Relaxation behaviour in blends of PEEK and PEI

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Abstract

Blends of poly(ether ether ketone) and poly(ether imide) have been produced in the composition range 2–20 wt% poly(ether ether ketone) and dynamic mechanical and dielectric behaviour of these materials have been investigated. A composition dependent α process was observed using both techniques, the temperature of which increased with increasing poly(ether imide) content. The low temperature relaxation behaviour of poly(ether imide) and the dielectric relaxation time in the glass transition region was found to be affected by the addition of poly(ether ether ketone). The variation of loss and storage permittivities showed that the asymmetric broadening was strongly dependent on the blend composition, indicating a high degree of interaction between the components. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Poly(ether imide) (PEI) is referred to as a high performance engineering thermoplastic material in that it displays good strength, high modulus and a high glass transition temperature. PEI also demonstrates good electrical properties and remains stable over a wide range of temperatures and frequencies. It is amorphous and when unmodified it is transparent and exhibits inherent flame resistance and low-smoke evolution. It also exhibits strong relaxations in the glass transition region, which is important for comparing dynamic mechanical and dielectric behaviour [1].

Poly(ether ether ketone) (PEEK) is well-known for excellent mechanical and thermal properties together with good environmental resistance. PEEK demonstrates good adhesion ability and can be used as a resin for either short of continuous fibres. The morphology of PEEK can be controlled by thermal treatment, it can be quenched from the melt into an amorphous state or crystallised to levels of 40% [2].

Blends of PEEK and PEI have been prepared to enable complimentary combination of the material properties exhibited by each component, these blends have been found to be miscible over the entire composition range [3]. This paper investigates the dynamic mechanical and dielectric behaviour of blend compositions in the range 2–20 wt% PEEK, and in particular the effect of composition on the α and β relaxations. The effect of temperature and composition on the relaxation time in the α transition region has also been investigated together with the breadth of the α relaxation as characterised by a Havriliak and Negami [4] analysis.

2. Experimental

A commercial grade of PEI, ULTEM 1000 was used as supplied by General Electrics Ltd. The material had a weight average molecular weight of 20 kg/mol. In addition PEEK, grade 450G was supplied by ICI Ltd. It had a number average and weight average molecular weight of 40.7 and 99.2 kg/mol, respectively.

Blends of these materials were prepared using an APV model MP2000 twin screw extruder. The moulding pellets of PEEK and PEI were dried in a vacuum oven at 160°C for 3 h prior to the production of a 50 wt% PEEK master batch. Blends containing 2, 5, 10 and 20 wt% PEEK were then prepared by dilution of the dried master batch with dried PEI. The granules were premixed to ensure good dispersion of the components and the system was purged with 500 g of PEI and the first 200 g of each blend extruded from the die head were discarded. The barrel temperature was set to 380°C and the flow rate through the extruder was adjusted to maintain a high torque thereby ensuring thorough mixing. The moulding pellets produced from the extruder were subsequently dried prior to compression moulding at

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380°C into sheets (150 × 150 × 2 mm). The sheets were quenched in ice/water.

Dynamic mechanical measurements were performed using a Polymer Laboratories DMTA MKII. Samples in the form of beams (40 × 10 × 1 mm) were mounted in dual cantilever geometry and the loss and storage moduli were recorded over a range of frequencies from 0.33 to 100 Hz. The temperature scan range was from −120 to 250°C at 2°C/min.

A Polymer Laboratories DETA was used to obtain dielectric measurements. The range for a temperature scan was again −120 to 300°C and the frequency range was, 100 Hz to 100 kHz. In order to ensure a good level of conduction between the surfaces of the sample and the electrodes, the sample was coated with gold using a Polaron E5000 sputter-coating unit. Step isothermal experiments were also carried out on the blends. The loss and storage permittivities at twenty frequencies were measured and recorded at temperatures from 180 to 250°C in steps of 5°C.

3. Results and discussion

3.1. α Relaxation

The dynamic mechanical behaviour of the blends containing 20, 10 and 5 wt% PEEK were investigated and Fig. 1 shows the variation of both the storage and loss moduli with temperature for a 20 wt% PEEK blend, measurements were made at a frequency of 1 Hz. The behaviour is typical for the blend compositions studied and exhibits several characteristic mechanical features. Over the temperature range of 100–150°C, the blend material exhibits a relatively high storage modulus and low loss modulus. This is characteristic of a glassy material and results from the fact that the chain conformations are frozen into an amorphous rigid network. In the range 150–210°C, a marked drop in storage modulus occurs, this is accompanied by a peak in the loss modulus, in this region the glass begins to transform to a liquid via a glass-rubber plateau. This transition involves long-range motion of the chain segments. Finally, in the range 210–250°C, there is a rubbery plateau in which both moduli remain constant. Here, the translatory motions that occur in the liquid state are prevented by chain entanglements that act as temporary cross-links.

From measurements of the storage and loss moduli, the loss tangent was calculated. This parameter corresponded to the ratio of loss to storage modulus. It can be seen in Fig. 2 that all the blend compositions studied show an α relaxation peak, analogous to the glass transition temperature measured using calorimetric techniques. The temperature at which this process occurred increased with increasing PEI content. A similar dependence was observed in the glass transition temperature as measured by differential scanning calorimetry. [3] A single glass transition was observed that varied linearly with composition between the homopolymer limits, it was concluded that a single glass transition resulted from the blend miscibility and that the glass transition varied continuously between that homopolymer limits because of increased rotational energy barriers associated with the PEI component. The same explanation can be applied to the dynamic mechanical data.

