

# Dynamic mechanical relaxation behaviour of poly(ether ether ketone)/poly(etherimide) blends

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The dynamic mechanical behaviour of miscible, amorphous blends of poly(ether ether ketone) (PEEK) and poly(etherimide) (PEI) was studied over a wide temperature range incorporating the  $\alpha$  transition and sub- $T_g$  transitions. The segmental motions responsible for the  $\alpha$  process were significantly slowed by blending and were dominated by PEI. Fits of the data to the Kohlrausch–Williams–Watts function showed increased broadening in the blends, arising from concentration fluctuations, and a reduction in the mechanical relaxation strength. The temperature dependence of the WLF shift factors, obtained from cooperativity plots, did not correlate with the stretched exponential broadness parameter in the manner predicted by the coupling model. Two sub- $T_g$  transitions in PEI and the blends, and one in PEEK, were detected. The PEI  $\beta$  transition, which occurred around 100°C at 1 Hz, was strongly affected by the presence of PEEK. The blend  $\gamma$  transition shifts its temperature position with composition in a linear manner between the PEEK  $\beta$  transition (–69°C at 1 Hz) and the PEI  $\gamma$  transition (–81°C at 1 Hz). © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Thermoplastic aromatic polyketones are frequently referred to as high performance polymers, as a result of their rigid aromatic backbone structure which confers outstanding physical and mechanical properties and enables them to be used in many engineering applications<sup>1</sup>. Poly(ether ether ketone) (PEEK) is the most widely studied polymer of this type, but is by no means the only one to be investigated. A number of other polyketones, with varying ether/ketone ratios, have been synthesized (and some commercialized), and the influence of this structural variable on the thermal properties and morphology of these materials has been reported<sup>2</sup>. Studies of this type confirm that polyketones are ideal for the study of thermoplastic structure/property relationships since wide variation in the morphology can be achieved by altering the thermal history<sup>3</sup>.

The  $\alpha$  and  $\beta$  relaxations in amorphous and semi-crystalline PEEK have been studied by dielectric and dynamic mechanical techniques<sup>4,5</sup>. The  $\alpha$  relaxation, which is assigned to the glass transition, has been shown to be very sensitive to the semi-crystalline morphology of PEEK, which in turn is governed by the processing history. In crystalline samples the  $\alpha$  relaxation is significantly broadened and raised in temperature compared with the amorphous sample, and this is attributed to constraints imposed by the crystallites on the segmental mobility of the amorphous regions<sup>6</sup>. For cold crystallized samples the glass transition temperature

(as defined by the maximum in the  $\tan \delta$ ,  $E''$  or  $\epsilon''$  peak) passes through a maximum as the crystallization temperature increases, and always remains above that of the amorphous sample<sup>5</sup>. Small-angle X-ray scattering studies suggest that this arises from an increase in the thickness of the amorphous interlayer,  $l_a$ , as crystallization temperature increases, thus leading to fewer constraints on the amorphous segments<sup>7</sup>. Both dielectric<sup>4</sup> and dynamic mechanical<sup>5</sup> studies indicate that the relaxation strength in semi-crystalline PEEK increases with temperature above the glass transition, and this has been explained in terms of a 'rigid amorphous phase' which remains immobile across the glass transition. An alternative model of the rigid amorphous phase, determined from X-ray studies on a range of semi-crystalline polymers, including PEEK, has recently been reported<sup>8</sup>.

Some interesting differences in relaxation behaviour in the sub- $T_g$  region in amorphous and semi-crystalline PEEK have been revealed, and the occurrence of these depend upon which experimental probe is used. At –155°C (dynamic mechanical, 7 Hz) and in the range –196°C to –73°C (dielectric, 200 Hz to 20 kHz) a  $\gamma$  relaxation occurs<sup>9</sup>. This is suggested to be due to a highly localized motion which does not involve phenyl group motion and is essentially non-cooperative, remaining unaltered by changes in PEEK morphology. The  $\gamma$  relaxation merges, at higher temperatures, with the  $\beta$  relaxation which arises from phenyl ring flips that free larger scale motions involving the polar units and thus make this relaxation dielectrically active. This process is considered to be cooperative in nature and is reported to be sensitive to morphology, water content and ageing history<sup>10</sup>.

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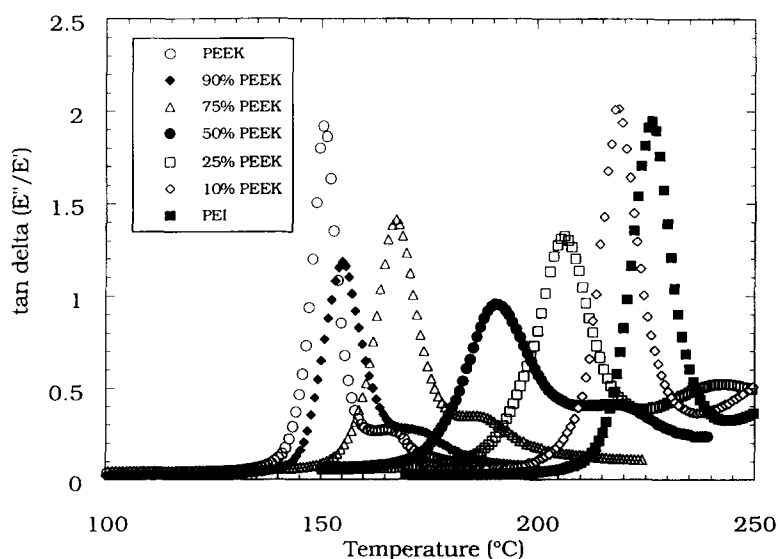


