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Compatibilizing effect of a poly(ester imide) on the properties of the blends of poly(ether imide) and a thermotropic liquid crystalline polymer: 1. Compatibilizer synthesis and thermal and rheological properties of the *in situ* composite system

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This study investigates the compatibilizing effect of a poly(ester imide) (PEsI) on the blends of poly(ether imide) (PEI, Ultem 1000 from G.E.) and thermotropic liquid crystalline polymer (TLCP) (poly(ester amide), PEA, Vectra B950 from Hoechst Celanese). The compatibilizer, PEsI, was synthesized. Composite fibres were prepared by extrusion. Compatibility, thermal and rheological properties of the compatibilized *in situ* composite have been analysed. PEI and PEA blends are known from previous studies to be immiscible. Differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.) results, however, show that PEsI is miscible with both PEI and PEA. This means that synthesized PEsI can be used as a compatibilizer for the PEI/PEA *in situ* composite system. The viscosity of the compatibilized *in situ* composite was increased by the compatibilizer owing to the strong interaction. Significant changes in the dispersion of the TLCP were observed when the compatibilizing agent was added. The size of the dispersed phase appears to be controlled by interfacial phenomena rather than rheological effects. Explanations for the interaction of PEsI with PEI and TLCP related to the interfacial phenomena are presented.

(Keywords: compatibilizer; poly(ester imide); thermal and rheological properties of *in situ* composite)

INTRODUCTION

In recent years, binary or ternary blends of flexible chain polymers and liquid crystalline polymers have been extensively studied due to the potential to generate *in situ* reinforced composites of high mechanical performance with a variety of processing options[1–10]. It is well known that maximum enhancement of the mechanical properties of short fibre composites can be achieved by very fine fibrils with a large aspect ratio and by strong interfacial adhesion between the fibres and the polymeric matrix. Under certain processing conditions the thermotropic liquid crystalline polymers (TLCPs) can develop a fibrillar morphology with a high degree of orientation leading to enhanced mechanical properties. Both engineering thermoplastics and commodity resins have been reinforced using various TLCPs[1–17]. Most of the thermoplastics studied so far are incompatible with TLCPs. This incompatibility between the matrix polymers and reinforcing TLCPs leads to poor interfacial adhesion. The reinforcing effect is less than that obtained from the miscible system. Good mechanical properties have been achieved for immiscible blends of poly(ether imide) (PEI) and TLCPs in the flow direction. However, the mechanical properties in the normal direction are quite poor, but would be improved if the blends were miscible or compatible[11]. To improve the composite properties, a TLCP miscible with PEI was recently synthesized and its effect was investigated[12].

Another way to generate compatibility of the *in situ* composite is to add a third component as a compatibilizer. Ternary blends present an attractive approach to the development of reinforced systems. Usually the main goal is to compatibilize two immiscible or partially miscible polymers through the use of a third polymer in which both are miscible[15–17]. This idea was applied to the PEI/poly(ether ether ketone)(PEEK)/TLCP system by Bretas and Baird[15]. They found experimentally that morphologies of the partially miscible system were quite different from that of an immiscible system. It was shown that ternary blends with high moduli could be

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obtained at high TLCP loadings, while compositions with high ultimate tensile strength could be obtained with high loadings of PEI or PEEK. Lee and DiBenedetto[16] also considered ternary blend systems of TLCP (K161, Bayer A.G.)/TLCP (PET/PHB60, Eastmann Kodak)/thermoplastics. They introduced the second thermotropic TLCP (PET/PHB60) as a compatibilizer to improve the adhesion and dispersion between the components of incompatible TLCP/thermoplastic blends.

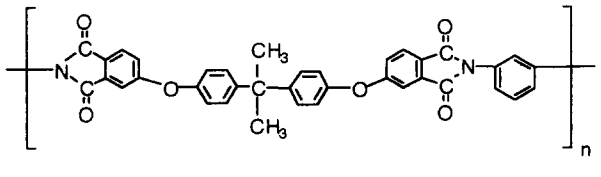
Compatibilizing agents are generally block or graft copolymers possessing segments with chemical structures or solubility parameters that are similar to those of the polymers being blended. Acting as polymeric surfactants, these reduce the interfacial tension, thus promoting interfacial adhesion, a finer dispersion and a more uniform distribution of the dispersed phase[17]. These result in improved mechanical properties of the blends. As mentioned before, compatibilization of thermoplastics with TLCPs has been attempted very recently and some aspects of the performance of the miscible system were reported in the literature[11,15–17]. However, to our knowledge, only Datta and his colleagues[17] have seriously tried to use a compatibilizer for immiscible blends of thermoplastics and TLCPs. They used a functionalized polypropylene (PP) to compatibilize the blend of PP with a TLCP. They observed that the key to property enhancement is improved interfacial adhesion, less phase separation and a more uniform TLCP distribution.

Poly(ether imide), an amorphous polymer commercially known as Ultem, has been blended with various TLCPs to prepare high-modulus and high-temperature *in situ* composites[4,5,13,17]. Ultem is known to be immiscible with poly(ester amide) TLCP[13]. The tensile strength and modulus of Ultem/PEA TLCP (Vectra B950) increase significantly in the flow direction but decrease in the normal direction. Also, elongation of the composite decreases significantly[14]. This is a loss of property for the blend. Improvement in mechanical properties without the sacrifice of other properties is desirable. The objective of this study is to synthesize a compatibilizer for a PEI/PEA *in situ* composite system, and to investigate its effect on the system properties.

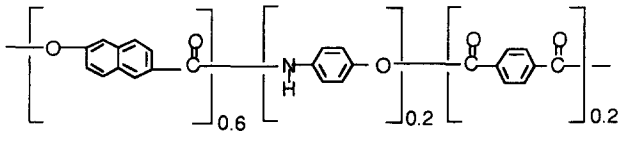
EXPERIMENTAL

Materials

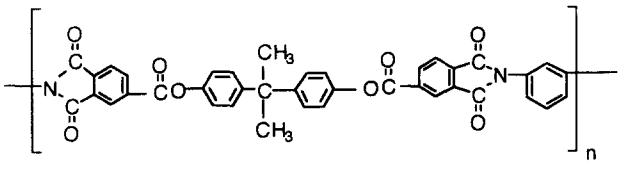
Ultem 1000 (PEI), an amorphous polymer made by G.E., was used as a matrix. The chemical structure of the repeating unit of Ultem is shown in *Scheme 1*. The chosen thermotropic TLCP was an extrusion grade resin, Vectra B950 (a copolymer based on 6-hydroxy-2 naphthoic acid (60%), terephthalic acid (20%), and aminophenol (20%) produced by Hoechst Celanese Co.). It possesses the chemical structure shown in *Scheme 2*.



