

Effect of Poly(esterimide)s as Compatibilizers on the Physical Properties of Poly(etherimide)/Thermotropic Liquid Crystalline Polymer *in-situ* Composites

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ABSTRACT: This study investigates the compatibilizing effect of poly(esterimide) (PEsI) on the blend of poly(etherimide) (Ultem 1000; Ultem from General Electric Company) and thermotropic liquid crystalline polyesteramide (Vectra B950; Vectra B from Hoechst Celanese). Two types of polyesterimide (PEsI) were prepared as compatibilizers to improve the interfacial adhesion of incompatible Ultem and Vectra B. Poly(ethyleneterephthalate) (PET) based PEsI (EI10) and poly(butylene terephthalate) (PBT) based PEsI (BI10) including 10 mol% of the imide are prepared. The binary Vectra B/PEsI and Ultem/PEsI blends were investigated in terms of thermal properties. This revealed that EI10 is more reactive (or compatible) with Vectra B, whereas BI10 is more compatible with Ultem. The effect of compatibilizer structures on the ternary Ultem/Vectra B/PEsI blends was also studied by thermal behavior, rheological properties, and mechanical properties. These results showed that BI10, more compatible with Ultem matrix, acts as a better compatibilizer in a ternary Ultem/Vectra B/PEsI blend system than EI10, more compatible with Vectra B phase. The optimum level of the compatibilizers turned out to be about 1–2 wt% for the blend systems.

KEY WORDS Polyesterimide / Interfacial Adhesion / Liquid Crystalline Polyesteramide / Poly(etherimide) / Compatibilizer /

In recent years polymer blends in which a thermotropic liquid crystalline polymer (TLCP) dispersed in a thermoplastic matrix, so called the *in-situ* composite, have frequently been studied to exploit the excellent mechanical properties of the TLCP such as high tensile strength/modulus, low thermal expansion coefficient, low dielectric properties, and low moisture pick-up.^{1–5} Furthermore, physical properties such as thermomechanical properties, transient viscosity, crystallization behavior, morphology, and rheological properties of TLCP/isotropic polymer blends have been lively investigated.^{6,7}

TLCP molecules can easily line up during shearing, thereby they reduce the resistance to flow. If a spinning process is performed, moreover, the oriented fibrillar species can be obtained in the solid state due to the long relaxation time of TLCP chains.^{5,8,9} *In-situ* composites can be produced by melt blending of two components in twin screw extruder or static mixer, followed by elongation. TLCP phases are usually deformed into microfibrils along the flow direction, and the matrix can be reinforced. In most cases, however, dispersed TLCP domain and thermoplastic matrix are immiscible. Thus, their *in-situ* composites show limited mechanical properties resulting from weak interfaces.

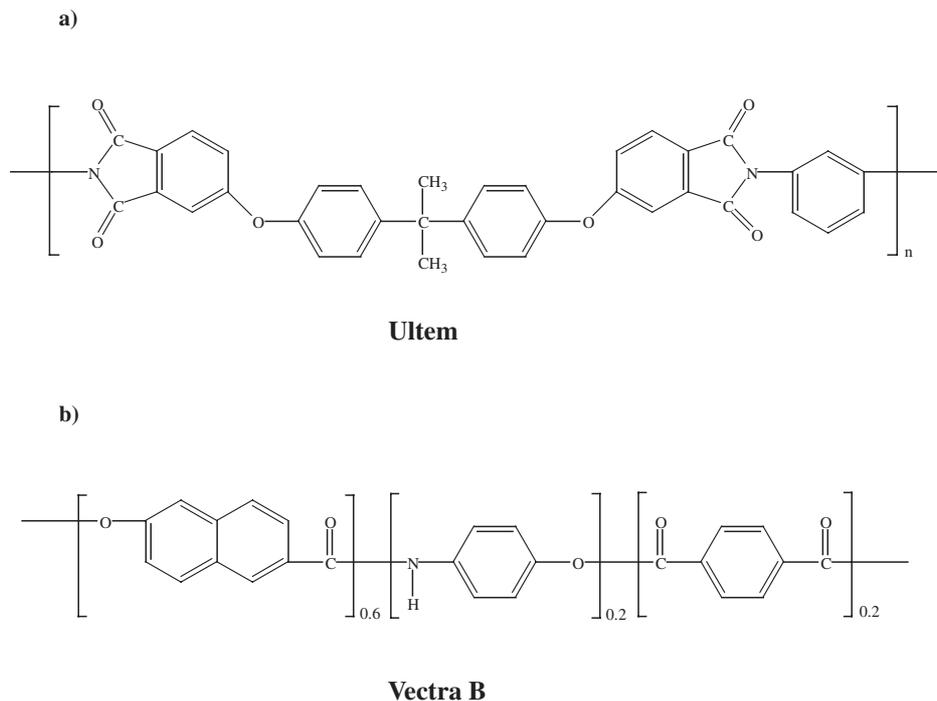
To obtain enhanced physical properties of the *in-*

situ composites, improved compatibility between the matrix polymer and the reinforcing TLCP has been required.^{10–12} It is well known that the compatibilization is a decisive factor to overcome the problems of poor dispersion and poor interfacial adhesion in the incompatible polymer blends resulting in melt flow instabilities and weak physical properties. To improve the compatibility, miscible TLCP/isotropic polymer blend systems have been evaluated by many researchers. Bretas and co-workers¹⁰ 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 blend is to use a third component as a compatibilizer or coupling agent. Lee and DeBenedetto¹¹ investigated the feasibility of introducing a second TLCP as a compatibilizer, or coupling agent, in order to improve the adhesion and dispersion between the components of incompatible TLCP/thermoplastic blends. However, physical properties such as thermal properties, rheological properties, and morphologies depending on different compatibilizers have not been fully un-

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Scheme 1. Chemical structure of (a) Ultem and (b) Vectra B.

derstood.

In this study, thermotropic polyesteramide (Vectra B), composed of 6-hydroxy-2-naphthoic acid, terephthalic acid, and *p*-aminophenol (approximately 60:20:20), was blended with thermoplastic polyetherimide (Ultem). Ultem is one of the leaders in special engineering plastics having appreciably good physical properties. However, it causes a high processing difficulty due to the high melt viscosity. As reported before, it would be very interesting to blend Ultem and TLCP (Vectra B) in the point of processibility.^{13–16} Addition of Vectra B to Ultem may increase the mechanical properties such as tensile strength and modulus, but the immiscible blend is brittle due to its poor interfacial adhesion.¹⁶ To improve the interfacial adhesion between Vectra B and Ultem, polyesterimide (PEI) was introduced as a compatibilizer in this paper. PEI as a compatibilizer enhanced processibility and mechanical properties of TLCP/PEI blends as reported in our earlier literature.^{16–18} Investigation of relationships between chemical structure and physical properties of Ultem/Vectra B blend containing chemically different PEI would be necessary to better understand the compatibilizing effects. Two types of PEI as compatibilizers for Ultem/Vectra B blend system were prepared based on polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) by melt polymerization. The structures of compatibilizers were designed for structural similarity of aromatic imide rings with Ultem. Probability of reaction with Vectra B by transesterification or transami-

nation is also considered. In addition, relationships among miscibility, structure, physical properties, and rheological properties of ternary Ultem/Vectra B/polyesterimide blends were investigated.

