

Phase behaviour of ternary blends of poly(ethylene naphthalate), poly(ether imide) and poly(ether ether ketone)

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The phase behaviour of melt mixed binary and ternary blends of PEN, PEI and PEEK were investigated using differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (DMTA) techniques. Both PEN/PEI and PEN/PEEK binary blends exhibit single glass transition temperatures (T_g s) in full composition range and PEN and PEEK were found to be immiscible particularly at mid-concentration range. When PEI is added to the immiscible PEN/PEEK system, first the blends form two separate PEN-rich and PEEK-rich phases below about 40% PEI concentration, and above this concentration, these three homopolymers form a miscible phase in the amorphous state exhibiting a single T_g . Based on the d.s.c. and DMTA results, an approximate ternary phase diagram is drawn. Three component Fox equations were found to describe the T_g s of the ternary blends in the miscible regions quite well. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: phase behaviour; ternary blends; thermal investigations)

INTRODUCTION

Ternary blends are gaining an important share in the field of polymer property diversification through blending. In the first systematic study on ternary polymer blends in 1977¹, the addition of poly(vinylidene fluoride) (PVF₂) to the immiscible pair poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) was reported. Since then, the list of ternaries investigated has been considerably enlarged. In these blends, generally a third component, either a homopolymer or copolymer, is added to an immiscible pair and miscibility is achieved in cases where this third component is miscible with each of the other polymers and/or can improve the adhesion between them by the modification of the interface properties. Besides experimental investigations, researchers studied the thermodynamics of the phase behaviour of ternary blends^{2–5} using Flory–Huggins theory or the lattice fluid theory of Sanchez and Lacombe.

The main purpose of this study is to investigate the miscibility of three high performance thermoplastics, PEN, PEI and PEEK, in order to develop candidate ternary blends that exhibit clarity and high T_g , while maintaining strain induced crystallizability. This deformation behaviour is the subject of a companion paper⁶. The binary blends of PEI/PEEK^{7–12} and PEN/PEI¹³ have already been reported to be completely miscible in their amorphous state over the whole composition range.

In this paper, the phase behaviour of PEN/PEEK and PEN/PEI/PEEK blends will be reported based on differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (DMTA) techniques. Although the T_g is subject to variations related to preparation procedures, the sample preparation procedures were kept constant in all

samples in order to minimize such behaviour. In this paper we also estimate the binary interaction parameters for PEN/PEI and PEN/PEEK blends using Flory–Huggins theory.

EXPERIMENTAL

Materials

Materials used in this study were poly(ethylene 2, 6-naphthalate), (PEN) (Eastman Kodak), Poly(ether imide), (PEI) (GE)(ULTEM 1000) and poly(ether ether ketone), (PEEK) (ICI) (381G). The thermal properties and the molecular weight data are summarized in *Tables 1* and *2*.

Preparation of the blends

In order to determine the miscibility of PEN/PEI/PEEK blends, 36 compositions on the ternary diagram were chosen as shown in *Figure 1* together with their numbered designations. Prior to processing, the pellets were dried in a vacuum oven at 140°C for 1 day. Like all polyesters, PEN is sensitive to the presence of moisture in its molten state. For this reason the ‘mini-max moulder’, used for mixing small quantities of specimens, was placed inside a ‘glove-box’ purged with dry nitrogen gas to minimize this effect. The three polymers were mixed at temperatures varying between 340 and 345°C. In order to limit the exposure time of PEN to this temperature, first PEEK and PEI was blended and in a subsequent stage PEN was added to this mixture until complete homogenization. After mixing was completed, the mixture was extruded through the die located at the bottom of this mixer into the ice-water bath in order to obtain amorphous samples.

In addition, three compositions 82.5/17.5, 70/30 and 50/50 of PEN/PEEK binary blends were prepared using a JSW co-rotating twin screw extruder, in order to compare the

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Table 1 Thermal properties of PEN, PEI, PEEK. (Heating rate: 10°C min⁻¹)

Material	T_g (°C)	T_m (°C)	T_m° (°C)	T_{cc} (°C)
PEN	123	258	337	223
PEI	218			
PEEK	146	340	384	173

T_g , Glass transition temperature; T_m , melting temperature; T_m° , equilibrium melting temperature; T_{cc} , cold crystallization temperature

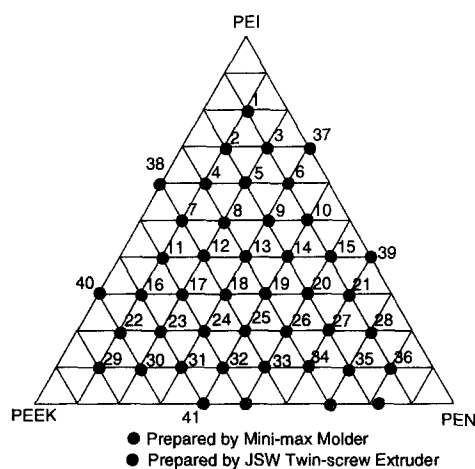
Table 2 Molecular weight data of PEN, PEI, PEEK

Material	\bar{M}_n	\bar{M}_w	\bar{M}_z
PEN ^a	12 500	42 000	66 000
PEI ^b	16 750	40 350	67 350
PEEK ^c	15 000	35 000	

\bar{M}_n , Number-average molecular weight; \bar{M}_w , weight-average molecular weight; \bar{M}_z , z-average molecular weight

^aSupplied by Eastman Kodak laboratories

^cSupplied by Victrex (distributor)

**Figure 1** Representation of the compositions of ternary blends on a ternary diagram

results on blends prepared by the two blending techniques used in this work.

Thermal behaviour

Thermal analysis of binary and ternary blends was performed with a DuPont DSC 9900 instrument. The machine was first calibrated with an indium standard. A sample size of 10 ± 1 mg was used. In the case of binary blends, in order to eliminate the traces of pre-existing crystalline residue, the blends were kept at temperatures above the equilibrium melting temperature (T_m°) for about 5 min prior to rapid quenching into the glassy state. These samples were then used for determination of T_g in the d.s.c. This procedure could not be applied to ternary blends, due to rapid degradation of PEN at T_m° of PEEK. For these samples, the quenched samples were first heated past the T_g region to 150°C, and then were rapidly quenched and rescanned. This ensured accurate determination of T_g without the spurious peaks that occasionally occur near the T_g . For all the experiments reported in this paper, the heating rate was kept constant at 10°C min⁻¹.

Dynamic mechanical thermal analysis

DMTA measurements were performed using Polymer

Laboratories (PL) DMTA equipment in bending mode. A rectangular 0.7 cm × 2 cm × 0.05 cm piece of the film was placed inbetween two thin metal sheets cut to the dimensions of the sample and the sandwiched sample was mounted on the cantilever frame from both ends. All experiments were performed with a strain of 4% and a frequency of 1 Hz. Storage and loss moduli (E' and E'') were recorded with a heating rate of 4° min⁻¹. The temperature at which the maximum in the $\tan \delta$ ($\tan \delta = E''/E'$) versus temperature curve occurred was taken as the T_g .

