Reactive Compatibilization of the Poly(Ethylene Terephthalate)/Liquid Crystalline Polymer Blends by Solid Epoxy Resin as a Coupling Agent

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SYNOPSIS

A selected reactive coupling agent can be served as an effective compatibilizer for certain immiscible and incompatible blends should both blend constituents possess the necessary functional groups that can react with the coupling agent at comparable rates. Solid epoxy resin with two epoxide endgroups per molecule was demonstrated to be an efficient reactive compatibilizer for the incompatible blends of poly(ethylene terephthalate) (PET) and co-polyester liquid crystalline polymer (LCP) by functioning as a coupling agent. The main chain structure of the epoxy resin is neither identical nor miscible with PET and LCP and tends to reside at interface during melt mixing. This preferential residence gives the epoxy compatibilizer greater opportunity to react with both PET and LCP simultaneously to produce the in situ-formed epoxy-b-PET-b-LCP mixed copolymer. This in situ-formed mixed copolymer is highly effective in compatibilizing the PET/LCP blends. This reactive epoxy compatibilizer enhances the LCP fibril formation and results in substantial improvements on stiffness and toughness of the PET/LCP blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

When blended with isotropic thermoplastics (TPs), the semirigid thermotropic liquid crystalline polymers (LCPs) tend to orient parallel to the flow direction to the fibrilar LCP morphology as in situ–formed reinforced composites. Since the pioneer work of Wilkes and Colleagues[1–3] on the polymer blends containing LCP in the early 1980s, this area of technology has attracted tremendous attention during last decade with hundreds of articles appearing in open literature and patents. A key to achieve the desirable reinforcement of the TP matrices with LCPs is the creation of LCP fibrils by use of appropriate processing conditions. This approach has been widely applied to various TP blend systems and was described in a few recent reviews.[4,5] Except for a few cases, most TP/LCP blends are considered to be immiscible and incompatible with poor interfacial adhesion. Poor interfacial adhesion of the TP/LCP blends is partially responsible for the lower mechanical properties usually observed when comparing with the theoretically predicted values. At first look, the solution seems to be obviously simple by compatibilizing the TP/LCP blends, a common approach similar to most compatibilized TP/TP blends. Compatibilization of TP/TP blends by either reactive or nonreactive compatibilizers has a much longer history and is relatively well understood as described in several recent reviews.[6–9] A well-compatibilized TP/TP blend is characterized with finer phase domains, lower interfacial tension in the melt state, increased interfacial adhesion in the solid state, higher morphological stability against coalescence, and improved mechanical properties. However, most compatibilized TP/LCP blends have the tendency to reduce the number and length of the resulted LCP fibrils or even convert the LCP fibrils into droplet domains.[10–12] Therefore, a typically compatibilized TP/LCP blend relative to the uncompatibilized counterpart, the gain achieved by the adhesion increase

may or may not be able to offset the loss due the reduction of the reinforced LCP fibrils. This is probably the reason why the observed mechanical properties of the compatibilization of TP/LCP blends varied with systems and conditions. This is probably also the reason why the compatibilization of TP/LCP blends has not received the same attention as the TP/TP blends.

Compatibilization of the TP/LCP blends have rarely been reported until very recently. The interchanged product between the blend constituents (one is LCP) were probably the first approach to compatibilize the TP/LCP blends. Amendola et al.[13] used the ester interchanged products of polycarbonate (PC) and copolyester LCP to compatibilize the PC/LCP blends. Most interchanged products as compatibilizers for their respective components usually result in inferior toughness and reduced crystallinity (if the TP is a crystalline polymer), which were described in details in our recent review.[9] Compatibilized blends of polypropylene (PP) with various LCPs[11,12,14-18] made up of more than half of all the reported compatibilized TP/LCP blends until present. The PP/LCP blends compatibilized with PP functionalized by maleic anhydride[14-17] and acrylic acid[18] resulted in higher strength and stiffness (tensile strength and modulus) but lower toughness (tensile elongation and impact strength). On the other hand, the PP/LCP blends compatibilized with epoxy-containing copolymers[11,12] or an ethylene-based reactive terpolymer[15] resulted in toughness improvement but suffered the loss of strength and stiffness. Polymer blends between LCP with polystyrene (PS) and Noryl [alloy of PS and poly(phenylene oxide) (PPO)] compatibilized by styrene-glycidyl methacrylate copolymer (SG) resulted in both toughness and stiffness improvements simultaneously.[10,19] Essentially, all abovementioned compatibilized TP/LCP blends utilized the reactive type compatibilizers or at least tried. Kobayashi et al. recently reported the use of nonreactive copolymer, a thermotropic liquid crystalline block-graft copolymer composed of thermotropic polycarbonate (LCPC) in the backbone, and PS segment in the side chain to compatibilize the incompatible blends between LCPC with PS (A/A-B/B type)[20] and with PPO (A/A-C/B type, where C and B are miscible).[21]

Poly(ethylene terephthalate) (PET)/LCP blends using various types of copolyester LCPs have been one of the most intensively investigated TP/LCP blend system. In fact, the earliest reported TP/LCP blends used PET as the matrix in the blends.[1-3] The miscibility or compatibility of the various PET/LCP blends vary depending on the LCP structure. Amano

and Nakagawa[22] studied the drawing behavior of the PET/LCP blends and reported that the orientation of the LCP was induced as well as that of the PET during drawing. Brostow et al.[23] investigated the thermophysical, rheological, and mechanical properties of the PET/LCP blends and developed an island model to explain the results. Zhuang et al.[24] showed substantial viscosity reduction and mechanical property improvement of the PET/LCP blends. Ko et al.[25] also investigated the structure-properties behavior of the extruder cast film of the PET/LCP blends. Shin and Chung[26] studied the interfacial adhesion and the mechanical properties of the PET/LCP blends and found that the interfacial adhesion was much improved by the introduction of a long flexible spacer in the LCP main chain. Silverstein et al.[27] studied the core and skin gradient structure of the injection molded blends of PET/LCP and showed the highest orientation in the flow direction at the mold surface and the lowest at core region. Perkins et al.[28] studied the effect of temperature, composition, and shear rate on the viscosity and morphology of the PET/LCP blends. Mithal et al.[29] studied the *in situ* composite fibers of the PET/LCP blends and found almost additive behavior with regard to tensile modulus and strength but resulted in a radical decline in tensile elongation. Kyotani et al.[30] reported the tensile modulus increases linearly with the increase of the LCP content for the blend containing >10% LCP but hardly contributed to the improvement of the tensile properties for <5% LCP. Seppala et al.[31] reported partial miscibility between PET and LCP and the presence of LCP serves as a nucleating agent to accelerate the PET crystallization. Heino and Seppala[32] reported that at high shear rate, the viscosity ratio of LCP/PET between 0.5 and 1.0 led to good fiber formation. Kim and Denn[33] reported some interactions between PET and LCP based on the observed melting and crystallization depression of the blends. Mehta and Deopura[34] also investigated the PET/LCP fibers and reported significant improvement in modulus and strength. Narayan-Sarathy et al.[35] blended PET with a novel LCP with a flexible side group and resulted in 80% reduction on the apparent viscosity for only 2-5% LCP presence in the blends.

