

Glass transition behaviour of poly(ether ether ketone)/poly(ether imide) blends

A. A. Goodwin* and G. P. Simon

Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia
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Differential scanning calorimetry (d.s.c.), dynamic mechanical thermal analysis (d.m.t.a.) and dielectric relaxation spectroscopy (DRS) have been used to study the α -relaxation in amorphous blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI). The composition dependence of the d.s.c. T_g is well described by the Couchman and Gordon–Taylor equations while the isothermal dielectric loss curves can be fitted by the empirical Havriliak–Negami (HN) function. The HN parameters can be represented in the form of cooperativity plots which show that they do not follow a weighted average with changing composition. The time scale for dipolar relaxation in the blends is dominated by PEI, which relaxes at a relatively slower rate compared with PEEK, while the composition dependence of the apparent activation energy shows a negative deviation from additive behaviour. It is likely that these observations are related to the interactions between the blend components which result in changes in the local molecular environment on blending.

(Keywords: polymer blends; glass transition; specific interactions)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is an aromatic polymer which is widely regarded as a high performance material with outstanding properties. These include excellent mechanical, thermal and chemical resistance properties, and permit unfilled PEEK to be used in many engineering applications, often in harsh environments¹. It also finds wide application in the reinforced form, containing either continuous or short fibres, and is a leading candidate amongst the thermoplastic composite group. PEEK is of interest in the study of structure/property relationships since the morphology can be controlled by simple thermal treatments. Thus, it can be quenched from the melt into a fully amorphous state or, alternatively, the degree of crystallinity can be developed to > 40 wt%². The crystallization and melting behaviour of PEEK has been the subject of a number of publications^{3–5} because semicrystalline samples are found to exhibit two melting peaks on heating in a differential scanning calorimeter. These have been attributed to existing morphological features⁶ as well as crystal reorganization during the scan⁷.

Another morphological feature of interest in semicrystalline PEEK is the 'rigid amorphous phase' (RAP) in which those amorphous chains that are in close proximity to crystalline regions are thought to be constrained and are only able to relax at temperatures above the glass transition. Experimental investigations of the rigid amorphous phase in PEEK have been carried out using differential scanning calorimetry (d.s.c.)⁵, dynamic mechanical analysis⁶ and dielectric relaxation

spectroscopy (DRS)^{7,8}. An alternative approach⁹ to glass transition behaviour in PEEK proposes a model which considers the non-crystalline interlamellar species to be completely constrained and therefore unable to contribute to the glass transition. Small-angle X-ray scattering studies indicate that the strength of the glass transition originates from the broad amorphous regions between lamellar stacks and, for semicrystalline PEEK crystallized at relatively high temperatures, the conventional RAP analysis is not required.

Poly(ether imide) is an amorphous high performance polymer with a glass transition temperature (T_g) of 215°C and useful mechanical properties, which forms a miscible blend in all proportions¹⁰ with PEEK. This gives the potential for enhancing properties through blending. Thermal analysis and X-ray scattering studies¹¹ have shown that PEI weakly influences the crystallization of PEEK and its melting temperature is only slightly depressed by the addition of PEI, while the degree of crystallinity of annealed PEEK remains constant with blend composition. At high crystallization temperatures PEI is displaced into interspherulitic regions, whereas at intermediate and low crystallization temperatures PEI segregates between PEEK lamellar bundles¹². High temperature crystallized blends, with high PEI content, show two loss peaks when investigated by dynamic mechanical¹¹ and dielectric¹³ spectroscopy. 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 interspherulitic regions rich in PEI that are totally demixed from PEEK, and in interlamellar amorphous regions containing mixed PEEK and PEI. In a thermally stimulated current study¹⁴ of crystallized blends the

* To whom correspondence should be addressed

glass transition region was found to cover approximately 60°C and this was explained in terms of the heterogeneous nature of the non-crystalline region trapped between the lamellae. No relaxations associated with a rigid amorphous fraction were found.

In this paper we report on the glass transition behaviour of PEEK/PEI blends as determined by a range of thermal analysis techniques. All measurements were conducted on amorphous samples.