Scheme 1



Scheme 2



Scheme 3

Table 1 Reagents used and their purification

Reagents	Company	Purification
Trimellitic anhydride	Fluka (Swiss)	Sublimation
p-Toluenesulfonylchloride	Junsei (Japan)	Dissolved in $CHCl_3$ and recrystallized in n-hexane
Bisphenol-A	Junsei (Japan)	Recrystallized from acetic acid
1,3-Phenylenediamine	Janssen (Belgium)	Recrystallized from EtOH
Pyridine	Kanto (Japan)	Refluxed with KOH for at least 3 days

Compatibilizer synthesis

The compatibilizer used in this study is a poly(ester imide) (PEsI) having the chemical structure shown in *Scheme 3*. This is similar to PEI but has an ester unit instead of an ether unit. We have synthesized PEsI following the scheme of Tanaka and Sakaguchi[18]. The reagents used and their purification method are summarized in *Table 1*. The typical polymerization procedure is described below.

First, 0.05 mol of trimellytic anhydride and 0.06 mol of *p*-toluene sulfonyl chloride were dissolved in 100 ml of pyridine with stirring at room temperature for 10 min under nitrogen atmosphere in a three-necked 500 ml round-bottomed flask equipped with stirrer and nitrogen inlet. Then 0.025 ml of bisphenol A was added to the mixture with vigorous stirring. As soon as *p*-toluene sulfonyl was added, an exothermic reaction took place and the solution turned a pale yellow colour. Prior to the addition of bisphenol A the reaction proceeded in a heterogeneous manner, but when bisphenol A was added, the reaction became homogeneous. Next, 0.025 mol of *m*-phenylene diamine was added to the reaction solution and stirring continued for 30 min. After a period of time, the mixture was poured into excess methanol (1 litre) to remove pyridine, by-products and unreacted monomers from the polymer, which was then isolated by filtration. The polymer (polyamic acid, PAA) was repeatedly washed with methanol, and then dried *in vacuo* for 48 h. The yield was over 95%. Synthesized PAA was ground into a powder to maximize the surface area. The powder was dried at 70°C for 1 h, then heated at 265°C, 275°C and 285°C for 20 min each in a heating oven. Nitrogen was purged in order to remove the evolved water.

Figure 1 shows the PEsI preparation procedure. The structure of the produced PEsI was confirmed by i.r. spectroscopy and ^{1}H n.m.r. *Figure 2* shows the i.r. spectra of the synthesized PAA and PEsI. The PAA spectrum shows characteristic peaks at 3416 cm^{-1} (OH stretching) and 1672 cm^{-1} (secondary amide deformation). After imidization these two peaks have almost disappeared. Four characteristic imide bands at 1780, 1720, 1370 and 720 cm^{-1} are clearly shown. The bands at 1780 and 1720 cm^{-1} are assigned to imide carbonyl stretching. The bands at about 1370 cm^{-1} result from imide carbon–nitrogen stretching and the band at 720 cm^{-1} from the bending of the imide ring. The band at 1740 cm^{-1} is assigned to ester carbonyl stretching. *Figure 3* shows the ^{1}H n.m.r. spectrum of PEsI. The signals were assigned as: ^{1}H n.m.r. (300 MHz in $CDCl_3$) δ (ppm) 1.75 (s, 6H, CH_3), 7.2 (d, 4H, aromatic H), 7.38 (d, 4H, aromatic H), 7.65 (t, 2H aromatic H), 8.13 (d, 2H, aromatic H), 8.68 (d, 2H, aromatic H), 8.76 (s, 2H, aromatic H).

