2978 *Macromolecules* **1997,** *30,* 2978−2988

Structure Development during Flow of Ternary Blends of a Polyamide (Nylon 46), a Thermotropic Liquid Crystalline Polymer (Poly(ester amide)), and a Thermoplastic Elastomer (EPDM)

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Received September 10, 1996; Revised Manuscript Received January 23, 1997[⊗]

ABSTRACT: It was shown that a fine fibril structure of a thermotropic liquid crystalline polymer (TLCP)-(poly(ester amide)) can be developed in a shear flow field of a thermoplastic matrix (polyamide, nylon 46) when the viscosity of the latter is lower than that of the former. Addition of a third component, a functionalized elastomer (maleic anhydride grafted ethylene−propylene−diene terpolymer, MA-EPDM) that interacts with the matrix polymer (nylon 46) and the thermotropic liquid crystalline polymer, facilitates the structural development of the TLCP by acting as a compatibilizer at the interface. Maleic anhydride grafted to EPDM reacts with TLCP and nylon 46. Morphological observation determined the significance of compatibilization in immiscible polymer blends. The compatibilizer brings about good adhesion at the interface, reduces the droplet size, and enables finely dispersed liquid crystalline polymer to be deformed in shear flow without strong elongation even though the viscosity of the matrix was much lower than that of the liquid crystalline polymer. Fibrous structural development was observed in the edge area of the extruding strand without elongation and also in the central region with weak elongation. Mechanical properties were significantly improved by good adhesion and fibril generation, which were ascribed to the produced compatibilizer. These results have important implications in that they provide a means to produce strong and tough *in situ* composites when the viscosity of the matrix polymer is lower than that of a dispersed liquid crystalline polymer that is immiscible with the matrix polymer.

Introduction

Thermotropic liquid crystalline polymers (TLCPs) have been 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 and makes these materials useful for a number of specialized applications.[1−3] Upon melting, TLCPs give rise to highly organized liquid phases (mesophases) that tend spontaneously to pack parallel to one another to form highly oriented domains. Under elongational processing conditions, these oriented domains can develop a fibril 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 instead forms when the material is cooled to a solid state. These blends have been called "*in situ*" composites because of their *in situ* shaping during 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.[3−5]

There have been innumerable studies of *in situ* composites and TLCP blends with commercial thermoplastics.[2,4] In order to obtain a self-reinforcing fibril structure, the rheological properties of TLCP blends should be carefully controlled.[1] Not all TLCP blends with commercial thermoplastics can produce *in situ* composites. Fibrils of the TLCP phase are usually formed near the die exit as a result of the extensional forces in the flow direction.[6] For special engineering plastics such as poly(ether−imides), polyarylates, poly(phenylene sulfides), and polyolefins that can retain high viscosities at high processing temperatures (at least higher than the crystal−nematic transition temperature) and hence have high melt strength, the elongation process is readily applicable. On the other hand, for polymers produced by condensation, such as polyamides (nylons) and polyesters, viscosities decrease rapidly with temperature. Their melt viscosities are usually 2 or 3 orders of magnitude lower than those of TLCPs at the processing temperature and shear rate. It is generally accepted that in blends that include a minor phase of lower viscosity, the minor phase becomes elongated and the blend viscosity is reduced.[7,8] It is also accepted that in a capillary rheometer, the minor phase of lower viscosity becomes elongated into fibrils, provided there is a sufficient quantity of the minority phase (for TLCP, greater than 10%) and there are extensional flows involved—such as high rates of flow through the entrance to the capillary rheometer or drawing after die exit.[9] Taylor[10] and others[11−13] studied two phase systems of Newtonian fluids and found that the viscosity ratio, interfacial tension, and applied shear stress were crucial to the resultant drop morphology. A number of workers have applied these ideas, including that of the importance of drop viscosity to matrix viscosity ratio (viscosity ratio) and elasticity ratio, to polymer blend systems.[9,14,15] However, the case in which the viscosity of TLCP is higher than that of the matrix has not yet been fully investigated.

All previous findings agree that some form of elongational deformation, as well as a higher viscosity of the matrix polymer than that of the TLCP phase, is necessary for the deformation of the TLCP phase.[12,13,16] Therefore, it is easily predicted that fine dispersion and

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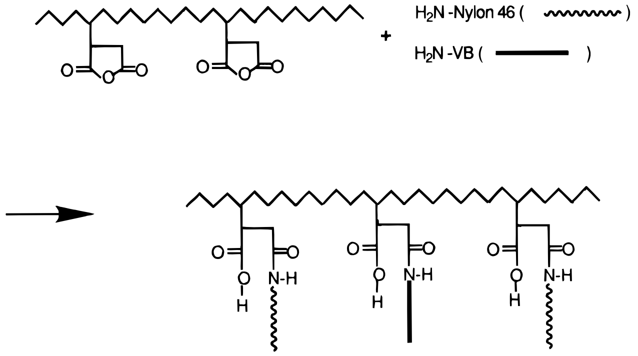
[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

S0024-9297(96)01343-5 CCC: $14.00

Scheme 1. Reaction between MA-EPDM and Nylon 46 or VB



fibril formation of TLCP will be very difficult in polyamides, one of the most widely used engineering plastics, because of their immiscibility with TLCPs and their low viscosities at the processing temperature and shear rate. Most previous experimental results support this prediction. The lack of miscibility between TLCPs and polyamides leads to poor dispersion and thereby degrades some mechanical properties of these blends.[2,4,17−19] In preliminary investigations of blends of the polyamide (nylon 6) and a TLCP (poly(ester amide)), no fibrils were formed in the shear flow.[17−19] The moduli were lower than those predicted by the theory for short-fiber oriented composites because of poor adhesion between the matrix and dispersed phase and incomplete fibrillation of the TLCP particles. Micrographs of the binary blends show that the TLCP is present in a droplet structure and little droplet deformation into elongated shapes could be observed, even with the high draw ratio of 100.[17] In another study, deformation of TLCP droplets (polyester, Vectra A 950) in nylon 6 could barely be observed when the shear rate was very high (2700 s^{-1}), where the viscosity of TLCP approaches that of nylon 6 (the ratio was about 4).[19]

