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Glass transition behaviour of poly(ether ether ketone)/poly(aryl ether sulphone) blends: dynamic mechanical and dielectric relaxation studies

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Abstract

Blends of poly(ether ether ketone) (PEEK) and poly(aryl ether sulphone) (PES) have been prepared in the whole composition range. The molecular dynamics and α-relaxation behaviour of these materials have been studied using dynamic mechanical and dielectric relaxation spectroscopy. From dynamic mechanical relaxation studies, two α-relaxation peaks corresponding to the segmental relaxation process of pure components in the blend was observed. Also, it was found that the temperature at which α-process of the homopolymers occurs, shows a slight change with blend composition, corresponding to a PEEK-rich and PES-rich phase. The relaxation intensities of the homopolymers in the blend compared to that in pure state were approximately proportional to their respective content in the blend. From the phase composition of the respective phases obtained using Fox equation, it has been inferred that PEEK dissolves more in PES than vice-versa. The α-relaxation of PES could not be detected from dielectric relaxation spectroscopy because of the possible influence of dc conduction and electrode polarization losses. Otherwise, the α-relaxation behaviour of PEEK-rich phase observed from dielectric relaxation studies agree with those inferred from dynamic mechanical relaxation studies. Furthermore, activation energies for molecular motions (E_a) at the α-relaxation have also been determined using an Arrhenius form of equation and it has been found that E_a for both PEEK-rich and PES-rich phase show variation with composition. Similarly, the relaxation times associated with the mobility of relaxing species in both PEEK and PES are influenced in the blends. It is likely that these observations are related to some interactions and a partial segmental mixing between the blend components, which result in changes in the local molecular environment on blending.

Keywords: Dielectric; Dynamic mechanical; Polymer blends

1. Introduction

In the last decade much attention has been paid to the development of polymeric blends. Blends offer the possibility of combining the unique properties of available materials and thus of producing materials with tailor made properties, which often has advantages over the development of completely new polymeric materials [1,2]. Since the properties of polymer blends depend strongly on the miscibility of the components, the miscibility of polymer blends has been studied with various methods [2], such as calorimetry [3,4], cloud point measurements [5–7], NMR [8,9], electron microscopy [10], thermally stimulated current [11], dynamic mechanical relaxation [12–14], and the dielectric relaxation method [15–17]. Of all the methods used for studying the miscibility between the blend components perhaps those based on glass transition behaviour are most widely reported. When a blend composed of polymers 1 and 2 is demixed, two glass transition temperatures T_g of the components will be observed. But an ideally mixed blend exhibits a single glass transition T_g at an intermediate temperature between the T_gs of the components.

Poly(ether ether ketone) (PEEK) is a semicrystalline engineering thermoplastic based on a relatively rigid *para*-connected aromatic backbone structure, and displays outstanding mechanical properties in combination with exceptional thermal and chemical resistance characteristics [18,19]. However, its engineering applications gets limited because of the low glass transition temperature of this polymer, which is around 150 °C. High wrapage is another problem in PEEK, which requires attention. Poly(aryl ether sulphone) (PES) is another useful high performance

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engineering thermoplastic with outstanding thermal and mechanical properties [20]. It has a high glass transition temperature (T_g) in the range of 220–230 °C. However PES, being an amorphous polymer, exhibits poor organic solvent resistance.

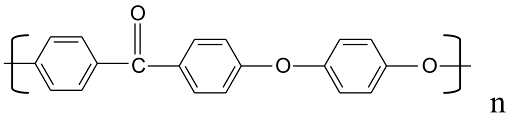
The two polymers have been blended in the past with an aim to reduce the drawbacks of both the polymers to minimum and at the same time bring some benefits into the system, which is inherited from both ingredients [21–25]. But conflicting results have been reported in the literature regarding shifts of T_g and miscibility in PEEK/PES blends. The apparent disagreement is thought to arise from differences in grades of homopolymers, blending procedure, and thermal history. Because of the exceptional behaviour reported to be shown by these blends and range of miscibility's reported, we have carried out an extensive study of PEEK/PES blends and have reported some of the results in the past [26,27]. From DSC studies, the melt blends were shown to form a multiphase system containing a PEEK-rich and a PES-rich phase.

In the present study, we report on the glass transition behaviour of PEEK/PES blends using dynamic mechanical and dielectric relaxation analysis. Dynamic mechanical and dielectric relaxation studies are a more sensitive tool for studying miscibility in polymer blends and offer some interesting possibilities for obtaining additional information on the structure of the material. Variable temperature measurements of dynamic mechanical and dielectric response within a broad frequency range can yield valuable information regarding modes of molecular and segmental motion in polymers in the vicinity of the glass-rubber relaxation.

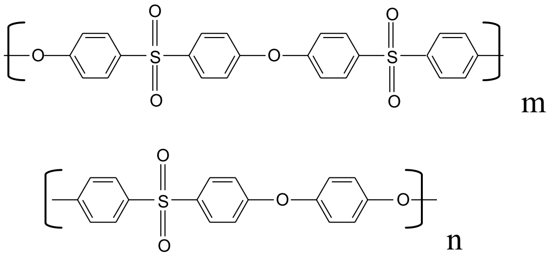
2. Experimental

2.1. Materials

PEEK was synthesized in the laboratory itself by following the reported procedure [28,29]. The purified polymer was then dried in a vacuum oven at 120 °C for 48 h. The inherent viscosity of the synthesized PEEK was measured in Ostwald viscometer at 25 °C using 98% sulphuric acid as a solvent, at a concentration of 1.00 g polymer/100 ml solvent and found to be 0.81 dl/g. The polymer is having the following general structure,



PES was procured from Amoco Performance Products Inc., USA under the trade name Radel (Grade A-300). Though the structure of this polymer has not been disclosed by the manufacturers, but was found to have the following repeating units in its general structure, by Ghosal et al. [30].



The ratio m/n probably varies in different grades of Radel A-PES available. Some of the important characteristics and their sources of PES and PEEK used in this investigation has been listed in Table 1.

2.2. Preparation of blends

PEEK and PES were blended in the ratio 100/0, 90/10, 75/25, 50/50, 25/75, 10/90, and 0/100 (w/w ratio), respectively. Before blending, the two polymers were completely dried overnight in an air-circulated oven at 150 °C. The two polymers were melt-blended in a Maxwell mixing extruder from Custom Scientific Instruments (CSI), USA (Model CS-194 AV) [31]. It is a laboratory mixing extruder featuring a screw less design. The Maxwell extruder has a 3/4 in. diameter rotor and produces a throughput in the range of 200 g/h. Before melt blending, the two polymers in appropriate weight ratios were thoroughly mixed by hand and then fed to the hopper of the mixing extruder in small batches. Temperature of both the rotor and die zone were set at 350 °C and the rotor was driven at 90 rpm for all blend compositions. Total residence time of the polymer mixture inside the mixing zone was 30 s approximately, and extrudate was obtained through a die of 3.5 mm diameter. The extrudates were further chopped into small granules and again passed through the mixing extruder to ensure a thorough mixing. The extrudates obtained were further converted to granules.

Table 1
Characteristics of the polymers used

Characteristics	PEEK	PES
$\bar{M}_w$	34 700[a]	42 500[b]
Density (ρ) (g/cm^3)	1.263[c]	1.370
T_g (°C)	147.6[c]	≈223.0[d]
T_m (°C)	339.1	–
Solubility parameter (δ) (cal$^{1/2}$ cm$^{-3/2}$)	10.5[e]	11.2[f]

[a] Molecular weight measured in our lab.
[b] Molecular weight data provided by the manufacturers.
[c] Data for completely amorphous samples.
[d] Slightly varies with thermal history.
[e] Solubility parameter calculated using Small's table.
[f] From Ref. [42].

2.3. Specimen preparation

For dynamic mechanical relaxation studies. Specimens for dynamic mechanical relaxation studies were prepared with a thickness of 3.50 mm. Granules of blends prepared in the extruder, kept between two halves of mold were placed between the platens of the press, which was already heated to 380 °C. A pressure of 200 kg/cm^2 was applied at this temperature for 15 min. After this the heating of the press was switched off and the molded samples were cooled inside the press under pressure in room temperature environment.

