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Dielectric relaxation studies of miscible polycarbonate/polyester blends

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Abstract

Blends of bisphenol-A polycarbonate and a thermoplastic polyester (Kodar) are miscible as shown by single DSC and DMTA glass transition temperatures at all compositions. Blends of polycarbonate and Kodar also display a strong, single dielectric α-relaxation. Conclusions regarding the molecular nature of the blends, the state of mixing and molecular cooperativity can be made by both quantitative and semi-empirical analysis of dielectric relaxation data. There is an increased broadening of the loss spectra on blending as determined by both Havriliak–Negami (HN) and Kohlrausch–Williams–Watts (KWW) fits to the dielectric data, and by analysis of the DMTA loss peaks. An increase of the relaxation time on blending is attributed to the temperature of measurement being below the glass transition of the rigid PC-rich component of the blends and that this is likely to have an effect because of micro-heterogeneity in the blends. Local regions of composition rich in Kodar or polycarbonate exist in these blends and this allows the molecular motion of the PC molecules to dominate the relaxation behaviour of the blends. Concentration fluctuation is thus the dominant feature controlling the dielectric response in these miscible, amorphous blends. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric relaxation; Miscible blend; Polyester

1. Introduction

The extent of miscibility in a polymer blend is commonly determined by characterisation of the glass transition temperature (T_g). A number of methods are available for determining the T_g in polymers and blends. These include differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), dielectric relaxation and dilatometry [1].

A miscible blend will form a single phase and will exhibit a composition-dependent T_g which generally falls between those of the homopolymer constituents. There are, however, limitations to the use of bulk techniques such as DSC and DMTA for miscibility studies in blends. In DSC, the T_g values of the component polymers should differ by at least 50°C to ensure that the T_g values of the blend phases can be resolved, and at least 10–20% of minor phase must be present or its contribution may not be detected [2,3]. The DMTA technique is found to be more sensitive [3,4], and Kaplan [5] concludes that the minimum detectable domain size by DMTA at 110 Hz is 150 Å. Therefore miscibility in a blend system is defined, practically, as homogeneity down to the scale that can be resolved by the particular experimental technique used [6]. Heterogeneity existing on a level below this scale may be characterised by techniques such as dielectric relaxation spectroscopy (DRS) or nuclear magnetic resonance (NMR), for example. DRS represents a method able to probe segmental motion and is therefore sensitive to this micro-heterogeneity.

DRS measures the interaction of an electromagnetic field with the electric dipole moments of the material under test. Chemical structure and polarity are the basic factors controlling dielectric response in polymers. However, it is necessary to take into account the conformation, packing and interaction of molecules because these factors determine the ability of dipoles to respond to the field [7]. Large changes in dielectric response occur at transitions such as the glass transition or at sub-T_g (secondary) relaxations that involve more local molecular motion, and are seen as dielectric loss maxima.

In a bulk, constrained environment, polymer chains and their attached dipoles do not move with a single relaxation time, but with a range of relaxation times dependent on the inter- and intramolecular interactions present. This results in a broader relaxation than predicted by a simple Debye function [8]. It is also often found that the spectrum of relaxation times is skewed to higher frequencies. It is most common for both these effects to occur in the dielectric measurement

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of polymers, and Havriliak and Negami [9] proposed a semi-empirical equation which combines both broadening (β_{HN}) and skewing (γ_{HN}) factors. The Havriliak–Negami (HN) equation parameters can be determined by direct fitting of isothermal relaxation spectra with the HN function by computer analysis.

Relaxation phenomena near the glass transition can also be modelled by the Kohlrausch–Williams–Watts expression (KWW) [10]:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau*}\right)^{\beta_{KWW}}\right] \tag{1}$$

where τ^* is the characteristic molecular relaxation time and β_{KWW} is a shape (broadness) parameter ranging from zero to unity. To fit this KWW function to dielectric relaxation data in the frequency domain (as occurs with the HN function) is difficult due to the lack of an analytical solution. A simple numerical procedure for evaluating the parameters has been given, for example, by Moynihan et al. [11].

A significant number of discussions of the segmental dynamics of polymer blends, as observed by the dielectric relaxation technique, have been published [7,12,13]. The dielectric technique requires the polymers to be dielectrically active, but it may be considered an advantage of this technique if only one component of a blend is dielectrically active, so that the segmental dynamics of this component can be observed independently of other blend components [7]. In this study, however, both polycarbonate and Kodar incorporate dipoles in the polymer backbone, so each polymer displays a strong dielectric α-relaxation (T_g). The dielectric relaxation behaviour is therefore more complex because the α-relaxation of the miscible blend will be a mixture of the relaxations of the two component polymers.

In polymer blends, as well as mixtures of small molecules, the local composition is thought to fluctuate about its average value, and such concentration fluctuations have been identified as a mechanism for broadening of the α-relaxation and glass transition generally in polymer blends [14,15]. A number of theories have been proposed to model the broad dispersion of relaxation times in polymer blends and solutions. The Fischer and Zetsche model [16] describes local composition fluctuations as a Gaussian distribution around the average composition and their effect on the relaxation of segments in that local environment. As one component will be rich in some areas, the T_g of that component will dominate the relaxation behaviour, leading to dynamic heterogeneity. Jonas et al. [17] developed a model which analyses the effect of nearest-neighbour contacts in a Flory–Huggins-type lattice on the local chain dynamics. In the coupling model [18–21] the shape and temperature dependence of the relaxation are governed by intermolecular cooperativity, onto which fluctuation of concentrations can also be imposed.

The coupling model attributes broadening of relaxation spectra to the intramolecular and intermolecular cooperative motion (primarily the latter) between polymer chain units [18,21], and is described by a coupling parameter ($n = 1 - \beta$). The nature of such cooperative motions can be described by time correlation functions [22–24]. Polymers with less flexible, more sterically hindered motions demonstrate broader relaxations [25], so from a purely physical point of view 'rougher' molecules, such as those with pendant, rigid moieties, will be more coupled than 'smoother ones' [19]. This was observed in the loss spectra of a butadiene/vinyl copolymer, where incorporation of additional, bulkier vinyl groups increases the coupling [20].

The polymer components of a blend will therefore have different intermolecular coupling, even when in the same environment [26]. In addition, the components of any mixture experience a distribution of local environments due to composition fluctuations. Therefore chain segments of a given component will experience different local environments and in mixtures each component will be associated with a range of relaxation times.