For polyesters, compatibility can be provided by reactive compatabilization with PET-based TLCPs.[20,21] However, most thermoplastics studied thus far are incompatible with TLCPs.[22] The reinforcing effect is less than that obtained from the miscible system. It has been claimed that compatibility between the TLCP and the matrix may be detrimental to fibril formation, so that the reinforcing effect may be lost.[23−25] The reason is that if polymers are too compatible, then the TLCP will form very small drops that are too small to be deformed into fibrils. On the other hand, just as in the case of blends of two flexible chain polymers, the complete lack of compatibility could lead to the deterioration of properties such as impact strength for the TLCP/thermoplastic blends, sometimes even if microfibrils are formed. This is more serious in the transverse direction. Provided compatibilization is optimized so as not to reduce the droplet size below the critical value for deformation, a compatibilized system can improve some properties of immiscible TLCP/thermoplastics blends.[26] One way to provide such compatibility in immiscible binary blends is to add a compatibilizer.[27] Ternary blends represent 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. Acting as polymeric surfactants, they reduce the interfacial tension, thus promoting interfacial adhesion and a finer and more uniform dispersion. Very recently, compatibilization of thermoplastic blends with TLCPs has been attempted.[4,22,26]

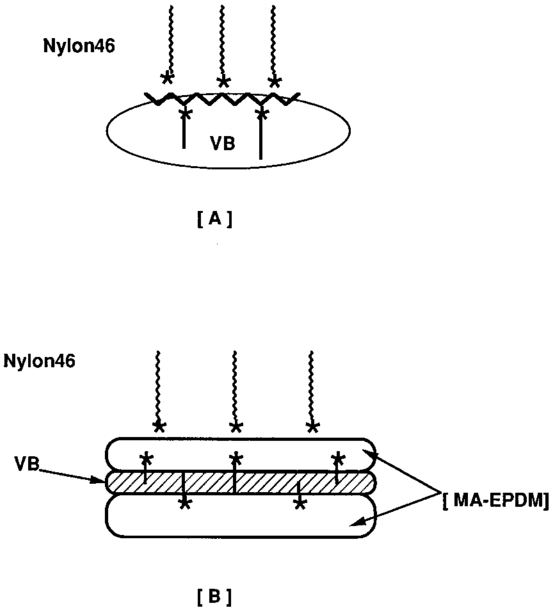


Figure 1. (A) Ideal configuration of a graft block copolymer at the interface between the nylon 46 phase and the VB phase. (B) Formation of the separate elastomer phase. The VB phase is surrounded by the elastomer phase. Asterisks mean the amide group formed by the chemical reaction in Scheme 1.

Our goal is to gain an understanding of the structure development of the TLCP phase in the ternary blends of nylon 46, TLCP, and a maleic anhydride grafted elastomer based on the molecular characteristics of the macromolecules and their processing conditions, especially when the matrix viscosity is lower than that of TLCP's. The method we used is based on the reactive extrusion. If the TLCP has an end group that can react with maleic anhydride grafted to EPDM, it will also form a compatibilizer that can work at the interface of the elastomer and TLCP phase (Scheme 1).[28,29] The product can act as a polymeric surfactant, thereby reducing the interfacial adhesion, inducing a finer and more uniform distribution of the dispersed phase. Depending on the amount of the elastomer, they can form either their own separate phases or an interphase between TLCP and the matrix polymer (Figure 1).

Experimental Section

Materials. The chosen TLCP was an all aromatic liquid crystalline poly(ester amide), Vectra B950 (VB) (a copolymer based on 6-hydroxy-2 naphthoic acid (60%), terephthalic acid (20%), and aminophenol (20%)) produced by Hoechst Celanese Co. Because of the high nematic transition temperature of VB (285 °C), nylon 46 (C2000NS, Teijin Co., Japan) whose melting temperature is 292 °C, was used as a matrix polymer. Maleic anhydride grafted EPDM (ethylene−propylene−diene terpolymer, MA-EPDM) was purchased from Uniroyal Chemical Co. (Royaltuf 465). Its maleic anhydride/acid content is reported as less than 1.5 wt %.

Instruments. Blending and Extrusion. The pellets of the nylon 46 and Vectra B were dried in a vacuum oven at 120 °C for at least 24 h before use. EPDM was dried in a vacuum oven at 60 °C for 72 h. The TLCP content was kept at about 25 wt %, at which level the composite showed a maximum fibril aspect ratio.[30] Dried pellets of VB, nylons, and MA-EPDM were mixed in a container before blending in the extruder. Blending was carried out in a 42 mm Brabender twin screw extruder (AEV651) at a fixed rotation speed of 20 rpm. It was equipped with a pulling unit imparting different draw ratio (DR), defined as the diameter at die exit to far down stream. A high draw ratio was not applicable because of the instability of nylon extrudates. Many strands of low DR (less than 8) were obtained. The extrusion temperatures of the feeding zone/transporting zone/melting zone/die were set as 140/300/300/295 °C, respectively.

FT IR Spectrum and FT Raman Spectrum. The FT IR spectrum was obtained using an Alpha Centauri Spectrometer (Mathson Instruments) with an average of 32 scans at 4 cm^{-1} resolution. FT Raman spectra were obtained using a Perkin-Elmer System 2000 instrument equipped with near-IR optics. Spectra were obtained with 4 cm^{-1} resolution, and typically required 10−15 min of acquisition time.

Thermal Properties. Differential scanning calorimetry (DSC) studies of the thermal property characteristics were performed on a Du Pont 910 DSC controlled by a 9900 thermal analyzer. Every thermogram was repeated at least twice to verify the reproducibility of the measurements. A Du Pont 2000 thermal gravimetric analyzer was also used to observe the degradation of samples. The heating rate was 10 °C/min and samples were heated up to 800 °C. Dynamic mechanical thermal analysis (DMTA) of the blends was carried out with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model 2) at a frequency of 1 Hz. A single cantilever clamping geometry in the bending mode was used.

