Interfacial Adhesion and Deformation of Thermotropic Liquid Crystal Polymers in Engineering Thermoplastics: Blends of a Poly(ester amide) with Nylon 6 and a Polyester with PBT

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ABSTRACT: A new method was sought to produce *in situ* composites by the addition of a third component that would react with matrix polymers and thermotropic liquid crystal polymers to form graft copolymers, which act as a compatibilizer at the interface. Morphological observation reveals the significance of compatibilization in immiscible polymer blends. Good adhesion at the interface by the produced compatibilizer enabled the finely dispersed liquid crystal phase to be deformed in shear flow without elongation, even when the viscosity of the matrix polymer was lower than that of the liquid crystal polymer. This study provides a way to produce a strong and tough *in situ* composite. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 359–366, 1997

Key words: *in situ* composite preparation; interfacial adhesion; reactive extrusion; TLCP droplet deformation

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) are one of the most interesting developments in the chemistry and technology of polymeric materials during the past two decades. Their spontaneous molecular orientation leads to impressive rheological (low melt viscosity) and mechanical (high modulus and strength) properties that make these materials useful for a number of specialized applications.[1–3] TLCPs give rise, on melting, to highly organized liquid phases (mesophases) which tend to spontaneously pack parallel to one another to form highly oriented domains. Under elongational processing conditions, these oriented domains can develop a fibrillar morphology with a high degree of orientation, leading to enhanced mechanical properties.[1] This property enables TLCPs to be used as a reinforcing filler that is not present as a solid phase during processing of the composite but rather forms when the material is cooled to a solid state. This class of composites is called *in situ* composites because of their *in situ* shaping during the processing.[2] *In situ* composites have attracted a great deal of interest because they can solve some problems that arise during the processing of conventional fiber-reinforced composites, such as increase in melt viscosity, thermal degradation, poor dispersion of fibers, processing machinery wear-out, and breakage of solid fibers.[3]

There have been numerous studies of *in situ* composites and TLCP blends with commercial thermoplastics.[2,4] In order to obtain a self-reinforcing fibrillar structure, the rheological property of TLCP blends should be carefully controlled. Not all TLCP blends with commercial thermoplastics can produce *in situ* composites. Fibrils of the TLCP phase are formed after the die exits as a result of the extensional forces in the flow direc-

tion. For special engineering plastics such as poly-ether–imides, polyarylates, polyphenylene sulfides or polymers produced by radical polymerization that can retain high viscosities at high processing temperatures (at least higher than crystal-nematic transition temperature), extension is readily applicable. On the other hand, for polymers produced by condensation, such as Nylon 6 and poly(butylene terephthalate) (PBT), viscosities rapidly decrease with temperature and are two or three orders lower than those of TLCPs at the processing temperature and shear rate. Hence extension is not readily applicable to these polymers, whereas it is definitely needed to produce *in situ* composites. Following Taylor's theory, at least qualitatively, La Mantia and Valenza studied the morphologies of TLCP blends which were determined by the particular viscosity ratios.[5] They insisted that large TLCP particles are formed when the viscosity of TLCP is much greater than that of the matrices; the fibrillation morphology occurs only when the viscosity of the thermoplastic matrix is higher than TLCP's viscosity. Following their arguments, it is expected that fine dispersion and fibril formation of TLCP will be very difficult for Nylon 6 and PBT matrices, two of the most widely used engineering plastics, because of their low viscosities at the processing temperature and shear rate.[6,7] The lack of miscibility between TLCPs and these matrices also invokes poor dispersion and deterioration of some mechanical properties.