EXPERIMENTAL

Materials

The PEEK used in this study was grade 381G, supplied by ICI Australia. The molecular weights are $M_w = 73\,000\text{ g mol}^{-1}$ and $M_n = 30\,600\text{ g mol}^{-1}$ (manufacturer's data). The PEI was Ultem 1000 supplied by GE plastics with molecular weights of $M_w = 30\,000\text{ g mol}^{-1}$ and $M_n = 12\,000\text{ g mol}^{-1}$ (ref. 6). A 50/50 blend, calculated as weight percent, was processed using a Haake Rheocord single-screw extruder at 400°C. Pure PEEK and PEI were also extruded at 400 and 300°C, respectively. The extruded materials were compression moulded at 400°C (300°C for PEI) and then quenched into ice/water to form amorphous sheets with thicknesses ranging from 0.2 to 0.4 mm.

Differential scanning calorimetry

A computer-controlled Perkin-Elmer DSC-7 was used to determine the glass transition temperatures of the homopolymers and blends. Samples weighing ~10 mg were scanned at 20°C min⁻¹ in an inert atmosphere and the glass transition temperature was taken as the mid-point of the heat capacity change. The temperature and heat flow response of the calorimeter was calibrated using high purity indium and zinc.

Dielectric relaxation spectroscopy

Dielectric data were obtained using a Gen Rad 1689 Digibridge interfaced to a Hewlett-Packard computer over the frequency range 15–10⁵ Hz. PEEK samples, 17 mm in diameter, were prepared for analysis by vacuum sputtering gold onto both polymer surfaces to ensure good electrical contact with the cell electrodes. The dielectric cells were three-terminal guarded and samples were equilibrated for some minutes in a Labmaster oven prior to data collection. All data were obtained in an isothermal mode, as a function of frequency at constant temperature, and the main variable determined was the dielectric loss, ϵ'' . For blends in which PEEK was the major phase the temperature range for isothermal measurements of the dielectric loss was limited by the low frequency limit of the dielectric bridge at low temperatures and by the tendency of PEEK to crystallize at high temperatures. An upper limit was chosen so as to ensure that the sample remained amorphous throughout data collection. PEEK crystallizes rapidly at temperatures above T_g and it is this feature which restricts dielectric measurements to a narrow temperature range in the homopolymer and in some blends.

Dynamic mechanical thermal analysis (d.m.t.a.)

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 mm × 10 mm × 0.5 mm, were scanned at 2°C min⁻¹ across the glass transition range. Loss modulus, storage modulus and $\tan \delta$ were recorded at a frequency of 1 Hz.

Curve fitting

Non-linear least-squares curve fitting of the dielectric data was accomplished by the use of the commercial 'PeakFit' software (Jandel Scientific, USA) which uses the iterative Marquardt-Levenberg fitting algorithm. 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. The ability of the software to fit two functions simultaneously was utilized to analyse the data in which low frequency conductivity and dipolar relaxation contribute to the dielectric loss. It is well known that the dielectric α -relaxation can be fitted to a number of empirical expressions and, in this study, we use the Havriliak-Negami (HN) function¹⁵:

$$\frac{[\epsilon^*(\omega) - \epsilon_\infty]}{(\epsilon_0 - \epsilon_\infty)} = \frac{1}{[1 + (i\omega\tau_{\text{hn}})^{\beta_{\text{hn}}}]^{\alpha_{\text{hn}}}} \quad (1)$$

where ϵ_0 and ϵ_∞ are the relaxed and unrelaxed permittivity, respectively; β_{hn} and α_{hn} characterize the broadness and skew, respectively; and τ_{hn} is a characteristic relaxation time. The conductivity contribution can be described by $\epsilon''_{\text{cond}} = a/f$, where a is a fitting parameter related to bulk conductivity. The total dielectric loss $\epsilon''_{\text{total}}$ is then equal to $\epsilon''_{\text{dipolar}} + \epsilon''_{\text{cond}}$, where $\epsilon''_{\text{dipolar}}$ results from segmental motions.