EXPERIMENTAL

Raw Materials

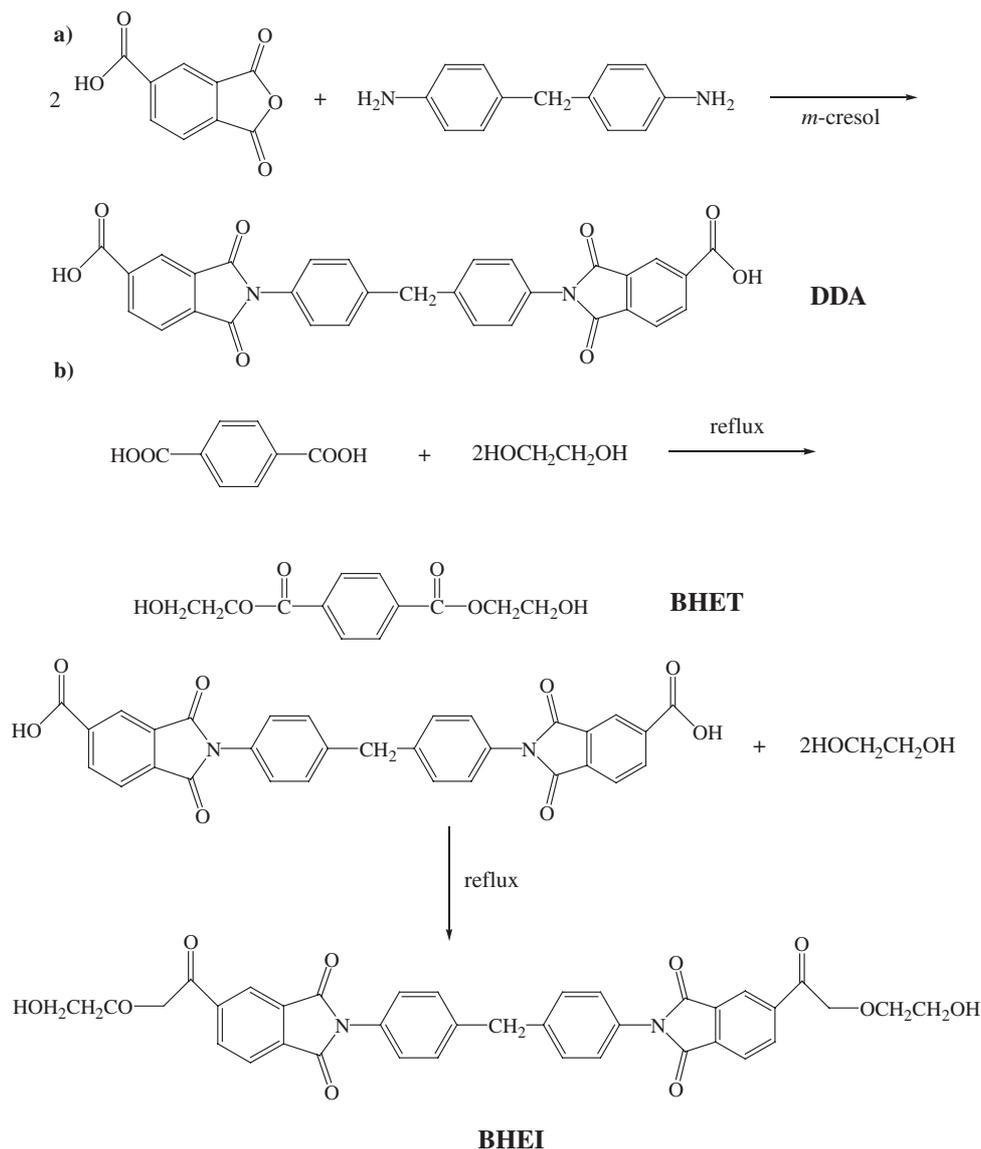
Vectra B and Ultem were supplied by Hoechst Celanese Corp. and General Electric Company, respectively. Chemical structures of Ultem and Vectra B are shown in Scheme 1.

Synthesis of Compatibilizers

PEI used as a compatibilizer was prepared as follows;

0.26 mol trimellitic anhydride (TMA) and 0.13 mol 4,4'-diamino diphenyl methane were reacted in 500 mL *m*-cresol at 150 °C for 6 h. Reaction mixture were cooled down and then filtered. The obtained yellow product was washed two times with methanol and ethyl ether, followed by filtering and vacuum drying. Obtained diphtalimidodicarboxylic acid (DDA) was purified by recrystallization in acetic anhydride.

Bishydroxyethylene terephthalate (BHET) and Bishydroxybutylene terephthalate (BHBT) were prepared by direct esterification reaction of terephthalic acids and diols at the mole ratio of 1:2.2 without any catalyst. 4,4'-Bis[(4-carbo-2-hydroxyethoxy)-phthalimido]-diphenylmethane (or bishydroxyethyl-diphthalimido-dicarboxylate; BHEI) and 4,4'-bis-[(4-



Scheme 2. Synthetic routes for (a) DDA, (b) BHEI, and (c) BHET. (Continued on next page)

carbo-4-hydroxybutoxy)phthalimido]-diphenylmethane (or bishydroxybutyldipthalimidodicarboxylate; BHBI) were prepared as following procedures;

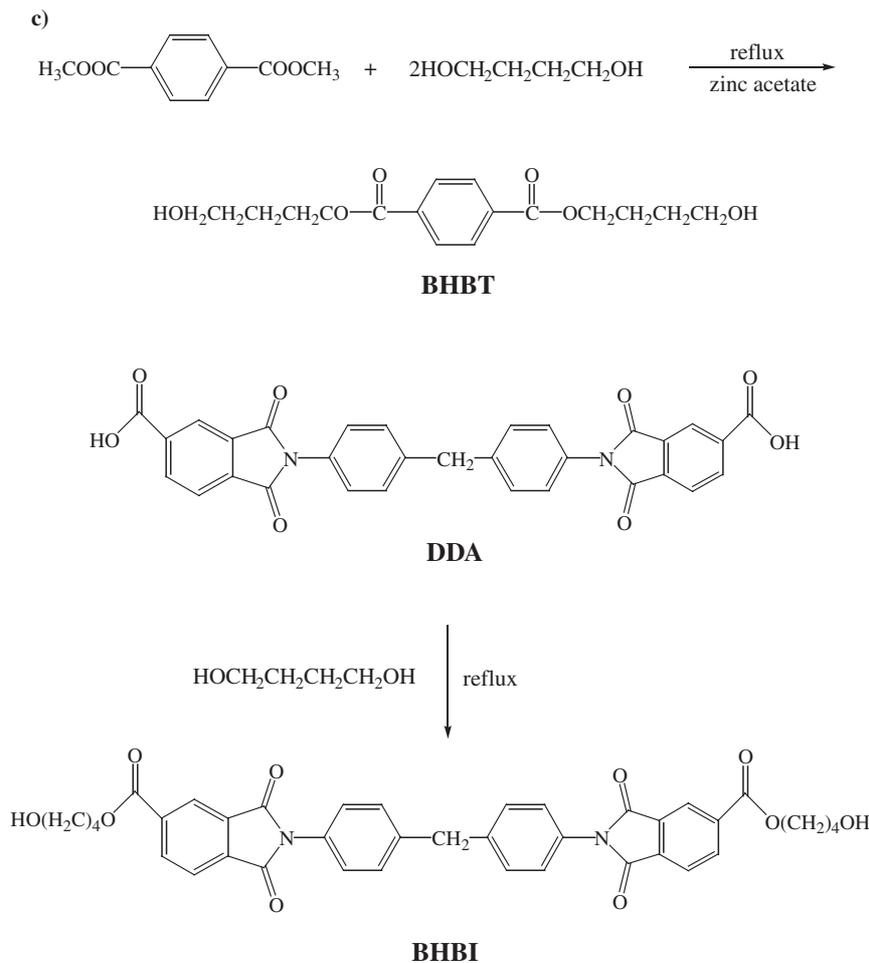
0.08 mol of DDA and 3.2 mol of diols were placed in a 200 mL three-necked round bottom flask equipped with a reflux condenser. The reaction mixture was stirred under nitrogen atmosphere at 198–235 °C for several hrs. Products were solidified on an aluminum pan and washed with methanol to remove the excess diols. The synthetic routes for DDA, BHEI, and BHBI are shown in Scheme 2.