Scanning Electron Microscopy and Optical Microscope. Scanning electron microscopy (SEM) observations of the composite samples were performed on a Hitachi S-2200C model. Fractured surfaces of the blends were prepared by cryogenic fracture in liquid nitrogen followed by coating with gold in an SPI sputter coater. The morphology was determined using an accelerating voltage of 15 keV. An optical microscope (Reichert-Jung Micro-star) equipped with a hot plate (Mettler FP82) was used to observe the liquid crystalline state.

Rheometry. Rheological properties of the blends and pure resins were measured using a Rheometrics Dynamic Spectrometer (RDS 7700, Rheometrics) on which a 25 or 50 mm diameter parallel plate was mounted. The frequency range was set at 0.1−500 rad/s and applied strain was 10%. The plate gap was set as 1.2 mm. Before the measurement, the samples were prepared using a compression molder. Measurement was done under a nitrogen atmosphere. Rheological measurement was also carried out using a capillary viscometer RH7(Rosand, England) at 300 °C. The capillary was 1 mm in diameter and had a length-diameter ratio of 32.

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

Results and Discussion

Thermal and Rheological Properties. Before the analysis of the ternary blends, binary blends of nylon 46 and VB were studied. The glass transition temperature, T_g, was evaluated by DSC and related to the DMTA point where tan δ had a maximum. The T_g of nylon 46 is 78 °C and that of VB is 145 °C. The maximum of tan δ from DMTA is shown in Figure 2. The lack of change of T_g indicates that they are immiscible with each other. The heat of fusion of different blends (Figure 3) decreases with TLCP content. This finding is ascribed to the low crystallization heat of TLCP at the nematic transition temperature. Crystallization exotherms of the blends at the cooling rate of 10 °C/min after melting at 330 °C are shown in Figure 4. The crystallization temperature of nylon 46 at 263 °C did not change with amount of TLCP indicating that VB does not act as the nucleating agent for nylon 46.[31,32] The maximum of tan δ of ternary blends, including 2%of MA-EPDM, is shown in Figure 5. The T_g values of nylon 46 and VB shifted toward each other. The positions corresponding to the glass transition temperature are slightly different for the DSC and DMTA results, because of the difference in heating rates used in the DSC (10 °C min^{-1}) and DMTA (2 °C min^{-1}) experiments.[33] The shift in T_g indicates that nylon 46 and VB become partially miscible in the ternary blend.[27] Depending on the amount of MA-EPDM, the elastomer forms its own separate phase and/or concentrates at the interface between nylon 46 and TLCP.

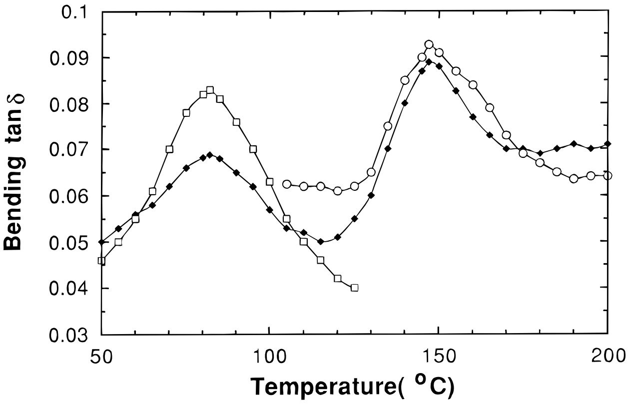


Figure 2. Normalized tan δ vs temperature for binary blend (nylon 46: VB = 75:25): (□) nylon 46, (○) Vectra B950; (◆) binary blend.

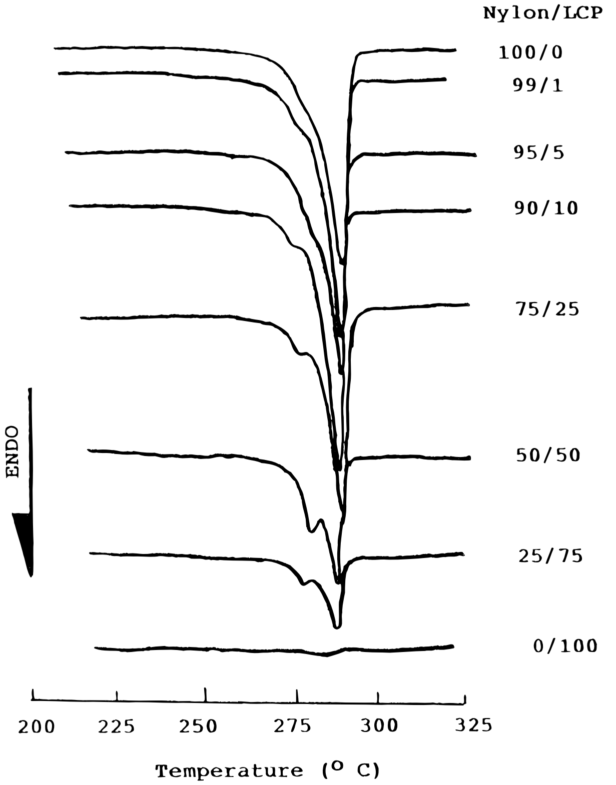


Figure 3. DSC thermograms of nylon 46/VB binary blend.

TGA thermograms of the binary and ternary blends are shown in Figure 6. Little thermal degradation results from the addition of the elastomer into the binary blend. This finding is ascribed to the compensation effect of TLCP and the elastomer. The low thermal properties of the elastomer seem to be supplemented by the higher thermal properties of TLCP.

