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In situ composites based on blends of a poly(ether imide) and thermotropic liquid crystalline polymers under injection moulding conditions

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This paper addresses a number of questions regarding the use of thermotropic liquid crystalline polymers (TLCPs) to reinforce thermoplastics. In particular, we concentrate on the effect of partial miscibility between the matrix and the TLCP, the effect of the properties exhibited by the TLCP itself, and why the properties of the blends pass through a maximum at an intermediate composition. Blends of an immiscible and partially miscible TLCP with a poly(ether imide) (PEI) were injection-moulded into mini-tensile bars and rectangular plaques, and their mechanical properties were evaluated. Interfacial and rheological properties along with morphological and molecular orientation analyses were carried out in order to explain the mechanical properties of the blends. Mechanical tests showed that both the tensile and flexural moduli deviate positively from the law of mixtures and, in addition, both blends showed a maximum in the tensile modulus at 90 wt% TLCP. This is believed to be due to a higher degree of molecular orientation observed for the blends than for the neat TLCPs. It was found that partial miscibility affected more strongly the stiffness of the *in situ* composite, whereas the ultimate properties of the TLCP dominated the ultimate properties of the PEI/TLCP composite.

(Keywords: *in situ* composite; thermotropic liquid crystalline polymers; polymer blends)

INTRODUCTION

The addition of a thermotropic liquid crystalline polymer (TLCP) to a thermoplastic matrix is attractive in at least two ways. First, the TLCP may act as a processing aid by reducing the viscosity of the matrix material, so that materials exhibiting extremely high viscosities may be processed with lower energy expenditure[1-5]. Second, the TLCP, under adequate processing conditions, deforms into elongated fibrils which often reinforce the thermoplastic matrix in a fashion analogous to glass fibres[6]. Enhancement of the mechanical properties of several polymer matrices upon addition of TLCPs has been reported by several research groups[7-14].

One of the most attractive properties of TLCPs is the intrinsic anisotropy of the mesophase, which can be used to create molecular orientation in fabricated articles[15]. One application of such a feature is fibre spinning, in which the orientation in the fibre is created by the elongational flow field prevailing in the spinning line. The effectiveness in orienting a liquid crystalline phase under melt spinning conditions is usually observed in the increase of the elastic modulus as a function of draw ratio[16-18]. For example, in studying the melt spinning of a thermotropic copolyester (Vectra A950), Chung[16] observed that the elastic modulus would increase exponentially with molecular orientation (measured as the Herman's orientation function). He obtained values of elastic modulus for this TLCP as high as 65 GPa, corresponding to a Herman's orientation function of 0.93.

However, in processes such as injection moulding, the effect of flow on the orientation of TLCPs is more complex. Due to the flow kinematics, moulded TLCP parts show a distribution in molecular orientation perpendicular to the principal direction of flow, i.e. the through-thickness direction[19]. The surface (skin) of the part is often formed of highly oriented fibrils, whereas in the centre (core) region, a less oriented TLCP phase is usually found. Because of this, moulded TLCP parts usually show lower values of mechanical properties relative to spun fibres. For instance, injection-moulded tensile bars (ASTM D638 type 5) of Vectra A950 show values of tensile modulus of about 12 GPa[19], which is considerably lower than the value of 65 GPa obtained in fibre spinning[16].

In reinforcing a thermoplastic by the addition of a TLCP, the objective is to deform the dispersed TLCP phase into elongated fibrils that will reinforce the polymeric matrix. However, this is a complex process that will depend primarily on the rheological and interfacial properties of the blend components, the flow

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strength and the volume fraction of the dispersed TLCP phase. Most often, Taylor's theory on the deformation of a Newtonian droplet suspended in a Newtonian medium is used to describe the deformation of a TLCP phase in *in situ* composites[20-22]. According to Taylor[20], under uniform shearing or plane hyperbolic flows, a spherical droplet of initial radius a deforms into a spheroidal form. The shape of the droplet depends on the viscosity ratio of the droplet phase (μ_d) to the medium (μ_m), $\lambda = \mu_d/\mu_m$, and the ratio of the product of the local shear stress and the droplet radius to the interfacial tension, often called the Weber or capillary number. This is defined as $We = (\mu_m \dot{\gamma} a)/\sigma$, where $\dot{\gamma}$ is the shear rate, a is the initial droplet radius and σ is the interfacial tension. When the interfacial tension effect dominates the viscous effect, the deformation parameter D is given by:

$$D = We\frac{19\lambda + 16}{16\lambda + 16} \tag{1}$$

where D is defined as

$$D = \frac{L - B}{L + B} \tag{2}$$

in which L and B are the length and breadth of the deformed droplet, respectively. Experimental data relating the Weber number and viscosity ratio to the droplet deformation phenomena have been reported by several authors[23-26]. According to these studies, a viscosity ratio between 0.1 and 1.0 will favour droplet deformation in simple shear flow conditions.

Dispersion, morphology and adhesion of the component phases, which are greatly affected by interfacial energies, are important in determining the mechanical properties of the blend. For instance, *in situ* composites with improved strength are obtained through enhancement of the interfacial adhesion between the blend components[13]. In addition, interfacial tension determines the wettability and compatibility of the blend components. Thus, determining the interfacial properties of *in situ* composites is of great importance due to their effect on mechanical properties and on the degree of dispersion of the TLCP phase. Interfacial tension studies on seven types of TLCPs in seven different matrices were recently carried out by Meretz *et al.*[27]. By measuring contact angles on the individual solid samples, they were able to calculate differences in polarities and surface tension and interfacial tension of the 49 possible TLCP/matrix combinations. This procedure led them to the selection of polyethylene terephthalate (PET) and a TLCP copolyester based on PET and hydroxybenzoic acid (HBA) as the most compatible TLCP/matrix pair. Minimized polarity and surface tension differences and interfacial tension were the criteria for compatibility. Through morphological studies they observed that very fine dispersions of the PET/HBA TLCP in the PET matrix could be achieved by blending the polymers through a piston mixer. The work of Meretz *et al.*[27] is important because it shows that measurements of the contact angle on solid samples can successfully be used to predict the compatibility of blend components in the melt state.

The mechanical properties of injection-moulded TLCP/polymer blends often show a variation with the TLCP concentration that is above the predictions of the simple rule of mixtures. A synergistic effect in the tensile modulus has been observed for blends of PET[28], poly(ether imide) (PEI)[29,30] and poly(ether ether ketone) (PEEK)[31] with several TLCPs. The reason for such a synergism is most often not completely understood. In addition, some TLCP/polymer blends have shown a maximum in the tensile modulus at intermediate TLCP concentrations[28-33].

Baird and co-workers[32,33] have recently studied blends of PEI with an amorphous and a semicrystalline TLCP. They have shown that the mechanical properties of the *in situ* composites studied were not only affected by the partial miscibility between blend components, but also by the ultimate properties of the TLCP used. They have also observed that, regardless of miscibility, the mechanical properties of the blends (obtained from mini-tensile bars) passed through a maximum at a TLCP concentration of 90 wt%. The observations of Baird and co-workers have shown agreement with earlier observations of Isayev and co-workers[30,31].

In this paper, the work of Baird *et al.*[33] is extended, and additional studies (X-ray diffraction, blend rheology and interfacial energies) are presented which will contribute to the understanding of the mechanical properties exhibited by TLCP/polymer blends. The primary objective of this paper is to determine the contributing factors which lead to the observed maximum in the mechanical properties of TLCP-based *in situ* composites at intermediate compositions. In addition, the effect of partial miscibility on the rheology and interfacial and mechanical properties is also addressed. Morphological and molecular orientation analyses are presented with the intent of explaining the mechanism by which the mechanical properties of these blends are generated during injection moulding.

EXPERIMENTAL

Materials

The matrix material used was a poly(ether imide) (PEI), commercially available as Ultem 1000 from General Electric Plastics. PEI is an amorphous engineering thermoplastic with a glass transition temperature at ~228°C and a processing temperature ranging from 340 to 380°C[4]. The semicrystalline TLCP used was a thermotropic copolyester composed of 73 mol% of *p*-hydroxybenzoic acid and 27 mol% of 2-hydroxy-6-naphthoic acid. This TLCP is commercially available as Vectra A900 from Hoechst-Celanese. Vectra A900 (henceforth referred to as Vectra A) exhibits a glass transition temperature of 105°C, a crystal–mesophase transition at 283°C[34], and a maximum stable processing temperature of 370°C[4]. The amorphous TLCP, supplied by Du Pont, is based on hydroquinone (HQ), terephthalic acid (TA) and other hydroquinone derivatives. This amorphous TLCP, referred to as HX1000, has a glass transition temperature of 185°C[32] and a processing temperature ranging from 290 to 365°C. Proposed chemical structures for these TLCPs may be found elsewhere[35].

Vectra A and HX1000 were selected based upon the following criteria: (1) they have an overlapping processing temperature relative to the engineering thermoplastic matrix used, thus thermal degradation of the TLCP is avoided; (2) HX1000, contrary to Vectra A, is partially miscible with PEI[32]. Thus, by selecting these two TLCPs, the effect of partial miscibility on the structure and properties of the blends may be determined.

Blend preparation and processing

Before blending, pellets of the above materials were dried at 115°C in a convection oven for at least 48 h. The dried pellets of PEI/Vectra A and PEI/HX1000 were then tumbled in a steel container on a weight percent basis. To study the effect of TLCP concentration on the structure and properties of PEI/TLCP blends, the TLCP concentration was increased from zero to 100 wt% in 10 wt% intervals. After dry blending, the mixed pellets were stored in a hermetically sealed container.