Most of the thermoplastics studied thus far are incompatible with TLCPs.[8] The reinforcing effect is less than that obtained from the miscible system. One way to provide compatibility in *in situ* composites is to add a compatibilizer.[9,10] Ternary blends present an attractive approach to the development of reinforced systems. 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.[9] Acting as polymeric surfactants, these reduce the interfacial tension, thus promoting interfacial adhesion and finer and more uniform dispersion of TLCP. Compatibilization of thermoplastic blends with TLCPs has been attempted very recently.[9–11]

In this report, we present a new method to produce *in situ* composites of Nylon 6 and PBT. The method we used is based on reactive extrusion and toughening of the matrix resin. The toughness of most thermoplastics can be considerably enhanced by the incorporation of a dispersed rub-bery phase. Addition of a rubber having two orders higher viscosity than Nylon 6 or PBT at the processing temperature and shear rate will substantially increase the viscosity of the blends at low shear rate. Since the brittle–tough transition of Nylon 6 and PBT depends on the rubber particle size, the size should be controlled to obtain the desired toughness. Such control is usually achieved by the addition of functionalized rubber, of which the functional group reacts with amine or hydroxyl end groups to form graft copolymers that act as the compatibilizer.[12] We expect that toughened Nylon 6 or PBT *in situ* composites can be prepared by the combination of a toughening process and *in situ* fibril formation. The significance of this report is to propose a new method for new TLCP blends that are tough and have a high modulus.

EXPERIMENTAL

Materials

The materials used in this work were commercial polymers. Nylon 6 (KN171 from KOLON Co., S. Korea) and PBT (HV1010 from LG Chemical, S. Korea) were used as matrices, maleic anhydride grafted ethylene–propylene–diene terpolymer (SA-*g*-EPDM; Royaltuf 465, Uniroyal, U.S.A.) was used as the reacting elastomer, and all-aromatic copolyesteramide (Vectra B950, Hoechst Celanese, U.S.A.) and copolyester (Vectra A950, Hoechst Celanese, U.S.A.) were used for LCP phases. Their chemical structures are shown in Schemes 1 and 2.
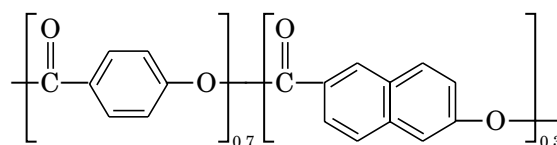
Scheme 1   Vectra A950.
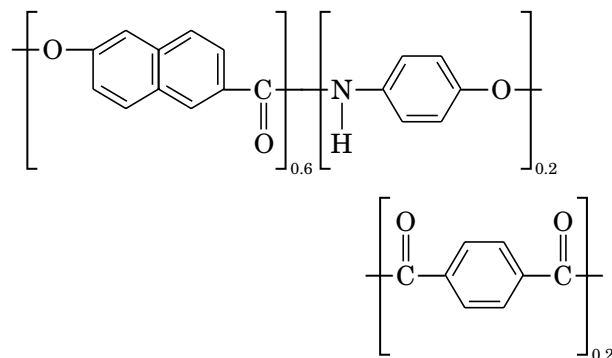
Scheme 2   Vectra B950.

(a)

