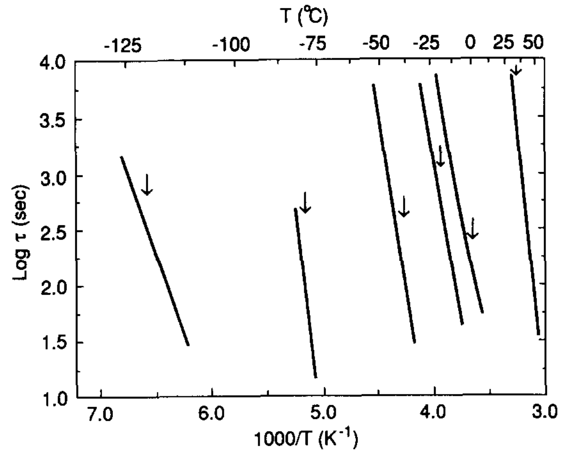


Figure 8 Arrhenius plots of relaxation time *versus* $1/T$. The values of τ were calculated by fractionally integrating the thermal sampling spectra in *Figure 7* for the blend of PBT with copolymer-2000. The vertical arrows indicate the T_p values. Here representative curves are only shown in the vicinity of the β relaxation (-110°C), the glass transition of the copolymer phase (-76°C), the ρ transition (-10°C) and the PBT glass transition (42°C). The full set of activation energies determined from Arrhenius curves for all the samples is given in *Figures 5* and *6*

to the work of Starkweather[16,17] on modelled viscoelastic relaxations using:

$$E_a = \Delta H\ddagger + RT = RT[22.92 + \ln(T/f)] + T\Delta S\ddagger$$
$$= RT[24.76 + \ln(T\tau)] + T\Delta S\ddagger \qquad (4)$$

where $\Delta H\ddagger$ and $\Delta S\ddagger$ are the activation enthalpy and entropy, respectively. Equation (4) was obtained by rearranging the activated states equation and solving for $\Delta H\ddagger$. The relationship $E_a = \Delta H\ddagger + RT$ was derived by Hoffman *et al.*[20]. The thick broken lines in *Figures 5b* and *6b*, which actually have a very slight amount of curvature, were calculated with the activation entropy ($\Delta S\ddagger$) set equal to zero and an equivalent frequency of 5×10^{-3} Hz with no adjustable parameters. The main feature that is emphasized in these plots is that the values of E_a only depart from the zero activation entropy curve for co-operative relaxations such as the glass transition. This can be related to the theory of Adam and Gibbs[21] who have suggested that the entropy maximizes at T_g due to the high degree of co-operativity of the relaxation at that temperature.

Because of conductivity background, it is generally difficult to obtain activation energies at temperatures $> \sim 80$°C above the T_g for a single component material. The values presented here at temperatures above 90°C are influenced by conductivity background and other non-dipolar processes so should only be judged by their qualitative trend.

The activation energies obtained from integrating the thermal sampling spectra and those determined by plotting the a.c. dielectric data in an Arrhenius relaxation plot of $\log f$ *versus* $1/T_{max}$ of the loss peak are compared in *Table 2*. The relaxation maps of glass transitions generally have some curvature[22] which is modelled with the Williams–Landel–Ferry (WLF) equation. For the higher temperature PBT glass transition we have compared activation energies determined by the two methods (*Table 2*). The techniques are in rough agreement considering the differences in frequency and the effect of WLF curvature. The values are systematically lower for the blends possibly due to a slight change in phase purity or morphology of the PBT phase in the blends. There are also many inaccuracies associated with analysis of these very high activation energy processes and conductivity could be contributing to some of the discrepancy.

The activation energy for the low temperature glass transition of pure copolymer-1000 was determined to be 35 ± 3 kcal mol^{-1} at 1000 Hz from a.c. dielectric data and 47 ± 5 kcal mol^{-1} at 5×10^{-3} Hz from the thermal sampling data in *Figure 6b*. These are again in reasonable agreement considering the WLF curvature in the relaxation map which causes the values of E_a to change with frequency. The values of E_a determined from the thermal sampling spectra (*Figures 5b* and *6b*) which maximize at the copolymer T_g, indicate that the values are essentially the same for the 20% copolymer blend and for the pure copolymers. Activation energies from a.c. dielectric spectroscopy could not be easily obtained for the glass transition of the 100% copolymer-2000 because of the overlap with its own β transition at $f > 2000$ Hz (*Figure 2*). Also, no values of E_a were obtained from a.c. dielectric spectroscopy in the blends because of the same problem and also because of significant overlap with the strong β transition of the PBT phase (*Figure 4*).

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