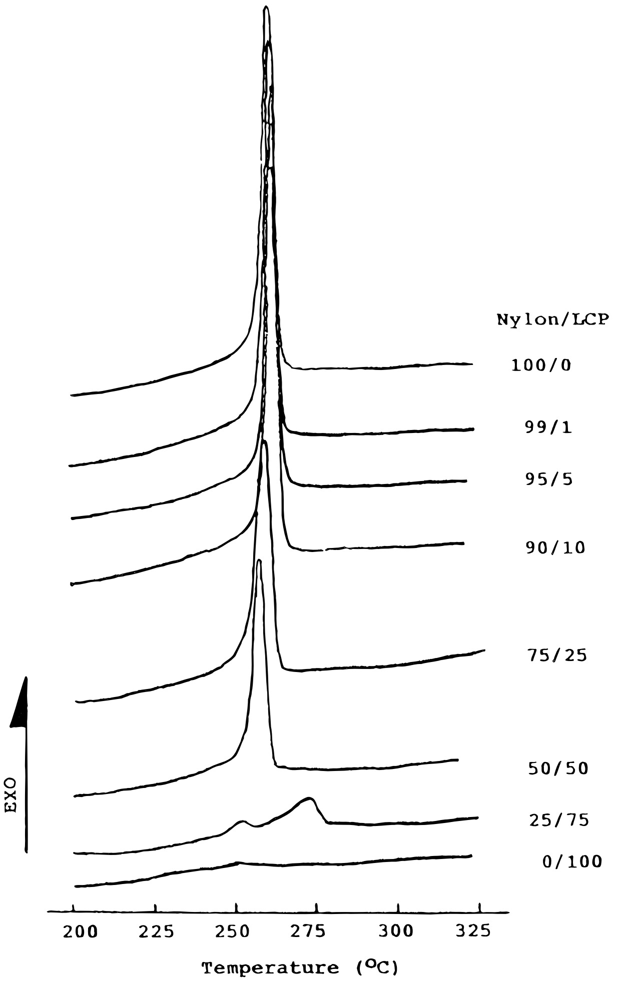


Figure 4. Crystallization exotherms of nylon 46/VB binary blend.

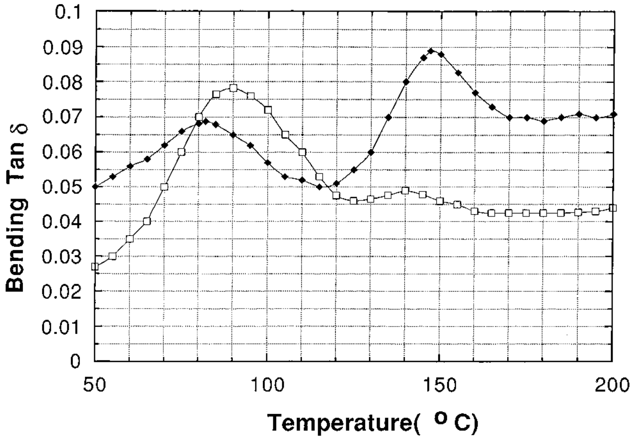


Figure 5. Normalized tan δ vs temperature for ternary blend (nylon 46:VB:MA-EPDM = 73:25:2): (◆) binary blend; (□) ternary blend.

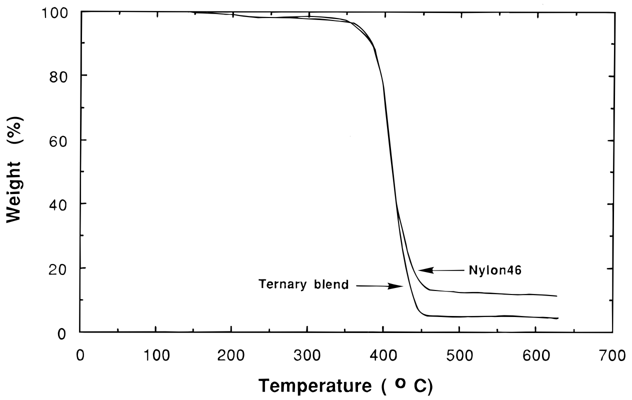


Figure 6. TGA thermograms of nylon 46 and ternary blend (nylon 46:VB:MA-EPOM = 60:25:15).

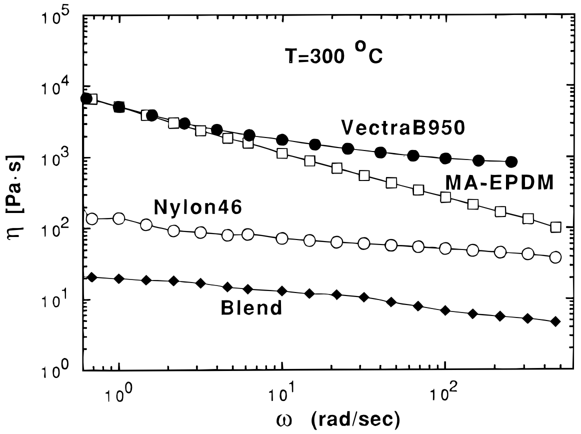


Figure 7. Dynamic viscosity vs frequency at 300 °C

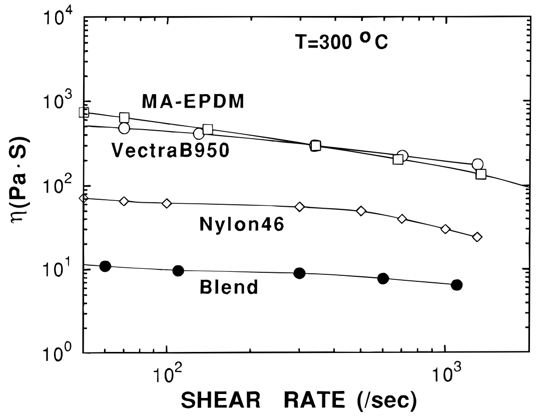


Figure 8. Viscosity−shear rate relationship of nylon 46, VB, MA-EPDM, and the blend (nylon 46:VB:MA-EPDM = 60:25:15) at 300 °C.

The flow curves of the pure components and ternary blend are presented in Figure 7. A general feature related to frequency response is the Cox−Merz rule, whereby the curve of the complex viscosity as a function of frequency should coincide with that of the steady-state viscosity vs shear rate. The Cox−Merz rule, invariably obeyed by ordinary polymeric liquids, does not generally hold true in TLCPs,[34] as demonstrated by Denn et al.[35] while Wissbrun and Griffin[36] found different behavior. Consideration of the long relaxation time of TLCP reveals that it does not work with TLCPs. Hence the complex viscosity of the blend vs the frequency is different from steady-state viscosity vs shear rate. It can be conjectured that the complex viscosity value will be higher than that of the steady-state viscosity since the TLCP phase in the oscillatory mode will be in a partially relaxed state, which makes the system similar to the heterogeneous filled system. This held true for this system as shown in Figures 7 and 8.