The physically mixed pellets were then injection moulded into mini-tensile bars (ASTM D638 type 5) and rectangular plaques (measuring approximately 75 mm × 85 mm × 1.75 mm) using an Arburg 221-55-250 Allrounder Injection Molder. The temperature settings of the injection moulding unit were 330, 345, 360 and 360°C for zones 1, 2 and 3 of the barrel and nozzle, respectively. The injection pressure was set at 7.0 MPa with a holding pressure of 5 MPa. The injection speed was set at a medium range, which gives a volumetric flow rate of $12\,\text{cm}^3\,\text{s}^{-1}$. The mould was held at 110°C and a cooling time of 40 s was used. The processing conditions were kept constant throughout all mouldings.

It is important to point out, however, that the samples were generated through injection moulding alone, without any previous melt blending of the tumbled pellets. Thus, all samples have only undergone the mixing history provided by the plasticating process in the injection moulding unit. It should be emphasized that the effect of mixing history on the structure and properties of TLCP-based *in situ* composites cannot be overlooked. The effect of mixing history on the morphology and mechanical properties displayed by a TLCP/polymer blend can be significant[33]. To some extent, depending on the ratio of viscosities and interfacial tension, mixing improves dispersion of the minor phase component in the blend, and finer structures are often obtained by increasing passes through a single- or twin-screw extruder[32]. However, depending on the TLCP/polymer system, improvements in the mechanical properties are not always observed upon increasing the mixing history[35]. As mixing reduces the dispersed phase particle size, larger hydrodynamic stresses, often not attained during processing, are necessary in order to elongate the droplet into fibrils.

Rheological characterization

Dynamic oscillatory shear viscosity data were obtained by means of a Rheometrics Mechanical Spectrometer (model 800) for all blend compositions as well as for the individual components. The tests were performed in the frequency sweep mode on samples cut from injection-moulded plaques. Parallel plate fixtures were used with a gap between 1.0 and 1.25 mm. The test temperature was set at 360°C, which matches the maximum temperature the samples were exposed to during injection moulding. Strain sweep experiments were carried out on the individual components and on 50/50 wt% blends to determine the limits of their linear viscoelastic behaviour. Within the range of strains investigated, from 0.5 to 14.5%, PEI, PEI/Vectra A 50/50 and PEI/HX1000 50/50 exhibited linear viscoelastic response. Only a small deviation from the linear viscoelastic behaviour was observed for Vectra A and HX1000 at strains > 10%. Hence, all the dynamic data were taken at 5% strain, which is well within the linear viscoelastic behaviour of the materials.

Interfacial tension

Interfacial tension calculations were performed to determine the degree of compatibility between the polymer pairs used. The harmonic mean method[36] of calculating interfacial tension is utilized here to determine the interfacial energy between PEI and Vectra A, and PEI and HX1000. Following Wu[36,37], the interfacial tension between two materials γ_{12} may be estimated according to the equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}}{\gamma_1^{\mathrm{d}} + \gamma_2^{\mathrm{d}}} - \frac{4\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}}{\gamma_1^{\mathrm{p}} + \gamma_2^{\mathrm{p}}} \tag{3}$$

where γ_i is the surface tension of material i ($i = 1, 2$), γ_i^{d} and γ_i^{p} are the dispersive and polar components of the surface tension of material i. Combining the harmonic mean equation of the interfacial tension [equation (3)] with the Young's equation for the contact angle[36] results in:

$$(1 + \cos\Theta)\gamma_{\mathrm{L}} = \frac{4\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}}}{\gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{L}}^{\mathrm{d}}} + \frac{4\gamma_{\mathrm{S}}^{\mathrm{p}}\gamma_{\mathrm{L}}^{\mathrm{p}}}{\gamma_{\mathrm{S}}^{\mathrm{p}} + \gamma_{\mathrm{L}}^{\mathrm{p}}} \tag{4}$$

where the indices L and S characterize the liquid and the solid phase, respectively. By measuring the contact angle (Θ) of two test fluids with known values of $\gamma_{\mathrm{L}}^{\mathrm{d}}$ and $\gamma_{\mathrm{L}}^{\mathrm{p}}$, two simultaneous quadratic equations can then be solved for $\gamma_{\mathrm{S}}^{\mathrm{d}}$ and $\gamma_{\mathrm{S}}^{\mathrm{p}}$.

Two probe liquids (distilled water and formamide) were used to measure the equilibrium contact angle on solid samples of PEI, Vectra A and HX1000. The surface tension as well as its dispersive and polar components for distilled water are 72.6, 21.7 and $50.9\,\text{mN}\,\text{m}^{-1}$, respectively. For formamide the values are 58.3, 32.3 and $26.0\,\text{mN}\,\text{m}^{-1}$, respectively. Injection-moulded samples of PEI, Vectra A and HX1000 were used in the tests. The contact angle of each sample was calculated by taking the average of at least eight measurements. Standard deviations were of the order of 1.6 to 7.4%. The average values of the contact angle were placed into equation (4) and the polar and dispersive components of the surface tension for each individual solid sample were determined. These results were then substituted into equation (3) and the interfacial tension for each polymer pair was calculated.

Morphological characterization and mechanical properties

The morphology of the injection moulded parts (moulded plaques and/or tensile bars) was investigated by means of scanning electron microscopy (SEM). A Cambridge Stereoscan-S200 instrument with an accelerating voltage of 25 kV was used. The samples were cryogenically fractured along and across the injection moulding flow direction after immersion in liquid nitrogen for at least 5 min. The samples were then mounted on aluminium stubs and sputter-coated with gold for enhanced conductivity. The fracture surfaces were scanned from the surface to the centre regions to determine the shape and size of the TLCP dispersed phase.

The mechanical properties of the injection moulded tensile bars and rectangular strips (measuring approximately 12 mm × 80 mm) cut from the injection moulded plaques were evaluated using an Instron universal testing instrument (model 4204). A crosshead speed of 1 mm min^{-1} was used. An extensometer was utilized to record the strain. Tensile strength and tensile (Young's) modulus were calculated from the stress–strain curves. The tensile modulus was determined from the best linear fit through the initial region of the stress–strain curve. Toughness was calculated as the area under the stress–strain curve through numerical integration. The mechanical properties reported are based on measurements made on at least five samples. In some cases, especially at high TLCP contents, the samples broke at the grips. In such cases, tensile strength and elongation at break are most probably underestimated. Error bars in the graphs indicate one standard deviation.

Molecular orientation

The degree of molecular orientation, assessed by wide-angle X-ray diffraction (WAXD) measurements, was specified by means of the Herman's orientation function f^{H} of the TLCP phase in the blend. An automated Philips diffractomer and nickel-filtered Cu$K\alpha$ radiation were used. Equatorial scans were collected in a fixed-time mode from 5 to 45° with a step size of 0.1°. Azimuthal scan traces of the strong equatorial 1 1 0 reflections of the TLCP were then performed and the value of the values of the Herman's orientation function f^{H}, defined by

$$f^{\mathrm{H}} = \frac{3\langle\cos^2\phi\rangle - 1}{2} \tag{5}$$

were determined. Calculated orientation functions were averaged over four quadrants, using both equatorial reflections. Background scattering was subtracted from the intensity profile. In equation (5), ϕ is the angle between the director of the liquid crystalline phase or domain, and the reinforcing fibril axis. The brackets $\langle\ \rangle$ indicate the average over all possible configurations. For a perfect orientation of the domains in the fibril direction $f^{\mathrm{H}} = 1$, and for a complete random orientation $f^{\mathrm{H}} = 0$.

RESULTS AND DISCUSSION

Mechanical properties

The results of mechanical tests performed on injection-moulded samples of PEI/Vectra A and PEI/HX1000 blends as a function of TLCP concentration are discussed in this section. Tensile and flexural properties are presented in order to illustrate the significance of partial miscibility and compatibility on the mechanical response of *in situ* composites. To better convey the findings of the mechanical tests, tensile properties are discussed first, followed by the results of the flexural tests.

Tensile properties. The effect of the addition of a thermotropic liquid crystalline polymer on the tensile modulus of a PEI matrix is discussed first. Following this, the ultimate properties (strength, elongation at break and toughness) are discussed. In addition, transverse mechanical properties are presented which will provide additional understanding of the effect of partial miscibility on the properties of PEI/TLCP blends.

Tensile modulus values obtained from injection-moulded mini-tensile bars of PEI/Vectra A and PEI/HX1000 blends as a function of TLCP concentration are presented in *Figure 1*. As observed, blending of either Vectra A or HX1000 with PEI leads to a significant increase in tensile modulus. However, the degree of modulus increase obtained by the addition of HX1000 is larger than that for the addition of Vectra A, in spite of both TLCPs showing similar values of tensile modulus themselves. For instance, at 30 wt% TLCP reinforcement, PEI/HX1000 shows a tensile modulus of 8.70 GPa, whereas for PEI/Vectra A, a value of 5.80 GPa is observed. This represents an increase in the modulus of the PEI by a factor of 2 or 3 by the addition of either Vectra A or HX1000, respectively. Furthermore, a maximum in the tensile modulus, although of different magnitude, is observed for both *in situ* composites at around 90 wt% TLCP concentration. The values of tensile modulus of the blends at this concentration are significantly higher than those of the neat TLCPs.