RESULTS AND DISCUSSION

Glass transition temperature

The composition dependence of the T_g , measured by d.s.c., is shown in Figure 1 and confirms the miscibility of this system at all proportions. This behaviour, for a miscible binary blend, can be described by an equation of the form

$$T_g = (w_1 T_{g1} + K w_2 T_{g2}) / (w_1 + K w_2) \quad (2)$$

where w is weight fraction and 1 and 2 refer to the lower and higher T_g component, respectively. In the Gordon-Taylor¹⁶ form of equation (2), $K = (\rho_1/\rho_2)/(T_{g1}/T_{g2})$ where ρ is density. If $\rho_1/\rho_2 = 1$ then equation (1) reduces

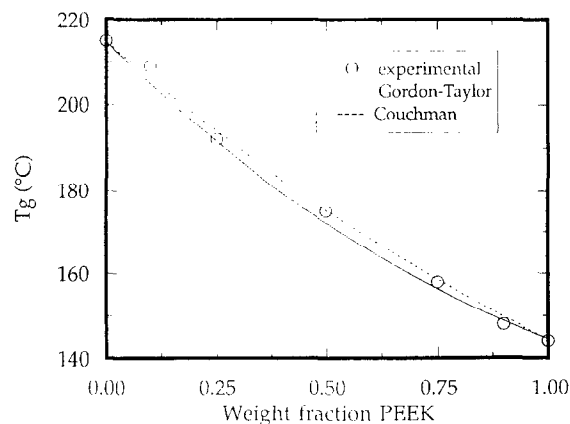


Figure 1 Composition dependence of the d.s.c. glass transition of amorphous PEEK/PEI blends

to the well-known Fox¹⁷ equation which describes volume additivity. The Couchman¹⁸ version of equation (2) puts $K = \Delta c_{p2}/\Delta c_{p1}$, where Δc_p is the change in specific heat capacity at T_g .

Also shown in Figure 1 are theoretical T_g -composition curves calculated with $K = 0.67$ (Gordon-Taylor) and $K = 0.79$ (Couchman), where these parameters are calculated using glass transition temperature (Gordon-Taylor) and specific heat capacity (Couchman) data from d.s.c. studies on the amorphous PEEK and PEI homopolymers. The resulting curves show good agreement with the experimental data. This can be confirmed from a linear plot of equation (2) with K as a fitting parameter, where a value of 0.79 ± 0.2 is found. A similar analysis of an earlier study¹⁹ gave a value of K , as a fitting parameter, of 0.84 ± 0.2 .

An equation developed by Lu and Weiss²⁰ puts

$$K = k + A/(T_{g2} - 1) \quad (3)$$

with

$$A = \frac{\chi R(T_{g1} - T_{g2})(\rho_1 - \rho_2)}{M_1 \Delta c_{p1}} \quad (4)$$

and

$$k = \frac{\Delta c_{p1}}{\Delta c_{p2}} \left[1 + w_1 \frac{\delta c_p^l}{\Delta c_{p2}} + w_2 \frac{\delta c_p^g}{\Delta c_{p1}} \right] \quad (5)$$

where Δc_p is the change in specific heat capacity at the glass transition; δc_p is the change in specific heat capacity, in the liquid (l) and glassy (g) states, due to mixing; M is the molar mass per chain segment of PEEK; and χ is a binary interaction parameter. When the interactions are relatively small or weak the effects of δc_p and A can be neglected and the Couchman version of equation (2) is found. According to this analysis, weak interactions result in negative deviations from linear additivity in the T_g -composition behaviour whereas strong interactions will produce positive deviations. It can be seen that, using a fitted K value of 0.79, and an experimental k value also equal to 0.79 in equation (3) (if we assume weak interactions between PEEK and PEI, i.e. $\delta c_p \approx 0$), χ is zero. Alternatively, if $K = 0.84$ is used then χ becomes -0.3 . This agrees well with $\chi = -0.4$ reported from melting point depression studies²⁰. This analysis indicates, therefore, that the specific interactions between PEEK and PEI are small and relatively weak.

Dynamical mechanical analysis

The dynamic viscoelastic response of PEEK, PEI and a 50/50 blend, in the glass transition region, is shown in Figure 2 with plots of storage modulus and $\tan \delta$. Both homopolymers exhibit a relatively narrow peak in $\tan \delta$ across the glass transition, where the temperature T_{\max} , corresponding to the maximum in $\tan \delta$, can be taken as the T_g . The small, high temperature shoulder on the PEEK damping curve is associated with dynamic cold crystallization of PEEK during heating and is accompanied by a steep rise in the storage modulus as the growing crystallites increase the sample stiffness. The 50/50 blend has a lower initial storage modulus and a damping peak that is both broader and lower in intensity. As with PEEK there is a small damping peak shoulder and an increase in storage modulus due to