In complex viscosity, MA-EPDM shows the typical elastomer's non-Newtonian flow behavior. Nylon 46 is in the Newtonian plateau region. The viscosity of the ternary blend is much lower than that of neat polymers at 300 °C, indicating a synergistic effect on reducing the viscosity of the TLCP composite and great processing ability on the part of the ternary blend. A previous study of the VB composite with nylon 6 indicated that rheological behavior of nylon 6/VB showed a deep minimum at 290 °C at a concentration range of 5−20% of the liquid crystalline component (VB).[9] The reduced viscosity of blends with TLCP has been attributed to the interlayer slip of the phases for two different reasons: (a) incompatibility between the two phases and (b) formation of elongated fibrils of the TLCP phase, which tend to lubricate the melt. Both are reasonable explanations, judging from the fact that elongated structures and spherical structures were observed in SEM microphotographs as shown later. Though it is more effective in the case of fibrils that arise usually because of elongational flow than for spherical particles often seen in blends undergoing simple shear flow, the fibrillation of TLCP in the nylon 46 matrix is a little unusual on account of the very low viscosity of the nylon 46 matrix, which cannot deform the spherical droplets of the dispersed TLCP phase by itself in shear flow. La Mantia et al.[9] reported that they could not observe any elongated structure of the TLCP (VB) phase in a nylon 6 matrix having a viscosity similar to that of nylon 46 at high shear rate of 1200 s^{-1}. However, the viscosity of the blend was lower than that of the polymer matrix (nylon 6), quite similar to the finding for the present case.[9,18]

The flow curves obtained from the capillary rheometer are shown in Figure 8. The MA-EPDM and TLCP curves show non-Newtonian behavior while the elastomer curve exhibits more shear thinning behavior. As mentioned, the Cox−Merz rule does not hold for the VB case. However, the viscosity values of the blend are close to complex viscosity. The viscosity of VB is in agreement with those obtained by LaMantia et al.[37] and is higher than that of nylon 46. Regarding the processing shear rate (apparent shear rate was about 40 s^{-1}), VB had an almost 1 order of magnitude higher viscosity than that of nylon 46. The viscosity of the blend in the investigated shear rate range was again lower than those of the neat polymers. Thus the role of TLCP as a processing aid is vividly seen. Even though the viscosity of the elastomer was slightly higher than or close to that of the VB's, the lower viscosity of the blend than that of neat polymers implies that the effect is less than the viscosity reduction resulting from the fibrous structural deformation.

Morphologies of the Blends. In an effort to provide more support for the compatibility of the ternary blend, the morphologies of binary (nylon 46/VB) and ternary (nylon 46/VB/MA-EPDM) blends were investigated. SEM micrographs of the fractured surfaces of binary blends are shown in Figure 9. These micrographs show two main TLCP features: the continuous phase is the nylon 46 until 50% of the TLCP phase and the TLCP particles are pulled from the matrix, showing poor adhesion between the two phases due to incompatibility. When the TLCP content is between 25 and 50%, void formation due to phase separation, a spherical dispersed phase, and poor adhesion between TLCP and the matrix are observed. The mechanical properties of the binary blends deteriorate as a result of this morphology, as shown later.

Studying the binary blend of nylon 6 and VB, La Mantia et al.[18] observed only spherical droplets from the fractured surface of fibers extruded through capillary rheometer. Even with the very high draw ratio of 100, few fibrils could be seen. Using the same VB in nylon 6, Berry et al.[19] reported the observation of some fibril shapes at a very high shear rate of 5400 s^{-1}, where the viscosity ratio of VB to nylon 6 is about 4. They observed the fractured surfaces of the free-falling strands from the capillary rheometer, but they did not consider the elongational effect due to gravity force. Neglect of the elongational effect raises a question about the validity of their conclusions.

SEM micrographs of binary (nylon 46/VB, 75:25) and ternary (nylon 46/VB/MA-EPDM, 60:25:15) blends are displayed in Figure 10. In the binary blend of nylon 46/VB (Figure 10a), the TLCP domains are relatively large because of immiscibility, thereby leading to poor dispersion. The ternary blend surface (Figure 10b) shows a different morphology. Droplet size is noticeably reduced. Some droplets are deformed into fibrous shapes in the edge region, where the shear rate is higher than in the core region. It should be emphasized again that no drawing was done (draw ratio was 1) and the shear rate was at a low level (about 40 s^{-1}), where the viscosity of nylon 46 is much lower than that of VB. The fibers in Figure 10b have a large aspect ratio. In Figure 11 we observe the enlarged fractured surfaces in the ternary blends. Finer dispersion and better adhesion clearly demonstrate the compatibilizing effect of MA-EPDM. The compatibilizer yields not only a reduction of the interfacial tension but also better adhesion, which invokes effective stress transfer at the interface. The final shape of the dispersed phase is a dynamic equilibrium between the shear stress and the compatibilizing action. Needless to say, the thermoplastics of high viscosity possess sufficient melt strength to withstand strong flow (elongational flow) that easily deforms small droplets; this is not possible with weak flow (shear flow). As verified experimentally by La Mantia et al.[17] for a nylon 6 blend with VB, the nylon 6 matrix does not easily deform the TLCP droplets in spite of a high elongational deformation (draw ratio of 100). Therefore, efficient stress transfer by the improved adhesion at the interface is the only practical way to achieve the deformation of TLCP droplets in the nylon matrix, even without high elongation. Depending on the compatibilizing action at the interface, relatively small droplets can also be deformed (Figure 11).

If wall slip does not exist at the die exit, the elongation process on the strand edge (die exit region) can be also considered. A change in axial direction velocity from 0 to some average value requires extension on the surface region, along with compression at the center region.[38] However, it can also be speculated that rapid cooling after die exit (water cooling) raises the modulus and viscosity of the TLCP phase more rapidly, so that deformation of the TLCP phase becomes more difficult in spite of elongational flow at the edge side. From the microphotographs of the binary blend (Figure 10a), we see that the elongation effect at the edge of the die (extrudate surface) is not strong enough to deform the TLCP droplets. Molecular orientation for fibers occurs mainly in the die. After die exit, the rapid cooling process prevents the deformation of TLCP domains.