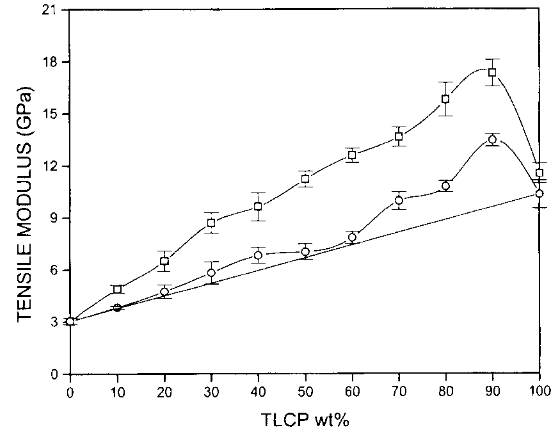

Figure 1 Tensile modulus of injection-moulded tensile bars of PEI/TLCP *in situ* composites as a function of TLCP concentration: ○, PEI/Vectra A; □, PEI/HX1000

The fact that TLCPs can act as a reinforcing agent in a blend has led some investigators to model the mechanical behaviour of TLCP/polymer blends according to composite theories[2,9,38,39]. One of the relationships most commonly used to predict the modulus of a composite from the moduli of the individual components is the Tsai–Halpin equation[40]:

$$E_{\mathrm{c}} = E_{\mathrm{m}}\left(\frac{1 + ABV_{\mathrm{f}}}{1 - AV_{\mathrm{f}}}\right) \tag{6}$$

with

$$A = \frac{E_{\mathrm{f}} - E_{\mathrm{m}}}{E_{\mathrm{f}} + BE_{\mathrm{m}}} \tag{7}$$

and, for the case of transversely isotropic composites, B given by:

$$B = 2\left(\frac{L}{D}\right) \tag{8}$$

where E_{c} is the composite modulus along the fibre direction, E_{m} is the modulus of the matrix, E_{f} is the modulus of the fibre, V_{f} is the volume fraction of fibre, and L/D is the aspect ratio of the fibre. For fibres with aspect ratios greater than 100, a linear relationship exists between the modulus of the composite and the volume fraction of reinforcement[9]. This suggests that, for uniaxially reinforced systems, a simple rule of mixtures may conveniently be applied to predict the theoretical modulus of composites reinforced with fibres of aspect ratio greater than 100.

However, in addition to fibre aspect ratio, the modulus of the reinforcing fibres (more specifically the ratio E_f/E_m) also plays an important role in the final modulus of the composite. In the case of TLCP/polymer blends, the difficulty lies in the proper selection of TLCP properties to use in the calculations. It is well known that the mechanical properties of TLCPs are significantly affected by the magnitude of the applied strain. Higher values of modulus and strength are usually obtained through melt spinning or post-extrusion drawing[4,16]. Therefore, in predicting the theoretical modulus of TLCP/polymer blends, one should be aware that the mechanical properties of the blends are directly dependent upon the processing history. Consequently, in estimating the TLCP/polymer blend properties, calculations should be performed with materials that have undergone comparable processing histories.

In *Figure 1*, the tensile moduli of the PEI/TLCP blends are compared with the moduli predicted by the simple rule of mixtures (indicated by the straight line). The modulus values used in the calculations are based on measurements made on injection-moulded samples of the blend constituents. Therefore, the processing histories of both individual components as well as the blends are alike. As noticed in *Figure 1*, a positive deviation from the rule of mixtures is observed for both blends. In the case of PEI/Vectra A, the blend moduli follow the rule of mixtures up to a Vectra A concentration of 60 wt%. Above this concentration, a synergism in the tensile modulus is observed. In the case of PEI/HX1000, the synergism in the tensile modulus is observed over the whole range of compositions investigated.

However, for comparison, the theoretical modulus of the blends was estimated using the modulus of spun TLCP fibres. If values of spun TLCP fibres are used and considering perfectly aligned fibres of aspect ratio of at least 100, the calculated theoretical modulus would be as follows. Using, for example, a tensile modulus for Vectra A fibres of 65 GPa[16] instead of 10.33 GPa as obtained in injection moulding, at 30 wt% Vectra A (which corresponds to 28 vol%) the theoretical modulus is estimated to be 20.4 GPa, which is considerably higher than the value of 5.83 GPa obtained in injection moulding. It is apparent that if the moduli of spun fibres were to be used in the theoretical calculations, the experimental values would be considerably lower than the theoretical value. This does not mean to imply that it might be better to use pregenerated TLCP fibres to reinforce PEI, as it may not be possible to keep the aspect ratio of the fibres at 100. Furthermore, the processing temperature is so high for PEI that Vectra fibrils would melt. However, it serves to show that the TLCP fibrils generated in injection moulding have not reached their optimum values.

We next turn out attention to the ultimate properties (strength, elongation at break and toughness) exhibited by the PEI/TLCP blends. The tensile strengths of PEI/Vectra A and PEI/HX1000 blends are presented in *Figure 2*. The tensile strength for all blend compositions is greater than that of the pure PEI. However, depending on the TLCP content, it seems that both partial miscibility and the ultimate properties of the TLCP phase may play significant roles in determining the tensile strength of the blend. At TLCP contents as high as 20 wt%, higher values of tensile strength are observed for the PEI/HX1000 system than for the PEI/Vectra A system. However, at high levels of TLCP, it seems that the tensile strength of the TLCP polymer dominates the tensile strength of the blend. The tensile strength of Vectra A (234 MPa) is almost twice that of HX1000 (126 MPa), and because of this, at high concentrations of TLCP, the tensile strengths of PEI/Vectra A blends are considerably higher than those of PEI/HX1000.

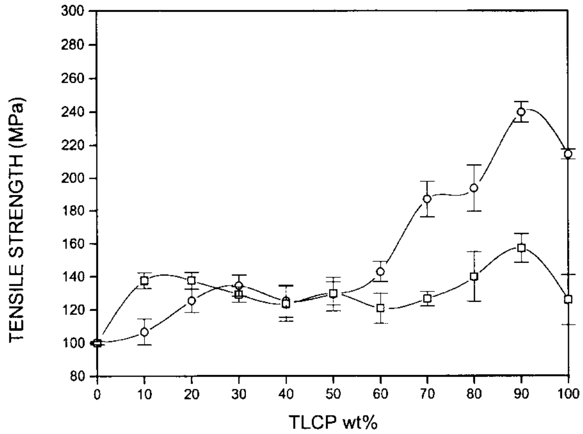

Figure 2 Ultimate tensile strength of injection-moulded tensile bars of PEI/TLCP *in situ* composites as a function of TLCP concentration: ○, PEI/Vectra A; □, PEI/HX1000

The transverse tensile strength is usually used as an indication of fibre–matrix adhesion in fibre composites[41]. It is usually found that variations in thermal treatment can substantially affect the transverse properties and consequently the fibre–matrix adhesion of a thermoplastic prepreg[41]. In the case of *in situ* composites, it is expected that the transverse tensile strength would also be sensitive to the miscibility between the matrix and the reinforcing TLCP. With this in mind, transverse tensile strength measurements were performed on selected compositions of PEI/Vectra A and PEI/HX1000 blends. Transverse tensile strength values of PEI/HX1000 and PEI/Vectra A for TLCP contents of up to 30 wt% are presented in *Table 1*. As one notices, even though HX1000 shows a value of transverse strength significantly lower than that of Vectra A, the values of transverse tensile strength obtained for PEI/HX1000 blends are slightly higher than those of PEI/Vectra A blends at TLCP concentrations of up to 20 wt%. At 30 wt% TLCP content, both blends exhibit similar values of transverse tensile strength. Considering that the transverse tensile strength of the neat HX1000 samples is lower than that of Vectra A, the slightly higher transverse values of the blends of PEI/HX1000 may be due to improved adhesion between the PEI and HX1000.

The elongation at break for both *in situ* composites is

Table 1 Transverse tensile strength (MPa) of PEI/HX1000 and PEI/Vectra A blends (standard deviations are given in parentheses)

Composition (wt%)	PEI/HX1000	PEI/Vectra A900
90/10	83.87 (3.59)	75.00 (3.90)
80/20	57.10 (3.92)	45.00 (4.10)
70/30	41.61 (2.74)	37.10 (3.30)
0/100	28.90 (2.01)	45.70 (1.80)

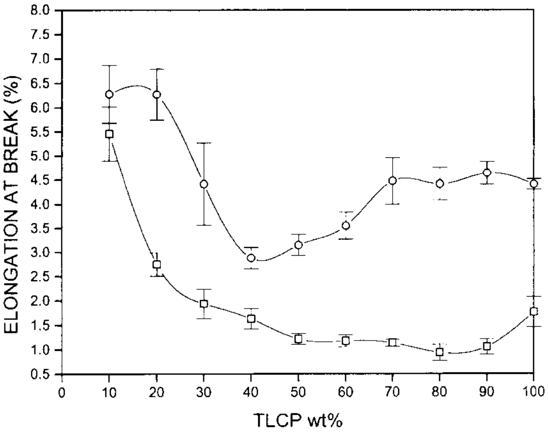

Figure 3 Elongation at break of injection-moulded tensile bars of PEI/TLCP *in situ* composites as a function of TLCP concentration: ○, PEI/Vectra A; □, PEI/HX1000

illustrated in *Figure 3*. The elongation at break of PEI/TLCP blends falls drastically as the TLCP content is increased because of the dramatic difference in ductility between the PEI and the TLCPs. PEI usually shows an elongation at yield of 7% and an elongation at break at 60%, whereas Vectra A and HX1000 show an elongation at break of 4.4 and 1.7%, respectively. The elongation at break of PEI/Vectra A blends is much higher than that for PEI/HX1000 blends, especially at high TLCP contents, because Vectra A is more ductile than HX1000. It seems that the elongation at break of the PEI/TLCP systems studied is influenced much more strongly by the intrinsic properties of the TLCP used as a reinforcement than by partial miscibility.

