

# Compatibilizing effect of a poly(ester imide) on the properties of the blends of poly(ether imide) and a thermotropic liquid crystalline polymer: 2. Morphology and mechanical properties of the in situ composite system

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Blends of a thermotropic liquid crystalline polymer (TLCP), [poly(ester amide), PEA, Vectra B950 from Hoechst Celanese] and poly(ether imide) (PEI, Ultem 1000 from G.E.) with the compatibilizer [poly(ester imide), PEsI] were extruded in a twin-screw extruder. The extruded strands were evaluated in terms of morphology and mechanical properties. The morphology of the compatibilized in situ composites was found to be significantly dependent on the concentration of the compatibilizer in the blend. For a TLCP phase content of 25 phr, a maximum reduction in phase size was observed when 1.5 phr by weight of compatibilizer was added to the blend. At high concentrations of the compatibilizer, flocculation of the TLCP phase was observed. Measurement of the tensile properties shows increased elongation as well as enhanced modulus and strength when properly compatibilized. This improvement is ascribed to better adhesion between the TLCP fibrils and the PEI matrix and better dispersion of the TLCP fibrils. Synthesized PEsI significantly improved the adhesion between the matrix phase (PEI) and fibril phase (PEA). However, maxima in tensile modulus, tensile strength and elongation were observed when excess compatibilizer was added. An emulsifying effect of the compatibilizer to coalesce the fibrils is believed to be the cause of the maxima in the tensile properties. Impact strength was seriously increased with the compatibilizer. A maximum in impact strength was also observed, but all compatibilized samples exhibited a higher impact strength than the non-compatibilized one. The reason is believed to be the failure mode difference between the tensile properties and the impact strength.

(Keywords: compatibilizer; emulsifying effect; flocculation)

#### **INTRODUCTION**

For high-performance composite systems, fibrous fillers (usually glass fibre or carbon fibre) have been used. Glass fibre is the most popular filler because it is inexpensive; however, the processing and fabrication of glass composites present some technical difficulties, such as wear (abrasion on screw and barrel walls of processing machinery), increased viscosity, difficulties in compounding, and breakage of the solid fibres that reduces the aspect ratio and consequently reduces the performance of the end product. For these reasons, self-reinforced composites have been sought to avoid the drawbacks of the fibre-reinforced system. Blending of thermotropic liquid crystalline polymers (TLCPs) with a less expensive thermoplastic offers the full advantage of using many of the desirable characteristics of the TLCP. Much work has been reported on improving the properties, in which the TLCP phase acts as a processing aid and a self-reinforcing material<sup>1-18</sup>. The blending morphology and properties of such composites are in many respects similar to those of the conventional glass fibre-filled composites.

Excellent mechanical properties have been achieved for blends of thermoplastics and TLCPs in the machine direction (fibril orientation). However, most thermoplastics that have been studied are incompatible with TLCPs. This incompatibility between the matrix polymers and reinforcing TLCPs gives rise to poor interfacial adhesion, which leads to a reinforcing effect for the mechanical properties less than that expected from

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the law of mixtures. Even worse is the poor performance in the normal direction. To obtain enhanced properties of the in situ composites, compatibility between the matrix polymer and the reinforcing TLCPs has been sought<sup>12,17–19</sup>. Compatibilization has been known to overcome the problems of poor dispersion and poor adhesion in blends of other incompatible polymers<sup>20</sup>. To improve the compatibility, miscible TLCP systems with the matrix polymer have been investigated by many researchers. Bafna and co-workers<sup>18</sup> studied the miscibility between various TLCPs with poly(ether imide) (PEI) (Ultem). In the blending system of TLCPs (HX1000 and HX4000 from DuPont) and PEI, they observed that morphologies of the partially miscible system were quite different from that of an immiscible system (which showed pull-out of TLCP microfibrils and large voids where the microfibrils were pulled out of the matrix, revealing poor matrix/fibril interfacial adhesion). In contrast, partially miscible blends did not show pulled out microfibrils. Using this partial miscibility between HX4000 and Ultem, Bretas and Baird<sup>16</sup> further investigated a ternary blend system of TLCP (HX4000)/PEI (Ultem)/poly(ether ether ketone) (PEEK) (Victrex 450G). The measurement of tensile properties showed that ternary blends with high modulus can be obtained at high TLCP loadings, while a composition with high ultimate tensile strength can be obtained with high loadings of PEI or PEEK.

Another way of compatibilizing an immiscible system is to use a third component as a compatibilizer or coupling agent. Lee and DeBenedetto<sup>17</sup> investigated the feasibility of introducing a second TLCP as a compatibilizer, or coupling agent, in order to improve the adhesion and dispersion between components of incompatible TLCP/thermoplastic blends. They used a wholly aromatic copolyester (K161) and an aliphaticcontaining TLCP (PHB60) as a dispersed phase and coupling agent. Polycarbonate (PC) and poly(ethylene terephthalate) (PET) were used as the matrix. They found that adhesion between the reinforcing K161 and the matrix PET depended on both the concentration of the coupling PET/PHB60 phase and the relative composition of the two TLCPs. Improved adhesion was also observed for the PC blend system. Mechanical properties of the composite system were improved. Datta et al.12 used a functionalized polypropylene (PP) as a compatibilizer for TLCP/PP blends. The mechanical properties of the compatibilized PP/TLCP (Vectra B) blends compared favourably with those of the glass-filled PP. Even though it was not applied to in situ composites, very recently King et al.<sup>21</sup> studied the effect of surface treatments to enhance fibre-matrix adhesion in carbon fibre/TLCP composites. They concluded that adhesion between the carbon fibre and the TLCP phase could be seriously enhanced by diamine or triamine treatments of the comingled tow.