Figure 1 Dynamic mechanical temperature scan for PEEK/PEI blends at frequency 1 Hz and heating rate  $2^{\circ}\text{C min}^{-1}$

A bi-modal nature to the  $\beta$  relaxation has been observed and is clearly seen in the dynamic mechanical spectrum<sup>10</sup>, with the lower temperature component being due to non-cooperative motions and the higher temperature one being assigned to local, cooperative motions of ordered regions in amorphous PEEK. It has been shown that, at comparable frequencies, the dielectric loss maxima occur at lower temperatures (compared with the dynamic mechanical loss), which suggests that the dielectric component is a high frequency part of the broad range of motions detected by the dynamic mechanical studies<sup>11</sup>.

The fine structure of the relaxation discussed above has been revealed by thermally stimulated current (TSC) studies on semi-crystalline PEEK<sup>12</sup>. These show two 'sub-modes' around the glass transition and in the sub- $T_g$  region. The high temperature relaxations are attributed to the glass transition of PEEK (at  $145^{\circ}\text{C}$ ) and the rigid amorphous fraction constrained by the crystallites (at  $162^{\circ}\text{C}$ ), whilst the low temperature processes are believed to be associated with cooperative movements in the amorphous crystallizable phase (at  $-110^{\circ}\text{C}$ ) and motions within the crystalline phase (at  $-75^{\circ}\text{C}$ ).

Another interesting aspect of PEEK is that it forms a miscible blend in all proportions with poly(ether imide) (PEI), which is an amorphous, engineering thermoplastic with a  $T_g$  of  $215^{\circ}\text{C}$ <sup>13</sup>. This blend has attracted some interest in the belief that there is potential for the enhancement of engineering properties, although to date it has proved more useful for understanding structure-property relationships in miscible blends than in finding a practical application. At high crystallization temperatures PEI is displaced into inter-spherulitic regions, whereas at intermediate and low crystallization temperatures PEI segregates between PEEK lamellar bundles<sup>14</sup>. High temperature crystallized blends with high PEI content which have been investigated by dynamic mechanical<sup>15</sup> and dielectric<sup>16</sup> spectroscopy, show two loss peaks. The main peak occurs close to the loss peak of pure PEI, and a shoulder appears at lower temperatures. These have been attributed to transitions occurring in inter-spherulitic regions which are rich in PEI that is

totally de-mixed from PEEK, and in interlamellar amorphous regions containing a mix of PEEK and PEI.

In a previous paper on this blend system we examined the dielectric behaviour around the glass transition<sup>17</sup>. In this work we report on the dynamic mechanical behaviour of PEEK/PEI blends at the glass transition temperature and below.

## EXPERIMENTAL

### Materials

The PEEK used in this study was grade 381G, supplied by ICI Australia. The molecular weights are  $M_w = 73\,000$  and  $M_n = 30\,600$  (manufacturer's data). The PEI was Ultem 1000, supplied by GE Plastics, with molecular weights of  $M_w = 30\,000$  and  $M_n = 12\,000$ <sup>14</sup>. Blends, calculated as weight percent, were processed using a Haake Rheocord single-screw extruder at  $400^{\circ}\text{C}$ . Pure PEEK and PEI were also extruded at  $400^{\circ}\text{C}$  and  $300^{\circ}\text{C}$  respectively. The extruded materials were compression moulded at  $400^{\circ}\text{C}$  ( $300^{\circ}\text{C}$  for PEI) and then quenched into ice/water to form amorphous sheets with thicknesses ranging from 0.2 to 0.6 mm. All samples were dried before blending, moulding and analysis.

### Dynamic mechanical thermal analysis

The dynamic mechanical response of the samples was monitored using a Rheometric Scientific DMTA MKII in the bending mode, with dual cantilever geometry. Rectangular samples, measuring  $30\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$ , were scanned isochronally at  $2^{\circ}\text{C min}^{-1}$  between  $-110^{\circ}\text{C}$  and  $300^{\circ}\text{C}$ , and isothermally around the glass transition. Loss modulus ( $E''$ ), storage modulus ( $E'$ ) and  $\tan \delta$  were recorded over the frequency range 0.03–200 Hz. All sub-ambient experiments were carried out in an inert atmosphere.

### Curve fitting

Non-linear least-squares curve fitting was accomplished by the use of the commercial 'PeakFit' software

(Jandel Scientific, USA) which uses the iterative Marquardt–Levenberg fitting algorithm. This involves estimating values for the adjustable parameters such that the function

$$\chi^2 = \sum_{i=0}^n \left[ \frac{f(x_i) - y_i}{\sigma_i} \right]^2 \quad (1)$$

is minimized, where  $y = f(x)$ , with  $f$  representing a model fitting function, and  $\sigma$  is the standard deviation. This procedure provides values for the adjustable parameters such that the fitting function is optimum in a least-squares sense. A fit is converged when  $\chi^2$  is unchanged within the eighth significant figure for five full iterations. The confidence intervals for the model parameters are determined at the 95% limit using a method outlined by Draper and Smith<sup>18</sup>. A graphical pre-fitting method was used to manipulate the fitting function on the screen to match the experimental data as closely as possible prior to fitting.