The toughness of PEI/Vectra A and PEI/HX1000 blends, calculated as the area under the stress *versus* strain curve, is presented in *Figure 4*. Not shown in the figure is the toughness of neat PEI, which is in excess of 10 GJ m^{-3}. The toughness of the PEI/Vectra A blends is much greater than that of PEI/HX1000 blends. This is consistent with the fact that higher values of ultimate properties (strength and elongation at break) are observed for Vectra A. The values of toughness calculated for the neat Vectra A and HX1000 are of the order of 6 and 1.3 GJ m^{-3}, respectively. It is observed that the lower toughness of HX1000 is carried over to the PEI/HX1000 blends. For HX1000 concentrations greater than 20 wt%, the toughness of the blend is now dominated by the HX1000. PEI/Vectra A blends, on the other hand, exhibited a peculiar behaviour. Once again, toughness of the blend decreased upon addition of Vectra A, but in this case, a minimum is observed at 40 wt% Vectra A concentration. Another important observation is the presence of the maxima at 90 wt% Vectra A concentration, which is a consequence of the maxima in the tensile strength observed at this same concentration. The experimental data suggest that, as in the case of elongation at break, the toughness behaviour of PEI/HX1000 and PEI/Vectra A blends is much more influenced by the properties of the TLCP used than by miscibility.

In summary, the above results show that greater values of tensile modulus are obtained in the system showing partial miscibility and, at high TLCP concentrations, the ultimate mechanical properties of the TLCP phase dominate the ultimate properties of the *in situ* composite. Therefore, the selection of a TLCP to reinforce a polymeric matrix becomes complex because not only is partial miscibility significant at low TLCP concentrations, the mechanical properties of the TLCP become important at high levels of TLCP (> 50%). Thus, it seems that the TLCP concentration in the blend becomes an additional factor to be considered in the final selection of a TLCP to reinforce a polymeric matrix.

Flexural properties. The flexural modulus and flexural strength for PEI/Vectra A and PEI/HX1000 blends are presented in *Figures 5* and *6*, respectively. In *Figure 5* it is shown that the flexural modulus of PEI/HX1000 blends exhibit a positive deviation from the simple rule of mixtures (shown by the straight line) for all HX1000 concentrations. On the contrary, the flexural modulus of PEI/Vectra A follows the rule of mixtures for most of the Vectra A concentrations. A small synergism appears only at Vectra A concentrations of 80 wt% and above. Nevertheless, as in the case of the tensile modulus, both blends once again show a maximum in modulus at 90 wt% TLCP.

Flexural strength values plotted as function of TLCP concentration for PEI/Vectra A and PEI/HX1000 blends are presented in *Figure 6*. As one notices, for TLCP concentrations of up to 20 wt%, for the system in which

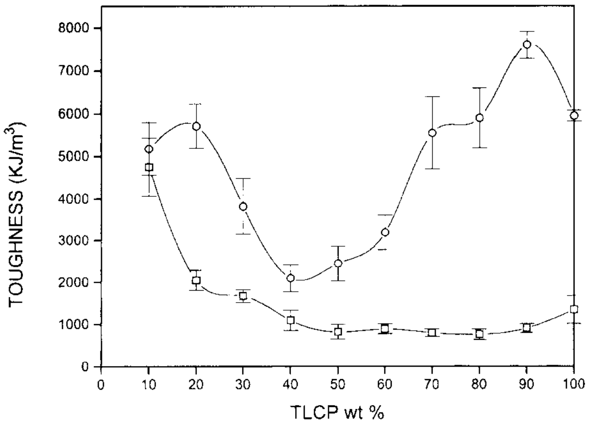

Figure 4 Toughness of injection-moulded tensile bars of PEI/TLCP *in situ* composites as a function of TLCP concentration: ○, PEI/Vectra A; □, PEI/HX1000

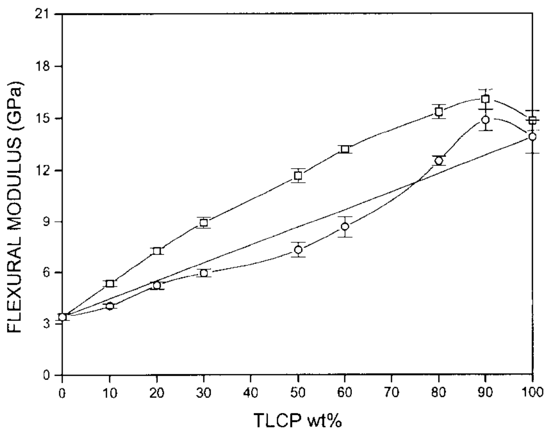

Figure 5 Flexural modulus of PEI/TLCP *in situ* composites as a function of TLCP concentration: ○, PEI/Vectra A; □, PEI/HX1000

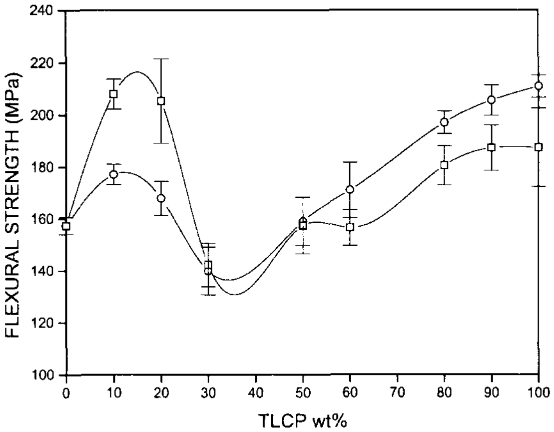

Figure 6 Flexural strength of PEI/TLCP *in situ* composites as a function of TLCP concentration: ○, PEI/Vectra A; □, PEI/HX1000

partial miscibility exists, a much stronger increase in the flexural strength is observed when compared with the immiscible system. For instance, the addition of only 10 wt% HX1000 increases the flexural strength of the PEI matrix from 150 to ~210 MPa, representing a 40% increase. On the other hand, at the same concentration, Vectra A contributes to a lesser increase in the strength (from 150 to ~180 MPa), in spite of showing a higher flexural strength than HX1000. However, at 30 wt% TLCP concentration, the flexural strength of both blends drops to a value of ~140 MPa. When increasing the TLCP concentration above 30 wt%, a monotonic increase in the strength, up to the value of the neat TLCPs, is observed.

The mechanical properties of PEI/Vectra A and PEI/HX1000 blends have been presented in this section. It appears that the system in which partial miscibility exists greater values of modulus are observed compared with the immiscible system. In the case of ultimate properties, the properties of the reinforcing TLCP phase are dominant at high TLCP concentrations. However, for TLCP contents up to 20 wt%, greater values of ultimate properties are found for the system showing partial miscibility. For example, even though HX1000 shows a lower value of ultimate tensile strength than Vectra A, PEI/HX1000 blends exhibit a greater value of tensile strength than PEI/Vectra A blends for TLCP concentrations up to 20 wt%.

Interfacial tension analysis

Interfacial tension results for PEI/HX1000 and PEI/Vectra A are presented in *Table 2*. As seen, the PEI/HX1000 system exhibits a lower value of interfacial tension than the PEI/Vectra A system. This suggests that a greater degree of interfacial adhesion may be expected for the PEI/HX1000 system relative to the PEI/Vectra A system. The work of adhesion and the work of cohesion are also presented in *Table 2*. For both *in situ* composites the work of interfacial adhesion is less than the work of matrix cohesion. This suggests that for both composites failure will most probably occur at the TLCP–matrix interface[42].

In *Table 2* a lower interfacial tension and a higher work of adhesion are observed for PEI/HX1000 than for PEI/Vectra A. This suggests that, in spite of the neat HX1000 showing lower values of ultimate mechanical properties than the neat Vectra A, the greater values of ultimate mechanical properties of PEI/HX1000 at low TLCP contents may be due to the higher interfacial adhesion (shown by the work of adhesion in *Table 2*) exhibited by the PEI/HX1000 system relative to the PEI/Vectra A system. In addition to the effect on ultimate properties, interfacial tension also plays an important role in the deformation of a TLCP phase into reinforcing fibrils. As seen from equation (1), lower interfacial tension will result in lower values of the Weber number at the same stress. Consequently, a higher magnitude of the deformation parameter D may be observed. For TLCP/polymer blends, a low value of interfacial tension may result in high aspect ratio TLCP fibres. Thus one may expect that, due to the lower value of interfacial tension, HX1000 fibrils of higher aspect ratio than Vectra A fibrils could be formed during injection moulding of the blends. Furthermore, the values of interfacial tension may also suggest that lower magnitudes of deformation rates (lower We) are necessary in order to elongate the HX1000 phase into reinforcing fibrils compared with the Vectra A phase. However, in addition to interfacial tension, the deformation parameter D also depends on the viscosity ratio of the dispersed phase to that of the suspending medium, which leads to the discussion of the rheological properties next.