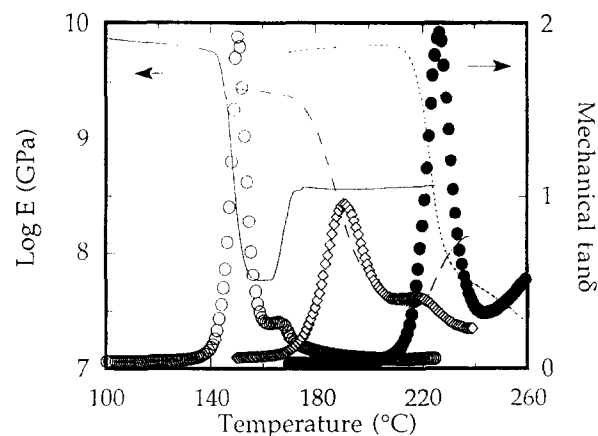


Figure 2 Dynamic mechanical spectra of storage modulus and $\tan \delta$ for the homopolymers and a 50/50 blend, scanned at 2°C min^{-1} and at a frequency of 1 Hz. (○), PEEK; (●), PEI; (◇), 50/50 blend. Storage modulus: (—), PEEK; (---), PEI; (- · - · -), 50/50 blend

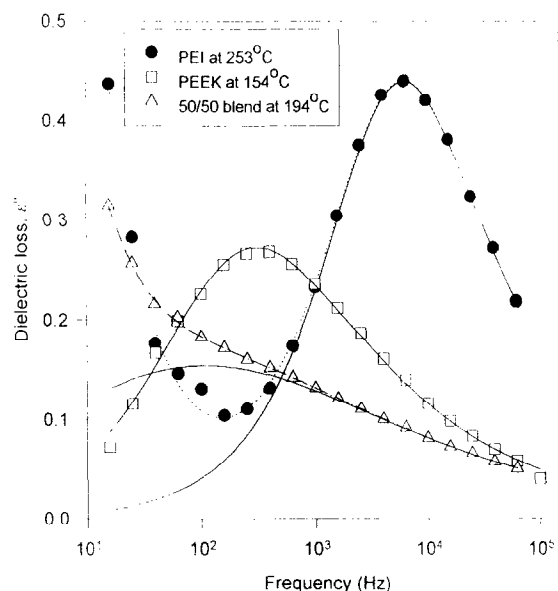


Figure 3 Isothermal dielectric loss curves for PEEK, PEI and a 50/50 blend. Solid lines are fits to HN function. Broken lines are summation of conductivity and dipolar loss

crystallization. However, the shoulder occurs at a relatively higher temperature and reflects the retarding effect of PEI on the crystallization kinetics of PEEK.

Dielectric relaxation

Figure 3 shows dielectric loss data, in the α -transition region, for PEEK, PEI and a 50/50 blend, along with curve fits from the HN and conductivity functions. The data are taken from isothermal measurements and are plotted as a function of frequency, at particular temperatures. They exhibit the broad and asymmetric shape typical of the dielectric response of pure amorphous polymers in the glass transition region. The steep rise in ϵ'' at low frequency for PEI and the blend is a result of ionic conductivity in the sample and was observed in all samples containing PEI. No such effects were found with PEEK homopolymer over the temperature range investigated here. The loss peak for the blend is partially masked by conductivity and has a

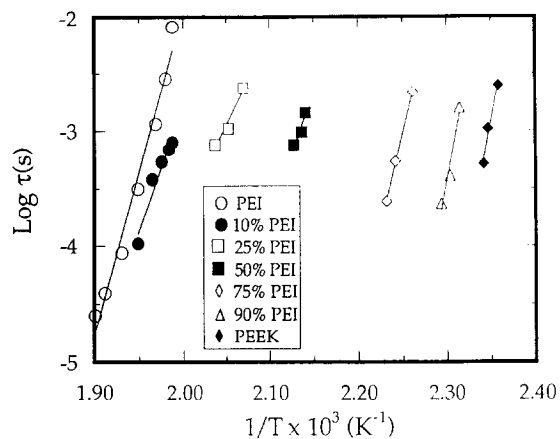


Figure 4 Inverse temperature dependence of logarithmic dielectric relaxation time for PEEK/PEI blends. Solid lines are curve fits to Arrhenius equation

Table 1 Apparent activation energy, E_{act} , for amorphous PEEK/PEI blends. Values were determined from Arrhenius fits to the data in Figure 4

Weight fraction PEI (%)	E_{act} (kJ mol ⁻¹)
0	750 ± 150
10	760 ± 160
25	600 ± 15
50	380 ± 135
75	290 ± 70
90	265 ± 5
100	540 ± 40

maximum in ϵ'' , according to the HN fit, of 0.15. This value is significantly below that of PEI (0.44) and PEEK (0.27).