In amorphous polymer blends, Karasz and MacKnight [27] investigated the difference between miscible and immiscible PPE/poly(styrene-*co*-4-chlorostyrene) (PSCCS) blends and found that the broadness of dielectric loss curves gave an indication of concentration changes in the material. This loss peak broadening was also found in polystyrene/poly(chlorostyrene) blends [28], PS/poly(cyclohexyl acrylate-*stat*-butyl methacrylate) blends [29] and in poly(vinyldiene fluoride)/poly(methyl methacrylate) (PVDF/PMMA) blends [30]. Broadening has also been observed by NMR [31], DMTA [12,32], and light scattering, and dynamic heterogeneities have also been observed by ESR spectroscopy [33].

Blends of PC and ThermX (a polyester related in structure to Kodar) display DMTA and dielectric relaxation spectra that are broader in the blends than in the homopolymers [34]. This broadening was attributed to both concentration fluctuation and intermolecular coupling in the blends. The composition of greatest broadening was dependent on the experimental technique and was skewed towards component of highest intermolecular coupling. The work by Spall et al. [34] follows a similar analysis to that of the miscible PC/Kodar blends undertaken in the present study. In both cases polycarbonate is blended with a polyester and forms miscible blends at all compositions.

2. Experimental

2.1. Materials and sample preparation

In this study a bisphenol-A polycarbonate (Lexan 141) was supplied by GE Plastics, the structure of which is shown in Fig. 1. Kodar was supplied by Eastman Chemical Products Inc. Kodar is a copolyester of 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic

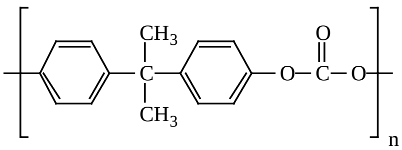

Fig. 1. Molecular structure of bisphenol-A polycarbonate.

acids, illustrated in Fig. 2, with the monomers derived from xylenes. By NMR the isophthalic/terephthalic acid ratio is 20/80 [35]. GPC measurements for PC were conducted using a Waters apparatus and Perkin–Elmer detector, and for Kodar a Viscotek V60A analyser with a 1 μl/min injection rate, and were determined in polystyrene equivalent units. The PC was dissolved in tetahydrofuran (THF). The Kodar did not dissolve in THF, so a mixture of 90% chloroform and 10% hexafluoroisopropanol was used as solvent. The values for PC were $M_w = 43,700$, $M_n = 20,500$ and the polydispersity was 2.1. For Kodar, $M_w = 36,700$, $M_n = 14,700$ and the polydispersity was 2.5.

Samples were blended using a 1.25 in. single screw Killion extruder after drying at 135°C for 4 h under vacuum. Flat 2 mm thick plaques were injection moulded using a Meiki 80 t injection moulder after the same drying. Processing temperatures ranged from 280°C for polycarbonate to 300°C for Kodar. All blends contain 0.3 wt% proprietary transesterification inhibitor. Fourier transform infrared spectrometry, solubility tests and NMR indicated that negligible transesterification had occurred [36].

Thin films for dielectric analysis were prepared by compression moulding at 270°C with a thin sheet of aluminium as a mould, and teflon impregnated glass fibre sheet as a mould release. This resulted in samples of 0.1–0.2 mm thickness. Circular samples of 23 mm diameter were cut from the films and sputter coated with gold in a Dynavac SC150 sputter coater to ensure good electrical contact between the sample and the electrodes of the dielectric apparatus. A vacuum of 0.5 Torr and carrier gas of high purity argon were used in the coating chamber. To prevent overheating and warpage of the samples six short bursts lasting 30 sec were applied to each side of the polymer with an operating current of 30–35 mA. A period of 1 min without current was used between bursts to allow the polymer to cool. A mask corresponding to the electrodes in the three-terminal, guarded cell was used to define the areas of sputtering.

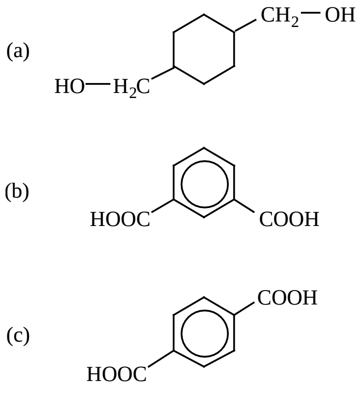

Fig. 2. Molecular structure of (a) 1,4-cyclohexanedimethanol; (b) isophthalic acid; and (c) terephthalic acid.

2.2. Experimental techniques

DSC scans were conducted using a Perkin–Elmer DSC-7 calorimeter at a scanning rate of 10°C/min. Dynamic Mechanical Analysis made use of a Perkin–Elmer DMA-7 at a scanning rate of 2°C/min, at a frequency of 1 Hz using a 2 mm round tipped probe in a compression configuration. Sample sizes used were approximately 10 mm × 10 mm.

In this study the dielectric response of the blends and corresponding unblended polymers was measured using a Genrad 1689 RLC Digibridge which was controlled by a personal computer running custom-written software. The associated electrode assembly was held in a thermostatically controlled oven.

Frequency scans over the range 15–63000 Hz were performed at a range of isothermal temperatures related to the range of the transitions observed in temperature scans. Dielectric relaxations occurred about 10–20°C above those determined by DSC temperature scans [7]. The Jandel Scientific Peakfit program was used to fit both HN and dc conductivity curves to the data.

3. Results and discussion

Polycarbonate/Kodar blends have been found to be miscible at all compositions by DSC [36], the T_g values for the blends falling close to, but just below values predicted by the Fox equation for miscible blends [36] using the T_g values of the PC and Kodar polymers. Illustrated in Fig. 3 are the T_g for DSC [36], DMTA and dielectric techniques, showing a single T_g value for all blend compositions. The values fall very close to, but just below an additive line between the component polymer values indicating the presence of weak

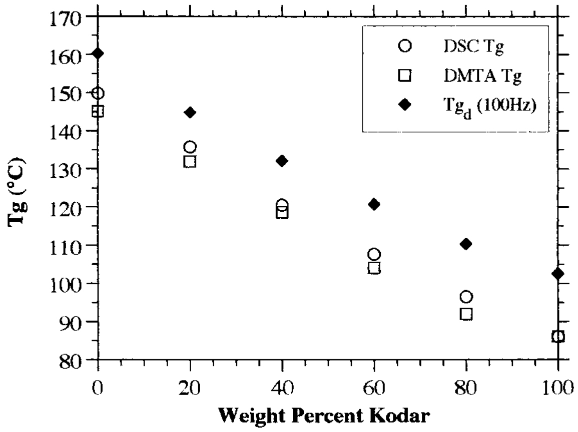

Fig. 3. T_g for PC/Kodar blends as determined by: DSC (○); DMTA loss peak (□); dielectric relaxation (●) at $f_{max} = 100$ Hz.