For dielectric relaxation studies. Specimens for dielectric relaxation studies were prepared with a thickness of 0.30 mm. Granules of blends prepared in the extruder, kept between two aluminum foils were placed between the platens of the press, which was already heated to 380 °C. A pressure of 100 kg/cm^2 was applied at this temperature for 10 min and then was immediately quenched from 380 °C to ice water.

2.4. Dynamic mechanical relaxation studies

Dynamic mechanical measurements were carried out in the temperature range of room temperature to 250 °C using a DMA 2980 dynamic mechanical analyzer (TA Instruments) in the bending mode with dual cantilever geometry. Data analysis was done on a thermal analyst 3100 (TA Instruments) thermal analyzer. Rectangular samples, measuring $60.00 \times 15.00 \times 3.50$ mm were scanned isochronally at 3 °C/min. Loss modulus (E'), storage modulus (E''), and tan δ were recorded in multifrequency mode at 1, 2, 5, 10, and 100 Hz.

2.5. Dielectric relaxation studies

Dielectric relaxation studies on the blend samples were carried using a DEA 2970 (TA Instruments) equipped with a thermal analyst 3100 (TA Instruments) data station. For this purpose ice quenched amorphous films of thickness 0.30 mm were used. The samples were analyzed using the parallel plate sensors. The sample was placed under a force of 500 N to ensure good contact between the specimen and the electrodes below T_g. A minimum plate spacing of 0.12 mm was specified so that the electrodes would maintain this displacement if the sample become soft or melted. The sample was heated at a rate of 2 °C/min from room temperature to 250 °C. The DEA cell was continuously purged with dry nitrogen adjusted to a flow rate of 200 ml/min. Data were obtained in the multifrequency mode at 10, 100, 1000, 10 000, and 100 000 Hz.

3. Results and discussions

3.1. Dynamic mechanical relaxation studies of pure polymers

Fig. 1 shows the dynamic mechanical spectra of pure PEEK recorded at different frequencies. A single mechanical transition has been observed in the temperature range studied and is recognized as the α-relaxation or the glass transition peak for pure PEEK. The α-relaxation is related to the Brownian motion of the main chain associated with the glass transition and the relaxation of segments associated with it. Onset of glass transition of PEEK is marked by a sharp decrease in its storage modulus, as shown in Fig. 1. The glass transition temperature of a polymer is usually taken from the peak position of loss modulus or tan δ versus temperature curves. Peaks of tan δ are typically found at somewhat higher temperatures depending on the intensity and/or width of the transition. Hence, glass transition temperature (T_g) of PEEK at 1 Hz based on loss modulus peak value was found to be around 157.5 °C, whereas based on damping (tan δ) peak it is around 164.2 °C. Also the loss modulus and tan δ peak temperatures show that the glass transition moves to higher temperatures as the analysis frequency increases. T_g determined using dynamic mechanical or dielectric analysis is generally higher than those determined using differential scanning calorimetry (DSC), because of the high frequency used during the measurement in the former cases [32]. With increasing frequency, the relaxation peak shifts to higher temperatures, which is due to the increasing speed of motion of the molecules.

Similarly, Fig. 2 shows dynamic mechanical spectra of pure PES(A-300) recorded at different frequencies. Again a single mechanical transition has been observed in the temperature range studied, characterized as the α-relaxation or glass transition of PES. Storage modulus remains more or less constant up to 190 °C and after that it sharply decreases around which glass transition of PES exists. T_g of PES as determined from the peak of loss modulus and tan δ curves at 1 Hz were found to be 221.6 and 234.5 °C, respectively.

3.2. Dynamic mechanical relaxation studies of blends

Fig. 3 shows the tan δ versus temperature curves for PEEK/PES blends of different compositions measured at a frequency of 1 Hz. As can be seen from the figures, all the blend compositions show the characteristic tan δ curves of immiscible blends with two peaks corresponding to the T_g of PEEK and PES phases. Also in the blend composition the, tan δ peak corresponding to PEEK phase appear at slightly higher temperatures, whereas those corresponding to PES phase appear at slightly lower temperature. This indicates that some PES segments are dissolved in PEEK phase, whereas some PEEK segments get dissolved in PES phase. Hence there is an existence of PEEK-rich and PES-rich phase in each blend composition.

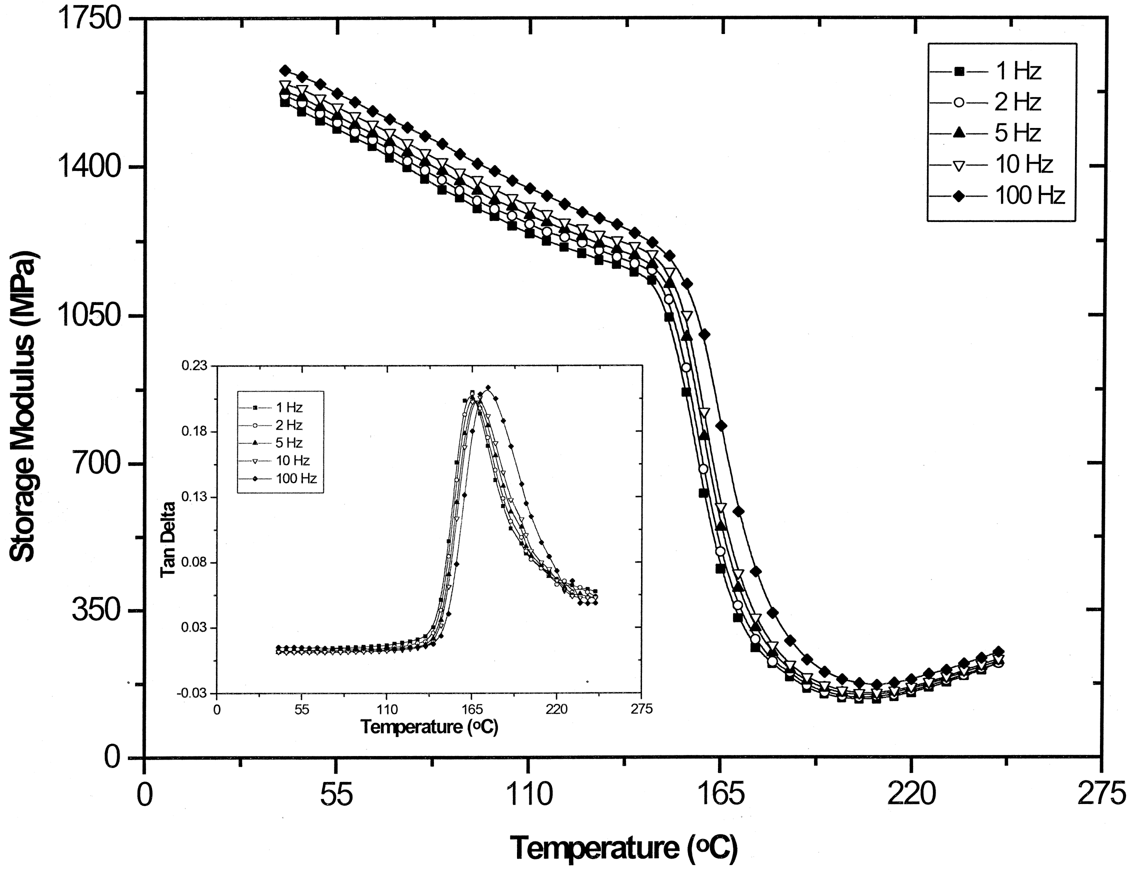


Fig. 1. Dynamic mechanical results for pure PEEK in multifrequency mode showing glass-rubber (α) relaxation.

Fig. 4 shows the variation of T_g(PEEK) and T_g(PES) with composition as determined using tan δ damping peaks for PEEK/PES blends. It can be observed that T_g(PEEK) in PEEK/PES blends determined from damping peaks increase by about 1–7 °C depending on composition, whereas T_g(PES) decreases by up to 11 °C compared to homopolymers. Further, the other significant observation from Fig. 4 is that T_g(PEEK) increases as PES weight fraction in the blend increases up to 25 wt% and then decreases with further increase in the PES weight fraction. Whereas T_g associated with PES-rich phase shows a continuous decrease with increasing concentration of PEEK in the blend. Similar type of behaviour had been observed from differential scanning calorimetry measurements (DSC) also Ref. [26]. One noteworthy observation of dynamic mechanical analysis results compared to DSC results is the fact that in compositions where no shift in the T_g of PEEK-rich phase was observed by DSC [26], dynamic mechanical analysis results do show a shift. In this respect it will be appropriate to give the explanation given by Dickie [33]. He has argued that changes in the location of maxima in the loss tangent or loss modulus characteristics of blend constituents do not necessarily imply changes in T_g relative to pure components, but may arise purely from mechanical reasons (attributed to changes in the state of deformation of each phase region as the mechanical properties of the constituents change with T_g). He further suggested that changes in the position of the maximum in tan δ or loss modulus might imply changes in the constituents T_gs only to the extent that the shifts in position differ from those predicted by continuum analysis.