(b)
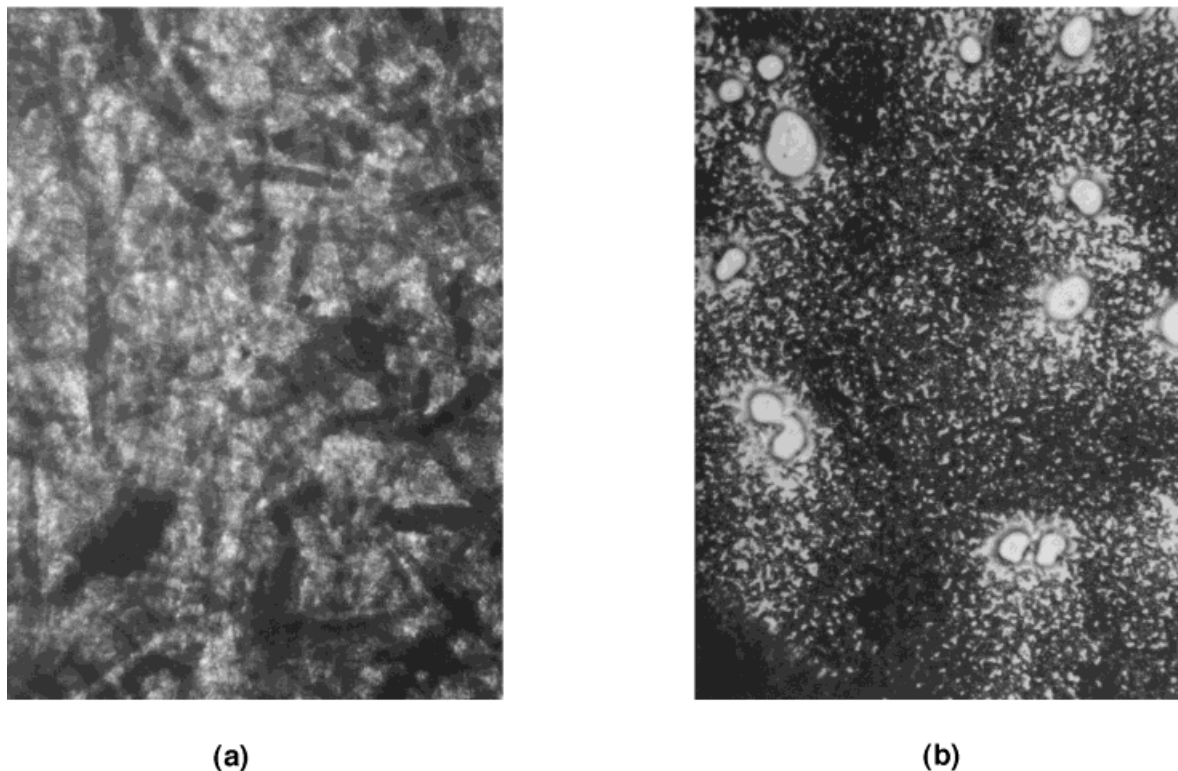
Figure 1   Polarized microscope photographs (×800). (a) PBT/TLCP/elastomer blend. Dark phase is the TLCP phase. (b) Nylon 6/TLCP/elastomer blend. Dark phase is the TLCP phase and large white one is the elastomer phase.

TLCP and elastomer contents were fixed as 25 wt % and 15 wt %, respectively. Vectra B was blended with Nylon 6/SA-*g*-EPDM and Vectra A was blended with PBT/SA-*g*-EPDM.

Preparation of Blends

The pellets of Nylon 6, PBT, and Vectra B950 were dried in a vacuum oven at 120°C for at least 24 h before use. Elastomer was dried in a vacuum oven at 60°C for 24 h. Blending was carried out in a Brabender twin screw extruder (AEV651). It was equipped with a pulling unit, but its pulling speed was set to match the extrusion speed so as not to extend the extrudate. Extrusion temperature was 290°C.

Observation of the Morphology and Other Physical Properties

Morphologies of extrudates were checked with a scanning electron microscope (SEM; Hitachi S-

2200C). Optical microscope (Reichter-Jung Micro-Star) equipped with hot plate (Mettler FP82) was used to see the liquid crystalline state. FT Raman spectra were obtained using a Perkin-Elmer System 2000 instrument equipped with near-IR optics. Testing of the mechanical properties of the blends was done using an Instron Universal Testing Machine 4204.