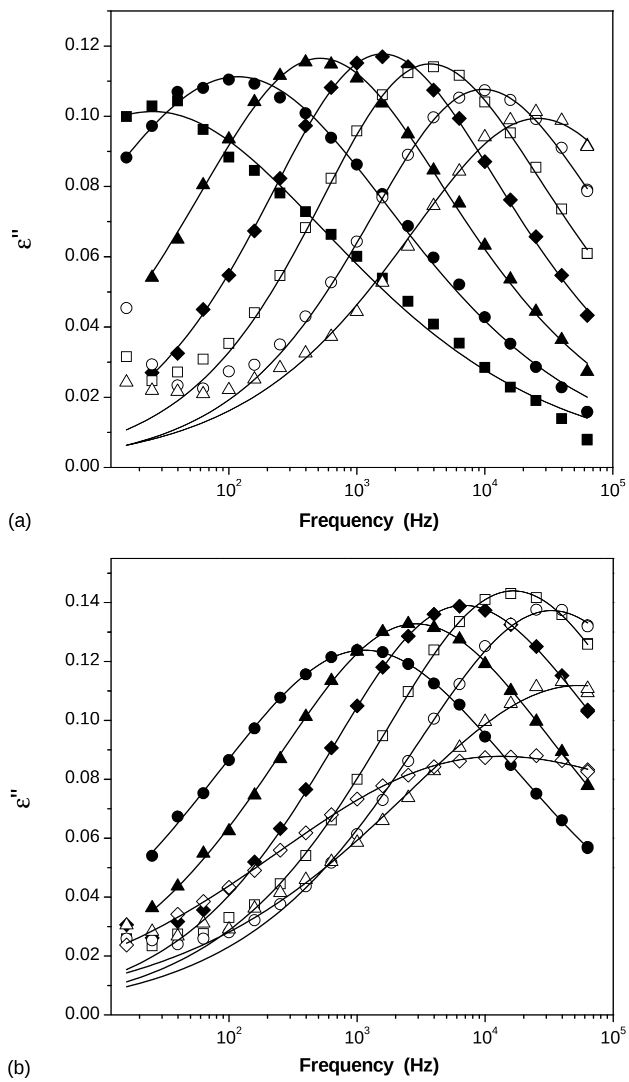

Fig. 4. (a) Isothermal dielectric loss scans of the α-relaxation in 100% polycarbonate at temperatures: (■) 158°C; (●) 161°C; (▲) 164°C; (◆) 167°C; (□) 170°C; (○)173°C; (△) 176°C. Curve fits of the HN equation are also shown (—). (b) Isothermal dielectric loss scans of the α-relaxation in 40% Kodar at temperatures: (●) 140°C; (▲) 143°C; (◆) 146°C; (□) 150°C; (○) 153°C; (△) 156°C; (◇) 159°C. Curve fits of the HN equation are also shown (—).

favourable interactions between the components in the blends [37]. The values for T_g determined by the dielectric technique are greater than those for DMTA which are in turn greater than those determined by DSC. This is a result of the different frequency, or effective frequency, of measurement, and the precise nature of relaxation of the polymer chains (thermal, mechanical or dipolar relaxation) measured by each technique.

The crystallinity in the samples prepared for dielectric analysis was found by DSC measurements to be negligible. This was due to the method of sample preparation, where crystallites were prevented from forming by using rapid quenching, at approximately 200°C/min, to cool the samples immediately after they were compression moulded at a temperature above the melting temperature of Kodar.

The dielectric loss spectra for polycarbonate and the 40% Kodar blend are shown in Fig. 4a and b. A separate spectrum is plotted for each temperature at which samples were isothermally scanned. For each isothermal frequency scan displayed in Fig. 4a and b a line is shown representing the computer fit of dielectric loss (ε'') to the HN equation [9],

$$\varepsilon^*(\omega) = \frac{\Delta\varepsilon}{(1 + (i\omega\tau_{\mathrm{HN}})^{\beta_{\mathrm{HN}}})^{\gamma_{\mathrm{HN}}}} \tag{2}$$

where $\Delta\varepsilon$ is the dielectric relaxation strength and τ_{HN} is the relaxation time. The broadness of the relaxation is described by β_{HN} and the skew of the curve is characterised by the parameter γ_{HN}. A simple Debye relaxation results in value of 1 for both β_{HN} and γ_{HN} [8]. Lower values of each (closer to zero) imply greater broadness or high frequency skew, respectively.

It is evident that as the temperature is increased, the frequency of the peak maximum is also increased, due to the polymer chains attaining greater mobility. In some cases the dielectric loss increases at low frequencies due to conductivity. This can be fitted mathematically so that its effect is removed from the analysis of the α-relaxation. The curves for polycarbonate (Fig. 4a) compare well with those of Ishida and Matsouka [38] which show dielectric loss peaks at temperatures of 150–170°C for frequency maxima in the range of 10–10^5 Hz.

The crystallisation of Kodar in these blends occurs at temperatures approximately 40–50°C above the DSC T_g [36], and as the dielectric scans are also conducted above the T_g it is important to take into account the possibility of crystallisation during the scans. Crystallisation is evident in the isothermal scans of the 40% Kodar blend, for example, shown in Fig. 4b, where the loss curves begin to broaden, decrease in strength and move to lower frequencies as the temperature is increased above 153°C. The decrease in strength is a result of the smaller amount of amorphous material available for relaxation, while the shift to lower frequencies is a result of the restriction of the amorphous material by the crystallised polymer. This restriction of molecular motion has been observed as result of crystallisation in a number of polymers and blends [12]. Broadening of the relaxation spectrum is a result of the greater range of relaxing environments existing when the polymer begins to crystallise, such as at the interface where a gradation in blend concentration and molecular mobility may occur [34]. Loss curves that displayed this behaviour were not used in any further analysis.