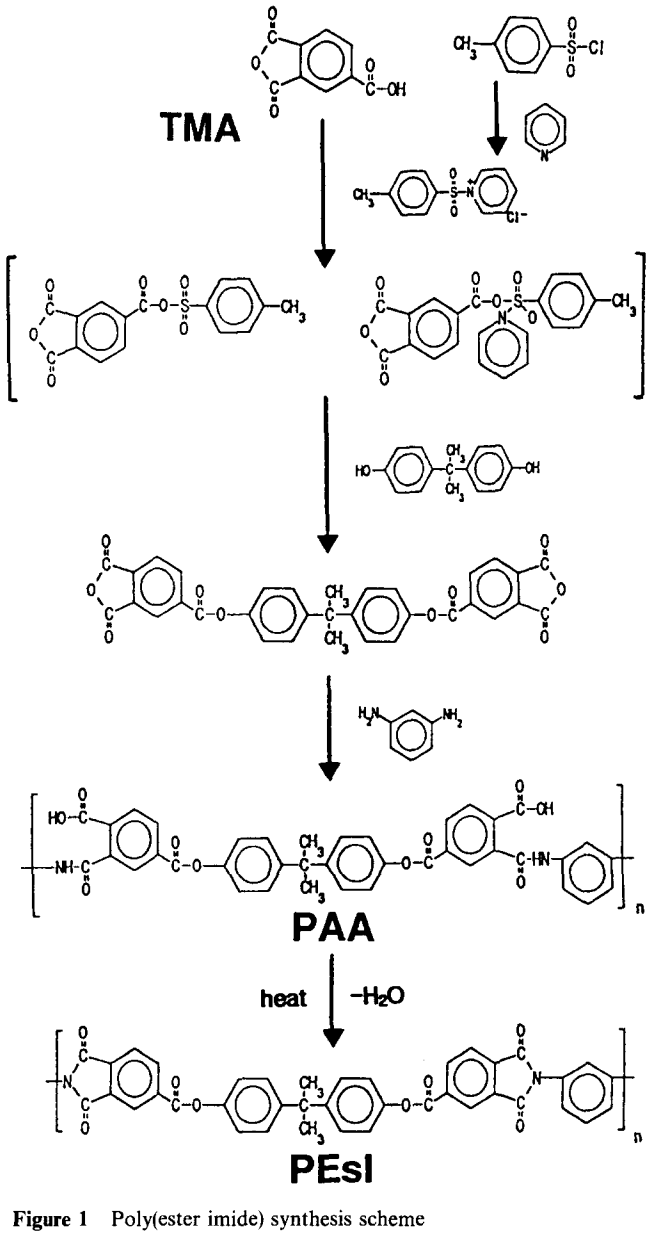


Figure 1 Poly(ester imide) synthesis scheme

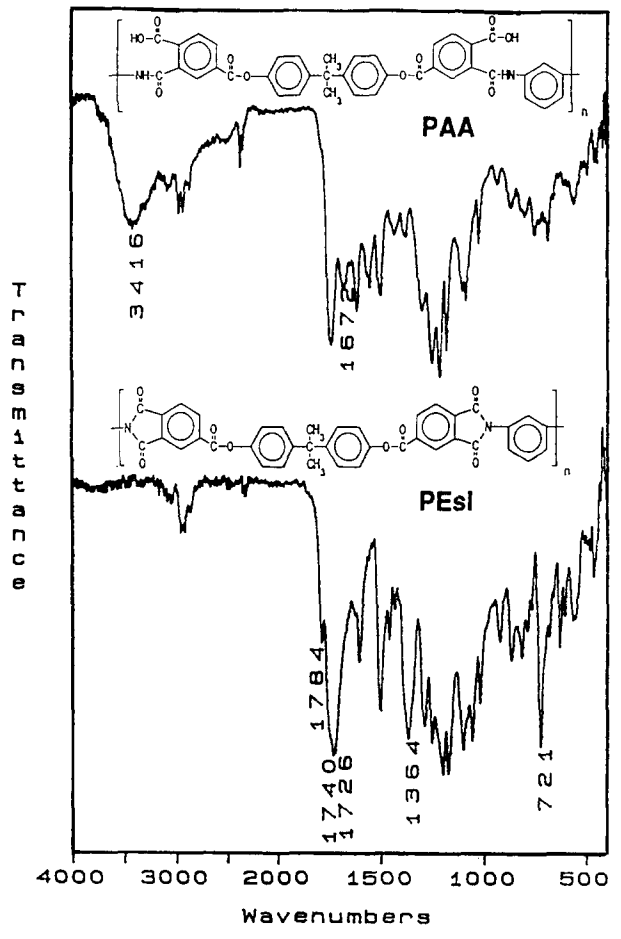


Figure 2 I.r. spectra of the synthesized PAA and PEsI

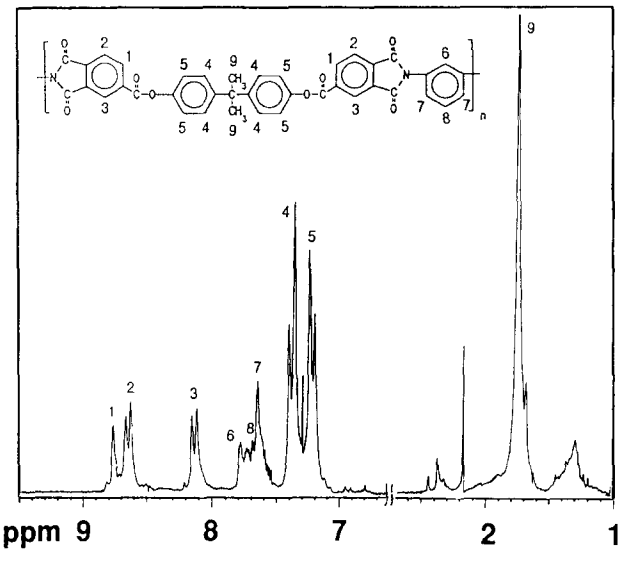


Figure 3 N.m.r. spectrum of synthesized PEsI

Instruments

Blending and extrusion. The pellets of PEI and Vectra B were dried in a vacuum oven at 120°C for at least 24 h before use. The TLCP content was kept as 25 phr, at which content the composite showed a maximum fibril aspect ratio[13]. Dried pellets of PEI and Vectra B were mixed in a container, then PEsI was added. Blending was carried out in a 42 mm Brabender twin-screw extruder (AEV651) at a fixed rotation speed of

30 rev min^{-1}. The extruder was equipped with a pulling unit imparting different draw ratios (DR), defined as the ratio between the diameter at the die exit to that far downstream. Many strands of different DR were obtained. The extrusion temperatures of the feeding zone/transporting zone/melting zone/die were set at 140/290/290/240°C. An internal mixer (Brabender W50EH) was also used for blending.

FT*i.r. spectra and* FT *Raman spectra.* Fourier transform infra-red (*FT*i.r.) spectra of the PEsI and PAA were taken using an Alpha Centauri Spectrometer (Mathson Instrument) with the average of 32 scans at 4 cm^{-1} resolution. *FT* Raman spectra were obtained using a Perkin–Elmer system 2000 instrument equipped with near-i.r. optics. Spectra were obtained with 4 cm^{-1} resolution, and typically took 10–15 min acquisition time.

Light-scattering apparatus. A light-scattering instrument was used for the measurement of the absolute M_w. It is a commercial instrument (Malvern 4700) equipped with a 64-channel, 8-bit digital correlator. It uses a 632.8 nm He/Ne laser (Spectra Physics 117-35) as the light source.

Thermal properties. Differential scanning calorimetry (d.s.c.) studies for the thermal property characterization were performed on a Du Pont 910 DSC controlled by a 9900 thermal analyser. The heating rate was 10°C min^{-1}, the cooling rate was 10°C min^{-1}, and the materials were scanned from 30 to 350°C. Every thermogram was repeated at least twice, and a duplicate blend was then analysed to verify the reproducibility of the measurement.

N.m.r. spectra. ^1H n.m.r. spectra were recorded on a Varian Gemini 300 spectrometer at 300 MHz with tetramethylsilane as the internal standard.

Scanning electron microscopy. Scanning electron microscopy (SEM) observations of the composite samples were performed on Hitachi model S-2200C. The samples, fractured in liquid nitrogen, were coated with gold to make them electrically conducting. The morphology of the inner surface parallel to the flow direction was also observed after peeling off the fibre surface.

Rheometry. Rheological properties of the blends and pure resins were measured using a Rheometrics Dynamic Spectrometer (RDS) (RDS 7700, Rheometrics, USA) on which a 25 mm diameter parallel plate was mounted. The frequency range was set at 0.1–500 rad s^{-1} and the applied strain was 15%. The plate gap was set at 1.2 mm. Before the measurement, the samples were prepared using a compression moulder at 350°C. Measurements were done under nitrogen atmosphere. The viscosity at high shear rates was evaluated by a capillary rheometer (Instron 3211) of which the capillary *L/D* ratio was 40 and the diameter was 1.27 mm. Dynamic mechanical thermal analysis (d.m.t.a.) of the blends was carried out with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model 2) at the frequency of 1 Hz. A single-cantilever clamping geometry in the bending mode was used.