RESULTS AND DISCUSSION

Polarized microscope pictures of Nylon 6/Vectra B/SA-*g*-EPDM blend and PBT/Vectra A/SA-*g*-EPDM blend are shown in Figure 1. The PBT blend exhibits the fibrillar structure of Vectra A. At the extrusion shear rate (about 20 s^{-1}) and a temperature of 290°C, the viscosity of PBT was at least two orders lower than that of TLCP. Although the addition of an elastomer phase lifts the blend viscosity (ten times higher than that of

(a)

(b)
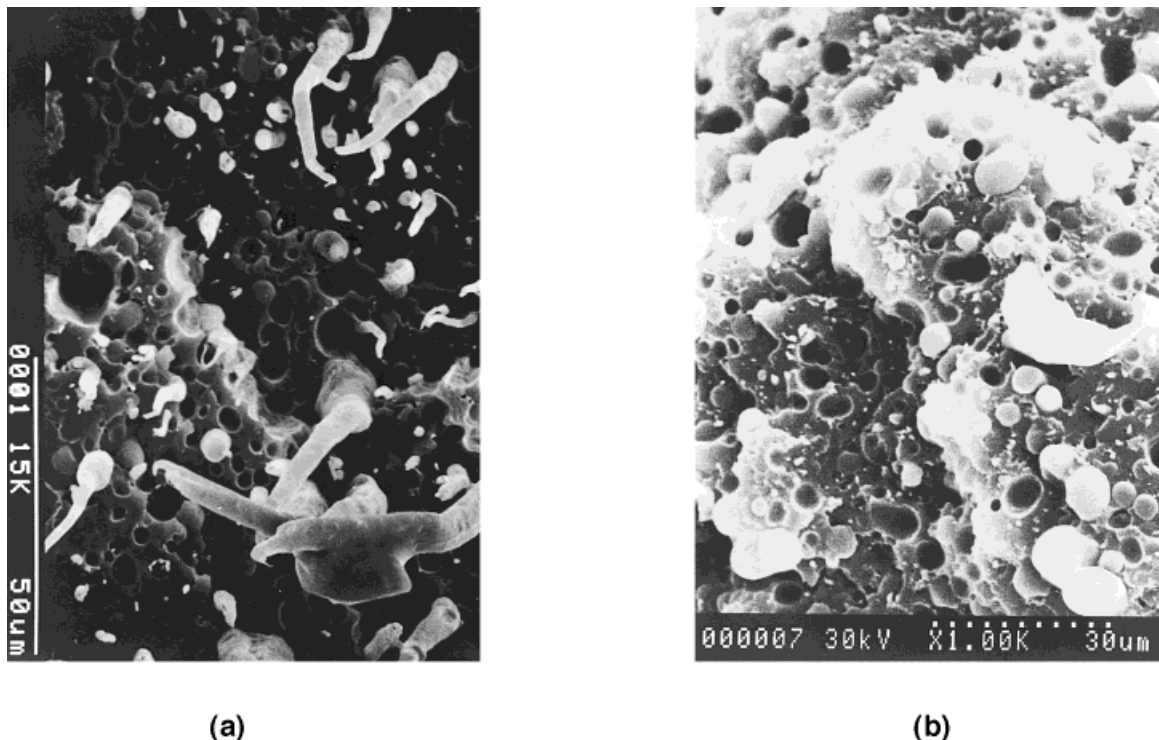
Figure 2 SEM photographs of fractured surfaces. (a) PBT/TLCP/elastomer blend. (b) Nylon 6/TLCP/elastomer blend.

PBT), this viscosity was still lower than that of Vectra A. At a similar shear rate, PBT of low viscosity could not by itself deform and break the spherical particles of the dispersed phase during flow. A more surprising feature is that no-drawing was applied to the extrudate. Most previous results were consistent with the finding that when the TLCP was the minor component, the viscosity ratio of the TLCP to that of the isotropic polymer was a decisive factor determining the deformation and structure development of the TLCP phase. Elongation and orientation of the TLCP phase takes place when the viscosity of the matrix polymer is higher than that of the suspended TLCP phase.[13] Therefore, high shear rate processing should be performed to lower the viscosity of the TLCP phase. The shear rate of this process was low (about 20 s^{-1}), and it should be emphasized again that the TLCP viscosity is higher than that of PBT. More details of the morphology can be observed in the SEM picture of the blend shown in Figure 2(a). We can obviously see the TLCP fibril shapes. Some appear to be coalesced into a large fiber shape, but fine fibrils can also be observed.