The onset of crystallisation observed by DRS, T_c (diel), was found to be similar to the cold crystallisation temperature (T_c (DSC)) determined by DSC [36]. Cold crystallisation appears as an exothermic peak maxima at temperatures above the glass transition and below the onset of melting (Fig. 5). The temperatures at which such crystallisation phenomena commenced were slightly lower

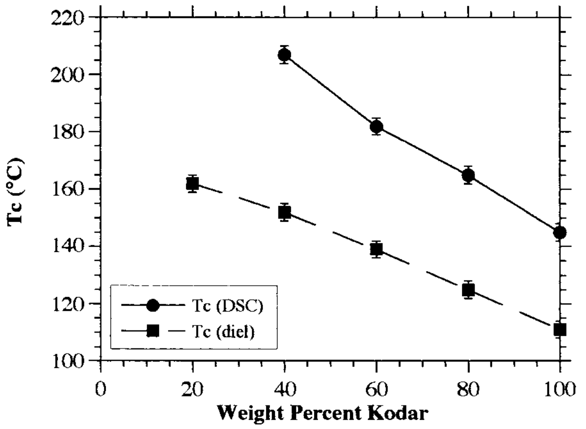

Fig. 5. Crystallisation temperature for PC/Kodar blends as determined by DSC at 10°C/min (●), and DRS (■).

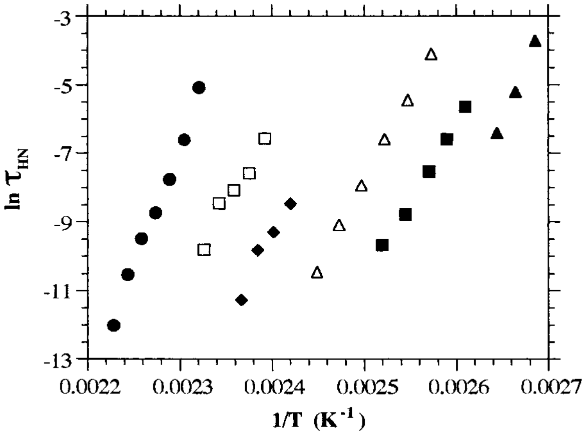

Fig. 6. Relaxation time (ln τ_{HN}) as a function of reciprocal temperature for PC/Kodar blends: (●) Polycarbonate; (□) 20% Kodar; (◆) 40% Kodar; (△) 60% Kodar; (■) 80% Kodar; (▲) Kodar.

in DRS than in DSC due to the slower effective heating rate in the stepped isothermal dielectric scans, compared to the relatively rapid heating (10°C/min) possible in the DSC scans.

To ensure that no crystallisation occurred at temperatures below T_c (diel), the onset of crystallisation during the dielectric experiments was confirmed by two methods of DSC analysis. The first method involved heating of the samples at a very slow scan rate of 0.5°C/min, which simulated the effective scan rate of the dielectric experiments. The temperatures of the onset of crystallisation at this heating rate by DSC were at least as high as those determined by dielectric analysis. For example, the onset of crystallisation of 60% Kodar by DSC at 0.5°C/min was determined to be 143°C, but the highest temperature scan used in the analysis of data from dielectric experiments was chosen to be 135°C. Secondly, blend samples were heated for 10 min at this limiting temperature for dielectric analysis, typically 3°C below the T_c (diel) value. The DSC scans after this heating were not significantly different from those of equivalent samples not subjected to this isothermal treatment, indicating that there was no change in the crystallisation and melting processes. Therefore, these two methods provide evidence that no crystallisation occurred during the dielectric scans at temperatures below the dielectric crystallisation temperature T_c (diel).

The relaxation time (τ_{HN}) for the isothermal scans of the PC/Kodar blends can be represented on a semi-log plot against reciprocal temperature (Fig. 6). In this format, each blend composition shows a monotonically increasing relaxation time with increasing $1/T$ (decreasing T). This represents a decrease in relaxation time as the temperature is reduced towards the T_g from above, as free volume decreases and the polymer molecules become less mobile. The position of the curves moves to lower temperatures with increasing Kodar in the blends, which is a result of the lower T_g values of blends containing more Kodar. The peak frequency (f_{max}) of each scan can also be represented against reciprocal temperature (Fig. 7). The loci of points are reversed relative to those of the relaxation time (Fig. 6) because the frequency of molecular motion increases as temperature increases. This latter representation is useful because it can be directly abstracted from the experimental data, whereas the relaxation time (τ_{HN}) data is determined by a mathematical fit to the data, which will introduce some error.

The change in relaxation time of the primary (α) relaxation in polymers is often best modelled by a Vogel–Fulcher dependence [39]

$$f_m = A \exp\left(\frac{-B}{R(T - T_0)}\right) \tag{3}$$

where A and B (J/mol) and T_0 (K) are fitted parameters. This predicts a rapid decrease in relaxation time on approaching the T_g from high temperatures due to a decrease in free volume [7,40]. However, the frequency–temperature loci in this work are quite linear due to the limited frequency

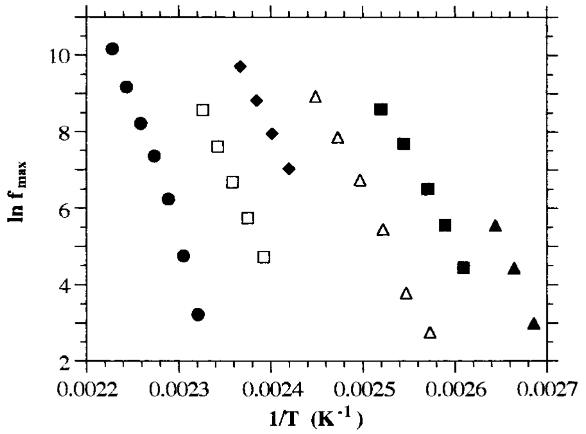

Fig. 7. Dielectric loss curve peak frequency (ln f_{max}) as a function of reciprocal temperature for PC/Kodar blends: (●) Polycarbonate; (□) 20% Kodar; (◆) 40% Kodar; (△) 60% Kodar; (■) 80% Kodar; (▲) Kodar.

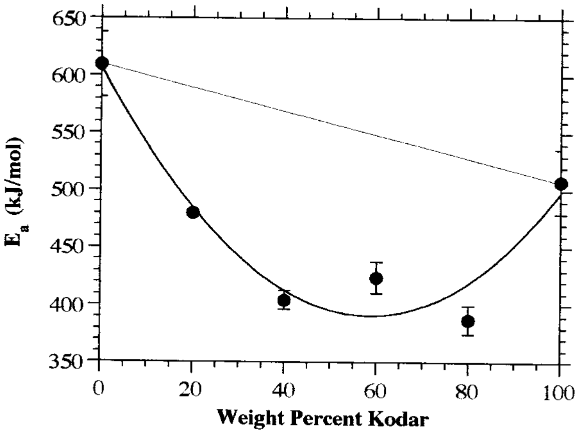

Fig. 8. Arrhenius activation energy (kJ/mol) for PC/Kodar blends. A polynomial of best fit illustrates the trend in E_a values. For comparison, a line of additivity (—) is also shown.