As can be seen, compatibility in in situ composite systems has attracted much research interest. However, to our knowledge, only the Baird group<sup>11</sup> have seriously tried to use a compatibilizer for immiscible blends of thermoplastics and TLCPs. In our previous paper 19, the thermal and rheological properties of the in situ composite of TLCP (Vectra B950) and PEI were correlated with compatibilizer amount and interaction. In this paper, the relationships between mechanical behaviour and compatibilizer interaction are studied with

respect to morphological changes. The tensile parameters of modulus, strength and elongation are investigated, as is impact strength. Samples of varying degrees of compatibilization were prepared under the same processing conditions. Materials were extruded from the twin screw extruder to which drawing equipment was attached. The extrusion temperatures of feeding zone/ transporting zone/melting zone/die were as 140/290/290/240°C. Details of these experiments were presented in our previous paper<sup>19</sup>. Here we simply add some other experimental methods. Experimental results have been interpreted in accordance with the morphological observations.

#### **EXPERIMENTAL**

Materials

Ultem 1000 (PEI), an amorphous polymer made by G.E., was used as a matrix. The TLCP was an extrusion grade resin, Vectra B950 (a copolymer based on 6-hydroxy-2 naphthoic acid (60%), terephthalic acid (20%), and aminophenol (20%) produced by Hoechst Celanese Co.). The compatibilizer, poly(ester imide) (PEsI), was synthesized as explained in a previous paper<sup>19</sup>.

#### Instruments

Testing of the mechanical properties of the blends was done using an Instron Universal Testing Machine (model 4204) at constant temperature and humidity. A gauge length of 30 mm and a crosshead speed of 10 mm min were used. All the reported results are averages of at least ten measurements. Impact testing was done using a pneumatic driving instrumented impact tester (Radmana ITR 2000) at constant temperature and humidity. All results are averages of at least ten measurements for each blending system.

# **RESULTS AND DISCUSSION**

Tensile properties of the blend system

Tensile properties of the compatibilized and the uncompatibilized extruded blends of PEI and TLCP are compared first to see the compatibilizing effect. Vectra composition was fixed at 25 phr, at which ratio the fibril aspect ratio was the maximum for this pair<sup>14</sup> and the

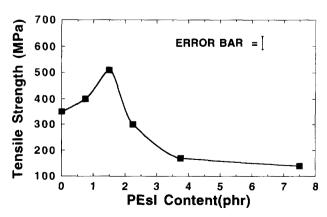


Figure 1 Tensile strength versus PEsI content for a PEI/TLCP in situ composite at a draw ratio of 4. The error bar shows a standard deviation

amount of Ultem was varied slightly depending on the amount of PEsI. Figure 1 shows the tensile strength versus added PEsI amount. The tensile strength is considerably improved with a small amount of PEsI but soon reaches a peak and decreases. When 1.5 phr PEsI was added, a tensile strength of 520 MPa was obtained, which is 50% higher than that of the PEI/TLCP blend without the compatibilizer. Figure 2 shows the tensile modulus of the compatibilized composite versus PEsI amount. Its trend is similar to that of tensile strength. Even though its maximum is not as evident as that of tensile strength, a peak value appears at 1.5 phr PEsI. As shown later, this is attributed to a more uniform distribution and finer fibril formation using the compatibilizer.

It is generally known that if miscibility exists between the matrix phase and dispersed TLCP phase, the adhesion

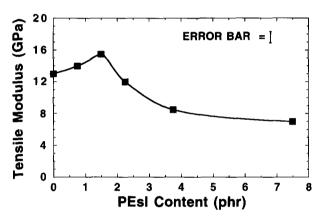


Figure 2 Tensile modulus versus PEsI content for a PEI/TLCP in situ composite at a draw ratio of 4. The error bar shows a standard deviation

at the interface will increase the mechanical properties, whereas it prevents fibril formation<sup>14</sup>. However, hindrance of fibril formation caused by adhesion between the matrix and TLCP droplets is not serious unless excess compatibilizer is used (which coalesces the TLCP droplets). This is because the dominant flow field for particle deformation is not shear flow but elongational flow. The classical analysis of Taylor<sup>22</sup> on the elongation of droplets in different suspensions shows that in simple shear flow of Newtonian fluids, the initial droplet is modified according to the relationship:

$$\frac{b_1 - b_2}{b_1 + b_2} = \frac{\dot{\gamma} \eta_0 b}{\sigma} \frac{19\delta + 16}{16\delta + 16} \tag{1}$$