It is well known that the dielectric  $\alpha$  relaxation can be fitted to a number of empirical expressions. In this study we first use the Havriliak–Negami function<sup>19</sup> to fit and define the shape of the isothermal loss curves. We then fit the resulting curves to the Kohlrausch–Williams–Watts function<sup>20,21</sup>

$$\phi = \exp[-(t/\tau)\beta_{\text{kww}}] \quad (2)$$

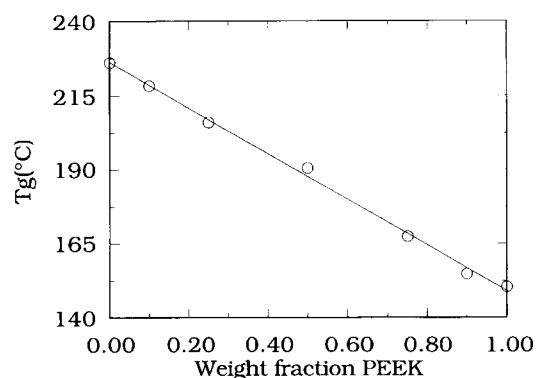
using the Fourier transform method developed by Moynihan *et al.*<sup>22</sup>. In equation (2)  $\phi$  is a relaxation function,  $\tau$  is a characteristic relaxation time and  $\beta_{\text{kww}}$  is related to the broadness of the relaxation.

## RESULTS AND DISCUSSION

### $\alpha$ relaxation

**Temperature scans.** The dynamic viscoelastic response of PEEK, PEI and blends, in the glass transition region, is shown in *Figure 1* as an isochronal plot of  $\tan \delta$ . Both homopolymers exhibit a relatively narrow peak in  $\tan \delta$  across the glass transition, where the temperature,  $T_{\text{max}}$ , corresponding to the maximum in  $\tan \delta$ , can be taken as the  $T_g$ . The loss curves for the blends are broader and generally have a lower maximum. The small, high temperature shoulder on each damping curve from PEEK homopolymer to 25% PEEK is associated with dynamic crystallization of the samples during heating. As the proportion of PEEK decreases, the shoulder occurs at a relatively higher temperature and reflects the retarding effect of PEI on the crystallization kinetics of PEEK. The blend containing 10% PEEK does not crystallize during the temperature scan. Taking the temperature at the peak maximum as the glass transition temperature, a plot of these values against blend composition, shown in *Figure 2*, exhibits close to linear additivity. This is a common feature of miscible blends and the data can be used to estimate the strength of interactions between the homopolymers<sup>23</sup>.

*Figure 3* shows dynamic mechanical loss data for PEEK, PEI and a 50/50 blend, along with curve fits from the HN function. The data are taken from isothermal measurements and are plotted at particular temperatures as a function of frequency. Although isothermal dynamic mechanical scans cannot extend over as wide a frequency



**Figure 2** Variation of dynamic mechanical  $T_g$  with composition for PEEK/PEI blends. Solid line is linear fit to data

range as dielectric scans, they have the advantages of: probing the sample at relatively lower temperatures, thereby reducing the chance of unwanted dynamic crystallization; not requiring polar groups for detection; and not being hampered by low frequency conductivity effects which can mask the  $\alpha$  relaxation. The curves shown in *Figure 3* exhibit the asymmetric shape typical of the glass transition process of amorphous polymers. According to the HN fit, the blend has a significantly reduced  $E''_{\text{max}}$  of 0.30 GPa compared with PEI (0.91 GPa) and PEEK (1.37 GPa).

**Relaxation times.** The relaxation times,  $\tau$ , for each of the homopolymers and blends were determined from HN fits to plots of loss modulus against frequency. They were then used in an Arrhenius plot to calculate an apparent activation energy,  $E_{\text{act}}$ , for the glass transition process. Values of  $E_{\text{act}}$  for the blends tended to be close to those of the homopolymers, and all had values of approximately  $1000 \text{ kJ mol}^{-1}$ , indicating that the barriers to rotation are unchanged by blending.

The temperature dependence of the relaxation times for miscible blends is not easily observed from inverse temperature plots, because the glass transition temperature shifts with composition and molecular mobility scales with distance of the experimental temperature from the d.s.c.  $T_g$ . It is more revealing simply to normalize the data using an arbitrary temperature  $T_\alpha$ , which is taken from outside the measuring range; often the d.s.c.  $T_g$  or the temperature at which the relaxation time is equal to 1 s is used. For low molecular weight glasses plots of relaxation time against  $T_\alpha/T$  are known as fragility plots, whereas for polymer systems they are referred to as cooperativity plots<sup>24</sup>. A cooperativity plot of  $\log \tau$  (where  $\tau = 1/2\pi f_{\text{max}}$ , with  $f_{\text{max}}$  corresponding to the peak temperature in isochronal scans) against  $T_g/T$ , where  $T_g$  is the d.s.c.  $T_g$  of the blends and homopolymers, is shown in *Figure 4*. This plot now shows that the mobility of the mechanical relaxing species in the blends is strongly influenced by PEI. Only the blend containing 90% PEEK remains close to the relaxation locus of PEEK homopolymer. The remaining blends have relaxation times that are shifted mainly beyond those of PEI homopolymer.