As shown in Figure 1(b), dispersion morphology for the Nylon 6/Vectra B/SA-g-EPDM blend was totally different from that of the PBT/Vectra A/SA-g-EPDM blend. TLCP phases were very uniformly and finely dispersed in the Nylon 6/Vectra B/SA-g-EPDM blend, and a large fibril shape observed in the PBT/Vectra A/SA-g-EPDM blend could not be seen under polarized microscope. It should be noted that the size of the dispersed TLCP phase is very small (submicron size). This small size of the TLCP phase in the Nylon 6/elastomer matrix was not observed by any others.[1,6,14,15] A closer look by SEM more obviously shows the dispersed state of Vectra B in the matrix [Fig. 2(b)]. TLCP phases are very finely and uniformly dispersed, with elongated shapes. Higher magnification showed dispersed microfibrils and their clusters in the TLCP phase (Fig. 3). It should be emphasized again that no extensional flow field was applied.

It is worth noting that there was good adhesion at the interface between the matrix (Nylon 6 and PBT) and dispersed phase (TLCPs and elastomer phase), as shown in Figures 2 and 3. This is ascribable to the graft copolymers, which act as a

compatibilizer at the interface. It is well known that amine groups of Nylon 6 and hydroxyl groups of PBT can react, during the melt mixing, with the anhydride group of the functional rubber as follows[12,17,18]:
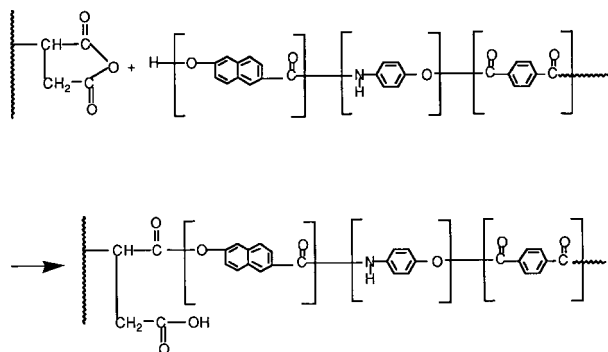
[REACTION 1]