Including the above mentioned literature, the application by adding a third component compatibilizer, reactive or nonreactive type, into an incompatible PET/LCP blend has not yet been found by the authors at present. We discovered that many epoxy-containing compounds or polymers are excellent in compatibilizing the polyester/polyester, polyester/polyamide,[36] polyester/PPO,[37] and poly-

amide/PPO[38] blends. The basic criterion for such an approach to be applicable is that both blend constituents must possess certain necessary functional groups that can react with the epoxy under melt conditions to form various copolymers containing segments of both blend components. The blends containing copolyester LCP with many thermoplastic polyesters are classified in the polyester/polyester blend system.

This paper reports the resultant structure–properties of the PET/LCP blends compatibilized by a solid-state bisphenol-A epoxy resin (MW 5000).

EXPERIMENTAL

The PET with IV-1.0 was obtained from the Shinkong Synthetic Fibers Corp. of Taiwan. The copolyester LCP, Vectra A900, was donated by the Hoechst Celanese Corp. The reactive compatibilizer, a bisphenol-A solid epoxy resin NPES-707 with MW 5000, was donated by the Nan Ya Plastics Corp. of Taiwan. The catalyst ethyl triphenylphosphonium bromide was purchased from Merck.

Melt blending was carried out on a 30-mm corotating twin-screw extruder. The extruded pellets were dried in an oven at 100°C for at least 10 h and injection molded into standard ASTM testing specimens using an Arburg 3-oz injection-molding machine. The detailed processing conditions for the extrusion and injection molding are listed in Table I. The torque versus time relation was obtained in a Torque Rheometer, system 90, from Hakke Co. at 285°C and under constant rotating speed of 30 rpm. Melt flow rates of the blends were carried out according to ASTM-D1238 at 285°C using a 2.16-kg load on an Automatic Flow Rate Timer, Model 3A of Ray-Ran Co. The capillary rheological measurements were carried out by following the ASTM-

D3835 method at 285°C by using a rheometer from Kayeness Company.

Thermal properties were studied by the differential scanning calorimetry (DSC) from −25 to 300°C at a heating rate of 15°C/min on a DSC analyzer from Seiko Co. of Japan. The percent of PET crystallinity in the blends was determined by the following equation:

$$Xc(\%) = (\Delta H_s / \Delta H_{PET})(100/x)$$

Where Xc is the percent crystallinity of the blend, ΔH_s is the measured heat of fusion of the PET component of the blend, ΔH_{PET} is the theoretical heat of fusion of the 100% crystallinity of the pure PET, and x is the mass fraction of the PET in the blends.

The morphologies of the cryogenically fractured surfaces of the injection-molded specimens were examined at core and skin regions perpendicular and parallel to the injection flow direction. The LCP fibrilar morphologies were also inspected by a hot-stage microscope by heating the sample at 275°C to melt the PET matrix while retaining the original LCP morphology.

Notched and unnotched Izod impact strengths were measured at ambient conditions according to ASTM-D256 methods. Standard tensile tests were also carried out at ambient conditions by following the ASTM-D638 method using a cross-head speed of 5 mm/min.

RESULTS AND DISCUSSION

Fundamentals on Reactive Compatibilization

A conventional C-X reactive compatibilizer in a binary A/B blend system has the nonreactive C segment structurally identical or miscible with com-

Table I Processing Conditions

Extrusion blending									
Stage:	1	2	3	4	5	6	7	8	9	Die
Temp. (°C)	180	270	275	280	285	285	280	280	280	285
Motor rate: 250 rpm
Feeder rate: 300 g/min

Injection molding				
Zone	1	2	3	Nozzle
Temp. (°C)	260	285	285	280
Screw rate: 200 rpm
Mold temperature: 80°C
Cycle time: 20 s

ponent A and the reactive X groups that are capable of a chemical reaction with component B of the blend to form *in situ* the C-X-B graft or block co-polymer during melt processing. By blending A, B, and C-X simultaneously, because the reactive C-X compatibilizer is inherently more miscible or more compatible with the component A, C-X is preferably to reside evenly in the A phase before the occurrence of the anticipated reaction. Therefore, the reaction between C-X and component B should take place at the interface and the *in situ*-formed C-X-B co-polymer tends to anchor along the interface to reduce the interfacial tension in the melt state. Not all added C-X compatibilizer in the blend has the chance to make contact and react with B component during a typical melt-mixing process and a portion of them may have the chance to react more than once. The extent of such *in situ* reactions depends on reactivity, blending sequence, presence of a suitable catalyst, processing conditions, and the X content in the C-X compatibilizer. C-X itself is not considered as a compatibilizer for the A/B blend; only the *in situ*-formed C-X-B copolymer is able to function as a compatibilizer of the blend. Such a reactive compatibilization approach is not universally applicable to all polymer pairs. Reactive compatibilization approach is potentially valid only for those blend pairs with at least one blend component possessing certain necessary functional groups (as chain ends or within main chain) that can be reacted with the reactive compatibilizer. In general, a blend component possessing chain-end functional groups is particularly suitable for such *in situ* reactive compatibilization. Typical examples are —COOH (and/or —OH) of polyester, —NH$_2$ of polyamide, and phenolic —OH of PPO. The functional groups X in C-X compatibilizer copolymer can also be as chain-ends or evenly distributed within the main chain to produce *in situ* the block or graft copolymer. For a graft type reaction by preblending the C-X compatibilizer with B component in a sequential blend process, excessive reaction tends to take place and produces the highly branched comb-like graft copolymer or even a crosslinked network, which is certainly undesirable. Usually, a lightly grafted co-polymer, one or a few grafts per main chain, is more efficient than the heavily grafted one.[39,40] Therefore, it is essential to properly control the extent of the graft reaction by optimizing the reactive group concentration, blending sequence, catalyst, and processing conditions to achieve the best performance of the resultant blends.[9]

If both blend components (A and B) contain the functional groups that can react with the reactive

compatibilizer with comparable rate, a fraction of the *in situ*-formed copolymers may include both A and B components. Evidence indicated that the formation of the mixed copolymer is advantageous and resulted in further improvement of the compatibilized blend.[19] The compatibilized Noryl/LCP blend improved more in morphological and mechanical properties than the corresponding compatibilized PS/LCP blend above their respective uncompatibilized blends. In the Noryl/LCP blend system, the reactive compatibilizer, SG, is able to react with both LCP and PPO (in Noryl) with comparable reactivity, and a certain amount of the mixed graft copolymer (SG-g-LCP-g-PPO) is expected to be formed.[19] In the PS/LCP system, PS is a nonreactive component, and only the SG-g-LCP graft copolymer is expected to be formed.[10] The mixed copolymer is expected to be more effective as a compatibilizer of the blend, which is probably responsible for the difference observed between these two blend systems.