Although normalization of the data by the d.s.c.  $T_g$  results in a horizontal shifting of each curve, the slope of each curve is unchanged from that of a conventional plot of  $\log \tau$  against  $1/T$ . *Figure 4* shows that some curves have a greater degree of non-linearity than others. For

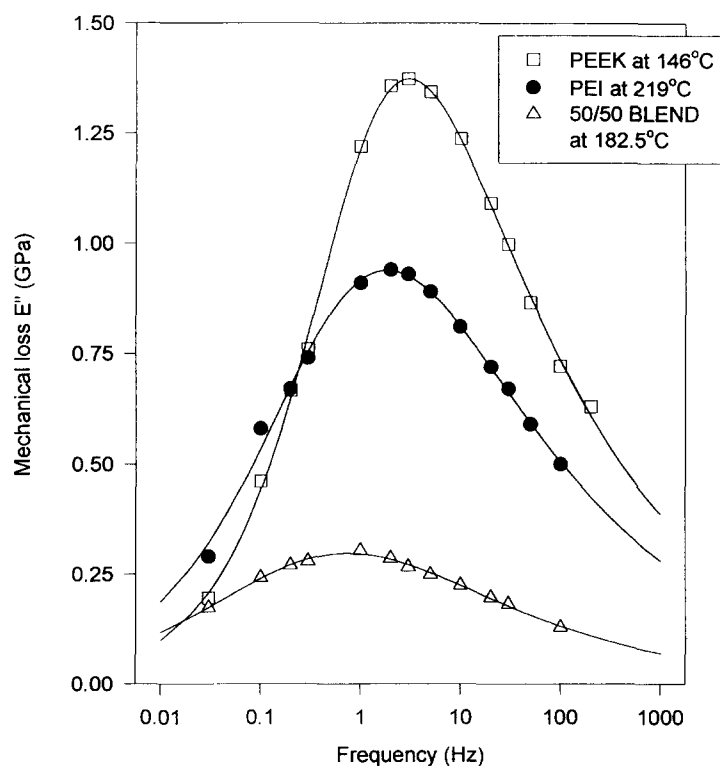


Figure 3 Isothermal mechanical loss curves for PEEK, PEI and a 50% blend. Solid lines are fits to the Havriliak–Negami function

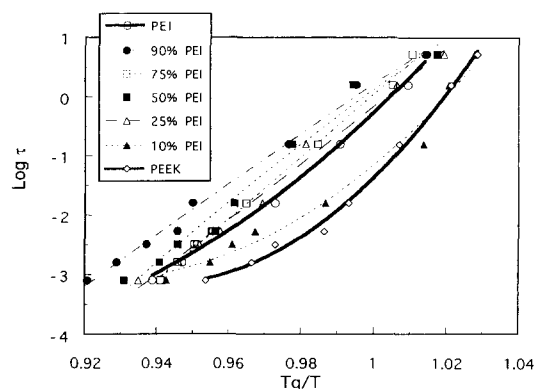


Figure 4 Cooperativity plot of relaxation times for PEEK/PEI blends.  $T_g$  is taken from d.s.c. studies. Solid lines are guides to the eye. Error in  $\log \tau$  is  $\pm 0.05$

closer examination of these data the cooperativity plot can be modified by plotting the relaxation data against blend composition at a constant value of  $T_g/T$ . This is shown in Figure 5 with  $T_g/T$  equal to 0.96; also shown in this plot is the corresponding analysis from our recent dielectric studies on this system<sup>17</sup>. For data that did not appear exactly at this point, linear extrapolation was used. With both experimental modes there is a pronounced positive deviation from linear additivity, with blends containing PEI as the major phase relaxing at a slower rate than either homopolymer. The slower motion of PEI is to be expected from an examination of the chemical structure of each homopolymer. PEI has two carbonyl groups attached to the imide ring and pendant methyl groups to impede relaxation, whereas the PEEK molecule contains a high proportion of relatively flexible ether groups. In the high PEI content blends the interactions between PEEK and PEI act to restrict motion even more. The observed increase in the dynamic

mechanical times compared with the dielectric ones results from the lower measuring frequency of dynamic mechanical. Krishnaswamy *et al.*<sup>5</sup> also found an offset in  $\tau$  measured by each technique for amorphous PEEK, which they attributed to different sensitivities of each probe with dynamic mechanical probing the longer range motions of the  $\alpha$  relaxation. Wetton *et al.*<sup>25</sup> suggest that the dielectric constant is formally equivalent to the mechanical compliance since both represent the ability of the system to move. However, as compliance is weighted towards large-scale molecular motions, better empirical correlation is usually found between  $\epsilon''$  and  $E''$  (or  $G''$ ). Although the same overall relaxation process is being monitored by dynamic mechanical and dielectric techniques, the loss peak locations are weighted by the coupling of the stress to the molecules and the experimental parameters chosen. Colmenero *et al.*, in a study on PVE<sup>26</sup>, report a correlation between the Kohlrausch–Williams–Watts (KWW) stretch exponent and the shift

factor which is consistent with the coupling model of relaxation, such that if stretch exponents determined by different techniques are equal the temperature dependences of the relaxation times will also be equal. The stretch exponent and shift factors with regard to the PEEK/PEI system will be discussed in the next section.