The blend system was also investigated using dielectric thermal analysis. Fig. 3 shows the variation of storage and loss permittivity with temperature for a 20 wt% PEEK blend
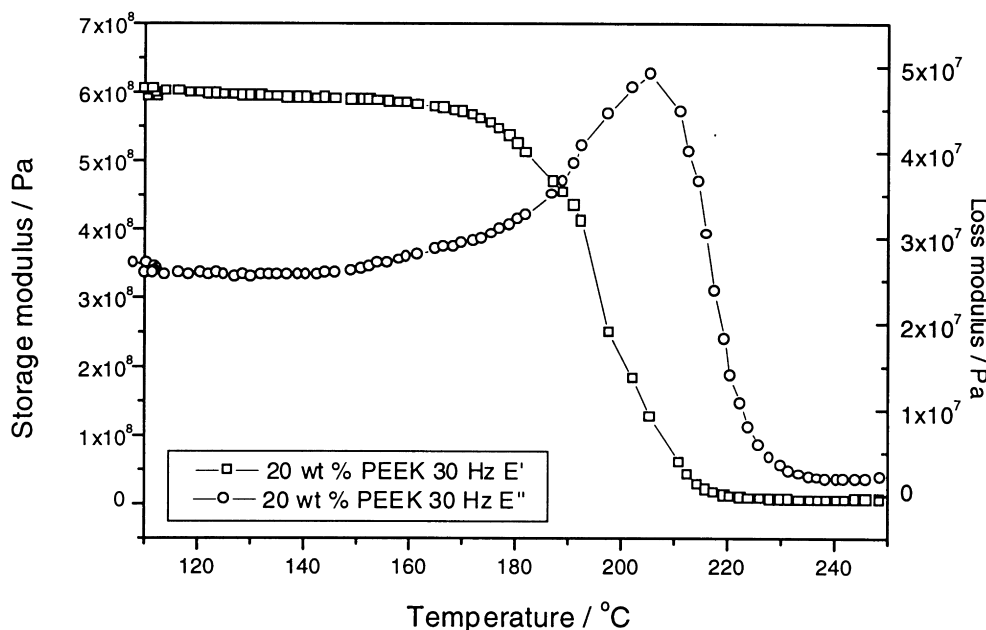

Fig. 1. The α transition for a 20 wt% PEEK blend as measured by DMTA at 30 Hz.
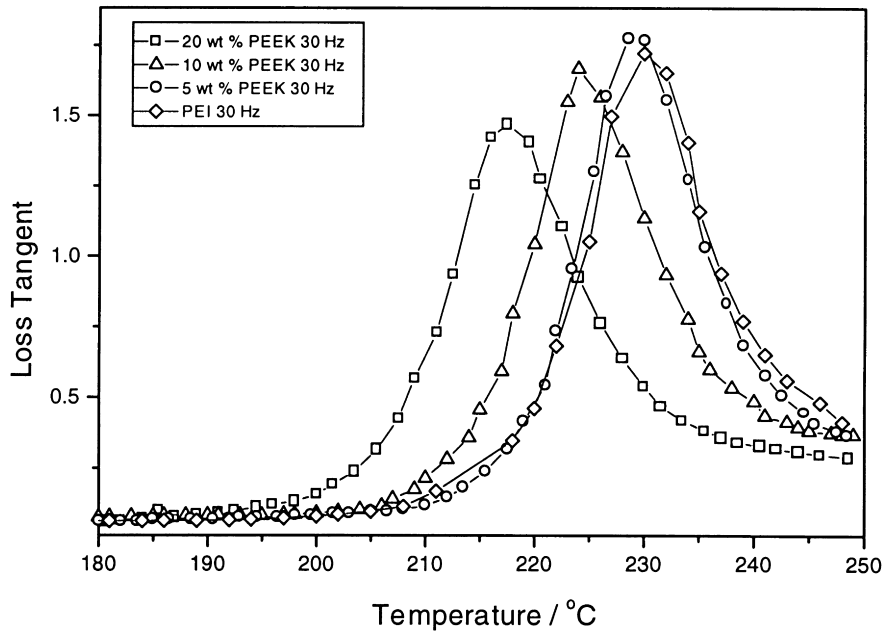
Fig. 2. The variation of the α transition temperature with blend composition as measured by DMTA at 30 Hz.

at 1 kHz. The loss curve has two prominent features, there is a peak centred at 225°C corresponding to the α relaxation process and there is a high temperature tail resulting from ionic conductivity within the sample.

The data for storage and loss permittivity can also be used to calculate a value for the loss tangent as in dynamic mechanical experiments. Again, a composition dependent α relaxation process is observed together with a high temperature tail resulting from the effects of ionic conductivity as shown in Fig. 4. This α process is also assumed to

be analogous to the glass transition temperature as observed using differential scanning calorimetry and varies with composition for the same reasons outlined in the case of the dynamical mechanical experiments.