Rheological properties

Rheological tests were performed to determine the viscosity ratio between the components of the PEI/TLCP blends studied. The complex viscosity as a function of frequency of PEI, Vectra A and HX1000 are shown in *Figure 7*. The rheological behaviour of PEI, for instance, shows a viscosity–frequency curve that is independent of frequency, similar to that of a Newtonian fluid. A slight deviation from Newtonian behaviour is only observed for frequencies above 10 rad s^{-1}. Vectra A, on the other hand, shows shear thinning behaviour throughout the range of frequencies investigated. For HX1000, however,

Table 2 Surface energies (mN m^{-1}) for PEI, HX1000 and Vectra A

Material	γ^d	γ^p	γ^t	X_p	γ_{12}	ΔX_p	W_a	W_c
PEI	10.50	42.30	52.80	0.801				105.60
Vectra A	20.59	11.57	32.16	0.360				
HX1000	13.00	23.10	36.10	0.640				
PEI/VA					20.80	0.441	64.16	
PEI/HX1000					7.20	0.161	81.70	

γ^d = Dispersive component of surface tension; γ^p = polar component of surface tension; γ^t = surface tension ($\gamma^d + \gamma^p$); X_p = polarity (γ^p/γ^t); γ_{12} = interfacial tension; ΔX_p = difference in polarities; W_a = work of adhesion; W_c = work of cohesion

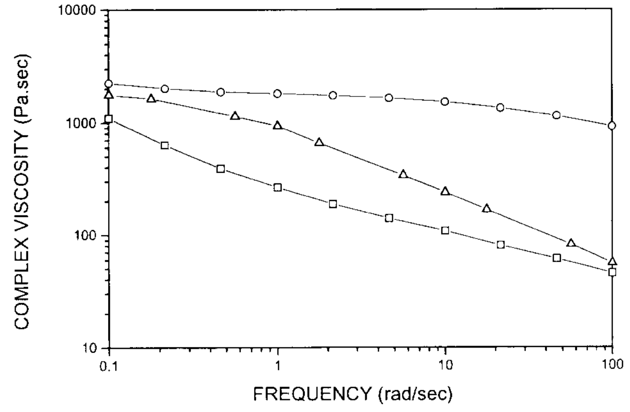

Figure 7 Complex viscosity *versus* frequency of PEI (○), Vectra A (□) and HX1000 (△) measured at 360°C and 5% strain

at frequencies of up to 1 rad s^{-1}, a pseudo-Newtonian plateau is observed and at frequencies above 1 rad s^{-1}, the material shear thins considerably. The complex viscosity of HX1000 decreases monotonically from ~1000 Pa s at 1 rad s^{-1} to ~55 Pa s at 100 rad s^{-1}, which represents a reduction of over one order of magnitude of the viscosity over two decades of frequency. In addition, the ratio of viscosities of the TLCPs and PEI (η_{TLCP}/η_{PEI}) is observed to vary drastically with frequency. In the case of PEI/HX1000, for example, a viscosity ratio of about 0.80 is observed at a frequency of 0.1 rad s^{-1}, and at 100 rad s^{-1}, the viscosity ratio has dropped to 0.06. Therefore, for most of the range of frequencies investigated, a viscosity ratio exists in the PEI/TLCP blends, which is favourable for the deformation of the TLCP phase into reinforcing fibrils.

The effect of the addition of TLCP to the blend viscosity is considered next. The complex viscosity as a function of frequency of PEI/Vectra A blends for Vectra A concentrations of 10, 50 and 90 wt% is presented in *Figure 8*. As shown, the addition of as little as 10 wt% of Vectra A to PEI reduces the viscosity of PEI by as much as 50% over the entire range of frequencies studied. Further, the dependence of the complex viscosity on the frequency for the 90/10 PEI/Vectra A blend resembles the behaviour observed for the neat PEI (i.e. nearly Newtonian behaviour over all frequencies). The reduction in the matrix viscosity upon addition of small amounts of a TLCP phase is typical behaviour reported for other TLCP/polymer blends[43–47] (reasons for such a behaviour have been attributed to: (1) incompatibility between the two phases; and (2) at small amounts, the low viscosity TLCP phase may act as lubricant to the polymeric matrix and reduce its viscosity[47]). At Vectra A concentrations of 50 and 90 wt%, however, pseudo-plastic behaviour is readily observed. The complex viscosity curves at high TLCP concentrations are, nonetheless, similar in shape to the one observed for the neat Vectra A. Due to the shape of the curves, one may speculate that for concentrations of Vectra A of 50 wt% and above the continuous phase is probably the TLCP. From this perspective, the increase in blend viscosity relative to the neat Vectra A could be related to the presence of a more viscous PEI phase.

The complex viscosity as a function of frequency of PEI/HX1000 blends for HX1000 concentrations of 0, 10, 20, 50, 90 and 100 wt% is illustrated in *Figure 9*. Once again, the addition of as little as 10 wt% of HX1000 considerably reduces the viscosity of the PEI matrix. The extent of viscosity reduction was >65%, considerably greater than the 50% reduction observed for PEI/Vectra A blends. However, increasing the concentration of HX1000 in the blend does not necessarily mean that the viscosity of the blend will continue to decrease. As a matter of fact, the contrary is observed. The reduction in the viscosity of the PEI matrix by the addition of 20 wt% HX1000 was much less significant than that by the addition of 10 wt%. The viscosity of PEI/HX1000 80/20 is much closer to that of the pure PEI than the PEI/HX1000 90/10 blend. Nevertheless, the nearly Newtonian behaviour observed in the neat PEI persists at HX1000 concentrations of as high as 20 wt%. This behaviour indicates that the viscosity response of the system at this concentration is clearly dominated by the PEI phase. A transition in the rheological response (from Newtonian to shear thinning) of the PEI/HX1000 blends begins at an HX1000 concentration of ~50 wt%.

In summary, the dynamic viscosity values have indicated that the viscosity ratio of the TLCP phase (HX1000 and Vectra A) to the viscosity of the PEI matrix falls within the optimum range for the deformation of the TLCP phase into reinforcing fibrils. In addition, the rheological tests have also shown that the

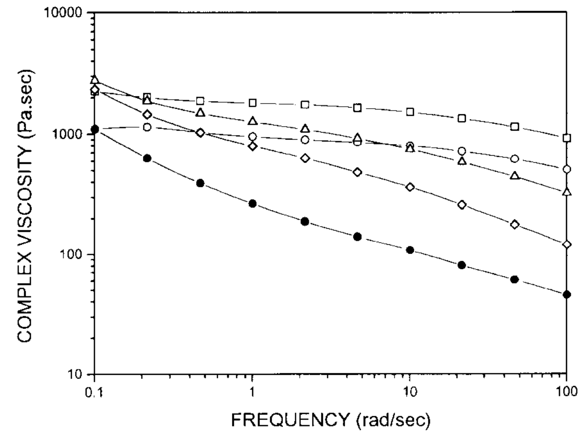

Figure 8 Complex viscosity *versus* frequency of PEI/Vectra A blends as a function of Vectra A concentration measured at 360°C and 5% strain: □, 100/0; ○, 90/10; △, 50/50; ◇, 10/90; ●, 0/100

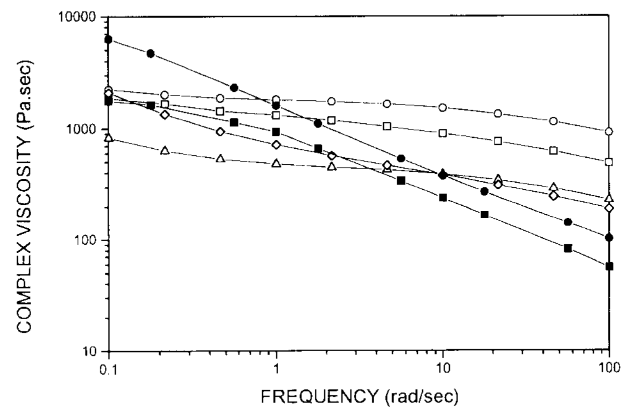

Figure 9 Complex viscosity *versus* frequency of PEI/HX1000 blends as a function of HX1000 concentration measured at 360°C and 5% strain: ○, 100/0; △, 90/10; □, 80/20; ◇, 50/50; ●, 10/90; ■, 0/100

addition of either Vectra A or HX1000 to PEI greatly reduces the viscosity of the blend relative to that of PEI. However, even though Vectra A shows a lower viscosity than HX1000, the extent of viscosity reduction is more significant for PEI/HX1000 than for PEI/Vectra A, especially at 10 wt% TLCP. This may be explained according to the following. Bafna *et al.*[32] have observed that the maximum shift in the glass transition of the PEI phase in the PEI/HX1000 blend occurs at 10 wt% HX1000. Thus, it is believed that the reduction of PEI/HX1000 viscosity at this particular concentration may be due to the existence of a fraction of the HX1000 which is miscible with PEI and having a lower viscosity than the neat PEI itself. The rheological tests also revealed that the blend viscosity for TLCP-rich compositions is significantly higher than the viscosity of the neat TLCPs.

Morphological analysis

The morphology developed during the injection moulding of PEI/Vectra A and PEI/HX1000 blends is discussed in this section. Knowledge of the structural development during injection moulding is important to understand the mechanical properties of the blends. First, the effect of the injection moulding flow kinematics on the structure development of PEI/Vectra A blends is presented. Following this, studies on PEI/HX1000 blends are presented.