Now from the glass transition temperatures of PEEK and PES in the PEEK/PES blends, we can estimate the apparent weight fractions of PEEK and PES dissolved in the PES-rich and PEEK-rich phases, respectively. It is reasonable to assume that variation of T_gs of each phase, i.e. the high T_g PES-rich phase and the low T_g PEEK-rich phase, with composition can be described by any of the several equations used to fit T_g versus composition data. Therefore, applying the equations to each phase and rearranging it, the composition of each phase can be obtained. We will use here the widely used Fox equation [34] for determining the composition of PEEK-rich and PES-rich phases. Fox equation is given by [34],

$$1/T_{gB} = w_1/T_{g1} + w_2/T_{g2} \tag{1}$$

where T_{gB} is the observed glass transition temperature of the copolymer or the blend; w_1, the weight fraction of homopolymer 1 having a glass transition temperature T_{g1}; w_2 is the weight fraction of homopolymer 2 having a glass transition temperature T_{g2}. Rearranging Eq. (1) and applying it to individual phases of the blend system, we

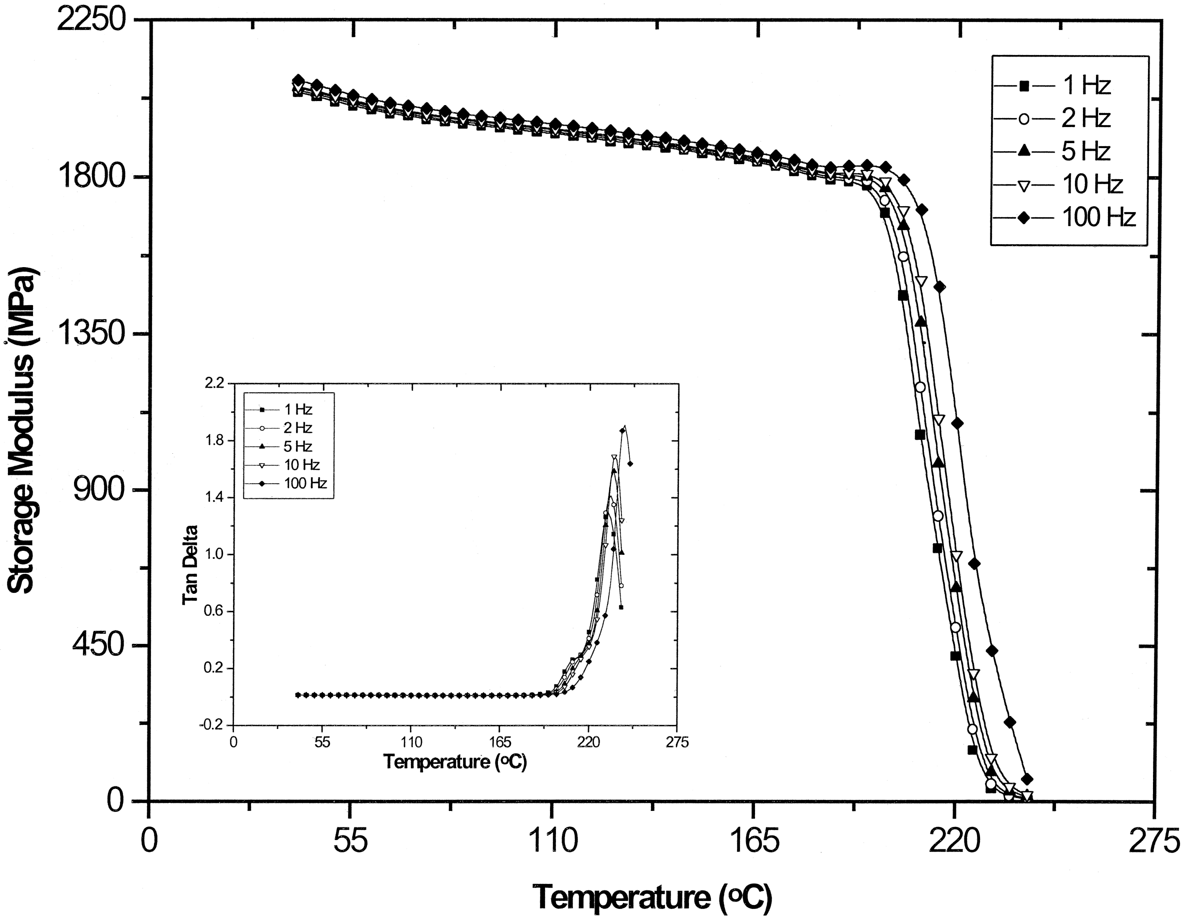


Fig. 2. Dynamic mechanical results for pure PES in multifrequency mode showing glass-rubber (α) relaxation.

will obtain,

$$w'_1 = T_{g1}(T_{g1,B} - T_{g2})/T_{g1,B}(T_{g1} - T_{g2}) \tag{2}$$

where w'_1 is the apparent weight fraction of polymer 1 in the polymer 1-rich phase; $T_{g1,B}$, the observed T_g of polymer 1 in the blends; T_{g1} and T_{g2} are the T_gs of unblended polymers 1 and 2, respectively. Weight fraction of polymer 2 in this phase will be given by,

$$w'_2 = 1 - w'_1 \tag{3}$$

Similarly, the weight fractions w''_1 and w''_2 of polymers 1 and 2 in the polymer 2-rich phase can be calculated. In this

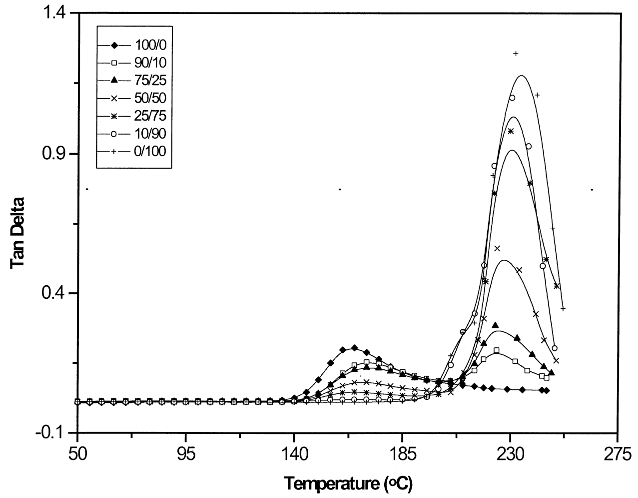


Fig. 3. Dynamic mechanical results of tan δ versus temperature for the various compositions of PEEK/PES blends at a frequency of 1 Hz.

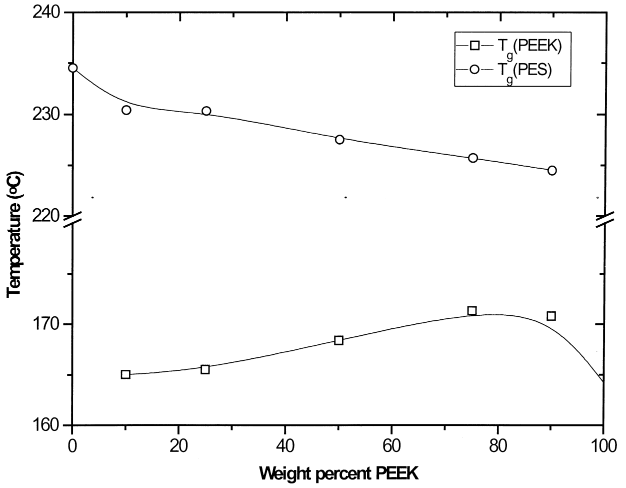


Fig. 4. Effect of composition on the dynamic mechanical T_g(PEEK) and T_g(PES) based on maximum in tan δ, for PEEK/PES blends at a frequency of 1 Hz.

manner we have calculated the apparent weight fractions of PEEK and PES in the PES-rich and PEEK-rich phases. Table 2 shows the composition of PEEK-rich and PES-rich phases for PEEK/PES blends determined using Fox equation based on tan δ peak T_g. As can be observed from the table, PEEK dissolves more in PES than vice-versa. Similar type of results has been obtained in case of PEEK/polyarylate blends also, where polyarylate-rich phase show considerable presence of PEEK segments in it, whereas PEEK-rich phase was almost pure [35].