The effect of draw ratio in the limited elongation is shown in Figure 12. As expected, more fibrillation takes place at a high draw ratio. At a draw ratio of 1, most TLCP phase remains spherical in the center region. At a draw ratio of 4, some TLCP fibrils can be seen even in the center region. The presence of spherical particles in the central region indicates that the drawing was not strong enough to deform the droplets, whose adhesion at the interface was not very strong.

Mechanical Properties. The morphological difference between the blends with and without MA-EPDM definitely affect their respective physical properties. The

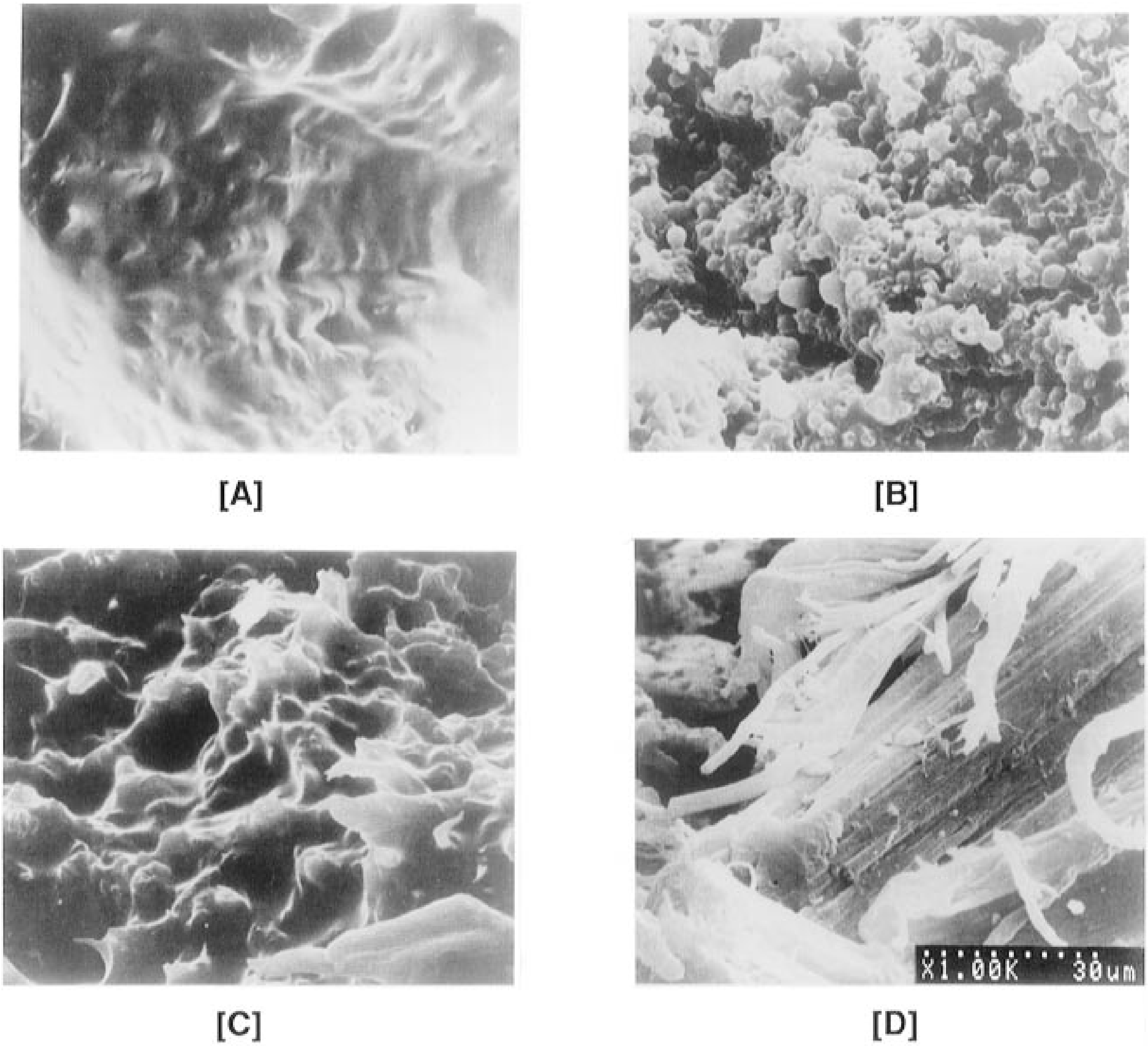


Figure 9. SEM photographs of fractured surfaces of nylon 46/VB binary blends at the draw ratio of 4: (a) 90/10; (b) 75/25; (c) 50/50; (d) 25/75.

tensile strength and tensile modulus of the binary blends vs TLCP content are shown in Figures 13 and 14. We observe a negative deviation from the rule of mixture, which is the typical sign of an immiscible system. The tensile strength of the nylon-rich phase decreases with TLCP content because of the loss of ductility and failure at the interface, whereas the tensile modulus of the TLCP-rich phase increases because of the molecular orientation and the high modulus of TLCP phase. Tensile properties increase rapidly when the TLCP content reaches 50%, where phase inversion occurs. The effect of draw ratio in this range is not so manifest because fibrillation of the TLCP phase hardly occurs and failure occurs in the matrix or at the weak interface.

The tensile strength and modulus of the ternary blend are presented in Figures 15 and 16. Contrary to the binary blend case, the addition of MA-EPDM increases the tensile properties with the draw ratio. This result is ascribed to the fibrillation of the TLCP phase and better adhesion with finer dispersion. After a monotonic increase with the draw ratio, this blend reaches a plateau in strength and modulus. The binary blend does not show much improvement in tensile strength with the draw ratio, whereas the ternary blend clearly shows the effect of the draw ratio. The tensile modulus for the ternary blend also shows a pronounced variation with a draw ratio, a natural effect of fibrillation. The tensile modulus and strength of the ternary blend increased to more than twice that of the binary blend with draw ratios of 4 and 6. The effect of the amount of elastomer on the tensile properties is seen in Figure 17. The relatively small variation with MA-EPDM content means that there is not much difference within the varied content because of the matrix failure mode variation (ductile−brittle) with the TLCP addition.