where  $b_1$  and  $b_2$  are the principal semiaxes of the deformed drops,  $\tilde{\gamma}$  is the shear rate,  $\sigma$  is the interfacial tension, b is the initial diameter of the drop,  $\eta_0$  is the viscosity of the suspending liquid and  $\delta$  is the ratio between the viscosity of the dispersed liquid and the viscosity of the suspending liquid,  $(\eta_0/\eta_m)^{22}$ . Taylor suggested<sup>22</sup> that when the maximum value of the pressure difference (which tends to disrupt the drop) across the interface between a suspending liquid and a dispersion exceeds the force due to surface tension (which tends to hold it together), the drop will burst. This occurs when<sup>4</sup>:

$$4\dot{\gamma}\eta_0 \frac{19\delta + 16}{16\delta + 16} > \frac{2\sigma}{h} \tag{2}$$

Taking into account the viscosities of Ultem and Vectra B950, the value of  $\delta$  is less than 0.1. It also decreases with the shear rate. Then equation (2) can reasonably be



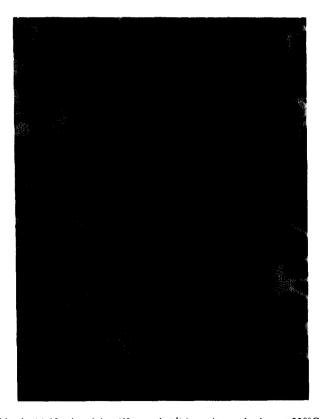


Figure 3 SEM photographs of fractured surfaces of typical PEI/TLCP blends: (a) 10 min mixing (60 rev min<sup>-1</sup>) in an internal mixer at 320°C; (b) 20 min mixing (60 rev min<sup>-1</sup>) in an internal mixer at 320°C

simplified to

$$\frac{2\dot{\gamma}\eta_0 b}{\sigma} > 1 \tag{3}$$

indicating that if the ratio of shear stress  $(\eta_0 \dot{\gamma})$  is larger than half of the interfacial energy  $(\sigma/b)$ , the droplet will elongate. Added compatibilizer reduces the interfacial tension  $\sigma$  and also reduces the initial diameter of the drop b. A number of workers have applied these ideas to TLCP blend systems<sup>2,4,14</sup>. However, all agree that some form of elongational deformation is necessary to produce fibrillation. Weiss et al..<sup>22</sup> showed that purely spherical droplets were formed when examining the morphology of polystyrene/TLCP blends following simple shear flow. Figure 3 shows the fractured surface morphology of the blends that were blended in an internal mixer under pure shear flow without elongation. The TLCP particles are purely spherical without any deformation. The lack of good alignment of the TLCP phase in shear flow is consistent with high interfacial tension in TLCP blends, as demonstrated by gross phase separation, poor adhesion and a resulting lack of deformation of the TLCP fibrils in the SEM photographs.

Elongational deformation is necessary to produce fibrils because the condition of equation (3) is not always satisfied if the polymer melt is non-Newtonian. In immiscible polymer blends, both the dispersed phase and the matrix phase may often show increasingly complex non-Newtonian and viscoelastic melt behaviour. Elasticity of the fluid plays a very important role in the particle deformation<sup>24</sup>. Its explicit expression for the deformation of TLCP particles for which elastic behaviour is important is different from usual polymeric melts. Even for simple steady shear flow, polymeric melts generally show shear-thinning behaviour under normal processing conditions, i.e. their viscosities decrease by two or three orders of magnitude with the shear rate. Relatively few results dealing with contributions to drop behaviour in viscoelastic systems have been published<sup>25-28</sup>. Viscoelasticity, and especially yield stress, may severely slow down or completely prevent the deformation of the drop and the occurrence of thread break-up. VanOene approaches the deformation and break-up of the particle, including the difference in 'elasticity' across the interface under laminar flow conditions<sup>25,26</sup>. Even though his thermodynamic equilibrium state assumption has been queried, he demonstrated the dominant influence of 'elastic' terms on composite morphology. According to VanOene's theory and expression, low shearing conditions such as those occurring in an internal mixer are usually sufficient, especially when the components stratify. However, when the difference in elasticity is large and the dispersed phase forms droplets, neither low shear nor high mixing is satisfactory, since the droplets resist deformation. Even in this case, VanOene concluded that a liquid droplet may still be drawn into a fibre by an elongational flow. Subsequent shearing may cause the fibre to break up. Elmendorp<sup>27</sup> showed that in model liquids exhibiting distinct yield stresses, no break-up occurs if yield stress is larger than the pressure difference that is generated in the thread by the different radii of curvature. His experimental results showed that the solution with higher normal stresses exhibited smaller deformations, although the viscosities of the two

components of the pair were equal. The droplets with higher normal stresses (higher 'elasticity') appeared the most stable. TLCPs are highly elastic and have long relaxation times. Hence their deformation by the stress transferred across the interface would be quite difficult, if not impossible.