RESULTS AND DISCUSSION

Thermal properties

Before the analysis of the ternary blends (PEI/TLCP/PEsI) was started, binary blends were studied. The glass transition temperature, T_g, was evaluated by d.s.c. and related to the d.m.t.a. point where tan δ had a maximum. *Figure 4* shows the dynamic mechanical response of PEI, TLCP, PEsI and binary blends of PEI/PEsI and TLCP/PEsI. In *Figure 4*, the magnitude of the tan δ peak in the amorphous PEsI is much higher than in TLCP, but is close to PEI. TLCP shows a broader and smaller tan δ than PEsI. Transition behaviours of the PEI/PEsI blend (50:50) and TLCP/PEsI blend (70:30) show miscibility. Two peaks corresponding to relaxation at T_g were observed for these blends. These two peaks move towards each other. When the original T_g of each polymer in a blend shifts towards that of the other polymer, partial miscibility is suggested and each coexisting phase is a mixture. This means the blends are biphasic[19]. D.s.c. results show similar behaviour. A representative d.s.c. heating scan for the Vectra B/PEsI (98:2) mixture is shown in *Figure 5*. The sample was

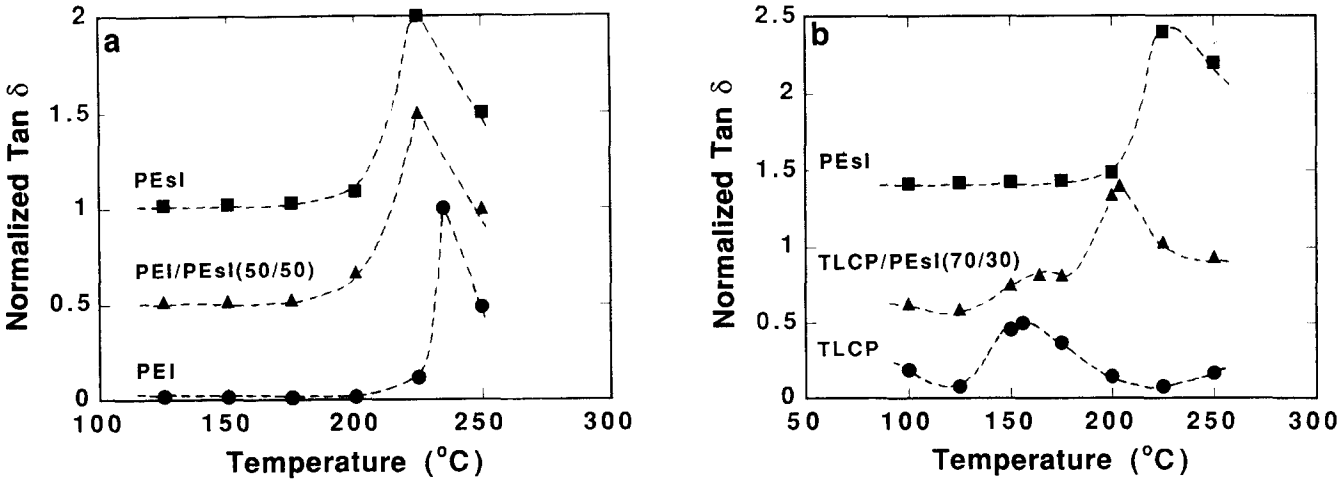


Figure 4 (a) Normalized tan δ *versus* temperature for PEI, PEsI and PEI/PEsI blends. (b) Normalized tan δ *versus* temperature for TLCP, PEsI and TLCP/PEsI blends

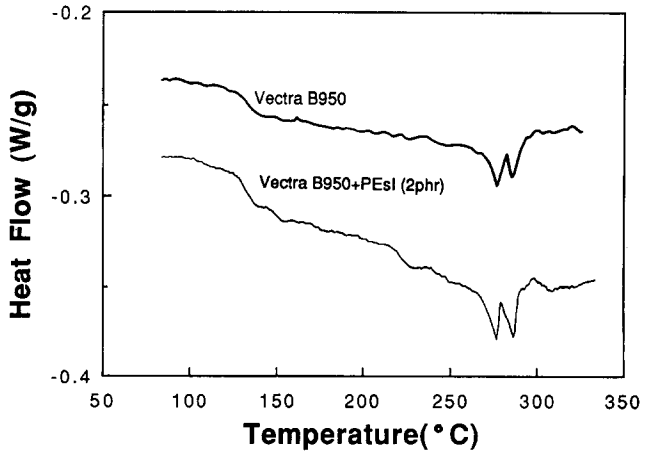


Figure 5 Ds.c. thermograms for TLCP/PEsI (98:2) blends

heated at 330°C for 10 min and cooled down to 115°C for 10 min before heating at 10°C min^{-1} when the trace was recorded. A double T_g and an intricate melting endotherm are present. The low T_g occurring at 124°C is the T_g of Vectra B. The second T_g at 152°C seems to be the glass transition of Vectra B/PEsI. It is much higher than the T_g of Vectra B and lower than that of PEsI (220°C). It indicates partial miscibility of this blend. The positions corresponding to the glass transition temperature are different for the d.s.c. and d.m.t.a. results. This might be due to the difference in heating rates used in the d.s.c. (10°C min^{-1}) and d.m.t.a. (2°C min^{-1}) experiments[2].

In the d.s.c. thermograms for Vectra B/PEsI blends, two sharp endotherm peaks are neighbouring. Complex melting phenomena are common in terephthalate polymers. They are attributed to the melting of tiny, imperfectly formed crystallites at low temperatures[20,21]. The nature of this complicated melting endotherm is controversial. Earlier, dual endothermic transitions at temperatures below the isotropic transition temperature were observed by several authors: Lin and Winter[22,23] on the 72/27 *p*-hydroxybenzoic acid (HBA)/6-hydroxy-2-naphthoic acid (HNA) copolyester (Vectra A900); Butzbach and co-workers[24] on the 58/42 HBA/HNA copolyester; Cheng and co-workers[25] on a thermotropic copolyester consisting of *p*-benzenedicarboxylic acid, phenylhydroquinone and (1-phenyl-ethyl) hydroquinone; and Nam and co-workers[26] on a thermotropic copolyester consisting of bisphenol E diacetate, isophthalic acid and 2,6-naphthalenedicarboxylic acid. Based on the results from wide-angle X-ray diffraction, Lin and Winter[22,23] attributed the existence of the slow process that occurs during a long-period isothermal annealing to high-temperature recrystallization, and Nam and co-workers[26] attributed it to melting and recrystallization. In contrast, Cheng and co-workers[25] attributed its existence to a solid–solid transformation. Based on these studies and their own experimental results for the rheological behaviour of poly[(phenylsulfonyl)-*p*-phenylene-1,10-decamethylenebis(4-oxybenzoate)], Kim and Han[27] observed similarities in complicated dual endothermic transitions for the TLCPs with vastly different chemical structures. They concluded that the underlying mechanism(s) responsible for the existence of dual transitions, may be independent of the chemical structures of the TLCPs and may be intrinsic to TLCPs. Details of the Vectra B950 are being investigated and will be reported in the future.