Comparing the positions of the peak in the loss tangent traces obtained from both dynamic mechanical and dielectric analysis at frequencies of 30 Hz and 1 kHz, respectively, shows a difference of the order of 10°C, this illustrates the effect of frequency of on the measured α process. Higher measurement frequencies result in
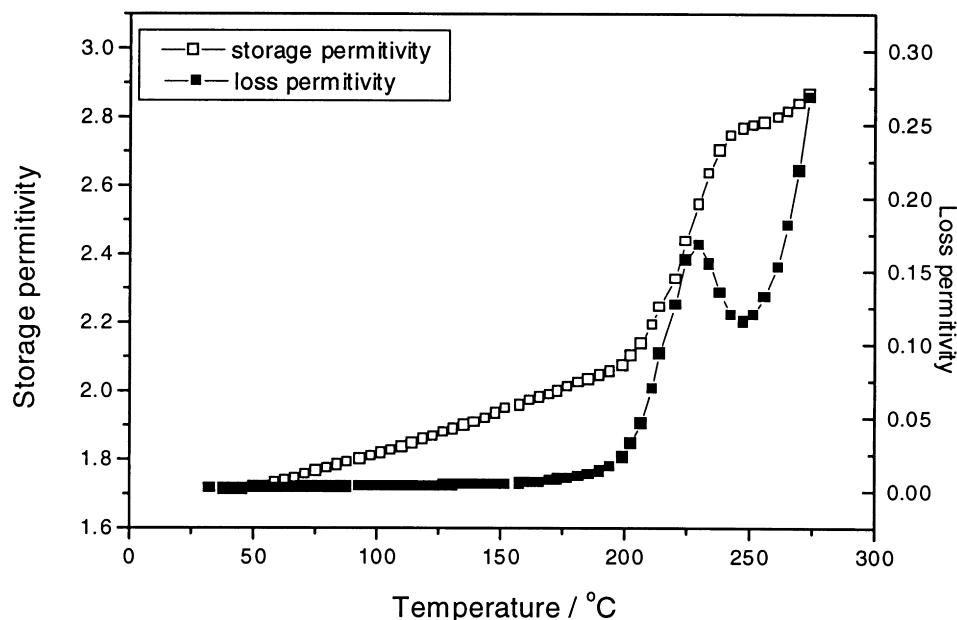

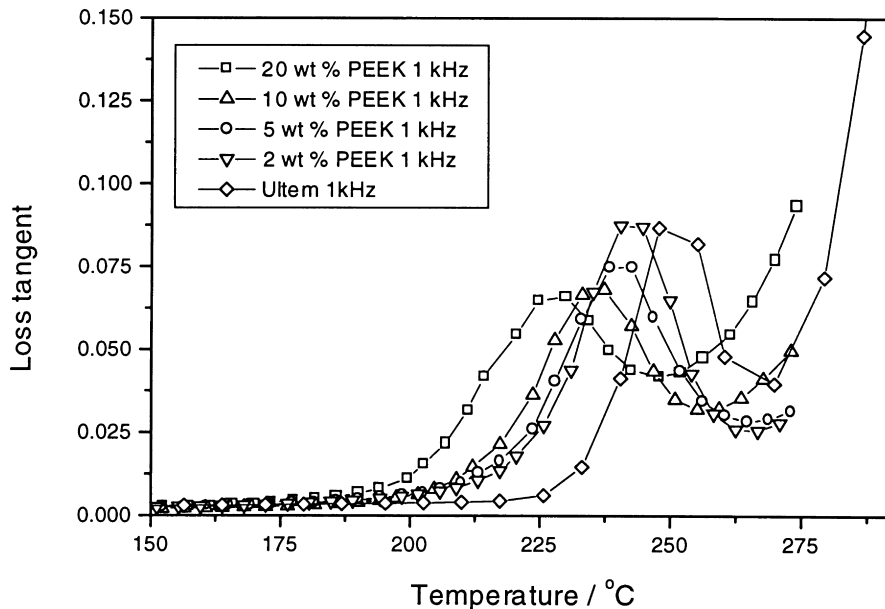Fig. 3. The α transition for a 20 wt% PEEK blend as measured by DETA at 1 kHz.

Fig. 4. The variation of the α transition temperature with blend composition as measured by DETA at 1 kHz.

increased peak temperatures: the relationship often used to describe the variation of peak position with measurement frequency is that described by Arrhenius.

3.2. β and γ Relaxations

Although long ranged molecular conformations are frozen in below the glass transition temperature, some limited motion of the side groups is possible, corresponding to the β and γ transitions. The low temperature relaxation behaviour of both PEEK and PEI was investigated to assess the effect of composition on these processes. The moisture content within the samples was allowed to equilibrate at room temperature and humidity. Fig. 5 shows the β and γ relaxations for PEI, the β process is centred at 70°C and the γ at −100°C. The β process is well documented and is attributed to main chain oscillation involving the aromatic and bezimide rings [5] and the γ process is assumed to result from an oscillation of a complex of water and a small part of the chain. [6] The γ process only occurs when moisture is present within the sample.