The results of Taylor's Newtonian model systems described above represent the simplest blend systems. The data of Blizzard and Baird<sup>29</sup> also indicated that pure shear flow induced only spherical droplets, and a similar trend can be seen in Figure 3. Increasing the amount of PEsI decreases the interfacial tension, which has the same effect as increasing the shear rate by acting only to decrease particle size. The smaller the particles become, the smaller the so-called capillary number,  $C_a$ , which is defined as the ratio of the shear force  $\tau$ , imposed by the flow field to the interfacial tension  $(\lambda/R)$  where  $\lambda$  is the interfacial energy and R the radius of the droplet. When the capillary number is below the critical value (for the Newtonian fluid, 0.5 from equation (3)), break-up of the droplet will not take place<sup>5,11</sup>. Small particles get less transferred energy from the flow field and are more difficult to deform. Weiss et al. 23 showed that the addition of small amounts of TLCP to polystyrene actually increased the viscosity in pure shear flow while similar additives in capillary flow reduced the viscosity. They proposed that the spherical droplets observed in shear

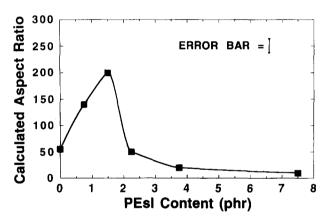


Figure 4 Calculated aspect ratio versus PEsI content for a PEI/TLCP in situ composite at a draw ratio of 4. The error bar shows a standard deviation

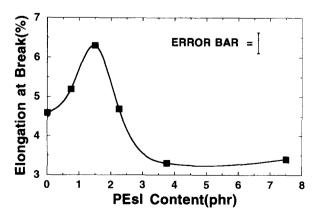


Figure 5 Elongation at break versus PEsI content for a PEI/TLCP in situ composite at a draw ratio of 4. The error bar shows a standard deviation

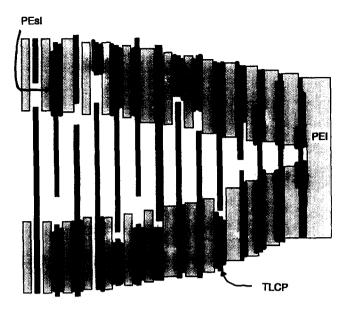


Figure 6 Schematic diagram showing some possible failure mechanisms along the cracked surface

flow rotate and tumble, increasing viscous dissipation and increasing viscosity. This agrees with the explanation of Crevecoeur and Groenickx that the bigger TLCP droplets are rather easily elongated by the flow field, and droplet deformation may be assumed to be affine with the macroscopic deformation<sup>5,6</sup>. For the lower TLCP contents (i.e. less than 7.5 phr) in this study, however, the particles are considerably smaller and the sizes are almost the same order of magnitude as the shear stress, so that droplet deformation will be less than affine. Therefore, a pure shear flow field cannot deform the particle to produce fibril shapes and the elongational flow field is indispensable for small droplet deformation. The effect of high shear rate in flow field is mainly to reduce droplet size without substantially improving the blend viscosity reduction due to fibrillar formation.

Addition of a compatibilizer enhances the mechanical performance of in situ composites by forming fibrils with finer and more uniform dispersion. The fact that the miscibility between the matrix and TLCP phases does not affect the TLCP phase fibril formation can be confirmed by the calculation of the aspect ratio for the

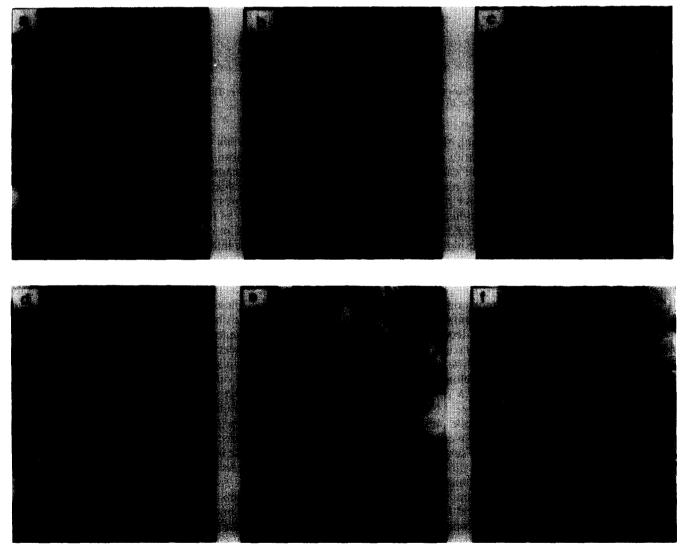


Figure 7 SEM photographs of fractured surfaces of PEI/TLCP blend fibres at a draw ratio of 1. The samples were fractured after freezing in liquid nitrogen. The amount of PEsI in the blends is: (a) 0 phr; (b) 0.75 phr; (c) 1.5 phr; (d) 2.25 phr; (e) 3.75 phr; (f) 7.5 phr