Scanning electron microscopy

To investigate the effect of the PEI concentration on the average particle size of the dispersed phase of the immiscible blends, scanning electron microscopy (SEM) pictures of PEN/PEEK (70/30) and two selected compositions in the two-phase regions were taken. For this purpose, the fracture surface of the strands obtained from the mini-max moulder was coated with gold using a Sputter Coater device model ISI-5400, and the pictures were taken with a SEM Hitachi S-2150 under 1000× magnification.

Estimation of interaction parameters for PEN/PEI and PEN/PEEK blends

After the phase behaviour of the prepared blends was determined by d.s.c. and DMTA techniques, we investigated the interaction parameters for PEN/PEI and PEEK/PEN blends using the equations for the spinodal condition based on Flory–Huggins theory. The Flory–Huggins theory for the free energy of mixing (ΔG_m) of three monodisperse homopolymers may be given in terms of volume fractions (ϕ_i) as

$$\tilde{G} = \left(\frac{\Delta G_m}{kT} \right) \left(\frac{v_0}{V} \right) \quad (1)$$

$$\tilde{G} = \left(\frac{\phi_1}{y_1} \right) \ln \phi_1 + \left(\frac{\phi_2}{y_2} \right) \ln \phi_2 + \left(\frac{\phi_3}{y_3} \right) \ln \phi_3 + \chi_{12} \phi_1 \phi_2 + \chi_{23} \phi_2 \phi_3 + \chi_{31} \phi_3 \phi_1 \quad (2)$$

where v_0 is the volume per lattice site, V is the mixture volume, y_i is the ratio of the volume of polymer i to the reference volume (v_0) and χ_{ij} is the interaction parameter between the segments of polymers i and j , which is assumed to be composition-independent. For a mixture to be a single phase, the requirement that $\Delta G_m < 0$ must be fulfilled. The boundary condition for the spinodal is given as

$$\frac{\partial^2 \Delta G_m}{\partial \phi_i^2} = 0 \quad (3)$$

$$y_1 \phi_1 + y_2 \phi_2 + y_3 \phi_3 - 2[y_1 y_2 (\chi_{12} + \chi_{21}) \phi_1 \phi_2 + y_2 y_3 (\chi_{23} + \chi_{32}) \phi_2 \phi_3 + y_3 y_1 (\chi_{31} + \chi_{13}) \phi_1 \phi_3] + 4y_1 y_2 y_3 (\chi_{12} \chi_{23} + \chi_{23} \chi_{31} + \chi_{31} \chi_{12}) \phi_1 \phi_2 \phi_3 = 0 \quad (4)$$

where

$$\chi_i = (\chi_{ij} + \chi_{ik} - \chi_{jk})/2 \quad (5)$$

Additionally equation of continuity is given as:

$$\phi_1 + \phi_2 + \phi_3 = 1 \quad (6)$$

After arrangements of equations (5) and (6) a second order equation dependent in ϕ_1 can be obtained:

$$a\phi_1^2 + b\phi_1 + c = 0 \quad (7)$$

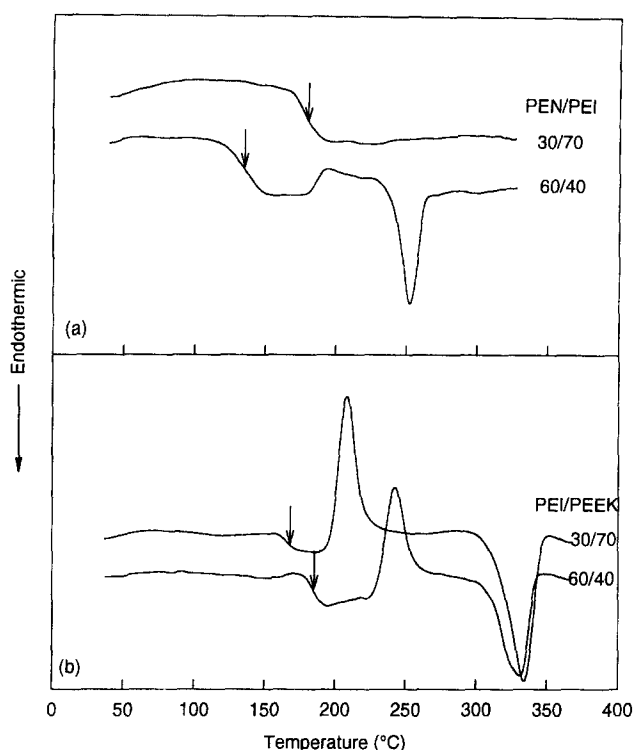


Figure 2 D.s.c. thermograms of (a) PEN/PEI (b) PEI/PEEK blends. Heating rate = $10^{\circ}\text{C min}^{-1}$

where

$$a = s_{12} - s_{123}\phi_3 \quad (8)$$

$$b = y_1 - y_2 - s_{12}(1 - \phi_3) - s_{13}\phi_3 + s_{23}\phi_3 + s_{123}\phi_3(1 - \phi_3) \quad (9)$$

$$c = y_2(1 - \phi_3) + y_3\phi_3 - s_{23}\phi_3(1 - \phi_3) \quad (10)$$

where

$$s_{12} = 2y_1y_2(\chi_1 + \chi_2) \quad (11)$$

$$s_{23} = 2y_2y_3(\chi_2 + \chi_3) \quad (12)$$

$$s_{13} = 2y_1y_3(\chi_1 + \chi_3) \quad (13)$$

$$s_{123} = 4y_1y_2y_3(\chi_1\chi_2 + \chi_2\chi_3 + \chi_1\chi_3) \quad (14)$$

By varying one of the volume fractions, the other two volume fractions can be obtained from equations (7)–(14) combined with equations (5) and (6).

The parameters that are needed for the solution of these equations are y_i and the binary interaction parameters χ_{ij} .

RESULTS

Binary blends

PEN/PEI blends were studied previously by Kim¹³. This blend pair was found to be miscible over the whole composition range although ΔT_g , which describes the breadth of the glass transition region, increases at the mid-concentration levels. Similarly the phase behaviour of PEI/PEEK blends was investigated^{11,8} and they were found to be miscible in the amorphous state over the whole composition range; the variation of T_g with composition was found to be nearly linear with the slightly negative deviation expected from a good miscible system¹⁴. In both