Further, the energy of activation (energy barrier to motion) associated with α-relaxation of PEEK-rich and PES-rich phases were calculated using Arrhenius plots of [log(frequency)] versus [$1/(T_{max})$], where T_{max} is the temperature, which corresponds to the tan δ peak maximum at a certain test frequency, f. Fig. 5(a) and (b) shows the Arrhenius plots for the glass-rubber relaxation of PEEK-rich and PES-rich phases of different compositions of PEEK/PES blends, respectively. Data of this kind are commonly fitted to the well-known empirical Vogel–Fulcher–Tammann–Hesse (VFTH) equation [36–38], which predicts a rapid increase in relaxation time as the glass transition is approached from above T_g due to the decrease of free volume. The VFTH equation has the following form,

$$\log f = \log f_0 - E_f / 2.303R(T_{max} - T_0) \tag{4}$$

where f_0, E_f (kJ/mol) and T_0 (K) are fitted parameters. f_0 is related to the relaxation rate at infinitely high temperature, E_f is an energy term related to bond rotational barriers, and T_0 is the temperature at which essentially no α-relaxation occurs, which is usually at about 50 °C below the value of T_g. But any meaningful application of VFTH equation requires the need to fit data over a wide range of frequency and temperature.

Table 2
Apparent weight fraction (w) of PEEK and PES components in the PEEK-rich phase and PES-rich phase of PEEK/PES blends as determined by Fox equation

Blend compositions [a]	Glass transition temperature (°C) [b]		PEEK-rich phase[c] (weight fraction)		PES-rich phase[c] (weight fraction)	
	T_{g1}	T_{g2}	w_1'	w_2'	w_1''	w_2''
1.00	164.2	–	1.0000	0.0000	–	–
0.90	170.8	224.5	0.8711	0.1289	0.1040	0.8960
0.75	171.3	225.7	0.8617	0.1383	0.0911	0.9089
0.50	168.4	227.5	0.9168	0.0832	0.0719	0.9281
0.25	165.5	230.3	0.9738	0.0262	0.0426	0.9574
0.10	165.0	230.4	0.9838	0.0162	0.0416	0.9584
0.00	–	234.5	–	–	0.0000	1.0000

[a] Blend compositions given as overall weight fraction of PEEK in PEEK/PES blends.

[b] Subscript 1 and 2 denote PEEK and PES, respectively. The glass transition temperature mentioned are measured using dynamic mechanical analysis at 1 Hz frequency.

[c] Single and double primes denote PEEK-rich phase and PES-rich phase, respectively.

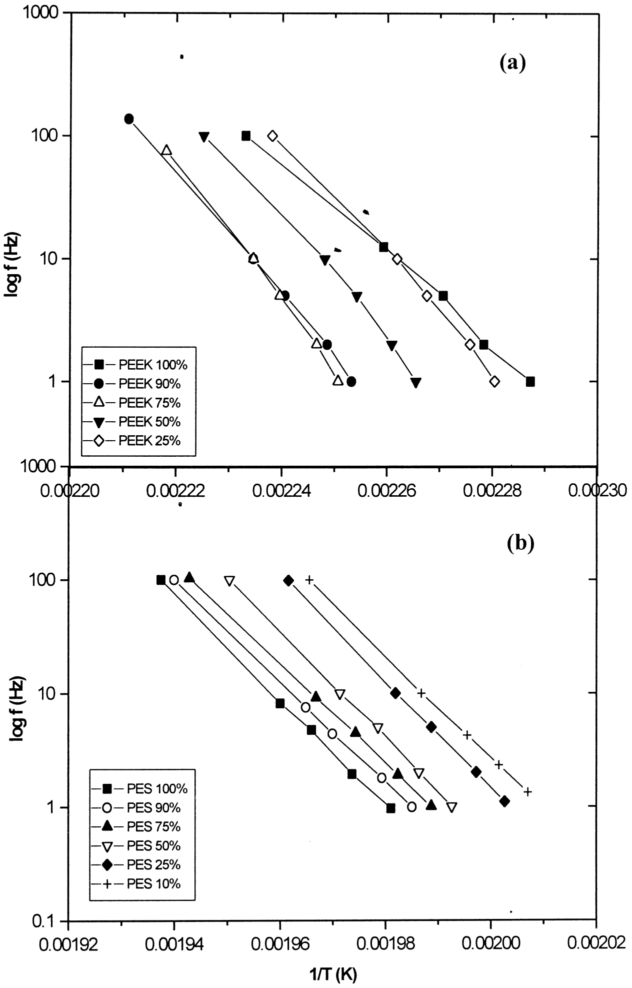


Fig. 5. Arrhenius plot for the dynamic mechanical glass-rubber relaxation of PEEK/PES blends obtained from tan δ—temperature—frequency plots: (a) for PEEK-rich phase, (b) for PES-rich phase. (Solid lines are guide to the eyes.)

Now alternately the temperature dependence of the α-relaxation loss peak can also be described by the Arrhenius

Table 3
Apparent activation energy (E_a) for the glass-rubber (α) relaxation of PEEK-rich and PES-rich phase in PEEK/PES blends. Values were determined from Arrhenius fits to the data in Fig. 5

Blend compositions	E_a (PEEK-rich phase) (kJ/mol)	E_a (PES-rich phase) (kJ/mol)
100/0	710.2	–
90/10	826.8	846.3
75/25	950.0	880.0
50/50	932.9	895.7
25/75	890.1	887.0
10/90	–	886.6
0/100	–	969.1