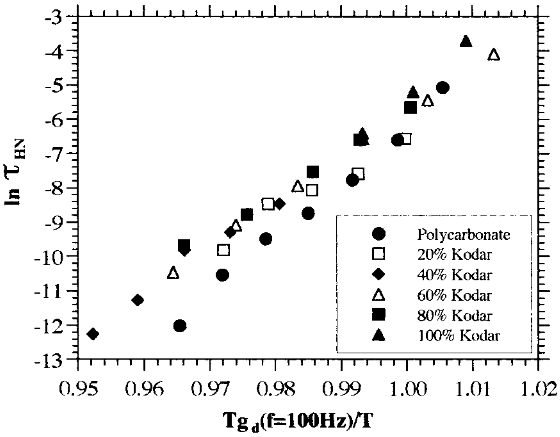

Fig. 9. Relaxation time (ln τ_{HN}) as a function of reduced temperature for PC/Kodar blends: (●) Polycarbonate; (□) 20% Kodar; (◆) 40% Kodar; (△) 60% Kodar; (■) 80% Kodar; (▲) Kodar.

range measured, and may be better fitted by an Arrhenius equation

$$f_m = A \exp\left(\frac{-E_a}{R(T)}\right) \tag{4}$$

where E_a (kJ/mol) is the activation energy or the energy barrier to rotation [7]. This approach was taken by Spall et al. [34], who showed that the slope of the line of best fit through the $\ln f_{max}$ against $1/T$ data (Fig. 7 in this study) could be used to calculate an activation energy and compare the data for a number of polymer blend compositions.

The curves in the $\ln f_{max}$ plot (Fig. 7) appear smoother, with less scatter than the ln τ_{HN} plot (Fig. 6), for the reasons mentioned above, and have thus been fitted to the Arrhenius equation to determine the activation energies (E_a) of the relaxations. The values of activation energy are plotted in Fig. 8 and show a greatly synergistic negative deviation from additivity for the blends, where the E_a values for all the blends are below those of either homopolymer. The minimum occurs between the 40 and 60% Kodar compositions. These results indicate that the energy barrier to rotation is lower in the blends than in the homopolymers. It is important to again note that it may be the combined relaxation of both polymers that is measured in the blends, as they are both dielectrically active.

It can also be seen that Kodar has a lower activation energy than polycarbonate. This can be explained by considering the structure of the two polymers. The bulky polycarbonate group consisting of aromatic rings and two pendant methyl groups has lower mobility than the Kodar molecule. This leads to the greater restriction to relaxation, or higher activation energy shown in Fig. 8.

In the polycarbonate/ThermX polyester blend system studied by Spall et al. [34] a small positive deviation from additivity in E_a was observed, indicating that the attractive interactions that cause miscibility may lead to energy barriers to motion that are greater than an average of those of the components. This was correlated with a decrease of free volume in the blends, relative to an additive behaviour, which revealed that closer molecular packing led to higher activation energies of motion [34]. Therefore, the molecular interactions in the PC/Kodar system appear to be quite different to those in PC/ThermX blends.

Positron annihilation lifetime spectroscopy data for PC/Kodar blends [36] show an average behaviour in free volume site size (V_f) and a negative deviation from additivity in the fractional free volume (f_v) on blending, which may be expected to result in some inhibition of molecular motion in the blends [36]. However, free volume as measured by PALS at ambient temperature (well below T_g) is generally thought to be an order of magnitude lower than that required for segmental motion at the higher temperatures of the glass transition [41], so it is not necessarily correct to directly relate these parameters. The observed negative deviation in the dielectric activation energy must be due to facilitation

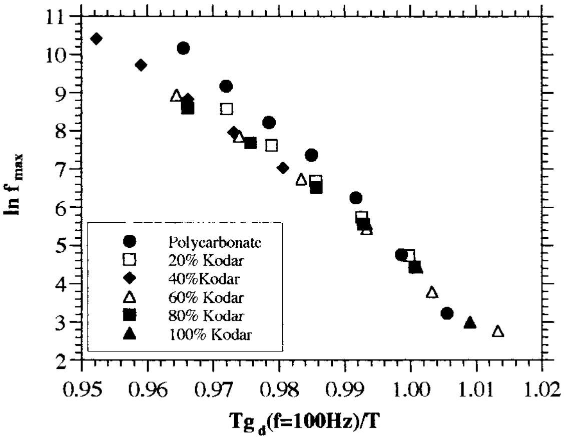

Fig. 10. Dielectric loss curve peak frequency (ln f_{max}) as a function of reduced temperature for PC/Kodar blends: (●) Polycarbonate; (□) 20% Kodar; (◆) 40% Kodar; (△) 60% Kodar; (■) 80% Kodar; (▲) Kodar.

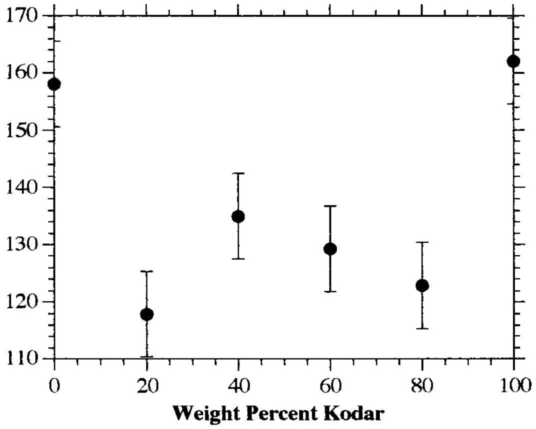

Fig. 11. Steepness parameter (S) for PC/Kodar blends.

of motion on a scale greater than that shown by PALS data. An increase in modulus for the blends and a decrease in elongation to break and toughness compared to a weighted average of the component polymer values [36] also corresponds to the f_v result, which indicates tighter molecular packing in the blends. It is possible, therefore, that the disruption of interactions between like molecules in the miscible blends may lead to enhanced mobility at the glass transition as shown by the synergistic decrease in the energy barrier to motion.