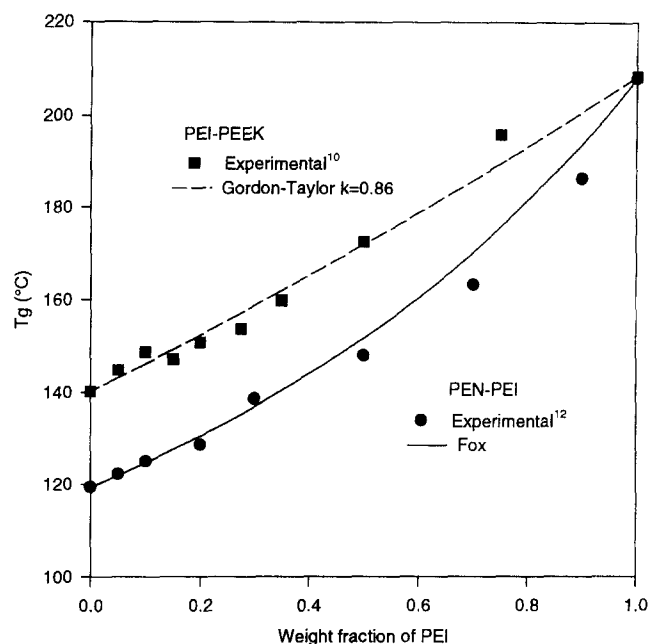


Figure 3 The change of the T_g s of PEN/PEI and PEI/PEEK blends with PEI concentration

cases, the miscibility of the blends was judged based on the existence of a single T_g . It has been suggested that the breadth of this transition region is indicative of increased levels of local concentration fluctuations that can be considered micro-heterogeneities^{11,15}, the blends exhibiting large values tend towards immiscibility. As shown in Figure 2, both the PEN/PEI and PEEK/PEI exhibit single glass transition regions of varying breadths. The PEN/PEI pair exhibit larger ΔT_g values. This polymer pair becomes non-crystallizable during the d.s.c. scan when the PEN concentrations drop below about 60–70%¹³ as a result of dilution effect. Chen and Porter also observed the increase of 'T_g width' at intermediate concentrations in solution blended PEEK/PEI blends, behaviour similar to that of PEN/PEI binary blends.

The T_g versus composition data is best correlated by the Fox equation¹³ for PEN/PEI blends (Figure 3).

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

where w_i is the weight fraction and T_{gi} is the glass transition temperature of component i .

On the other hand, the composition effect on T_g of PEI/PEEK blends follow Gordon-Taylor equation (Figure 3)

$$T_g = (T_{g1}w_1 + kT_{g2}w_2)/(w_1 + kw_2)$$

with the value of 0.86 for constant k ¹⁰. It should be noted that the negative deviation from linearity is larger in the PEN/PEI pair as compared to the PEEK/PEI pair indicating lesser affinity between these two polymers as compared to the PEEK/PEI pair¹⁴.

Since PEN/PEI and PEEK/PEI binary blends were extensively studied in the literature, no further investigation was performed on these blends.

We then concentrated on the phase behaviour of the remaining binary pair, PEN/PEEK. As indicated earlier, we prepared two sets of blends of series of identical composition using the mini-max moulder and a JSW twin screw extruder. The d.s.c. scans of binary blends of PEN/PEEK exhibit two T_g s as detected by d.s.c. (Figure 4). The mixing method does not have any effect on these results. These

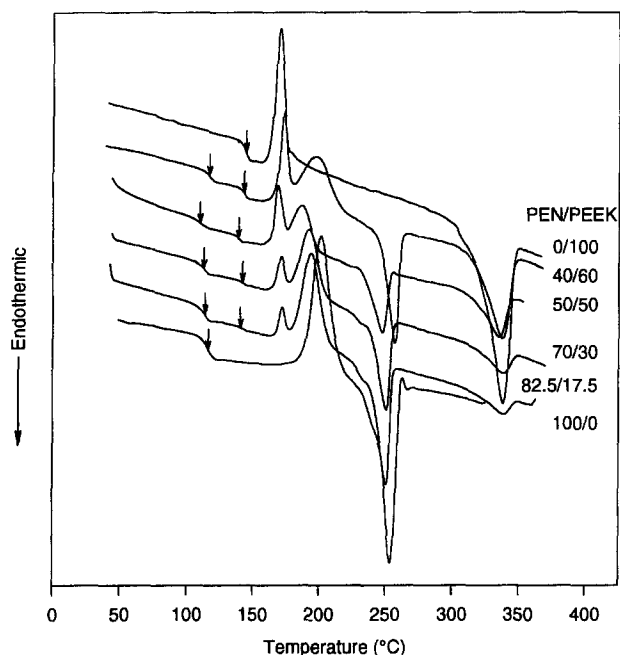


Figure 4 D.s.c. thermograms of PEN/PEEK blends. Heating rate: 10°C min⁻¹

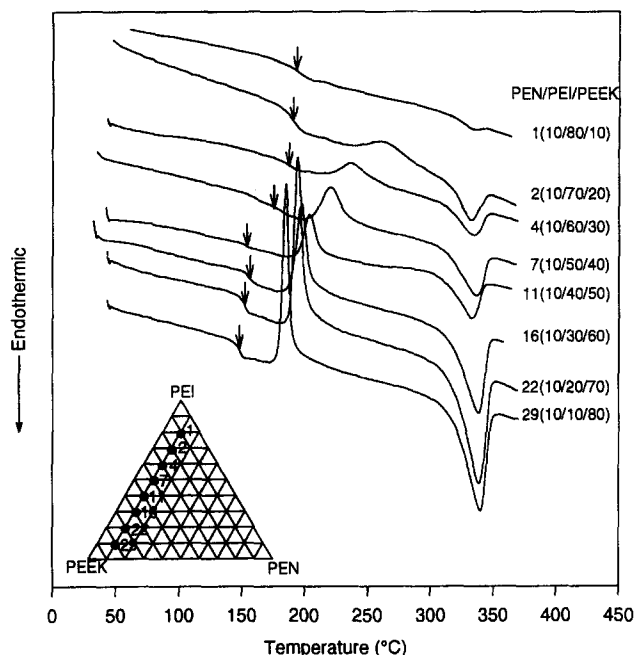


Figure 5 D.s.c. thermograms of some selected compositions of PEN/PEI/PEEK blends (10% PEN). Heating rate: 10°C min⁻¹

scans also show two cold crystallization (T_{cc}) and two melting (T_m) peaks. The lower T_{cc} and the higher T_m correspond to PEEK crystallization and melting respectively, and the remaining peaks correspond to those of PEN. Table 3 shows the dependence of T_g of the two phases on the blend composition. Usually, in a blend, when the original T_g s of each polymer shift towards that of the other polymer, partial miscibility is suggested and each coexisting phase is a mixture of two polymers. In our case, both T_g s do not change significantly with composition and the lower T_g is very close to the T_g of PEN and the higher T_g to that of PEEK. This is indicative of two distinct phases, where each phase consists of almost pure homopolymer. Even if PEN

Table 3 Glass transition of PEN-rich and PEEK-rich phase in PEN/PEEK blend

%PEN in the blend	T_g of PEN-rich phase (°C)	T_g of PEEK-rich phase (°C)
40	116.36	143.30
50	111.20	138.85
70	111.84	143.68
82.5	113.47	143.26

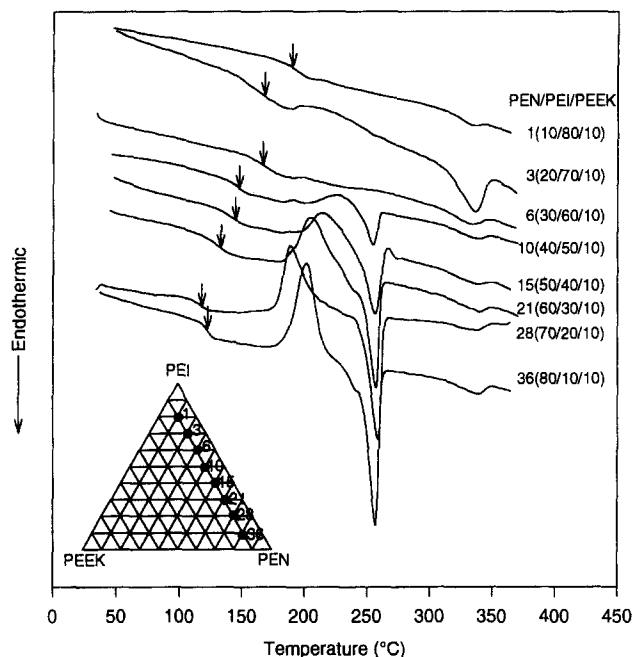


Figure 6 D.s.c. thermograms of some selected compositions of PEN/PEI/PEEK blends (10% PEEK). Heating rate: 10°C min⁻¹

phase or PEEK phase contains small amount of the other polymer, this is not detectable with the d.s.c. instrument in the compositions investigated in this research. It should be noted that the binary blends of PEN/PEEK containing less than 40% PEN and more than 80% PEN were not investigated, as they are beyond the scope of interest in this research.