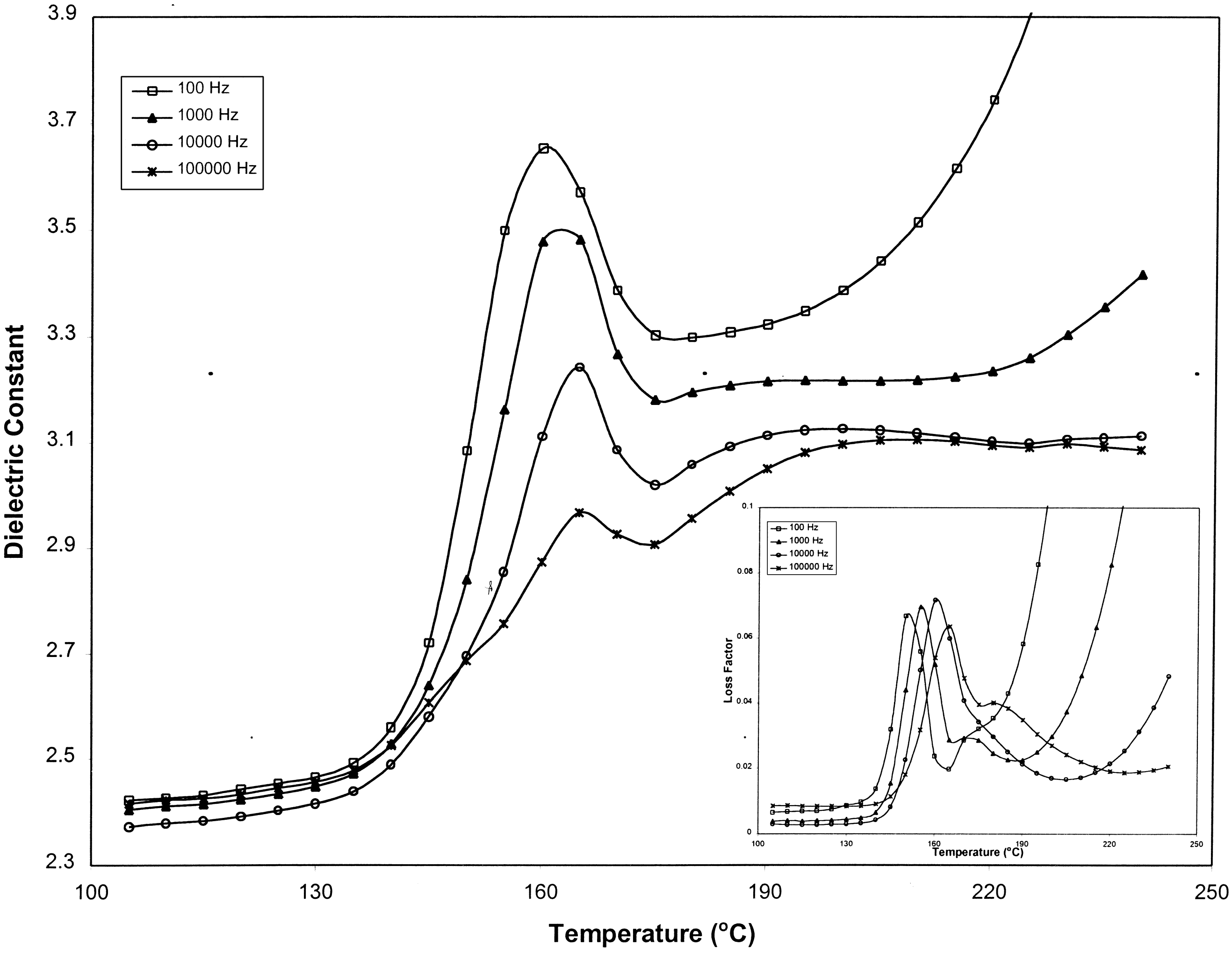


Fig. 6. Dielectric results for pure PEEK in multifrequency mode showing glass-rubber (α) relaxation.

relationship (especially over a limited frequency range) [17,39],

$$\log f = \log A - 2.303E_a/RT_{\max} \quad (5)$$

where A is the pre-exponential factor, E_a in this case is the apparent activation energy for the glass-rubber relaxation, and R is the universal gas constant. The slope of the resultant plot when multiplied by 2.303 and the gas constant R reveals the apparent activation energy. As a first approximation, $\log f$ versus $1/T_{\max}$ traces in Fig. 5(a) and (b) can be regarded as a straight line, which allows the evaluation of apparent activation energy based on the Arrhenius relation as given by Eq. (5). So keeping in view the limitation in using VFTH equation and as mean to compare the data obtained, the data in Fig. 5(a) and (b) were fitted to the Arrhenius equation to achieve an estimate of the composition dependence of the apparent activation energy for glass-rubber relaxation process over the limited frequency (temperature) range.

Table 3 shows the apparent activation energy (E_a) calculated from Fig. 5(a) and (b) and using Eq. (5). Activation energies were found to be 710 kJ/mol for pure PEEK and 969 kJ/mol for pure PES. The slightly low activation energy of PEEK compared to PES can be explained by the presence of comparatively larger fraction of ether linkages in PEEK main chain compared to PES, which imparts a more flexible character in the former. From Table 3 it can be observed that E_a for the glass-rubber relaxation of PEEK-rich phase increases with incorporation of PES and maximum is observed around 75 wt% of PEEK, after which it again decreases. Further, the E_a for the glass-rubber relaxation of PES-rich phase decreases slightly with the incorporation of PEEK in it, though the variation is not much along the composition range. The increase in E_a for PEEK-rich phase can be explained considering the miscibility behaviour observed in PEEK/PES blends. The PES segments, which are dissolved in PEEK-rich phase, enhance the barrier for movement of PEEK segments, as the former are relatively immobile at the glass-rubber relaxation temperature of PEEK. This results in increased energy barrier for the motion of PEEK segments. The maximum observed for the composition with 75 wt% PEEK is in accordance with the fact that PES weight fraction contained in PEEK-rich phase is maximum here. Similarly, the

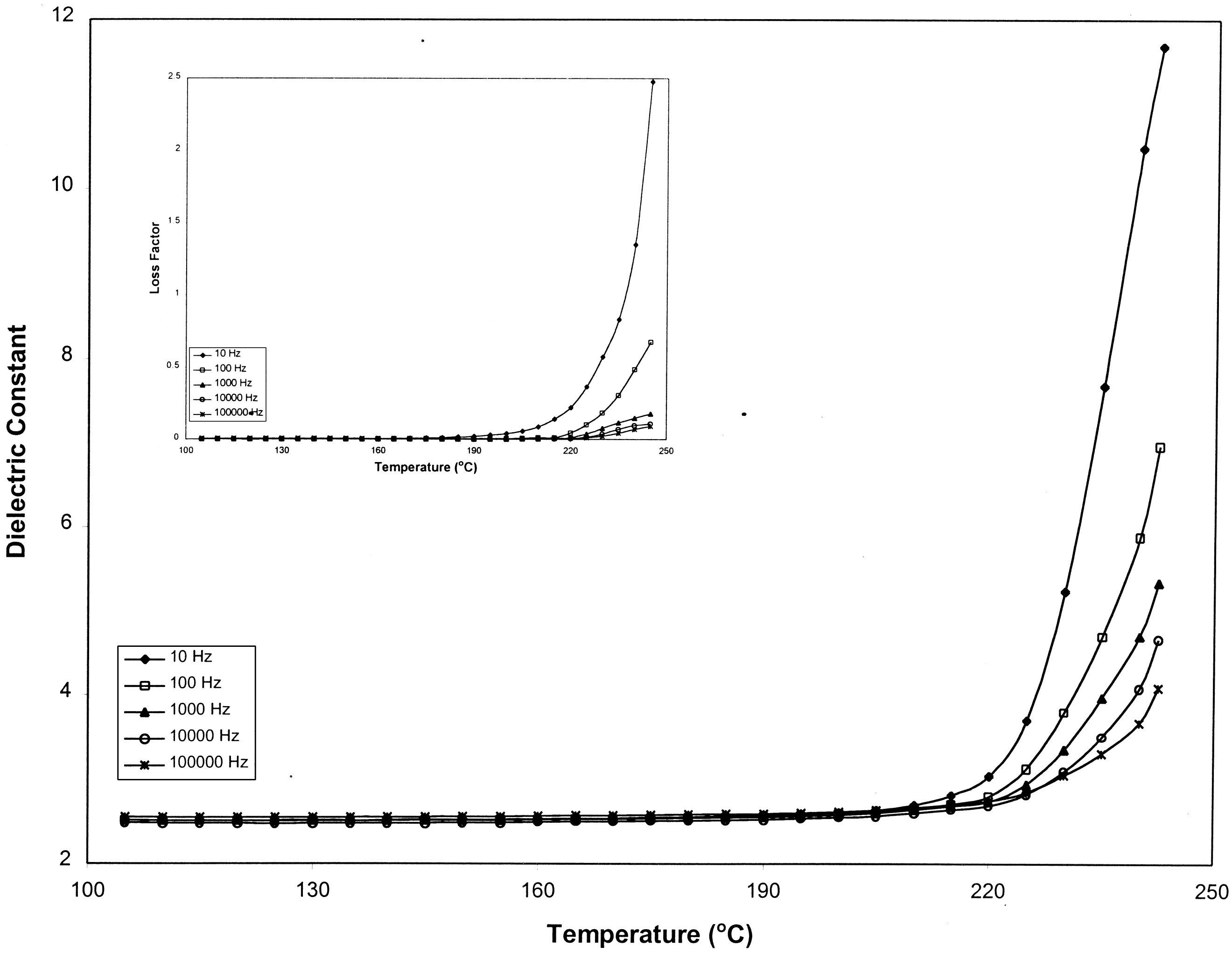


Fig. 7. Dielectric results for pure PES in multifrequency mode.

variation observed for the E_a of PES-rich phase can be explained considering the presence of relatively flexible PEEK segments, which are sufficiently mobile at the glass-rubber relaxation of PES.