**Relaxation broadness.** The parameter  $\beta_{\text{kww}}$ , which is inversely related to the broadness of the relaxation process, is plotted in Figure 6 as a function of composition at constant  $T_g/T$ . The coupling model<sup>24</sup> relates the degree of broadening to the extent of intermolecular cooperativity, which in turn correlates with chain structure. Specifically, the more rigid and inflexible a polymer backbone is, the more coupled it is to the motion of its near neighbours (i.e. broader relaxation) and the stronger its time and temperature dependence will be. This implies that, using a dynamic mechanical probe, chain motions of PEI are more intermolecularly coupled than PEEK chain motions (Figure 6); this is consistent with Figure 5 which shows that PEI relaxes at a relatively slower rate than PEEK, and with the bulkier chain structure of PEI. The  $\alpha$  relaxation of blends is broadened, compared with that of the homopolymers, which is consistent with what has been found for miscible blends generally where peak broadening, associated with concentration fluctuations, is commonly observed<sup>27</sup>. Also shown in Figure 6 is a KWW analysis of our previous dielectric studies<sup>17</sup> which shows similar blend broadening. In this case, however, PEEK motions are more intermolecularly coupled. These findings reinforce the notion that the two probes are sensitive to different aspects of the  $\alpha$  relaxation, with the mechanical technique perhaps sampling a larger kinetic unit with greater coupling, compared with the dielectric technique which probes smaller, dipolar units.

In comparison with other investigations of PEEK/PEI blends, it is interesting to note that the width of the glass transition measured by d.s.c. reported by Chen and Porter<sup>28</sup>, is slightly broadened in the blends, with maximum broadening at the 40% composition. On the other hand, in a miscible blend of TMBPA-PC and BPA-PC, Katana *et al.*<sup>28</sup> observed no significant d.s.c. broadening in the blends yet did observe dielectric broadening. As both homopolymers experience similar changes in free volume and entropy around the glass transition, they suggest that local concentration fluctuations in the blends would not be detectable by d.s.c.

The broadness, and hence cooperativity, of the  $\alpha$  relaxation has been shown, for many polymer and small-molecule glasses, to be correlated with the temperature dependence of the relaxation times in a manner that is consistent with the hypothesis of the coupling model<sup>30</sup>. Larger values of  $\beta$  (lower intermolecular cooperativity) signify relaxation times that are less sensitive to changes in temperature. In miscible blends this situation is complicated by the fact that broadening also occurs as a result of a distribution of local environments (and hence coupling) arising from concentration fluctuations. The coupling model has been shown to be applicable to these systems; for example, in the TMPC/PS and PVME/PS blends studied by Roland *et al.*, a correlation is found between  $\beta$  and time/temperature dependence<sup>31,32</sup>. Both systems were investigated by dielectric spectroscopy which takes advantage of the relatively small dipole moment of PS, making it largely dielectrically inactive.

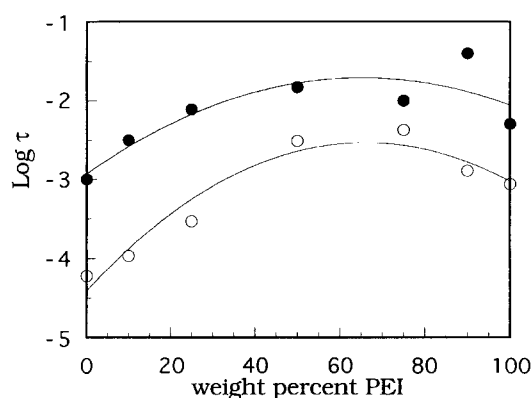


Figure 5 Composition dependence of relaxation times for PEEK/PEI blends: (●) dynamic mechanical ( $T_g/T = 0.96$ ); (○) dielectric ( $T_g/T = 0.90$ ). Solid lines are second-order polynomial fits to the data. Error in  $\log \tau$  is  $\pm 0.10$

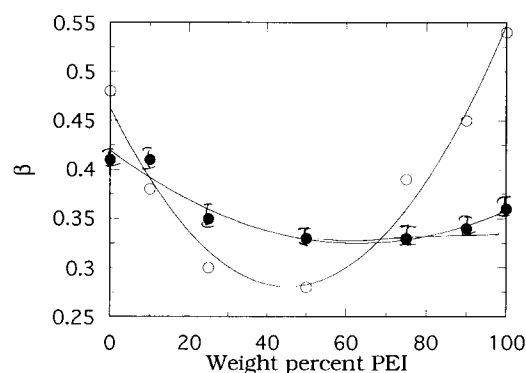


Figure 6 Composition dependence of broadness parameter,  $\beta$ , for PEEK/PEI blends at constant  $T_g/T$  from fits to KWW function: 1 (●) dynamic mechanical; 2 (○) dielectric. Solid lines are second-order polynomial fits to 1 and 2. Error in  $\beta$  is  $\pm 0.02$

The temperature dependence of the viscoelastic relaxation times, and hence the steepness of the cooperativity curve, can be described by the WLF equation<sup>33</sup>, given by

$$\log a_T = \log \left( \frac{\tau^*}{\tau_R} \right) = \frac{-C_1(T - T_R)}{C_2 + T - T_R} \quad (3)$$

where  $a_T$  is a shift factor,  $\tau^*$  and  $\tau_R$  are the relaxation times at temperature  $T$  and  $T_R$  respectively, and  $C_1$  and  $C_2$  are constants. The shift factor for the PEEK/PEI system were determined from isothermal dynamic mechanical  $\log E'$  against  $\log f$  curves. This is a useful method for obtaining time-temperature superposition data over a wide temperature range. The results are shown in Figure 7, for PEEK, PEI and the 50% blend, as a cooperativity plot, with  $T$  normalized by the temperature at which  $\log a_T$  is equal to 1. This graph indicates that PEI has the greatest intermolecular coupling while the 50% blend is least coupled (and PEEK is intermediate). The remaining blends exhibited cooperativity behaviour between that of the 50% blend and PEI and are therefore not plotted. Since the broadness parameter  $\beta_{\text{kww}}$  is identical, within error, for PEI and the 50% blend, and both are more coupled than PEEK, the temperature dependence of the relaxation times may not be totally explained by the coupling