Ternary blends

Thermal behaviour and miscibility. The d.s.c. curves of ternary PEN/PEI/PEEK blends are shown in Figures 5–8. Figure 5 shows the blends containing 10% PEN with varying proportions of PEI and PEEK indicated graphically by the dark symbols and their numbered designations in the ternary diagram.

D.s.c. thermograms show that although PEEK readily crystallizes during the d.s.c. scan for all the blend compositions even in the blends containing only 10% PEEK (Figure 6), PEN remains noncrystallizable for the blends containing 10% (Figure 5), 20% and some containing 30% PEN (1,3 and 6 in Figure 6). Although PEEK has higher T_g (145°C) it crystallizes from the glassy state at a lower temperature ($T_{cc} \sim 170^\circ\text{C}$) as compared to PEN ($T_g = 120^\circ\text{C}$ and $T_{cc} \sim 190^\circ\text{C}$), indicating that its ability to crystallize is faster, despite the fact that it generally exhibits higher viscosities in this temperature range^{16–18}. Figure 7 shows the d.s.c. curves of the samples containing 10% PEI. Except at two extreme ends (29,30,36) these blends exhibit two T_g s. We also note that when the two T_g s are observed,

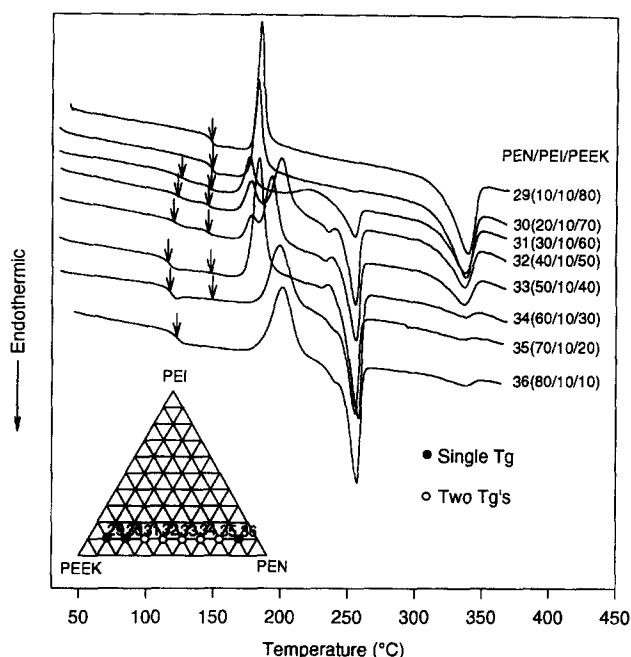


Figure 7 D.s.c. thermograms of some selected compositions of PEN/PEI/PEEK blends (10% PEI). Heating rate: $10^{\circ}\text{C min}^{-1}$

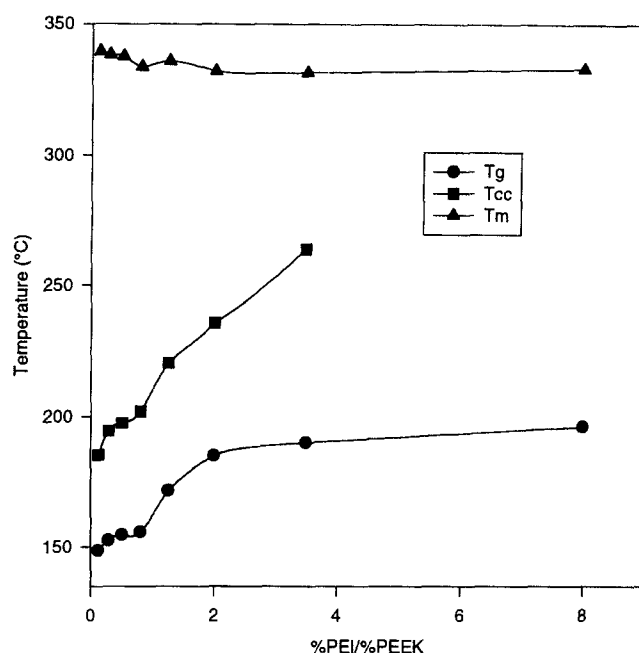


Figure 9 The dependence of T_g , T_{cc} and T_m with PEI/PEEK fraction for the blends containing 10% PEN

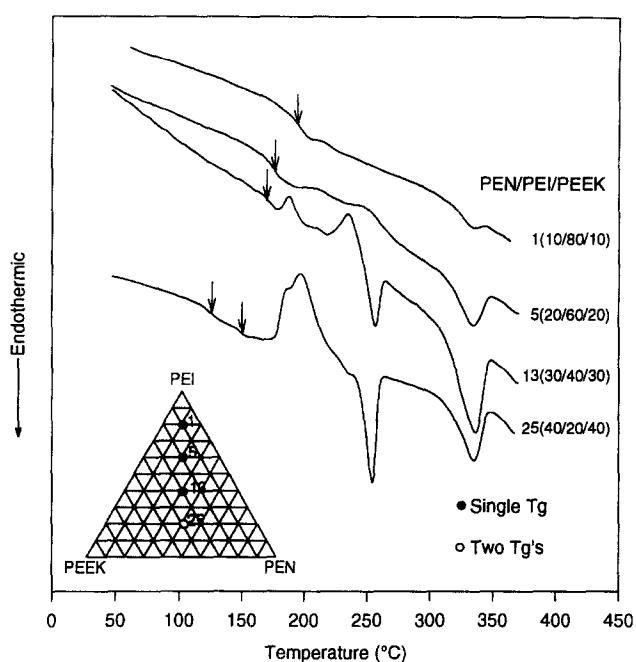


Figure 8 D.s.c. thermograms of some selected compositions of PEN/PEI/PEEK blends (wt% PEN/wt% PEEK = 1). Heating rate: $10^{\circ}\text{C min}^{-1}$