Fig. 5(a) and (b) also yield information on the dynamics of glass-rubber relaxation of PEEK-rich and PES-rich phases in PEEK/PES blends. In case of miscible blends, the temperature dependence of the relaxation times is not easily observed from the inverse temperature plots like Fig. 5, because the glass transition temperature shifts with composition and molecular mobility scales with distance of the experimental temperature from the DSC T_g. So, it is more revealing simply to normalize the data using an arbitrary temperature T_α, which is taken from outside the measuring range; often the DSC T_g or the temperature at which the relaxation time is equal to 1 s is used. For polymer systems, plots of $\log f$ against T_α/T are referred to as cooperativity plots [40]. But, in the present case, considering the small variation in the T_g of PEEK-rich and PES-rich phases, we will directly refer to Fig. 5(a) and (b) as such. The plots show that mobility of mechanical relaxing species in both PEEK and PES are influenced in the blends. The relaxation times associated with PEEK-rich phase tend to increase with composition, whereas PES-rich phase tend to relax faster in the blend. This again can be explained considering the relatively rigid structure of PES because of which it has higher relaxation times for glass-rubber relaxation compared to PEEK.

3.3. Dielectric relaxation studies of pure polymers

Dielectric relaxation results in the temperature range 100–250 °C are shown in Fig. 6 for quenched amorphous PEEK sample for several frequencies. The value of dielectric constant (ε') is nearly constant prior to start of the relaxation process. The glass transition relaxation begins at around 150 °C and ε' increases strongly to a maximum at about 160 °C. This event is frequency dependent indicating that it is a relaxational or time dependent transition. Rapid crystallization of the amorphous film above 164 °C results in a sudden decrease in ε'. The loss factor ($\tan \delta$), shown in the inset of Fig. 6, is similarly affected by crystallization.

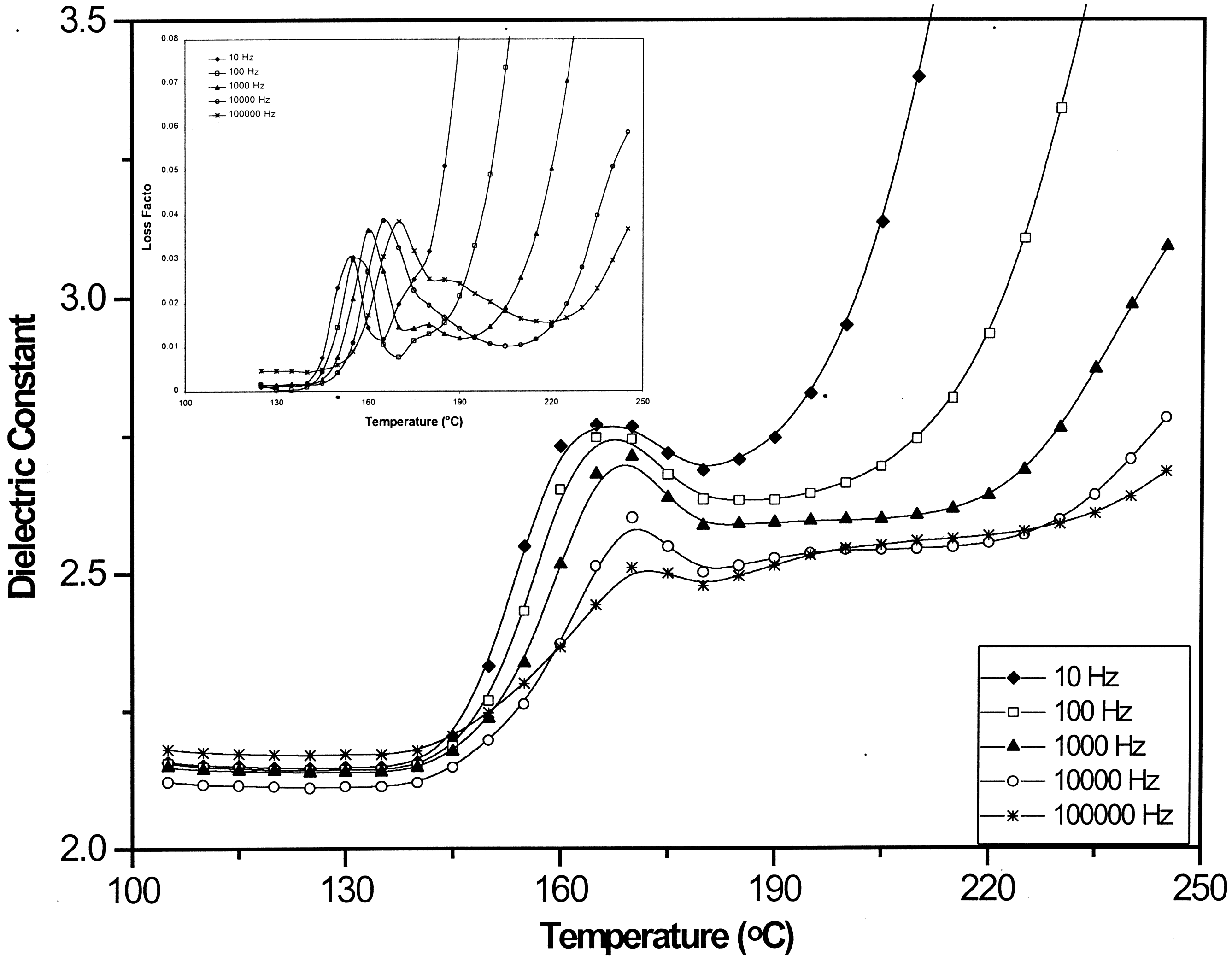


Fig. 8. Dielectric results for PEEK/PES: 75/25 blend in multifrequency mode showing glass-rubber (α) relaxation.

First, the amorphous film undergoes its glass transition relaxation and tan δ shows a strong maximum, which shifts slightly to higher temperature with increasing frequency. Then, tan δ decreases sharply due to crystallization and an additional relaxation is seen at higher temperature (around 190 °C at 10^5 Hz frequency). The second peak is due to relaxation of the now crystalline sample whose amorphous portion becomes constrained (called the rigid amorphous fraction) by the existence of crystals and therefore has a higher glass transition temperature. At temperatures above 200 °C, the dielectric constant shows a significant increase. This is due to the increased mobility of the amorphous phase as the temperature increases. Also, there may be small, imperfect crystallites continuously melting above 200 °C. One more reason for the upturn in the loss factor at high temperatures is the increased ionic conductivity above 200 °C.

Fig. 7 shows the dielectric relaxation results in the temperature range of 100–250 °C for PES sample for several frequencies. The value of ε' is nearly constant up to 200 °C, around which glass transition relaxation of PES begins and then ε' increases strongly. However, the glass-rubber transition temperature could not be detected for PES in the temperature range studied, since ε' shows a continuous increase. This illustrates one of the possible shortcomings of the dielectric method in the detection of glass-rubber transition of some polymers. In these cases the dc conduction and possibly electrode polarization (which results from accumulation of charge at the sample electrode interface) becomes so important at relatively low temperatures that the higher temperature α-relaxation is obscured. Although it is common for such losses to be modeled by using a power law or multiple power law and subtract it from the experimental loss, the conduction losses can be so large as to render this ineffective [41]. The contribution of conduction and electrode polarization to the dielectric loss is inversely dependent on frequency and generally is of no particular difficulty in certain cases because higher frequency measurements unmask the high temperature relaxation processes [41]. But as seen in PES, this is not always the case as here even at highest frequency the α-relaxation of PES could not be unmasked.