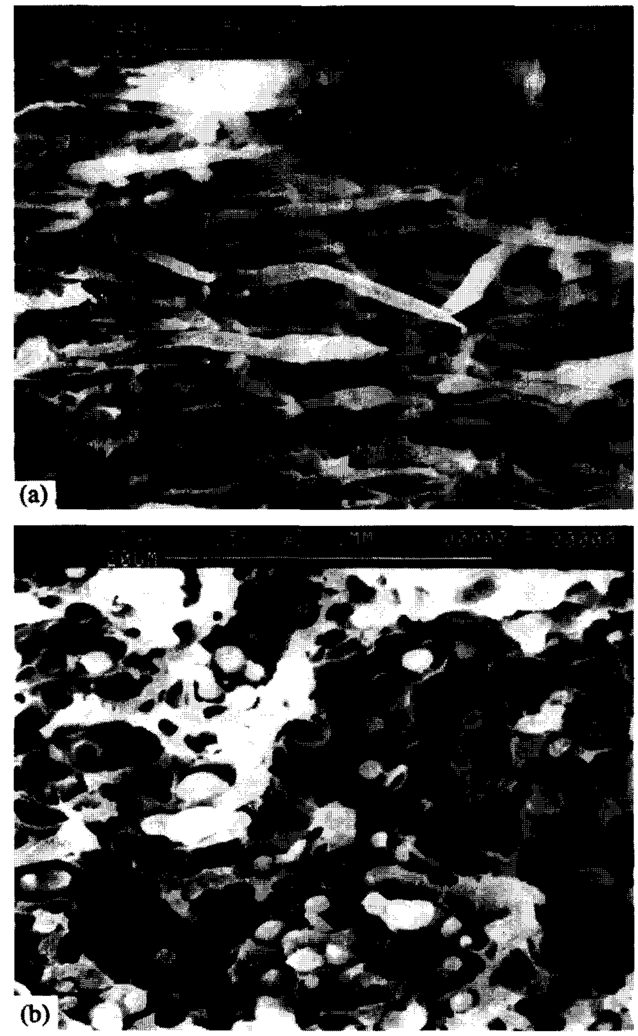

Figure 10 SEM photomicrographs of moulded plaque of PEI/Vectra A 80/20 composition ratio: (a) skin and (b) core regions

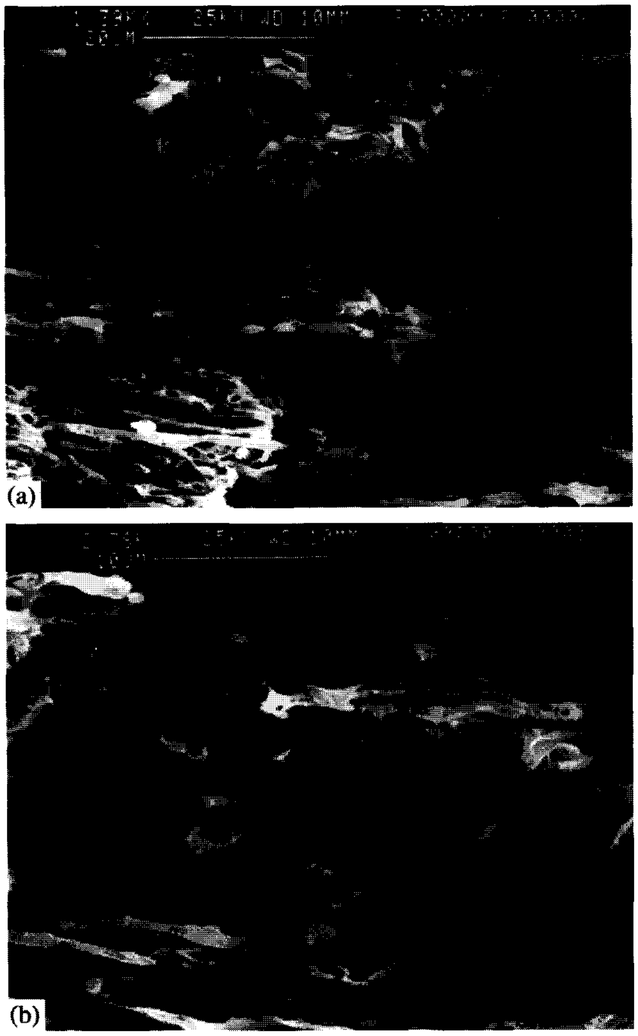

Figure 11 SEM photomicrographs of moulded tensile bar of PEI/Vectra A 60/40 composition ratio. Centre region seen at (a) 1390× and (b) 2780× magnification

Scanning electron micrographs of fracture surfaces of injection-moulded plaques of PEI/Vectra A 80/20 composition ratio are presented in *Figures 10a* and *b*. The samples were fractured along the flow direction. The effect of the kinematics of the injection moulding process on the morphology of the *in situ* composite is apparent. The combination of elongational flow from the advancing front and strong shear gradients at regions closer to the mould walls leads to the formation of fibres of the Vectra A phase in the blend. Hence, in *Figure 10a*, fibres with high aspect ratios are observed in the skin region. On the other hand, approaching the centre region of the moulded sample, the flow weakens and the TLCP phase remains as drops (*Figure 10b*). Near the centre region, the shear stresses are not strong enough to overcome the interfacial tension forces, and undeformed TLCP drops are found. It should be noted that the adhesion between the PEI and Vectra A phase is poor. Large voids around the Vectra A phase are particularly observed in the core region.

As the concentration of Vectra A is increased, the morphological structure of the PEI/Vectra A *in situ*

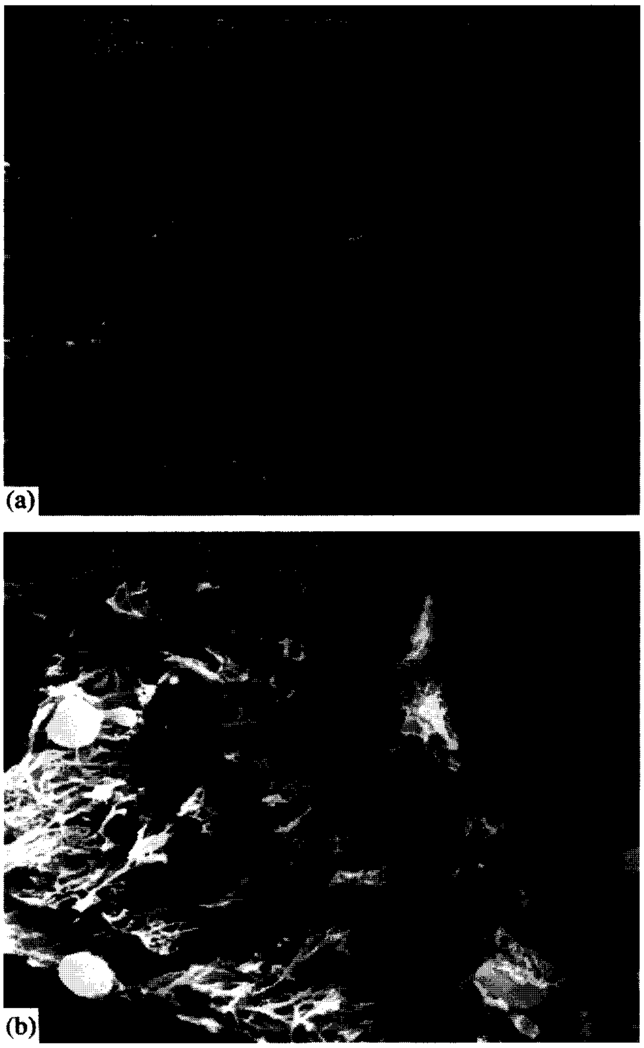

Figure 12 SEM photomicrographs of moulded tensile bar of PEI/Vectra A 10/90 composition ratio: (a) skin and (b) centre regions

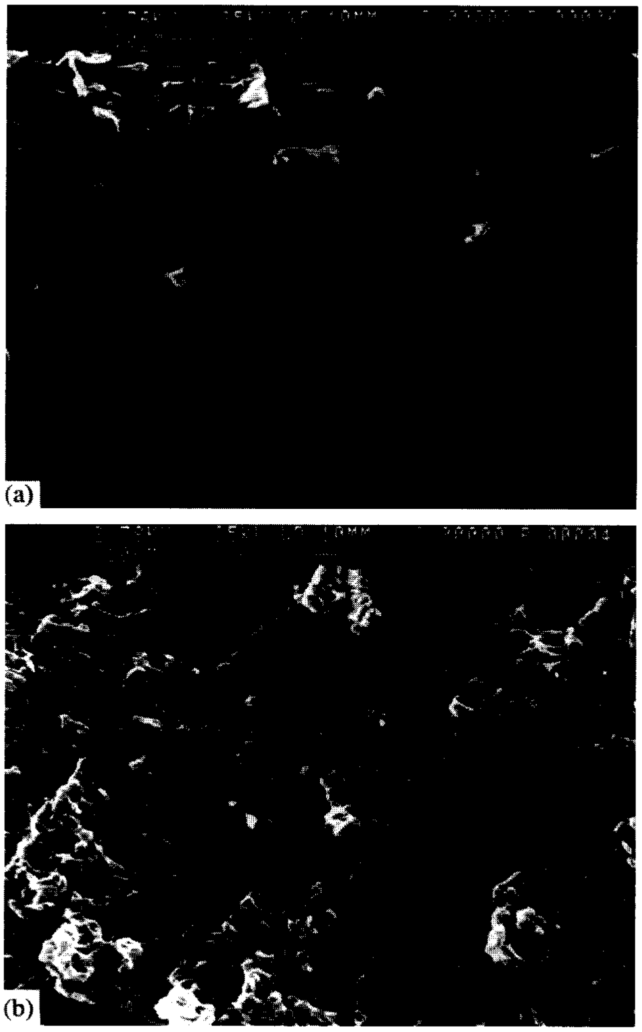

Figure 13 Scanning electron micrographs of fractured surfaces of moulded tensile bars of PEI/HX1000 90/10 composition ratio. The samples were fractured along the injection moulding flow direction: (a) skin and (b) centre regions

composite changes considerably. This is illustrated in *Figure 11*, where micrographs of fracture surfaces of injection moulded tensile bars of PEI/Vectra A 60/40 blend are shown. The sample has been fractured parallel to the principal direction of flow. One notices from *Figure 11* that at a Vectra A concentration of 40 wt% a co-continuous structure is observed. As detailed in *Figure 11b*, the structure is closely related to that of an interpenetrating network. This co-continuous morphology is of particular interest because mechanical tests have shown that a minimum in toughness for this particular composite appeared at this Vectra A concentration. This observation suggests that phase morphology also plays an important role in determining the mechanical performance of an *in situ* composite.