The ln τ_{HN} and ln f_{max} plots have been normalised with the T_g value determined by dielectric spectroscopy (T_{g_d}) at a constant frequency (100 Hz), and are shown in Figs. 9 and 10, respectively. This normalisation allows the data to be converted into fragility or cooperativity plots, as discussed in the introduction. All curves converge at the value $T_{g_d}/T = 1$ due to the choice of T_{g_d}. From this point on the ln τ_{HN} plot, the gradient can be determined, which corresponds to the steepness (S) as described by Ngai and Plazek [41]. In amorphous polymers a direct correlation has been shown between the steepness parameter (S) and the coupling parameter (n) [19].

$$S = \frac{\partial(\ln \tau)}{\partial\left(\frac{T_g}{T}\right)_{T=T_g}} \tag{5}$$

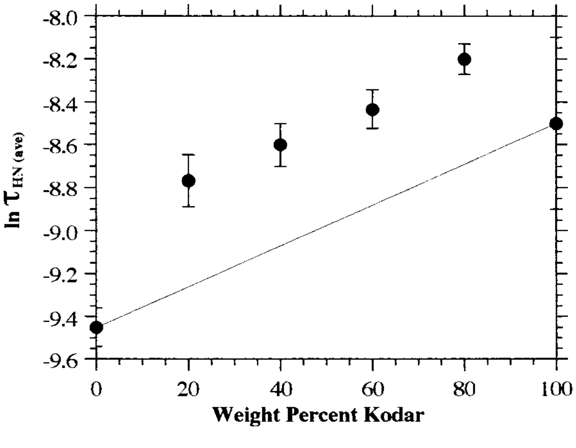

Fig. 12. Average relaxation time (ln $\tau_{HN\ (ave)}$) at the reduced temperature $T_{g_d}/T = 0.98$ for PC/Kodar blends. For comparison, an additive line (—) is also shown.

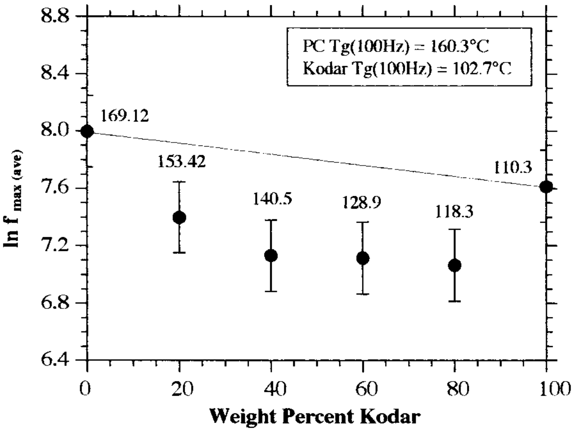

Fig. 13. Average dielectric loss curve peak frequency (ln $f_{max\ (ave)}$) at the reduced temperature $T_{g_d}/T = 0.98$ for PC/Kodar blends. For comparison, an additive line (—) is also shown.

A larger value of S indicates a higher degree of cooperative motion. Fig. 11 shows the values of the steepness parameter (S) plotted as a function of composition of the blends. There is only a slightly negative deviation of the blend S values compared to those of the pure polymer values due to the large errors associated with calculation of S. The close contact between the chains that drives miscibility does not increase intermolecular coupling, perhaps because of the different nature of conformation of the homopolymer chains compared to that in the blended state.

By determining the parameters of the HN function at a constant reduced temperature (T_{g_d}/T) it is possible to see the effect of blend composition on the shape of the loss spectrum. To do this, a plot of a parameter, relaxation time for example, against reduced temperature (Fig. 9) was analysed at three fixed T_{g_d}/T values (0.99, 0.98 and 0.97). By fixing these reduced temperatures it is meaningful to compare data between samples at the same relative ratio to T_g. Due to scatter in results, the average parameter over these three temperatures is calculated and plotted against the composition. The plot for the average relaxation time is shown in Fig. 12 and that for ln $f_{max\ (ave)}$ in Fig. 13. These two parameters are closely linked ($\omega\tau = 1$ in a single relaxation time system) and the plots thus show trends that are the inverse of each other. A minimum in the frequency of relaxation is observed at intermediate blend compositions at the given normalised temperature of $T_{g_d}/T = 0.98$, and a corresponding maxima in the relaxation time is also observed. Polycarbonate is the slower relaxing polymer, and this may be due to the large pendant methyl groups in the PC structure [34].

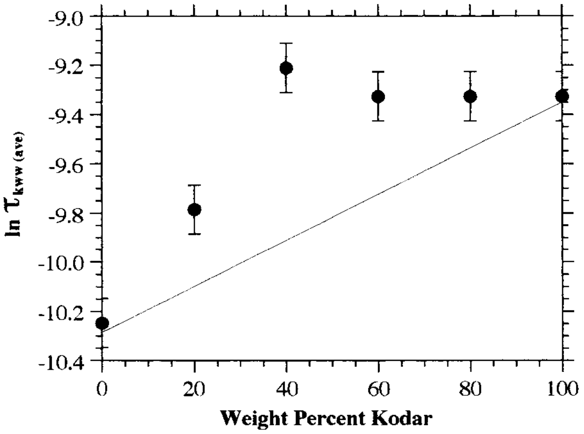

Fig. 14. Average KWW relaxation time ($\ln \tau_{\mathrm{KWW\ (ave)}}$) at the reduced temperature $T_{g_d}/T = 0.98$ for PC/Kodar blends. For comparison, an additive line (—) is also shown.

The relaxation time determined by the KWW method described in the introduction is shown in Fig. 14. There is an increase in relaxation time from the polycarbonate to the Kodar polymer although there is now an almost synergistic positive deviation from additivity. There is a rapid rise of relaxation time up to the 40% Kodar blend, and for higher Kodar contents the relaxation time is constant. This behaviour closely mirrors the $\ln f_{\mathrm{max\ (ave)}}$ data determined by the HN function.

One way to interpret such synergistic behaviour is to consider the different nature of packing on blending. Miscibility may lead to lower degrees of free volume, but this can only be speculation since the PALS measurements mentioned previously in this work were measured at ambient temperature, well below the temperature of the α-relaxation.