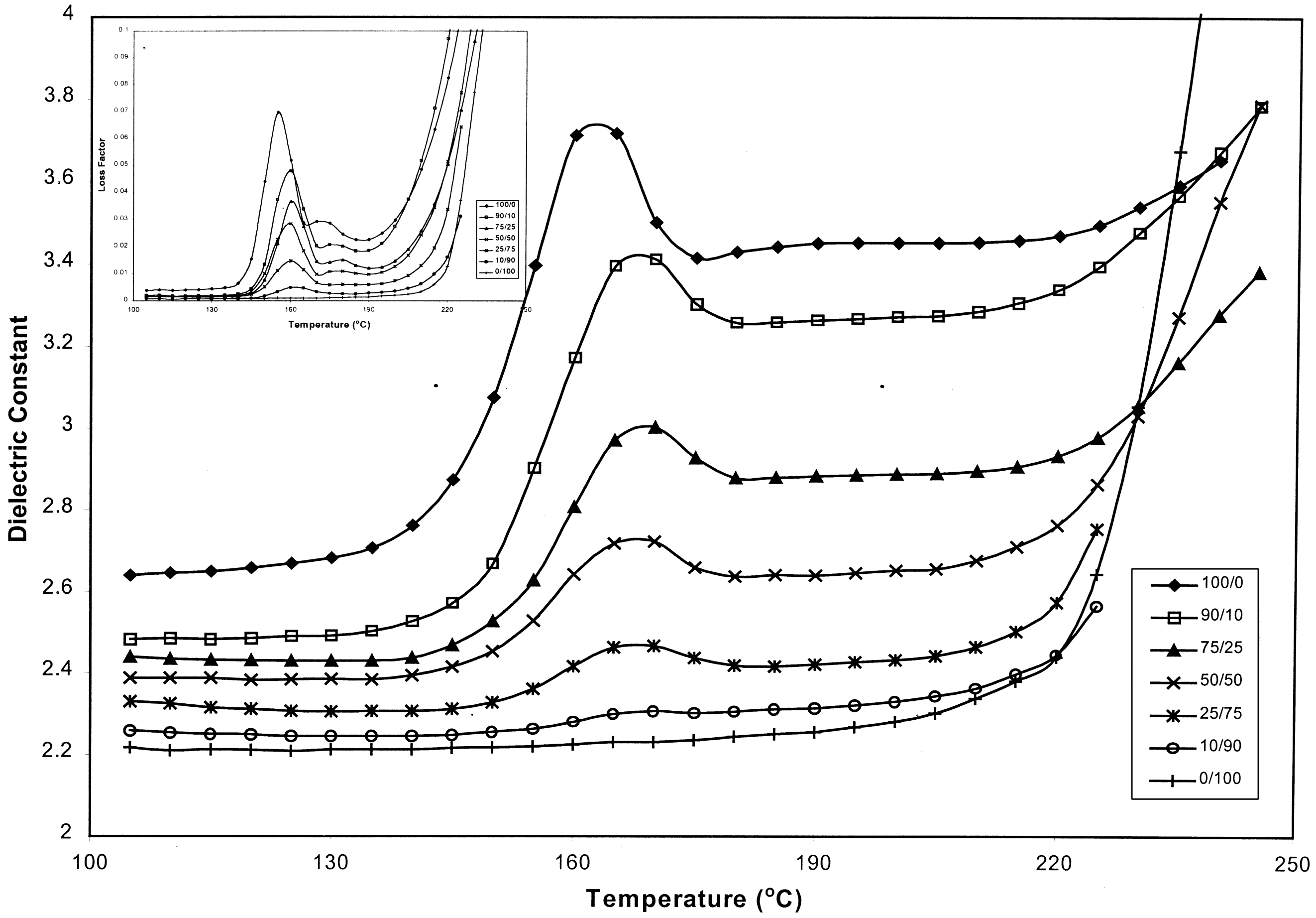


Fig. 9. Dielectric results for the various compositions of PEEK/PES blends at a frequency of 1 kHz.

3.4. Dielectric relaxation studies of blends

Fig. 8 shows the dielectric relaxation results of 75/25 PEEK/PES blend in the temperature range 100–250 °C for several frequencies as a representative dielectric analysis result of PEEK/PES blends. The results are almost same as for pure PEEK, except that a shift in the peak values of ε' and loss factor corresponding to the α-relaxation of PEEK to higher temperature was observed in the blends. As in the case with dynamic analysis results, this shift in the α-relaxation of PEEK to higher temperature is due to the presence of a PEEK-rich phase in which some segments of PES have dissolved. As can be seen from the figure, α-relaxation of PES is not discernible because of the reasons already explained.

Fig. 9 shows the dielectric relaxation results of various compositions of PEEK/PES blends between 100 and 250 °C at a frequency of 1 kHz. In all the compositions the α-relaxation of PEEK phase is clearly visible and maximum shift in this relaxation were observed for the 75/25 PEEK/PES blend. From Fig. 9, the absolute value of T_g(PEEK) were measured using standard dielectric analysis and its variation with composition is shown in Fig. 10. The figure shows that the maximum solubility of PES in PEEK phase occurs around 75/25 compositions, after which the miscibility of PES in PEEK phase decreases. The results agree with those observed from DSC [26] and dynamic mechanical measurements.

The relaxation maps of PEEK and its blends with PES are shown in Fig. 11 at temperature near to the glass transition of the PEEK phase. The curves shown in Fig. 11 (loss factor v/s log (frequency)) show an asymmetric broadening, or skew, on the high frequency side, which is typical, although relatively unexplained, feature of the dielectric response of amorphous polymers. The steep rise in loss factor at low frequency for blends is a result of ionic conductivity in the sample and was observed for all samples containing PES. However, for pure PEEK no such effects were found over the temperature range studied. Also from the figure it can be seen that the intensity of loss factor peak decreases with increasing concentration of PES in the blend. A slight broadening in the peak, on the high frequency side, was also observed which might be because of the presence of PES segments in PEEK phase, which results in concentration fluctuation in the latter.

The frequency dependent nature of various molecular

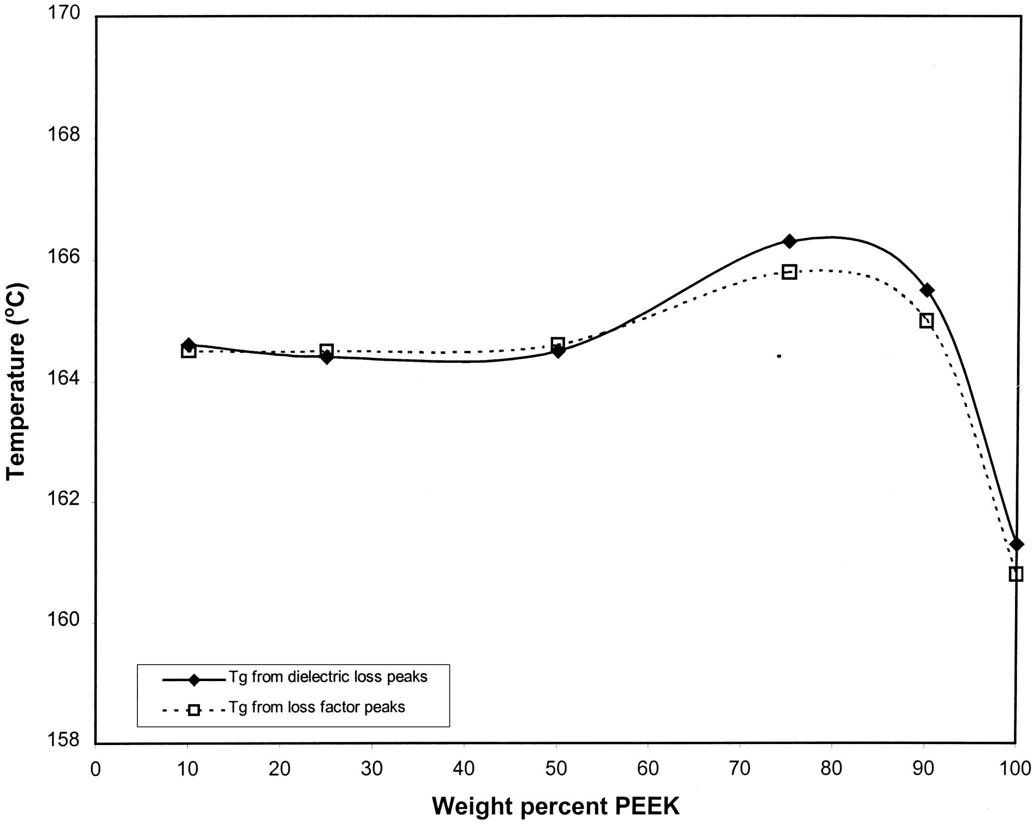


Fig. 10. Effect of composition on the dielectric T_g(PEEK) based on maximum in dielectric constant and loss factor at a frequency of 1 kHz for PEEK/PES blends.