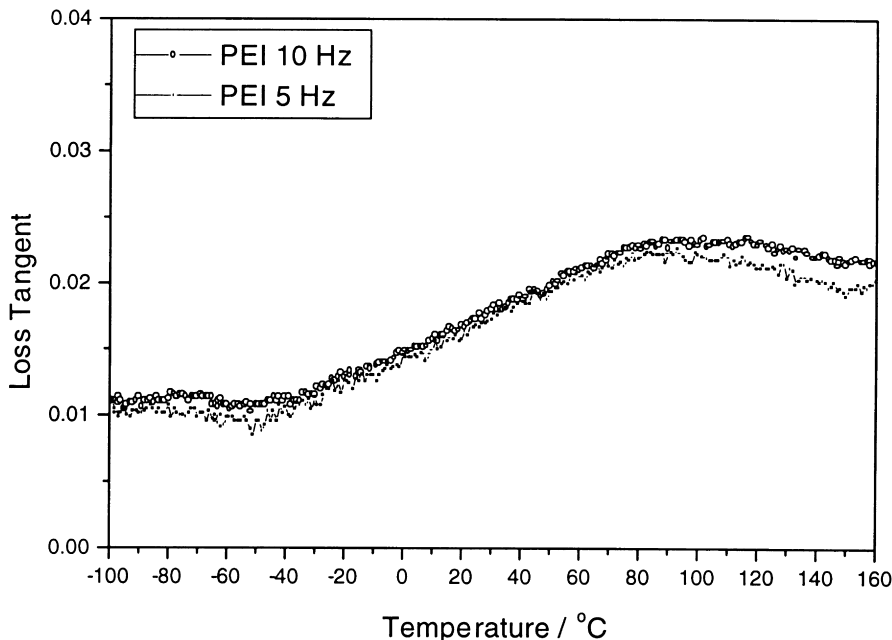The low temperature relaxation behaviour of PEEK has

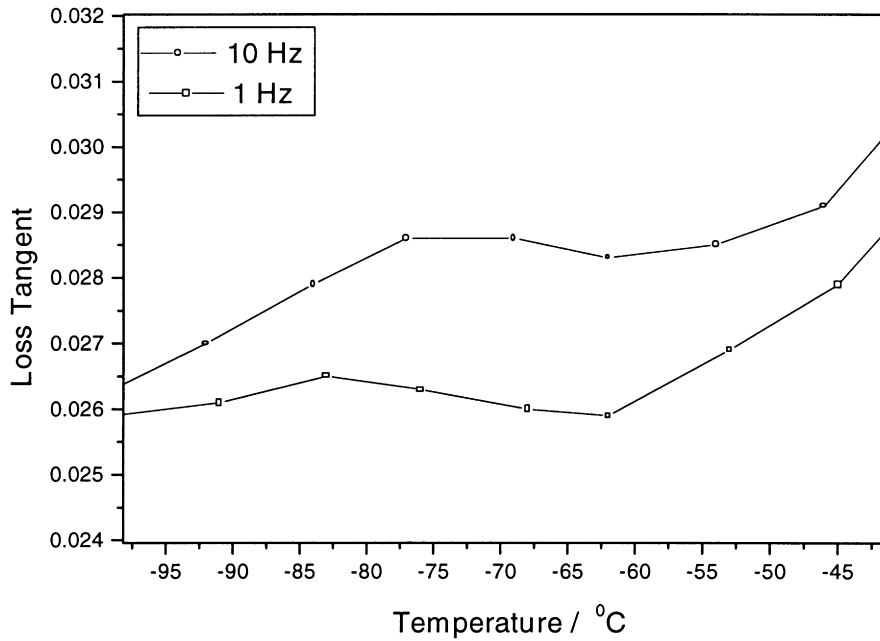Fig. 5. The β and γ relaxations in PEI as measured by DMTA at 5 and 10 Hz.

Fig. 6. The β relaxation in PEEK as measured by DMTA at 1 and 10 Hz.

also been investigated, Fig. 6 shows the variation of loss tangent with temperature, it can be seen that there is a distinct β process occurring at −95°C. This is believed to result from phenyl ring flips and motions of the polar bridges, it is more pronounced when there is moisture present. A γ process has also been reported at a temperature of −155°C, resulting from highly localised non-cooperative motions. [7]

Analysis of the low temperature blend relaxations was also possible using dielectric analysis, with the much higher measurement frequencies activating the transitions at higher

temperatures. It can be seen in Fig. 7 that the α and β transitions occur at higher temperatures, −100 and −52°C, respectively.