Alternatively, an explanation of the variation of frequency maxima, or blend relaxation time, with T_{g_d}/T takes account of the T_g values of the two homopolymers and the actual experimental measurement temperature corresponding to each of the points on the graph, as noted in Fig. 13. As the content of Kodar in the blends increases, it is clear that the experimental temperature is progressively lower. It is also evident that the speed of motion of the polymers in the blends is constant between 40 and 80% Kodar, and it is proposed here that this may be due to the T_g values of the blends. As the amount of Kodar is increased, the measurement temperature is reduced further below that of the PC T_g. If there remain, however, local regions of PC in blends of all compositions, there would be a range in the magnitude of intermolecular constraints on segmental motion [42]. As the blend composition moves to higher wt% Kodar, there is progressively less PC in the blends, but the measurement temperature progressively moves further below the glass transition of PC. Therefore the lower levels of PC may have a larger specific effect on restricting molecular motion in the blends due to the measurement temperature, resulting in an equivalent average frequency of relaxation in the blends.

This argument relies on the concept of concentration micro-heterogeneity in the blends, even though these blends are miscible as determined by the behaviour of the T_g in DSC, DMTA and dielectric measurements. A number of authors have found that blends characterised as miscible show some heterogeneity on a finer scale by techniques such as NMR [43,44]. The degree of homogeneity detected in a blend is highly dependent on the experimental technique used [45]. For example, DRS is believed to probe local segmental motion of a few units up to 10 bonds, whereas DMTA probes relaxations involving segments of the order of 50 bonds [45]. The presence of these concentration fluctuations [16,45] means that the composition of local regions is distributed around the macroscopic mean, which leads to fluctuation in the time dependent properties of the blend. In such cases it is possible, therefore, that the polymers in some local regions could behave similarly to their unblended state. Mansour and Madbouly reported [46,47] that PC/TMPC blends, that were determined to be miscible by DSC, were in fact not miscible on a segmental level, but rather on a larger structural level which led to no change in the local environment of the polymers on blending.

The intermolecular coupling of molecules in a blend is dependant on the strength of the coupling in the homopolymer components [45]. The presence of fluctuations in concentration leads to a range of local environments which in turn leads to variation in the coupling of the homopolymers. As shown above by the cooperativity plots, in PC/Kodar blends there is no more coupling than is evident in the pure polymers. If there are regions of sufficient size rich in each component polymer, then the average effect may be to increase the relaxation time because of significant concentrations of the rigid component which may act as in the homopolymer and restrict the total relaxation of the blend. Therefore the reduction in speed of relaxation, or increase in relaxation time, may be a result of concentration fluctuations in the blends averaging to give the above result.

This restriction of molecular motion by the rigid component in the blends also leads to broadening of the relaxation peak. This has been attributed to two factors; the coupling of molecular motion in the blends, and the concentration fluctuations that are expected when mixing two polymers [48]. Colmenero and coworkers [48] found in blends of poly(vinylethylene) (PVE) and 1,4-polyisoprene (PIP) that greater intermolecular coupling led to broader relaxation spectra due to greater coupling in the local regions of higher concentration of PVE (the higher T_g component). Therefore, greater broadening of the relaxation was observed in the low frequency side of the spectra due to the dominant constraining effect of the high-T_g component. Recent work on the PIP/PVE blend system by Arbe et al. [49] has shown that the PIP in the blends behaves as pure PIP, but the PVE α-relaxation is greatly plasticised. The behaviour of the PIP component may be understood in terms of the

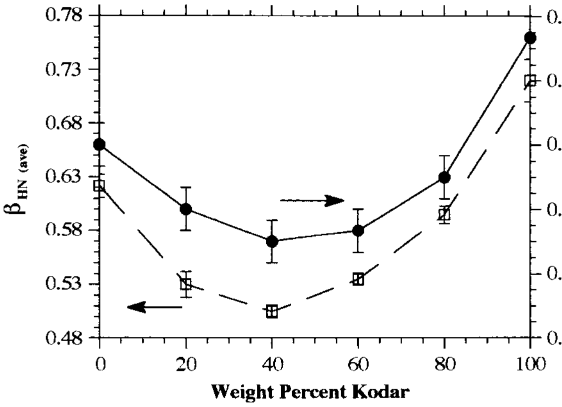

Fig. 15. Average relaxation broadness (β) at reduced temperature $T_{g_d}/T = 0.98$ by HN (□) and KWW (○) functions for PC/Kodar blends.

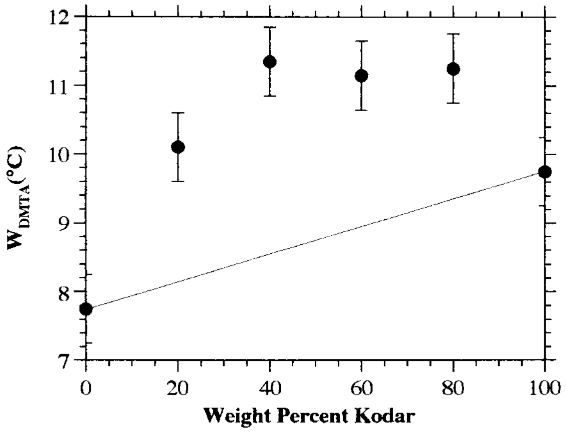

Fig. 16. DMTA loss modulus full width at half maximum height for PC/Kodar blends. For comparison, and additive line (—) is also shown.

thermodynamic theory of microphase separation proposed by Khokhlov and Erukhimovich [50] which predicts local demixing in miscible blends. This could have a strong effect on the local dynamics, but in the nanoheterogeneous structure predicted both components should behave as in the homopolymer state [49]. The principles of the coupling model [18], however, were considered suitable for explaining the existence of two different segmental relaxations in a blend, each related to one of the components [49].

The values of the broadness of the relaxation peaks measured from both HN and KWW fits of the relaxation data (β_{HN} and β_{KWW}) have been determined for an average reduced temperature of $T_{g_d}/T = 0.98$, and are plotted in Fig. 15. These two parameters are expected to behave similarly, even though they are not numerically equivalent [19,34]. The values determined by the KWW method are numerically lower than those determined by the HN function. With the KWW model the relaxation peak will appear broader because any skewing is incorporated as a contribution to broadness, whereas in the HN fit skewing is a separate parameter.

It is evident that there is considerable broadening of the glass transition relaxation in the blends, shown as a large negative deviation from additive behaviour as a function of composition of the blends. There is a minimum at 40% Kodar, and all blends display broader relaxations than the pure polymers. This is also reflected in the broadness of the DMTA loss peaks (W_{DMTA}) where a large positive deviation from additive behaviour (broader) is observed (Fig. 16). Relaxation processes as measured by DMTA and dielectric techniques have been related, and it has been shown that relaxation data (for PC) falls on the same $f_{\max}$/temperature curve [12].