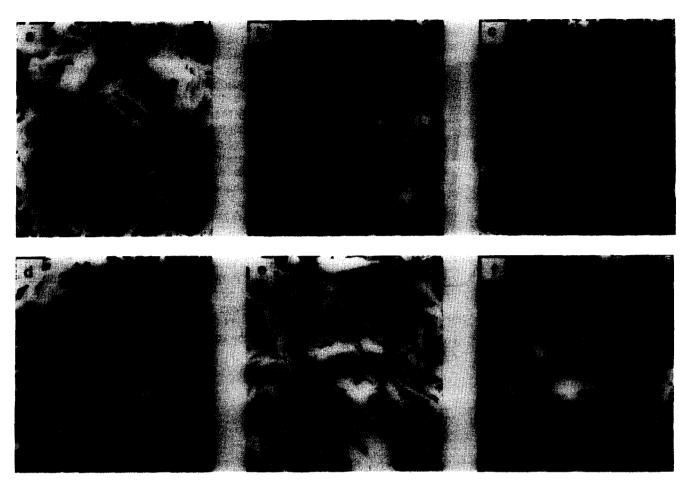


Figure 8 SEM photographs of fractured surfaces of PEI/TLCP blend fibres at a draw ratio of 4. The amount of PEsI in the blends is: (a) 0 phr; (b) 0.75 phr; (c) 1.5 phr; (d) 2.25 phr; (e) 3.75 phr; (f) 7.5 phr

TLCP fibrils in the composite. Using the well known Halpin-Tsai equation<sup>30</sup>, the aspect ratios of TLCP fibrils were calculated. Figure 4 shows the calculated aspect ratio versus PEsI content. Aspect ratios reach a maximum value at 1.5 phr of PEsI. Fibril aspect ratios decreased when more than 1.5 phr of compatibilizer was added. This is ascribed to the flocculation and coalescence of the TLCP fibrils, as explained later using morphological observations.

Figure 5 shows the elongation at break for the same blend. Surprisingly, the maximum peak appears at 1.5 phr of PEsI. Elongation at this composition is higher than the uncompatibilized system. For immiscible reinforced composites, the elongation generally decreases when the tensile modulus and tensile strength increase<sup>31</sup>. Generally, the higher the modulus of the composite, the harder the composite and the lower the elongation. These unexpected phenomena, however, are ascribed to the surfactant role of the compatibilizer. Simultaneous increase of tensile strength (or tensile modulus) and elongation can be explained by improved adhesion due to compatibilizer at the fibril surface and the micromechanism of fracture in the composite. Fibrous composites can fail during monotonic loading by a number of competing micromechanisms of fracture, e.g. by fibre breakage, matrix cracking and fibre pull-out<sup>32</sup>. Depending on the form in which stored elastic strain energy in the fibre is released, and on the strength and toughness of the fibre, fibre-matrix interface and the matrix, brittle fractures result from the earliest failure

event (matrix crack for instance) and the distribution of flaws. A short fibre is pulled out if the force on the fibre is sufficient to cause some debonding. In contrast, for long fibres embedded in a matrix under tensile stress, the fraction of fibres pulled out rather than broken approaches zero as the fibre length increases. This means that such fibres must fracture along a common crack plane or fracture into smaller segments before pulling out of the matrix (Figure 6) $^{33}$ . Examination of the fracture surface of the composite (Figure 7) reveals broken fibres of various lengths protruding above the fracture surface of the matrix. These breaks occur because of a variation in strength of the fibre at weak points beneath the surface of the cracked matrix. When a fibre fractures, in order for the new surfaces to move apart, the matrix must crack or plastically deform and the next fibre must fracture in the crack plane or beyond the crack plane. It is then axially pulled out of the matrix<sup>32</sup>. The matrix plastic deformation and fibre pull-out require additional energy input to the material and provide a means of dissipation of the energy decrement necessarily associated with fracture. Since the frictional shear force opposes any force applied to extract the fibre, work must be done in overcoming this frictional force. Compatibilized composites have more frictional shear force due to strong adhesion at the interface between the matrix and the fibre, which requires more energy to pull out the fibrils. As a result, the tensile strength (or toughness) of the system increases. Provided the fibre still maintains contact with the sheath of matrix surrounding it, work

must be done in pulling the fibre fragments against a restraining frictional force at the fibre-matrix interface. If the fibre does not maintain contact with the sheath of the matrix, the fibres can be easily pulled out and elongation cannot be increased. However, additional energy should be expended to break strong adhesion at the interface for the compatibilized system. Fibres will not be simply debonded. The fibril is sustained over the gap between crack surfaces until additional energy is supplied. This allows blends containing a small amount of compatibilizer to gain higher elongation at break than non-compatibilized systems. Excess compatibilizer, however, leads to coalescence of the dispersed phase. Owing to poor dispersion, tensile strength and modulus are decreased, and so is the elongation because the total contacting area is decreased and the energy restraining the crack is also decreased.