SA-g-EPDM   nylon 6

(SA-g-EPDM)-g-nylon 6

[REACTION 2]
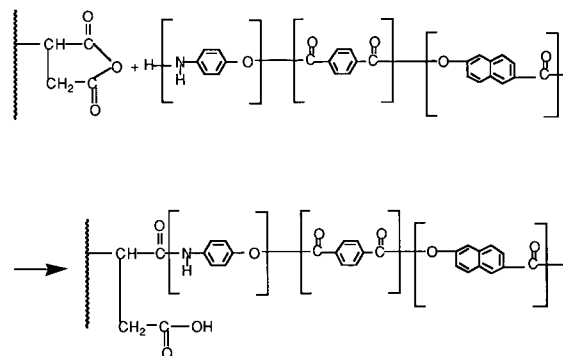
SA-g-EPDM   PBT

(SA-g-EPDM)-g-PBT
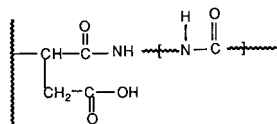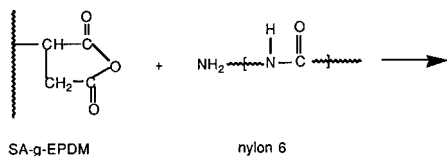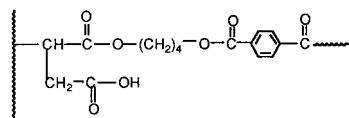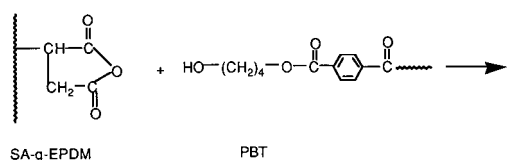
Good adhesion of TLCP phase with the matrix polymer suggests that the following chemical reactions might be occurred between SA-*g*-EPDM and Vectra B:
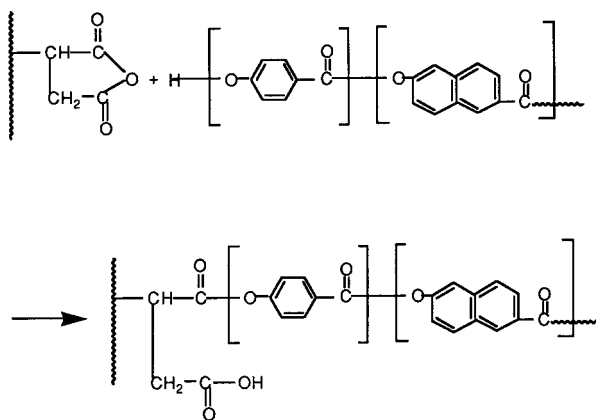
[REACTION 3]

or

[REACTION 4]

and the following reaction for Vectra A and SA-*g*-EPDM during the melt processing:

[REACTION 5]

Transesterification between PBT and Vectra A would be also possible, but does not seem to happen so much remarkably based on the SEM observation of the binary blend.[19] After the chemical reactions, it is apparent that products (graft copolymers) act as polymeric surfactants (compatibilizers). As a result, a uniform and very fine dispersion of the TLCP phase could have taken place. From the SEM photographs (Fig. 2) the compatibilizing action of Vectra B grafted copolymer appears to be more vivid than that of Vectra A grafted copolymer, because the dispersed TLCP phase domain is very small compared to that of the PBT blend.

In simple shear flow of Newtonian fluids, dispersed droplet will be elongated if

$$\frac{2\dot{\gamma}\eta_0 b}{\sigma} > 1 \qquad (1)$$

indicating that the ratio of shear stress ($\eta_0\dot{\gamma}$) should be larger than half of the interfacial energy
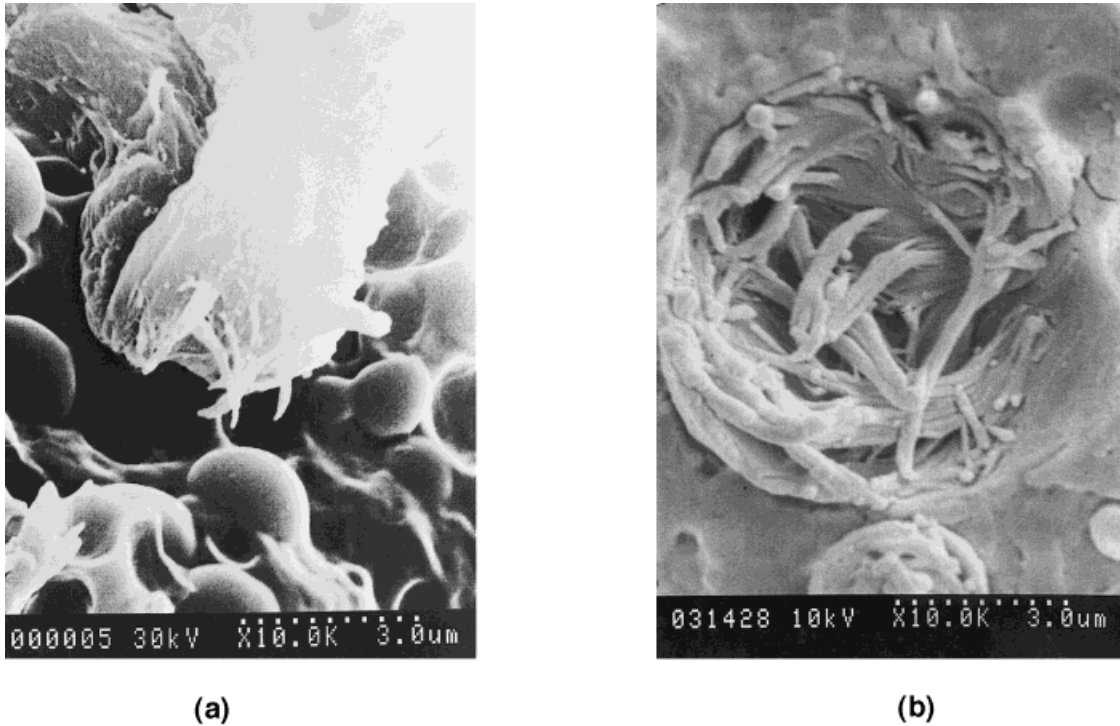
Figure 3 Higher magnification of SEM photographs of Nylon 6/TLCP/elastomer blend. (a) Dispersed fine microfibrils of TLCP. (b) Cluster of TLCP microfibrils.