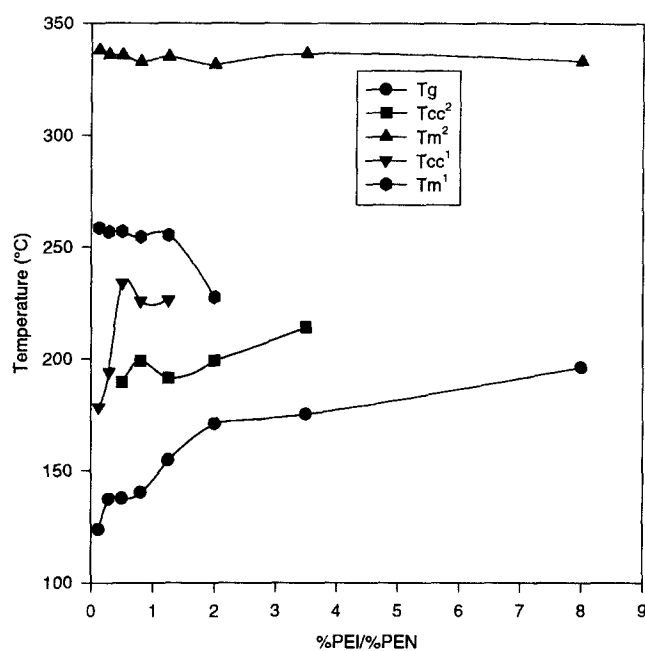


Figure 10 The dependence of T_g , T_{cc} and T_m with PEI/PEEK fraction for the blends containing 10% PEEK

two distinct cold crystallization peaks also appear confirming that PEN and PEEK are already separated into two distinct amorphous domains prior to the d.s.c. scan. They crystallize at their respected temperatures ($\sim 170^{\circ}\text{C}$ for PEEK and $\sim 190^{\circ}\text{C}$ for PEN) during the d.s.c. scan. Figure 8 shows the d.s.c. scans of blends containing equal proportion of PEN and PEEK with decreasing fraction of PEI in blends 1, 5, 13 and 25. The blends containing less than about 40% PEI exhibit two T_g 's, clearly demonstrating that the two phase region in the phase diagram extends to these levels.

It can be seen from Figure 9 that when the PEN concentration is kept constant, increasing PEI to PEEK ratio

increases the T_g of the blend $T_{cc}(\text{PEEK})$ and decreases $T_m(\text{PEEK})$. Similar observations are made for other blend compositions. In the case of binary blends containing one crystallizable and one amorphous component, the increase in cold crystallization temperature with increasing concentration of the non-crystallizable component has been attributed to the reduction of the crystallization rate as a result of the dilution effect¹⁹, as well as to the increase in viscosity of the surroundings of the growing front, particularly in those blend pairs in which the non-crystallizable component exhibits the higher T_g . In the ternary blends, we found that both $T_{cc}(\text{PEN})$ and $T_{cc}(\text{PEEK})$ increase with the increase of PEI fraction (See Figures 9

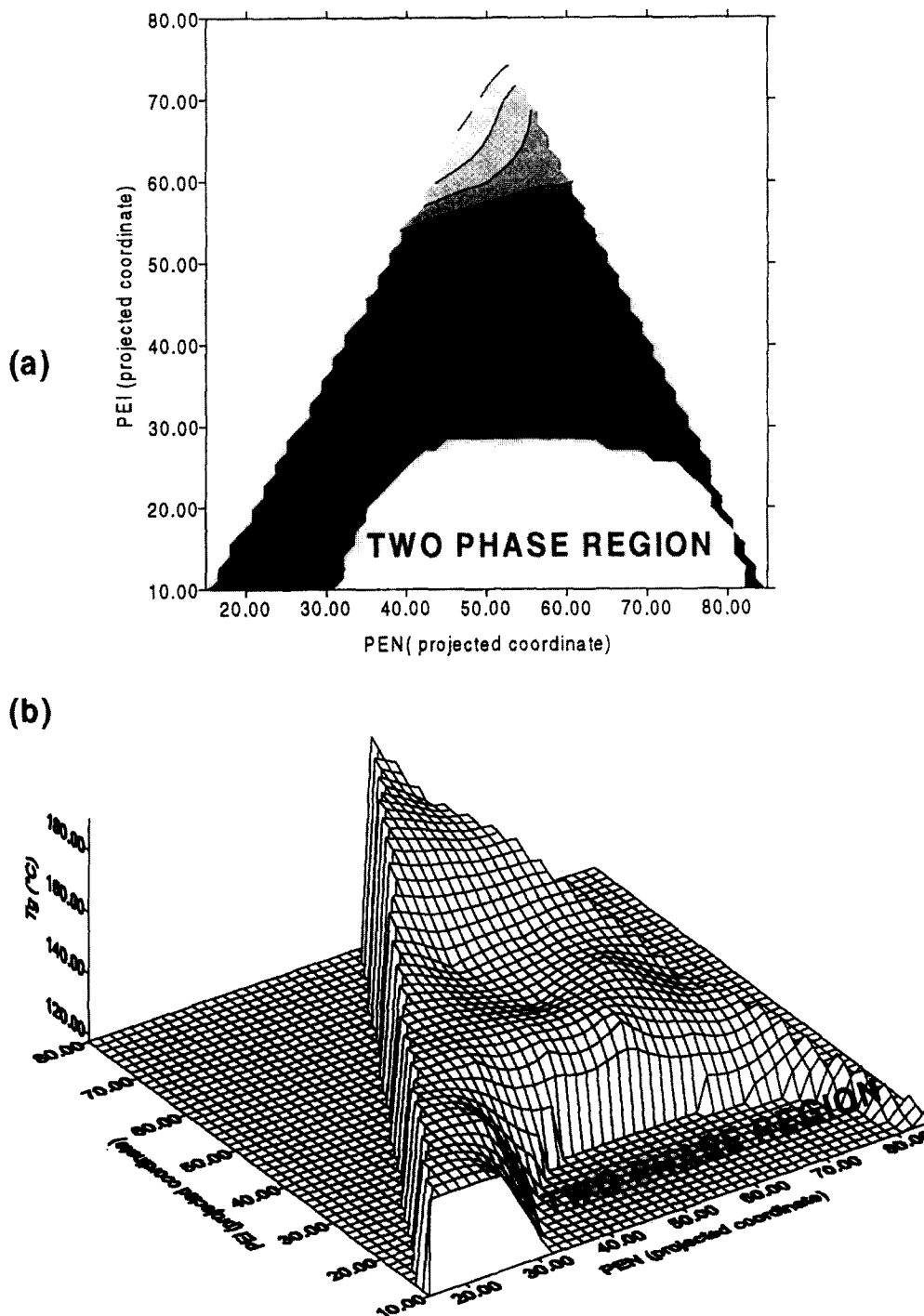


Figure 11 Representation of the T_g of miscible ternary blends: (a) contour plot; (b) three-dimensional view

and 10) indicating that the crystallization of PEN and PEEK are hindered by PEI, due to the increases in the overall T_g of the mixture caused by molecular level mixing with the stiffer PEI chains.

Figure 11 shows the variation of T_g with composition on the ternary diagram for all 36 compositions. Due to the high T_g of PEI, the T_g of the miscible blends is higher in the region closer to the PEI corner of the diagram. In the miscible regions one can fit roughly a flat surface over these data. This will be discussed further below.