The morphology of a PEI/Vectra A 10/90 blend is presented in *Figure 12*. At this concentration, PEI is the dispersed phase and Vectra A is the continuous phase. At this condition, the viscosity ratio between the PEI dispersed phase and the Vectra A continuous phase (η_{PEI}/η_{VA}) is much greater than 1. Nonetheless, even for this unfavourable viscosity ratio condition, deformation of the dispersed PEI phase into fibrils is evident in the skin region of the moulded tensile bar as illustrated in *Figure 12a*. In the skin region, the flow is strong enough to overcome the extremely high viscosity ratio and deformation of the PEI dispersed phase into fibres is observed. However, as shown in *Figure 12b*, undeformed droplets of the PEI phase are apparent in the centre region.

Scanning electron micrographs of a fractured surface of an injection moulded tensile bar of PEI/HX1000 90/10 composition ratio are shown in *Figure 13*. The sample was fractured along the flow direction. At this concentration, the PEI/HX1000 blend exhibits a morphological structure closely resembling a homogeneous system. In the skin region, illustrated in *Figure 13a*, very fine high aspect ratio fibres of at least 10 μm in length and $< 1\ \mu$m in diameter are observed. In the core region, illustrated in *Figure 13b*, submicrometre-sized drops are observed. In addition, the adhesion between the phases appears to be better than in the PEI/Vectra A system.

The effect of partial miscibility on the morphology of PEI/TLCP blends is better illustrated by a direct comparison of the morphologies exhibited by the PEI/Vectra A system and the PEI/HX1000 system. In *Figure 14* a scanning electron micrograph of a fracture surface of PEI/HX1000 80/20 composition ratio is shown. By

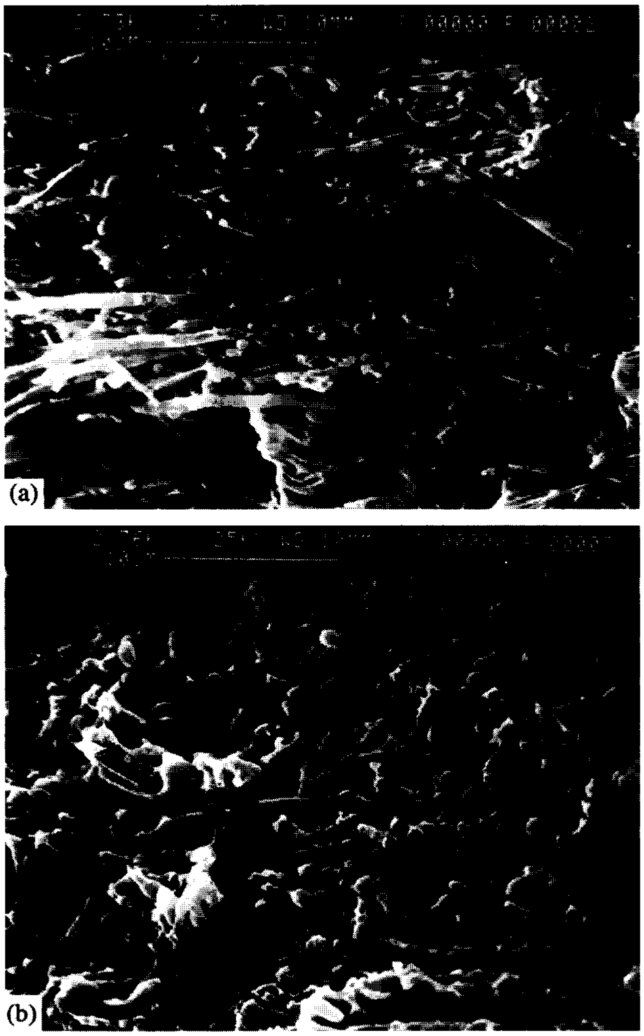

Figure 14 Scanning electron micrographs of fractured surfaces of moulded tensile bars of PEI/HX1000 80/20 composition ratio. The samples were fractured along the injection moulding flow direction: (a) skin and (b) centre regions

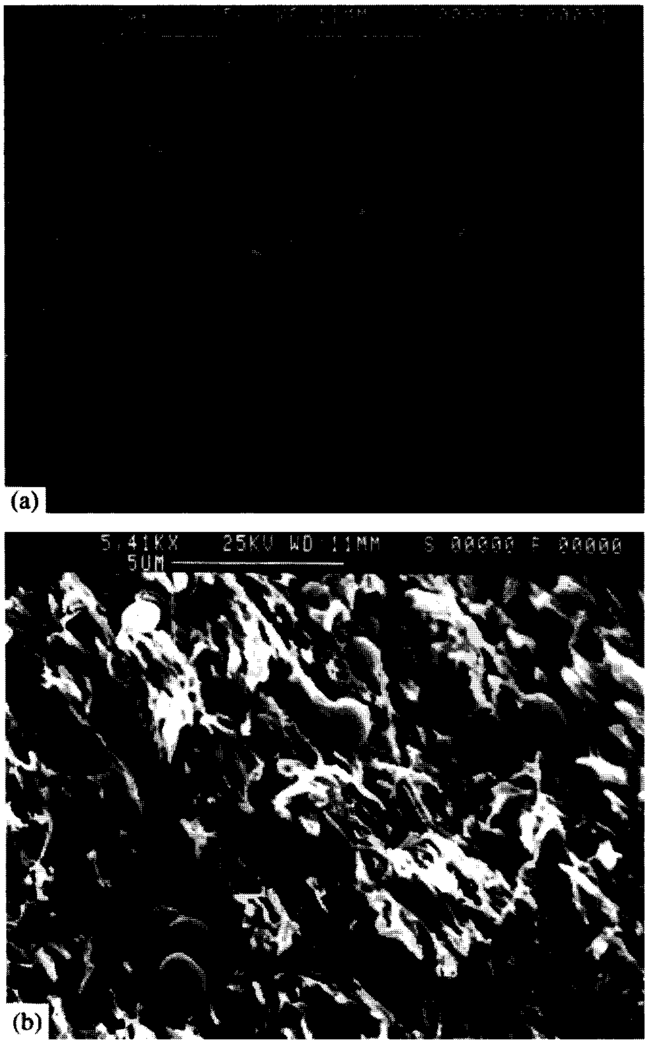

Figure 15 Scanning electron micrographs of fractured surfaces of moulded tensile bars of PEI/HX1000 10/90 composition ratio. The samples were fractured along the injection moulding flow direction: (a) skin and (b) centre regions

comparing the morphologies observed in *Figure 14* with that of *Figure 10*, the effect of partial miscibility on the morphologies of the blends is more apparent. The higher degree of compatibility of the PEI/HX1000 system, which arises from the partial miscibility, leads to a much finer structure than is observed for the PEI/Vectra A system. Furthermore, from *Figure 14b* one notices that HX1000 fibres can even be found in the core region of the moulded tensile bar. This observation indicates that higher average aspect ratio HX1000 fibrils may exist in the PEI/HX1000 system compared with the PEI/Vectra A system.

The effect of partial miscibility on the morphology of the PEI/HX1000 system is also observed at high HX1000 concentrations. In *Figure 15* a scanning electron micrograph of a fracture surface of PEI/HX1000 10/90 composition ratio is presented. At this HX1000 concentration, the dispersed phase is of PEI, and the viscosity ratio between the dispersed PEI phase and the continuous HX1000 phase ($\eta_{\mathrm{PEI}}/\eta_{\mathrm{HX}}$) is again much greater than 1. Nevertheless, in *Figure 15a*, fibres of the PEI phase are observed in the skin region of the moulded sample. This again emphasizes the effectiveness of the elongational flow in the advancing front in deforming the dispersed PEI phase into elongated fibrils, even at an unfavourable viscosity ratio. The core region, illustrated in *Figure 15b*, is again composed of undeformed PEI drops, but in this case the drops are considerably smaller.

Molecular orientation

The orientation parameters, f^{H}, obtained for PEI/Vectra A and PEI/HX1000 blends are discussed in this section. The experiments were performed with the intent of determining whether the observed tensile modulus of the blends could be correlated to the degree of molecular orientation of the TLCP phase. Injection-moulded plaques were used in these studies. Values of molecular orientation were obtained from the skin, core and full sample thickness. The results from these studies are presented next.

The tensile modulus of thermotropic liquid crystalline polymers is observed to increase with the increase in the draw down ratio, as for example in fibre spinning[16,48]. Chung[16] has shown that, along with modulus, molecular orientation (measured as the Herman's orientation function) also increases with draw ratio. Chung[16] observed

Table 3 Molecular orientation parameters for PEI/Vectra A and PEI/HX1000 blends

	PEI/Vectra A			PEI/HX1000		
Composition (wt%)	skin	core	full	skin	core	full
0/100	0.82	0.66	0.67	0.79	0.67	0.70
10/90	0.82	0.65	0.75	0.80	0.72	0.77
20/80	0.75	0.64	0.73	0.77	0.68	0.75

that in fibres of Vectra A, the orientation of the TLCP varied exponentially with modulus. For instance, an orientation factor of 0.88 correlated with a modulus of 40 GPa, and for an orientation of 0.93 a modulus of 65 GPa was observed. This suggests a direct correlation between molecular orientation and modulus. With this in mind, molecular orientation analyses were performed on selected samples of PEI/Vectra A and PEI/HX1000 blends to determine whether the maximum in the tensile modulus observed at 90 wt% TLCP could be related to a higher molecular orientation of the TLCP phase in the blend compared with the neat TLCP.

The values of the orientation parameter measured for PEI/Vectra A and PEI/HX1000 blends are presented in *Table 3*. As may be observed, the overall values of the orientation function (skin, core and full) of the PEI/TLCP blends at 90 wt% TLCP are significantly higher than those of the heat TLCPs. Further, one also observes that PEI/HX1000 shows a slightly higher degree of overall molecular orientation than PEI/Vectra A. The values of molecular orientation obtained from the skin indicate that highly oriented Vectra A fibrils have been formed in the outer layers of the moulded plaque. However, this orientation drops drastically in the centre regions of the sample. From the analysis presented above, it is clear that the maximum in the modulus found in the PEI/TLCP blends at 90 wt% TLCP concentration is a consequence of the higher molecular orientation shown by the blends at this concentration.