(σ/b), where $\dot{\gamma}$ is the shear rate, σ is the interfacial tension, b is the initial diameter of the droplet, and η_0 is the viscosity of the suspending liquid.[5,9] Until now, most studies about *in situ* composite preparation focused on the supply of high shear stress to dispersed phase for the droplet deformation. Hence the easiest way to provide high shear stress is to increase the viscosity of matrix, which requires the use of special engineering plastics or additionally polymerized plastics of high viscosities. However, good adhesion at the interface is as efficient as the high viscosity for the stress transfer to deform the dispersed phase.[12] Since the fluid temperature is higher than the glass transition temperature and nematic transition temperature of the TLCP phase, the droplet can be deformed if stress higher than the minimum requirement is provided. The com-

patibilizing effect of the generated block or graft copolymer enforces a good adhesion at the interface (this can be seen in Fig. 3) and good stress transfer. Hence we believe enough amount of shear stress was transferred to the TLCP phase to deform it into the fibrous shape.

Since the elastomer would react with both the Nylon 6 and Vectra B, it remains at the interphase between those two or dispersed in the matrix, depending on the amount of the elastomer. Some of them coalesce into a bigger elastomer droplet. Immiscibility between TLCP and matrix produces only dispersed TLCP droplets. But TLCP droplets compatibilized by the elastomer phase would be surrounded by the elastomer. Figure 4 depicts the deformation scheme of a dispersed TLCP phase in the compatibilized blend. We speculate the TLCP deformations as follows:
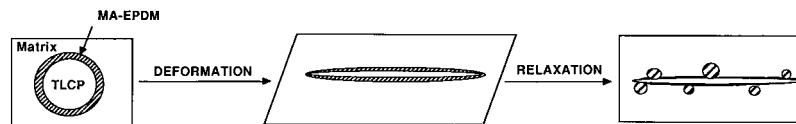

Figure 4 Deformation of a TLCP droplet. After relaxation, the long relaxation time of TLCP keeps its deformed shape, while the elastomer phase is already relaxed due to its short relaxation time.

Immediately after the deformation, the matrix, elastomer phase, and TLCP phase are in the affinely deformed state. After some time, the elastomer phase retracts to relaxed state due to its short relaxation time, while the TLCP phase still keeps its deformed shape, since it has a long relaxation time. Thus, the TLCP phase in the extended shape, whereas the elastomer phase has returned to spherical shape. A small portion of the elastomer phase may surround the TLCP surface. By the aggregation of the elastomer phase, the deformed TLCP phase is buried in the elastomer phase, as shown in Figure 3(a), when the surrounding elastomer layer is thick, or it forms a cluster of fine microfibrils, as shown in Figure 3(b), when the surrounding layer is thin or scarce.