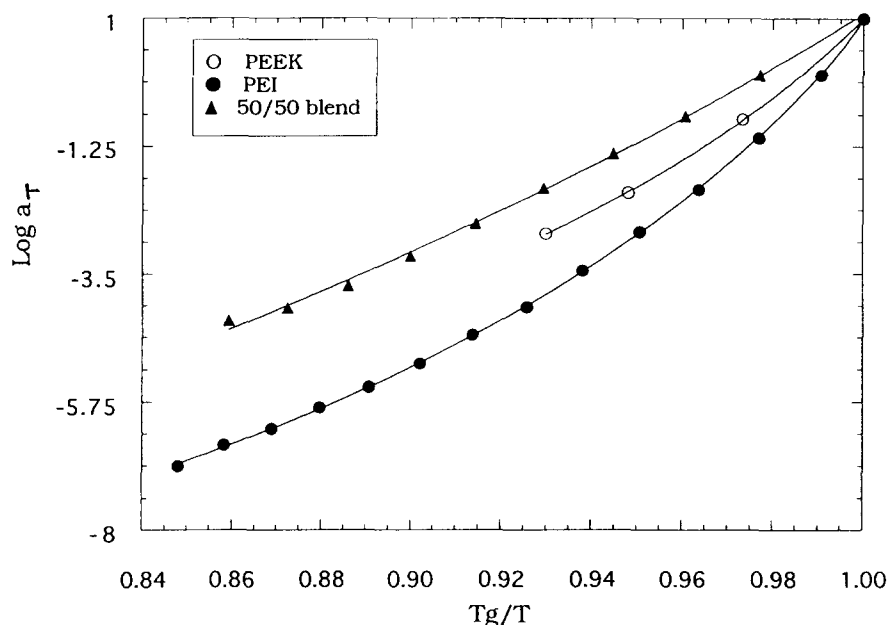


Figure 7 Cooperativity plot of WLF shift factors for PEEK, PEI and a 50% blend.  $T_g$  is taken as the temperature at which  $\log a_T = 1$ . Solid lines are fits to the WLF equation

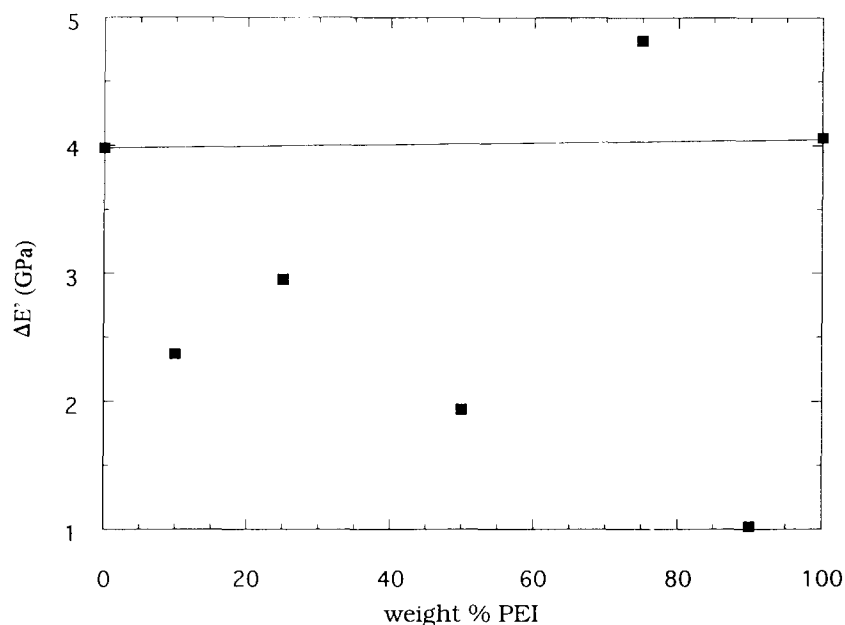


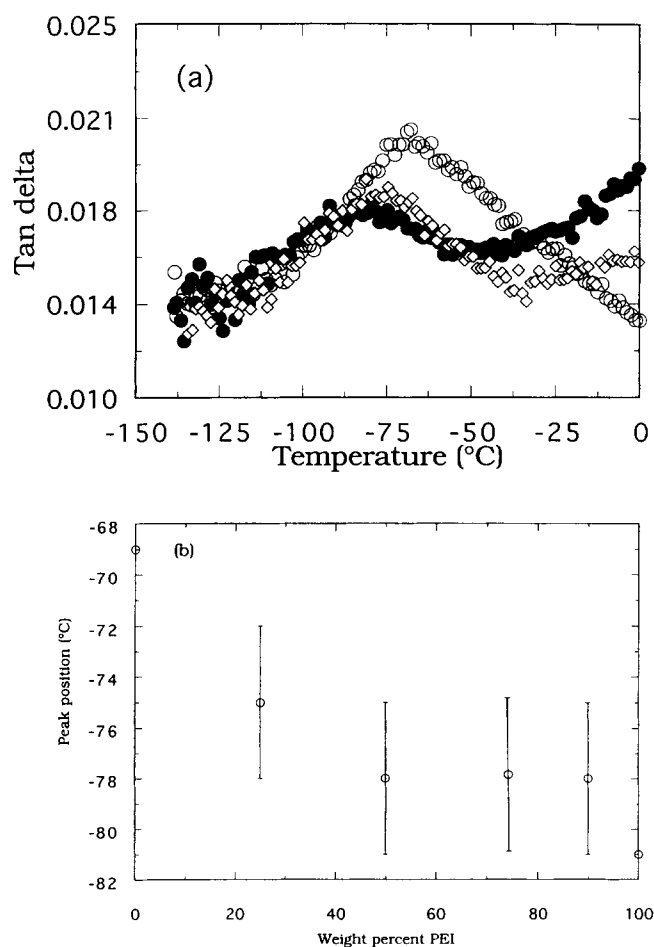
Figure 8 Composition dependence of dynamic mechanical relaxation strength for PEEK/PEI blends at constant  $T_g/T$ . Error in  $\Delta\epsilon$  is  $\pm 0.10$