#### Morphologies of the in situ composites

The previous explanations can be corroborated by morphological observations. Figure 7 shows the fractured surfaces of the non-compatibilized and compatibilized Ultem/Vectra B950 blends at a draw ratio of 1. The samples were fractured normal to the flow direction. The TLCP domains are relatively large in non-compatibilized blends, indicating poor dispersion. The micrographs also demonstrate poor adhesion between the two phases (Figure 7a), which leads to an open ring hole around the TLCP domain and whole TLCP being pulled out during the fracturing of the samples. In contrast, the fracture is seen to occur within the fibrils in the compatibilized blends with a low content of PEsI (Figure 7b and c), and there is no open ring around the TLCP domain, reflecting better bonding on adhesion between the two phases. Furthermore, TLCP fibrils are more evenly distributed and finer in size than in the uncompatibilized blend. For blends containing more than 2.2 phr of PEsI, TLCP fibrils are poorly distributed and thicker than when 1.5 phr PEsI is added to the composite. This excess compatibilizer leads to flocculation of the fibrils. The same trend is observed for the fibre of draw ratio equal to 4, as shown in Figure 8. When the draw ratio is 4, fine fibril formation is clearly observed for the composites containing PEsI with less than 1.5 phr and is hampered by the addition of more compatibilizer. This is similar to the behaviour of a surfactant in an emulsion system<sup>34</sup>.

From emulsion studies, flocculation of the dispersed phase is known to occur because of strong interparticle interactions. The quantity of surfactant required to cover an interface fully is related to many variables. The maximum quantity beyond which significant size reduction of the dispersed droplet no longer occurs is 1.5 phr PEsI. Instead of size reduction, excess compatibilizer tends to coalesce the dispersed TCP phase (Figure 7d, e and f). The flocculation and coalescence of the TLCP phase result in poor dispersion of the TLCP. The interfacial area between the matrix and TLCP is reduced. Excess amounts of the compatibilizer coalesce the TLCP particles before fibrils are formed. Particle coalescence prevents fine fibril formation. Even the fibril domains are not homogeneous. They may include part of the compatibilizer in the fibril, which acts as a defect in the fibre. As a result, the tensile properties of the drawn fibres become even worse than those of the pure

PEI/TLCP blend when excess amounts of compatibilizer are added. This is clearly seen in Figure 7f and Figure 8f. When 7.5 phr of PEsI is added, the TLCP phase does not form fibril shapes at a draw ratio of 4; it still remains as a stubby particle. Plochocki et al.35 similarly observed a minimum of dispersed phase size with compatibilizer amount in a blending system of low-density polyethylene/ polystyrene.

Figure 9 shows SEM micrographs of the fractured surface after tensile testing. For the immiscible Ultem/Vectra B950 blends, numerous microfibrils are observed to be pulled out from the surface (Figure 9a). Many matrix voids generated by the pull-out of microfibrils reveal poor matrix/fibril interfacial adhesion for this system. In the case of composites containing compatibilizer, matrix voids are barely observed. The interfacial adhesion looks good, suggesting that the compatibilization takes place at the interface. However, TLCP domains grow with the amount of compatibilizer due to flocculation and coalescence. This is clearly seen in Figure 9f. Diminished interaction between the TLCP phase and the matrix can be seen from the pulled-out large holes.

In order to see the effect of compatibilizer more clearly, SEM micrographs of the peeled-back exposed surface of the spun fibres are shown in Figure 10. In a non-compatibilized blend, the long TLCP fibrils are bundled together (Figure 10a). The fibril surface looks quite clean and smooth along the flow direction, which indicates poor adhesion between TLCP and the matrix. In contrast, the compatibilized composites containing less than 1.5 phr of PEsI exhibit much finer fibrils with rough and rugged surfaces. This definitely shows good adhesion between the TLCP fibrils and the matrix phase. The tendency of TLCP to coalesce, however, proceeds with more compatibilization, as shown in Figure 10c. Thick fibril bundles appear as more PEsI is added, but their surfaces are still rough due to strong interactions. Figure 11 shows an enlarged micrograph of a fibril surrounded by the matrix, which demonstrates the adhesion of the matrix on the fibril surface.

# Impact strength of the in situ composites

Non-compatibilized in situ composites show good mechanical properties in the machine direction due to fibril formation of the TLCP phase, but have poor properties in the transverse direction. We already saw that the compatibilized system had better mechanical properties in the machine direction. Since only the fibre was prepared, the mechanical property test could not be done in the transverse direction. Instead, we checked the impact strength in the normal direction. ASTM D256 testing could not be followed because the extruded fibres were not reprocessable without destroying the liquid crystal structure. Instead, fibres of the same draw ratio were used for the impact test. After directly hitting the fibre in the direction normal to flow, the impact strength values were normalized by the value of the noncompatibilized system. Figure 12 shows the impact strength on a normalized scale for the strands of draw ratio equal to 1. The transverse direction strength of the compatibilized system is at least twice that of the non-compatibilized system. An interesting fact is that the impact strength also shows a maximum when 1.5 phr