The low temperature relaxation behaviour of the blends shown in Fig. 8 reveals a single β transition centred at −70°C, since the β process for PEI occurs at 70°C the observed process is likely to originate in the PEEK component. The temperature at which this transition occurs is shifted by 25°C in the blend systems. The increased intensity of the β process in the 20 wt% PEEK is likely to result from compositional variation in the sample. No further β
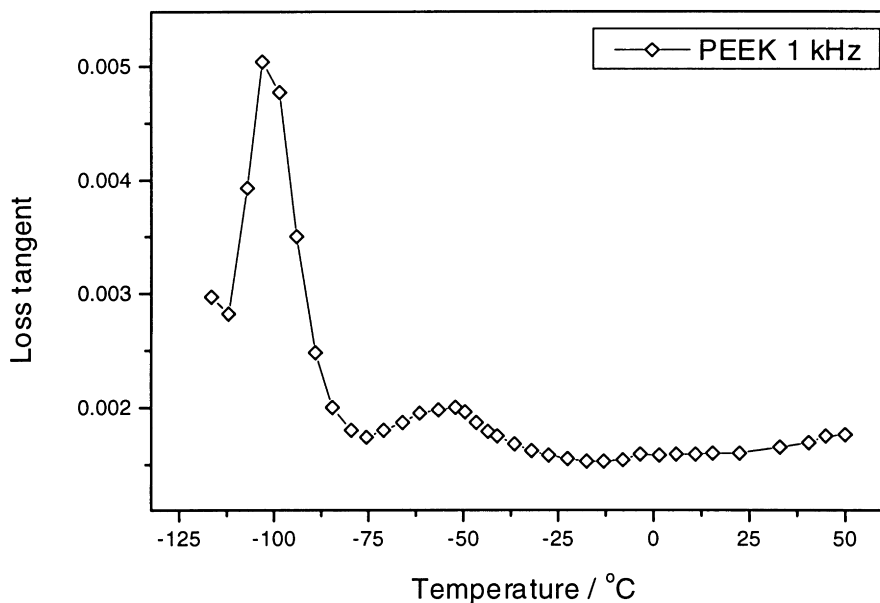

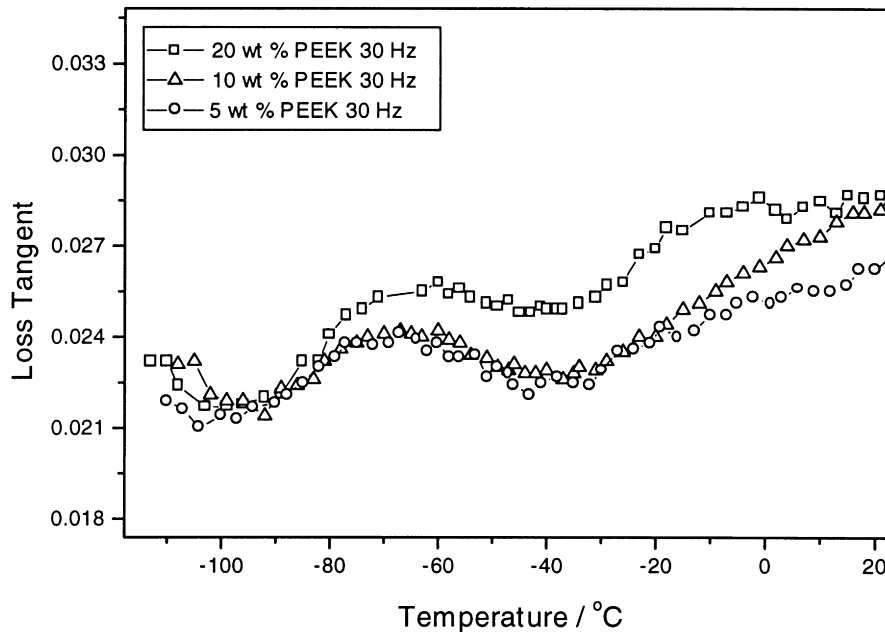Fig. 7. The β and γ relaxations in PEEK as measured by DETA at 1 kHz.

Fig. 8. The β relaxation for blends in the composition range 5–20 wt% PEEK as measured by DMTA at 30 Hz.

relaxation processes were detected, this indicates that the relaxation behaviour of the PEI component is affected by the addition of PEEK.

3.3. Effect of composition on the relaxation time

The effect of blend composition on the dielectric relaxation time in the glass transition region was investigated by measuring the isothermal frequency response of the blends. The variation of loss permittivity with frequency and

storage permittivity for a 20 wt% PEEK blend at 245°C are shown in Figs. 9 and 10, respectively. The frequency dependence of the loss permittivity shows two characteristic features, there is a low frequency tail resulting from ionic conductivity and a peak in the loss curve corresponding to the α relaxation.

The temperature dependence of the α relaxation times are shown in the Arrhenius plot in Fig. 11, but the effect of blend composition on the temperature dependence of the frequency and calculated relaxation time is not readily
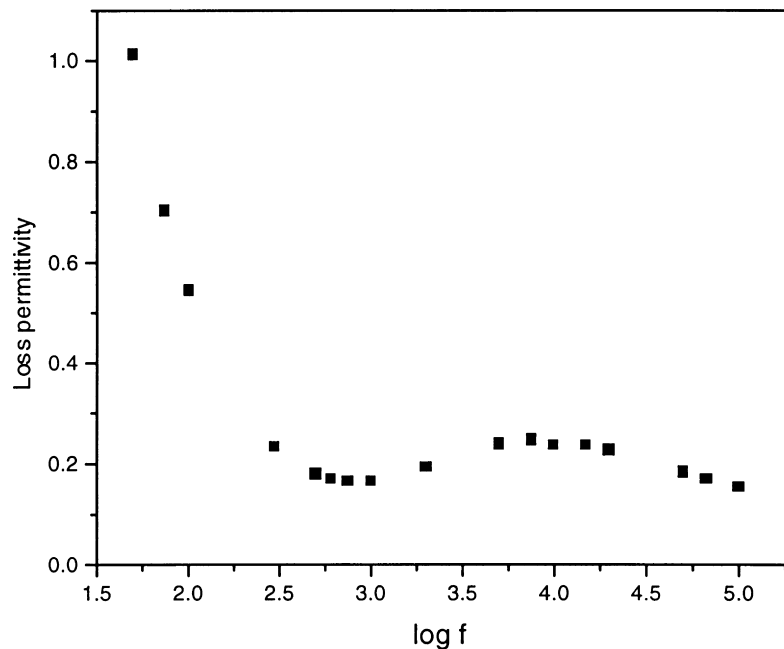