If the *in situ*-formed mixed copolymer is indeed more effective in compatibilizing a blend where both blend components possessing the necessary functional groups, then the presence of the C segment and its miscibility with component A required for a conventional reactive C-X compatibilizer may not be critical or even undesirable. That means a compound C-X, a small molecule, an oligomer, or a polymer containing multiple X functional groups should also act as a reactive compatibilizer for the A/B blend, disregarding the miscibility between the C segment in C-X and one of the blend constituents. In that sense, C-X simply functions as a coupling agent to produce the mixed copolymer containing both A and B components. Realistically, lower compatibility between C segment with blend constituents A and B is actually desirable because the C-X coupling agent would prefer to reside at interface and has a better opportunity to contact and react with both A and B components simultaneously. Therefore, blends between copolyester LCP with many thermoplastic polyesters are expected to be compatibilized by any epoxy compound with multiple epoxy functional groups. Both copolyester LCPs and thermoplastic polyesters possess similar —COOH and —OH endgroups, and their reactivities with epoxy are also expected to be comparable. Therefore, a fraction of the *in situ*-formed products should be in the form of mixed copolymer. Several blend systems including the LCP component have been demonstrated by us that such a coupling agent approach is highly efficient when both blend components contain the necessary functional

Table II Extruder Current and Die Swelling Ratio

Composition	Extruder Current (Amp)	Die Swelling Ratio
PET	23.5	1.35
PET/LCP 90/10	21.2	1.38
PET/LCP/Epoxy 90/10/0.5	21.5	1.35
PET/LCP/Epoxy 90/10/1	21.6	1.35
PET/LCP/Epoxy 90/10/2	21.2	1.31
PET/LCP/Epoxy/Cat 90/10/2/0.02	22.1	1.31

Extruder temperature range; 270–285°C; screw rotation rate; 250 rpm; feeding rate, 60 g/min.

groups. The main segment structure of the coupling agent used in this study (solid epoxy resin) is neither identical nor miscible with the blend components LCP and PET. This intermediate molecular weight epoxy resin with two epoxy endgroups simply functions as a coupling agent unlike most other conventional reactive compatibilizers. A low-molecular-weight multiple functional epoxy compound was demonstrated to be even a better reactive compatibilizer,[41] resulting in drastic improvements in mechanical properties. As mentioned earlier, this unconventional reactive compatibilization through in situ coupling reaction can be applied to many blend systems as long as both blend constituents containing the needed functional groups that can react with the reactive coupling agent with comparable reactivity. If one of the blend component is innert, it can be prefunctionalized with certain reactive groups, partially or fully, and the same coupling approach is still valid. Polypropylene is a nonreactive component in the blends of PP/polyamide and PP/PBT. By functionalizing a small fraction of the PP with maleic anhydride (MPP), the ethylene-glycidyl methacrylate (EGMA) became a effective reactive compatibilizer for the blends of PP/polyamide[42] and PP/poly(butylene terephthalate (PBT)[43] by functioning as a coupling agent to form the EGMA-g-PP-g-PA and EGMA-g-PP-g-PBT mixed copolymers, respectively.

Processibility

Processing of this PET/LCP blend system at lower LCP content is rather smooth even without the presence of the compatibilizer. At higher LCP content (15%), processing problems such as die swelling or melt fracture occasionally occurred. In generally, the presence of the compatibilizer did improve the extrusion processibility and resulted in smoother extrusion. Table II shows the summarized results of the required extruder power outputs and the die

swelling ratios based on the PET/LCP = 90/10 blend series. The extruder currents of the blends, with and without compatibilizer, are less than the pure PET. Addition of small amount of LCP improves the TP matrix processibility by lowering its shear viscosity which has been well reported.[24,28,32,35] The increase of the extruder current due the expected molecular weight increment by the reactive compatibilizer is not very significant. The observed die swelling problem of the uncompatibilized blends has been reduced after compatibilization.

Torque Versus Time

Figure 1 illustrates the torque versus time curves for PET and the uncompatibilized and compatibilized PET/LCP 90/10 blends. Pure PET and the uncompatibilized blend show torque decline continuously with time, an indication of thermal degradation. The compatibilized blend maintains its torque fairly steady up to 600 min. The compatibilized blend containing 200 ppm catalyst results in slight increases of the resultant torque value. Obviously,
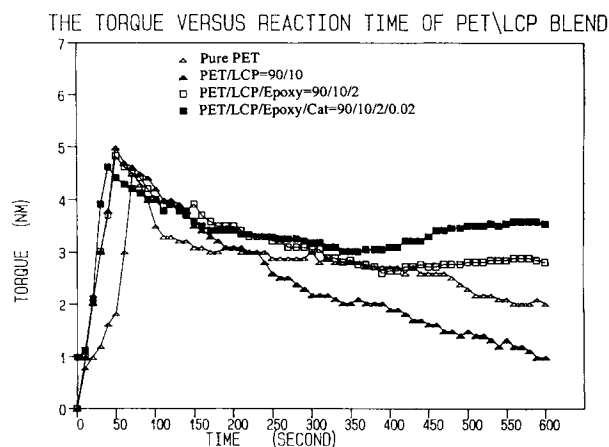

Figure 1 Torque versus time curves for PET and various PET/LCP 90/10 blends.

thermal stability improvement is an additional advantage by using the reactive compatibilizer.

Melt Flow Rates (MFRs)

Table III gives the MFR data of all the blends investigated. Without the presence of the compatibilizer, the PET/LCP blends result in higher MFR as would be expected. The MFR decreases from all three blend series with the increase of the quantity of the compatibilizer and the presence of the catalyst. Molecular weight increase from the anticipated reactions between the epoxy with PET and LCP is believed to be responsible for the observed lower MFR from the compatibilized blends. The interfacial friction caused by the in situ-formed copolymer anchoring along the interface may also partially contribute to the shear viscosity increase.

Capillary Rheometry

Figure 2 shows the apparent viscosity versus shear rate curves for pure PET and uncompatibilized and compatibilized PET/LCP 90/10 blends. Substantial reduction on the PET viscosity after blending with 10% LCP has been observed. The addition of 2 phr of the epoxy compatibilizer does not cause any viscosity increase, and it actually decreases the viscosity slightly. However, the compatibilized blend containing 200 ppm catalyst results in substantial viscosity rise but still lower than that of the pure PET.