The elongation at break was slightly affected by the addition of MA-EPDM but no noticeable change was induced as shown in Figure 18. The addition of 15 wt % MA-EPDM did not alter the brittleness of the binary blend system. The addition of brittle TLCP to ductile nylon promoted the propagation of fracture before the matrix reached its break point. Hence the small elongation of the blend compared with that of neat nylon 46 indicates that the specimen was acting as a two- (or three-) phase structure that could separate and fail prematurely instead of acting as an integral specimen.

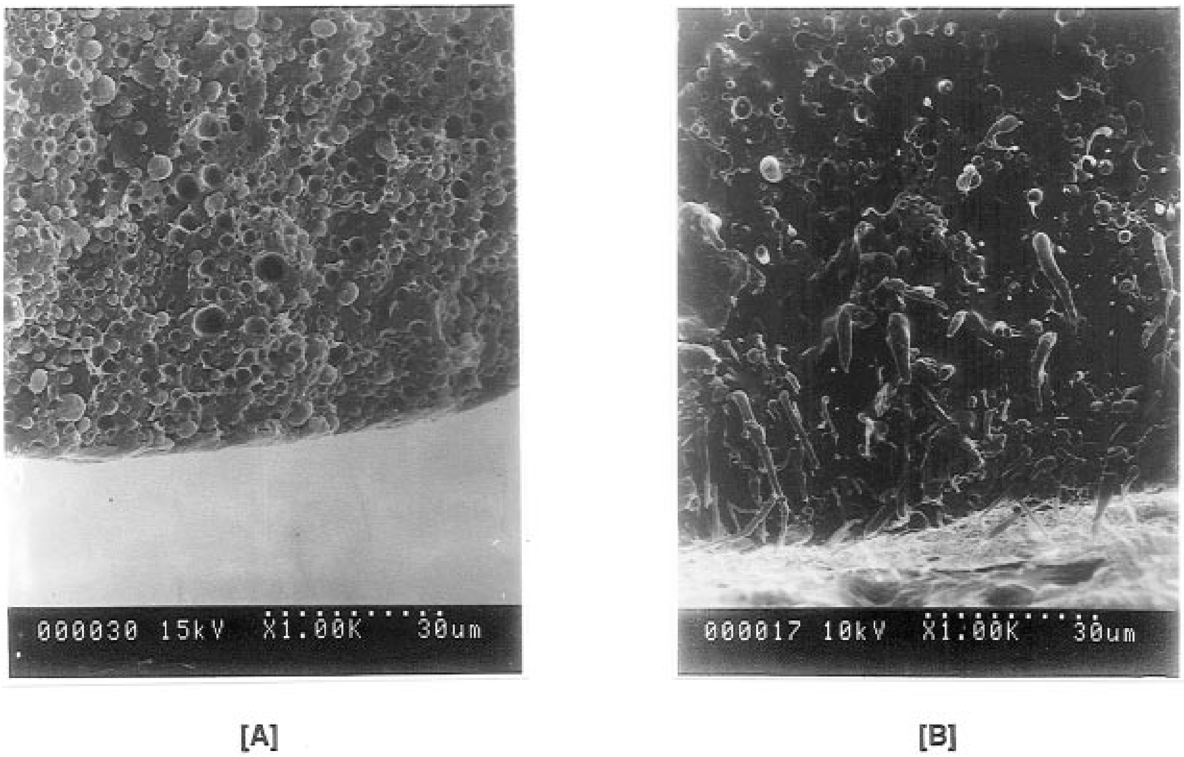


Figure 10. SEM photographs of fractured surfaces of (a) nylon 46/VB binary (75:25) and (b) ternary blends (nylon 46:VB:MA-EPDM = 60:25:15) at the draw ratio of 1.

Figure 11. SEM photographs showing adhesion between TLCP and the matrix.

Elongation of the blends decreased with the addition of the elastomer.

Most noncompatibilized *in situ* composites showed good mechanical properties in the flow direction because of fibril formation of the TLCP phase but had poor properties in the transverse direction. Since only the fiber was prepared, the mechanical properties in the transverse direction could not be measured. Instead, we checked the impact strength according to ASTM D256. The specimens were prepared by compression molding at 310 °C. It was anticipated that this high temperature might destroy the TLCP structure, but some information on the interfacial property could be obtained. The impact strength on a normalized scale for the specimen of the ternary blend is shown in Figure 19. Though a small amount of MA-EPDM did not show pronounced improvement in impact strength, a toughening effect was evident with the addition of more elastomer phase.[39] The addition of 15 wt % elastomer increased the impact strength to more than 3 times that of the binary blend. Improved impact strength means improved interfacial adhesion between the elastomer phase and the matrix. Simultaneous incorporation of hard (VB) and soft (MA-EPDM) materials both interacting with each other into nylon 46 improves not only the tensile properties but also the impact strength. In other words, we can effectively prepare a nylon composite whose components can interact with each other to improve the dispersion state, interfacial adhesion, and morphology and hence tensile properties and impact strength as well.