Fig. 9. The variation of loss permittivity with frequency for a 20 wt% PEEK blend at 245°C.
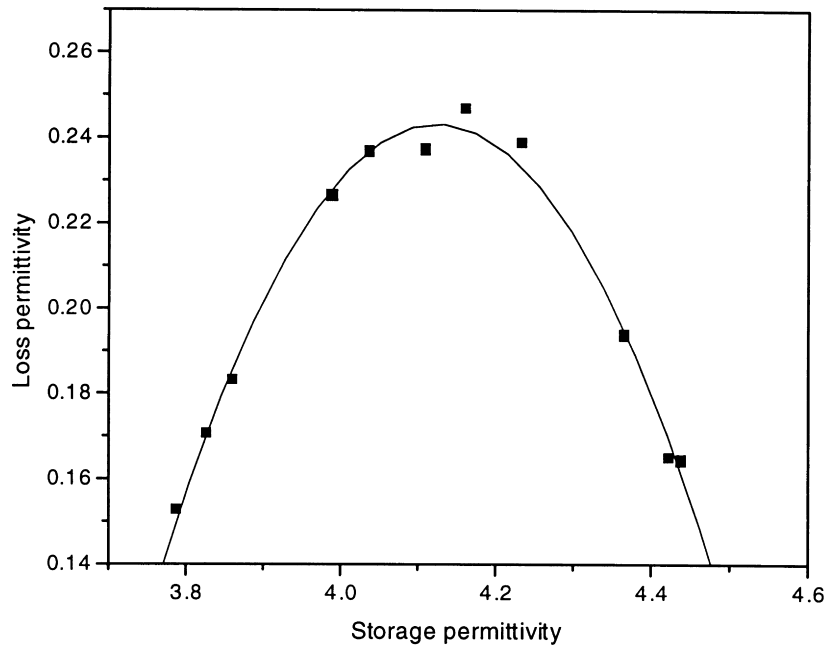
Fig. 10. The variation of loss with storage permittivity for a 20 wt% PEEK blend at 245°C.

found from this type of plot. The main reason for this is due to the fact that the molecular mobility scales with the distance from the glass transition temperature, and since each blend has a different glass transition temperature direct comparison is not possible. Therefore to enable comparison, the data must be scaled by plotting the relaxation time against T_α/T, where T_α is an arbitrary temperature outside the measuring range. This type of plot is often called a 'cooperativity' plot [8]. The data shown in Fig. 11 were normalised by scaling according to the blend glass transition

temperatures as measured by differential scanning calorimetry. The result is shown in Fig. 12.

It can be seen that there is a change in relaxation time with composition, indicating that the relaxation behaviour is affected by the level of PEEK within the blend. The compositional variation of the data shown in the cooperativity plot can be illustrated more clearly by expressing the relaxation time of each composition at a common value of T_g/T. This value was fixed at 0.87 and the value for the relaxation time of each blend was expressed as a function of weight
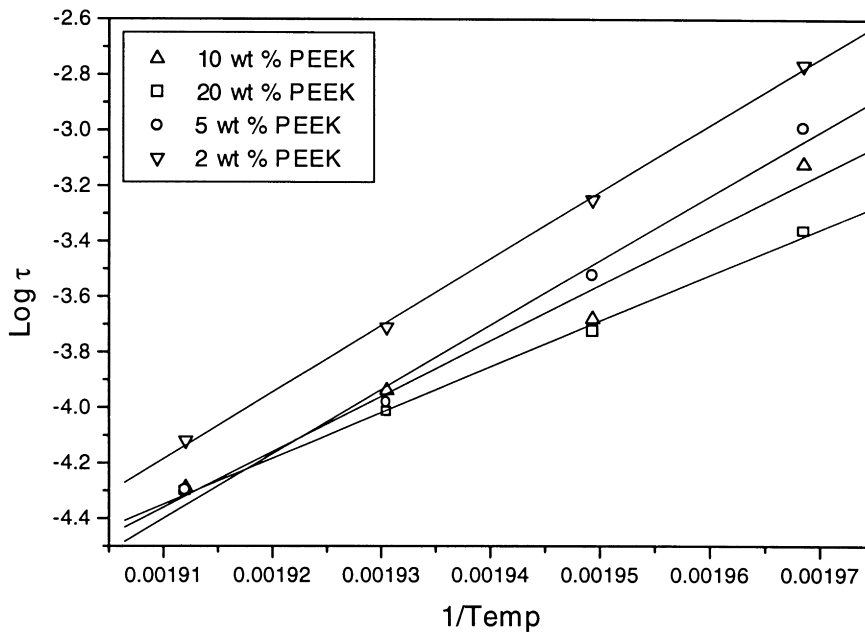