Table III   MFR of the PET/LCP Blends

Composition	MFR (g/min)
PET	40.6
PET/LCP 95/5	42.2
PET/LCP/Epoxy 95/5/0.5	38.5
PET/LCP/Epoxy 95/5/1	30.3
PET/LCP/Epoxy 95/5/2	27.5
PET/LCP/Epoxy/Cat 95/5/2/0.02	25.5
PET/LCP 90/10	44.2
PET/LCP/Epoxy 90/10/0.5	33.5
PET/LCP/Epoxy 90/10/1	27.2
PET/LCP/Epoxy 90/10/2	20.0
PET/LCP/Epoxy/Cat 90/10/2/0.02	18.0
PET/LCP 85/15	45.3
PET/LCP/Epoxy 85/15/0.5	33.1
PET/LCP/Epoxy 85/15/1	30.5
PET/LCP/Epoxy 85/15/2	20.3
PET/LCP/Epoxy/Cat 85/15/2/0.02	18.6

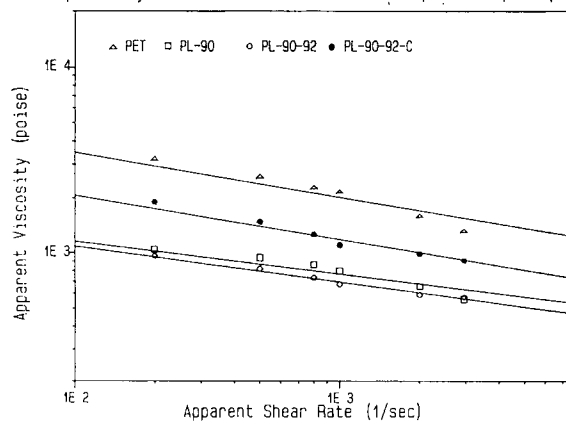Load, 2.16 kg; Temperature, 285°C.

Figure 2   Apparent viscosity versus shear rate curves for PET and various PET/LCP 90/10 blends.

DSC Analyses

Thermal properties analyzed by DSC for pure PET and various blends are summarized in Table IV. The T_gs and T_ms of the PET component in the blends are only slightly higher than the pure PET but are not very substantial. The PET crystallinity increases by blending with a small amount of LCP, which has been well-recognized. The presence of LCP can serve as a crystallization nucleation agent to promote PET crystallization. The presence of the epoxy compatibilizer further increases the PET crystallinity for the blends containing 5 and 10% of LCP. The epoxy compatibilizer results in finer LCP domains, which should provide greater surface contacting area between phases to induce higher PET crystallinity. However, in the PET/LCP 85/15 blends, the compatibilized blends show slight decrease of the PET crystallinity. The addition of 200 ppm catalyst in the compatibilized blends results in substantial reduction of the PET crystallinity. The compatibilized blends containing catalyst indeed cause further reduction of the LCP domain size but result in lower PET crystallinity unexpectedly. Greater mutual solubility by the better compatibilized blends (with catalyst) may have higher contents of LCP and the mixed copolymer dissolving in the PET phase, hindering the PET crystallization.

Scanning Electron Microscopy (SEM) Morphologies

Figure 3 illustrates the schematic diagram showing the four locations of an injection molded specimen, from the planes parallel and perpendicular to flow direction at core and near skin regions, that have

been examined by SEM. Because the LCP spherical dimension is at the core region, the morphologies viewing from both directions (locations 2 and 4 in Fig. 3) are essentially the same. Therefore, only the morphologies parallel to the flow (location 4) are presented here. Figure 4(A)–(C) shows the SEM micrographs of the uncompatibilized PET/LCP 95/5 blend taken from three locations: 1, 3, and 4. No LCP fibril can be detected from this blend with low LCP content. LCP in the blend has to exceed a critical level to form the fibril morphology depending on processing conditions. Figure 4(D) and (F) gives the micrographs of the PET/LCP/Epoxy 95/5/1 compatibilized blend taken at the same three locations. At the core region [Fig. 4(D)], the sizes of the LCP spherical particles are comparable with that of the corresponding uncompatibilized blend [Fig. 4(A)]. Figure 4(E) is the micrograph parallel to flow near skin region (location 3) that clearly shows the formation of the long LCP fibrils. Figure 4(F) shows the micrograph perpendicular to the flow (location 4) where great numbers of the small circular LCP domains are present. By comparing Figure 4(E) and (F) for the same spot but viewed by two different angles, these circular LCP domains can be confirmed as the fractured fibrils rather than as the droplet LCP particles. The results observed from Figure 4 reveal that the presence of 1 phr epoxy reduces the LCP domain size and induces greater fibril formation near skin region but is relatively unaffected at core region. Figure 5(A)–(C) shows the morphologies of the uncompatibilized PET/LCP 90/10 blend viewing from the same three locations. Coarse LCP
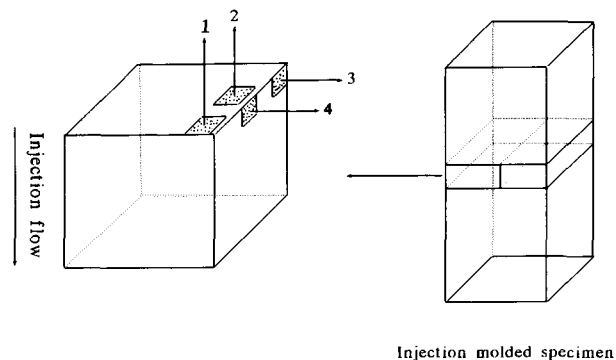

Figure 3 Schematic diagram shows the directions and locations where SEM micrographs were taken.

fibrils now can be found near the skin region [Fig. 5(B) and (C)] whereas the LCP phase still remains as droplet domains at the core region [Fig. 5(A)]. Figure 5(C) shows the pullout fibrils from the fracture surface near the skin region of the uncompatibilized blend, an indication of poor interfacial adhesion. Figure 5(D)–(F) gives the morphologies of the compatibilized PET/LCP/Epoxy 90/10/1 blend. At the core region [Fig. 5(D), location 4], the LCP spherical particles are relatively smaller than those of the uncompatibilized blend [Fig. 5(A)]. Near the skin region [Fig. 5(E), location 3], the LCP fibrils become finer with significantly higher aspect ratio relative to the uncompatibilized blend [Fig. 5(B)]. Figure 5(F) shows the fractured LCP fibrils without any single pullout fibril being found. Improved interfacial adhesion results in fibril fracture instead of fibril pullout during sample cryogenical fracture.