The differences in molecular orientation between the blends and neat TLCPs may be related to the following. Rheological tests have revealed that the values of complex viscosity of PEI/Vectra A and PEI/HX1000 at 90 wt% TLCP concentration were significantly higher than those of the pure TLCPs. In addition, the processing conditions were kept constant during injection moulding of the samples. Consequently, since the samples must have experienced similar rates of deformation during processing, the stresses generated must depend directly upon the viscosity of the system. Hence, materials exhibiting higher values of viscosity will experience higher magnitudes of stress. Therefore, it is believed that stress-induced molecular orientation of the TLCP phase may have occurred at 90 wt% TLCP concentration. This suggests that the criterion for the maximum in properties observed in TLCP/polymer blends is related to the viscosity of the flexible-chain polymer relative to that of the TLCP.

CONCLUSIONS

In the injection moulding process, the deformation of the TLCP phase into reinforcing fibrils will depend upon its position in the flow. Closer to the mould walls, where elongational flow from the advancing front and strong shear gradients exist, the TLCP phase deforms to a higher extent than in the centre regions of the moulded part, where weaker shear flows are present. In addition, partial miscibility plays an important role in determining the final structure of the moulded part. Finer higher aspect ratio TLCP fibrils were observed in the PEI/HX1000 system, where higher partial miscibility exists, relative to the PEI/Vectra A system. Tensile and flexural moduli were found to correlate well with the observed morphology. For instance, tensile and flexural moduli of PEI/HX1000 blends were greater than those of PEI/Vectra A blends throughout the range of compositions investigated.

For both blends a maximum in the tensile modulus, which has also been observed in other systems[28–33], occurred at a TLCP concentration of approximately 90 wt%. This maximum in tensile modulus at 90 wt% TLCP concentration was attributed to a higher molecular orientation of the TLCP phase in the blend than in the neat TLCP, as revealed by WAXD measurements. It is believed that, due to a higher blend viscosity at this concentration, stress-induced molecular orientation of the TLCP phase may have occurred. The higher molecular orientation would lead to higher modulus TLCP fibres in the blend relative to the pure TLCP.

Tensile strength properties, depending on the TLCP concentration, were affected by either interfacial adhesion or ultimate tensile strength of the TLCP. At low TLCP concentrations, up to 20 wt%, interfacial adhesion was important. In such cases, PEI/HX1000 blends, which have shown greater interfacial adhesion, exhibited higher tensile strengths than PEI/Vectra A blends. For instance, at 10 wt% TLCP concentration, tensile strengths of ~110 and 140 MPa were observed for PEI/Vectra A and PEI/HX1000, respectively. However, at TLCP concentrations of 70 wt% and above, the tensile strength properties were dominated by the ultimate strength of the TLCP. The TLCPs used, Vectra A and HX1000, show tensile strengths of ~215 and 126 MPa, respectively. Therefore, PEI/Vectra A blends have shown, at these concentrations, considerably higher values of tensile strength than PEI/HX1000.

PEI/HX1000 blends have also shown, at low TLCP concentrations, a higher value of transverse tensile strength than PEI/Vectra A blends. This agrees with the fact that a higher interphase adhesion was observed for the PEI/HX1000 system compared with the PEI/Vectra A system.

Although partial miscibility has a strong effect on the stiffness of an *in situ* composite, the ultimate properties of the TLCP strongly dominate the ultimate properties of the TLCP/polymer composite. Therefore, PEI/Vectra A blends have shown higher values of toughness throughout the range of compositions studied than the PEI/HX1000 blends. Consequently, the selection of a TLCP to reinforce a polymer matrix will not only depend upon whether partial miscibility between the TLCP and the matrix polymer exists, but also on the overall mechanical properties of the TLCP.

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REFERENCES

1 Siegmann, A., Dagan, A. and Kenig, S. *Polymer* 1985, **26**, 1325
2 Isayev, A. I. and Modic, M. *Polym. Compos.* 1987, **8**, 158
3 Malik, T. M., Carreau, P. J. and Chapleau, N. *Polym. Eng. Sci.* 1989, **29**, 600
4 Sun, T., Baird, D. G., Huang, H. H., Done, D. S. and Wilkes, G. L. *J. Compos. Mater.* 1991, **25**, 788
5 Beery, D., Kenig, S., Siegmann, A. and Narkis, M. *Polym. Eng. Sci.* 1992, **32**, 73
6 Baird, D. G. and Ramanathan, R. 'Contemporary Topics in Polymer Science', Vol. 6: Multiphase Macromolecular Systems' (Ed. B. M. Culberton), Plenum Press, New York, 1989
7 Li, J., Silverstein, M., Hiltner, A. and Baer, E. *J. Appl. Polym. Sci.* 1992, **44**, 1531
8 Chung, T. S. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1549
9 Crevecoeur, G. and Groeninckx, G. *Polym. Eng. Sci.* 1990, **30**, 532
10 Isayev, A. I. and Subramanian, P. R. *Polym. Eng. Sci.* 1992, **32**, 85
11 Seppala, J., Heino, M. and Kapanen, C. *J. Appl. Polym. Sci.* 1992, **44**, 1051
12 Kiss, G. *Polym. Eng. Sci.* 1987, **27**, 410
13 O'Donnel, H. J. *Ph.D. dissertation*, Virginia Polytechnic Institute and State University, 1994
14 O'Donnel, H. J. and Baird, D. G. *SPE Antec Technical Papers XL* 1994, 1606
15 Marrucci, G. in 'Thermotropic Liquid Crystal Polymer Blends' (Ed. F. P. La Mantia), Technomic, Lancaster, PA, 1993
16 Chung, T. S. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1549
17 Sukhadia, A. M. *Ph.D. dissertation.* Virginia Polytechnic Institute and State University, 1991
18 Dutta, D., Fruitwala, H., Kohli, A. and Weiss, R. A. *Polym. Eng. Sci.* 1990, **30**, 1005
19 Joseph, E. G., Baird, D. G. and Wilkes, G. L. *Polym. Eng. Sci.* 1985, **25**, 377
20 Taylor, G. I. *Proc. Roy. Soc.* 1934, **A146**, 501
21 Taylor, G. I. *Proc. Roy. Soc.* 1932, **A138**, 41
22 Taylor, G. I. *Proc. Roy. Soc.* 1954, **A226**, 289
23 Bentley, B. J. and Leal, L. G. *J. Fluid Mech.* 1986, **167**, 241
24 Goldsmith, H. L. and Mason, S. G. *J. Coll. Sci.* 1962, **17**, 448
25 Grace, H. P. *Chem. Eng. Commun.* 1982, **14**, 225
26 Elmendorp, J. J. and Maalke, R. J. *Polym. Eng. Sci.* 1985, **25**, 1041
27 Meretz, S., Kwiatkowski, M. and Hinrichsen, G. *Int. Polym. Proc.* 1991, **6**, 239
28 Blizard, K. G., Sukhadia, A. M., de Souza, J. P. and Baird, D. G. *Polym. News* 1990, **15**, 309
29 De Souza, J. P. and Baird, D. G. *SPE Antec Technical Papers XXXIX*, 1993, 1716
30 Isayev, A. I. and Swaminathan, S. *US Pat. 4 835 047*, 1990
31 Metha, A. and Isayev, A. I. *Polym. Eng. Sci.* 1991, **31**, 971
32 Bafna, S. S., Sun, T., de Souza, J. P. and Baird, D. G. *Polymer* 1993, **34**, 708
33 Baird, D. G., Bafna, S. S., de Souza, J. P. and Sun, T. *Polym. Compos.* 1993, **14**, 214
34 Cao, M. Y. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 521
35 Magagnini, P. in 'Thermotropic Liquid Crystal Polymer Blends' (Ed. F. P. La Mantia), Technomic, Lancaster, PA, 1993
36 Wu, S. 'Polymer Interface and Adhesion', Marcel Dekker, New York, 1982
37 Wu, S. *J. Phys. Chem.* 1970, **74**, 632
38 Mitchel, G. R. and Windle, A. H. in 'Developments in Crystalline Polymers' (Ed. D. C. Basset), Elsevier, London, 1988
39 Kohli, A., Chung, N. and Weiss, R. A. *Polym. Eng. Sci.* 1989, **29**, 573
40 Halpin, J. C. and Kardos, J. L. *Polym. Eng. Sci.* 1976, **16**, 344
41 Kelly, J. *Ph.D. dissertation*, Virginia Polytechnic Institute and State University, 1991
42 Folkes, M. J. 'Short Fiber Reinforced Thermoplatics', John Wiley and Sons, New York, 1982
43 Blizard, K. G. and Baird, D. G. *Polym. Eng. Sci.* 1987, **27**, 653
44 Zhuang, P., Kyu, T. and White, J. L. *Polym. Eng. Sci.* 1989, **28**, 1095
45 Nobile, M. R., Amendola, E., Nicolais, L., Acierno, D. and Carfagna, C. *Polym. Eng. Sci.* 1989, **27**, 244
46 Valenza, A., La Mantia, F. P., Paci, M. and Magagnini, P. L. *Int. Polym. Proc.* 1991, **6**, 247
47 Lin, Q., Jho, J. and Yee, A. L. *Polym. Eng. Sci.* 1993, **33**, 789
48 Itoyama, K. *J. Polym. Sci., Phys. Edn* 1988, **26**, 1845