Figure 6 shows that the exotherm peak represents the crystallization process upon cooling from the melt. Crystallization temperature shifts to a lower value on blending with PEsI. When the sample is cooled after heating at 330°C for 1 min and 10 min, the peak becomes broader and broader due to PEsI which acts as an impurity in crystallization. *Table 2* shows the crystallization temperature and nematic transition temperature of Vectra B with different amounts of PEsI. The d.s.c. thermogram of 50/50 PEI/PEsI blend shows a single T_g formed near that of PEI. Since the T_g values of PEI and PEsI are so close, it is not easy to tell whether they are miscible. However, previous d.m.t.a. results (*Figure 4b*) show that they form a miscible blend. *Table 3* shows the thermal properties of a ternary system where PEsI is added to PEI and TLCP blends. Since PEsI is amorphous, the heat of fusion per unit mass of TLCP (ΔH_m) is decreased by PEsI. The T_g of the PEI phase is also decreased by PEsI. This corroborates the d.m.t.a. result. The heat of crystallization (ΔH_c) and crystallization temperature of the TLCP phase are decreased. More details of the binary blends are reported elsewhere[28].

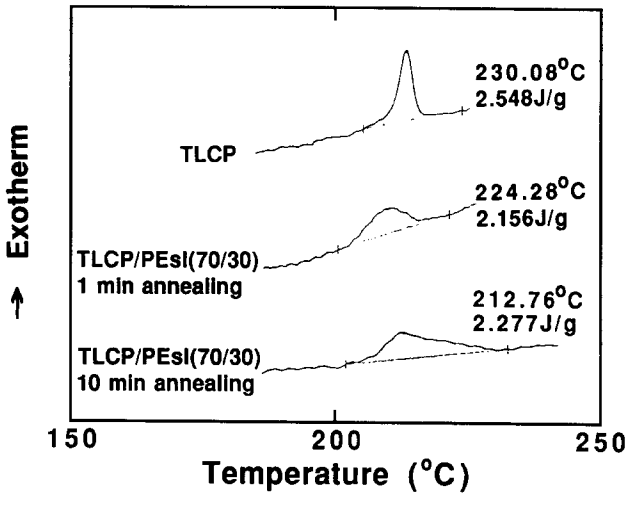


Figure 6 Crystallization exotherms for TLCP, TLCP/PEsI blend at the cooling rate of 5°C min^{-1}

Table 2 T_c and T_m values of Vectra B blends with PEsI

PEsI amount (phr)	T_c (°C)	T_m (°C)
0	230	281
1	226	279
2	227	279
5	230	280

Table 3 Thermal properties of PEI/TLCP blends

Composition (phr) PEI/TLCP/PEsI	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
100/0/0	218.6	–	–	–	–
75/25/0	214.2	272.9	0.87	229.4	0.45
74.25/25/0.75	213.4	272.9	0.87	229.4	0.45
73.5/25/1.5	212.2	271.9	0.51	228.5	0.33
67.5/25/7.5	212.1	275.8	0.27	220.0	0.17

Rheological properties

The molecular weight of synthesized PEsI was measured using a light-scattering instrument. Dimethylformamide was used as solvent. The M_w of PEsI is 16000 g mol^{-1}, which is lower than that of PEI. The flow curves at 340°C for the compatibilized TLCP/PEI blends are shown in *Figure 7*. All the melts in the shear rate range studied exhibited non-Newtonian flow behaviour. The TLCP amount was fixed as 25 phr. The viscosity of the blends is increased by the compatibilizer. Generally, the addition of a low-molecular-weight component to immiscible blends results in decreasing viscosity due to plasticizing action by the added component[19]. However, interaction by the compatibilizer in this blend system increases the viscosity. This is due to the strong interaction by chemical reaction as shown later. The location of the compatibilizer at the phase boundary, together with chemical bonding of the two phases, reduces the free volume and the chain mobility; hence it induces the increased viscosity.

We also observed the viscosity variation with time at constant shear rates using the RDS. Time sweep measurements were done on the RDS at a frequency of 10 rad s^{-1} and at a temperature of 335°C. The result is shown in *Figure 8*. This blend displays a complicated

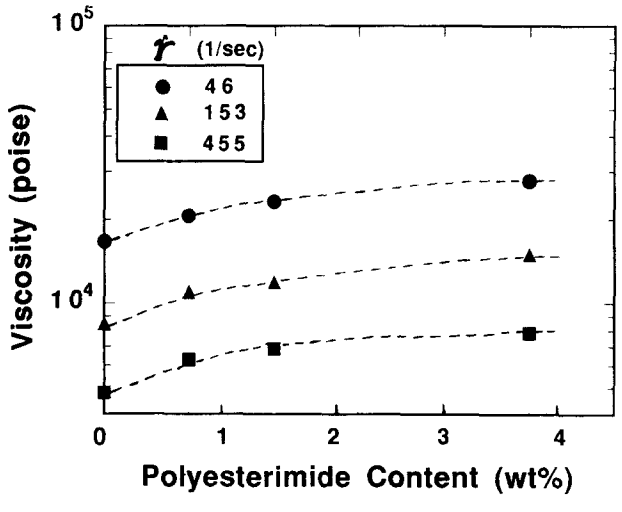


Figure 7 Complex viscosity of the PEI/TLCP/PEsI blends

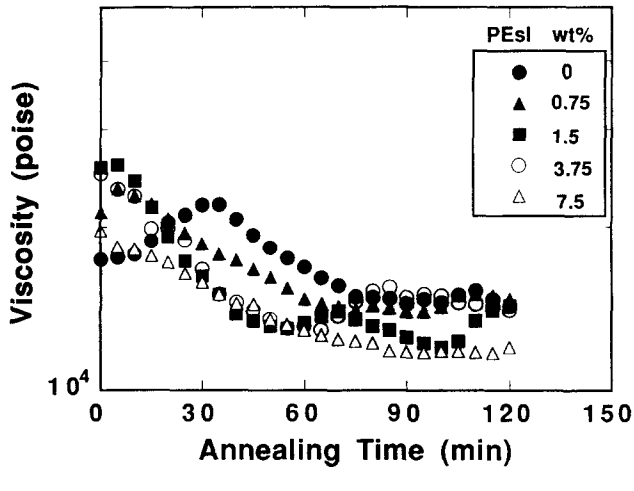


Figure 8 Viscosity *versus* annealing time for PEI/TLCP/PEsI blends

behaviour with the amount of PEsI. In obtaining the results in *Figure 7*, an as-cast specimen was placed in the parallel-plate fixture, which had been heated to a predetermined temperature. In the rheometer, a sample was heated to 335°C, held for 2 min and then measurements were taken at intervals of 2 min. Complex viscosity and storage modulus of PEI/Vectra B increased slightly at the start, but eventually decreased very slowly. After some time had passed, slight increases of the complex viscosity and the storage modulus were observed. Similar phenomena were observed in the rheological behaviour of TLCP melts. For the non-compatibilized system, this might be ascribed to the formation of a crystal-like phase[23]. As with the dual endothermic transitions, the intrinsic nature of this phenomenon is quite controversial. According to the experimental results of Kim and Han[27], it is attributable to the formation of a crystal-like phase. Using n.m.r. spectroscopy and wide-angle X-ray diffractometry, this is under investigation and results will be presented in the future[29]. Transesterification or other chemical reaction probably occurred in the ternary system.