Table IV Thermal Properties of the PET/LCP Blends

Composition	ΔH_{PET} (J/g)	% PET Crystallinity	T_g (°C)	T_m (°C)
PET	26.4	22.6	80.1	248.1
PET/LCP 95/5	28.4	25.6	82.8	250.6
PET/LCP/Epoxy 95/5/0.5	29.6	26.7	81.2	250.6
PET/LCP/Epoxy 95/5/1	32.6	29.7	82.1	250.7
PET/LCP/Epoxy 95/5/2	28.2	26.0	82.2	250.6
PET/LCP/Epoxy/Cat 95/5/2/0.02	20.4	18.8	83.6	248.9
PET/LCP 90/10	30.2	28.8	80.7	248.7
PET/LCP/Epoxy 90/10/0.5	31.1	29.8	81.0	250.0
PET/LCP/Epoxy 90/10/1	30.0	28.9	80.8	250.0
PET/LCP/Epoxy 90/10/2	32.0	31.9	81.1	249.5
PET/LCP/Epoxy/Cat 90/10/2/0.02	26.6	25.8	82.8	249.8
PET/LCP 85/15	26.0	26.2	82.8	250.0
PET/LCP/Epoxy 85/15/0.5	24.4	24.7	82.6	250.6
PET/LCP/Epoxy 85/15/1	25.4	25.9	81.8	251.2
PET/LCP/Epoxy 85/15/2	25.0	25.7	82.0	251.3
PET/LCP/Epoxy/Cat 85/15/2/0.02	24.2	24.9	82.2	251.6

A: PET/LCP=95/5, at core and parallel to flow (location #4)

B: PET/LCP=95/5, near skin and parallel to flow (location #3)

C: PET/LCP=95/5. near skin and perpendicular to flow (location #1)

D: PET/LCP/Epoxy=95/5/1 (location #4)

E: PET/LCP/Epoxy=95/5/1 (location #3)
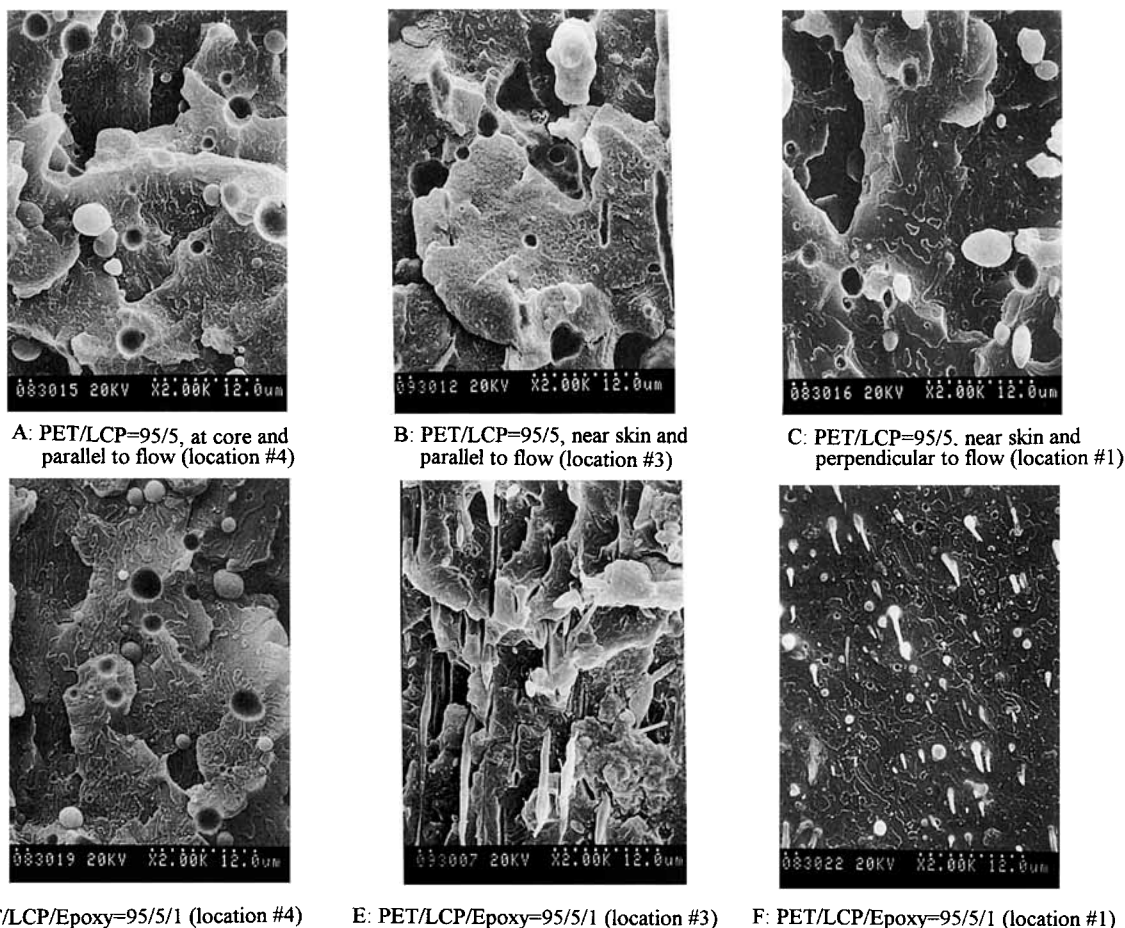
F: PET/LCP/Epoxy=95/5/1 (location #1)

Figure 4 SEM micrographs of the uncompatibilized and compatibilized PET/LCP 95/5 blends. (A) PET/LCP 95/5, at core and parallel to flow (location 4); (B) PET/LCP 95/5, near skin and parallel to flow (location 3); (C) PET/LCP 95/5, near skin and perpendicular to flow (location 1); (D) PET/LCP/Epoxy 95/5/1 (location 4); (E) PET/LCP/Epoxy 95/5/1 (location 3); (F) PET/LCP/Epoxy 95/5/1 (location 1).

Again, the results observed from Figure 5 demonstrate that the compatibilization of the PET/LCP blend breaks down the originally coarse fibrils into greater numbers of the finer LCP fibrils. Additionally, the adhesion between fibrils and the PET matrix has been enhanced.