In our studies, we used T_g as criterion for the miscibility of ternary blends. Although we observe a region in the ternary diagram where the blends exhibit two T_g s indicating immiscibility, the phase behaviour is far from simple. As shown in Figure 12, the addition of PEI into the blend

causes simultaneous increase in the two observed T_g s. This indicates that PEI mixes well with both PEEK and PEN in this region rather than remaining in its own distinct third phase. Beyond 40% PEI concentration, the three-component system exhibits essentially one phase. If we assume that PEI distributes itself equally in two phases namely PEN-rich phase and PEEK-rich phase where the other component is only PEI, the calculation of the T_g of two components and three components phases using Fox equation gives the lines shown in Figure 13. When the experimental data points are compared with the theoretical calculations, we observe that the higher T_g phase is closer to the PEEK-rich phase and the lower T_g phase is closer to the PEN-rich phase in the multi-phase blends containing less than 40% PEI. Those blends exhibiting single T_g s above 40% PEI concentration follow

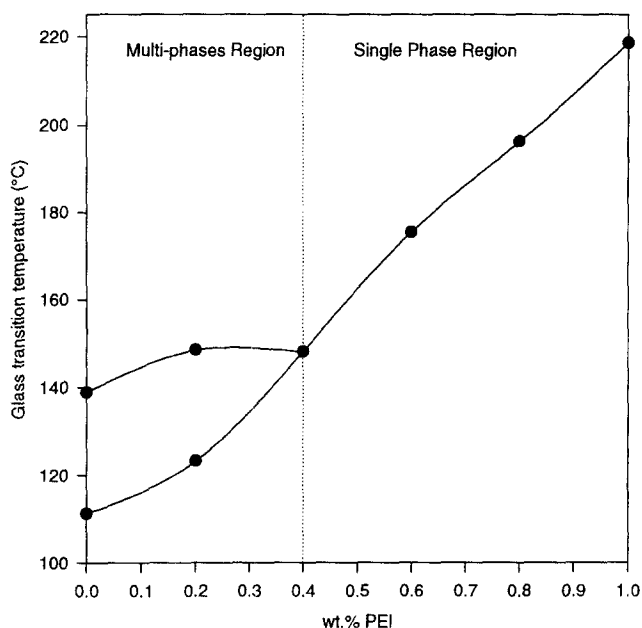


Figure 12 The change of the T_g of the blend with PEI concentration (wt% PEN/wt% PEEK = 1)

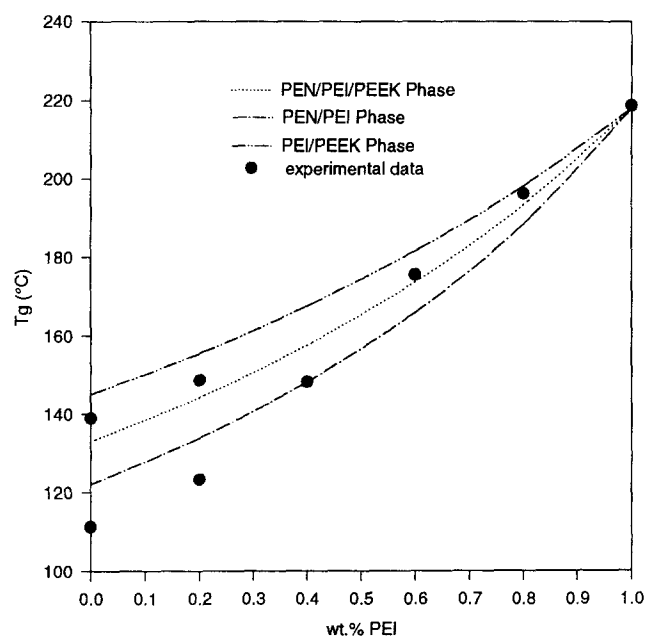


Figure 13 Comparison of the experimental T_g s with calculated T_g s of possible phases in the ternary blends

the theoretically calculated T_g s of a single phase region. This indicates that PEI in this ternary system acts as a common solvent for PEN and PEEK.

This is also observed from SEM pictures, where the addition of PEI to the immiscible blend of PEN and PEEK reduces the average particle size of the dispersed phase. Well separated domains of PEN/PEEK (70/30) blend can be observed in Figure 14. Since PEN concentration is much higher than PEEK concentration, PEN is expected to be the continuous phase in this particular blend. The addition of 10% PEI causes the domain sizes to decrease (See Figure 15), and further increase of PEI concentration to 20% causes the disappearance of the distinct domain boundaries, resulting in homogenization of the blend. (See Figure 16).



Figure 14 SEM micrograph on fracture surface of blend 70/0/30 PEN/PEI/PEEK showing ball-like phase separated regions of PEEK