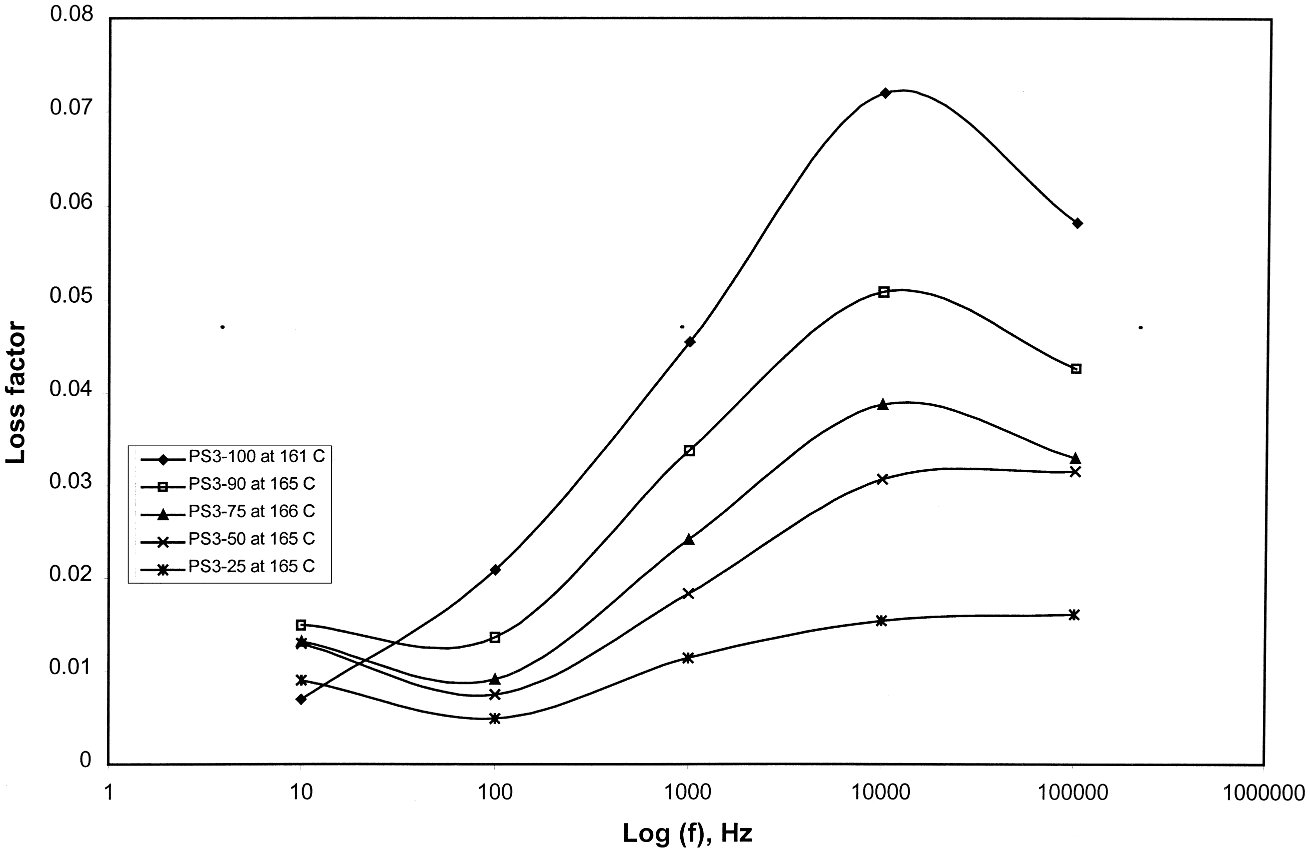


Fig. 11. Isothermal dielectric loss curves for PEEK/PES blends at selected temperatures.

relaxations allows the calculation of their activation energies. Hence, as in dynamic mechanical analysis, the apparent activation energy associated with the α-relaxation of PEEK-rich phase can be found here also using Arrhenius plots. Fig. 12(a) and (b) shows Arrhenius plots of log[frequency] versus $1/T_{max}$, where T_{max} is the temperature which corresponds to either dielectric loss or the loss factor peak maximum at a certain test frequency. The curves showed relatively linear behaviour, over the experimental frequency range and can therefore be fitted to the Arrhenius equation.

The apparent activation energies so obtained for the T_g of PEEK phase has been shown in Table 4. Activation energies were found to be 798 kJ/mol when tan δ peak values were used and 845 kJ/mol when dielectric loss peak values were used. The slight difference observed between dynamic mechanical relaxation and dielectric relaxation activation energies value may be because of the difference in the frequency range over which it has been measured by the two methods and also because of the difference in the nature of specimens used for respective analysis. The variation in the activation energy associated with the glass-rubber relaxation of PEEK-rich phase observed from Table 4 is same as that seen from dynamic mechanical analysis results and all explanations discussed there are equally applicable here. The relaxation time behaviour observed from Fig. 12(a) and (b) also show trend similar to that observed from dynamic mechanical analysis.

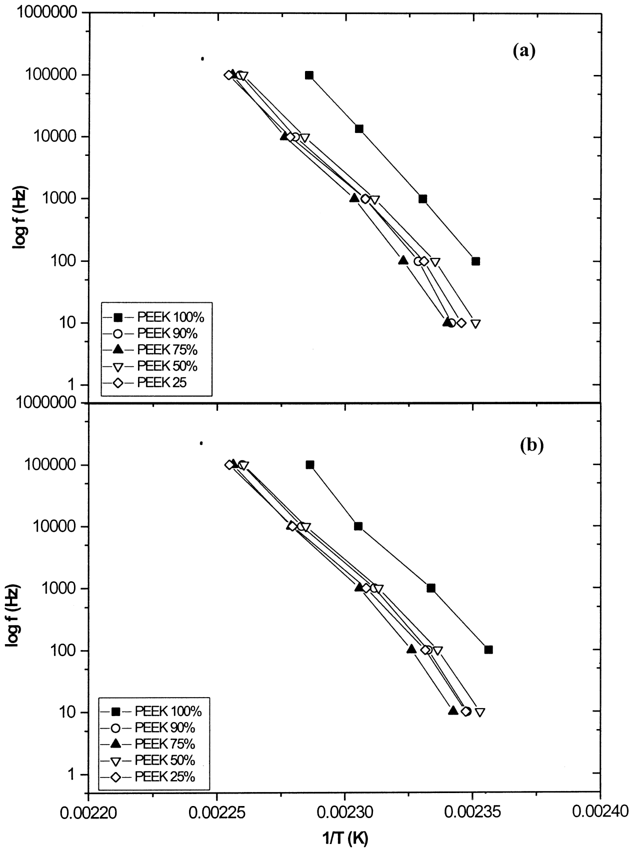


Fig. 12. Arrhenius plots for the dielectric glass-rubber (α) relaxation of PEEK-rich phase of PEEK/PES blends: (a) as obtained from dielectric loss-temperature-frequency plots, (b) as obtained from loss factor-temperature-frequency plots. (Solid lines are guide to the eyes.)

Table 4
Apparent activation energy (E_a) for the glass-rubber (α) relaxation of PEEK-rich phase in PEEK/PES blends. Values were determined from Arrhenius fits to the data in Fig. 12

Blend compositions	E_a (from ε'' peak values) (kJ/mol)	E_a (from tan δ peak values) (kJ/mol)
100/0	798.0	845.5
90/10	839.4	881.3
75/25	865.9	883.1
50/50	801.9	811.9
25/75	799.0	803.3
10/90	–	–
0/100	–	–

4. Conclusions

The phase behaviour and molecular dynamics of PEEK/PES blends have been examined over a wide temperature range using dynamic mechanical and dielectric relaxation studies. Two α-relaxation peaks corresponding to the glass transition of respective homopolymers were observed for each composition using dynamic mechanical analysis. The temperature at which the α-process occurs shows some variation with composition in the blend, signifying the presence of a PEEK-rich and a PES-rich phase. Also the variation in the α-relaxation temperature with composition has been found to vary in a way similar to that observed by differential scanning calorimetry and reported by us previously. From the phase composition of the PEEK-rich and PES-rich phases obtained using Fox equation, it has been shown that PEEK dissolves more in PES than vice-versa. Similar results were obtained from dielectric relaxation studies also except that the α-relaxation of PES was not discernible in the dielectric spectra because of the possible effect of dc conduction and electrode polarization losses. The apparent activation energies of the α-relaxation of both PEEK-rich and PES-rich phase was found to be slightly composition dependent. Also, the relaxation time associated with the mobility of the relaxing species in both PEEK and PES was affected by the presence of the other component in the blend. These observations imply that the dynamical environment for the motional units involving the α-relaxation in PEEK and PES are influenced in the blend. The cause of this effect is probably some molecular interactions that result in a limited segmental mixing between the two homopolymers.

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