BHET and BHEI, BHBT and BHBI were transformed into polyesterimide by melt-transesterification reaction. BHET/BHEI and BHBT/BHBI were placed with catalyst (Sb_2O_3 for BHET/BHEI and $\text{Ti}(\text{O}i\text{Bu})_4$ for BHBT/BHBI, respectively) in glass reactors. The reaction temperature was then increased to 280 °C un-

der controlled pressure of 3 mmHg. After a period of time the stirring rate was slowed down due to the enhanced melt viscosity of polymer product, and then nitrogen gas was purged to inject the product into water bath. The obtained polymer was washed with methanol several times. The resulting polymers were named after the corresponding polyesters. PET based PEI prepared from 10 mol% of imide monomer was named as EI10. PBT based PEI prepared from 10 mol% of imide monomer was also named as BI10.

Polymer Characterization

Melting and glass transition temperatures were measured by Du Pont 910 DSC. IR spectra of BHEI and BHBI were obtained by Mattson FT-IR with 32 scans at 4 cm^{-1} resolution. ^1H NMR spectra were obtained in $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (3/1 vol%) solvent on a

**Scheme 2.** (Continued)

300 MHz NMR spectrometer (Bruker AM300) with tetramethylsilane as an internal standard. The molecular weights of polymers were measured by Waters Basic gel permeation chromatography (GPC) using *o*-chlorophenol as an eluent at 100 °C. Inherent viscosities of polymers were measured by Ubbelohde viscometer using *o*-chlorophenol as a solvent at 35 °C.

Binary Blends

Binary Ultem/EI10 blend and Ultem/BI10 blend were prepared by solution precipitation method at the weight ratio of 10/90, 30/70, 50/50, 70/30, and 90/10 for each. The miscibility of binary blend was investigated by measurement of glass transition temperatures.

Binary Vectra B/EI10 blend and Vectra B/BI10 blend were melt-mixed by Mini-Max injection molder CS-183 MMX (CSI Co.) at 290 °C. Glass transition temperatures were measured by dynamic mechanical analyzer (DMA).

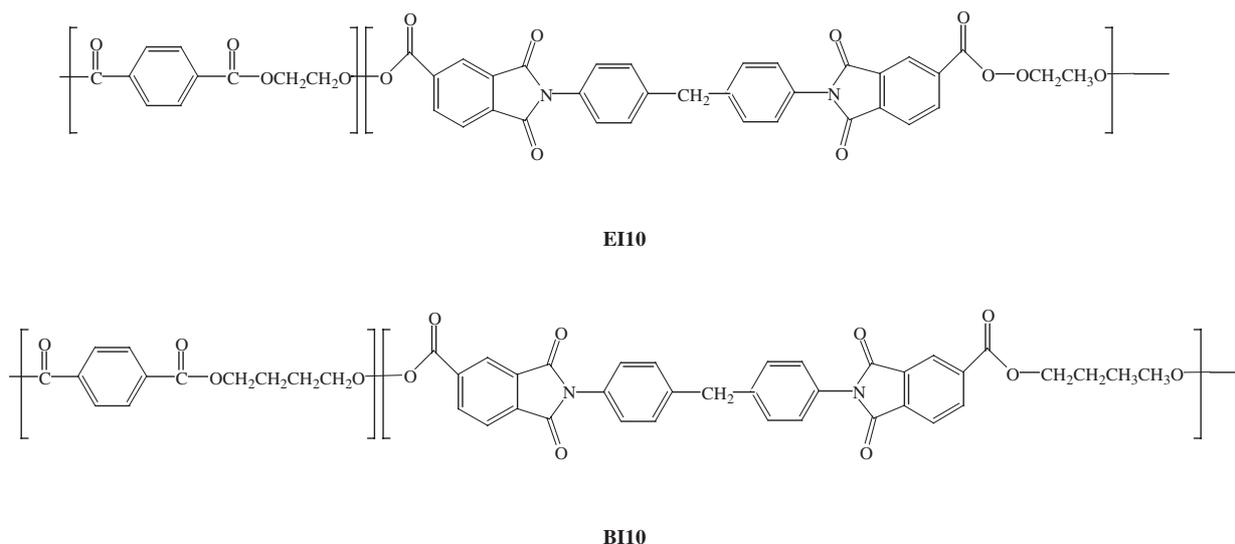
Ternary Ultem/Vectra B/PESl Blends

Pellets of Ultem, Vectra B, and PESl's were dried in vacuum oven at 90 °C for 24 h before use. In the Ul-

tem/Vectra B (75/25) blend system which showed maximum fibril aspect ratio, the loading level of PESl was varied as 1, 2, 5, and 10%.¹⁵ Blending was carried out in Brabender W50EH internal mixer at a fixed rotation speed 30 rpm at 330 °C. Fiber spinning was performed with Rosand RH7-8/4 capillary rheometer equipped with converging capillary die of 2 mm diameter and 16 mm length ($L/D = 8$) at the shear rate of 1500 s^{-1} . Spin draw ratios, defined as a diameter ratio at the die exit to that of far down stream was controlled by the speed of the take-up roll. The spinning temperatures was between 300 and 330 °C.

Measurements of Physical Properties

Dynamic mechanical analysis (DMA) was carried out with Dynamic Mechanical Thermal Analyzer MK III (Rheometric Scientific Ltd. UK) in bending mode. Rectangular-shaped samples for DMA measurements were prepared by using a minimax molder CS-183 MMX (CSI Co.) at 290 °C. The measurement was performed at the heating rate of 5 °C/min in the range of 10 °C–200 °C at the frequency of 1 Hz. Rheological properties of ternary blends were measured by Rheometrics Dynamic Spectrometer (RDS 7700) on

**Scheme 3.** Chemical structure of prepared polyesterimides.**Table I.** Characterization of prepared monomers

	M.P.	Elemental Analysis		¹ HNMR
		Exp.	Cal.	
BHEI	236 °C	C: 65.24	C: 66.24	8.85(s), 8.62(d), 8.13(d), 7.41(d), 7.34(d), 4.82(t), 4.66(t), 4.24(s), 4.17(d)
		H: 4.03	H: 4.13	
		N: 4.25	N: 4.41	
BHBI	367 °C	C: 69.58	C: 68.13	8.70(s), 8.67(d), 8.17(d), 7.31(d), 7.28(d), 4.62(t), 4.51(t), 4.12(d), 3.98(s), 2.01(t), 1.93(t)
		H: 3.43	H: 3.32	
		N: 4.94	N: 5.13	

which 25 mm diameter parallel plates of 1.2 mm gap mounted. Frequency range was set at 0.1–500 rad/s and applied strain was 10%. Mechanical properties of the ternary blends were measured by Instron universal testing machine (model 4201) at a gage length of 30 mm and a crosshead speed of 10 mm/min. Average values of seven specimens of tensile strength and tensile modulus were taken. Tensile fractured surfaces were observed on Hitachi S-2200C SEM. Samples were coated with gold to make them electrically conductive.