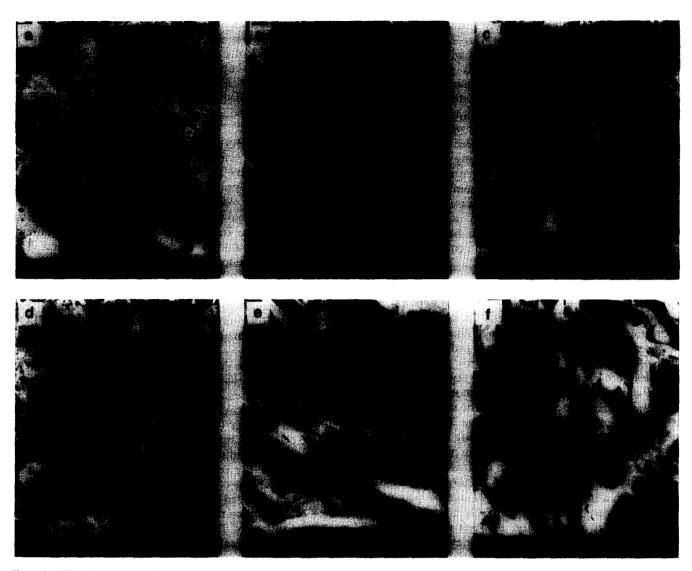


Figure 9 SEM photographs of fractured surfaces of PEI/TLCP blend fibres after tensile test (×3000). The draw ratio is 4. The amount of PEsI in the blends is: (a) 0 phr; (b) 0.75 phr; (c) 1.5 phr; (d) 2.25 phr; (e) 3.75 phr; (f) 7.5 phr

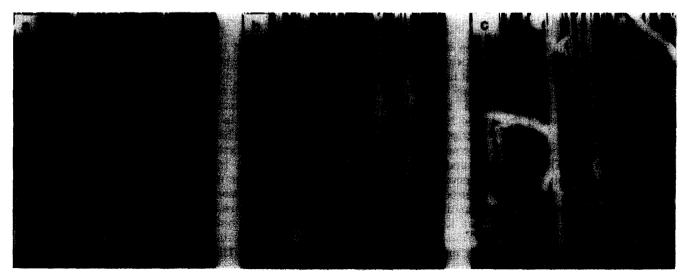


Figure 10 SEM photographs of peeled back surfaces of PEI/TLCP blend fibres. The draw ratio is 4. The amount of PEsI in the blends is: (a) 0 phr; (b) 0.75 phr; (c) 3.75 phr

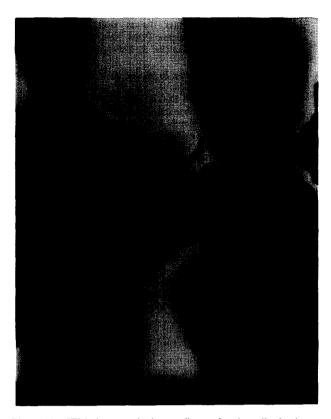


Figure 11 SEM photograph after tensile test showing adhesion between the TLCP fibril and the matrix (PEI). The PEsI content was 7.5 phr and draw ratio was 4

PEsI is added. This is similar to the tensile properties. Coalescence of the TLCP droplets and reduced surface area with an excess amount of PEsI are believed to be the reasons for the reduction in impact strength. However, compatibilized systems still have higher impact strength than non-compatibilized systems, which is different from the case for the tensile properties (see Figures 1, 2 and 5). This can be surmised from the difference of failure modes between tensile test and impact strength test. In impact strength tests, a propagating stress is transmitted to the TLCP phase through the compatibilizer, which deforms the TLCP phase. Excess energy is consumed by plastic deformation of the TLCP particles or fibril shapes. In a non-compatibilized system, a propagating stress passes around the TLCP phase since they are immiscible and the phases are separated. Hence, good adhesion enables the compatibilized system always to have higher impact strength. On the other hand, compatibilizer is included in the coalesced TLCP phase (Figure 3d-f) which decreases the tensile modulus and tensile strength of the TLCP phase. Under tensile stress, breakage can happen at the contacting surface area of the TLCP particles, which is occupied by the compatibilizer. Also, as we noted, excess compatibilizer brought poor dispersion of the TLCP phase. Hence the excessively compatibilized system always has lower tensile properties than the non-compatibilized system.

# CONCLUSIONS

Synthesized PEsI was used as a compatibilizer for a PEI/Vectra B950 in situ composite system. Morphological evidence demonstrated that addition of the correct

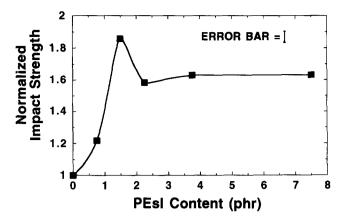


Figure 12 Normalized impact strength versus PEsI content for a PEI/TLCP blend. The draw ratio is 4. The error bar shows a standard deviation

amount of PEsI reduces the TLCP particle size and induces a fine distribution. However, optimum amounts of compatibilizer for the best mechanical properties and dispersion of the TLCP phase were observed. Excess amounts of PEsI coalesce the TLCP particles. The effectiveness of the compatibilizer depended on the absolute content of the compatibilizer. In the system studied, the adhesion at the interface was good due to chemical reaction and strong interaction 19. Tensile properties are enhanced with an optimum amount of the compatibilizer while impact strengths are always higher for compatibilized systems than for non-compatibilized ones. This is ascribed to the difference of the failure modes between these two tests.