The value of β_{HN} as determined by the dielectric relaxation technique is greater for Kodar than PC, as is W_{DMTA}. However, the blend compositions at which the maximum broadening occurs is different. Variation between the techniques may be due to the different size kinetic units involved in dielectric and mechanical relaxation [34]. Despite some scatter in the fitted values, the β_{KWW} parameter shows a slightly lower temperature dependence in the blends compared to the homopolymers (Fig. 17). In the PC/ThermX blends studied by Spall et al. [34] the α-relaxation is also broadened in the blends. The broadening, as determined by the HN function, is skewed more in the PC-rich blends, similar to the values obtained for PC/Kodar blends. In both cases the PC has a higher T_g than the polyester component of the blends. Therefore, the PC has a greater influence on broadening than the Kodar or ThermX polymers in the blends.

The strength of the loss peak ($\Delta\varepsilon_{\mathrm{HN}}$ and $\Delta\varepsilon_{\mathrm{KWW}}$) shows an additive relationship between the homopolymer values (Fig. 18) indicating that the polymers contribute on a weighted average basis to the strength of the relaxation. The Kodar polymer has a higher relaxation strength than polycarbonate or the blends. The relaxation strength is a function of many factors such as temperature, density, number of dipoles per unit volume, chain conformation and interaction. Linear changes in $\Delta\varepsilon$ have also been

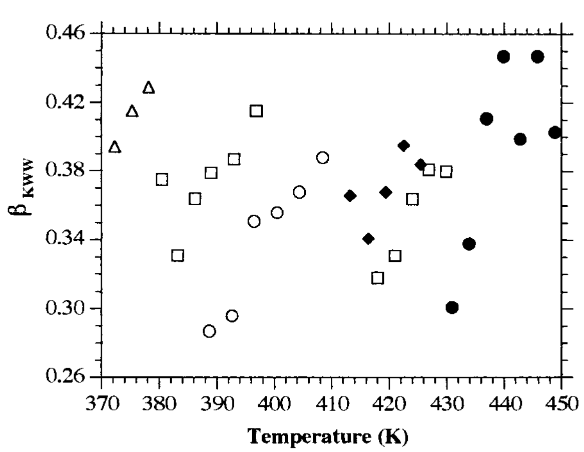

Fig. 17. Temperature dependence of β_{KWW} for PC/Kodar blends: (●) Polycarbonate; (□) 20% Kodar; (◆) 40% Kodar; (○) 60% Kodar; (□) 80% Kodar; (△) Kodar.

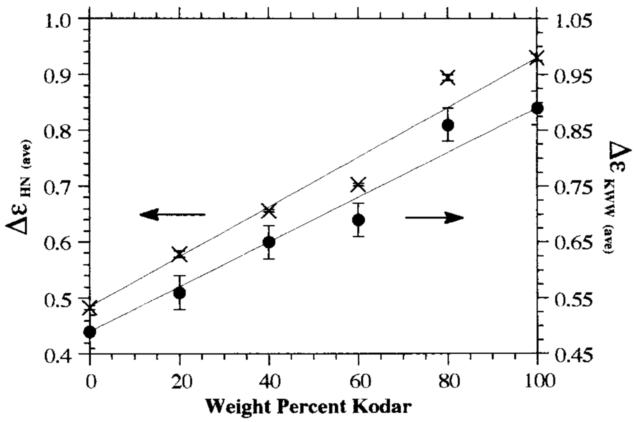

Fig. 18. Relaxation strength at the reduced temperature $T_{g_d}/T = 0.98$ by HN (×) and KWW (○) functions for PC/Kodar blends. For comparison, additive lines (—) are also shown.

attributed to changes in the volume of cooperativity of the α-relaxation [46,51,52], where a lower relaxation strength accompanied a greater cooperative motion. An additive change in relaxation strength has previously been found to be a feature of the miscible PC/ThermX blend system where both components are polar [34], as in this case of PC/Kodar blends.

Katana et al. [29] found that in the miscible blends of PC and tetramethylbisphenol-A polycarbonate (PC/TMPC) that the maximum in the width at half height of the dielectric spectra was skewed towards the PC-rich compositions. Therefore, in blend systems where both components are polar, the relative relaxation strengths of the components may influence the appearance of the spectrum [34]. In PC/ThermX blends Spall et al. [34] showed that PC had a much lower dielectric relaxation strength and slightly lower coupling than ThermX, so the observed bias of broadening towards the PC value indicated that coupling was important in this system. In the PC/Kodar blend system studied here, PC has a lower relaxation strength and the broadening of the dielectric α-relaxation (β_{HN} and β_{KWW}) in the blends is skewed slightly towards PC. Therefore, following the argument of Spall et al. [34], these results would indicate that coupling does have some importance in the relaxation behaviour of the PC/Kodar blends.

Despite the relaxation broadness in the PC/Kodar system increasing on blending (lower β), the intermolecular coupling is not greater in the blends than in the component polymers, as determined by the steepness parameter (S) [18,19]. This indicates that concentration fluctuation must be the cause of relaxation broadening. These fluctuations were also used as the justification of the dependence of relaxation time (ln τ) on composition discussed above. It is therefore evident that even in blend systems as similar as PC/Kodar and PC/ThermX, greatly different relaxation behaviour can be observed. The relationship between molecular state and the observed relaxation behaviour is therefore extremely important. In instances where both increased coupling and broadness occur in blend systems, it would be much more difficult than in the case presented in this study to separate those effects, particularly where both species contain strong dipoles.

4. Conclusions

Concentration fluctuation is the dominant feature which controls the dielectric response in the miscible amorphous polycarbonate/Kodar blends studied. There is an increased broadening of the loss spectra on blending as determined by both HN and KWW fits to the dielectric data, and by analysis of the DMTA loss peaks. There is decreased activation energy in the blends, and the steepness of the cooperativity plot indicates there is no increase in intermolecular coupling on blending. Hence, the increased broadening in the PC/Kodar blends must primarily be due to fluctuations in concentration about the average.

The relaxation time is increased on blending, and this is attributed to the temperature of measurement being below the glass transition of the rigid PC-rich component of the blends that exists because of the large concentration fluctuations present. This hypothesis relies on the assumption of some micro-heterogeneity in the blends, which allows the molecular motion of the PC molecules to dominate the relaxation behaviour of the blends to a greater extent than may be expected from a homogeneous mixture of the blend components. Thus, local regions of composition rich in Kodar or polycarbonate exist in these blends, even though they are miscible on the larger scale demonstrated by the appearance of a single T_g as determined by techniques such as DSC, DMTA and dielectric relaxation.

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