RESULTS AND DISCUSSION

Preparation of Compatibilizers

Chemical structures of prepared PEI used as compatibilizers in this study are shown in Scheme 3. Melting points, elemental analysis results, and ¹HNMR data for BHEI and BHBI are summarized in Table I. Figure 1 shows the FT-IR spectra of BHEI. It shows the characteristic OH stretching at 3466 cm⁻¹ and four characteristic imide bands at 1777, 1723, 1383, and 727 cm⁻¹. The bands at 1777 and 1723 cm⁻¹ are assigned to imide carbonyl stretching and band at 1383 cm⁻¹ is assigned to stretching of nitrogen in

imide ring. The peak at 727 cm⁻¹ shows the bending motion of the 5-membered imide ring. BHBI has a similar tendency with BHEI in the FT-IR spectrum. Most moieties are assigned as mentioned in Figure 1. ¹HNMR spectra and assignments to the structure of EI10 and BI10 are as follows:

¹HNMR spectrum of EI10: δ 8.19, 7.39–7.19 (aromatic proton); 4.95, 4.90 (aliphatic proton) ppm.

¹HNMR spectrum of BI10: δ 8.12, 7.39–7.22 (aromatic proton); 4.52, 2.02 (aliphatic proton) ppm.

The composition of the PEI was determined by integration ratio of the peak. Molecular weights, inherent viscosities, and transition temperatures of PEI are summarized in Table II.

Thermal Behaviors of Binary Blend

Compatibility and phase separation behaviors of polymer blends can be inferred from the analysis of thermomechanical behavior of *in-situ* composite based on Ultem and TLCP. Martinez *et al.* tried to blend PEI with crystalline polyester.^{20,21} However, PET and PBT based blends exhibited crystallization induced phase separation and low heat distortion temperature (HDT) due to their high crystallizability. In this point of view, incorporation of imide rings into

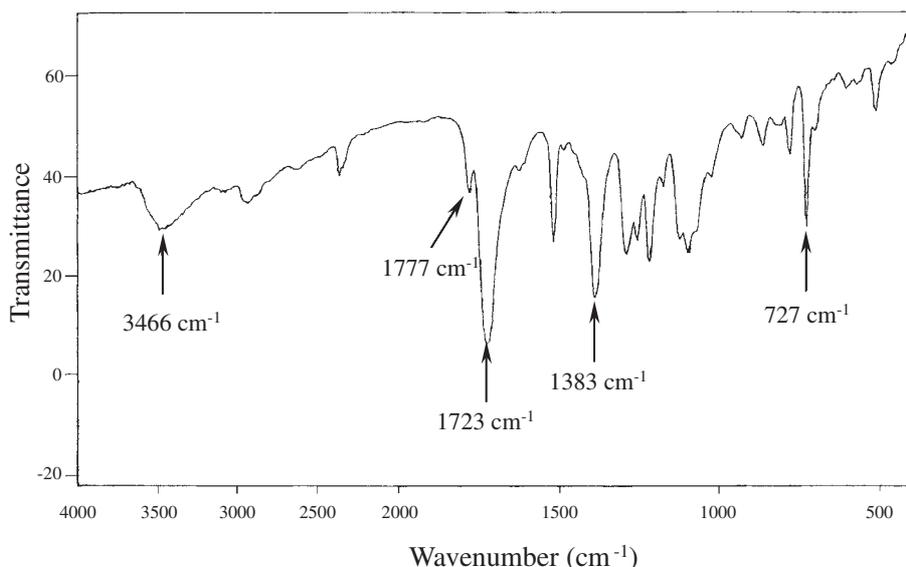


Figure 1. IR Spectrum of BHEI.

Table II. Characterization of prepared polyesterimides

	Composition ¹	Mn ²	IV ³	T _g ³ (°C)	T _m ³ (°C)	Solubility parameter ⁴
EI10	7.3	24600	0.59	91.6	225.7	11.60
BI10	7.6	29400	0.71	50.2	208.7	11.02

¹Characterized by ¹HNMR with CF₃COOD/CDCl₃ (3/1) as solvent.

m: 8.17 ppm, *n*: 7.34 ppm for EI10

m: 8.15 ppm, *n*: 7.34 ppm for BI10

$[4x + 2(1 - x)] : [8(1 - x)] = m : n$,

$x = (4m - n)/(4m + n)$

Imide content = $(1 - x) \times 100$ (%)

²Characterized by high temp. GPC using *o*-chlorophenol as an eluent at 100 °C

³*o*-chlorophenol as a solvent at 30 °C

⁴Calculated by group contribution method (Ultem: 11.05 (cal/cm³)^{0.5})

these polyesters as compatibilizers for immiscible Ultem/Vectra B blend system can reduce their crystallizability.²⁰

Glass transition temperatures of binary Ultem/EI10 and Ultem/BI10 blend are shown in Figure 2. The *T_g*'s of EI10 shifted to upper temperatures by about 70 °C and those of Ultem shifted to lower temperature about 40 °C as shown in Figure 2a. These shifts of *T_g*'s of each component reflect partial miscibility in Ultem/EI10 blend system. On the other hand, the single glass transition temperature is measured in the full composition range in the case of Ultem/BI10 blends (Figure 2b). The *T_g*'s of Ultem/BI10 blends are dramatically increased by about 170 °C as shown in Figure 2b. This result reveals that Ultem/BI10 blend exhibits better miscibility than Ultem/EI10 blend. In addition, the curve in Figure 2b follows additivity rule with negative deviation probably resulted from the re-

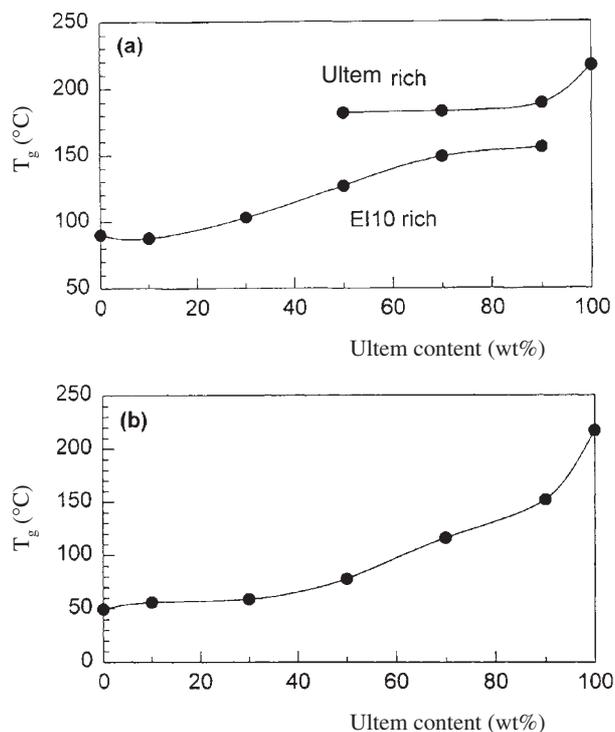


Figure 2. Glass transition temperatures of (a) Ultem/EI10 and (b) Ultem/BI10 blends.

duction of crystallinity due to plasticization effect by each other. We confirm that binary Ultem/BI10 binary blend is more compatible and more flexible than Ultem/EI10.