Fig. 11. The temperature dependence of the α relaxation time for blends in the composition range 2–20 wt% PEEK.
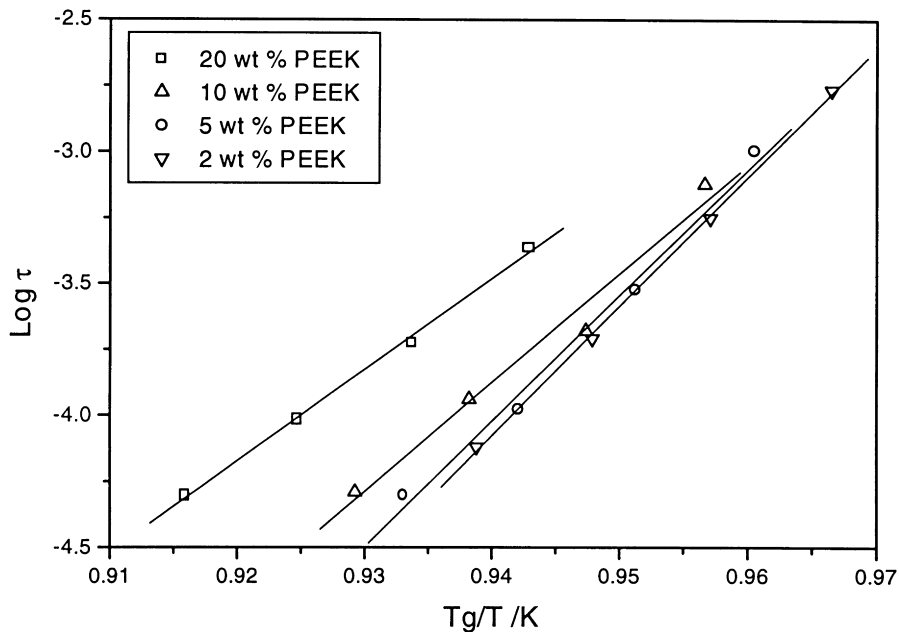
Fig. 12. A normalised 'cooperativity' plot of the temperature dependence of the blend α relaxation time.

fraction of PEI, as shown in Fig. 13. It can be seen that there is an increase in relaxation time with increasing PEEK content and that there is a non-linear dependence of relaxation time on composition. Again, PEEK appears to affect the relaxation behaviour of PEI.

The variation of the loss with storage permittivity was analysed in terms of the Havriliak and Negami equation, which described the breadth of the relaxation in terms of two parameters, an α parameter describing the asymmetric broadening and a β parameter describing the symmetric

broadening. It was found that there was a change in peak breadth with temperature and composition. The broadening of loss peaks in polymer blends has been found previously [8] and has been ascribed to compositional fluctuations within the blend samples. This fluctuation creates a range of local environments, which in turn gives rise to inhomogeneous broadening of the relaxation peak. The relaxation behaviour of the individual blend components can also affect the relaxation behaviour of the blend. [9] The variation of α with temperature is shown on the normalised
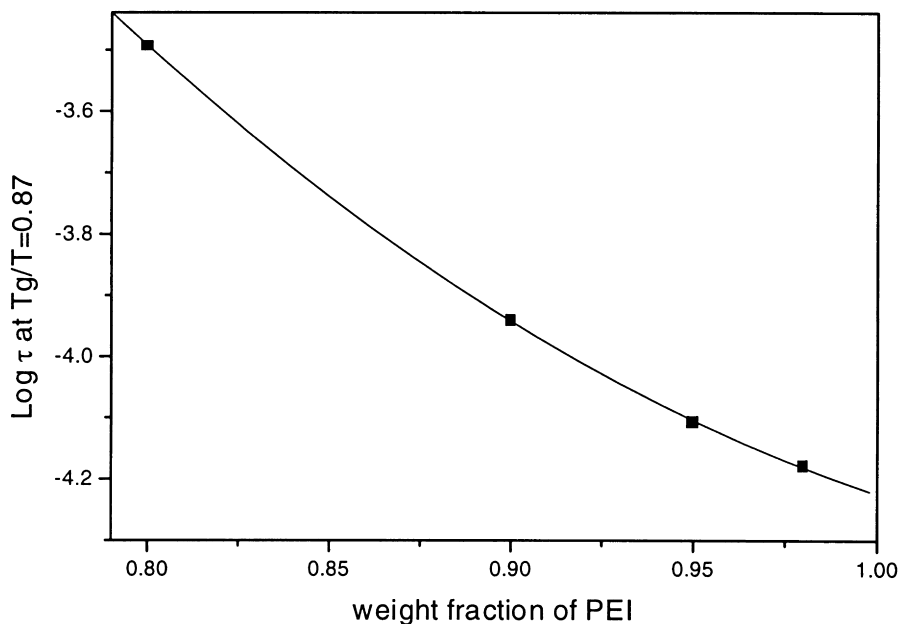