Figure 15 SEM micrograph on fracture surface of blend 60/10/30 PEN/PEI/PEEK

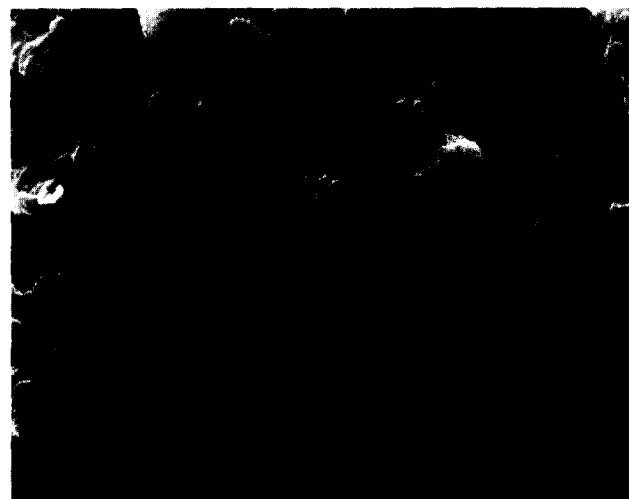


Figure 16 SEM micrograph on fracture surface of blend 50/20/30 PEN/PEI/PEEK

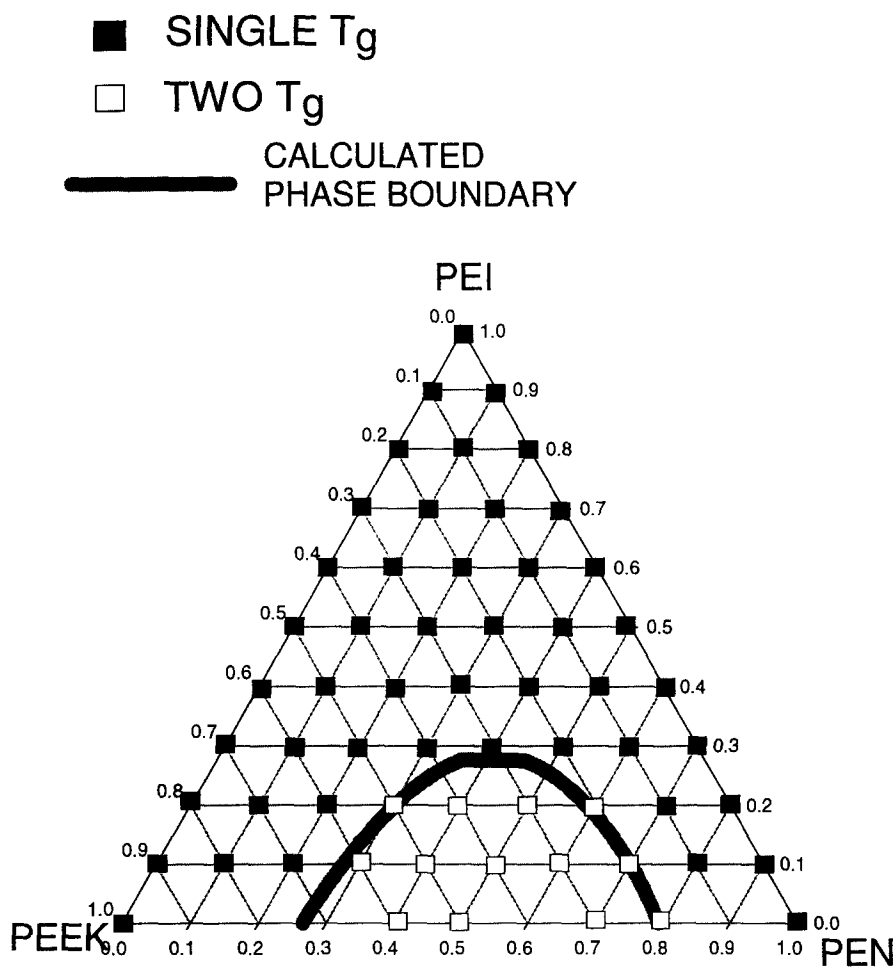


Figure 17 Ternary phase diagram (weight fraction) of blends indicating experimentally determined one or two T_g (s) and calculated phase boundary based on Flory-Huggins theory

Figure 21 compares the experimental T_g s of miscible blends with the ones calculated theoretically using three-component Fox equations. Among the existing theories, Fox equation was found to best correlate the dependence of T_g with the blend composition.

However, the existence of a single T_g does not necessarily imply the presence of a single phase. As shown in Figure 13, the T_g s of PEN-rich and PEEK-rich phases are very close to each other ($\leq 30^\circ\text{C}$). It is quite possible that the T_g regions of two phases overlap and become undetectable within the sensitivity limits of the d.s.c. instrument.

From the d.s.c. results, it is possible to establish a ternary phase diagram which shows the region of compositions with a single T_g or a single phase region (filled symbols), and the region of compositions with two T_g s or a biphasic region (unfilled symbols) (Figure 17).

Dynamic mechanical thermal analysis

The T_g was evaluated at the point where $\tan\delta$ exhibits a maximum. Figure 18 shows the dynamic mechanical response of PEN, PEI and PEEK. The curves are vertically shifted for clarity. Also, it should be noted that this data represents relative values since the samples were sandwiched in between two thin metals. The reason for using these metal sheets was to prevent the buckling of the sample above the T_g and extend the measurable range at high temperatures. This sandwich arrangement certainly affects the accuracy of E' and E'' , but it allows us to look into

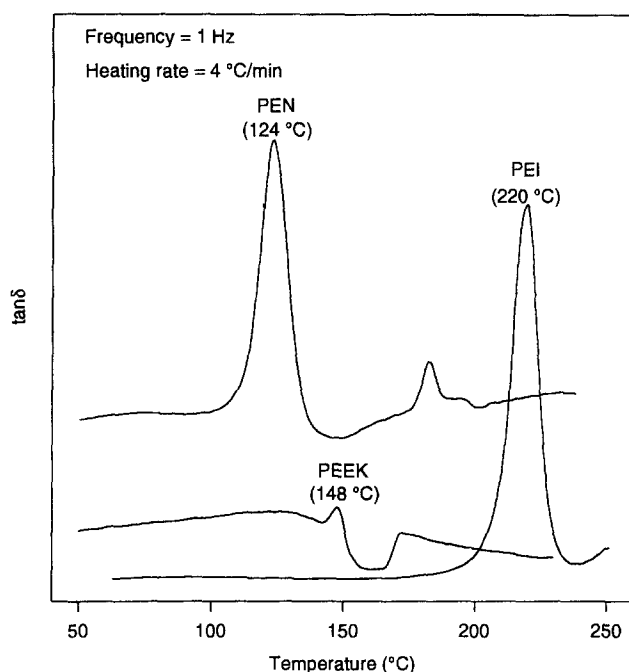


Figure 18 Temperature dependence of the dynamic mechanical loss tangents of PEN, PEI and PEEK at 1 Hz

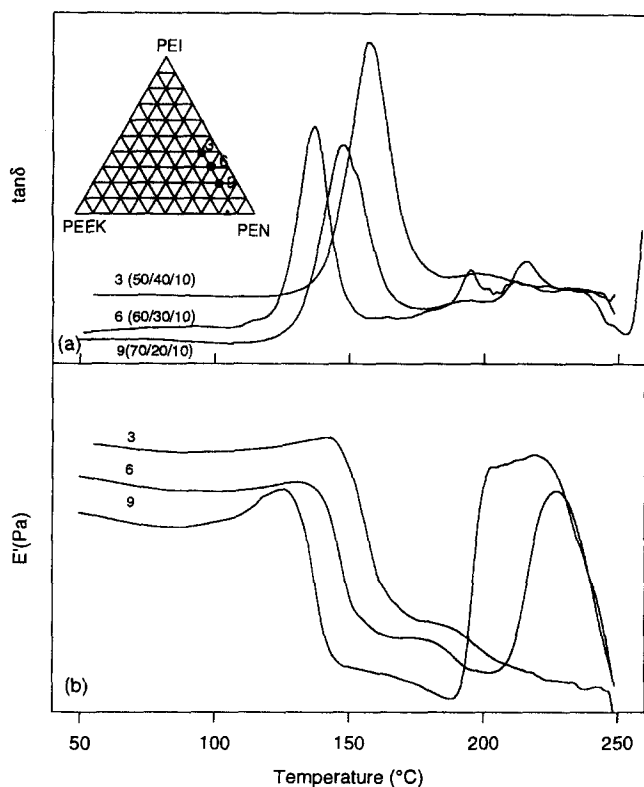


Figure 19 A comparison of 1 Hz dynamic mechanical (a) loss tangents and (b) storage moduli of PEN/PEI/PEEK blends containing 10% PEEK

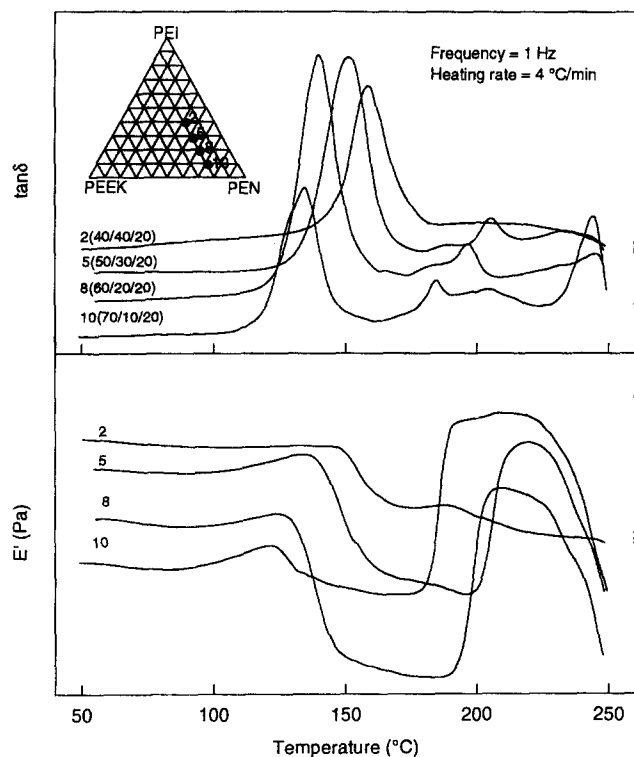


Figure 20 A comparison of 1 Hz dynamic mechanical (a) loss tangents and (b) storage moduli of PEN/PEI/PEEK blends containing 20% PEEK

transitions at higher temperatures. The sharp peaks on $\tan\delta$ versus temperature curves reflect segmental or micro-Brownian motion associated with the glass-rubber relaxation. The maxima for PEN, PEEK and PEI are observed at 124, 148 and 220°C respectively. These values