model. A recent study of substituted rigid polyphenylenes by Connolly *et al.*<sup>34</sup> also found a similar lack of correlation between coupling and time/temperature dependence. In this case they correlated the time/temperature dependence of these polymers with relative changes in free volume at the  $T_g$ , rather than by reference to the coupling model.

Another feature of the  $\alpha$  relaxation of miscible blends is low frequency broadening of the loss curves caused by a distribution in intermolecular cooperativity arising from concentration fluctuations, which results in a 'reversal of asymmetry' (symmetrical broadening). This effect was not apparent in this system—all blend loss curves remained skewed (according to fits to the

Havriliak–Negami equation) towards high frequencies. Asymmetric broadening has been found to occur in the dielectric spectra of PVME/PS and PVE/PIP blends where it is attributed to a divergence of the relaxation times of the components at low frequencies<sup>35</sup>.

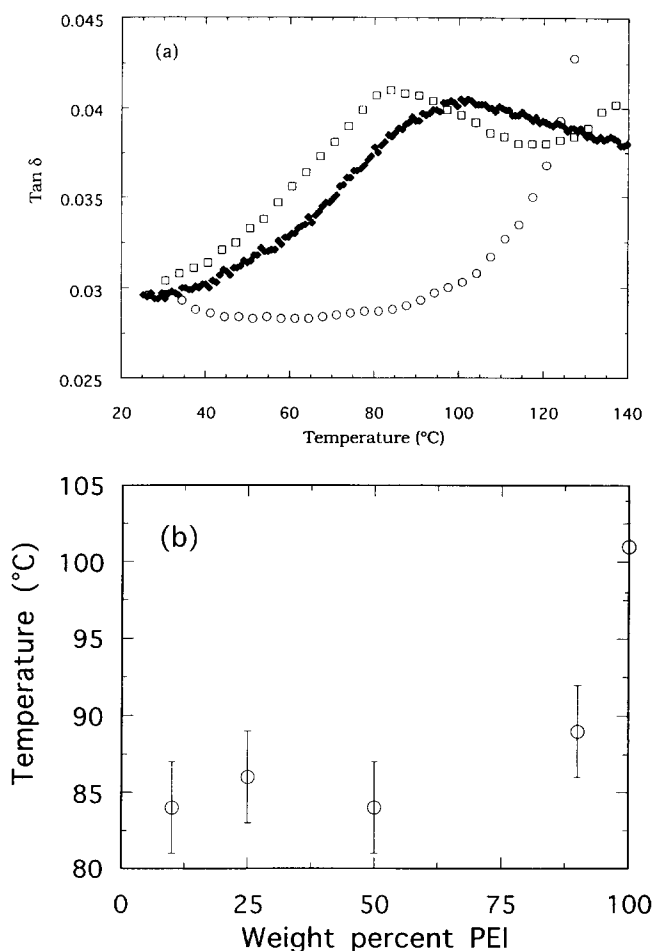
*Relaxation strength.* Although a number of theories exist which relate the dielectric relaxation strength,  $\Delta\epsilon$ , to the molecular dipole moment through dipole concentration and intra- and interdipolar correlations<sup>36</sup>, no such equivalent exists for the viscoelastic case. Nonetheless, the dynamic mechanical relaxation strength ( $\Delta E'$ ) is able to give useful, if qualitative, information on conformational changes brought about by blending.



**Figure 9** (a) Low temperature dynamic mechanical scan at frequency 1 Hz and heating rate  $2^{\circ}\text{C min}^{-1}$  for PEEK ( $\circ$ ) ( $\beta$  transition), PEI ( $\bullet$ ) ( $\gamma$  transition) and a 50% blend ( $\square$ ). (b) Composition dependence of  $\tan \delta$  peak temperature for PEEK/PEI blends in the low temperature region

The mechanical relaxation strength is defined as  $(E'_0 - E'_\infty)$ , where  $E'_0$  is the relaxed (low frequency) modulus and  $E'_\infty$  is the unrelaxed (high frequency) modulus. It is an indication of the response of the polymer chains to the imposition of a mechanical stress. Such changes in strength are indicated by the composition dependence of  $\Delta E'$  (derived from KWW fits) shown in Figure 8, which indicates a general reduction in mechanical relaxation strength in the blends, compared with the homopolymers. Although PEEK and PEI have identical relaxation strengths, blending may reduce the ability of the mixed chains to relax over all spatial directions, thus reducing the strength.