Interaction by the compatibilizer

Figure 9 shows SEM microphotographs of the fractured surfaces of non-compatibilized and compatibilized PEI/Vectra B blends of draw ratio 1. The samples were fractured normal to the flow direction. The TLCP domains are relatively large in the non-compatibilized blends, indicating a poor dispersion. The micrographs also demonstrate the poor adhesion between the two phases (*Figure 9a*); an open ring hole is seen around the TLCP domain and a whole TLCP fibril was 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 9b*), and there is no open ring around the TLCP domain. This indicates better adhesion between the two phases.

The interfacial adhesion between PEI and Vectra B is possibly ascribed to the chain interactions of the compatibilizer with PEI and Vectra B. The synthesized compatibilizer (PEsI) has almost the same structure as PEI except for the ester group. Electronic polarization (or charge transfer) can be expected between the π-electron-sufficient diamine-derived moiety and the highly π-electron-deficient anhydride-derived moiety[30]. There are possible interactions between PEsI and Vectra B. The first is a transesterification or ester–hydroxyl interchange reaction. The second, which is hardly likely to occur, is the amic acid reaction with Vectra B. We believe imidization was completed by thermal treatment. However, low heat conductivity of the imide prevents thermal energy from propagating into the inner part of the poly(amic acid) powder. Even with enough thermal energy, the reaction rate constant for the second imidization on the poly(amic acid) is much lower than for the first imidization[31]. If it remains, poly(amic acid) can react with Vectra B to form a block copolymer which acts as a compatibilizer[32]. However, the i.r. spectrum (*Figure 2*) does not show the characteristic peak of PAA after the imidization.

At present, we lack detailed information on the molecular weight and molecular weight distribution of Vectra B. A normal liquid crystalline polymer does not dissolve in common solvents. Therefore we do not know

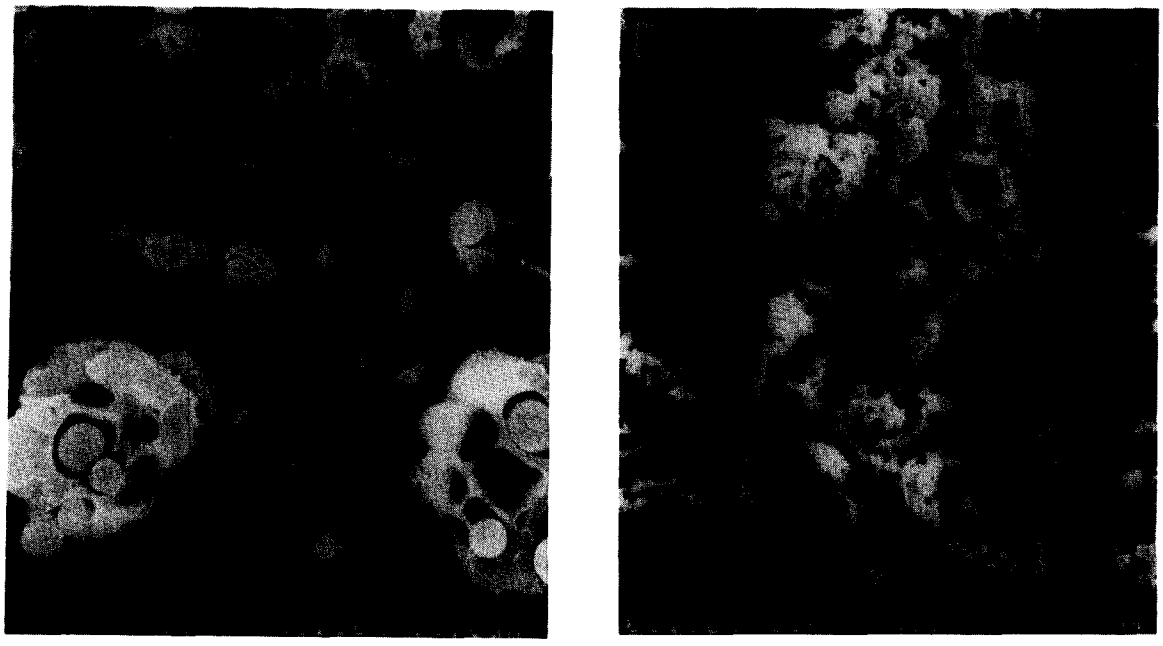


Figure 9 SEM photographs of fractured surfaces of PEI/TLCP/PEsI blend fibres at a draw ratio of 1. The samples were fractured after freezing in liquid nitrogen. The amount of PEsI in the blends is: (a) 0 phr; (b) 0.75 phr

what reaction occurred, but we believe that some chemical reactions have taken place. To confirm this, Vectra B and PEsI were blended in 70:30 weight ratio in a twin-screw extruder. The blended extrudate was dissolved by stirring CH_2Cl_2 for a week. Since synthesized PEsI dissolves very well in CH_2Cl_2, almost all of the free PEsI should have been extracted. The remnant was dried for a day in a vacuum oven at 60°C. We could not use *FT*i.r. spectroscopy, because the remnant was not easily blended with KBr, so a *FT* Raman spectrum was taken. *Figure 10* shows the Raman spectra of Vectra B, PEsI and the remnant of the blend. A new peak appears in the spectrum of the remnant at 1782 cm^{-1}, which is characteristic of imide compounds. Hence we believe that a chemical reaction occurred between PEsI and Vectra B. Through this chemical reaction, PEsI forms a block or graft copolymer at the surface of Vectra B, which acts as the compatibilizer.

To investigate the strength of interaction that occurred between PEsI and PEI or PEsI and Vectra B, different mixtures were prepared. We adopted two-step mixing. This was performed by preparing a blend of PEsI and PEI or Vectra B and then mixing it with the other component. By preblending the compatibilizer with the TLCP dispersed phase, if PEsI has a higher affinity for Vectra, it is possible that during melt mixing this affinity would ensure a random distribution of the compatibilizer within the dispersed TLCP phase rather than a high concentration of compatibilizer at the PEI/Vectra B interface. Also, if the interaction is stronger between PEsI and PEI, then the high affinity of the PEsI for the PEI may result in a preferential concentration of compatibilizer at the interface, producing a finer dispersion than in the former case. A diagrammatic representation of this effect is shown in *Figure 11*. Blending was done in the internal mixer at 340°C for 20 min. The fracture surfaces for these blends are shown in *Figure 12*. Compatibilized blends clearly show finer dispersions than non-compatibilized systems. The weight-average particle diameter, defined as $d_w = \Sigma N_i d_i^2 / \Sigma N_i d_i$, is given in *Table*