DMA thermograms of EI10/Vectra B (3/7) and BI10/Vectra B (3/7) melt blends are shown in Figure 3. The two peaks of $\tan \delta$ in this figure correspond to the characteristics of the two immiscible phase systems.²² However, as shown in Figure 3a,

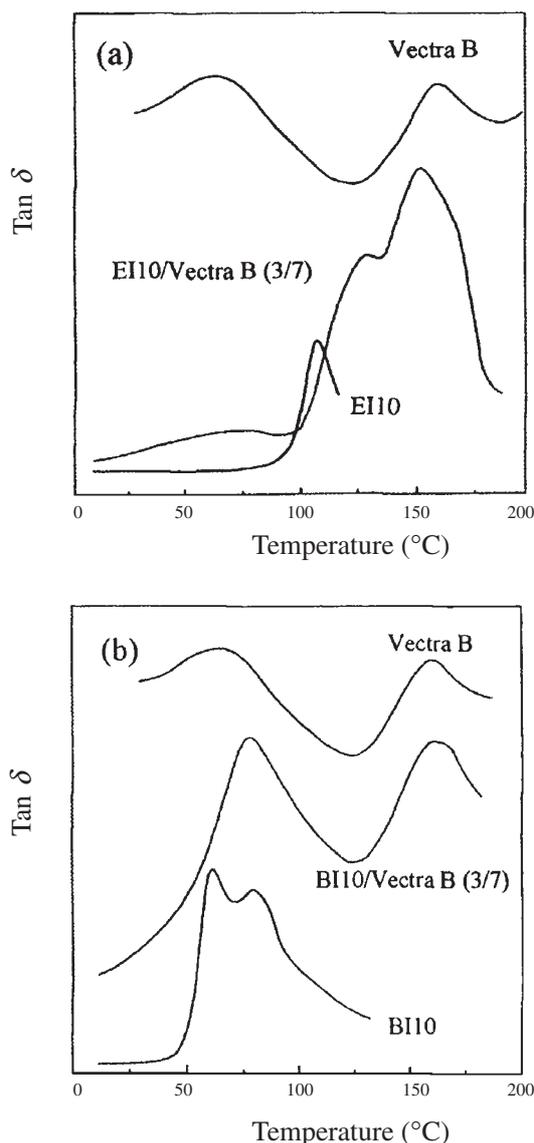


Figure 3. DMA thermograms of (a) EI10/Vectra B (3/7) and (b) BI10/Vectra B (3/7) blends.

the maximum $\tan \delta$ peaks merged into one broad asymmetric curve of the two phase systems. In the case of BI10/Vectra B (3/7), Figure 3b, the maximum $\tan \delta$ peak of BI10 shifted upward whereas that of Vectra B remain constant, which reflects that the flexible PEsi can rarely be dissolved into the rigid and high crystalline LCP phase although transreaction can occur between the two polymers.

This indicates that both EI10 and BI10 can be used as compatibilizers in binary Ultem/Vectra B blend system. Especially, EI10 is more reactive (or compatible) with Vectra B, whereas BI10 is more compatible with Ultem, which might be expected by the solubility parameter values. The solubility parameter of BI10 ($11.02 \text{ (cal/cm}^3)^{0.5}$) is much closer to that of Ultem ($11.05 \text{ (cal/cm}^3)^{0.5}$) than EI10 ($11.60 \text{ (cal/cm}^3)^{0.5}$) (see Table II). Consequently, BI10 can be easily dis-

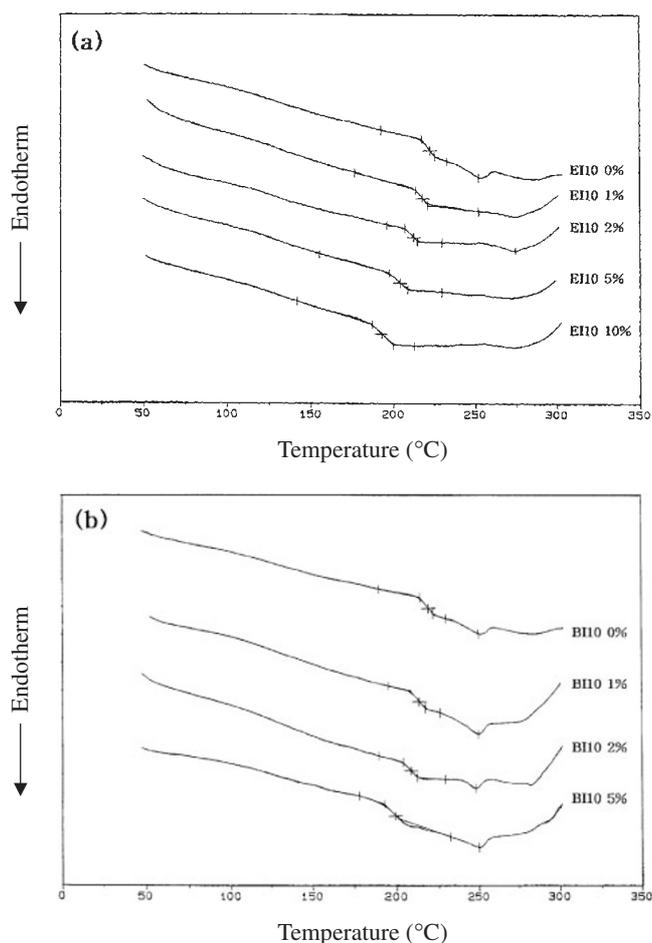


Figure 4. DSC thermograms of (a) Ultem/Vectra B (75/25) blends containing EI10 and (b) Ultem/Vectra B (75/25) blends containing BI10.

solved into Ultem matrix, hence be more compatible with Ultem matrix than EI10.

Thermal Behaviors of Ternary Blends

DSC thermograms of ternary Ultem/Vectra B/compatibilizer blends are shown in Figure 4. The T_g of Ultem rich phases in binary 75/25 Ultem/Vectra B blend appeared at 219°C . As the compatibilizer content is increased, the T_g of Ultem rich phases decreased almost linearly (Figure 5). The inclination of T_g shift up to 5 wt% content of compatibilizers is larger in ternary blends containing BI10 than that of blends containing EI10, which has a similar tendency with the results of binary blends. This indicates that BI10 is more compatible with Ultem matrix resin than EI10.

It is well known that the double melting behavior of Vectra B might result from the melting-recrystallization-remelting behavior of two different kinds of crystallites.²³ The melting peak behaviors were also reported by a number of researchers for polyesters containing terephthalate units.^{24,25} However, in the

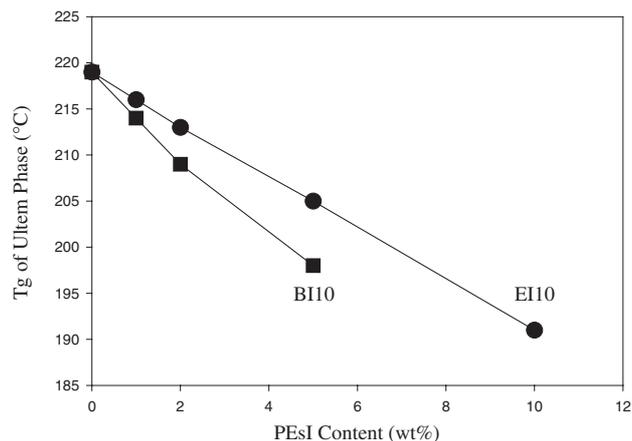


Figure 5. Glass transition temperatures of Ultem rich phases in Ultem/Vectra B (75/25) blend containing EI10 and Ultem/Vectra B (75/25) blend containing BI10.

case containing EI10 (Figure 4a), the melting peaks of Vectra B disappeared with increase in the small amount of compatibilizer, while those in (b) remained constant. These results exhibit good agreement with the results of binary blends (Figure 3). It suggests that compatibility is increased by melting point depression. Again that is, EI10 is more reactive to Vectra B than BI10.