*Sub- $T_g$  relaxations.* Temperature scans were also carried out in the sub- $T_g$  region, between  $-110^{\circ}\text{C}$  and  $180^{\circ}\text{C}$ . Figure 9a shows the temperature dependence of  $\tan \delta$  at 1 Hz for PEEK, PEI and a 50% blend. In the sub-ambient region corresponding to the PEEK  $\beta$  process (Figure 9a) broad, asymmetric loss peaks are observed. The PEEK scan is similar in nature and position to those discussed in the Introduction in which the  $\beta$  process is believed to result from non-cooperative and cooperative motions involving phenyl ring flips. The PEI scan is similar to that reported by Harris and Robeson<sup>13</sup> which they attribute to local motions of the polyimide chain. They also observed a similar transition in a 50/50 blend. The



**Figure 10** (a) Dynamic mechanical scan at frequency 1 Hz and heating rate  $2^{\circ}\text{C min}^{-1}$  for PEEK ( $\circ$ ), PEI ( $\bullet$ ) and a 50% blend ( $\square$ ) in the region of PEI  $\gamma$  transition. (b) Composition dependence of  $\tan \delta$  peak temperature for PEEK/PEI blends around the PEI  $\gamma$  transition

composition dependence of the  $\tan \delta$  peak temperature is shown in Figure 9b. This follows a weighted average between the PEEK and PEI positions, with the PEI process occurring at a lower temperature, and therefore relaxing faster, compared with PEEK. The peak heights (not shown here) also exhibit linear additive behaviour. These findings indicate that these particular relaxation processes of PEEK and PEI are unchanged by blending and that the changes observed arise from simple dilution effects. By contrast, Mansour *et al.* found the  $\beta$  relaxation in miscible blends of TMPC/PC and TMPC/PS to be unchanged at all compositions<sup>37,38</sup>. Secondary relaxations in miscible blends exhibit a range of behaviours from no effect to suppression and enhancement<sup>39</sup>.

A broad loss peak was also detected in PEI near  $100^{\circ}\text{C}$  (Figure 10a) but was absent in PEEK. (The steep upturn above  $100^{\circ}\text{C}$  in  $\tan \delta$  for PEEK is due to the approaching  $\alpha$  relaxation.) It was, however, detectable in the blends; these are similar findings to those reported by Hanchi *et al.*<sup>40</sup>. The temperature position of the  $\tan \delta$  peak with changing composition is shown in Figure 10b. Unlike the low temperature relaxation in these blends, this process is strongly modified by blending as small amounts of PEEK shift the transition to lower temperatures. In this case the PEEK acts as a plasticizer to speed up the PEI relaxation. Our findings do not allow us to assign particular molecular motions in these systems, so it is

worth noting the findings of a recent n.m.r. dielectric and dynamic mechanical study of a semi-crystalline polyimide, similar in structure to PEI, by Cheng *et al.*<sup>41</sup>. Two sub- $T_g$  processes were observed: a low temperature  $\gamma$  transition ( $-100^\circ\text{C}$  at 0.1 Hz) being assigned to motions of the phenoxy rings; and an intermediate temperature  $\beta$  transition ( $100^\circ\text{C}$  at 0.1 Hz) assigned to motions of the aromatic imide groups. Since the PEI repeat unit also contains both groups there is the possibility of some similarity in the molecular motions of both systems, although further investigations of PEI are required to verify this.

## CONCLUSIONS

The molecular dynamics of amorphous PEEK/PEI blends has been examined over a wide temperature range using dynamic mechanical spectroscopy. The  $\alpha$  relaxation has a longer relaxation time and increased broadness in the blends, compared with the pure components. This can be attributed to the concentration fluctuations and increased range of coupled environments generally found in miscible blends. However, the temperature dependence of the blend relaxation times is not satisfactorily explained by the coupling model. This suggests that concentration fluctuations may exert a greater influence on the relaxation broadening of the blends and that intermolecular coupling of chain motions is less important. The mechanical relaxation strength decreases sharply in the blends, suggestive of significant conformational changes on blending. Comparisons with previous data taken from a dielectric study indicate that the two techniques are probing different aspects of the glass transition process.

In the sub- $T_g$  region two broad relaxation processes (denoted  $\gamma$  and  $\beta$ ) occur in PEI and the blends while one broad process is present in PEEK (denoted  $\beta$ ). The  $\beta$  transition in PEEK has been attributed to phenyl ring flips; the sub- $T_g$  transitions in PEI have yet to be definitively assigned, although there is evidence from other studies that the  $\gamma$  process may be due to phenoxy group motions while the  $\beta$  process is due to movement of imide groups. From a structural aspect this seems a reasonable argument. The low temperature transition observed in the blends shifts, with composition, between the PEI  $\gamma$  and the PEEK  $\beta$  transitions, according to simple dilution effects. The  $\beta$  process in PEI is strongly affected by the presence of PEEK, such that it shifts to lower temperatures (therefore faster motions) in the blends.

Some or all of these findings may be explained by simple changes in unoccupied volume on blending, since Chen and Porter<sup>28</sup> have reported an increase in density in PEEK/PEI blends compared with homopolymers. This presumably arises from the favourable specific interactions which exist between PEEK and PEI in the mixed state. A second mechanism, based on the coupling model, has been proposed which attributes changes in relaxation behaviour in miscible blends to changes in intermolecular cooperativity. The dominant

mechanism can be determined, using the coupling model, from knowledge of the respective crossover times<sup>42</sup>.

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