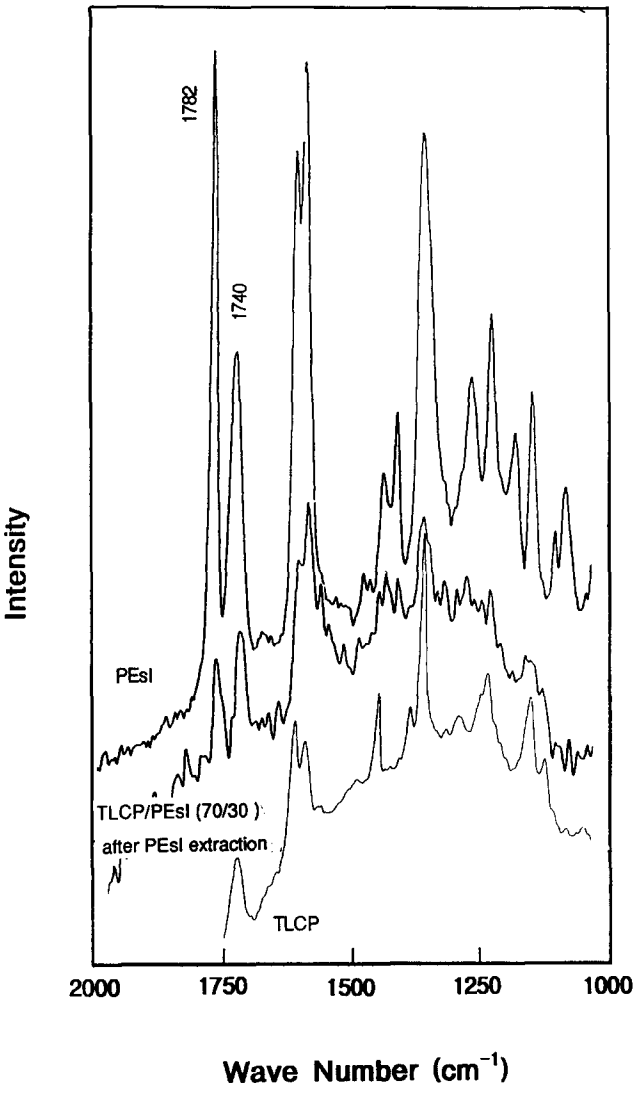


Figure 10 *FT* Raman spectra of PEsI, TLCP and the TLCP/PEsI blend after PEsI extraction

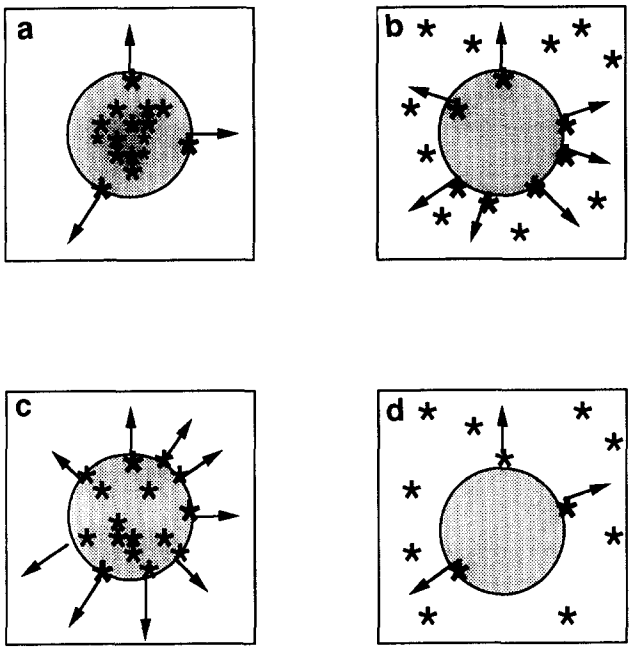


Figure 11 Speculative model of the interactions between the PEsI and the matrix (PEI) and dispersed phase (TLCP) during two-step mixing. The circles represent the TLCP particles and the stars represent the compatibilizer. Arrows represent interactions across the PEI/TLCP interface (after Willis and Favis[33]). (a, b) When PEsI has a greater affinity for TLCP: ((a) preblended with TLCP; (b) preblended with PEI). (c, d) When PEsI has a greater affinity for PEI: ((c) preblended with TLCP; (d) preblended with PEI)

Table 4 Weight-average diameter of TLCP for different mixing processes

Mixing process[a]	Diameter (μm)
PEI/TLCP	2.2 ± 0.1
PEI/m-TLCP (premixed with 1.5 phr PEsI)	1.88 ± 0.07
m-PEI (premixed with 1.5 phr PEsI)/TLCP	1.68 ± 0.06

[a] TLCP portion was 25 phr

4, where N_i is the number of particles whose size is d_i. The dimension of the dispersed phase is smaller when PEsI is preblended with PEI than when it is preblended with TLCP. This means that PEsI has a greater affinity for Vectra B than for PEI. Again, this implies that some interactions clearly exist between PEsI and Vectra B or PEI. However, there is only a negligible change in the viscosities of the blends prepared by the different mixing processes at a PEsI concentration of 1.5 phr. Hence, the influence of the mode of mixing on the size of the dispersed phase is related to interfacial phenomena rather than rheological effects[33].

CONCLUSION

A poly(ester imide) with a similar structure to PEI was synthesized. The miscibility between PEsI and PEI or Vectra B was determined by measuring the T_g shift by d.s.c. and d.m.t.a. Complicated endothermic peaks were observed near the crystalline transition temperature. The crystallization temperature of TLCP shifts to lower temperature when blended with PEsI. Addition of PEsI to PEI/TLCP blends results in increased viscosity. Transient rheological behaviours of the compatibilized systems were quite complicated.

In situ composites of PEI/TLCP (25 phr)/PEsI were prepared. The addition of PEsI as a compatibilizer results in a dramatic reduction of the dispersed LCP size. The compatibilized system shows good adhesion at the interface. From SEM micrographs of fractured surfaces, the addition of the compatibilizer to PEI/TLCP blends was found to increase the adhesion between the matrix and the dispersed phase. The compatibilized blends displayed a much finer dispersion of the minor phase in the matrix polymer. The emulsifying ability of the compatibilizer also induced a reduction in the particle size. A chemical reaction is believed to occur between PEsI and Vectra B to produce a block or graft copolymer which provides a strong interaction at the interface. A speculative description of the interactions that may exist across the matrix/dispersed phase was suggested to interpret the morphological observations made on these