Rheological Properties

Rheological properties of the TLCP blend systems have been explored.^{26–28} Dynamic shear viscosities of ternary blends containing EI10 and BI10 are shown in Figure 6. All blend melts in this shear rate range exhibited non-Newtonian and shear thinning behavior. Furthermore, melt viscosities were decreased with increase in the compatibilizer content. Compatible blends generally tend to show higher melt viscosities than incompatible blend system. Because incompati-

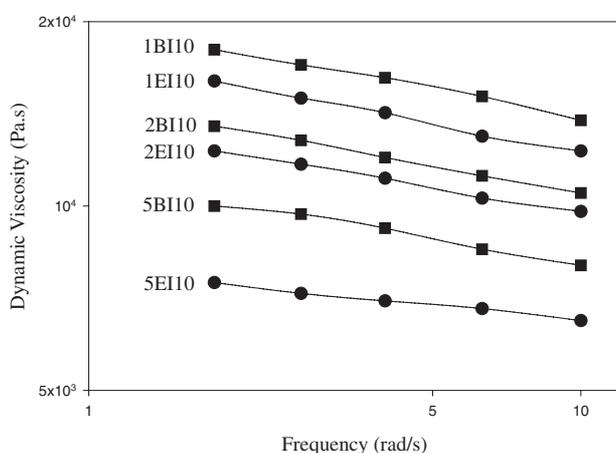


Figure 6. Viscosity curves of Ultem/Vectra B (75/25) blends at various PEI compatibilizer contents at 290 °C.

ble blends show interlayer slip due to their sharp interface and poor interaction between phases, they exhibit reduced viscosities. In addition, low molecular weight polymer added into the incompatible blend as a compatibilizer causes the viscosities of blend to be decreased because the polymer roles as a plasticizer. Han *et al.*^{29,30} also reported a high melt viscosity of compatibilized blends. In this study, however, the viscosities of ternary blends gradually decrease with increase in the compatibilizer content. This result comes from not low compatibilizability of EI10 and BI10 but very low T_g (EI10; 91.6 °C, BI10; 50.2 °C) and low T_m (EI10; 225.7 °C, BI10; 208.7 °C) of compatibilizers compared with high melt viscosity and high melt processing temperatures (Ultem; 330–400 °C, Vectra B; 300 °C) of matrices. Moreover, the bulky imide ring decreases structural regularity of the main chain and hinders the dense chain packing. Hence, it decreases T_m of crystallites although EI10 and BI10 containing imide ring interact with imide structure of Ultem.¹⁷ Thus, EI10 and BI10 decrease viscosities of the Ultem/Vectra B blend systems because EI10 and BI10 have very low viscosities in the processing temperature of 290–340 °C. Even though we reported T_g and T_m increase with increase of PEI contents in the ternary blend system, The PEI (T_g ; 220 °C) used in the previous reports has much higher T_g than BI10 and EI10.¹⁷ These results suggest that alkyl chains in the backbone significantly reduce thermal stability of the compatibilizers. Even though the blends are miscible, therefore, the resulting ternary blends have lowered T_g and T_m with increase of the compatibilizer content.

Melt viscosities of ternary blends containing BI10 are higher than those of blends containing EI10 at the same shear rate and composition although T_m of BI10 is lower than that of EI10. This is because the increase of contact area between the matrix and the dispersed phase and the enhancement of adhesiveness caused by reduction of interfacial tension are more noticeably increased in ternary blends containing BI10 than ternary blends containing EI10; we will see later this morphology by means of scanning electron microscopy. When more compatibilizer was added (about 5 wt%), however, the decrease of the viscosity of the blend containing EI10 was significantly reduced even though it was still lower than that of the system without the compatibilizer. This may be due to the easy processability of EI10 resulting from lower molecular weight than that of BI10.^{16–18} Details are under investigation and will be reported in the future.

Mechanical Properties

It is well known that compatibilization of immiscible polymer blend enhance the mechanical properties

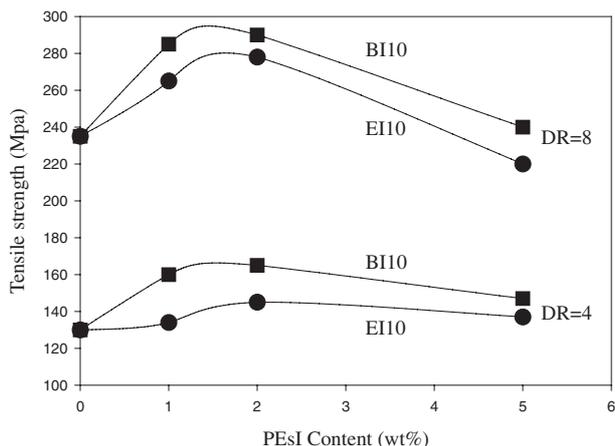


Figure 7. Tensile strength of 75/25 Ultem/Vectra B at various compatibilizer contents at the draw ratio of 4 and 8.

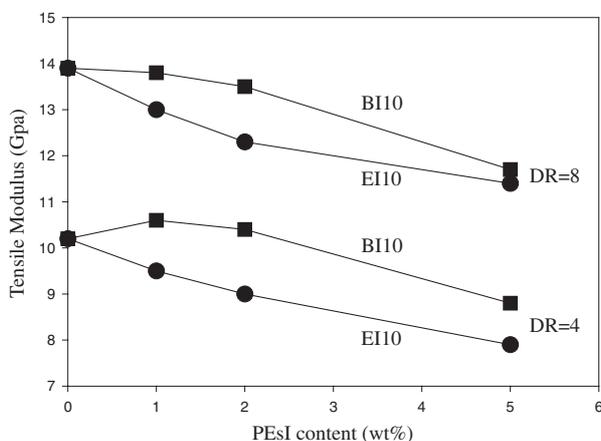


Figure 8. Tensile modulus of 75/25 Ultem/Vectra B at various compatibilizer contents at the draw ratio of 4 and 8.

of the blends.¹⁷ Tensile strength and tensile modulus data with various compatibilizer contents are presented in Figure 7 and Figure 8, respectively. Tensile strength is increased with increase in the amount of compatibilizer at low level. However, tensile strength is decreased as the compatibilizer content exceeds about 2 wt%. The optimum compatibilizer amount turned out to be about 1–2 wt% in 75/25 Ultem/Vectra B blend system. This result might come from the difference of solubility parameters between PEI and Ultem matrix as well as the dissolution of the PEI into the matrix resin rather than to be located between two phases. Maximum value of tensile strength is higher than that of uncompatibilized resin by *ca.* 25%. Decrease of tensile strength in high compatibilizer content results from the reverse action of compatibilizer. Above this optimum value, it gives rise to coalescing of the LCP fibrils that will be shown in morphology. It is well known that crystallization rate of PBT is faster than that of PET. In this respect, it means that PBT based BI10 brings about more self-re-

inforcing solidified species than PET based EI10 during fiber spinning processing. Thus we found that tensile strength of the Ultem/Vectra B blend containing BI10 is higher than that of the blend containing EI10. From these results of tensile strength measurements, it can be concluded that BI10, more compatible with Ultem matrix, roles as a good compatibilizer to improve mechanical properties than EI10, more compatible with Vectra B. Therefore, we insist that the maximum compatibilizing effect can be obtained not only from optimized compatibilizer content but also from developed crystallites and orientation of LCP microfibril during melt spinning process.

On the contrary, tensile modulus of compatibilized blends tends to decrease with increase in the PEI content. It can be explained by the fact that the compatibilizers have low modulus (1.1–1.7 GPa: flexural mode) compared with the value of Ultem (3 GPa) and Vectra B (much higher), and they give plasticizing effect in the Vectra B/Ultem interfaces during tensile test. Consequently, ternary blends containing BI10 show better mechanical properties. In other words, a compatibilizer should be more compatible with matrix than LCP domain. A compatibilizer compatible with LCP fibril might prevent from fine fibrillation.