Fig. 13. The variation of relaxation time at $T_g/T = 0.87$ with blend composition.
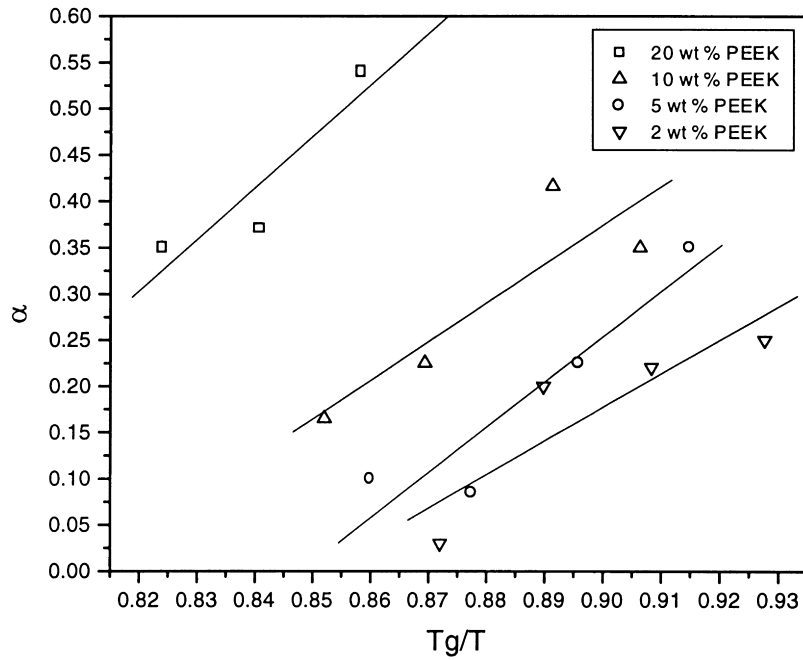
Fig. 14. A normalised 'cooperativity' plot of the temperature dependence of the asymmetric broadening parameter α.

cooperativity plot in Fig. 14 and the compositional variation at $T_g/T = 0.87$ is shown in Fig. 15.

It can be seen that there is an increased tendency to asymmetric broadening with increasing PEI content, which results from a combination of compositional fluctuations and differences in the relaxation behaviour of the blend components. No clear trend was observed for the variation of symmetric broadening with composition.

4. Conclusions

Blends of PEEK and PEI containing low percentages of PEEK have been found to exhibit a composition dependent α process that can be observed by both dynamic mechanical and dielectric analysis. The temperature at which the process occurs has been found to vary in a similar way to the glass transition temperature as measured by differential scanning calorimetry. The low temperature relaxation
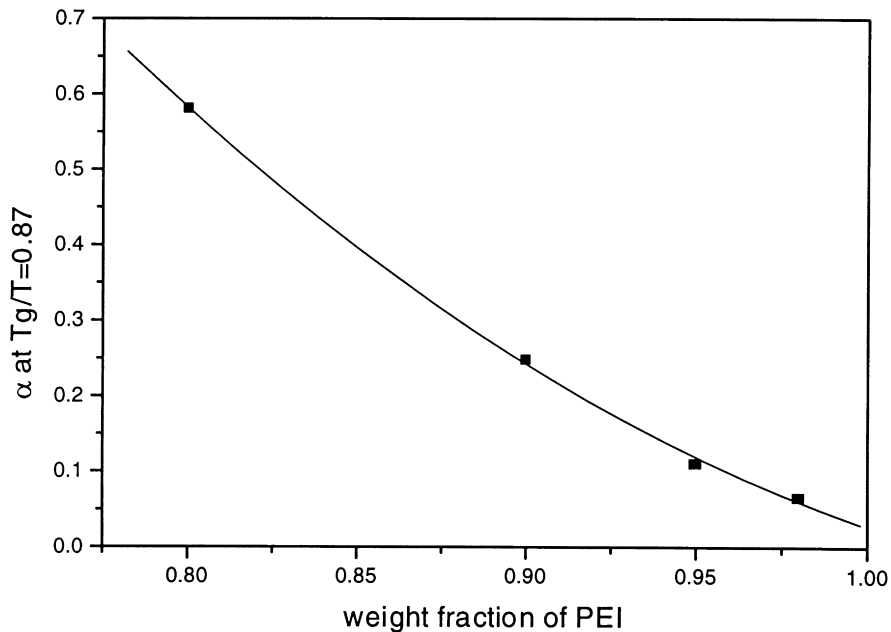

Fig. 15. The variation of the asymmetric broadening parameter α at $T_g/T = 0.87$ with blend composition.

processes were also analysed and the β process that originates within the PEEK component was found to be shifted by 25°C, no process was observed within the PEI β relaxation region. It was assumed that the relaxation behaviour of both components was affected by the presence of the other. The cause of the effect is probably the molecular interactions that result in the blend miscibility.

Further evidence of molecular interaction was found by analysing the isothermal frequency response of the blends in the glass transition region. The temperature dependence of the frequency at which the peak in loss permittivity occurs was found to vary with temperature, to enable comparison between the blend compositions that exhibit different glass transition temperatures the data was presented in the form of a cooperativity plot. The temperatures were normalised according to the glass transition temperatures as measured by differential scanning calorimetry. Expressing the values of the relaxation time at a fixed value of T_g/T revealed a non-linear dependence of relaxation time on blend composition. Again, this is probably the result of molecular interaction.

The breadth of the relaxation spectrum was also found to be dependent on composition, a Havriliak and Negami analysis of the isothermal frequency response showed that the asymmetric broadening parameter was strongly dependent on composition. Although no obvious trend was found in the symmetric broadending parameter. Molecular interactions result in the blend miscibility found in the PEEK/PEI system, but these interactions also affect the relaxation behaviour of the blend system and this has been observed in the dynamic mechanical and dielectric analysis.

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