With the goal of applying compatibilizer to an in situ composite, it is envisioned that this study can be expanded to explore the development of 'in situ' coupling between thermally stable thermotropic fibres and incompatible thermoplastic matrices using compatibilizers, in much the same fashion as compatibilizers have been applied in polymer blends<sup>36,37</sup>. This study would seem to stimulate more interest in the development of the compatibilized in situ composites.

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### REFERENCES

- Isayev, A. I. and Limtasiri, T. 'International Encyclopedia of Composites' (Ed. S. M. Lee), Vol. III, VCH Publishers, New York, 1990
- Turek, D. E., Siron, G. P., Tiu, C. and Tiek-Siang, O. Polymer 1992, 33, 4322
- 3 Dutta, D. and Weiss, R. A. Polym. Compos. 1992, 13, 394
- Carfagna, C., Amendola, E., Nicolais, L., Acierno, D., Francescangeli, O., Yang, B. and Rustichelli, F. J. Appl. Polym. Sci. 1991, 43, 839
- Crevecoeur, G. and Groenickx, G. Polym. Compos. 1992, 13, 244
- Crevecoeur, G. and Groenickx, G. Polym. Eng. Sci. 1990, 30, 532 6
- Sukhadia, A. M., Done, D. and Baird, D. G. Polym. Eng. Sci. 1990, 30, 9
- Lee, W. and DiBenedetto, A. T. Polym. Eng. Sci. 1992, 32, 400
- LaMantia, F. P., Cangialosi, F., Pedretti, U. and Roggero, A. Eur. Polym. J. 1993, 29, 671

- Carfagna, C., Netti, P. A., Nicolais, L. and DiBenedetto, A. T. 10 Polym. Compos. 1992, 13, 169
- Kiss, G. Polym. Eng. Sci. 1987, 27, 410 11
- Datta, A., Chen, H. H. and Baird, D.G. Polymer, 1993, 34, 759 12
- 13 Blizzard, K. G., Federic, C., Federico, O. and Chapoy, L. L. Polym. Eng. Sci. 1990, 30, 1442
- Lee, S., Hong, S. M., Seo, Y., Park, T. S., Kim, K. U., Hwang, 14 S. S. and Lee, J. W. Polymer, 1994, 35, 519
- Shin, B. Y. and Chung, I. J. Polym. Eng. Sci. 1990, 30, 13
- Bretas, R. E. S. and Baird, D. G. Polymer 1992, 24, 5233 16
- Lee, W. C. and DiBenedetto, T. Polymer 1993, 34, 684 17
- Bafna, S. S., Sun, T. and Baird, D. G. Polymer 1993, 34, 708 18
- Seo, Y., Hong, S. M., Hwang, S. S., Park, T. S., Kim, K. U., Lee, 19 S. M. and Lee, J. W. Polymer 1995, 36, 515
- 20 Utracki, L. A. 'Polymer Blends and Alloys', Hanser, New York, 1989
- King, J. A., Buttry, D. A. and Adams, D. F. Polym. Compos. 21 1993, 14, 292
- Taylor, G. I. Proc. R. Soc. A. 1934, 146, 501
- Weiss, R. A., Huh, W. and Nicolais, L. Polym. Eng. Sci. 1987, 23
- Han, C. D. 'Multiphase Flow in Polymer Processing'. Wiley, 24
- VanOene, H. J. Colloid Interface. Sci. 1972, 40, 448 25

- VanOene, H. in 'Polymer Blends' (Eds. D. R. Paul and 26 S. Newman), Vol 1, Academic Press, New York, 1978, Ch. 7
- 27 Elmendorp, J. J. and Maalcke, R. J. Polym. Eng. Sci. 1985, 25,
- Lee, W. K. and Flumerfelt, R. W. Int. J. Multiphase Flow 1981, 28
- 29 Blizzard, K. G. and Baird, D. G. Polym. Eng. Sci. 1987, 27, 653
- Nielsen, L. E. Mechanical Properties of Polymers and 30 Composites', Vol. 2, Marcel Dekker, New York, 1974
- 31 Gent, A. N. in 'Science and Technology of Rubber' (Ed. F. Eirich), Academic Press, New York, 1989, Ch. 10
- 32 Beaumont, P. W. R. and Schultz, J. M. 'Failure Analysis of Composite Materials', Delaware Composite Design Encyclopedia, Vol. 4, Technomic, Lancaster, PA, 1990
- Harris, B. and Phillips, D. C. J. Mater. Sci. 1975, 10, 2050
- 34 Piirma, I. 'Polymeric Surfactants', Marcel Dekker, New York,
- 35 Plochocki, A. P., Dagli, S. S. and Andrews, R. D. Polym. Eng. Sci. 1990, 30, 741
- Lee, W. C. and DiBenedetto, A. T. Polym. Eng. Sci. 1992, 36 32, 400
- 37 Paul, D. R., Barlow, J. W. and Keskkula, H. in 'Encyclopedia of Polymer Science and Engineering' (Eds. H. F. Mark et al.), Vol. 12, 2nd edn., Wiley, New York, 1988, p. 399