Morphology

Spherical LCP domains are observed in LCP/thermoplastic polymer blend.^{30–32} However, these structures are deformed by elongational shear flow, composition, viscosity ratio, the degree of orientation, and so on. Figure 9 and Figure 10 show the tensile fractured surfaces of ternary Ultem/Vectra B/EI10 blend fibers and Ultem/Vectra B/BI10 blend fibers at the draw ratio of 4, respectively. As shown in these figures, the Vectra B domains are relatively large in non-compatibilized blends indicating a poor dispersion (domain sizes are 1–5 μm and 2–5 μm in Figure 9a and 10a, respectively), which results in open ring hole around the domain and the whole LCP fibrils being pulled out. As the compatibilizer content increases up to 2 wt%, LCP fibrils are more uniformly distributed and finer in size (domain sizes are respectively 0.3–1 μm and 1–2.5 μm in Figure 9c and 10b.) than those of uncompatibilized blend fibers. The difference of domain size between compatibilized blend fibers can be explained by processability resulting from the difference of molecular weight. That is, processability of EI10 is better than that of BI10. (EI10 M_n ; 24,600, BI10 M_n ; 29,400) Therefore, the domain size of Vectra B at Ultem/Vectra B/EI10 is smaller than that at Ultem/Vectra B/BI10. However, when the excess amount of compatibilizer (5 wt%) is used, the LCP domains are coalesced each other to larger ones. In addi-

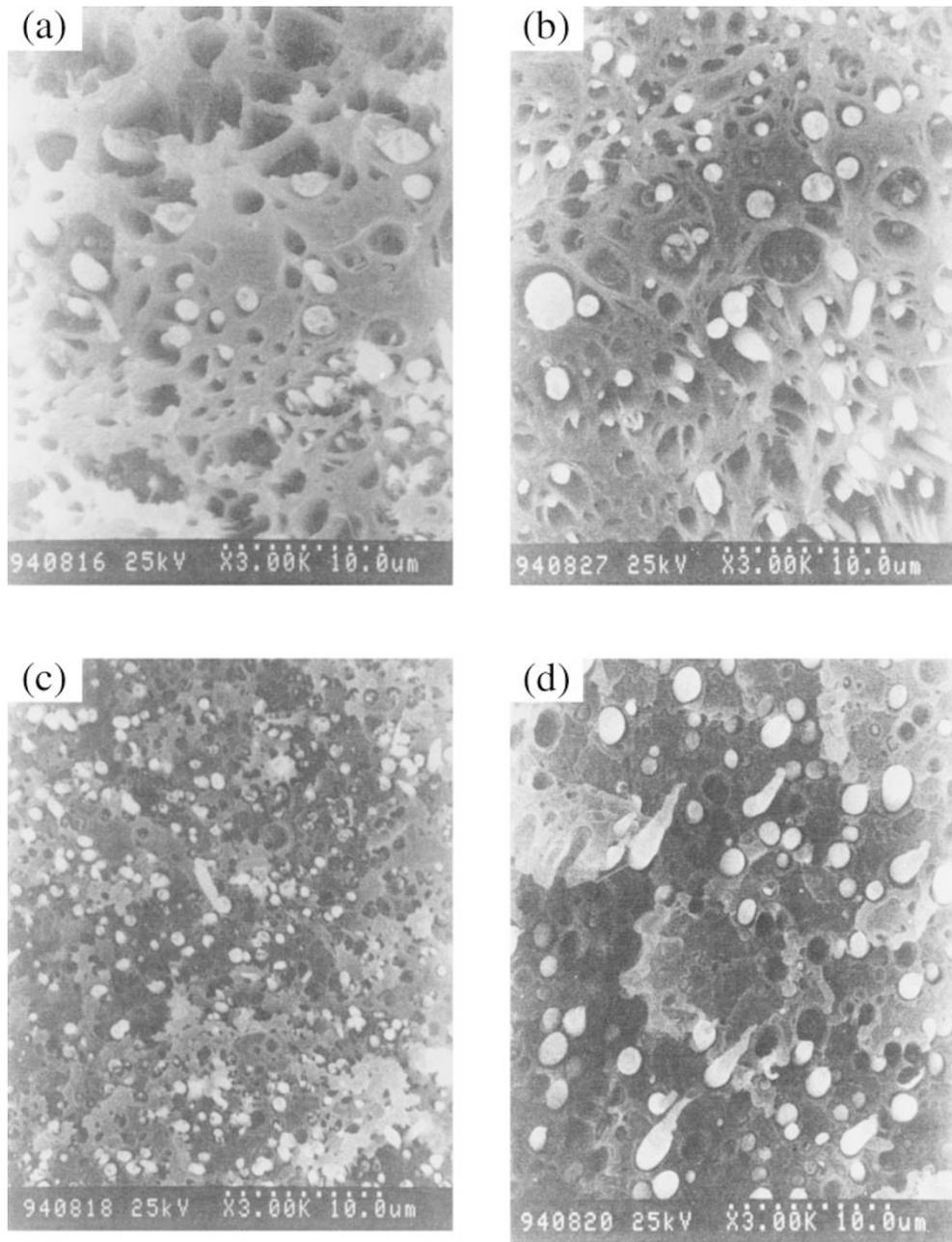


Figure 9. SEM images of tensile fractured surfaces of Ultem/Vectra B/EI10 *in-situ* composite at the draw ratio of 4; (a) 0 wt% EI10, (b) 1 wt% EI10, (c) 2 wt% EI10, and (d) 5 wt% EI10 ($\times 3000$).

tion, a decrease in total cross-section area accompanied by coalescence would also contribute the deterioration in mechanical properties.

This behavior is similar to that of the surfactant in emulsion system, in which flocculation of dispersed phase results from strong interparticle interactions of surfactant adsorbed on the surfaces of dispersed phases. These representations of different LCP domain geometries can be explained by considering of the micro-rheology of the blend during the fiber spinning process. Assuming the blend melt is a suspension system composed of the dispersed LCP domains suspended in Ultem matrix, suspension rheology theory can be

successfully applied. Deformation of the dispersed particles in different suspended medium was studied by Taylor.³⁴ He extended Einstein's theoretical treatment of the viscosity of a suspension of rigid particles to the case of small immiscible fluid spheres. He found that a droplet could be deformed according to the following relationship in a simple shear flow of Newtonian fluid. If the maximum value of pressure difference across the interface between a suspending liquid and a dispersion exceeds the force, the dispersed droplet will burst according to his report. This occurs when;