In the ternary blend, one more intriguing fact is the role of the compatibilizer to reduce the interfacial tension between the matrix and TLCP phase as well as to make a good adhesion. This is a complex phenomenon, because it also reduces dispersed droplet size.[8,11] A too finely dispersed phase below the critical capillary number is quite difficult to deform. The final size of the TLCP droplet should be decided by the balance of the two forces in eq. (1). Since the brittle–tough transition of Nylon 6 and PBT depends on the rubber particle size, the size should be controlled to obtain the desired toughness. A more systematic approach is desired to get the optimized composition.[19] Needless to say, if highly strong flow (extensional flow) field is applied to the fluid, the dispersed droplet will be inevitably deformed into micro fibrils, though the particle size might be reduced.[5,13,16]

For the PBT blend, the TLCP particles were considerably large, so that the droplet deformation occurred at the processing shear rate.[20,21] Because of the interfacial adhesion, deformation stress was well transferred to the TLCP phase. On the other hand, TLCP droplet size in the Nylon 6 blend was very small because of the high activity of the Vectra B grafted copolymer. However, it looks as if the particle size is above the critical value for the shear deformation.[20] Good adhesion at the interface enables applied stress to be transferred to the dispersed phase, and affine deformation could produce fine fibrils without an elongational flow field (Fig. 4). If the extrudate is under a high extensional process (extensional flow field by postextrusion drawing), an *in situ* microfibrillar reinforcing phase can be more vigorously formed.[20]
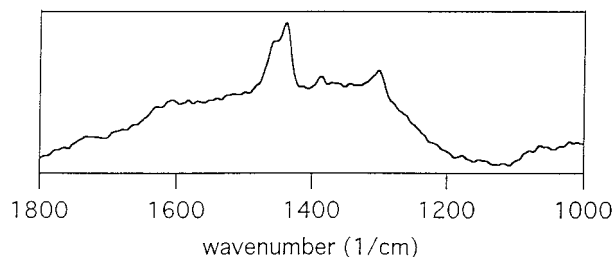
Figure 5 FT Raman spectra of the extract from the SA-g-EPDM and Vectra B binary blend.

We just briefly investigated interfacial adhesion and deformation of a TLCP phase dispersed in Nylon 6 and PBT by morphological observation. Formation of a block copolymer was also investigated by FT Raman spectroscopy. Using the sohxlet extractor, the soluble part (EPDM) was extracted from the binary blend of SA-*g*-EPDM and Vectra B with boiling xylene. Extracts were filtered and dried in a vacuum oven at 70°C for a week to evaporate the solvent. Figure 5 displays the FT Raman spectra of the extracts that shows the existence of an aromatic unit at 1620 cm^{-1} and ester peaks at 1473 and 1732 cm^{-1}, which means that a kind of block or grafted copolymer was formed (by reaction 3 or 4). The tensile modulus of the Nylon 6 blend increased almost twice (from 0.8 GPa to 1.5 GPa with the addition of elastomeric phase) with 15% standard deviation. Due to the scattering of the measurement, it is still under investigation. However, in spite of experimental errors, this is a little bit unusual, since the addition of the elastomer phase usually reduces the tensile modulus. Our result is contrary to this fact, and we believe that is because of TLCP fibrillation and good adhesion at the interface due to the compatibilizing effect. More details of the physical properties, chemical identification, and morphologies of the *in situ* composites will be presented in a forthcoming paper.[19]

CONCLUSION

In this study, we propose a new method to produce *in situ* composites at a low shear rate even without drawing of the extrudates when the viscosity of the matrix is lower than that of the TLCP phase. The addition of a functionalized elastomer (SA-*g*-EPDM) can provide toughness to the matrix phase as well as a higher modulus by the TLCP phase deformation.[13] Deformation of the finely dispersed TLCP phase by low viscosity ma-

trix is ascribed to the good adhesion that occurred by the compatibilizing effect of the produced graft copolymer. In principle, these results demonstrate that it is possible to obtain strong and tough Nylon 6 and PBT *in situ* composites with balanced mechanical properties. Many other intriguing features and more details about mechanical properties for these *in situ* composites are under investigation and will be reported in the future.[19]

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