The relaxation times of the homopolymers and blends, determined from HN fits to the dielectric data, are plotted in Figure 4 in an Arrhenius form. Data of this kind are commonly fitted to the Vogel–Fulcher equation²¹; however, in this case the limited range over which measurements were possible (due to sample crystallization) precludes the use of this equation. As an alternative the data were fitted to the Arrhenius equation to achieve an estimate of the composition dependence of the apparent activation energy, E_{act} , for the glass–rubber relaxation process over this limited temperature range. Values of E_{act} are listed in Table 1 and, despite the large errors in some instances, a clear trend is seen in which the activation energy is reduced below that of both homopolymers, as the content of PEI increases.

The effect of blend composition on the temperature dependence of the relaxation times is not easily discerned 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 . Therefore, in order to scale the data, the relaxation times can be plotted against T_α/T , where T_α is an arbitrary temperature outside the measuring range. For polymer systems these are commonly referred to as ‘cooperativity’ plots and the slope of such plots can be related to the degree of intermolecular cooperativity²². A cooperativity plot of the data shown in Figure 4 is plotted in Figure 5 using the d.s.c. glass transition (T_g) data as T_α .

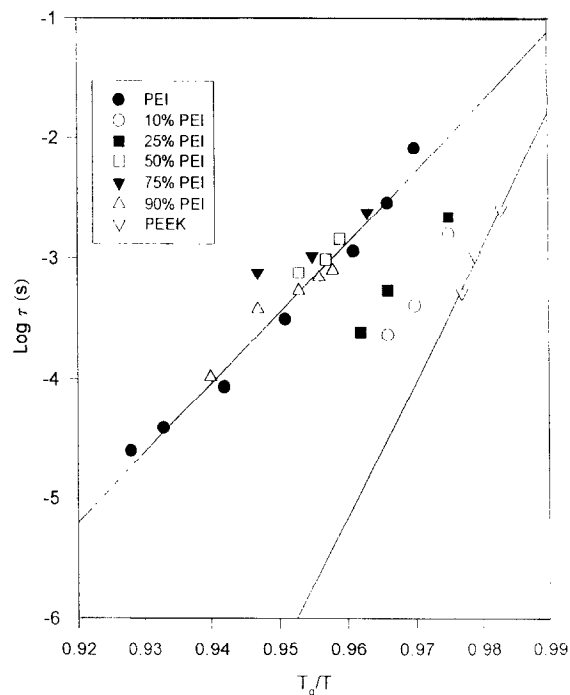


Figure 5 Cooperativity plot of logarithmic dielectric relaxation time for PEEK/PEI blends. T_g is d.s.c. glass transition temperature. Solid lines are linear fits to PEEK and PEI and are intended to guide the eye

Normalizing the temperature scale by T_g/T reveals that the rate of dipolar reorientation in the PEEK/PEI system, in the glass transition region, is strongly influenced by PEI. For example, the blend containing 25% of PEI lies approximately half-way between the homopolymer relaxation loci. When PEI becomes the major phase the relaxation times are shifted close to those of pure PEI.

To further investigate the composition dependence of the relaxation parameters derived from the HN analysis, the basic cooperativity plot can be modified such that data are plotted at a constant value of T_g/T where the independent variable is now blend weight fraction. In this study a T_g/T value of 0.96 was chosen as this is close to the middle of the measurable data range which spans T_g/T from 0.93 to 0.98. For those blends where the measurement range does not extend to this value, the data were considered to vary in a linear fashion with temperature. We believe that, over a relatively narrow temperature range, this is a reasonable assumption. Plots of this type are shown in Figure 6 as the composition dependence of the HN parameters. Figure 6a shows relaxation times at constant T_g/T which reveal a positive deviation from linear additivity behaviour, thus confirming that dipolar relaxation in PEI occurs at a slower rate than in PEEK.