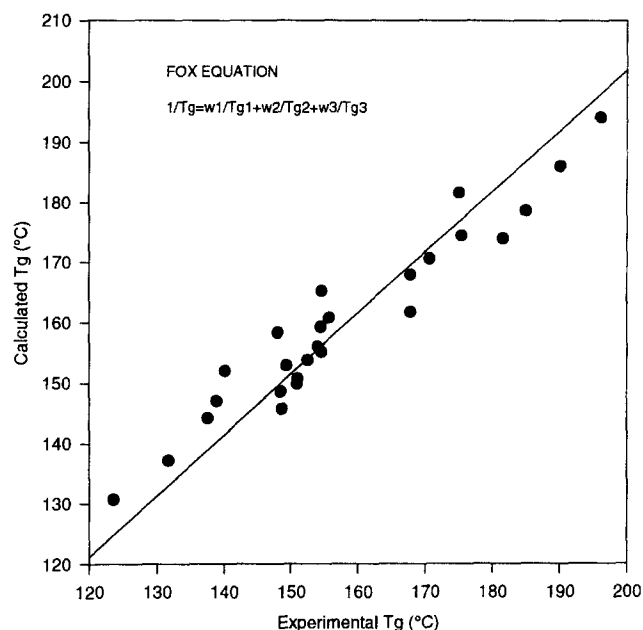


Figure 21 A comparison of the glass transitions of selected ternary blends found from DMTA measurements with those calculated by the Fox equation

Table 4 Comparison of the T_g s found from d.s.c. with those found from DMTA

Composition	T_g (DMTA) (°C)	T_g (d.s.c.)(°C)
1(30/40/30)	159	154
2(40/40/20)	159	153
3(50/40/10)	157	152
4(40/30/30)	153	148
5(50/30/20)	150	147
6(60/30/10)	149	144
9(70/20/10)	137	D128

are about 1–2°C higher than the T_g s found by d.s.c. (see *Table 1*, second column), which are within the experimental error.

Figures 19 and 20 show the dynamic mechanical responses of some of the ternary blends. In all of these blends only a single peak appears at a temperature which is inbetween the T_g s of three polymers. Although DMTA supported the d.s.c. results for most compositions, it was not able to detect the two transitions associated with PEN-rich and PEEK-rich phases. This may be due to the fact that the T_g s of these phases are close to each other and the related peaks overlap. The peaks which appear above the T_g are cold crystallization peaks. It can be seen from the storage modulus versus temperature curves that there is an increase in modulus due to the crystallization process. Except for compositions 8 and 10, the DMTA results agree well with those of d.s.c. where a single T_g was observed for these compositions. *Table 4* compares the T_g s found from DMTA with the T_g s found from d.s.c., and *Figure 21* compares the experimental DMTA T_g s with the T_g s calculated from the three-component Fox equation.

Estimation of interaction parameters

Among the interaction parameters of binary blends of PEN/PEI/PEEK ternary system, only the interaction parameter of PEI/PEEK blend is known from the open literature. This value was calculated by Chen and Porter¹² to be $\chi(\text{PEI/PEEK}) = -0.4$, using the melting point depression of PEEK

Table 5 Molecular parameters used for calculation of phase diagram

Polymer	M_{unit} (g mol ⁻¹ , weight of one repeat unit)	V_r (cm ³ mol ⁻¹ , volume of one repeat unit)	V_i (cm ³ mol ⁻¹ , polymer volume)	y_i^a	ρ (g cm ⁻³)	χ^b (segmental interaction parameter, Scott–Tampa)
PEN	242.23	182.82	9433.96	52	1.325	
PEI	592.00	466.14	13188.98	72	1.27	
PEEK	288.00	228.03	11876.48	65	1.263	-0.0139 ¹¹

$$^a y_i = \frac{\left[\frac{\bar{M}_n}{\rho} \right]_i}{V_r}$$

$$^b \xi_{ij}(\text{Flory}) = y_i \chi_{ij} \text{ (Scott–Tampa)}$$

in PEI/PEEK blends. It was shown in Section 2 that these three interaction parameters are related by the equations of spinodal boundary conditions using Flory–Huggins theory. With *a priori* knowledge of these three parameters, one can estimate the phase boundary theoretically. But since we do not know all of these parameters we could not apply this approach to our system. Instead, we estimated the unknown parameters $\chi(\text{PEN/PEI})$ and $\chi(\text{PEI/PEEK})$ by fitting the calculated phase boundary with the experimentally determined phase boundary. The degree of polymerization for each homopolymer was calculated from the ratio of the weight-average molecular weight to the molecular weight of the repeating unit. It should be pointed out that experimental phase boundary is not a definite separation between the single phase region and the multi-phase region, and as we discuss in great detail above it represents a diffuse boundary. We can see from *Figure 17* that the shape of the boundary is asymmetrical and skewed towards the 100%PEN corner in the ternary diagram. This shows that affinity of the PEEK/PEI pair is larger than the PEN/PEI pair.

Assuming the literature value for $\chi(\text{PEEK/PEI}) = -0.0138$ ¹¹ to be correct for our system, we fitted the experimentally determined phase diagram through iterative computer program. This calculation resulted a value $\chi(\text{PEI/PEN}) = -0.001$ and a value of $\chi(\text{PEEK/PEN}) = 0.048$ for best fit. The molecular parameters used for this calculation process are given in *Table 5*. The repeat unit volume of PEN—being the smallest—was chosen as the reference volume of the three polymers indicated in *Table 5*.

CONCLUSIONS

Based on the d.s.c. and DTMA analysis we established an approximate phase diagram for PEN/PEI/PEEK ternary blends. PEEK and PEN are immiscible and the addition of PEI increases the miscibility. The blends containing less than about 40% PEI exhibit 'multi-phase' behaviour, as PEI gets incorporated into both PEEK- and PEN-rich domains, whose T_g 's vary with the PEI fraction in the medium. This is particularly true for compositions containing equal or near equal proportions of PEN and PEEK. Based on our

experimental results, we estimated the segmental (Scott–Tampa) interaction parameters as $\chi(\text{PEI/PEN}) = -0.001$ and $\chi(\text{PEEK/PEN}) = 0.048$. In addition, it was shown that the three-component Fox equation predicts the experimental data quite well in the miscible regions of the ternary diagram.

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