Effect of Shear Rate on Fibril Formation by Hot-Stage Microscope

The original dimension of the LCP component in the blend can be easily examined by the hot-stage optical microscope at a temperature above the T_m of the PET but still below the T_m of the LCP. The strings from the capillary rheometrical measurements by varying the shear rates were used to study the effect of shear rate on the LCP fibrilar structure. Three different shear rates, $\gamma = 1 \times 10^2$ s^{-1}, 8×10^2

s^{-1}, and 2×10^3 s^{-1} were adopted in this investigation. Figure 6 shows the hot-stage micrographs of the uncompatibilized PET/LCP 90/10 blend at different shear rates where the LCP domains are irregular nonfibrillar structure, regardless of shear rate. For the blend containing lower epoxy content, PET/LCP/Epoxy 90/10/0.5, the LCP fibrilar structure begins to be formed at the intermediate shear rate [Fig. 7(B), $\gamma = 8 \times 10^2$ s^{-1}]. At high shear rates ($\gamma = 2 \times 10^3$ s^{-1}), the well-established long LCP fibrils can be clearly observed in the blend [Fig. 7(C)]. Figure 8 shows the micrographs of the compatibilized blend containing higher epoxy content (2 phr). At low shear rate ($\gamma = 1 \times 10^2$ s^{-1}), the LCP phase of this compatibilized blend is still existed as a droplet morphology [Fig. 8(A)]. At higher shear rates, the LCP fibrils are produced [Fig. 8(B) and (C)]. For the compatibilized blend containing the
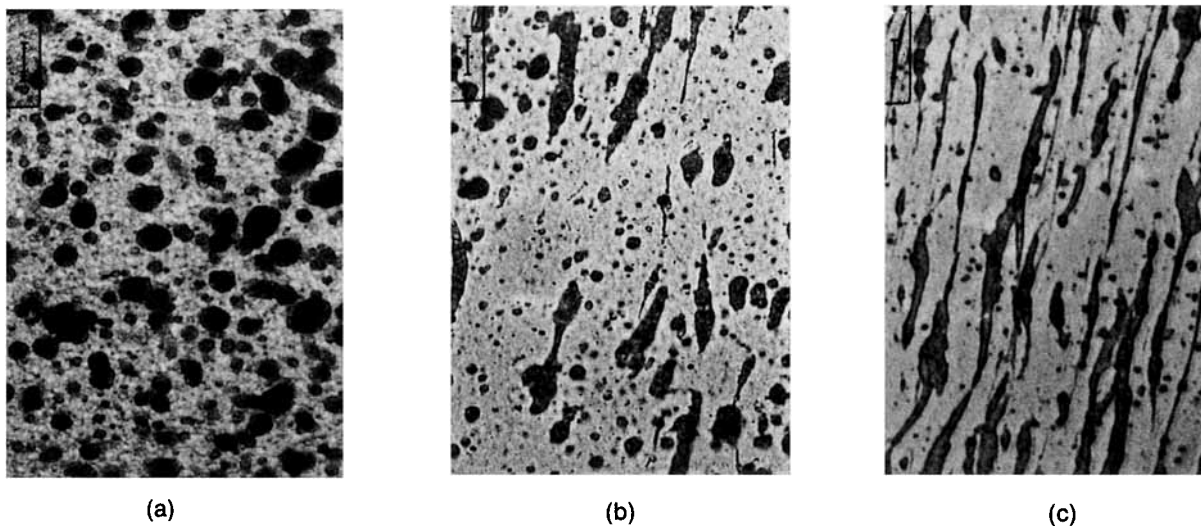
A: PET/LCP=90/10 (location #4),   B: PET/LCP=90/10 (location #3)   C: PET/LCP=90/10 (location #1),

D: PET/LCP/Epoxy=90/10/1 (location #4)   E: PET/LCP/Epoxy=90/10/1 (location #3)   F: PET/LCP/Epoxy=90/10/1 (location #1)

Figure 5   SEM micrographs of the uncompatibilized and compatibilized PET/LCP 90/10 blends. (A) PET/LCP 90/10 (location 4); (B) PET/LCP 90/10 (location 3); (C) PET/LCP 90/10 (location 1); (D) PET/LCP/Epoxy 90/10/1 (location 4); (E) PET/LCP/Epoxy 90/10/1 (location 3); (F) PET/LCP/Epoxy 90/10/1 (location 1).

(a)   (b)   (c)

Figure 6   Hot-stage micrographs of the PET/LCP 90/10 blend under different shear rates. (A) $\gamma = 1 \times 10^2$ s^{-1}; (B) $\gamma = 8 \times 10^2$ s^{-1}; (C) $\gamma = 2 \times 10^3$ s^{-1}.

(a) (b) (c)

Figure 7 Hot-stage micrographs of the PET/LCP/Epoxy 90/10/0.5 blend under different shear rates. (A) $\gamma = 1 \times 10^2$ s^{-1}; (B) $\gamma = 8 \times 10^2$ s^{-1}; (C) $\gamma = 2 \times 10^3$ s^{-1}.

additional 200 ppm, catalyst results in much finer fibrils at high shear rate [Fig. 9(C)]. A critical shear rate is required to form the LCP fibrils and has been widely reported. However, it is still a controversial issue whether the compatibilization will enhance, reduce, or even inhibit the LCP fibril formation. Based on the limited literature reported in the area of compatibilization of TP/LCP blends, most systems tend to reduce or inhibit the LCP fibril formation after compatibilization including two of our previous papers on PS/LCP[10] and PP/LCP[11] blends. In addition to the present study, the Noryl/LCP blends[19] and other PET/LCP blends compatibilized by a small MW epoxy resin[41] are the only three TP/

LCP blend systems known by the authors that the fibril formation is enhanced by compatibilization. Therefore, we believe that the effect of compatibilization on fibril formation depends on blend system and the processing conditions. More studies on additional compatibilized TP/LCP blend systems must be carried out to tell what factors are important to enhance the fibril formation.

Mechanical Properties

The summarized tensile properties and unnotched impact strengths are listed in Table V and Figures 10 and 11. The PET/LCP 90/10 blend series shows
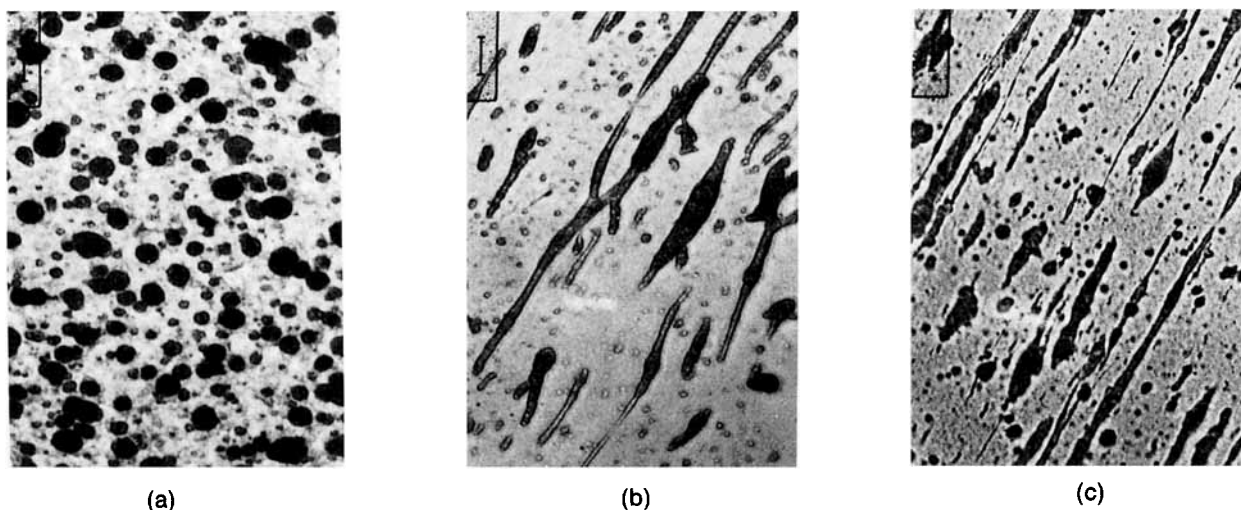