The broadening of loss peaks in blends is well known²³. One cause of this is concentration fluctuations where the local composition within a blend fluctuates about an average value. This places the relaxing segments into a range of local environments which gives rise to inhomogeneous broadening of the relaxation. Another cause of broadening is the intrinsic differences in the relaxation behaviour of the components²⁴. A recent model proposed by Zetsche and Fischer²⁵ analyses this behaviour in a quantitative

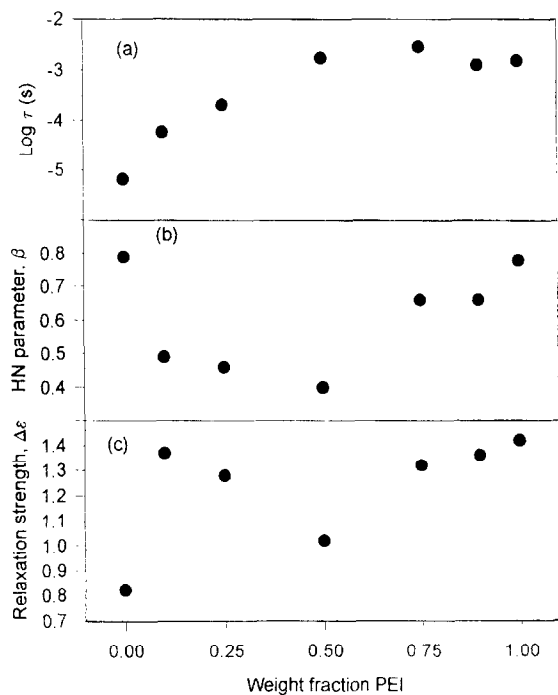


Figure 6 Composition dependence of HN parameters at constant T_g/T of 0.96: (a) logarithmic dielectric relaxation time, τ ; (b) broadness parameter, β ; (c) relaxation strength, $\Delta\epsilon$

fashion for poly(vinylmethyl ether)/poly(styrene) (PVME/PS) blends and calculates the volume of cooperative dipole relaxation to have a radius of 4 nm at 20 K above the glass transition. The composition dependence of the HN β parameter is shown in Figure 6b. The homopolymer loss curves are of equal broadness whereas, with the blends, the increase in broadness is significantly larger when PEEK is the major phase. The HN analysis also describes the skew or asymmetry of the loss curves and, although the results are not shown here, they can be summarized by stating that the loss peaks for all samples exhibited some degree of high frequency skew which did not show a clear trend with composition. This is in contrast to the symmetrical broadening (reversal of asymmetry) of viscoelastic spectra reported for poly(vinylethylene)/poly(isoprene) (PVE/PIP) and PVME/PS blends²⁶, where this effect is attributed to a divergence in the relaxation times of the components at low frequencies.

The composition dependence of the relaxation strength $\Delta\epsilon$, shown in Figure 6c, suggests that the PEI homopolymer has a greater effective dipole strength. As PEEK and PEI have similar densities, and therefore similar concentrations of dipoles, this may result from a greater dipole moment of the PEI repeat unit or from conformational effects which lead to some dipole cancellation in PEEK. A definite pattern with composition is difficult to ascertain because of the variation of the blend data, yet if the results for 10% and 25% PEEK are removed it appears that $\Delta\epsilon$ varies as a weighted average of the homopolymer values. A weighted average would suggest that the Onsager-Kirkwood²⁷ correlation parameter, g , is unchanged by blending. This parameter accounts for the effect of intra- and intermolecular correlations on the dielectric response and is sensitive to changes in local environments and the dipole interactions of the components.

CONCLUSIONS

Analysis of the composition dependence of the glass transition behaviour of amorphous PEEK/PEI blends, which has been investigated as a function of temperature and frequency, shows that the interactions between PEEK and PEI are weak, as previously reported. However, these are sufficient to produce a miscible blend in all proportions. The apparent activation energy of the blend glass transition exhibits a negative deviation from weighted additivity behaviour, while the dielectric relaxation time is dominated by PEI. The latter is not a surprising finding since PEI not only relaxes at a relatively slower rate, compared with PEEK, but is also likely to exist in small 'glassy' domains, if concentration fluctuations are present. At the same time the barriers to rotation in the blend are lowered and this is probably associated with the specific interactions between PEEK and PEI resulting in new conformational states with different distributions of orientational energy barriers.

The α -relaxation of the blends is broader than that of either homopolymer, and is broadest when PEEK is the major phase. The relaxation strength data are inconclusive as to the composition dependence, although a weighted average would indicate that the spatial arrangements of the dipoles in PEEK and PEI are unchanged on blending. However, it should be noted the other HN parameters do not vary with composition in such an additive manner.

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