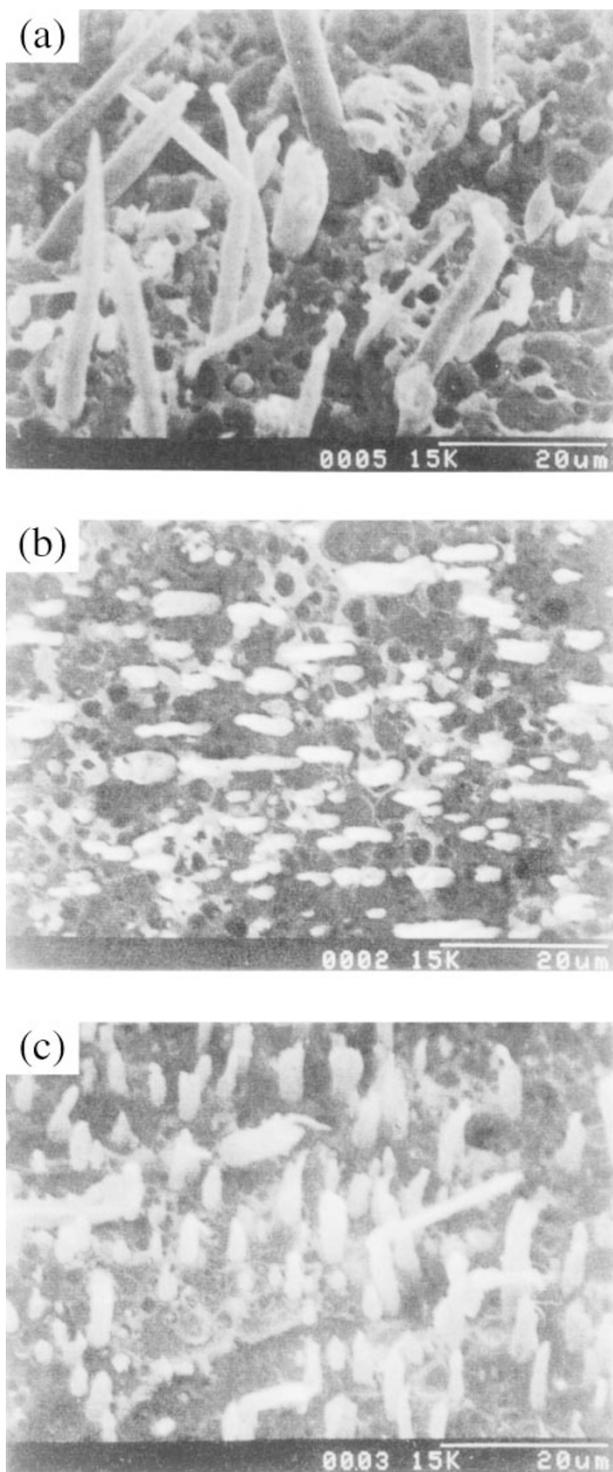


Figure 10. SEM images of tensile fractured surfaces of Ultem/Vectra B/BII0 *in-situ* composite at the draw ratio of 4; (a) 0 wt% BII0, (b) 2 wt% BII0, and (c) 5 wt% BII0 ($\times 1500$).

$$4\gamma\eta_0 = \frac{19\delta + 16}{16\delta + 16} > \frac{2\sigma}{b} \quad (1)$$

where γ is the shear rate, σ is the interfacial tension, η_0 is the viscosity of matrix, δ is the ratio of the viscosity of the dispersion to that of the suspending liquid, and b is initial diameter of the droplet. If the vis-

cosities of Ultem and LCP are considered, the value of δ is less than the order of 0.1 at the processing temperature (330 °C), and the equation can be reasonably simplified to^{16,18}

$$2\gamma\eta_0 > \frac{\sigma}{b} \quad (2)$$

This expression indicates that if the viscosity of the matrix is large enough, with respect to the interfacial tension, the droplet will elongate. This equation also suggests that the dispersed domain size would deform into smaller size if the interfacial tension (σ) can be lowered by addition of compatibilizer and the interfacial tension varies little beyond the critical micelle concentration of the compatibilizer. Roe *et al.*³⁵ confirmed this explanation. Coalescence of the domains occurs because the compatibilizers cannot exist in the interfacial region but dissolved into the matrix phases in the process of micelle formation.

Similar results for compatibilized Nylon/hydrogenated nitrile rubber blend system were reported by Bhoumick *et al.*³⁶ Beyond the optimum level of compatibilizer, the Nylon/rubber interfacial thickness no longer increased but the compatibilizer caused the domains to be clustered in their report.

Figure 11 shows the peeled surfaces of ternary *in-situ* composites with various amount of BII0 at the magnifications of 200. The finest LCP fibrils at the draw ratio of 4 are obtained in the case of 2 wt% of BII0. This implies that optimum content of the compatibilizer decreases the interfacial tension. This phenomenon has a similar tendency with increase in shear rate acting only to decrease the particle size. Hence the elongational flow also causes the spherical liquid droplets to be drawn into fibrillar domains.

CONCLUSIONS

In-situ composites containing polyesterimide compatibilizers were studied. Two types of polyesterimides were prepared by melt polymerization. The structural effects of compatibilizing actions of these polyesterimides were also investigated. Incorporation of the synthesized compatibilizers reduced the T_g 's of Ultem phases in Ultem/Vectra B (75/25) blends. BII0 was more effective than EI10 in compatibilizing action. Compatibilizers having a lower melting temperature reduced the viscosities of incompatible Ultem/Vectra B blends. However, the blend viscosities containing BII0 were higher than those containing EI10, which might be caused by better interfacial adhesion. Improved interfacial adhesion between immiscible phases increased the tensile strength of Ultem/Vectra B (75/25) blends. The optimum level of the compatibilizers turned out to be about 1–2 wt% for the blend systems. Addition of proper amount of com-

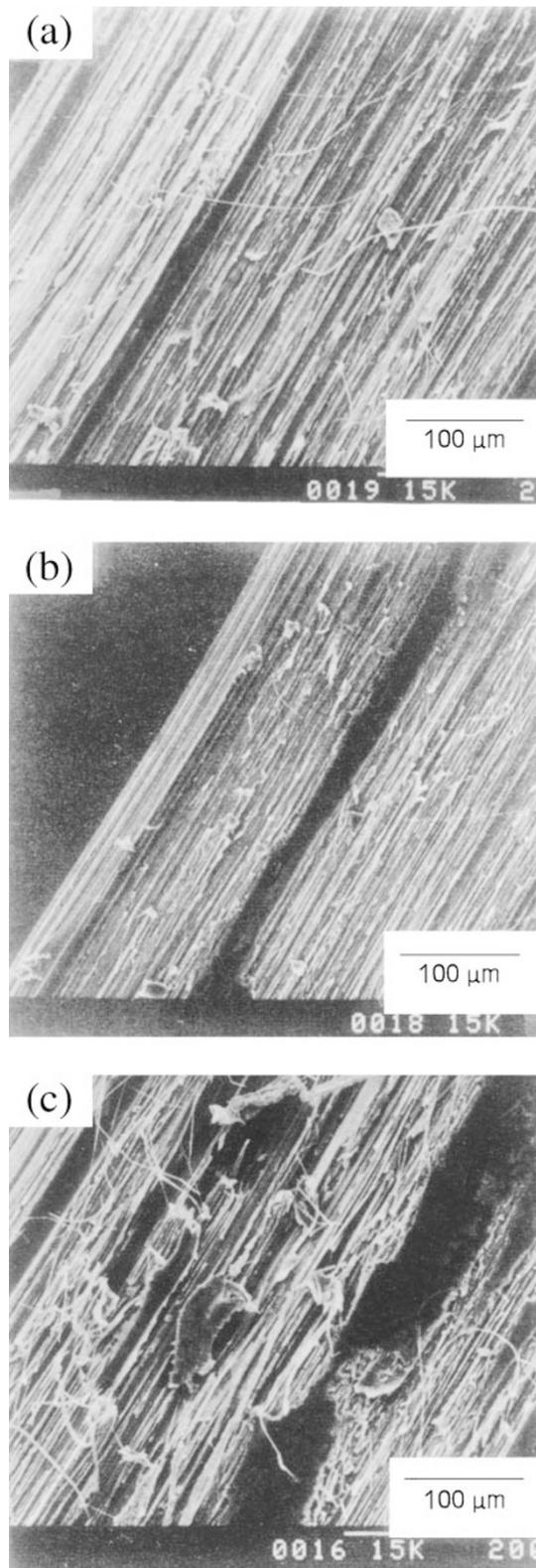


Figure 11. SEM images of peeled surfaces of Ultem/Vectra B/BI10 *in-situ* composite at the draw ratio of 4; (a) 1 wt% BI10, (b) 2 wt% BI10, and (c) 5 wt% BI10 ($\times 200$).

patibilizer reduced the dispersed LCP particle size and fine distribution. Excess amount of compatibilizer, however, made the LCP domains coalesce and consequently deteriorate the physical properties of this sys-

tem. From the results of the interrelationships among the thermal properties, physical properties, and microstructures, we found that compatibilizing action of BI10 was more efficient than EI10 in the immiscible 75/25 Ultem/Vectra B blend. In addition, we concluded that a compatibilizer should be more compatible with matrix than with LCP fibrillar domains. It implies that a compatibilizer compatible with dispersed LCP domains might prevent from fine fibrillation and deformation of reinforcing species along the flow direction in the solid state.

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