(a) (b) (c)

Figure 8 Hot-stage micrographs of the PET/LCP/Epoxy 90/10/2 blend under different shear rates. (A) $\gamma = 1 \times 10^2$ s^{-1}; (B) $\gamma = 8 \times 10^2$ s^{-1}; (C) $\gamma = 2 \times 10^3$ s^{-1}.

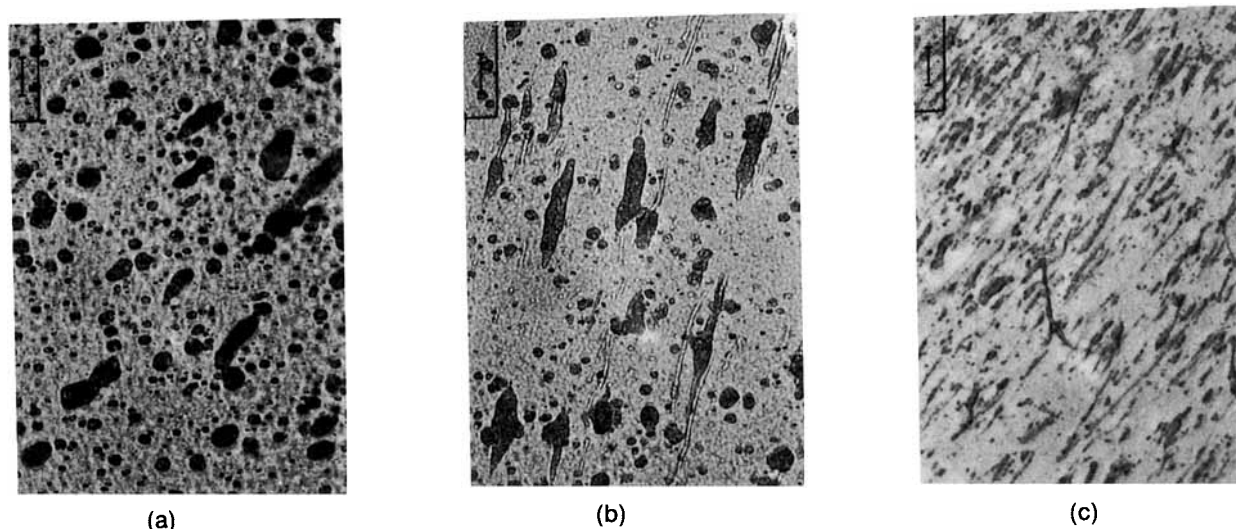(a)   (b)   (c)

Figure 9 Hot-stage micrographs of the PET/LCP/Epoxy/Cat 90/10/2/0.02 blend under different shear rates. (A) $\gamma = 1 \times 10^2$ s^{-1}; (B) $\gamma = 8 \times 10^2$ s^{-1}; (C) $\gamma = 2 \times 10^3$ s^{-1}.

a definite trend of property improvement according to the extent of compatibilization, whereas the trend in other series is somewhat less consistent. If we consider the tensile strength and modulus as the material stiffness, then the tensile elongation to break and impact strength is the material toughness. Figure 10 shows the stiffness (tensile modulus and strength) improvement with the increase of the epoxy compatibilizer quantity and the presence of catalyst. Figure 11 shows similar trend for the toughness (tensile elongation and impact strength) enhancement. Overall, both stiffness and toughness are enhanced through compatibilization for this PET/LCP blend system. With only a few excep-

tions,[10,19] essentially all previously reported compatibilized TP/LCP systems result in either stiffness improvement (but lower on toughness) or toughness enhancement (but lower on stiffness) relative to the uncompatibilized counterparts. Two major factors are important in dictating the mechanical properties of the resultant TP/LCP blends: the formation of the fibrilar LCP structure and the increase of the interfacial adhesion. Compatibilization of any polymer blend will increase the interfacial adhesion without any doubt by all. As mentioned above, compatibilization of a TP/LCP blend may enhance, reduce, or even inhibit the LCP fibril formation depending on systems and processing conditions. In

Table V   Tensile and Impact Properties of the PET/LCP Blends

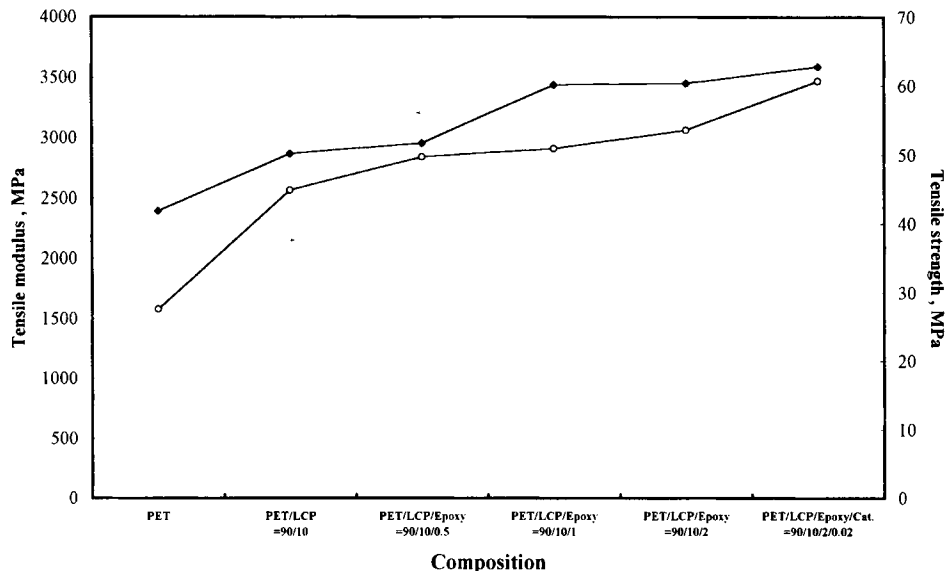| Composition	Tensile Modulus (MPa)	Tensile Strength (MPa)	Tensile Elongation (%)	Unnotched Impact (J/m)
PET/LCP 95/5	2630	24.7	7	766
PET/LCP/Epoxy 95/5/0.5	2361	25.3	> 100	802
PET/LCP/Epoxy 95/5/1	2601	27.1	> 100	735
PET/LCP/Epoxy 95/5/2	2782	28.2	> 100	778
PET/LCP/Epoxy/Cat 95/5/2/0.02	2952	40.1	> 100	810
PET/LCP 90/10	2868	44.9	5	386
PET/LCP/Epoxy 90/10/0.5	2954	49.7	7	432
PET/LCP/Epoxy 90/10/1	3437	50.9	10	562
PET/LCP/Epoxy 90/10/2	3452	53.6	12	616
PET/LCP/Epoxy/Cat 90/10/2/0.02	3589	60.7	15	620
PET/LCP 85/15	3891	67.7	3	322
PET/LCP/Epoxy 85/15/0.5	3979	71.6	5	383
PET/LCP/Epoxy 85/15/1	3698	79.0	6	444
PET/LCP/Epoxy 85/15/2	4200	70.8	10	520