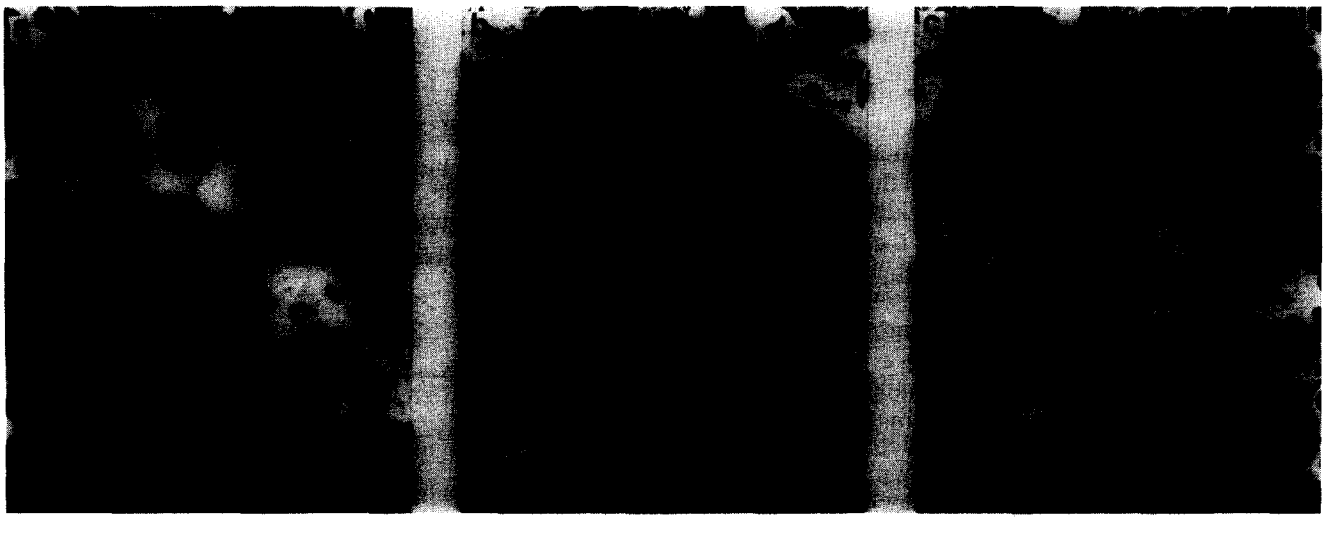


Figure 12 SEM micrographs of fractured surfaces of the blends prepared with different mixing processes. (a) No PEsI; (b) PEI/TLCP (TLCP was preblended with PEsI); (c) PEI/TLCP (PEI was preblended with PEsI)

in situ composites. PEsI shows a stronger interaction with Vectra B than with PEI. The effect of the compatibilizer is almost the same as that of the emulsifier. Its effect on the mechanical performance of PEI/TLCP *in situ* composite is presented in the accompanying paper[34].

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REFERENCES

1 Isayev, A. I. and Limtasiri, T. 'International Encyclopedia of Composites' (Ed. S. M. Lee), Vol. III, VCH Publishers, New York, 1990
2 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
4 Carfagna, C., Amendola, E., Nicolais, L., Acierno, D., Francescangeli, O., Yang, B. and Rustichelli, F. *J. Appl. Polym. Sci.* 1991, **43**, 839
5 Crevecoeur, G. and Groenickx, G. *Polym. Compos.* 1992, **13**, 244
6 Sukhadia, A. M., Done, D. and Baird, D. G. *Polym. Eng. Sci.* 1990, **30**, 9
7 Lee, W. and DiBenedetto, A. T. *Polym. Eng. Sci.* 1992, **32**, 400
8 LaMantia, F. P., Cangialosi, F., Pedretti, U. and Roggero, A. *Eur. Polym. J.* 1993, **29**, 671
9 Carfagna, C., Netti, P. A., Nicolais, L. and DiBenedetto, A. T. *Polym. Compos.* 1992, **13**, 169
10 Kiss, G. *Polym. Eng. Sci.* 1987, **27**(6), 410
11 Bafna, S. S., Sun, T. and Baird, D. G. *Polymer* 1993, **34**, 708
12 Ryu, C., Seo, Y., Hwang, S. S., Hong, S. S., Park, T. S. and Kim, K. U. *Int. Polym. Proc.* 1994, **9**(3), 266
13 Lee, S., Hong, S. M., Seo, Y., Park, T. S., Kim, K. U. and Lee, J. W. *Polymer* 1993, in press
14 Shin, B. Y. and Chung, I. J. *Polym. Eng. Sci.* 1990, **30**, 13
15 Bretas, R. E. S. and Baird, D. G. *Polymer* 1992, **24**, 5233
16 Lee, W. C. and DiBenedetto, T. *Polymer* 1993, **34**, 684
17 Datta, A., Chen, H. H. and Baird, D. G. *Polymer* 1993, **34**, 759
18 Tanaka, H. and Sakaguchi, M. in 'Polyimides: Materials, Chemistry and Characterization' (Eds C. Feger, M. M. Khojasteh and J. E. McGrath) Elsevier, Amsterdam, 1989, p. 363
19 Utracki, L. A. 'Polymer Blends and Alloys', Hanser, New York, 1989
20 Laivins, G. V. *Macromolecules* 1989, **22**, 3974
21 Ponnusamy, E. and Balakrishnan, T. *Polym. J.* 1987, **19**, 1209
22 Lin, T. G. and Winter, H. H. *Macromolecules* 1988, **21**, 2439
23 Lin, T. G. and Winter, H. H. *Macromolecules* 1991, **24**, 2877
24 Butzbach, G. D., Wendorf, J. H. and Zimmerman, H. J. *Polymer* 1986, **27**, 1337
25 Cheng, S. Z. D., Zhang, A., Johnson, R. L., Wu, Z. and Wu, H. H. *Macromolecules* 1990, **23**, 1196
26 Nam, J., Fukai, T. and Kyu, T. *Macromolecules* 1991, **24**, 6250
27 Kim. S. S. and Han, C. D. *Macromolecules* 1993, **26**, 3176
28 Lee, S. M. *PhD Dissertation*, Sogang University, Seoul, Korea, 1993
29 Seo, Y. *et al.* unpublished results
30 St Clair, T. L., Pratt, J. R., Stoakley, D. M. and Burks, H. D. in 'Polyimides, Materials, Chemistry and Characterization' (Eds C. Feger, M. M. Khojasteh and J. E. McGrath), Elsevier, Amsterdam, 1989, p. 243
31 Pyun, E., Mathiesen, R. J. and Sung, C.S.P. *Macromolecules* 1989, **22**, 1974
32 Ide, F. and Hasegawa, A. *J. Appl. Polym. Sci.* 1974, **18**, 963
33 Willis, J. M. and Favis, B. D. *Polym. Eng. Sci.* 1988, **28**, 1416
34 Seo, Y., Hong, S. M., Hwang, S. S., Park, T. S., Kim, K. U., Lee, S. and Lee, J. *Polymer* 1995, **36**, 525