Figure 10 Effect of epoxy compatibilizer and catalyst on tensile modulus and tensile strength.

addition to the expected interfacial adhesion increase, the enhanced LCP fibril formation in this compatibilized PET/LCP blends is responsible for the improvements on both stiffness and toughness.

Mechanism of Compatibilization

In the PS/LCP[10] and Noryl/LCP[19] blends, both stiffness and toughness were improved to different

levels after compatibilizing by the SG reactive compatibilizer. The compatibilized Noryl/LCP blends give much more improvements than that for the PS/LCP blends reflecting by the dimensional changes of the LCP fibrils. For the Noryl/LCP blend system, the LCP fibrils were mostly retained and even converted into finer fibrils with higher aspect ratio after compatibilization. For the PS/LCP system, on the contrary, compatibilization caused reduction on the number of the fibrils or even transformed into drop-
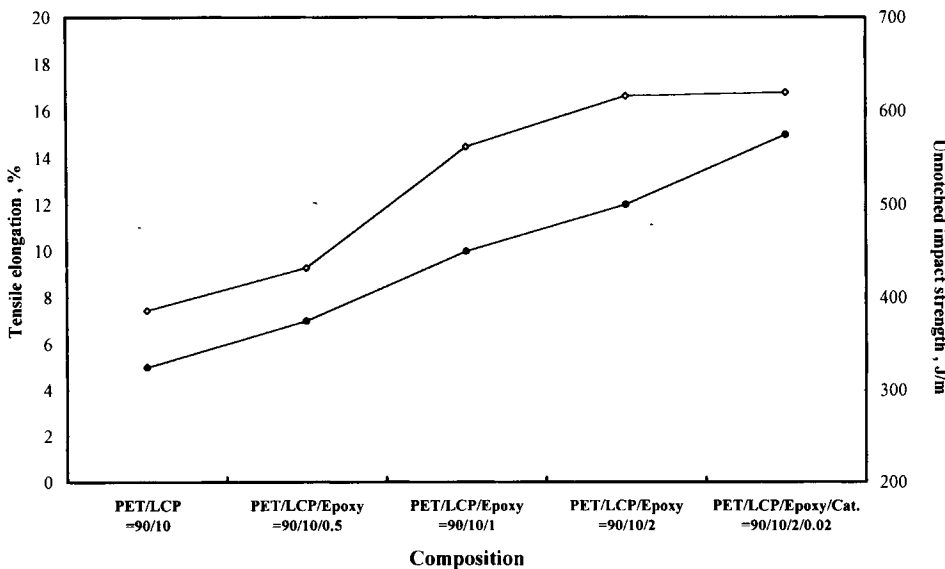

Figure 11 Effect of epoxy compatibilizer and catalyst on unnotched impact strength and tensile elongation.

let morphology after compatibilization. One major difference between this two-blend systems comes from the chemistry of the reaction involved. In the PS/LCP blend, the reactive SG compatibilizer can only react with LCP component to form the expected SG-*g*-LCP copolymer because the PS is the nonreactive component of the blend. In the Noryl/LCP system, this SG compatibilizer is able to react with both LCP and PPO in Noryl to form some of the mixed SG-*g*-LPC-*g*-PPO copolymer with comparable reactivity.[19] This mixed graft copolymer with its long PPO branch deeply penetrating into the Noryl phase and the LCP branch penetrating into the LCP phase is able to anchor along the interface more firmly than that of the SG-*g*-LCP copolymer and acts as a more effective compatibilizer. Therefore, the SG copolymer in the Noryl/LCP blends can functions as a coupling agent type compatibilizer in addition to the conventional type reactive compatibilizer. One drawback for the SG copolymer to function as coupling agent is the miscibility between SG and Noryl component in the Noryl/LCP blend. The SG copolymer tends to dissolve evenly into the Noryl phase, and the *in situ* reaction can take place only at interface with considerably less chance to make contact with LCP phase during melt mixing. When the epoxy containing compatibilizer with relatively poor miscibility with both blend constituents is used, such as the epoxy resin used in the current study, this inherently incompatible epoxy resin should preferentially reside along the interface and the chance of the *in situ* reaction involving both blend components should increase. The main chain structure of the solid epoxy resin used in this study is neither structurally identical nor miscible with PET and LCP. Therefore, we expect that this epoxy resin can react with both PET and LCP easier to form the desirable mixed copolymer. Indeed, the quantity of epoxy resin required in this PET/LCP system to achieve the maximum compatibilization is considerably less than that of the Noryl/LCP blend. Therefore, a coupling agent type reactive compatibilizer can be more efficient than the conventional reactive compatibilizer should both blend constituents contain the necessary functional groups with comparable reactivity.

CONCLUSIONS

A selected reactive coupling agent can be used to compatibilize certain incompatible blends with high efficiency if both blend components possess the necessary functional groups with comparable reactivity.

Solid epoxy resin with two epoxide end-groups per chain has been demonstrated to be an effective compatibilizer for the incompatible PET/LCP blends by functioning as a coupling agent. The epoxy resin is neither structurally identical nor miscible with PET and LCP and tends to reside at interface. The *in situ*–formed epoxy-*b*-PET-*b*-LCP mixed copolymer is believed to be a highly effective compatibilizer for the PET/LCP blends. The LCP fibril formation is also enhanced after compatibilization and results in substantial improvements on both stiffness and toughness of the resultant blends. In comparing the conventional reactive compatibilizer, this coupling type reactive compatibilizer provides many advantages. Many epoxy compounds are readily available commercially with minimum cost rather than the complicated procedures usually involved in the lab synthesized reactive copolymer. Several additional blend systems using the reactive coupling agent-type reactive compatibilizers will be reported later.

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