Interfacial Reaction. The enhancement of mechanical properties by the addition of MA-EPDM can be ascribed to two possible mechanisms: the occurrence of a reaction, or an interaction such as hydrogen bonding. Recently O'Donnel and Baird[40] investigated the possibility of these two mechanisms for ternary blends of polypropylene/maleic anhydride grafted polypropylene/TLCPs (Vectra A 950, Vectra B950, LC 3000). On the basis of their IR analysis, they concluded that hydrogen bonding between maleic anhydride and TLCP is the mechanism leading to the compatibilization. They conducted comparison testing only for the ternary blend of PP/MA-PP/Vectra A with the binary blend of PP/PP-MA by quantifying the maleic anhydride content obtained from the absorption peak at 1784 cm^{-1}. However, their results are somewhat uncertain because of experimental errors. For better analysis, the maleic anhydride content of the binary blend of VB and MA-EPDM should be compared with that of MA-EPDM. We prepared a binary blend of VB and MA-EPDM (50:50

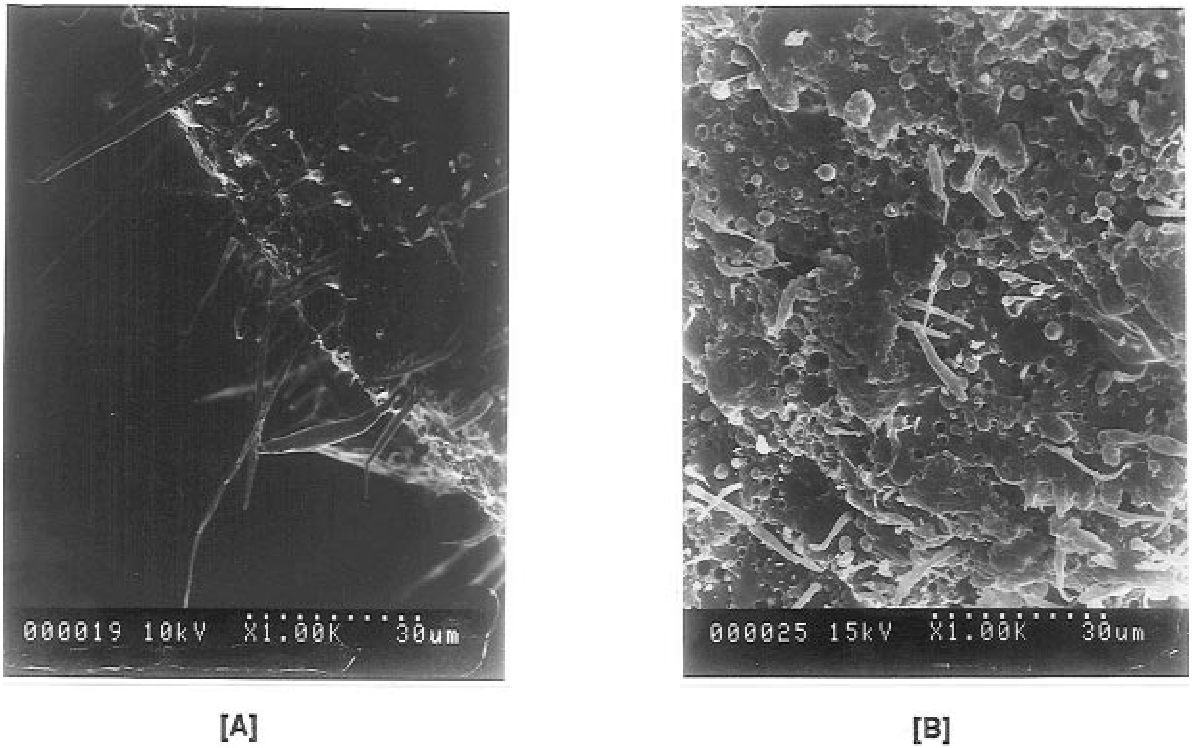


Figure 12. SEM photographs of fractured surfaces of nylon 46/VB/MA-EPDM ternary blends (nylon 46:VB:MA-EPDM = 60:25:15) at the draw ratio of 4: (a) edge surface, where the surface was rotated for a better view; (b) core region.

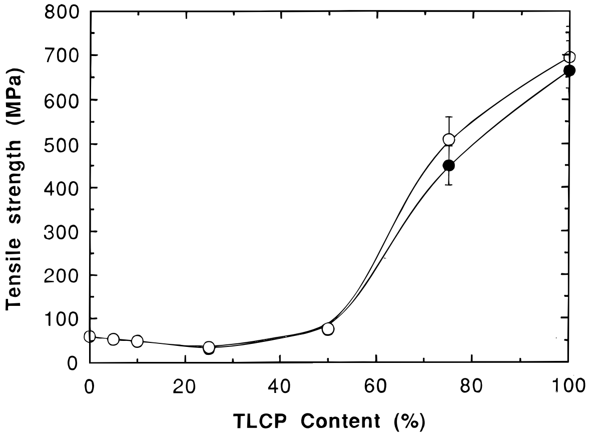


Figure 13. Tensile strength vs TLCP content for nylon 46/VB binary blend fibers: (●) draw ratio = 4; (○) draw ratio = 6.

ratio) under the same processing conditions. Then, using a Soxhlet extractor with boiling xylene, we extracted the soluble part (elastomer phase). After 2 days of extraction, the extracted solution was poured into the ethanol. The precipitate was dried in a vacuum oven at 60 °C for 2 weeks to remove any solvent residue. An FT Raman spectrum was taken for the remnants. The Raman spectra of MA-EPDM, VB, and the extracts are shown in Figure 20. Characteristic aromatic and ester peaks which can not be seen in the MA-EPDM spectrum are observable at 1400, 1620, and 1742 cm^{-1}. This means that the VB moiety is included in the extracts. Since VB is not soluble in xylene, we speculate that some reaction occurred to create graft copolymers. Recently we proposed that certain reactions occur between the maleic anhydride group and the end groups of nylon 6 or VB.[29] It is well-known that a maleic anhydride grafted elastomer can react with the amine ends of nylons.[28] Hydroxyl end groups can also react with the maleic anhydride to produce graft copolymers.

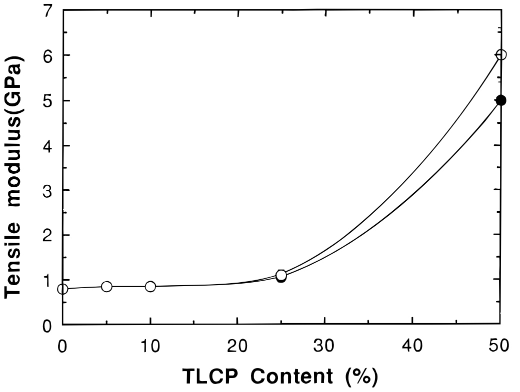


Figure 14. Tensile modulus vs TLCP content for nylon 46/VB binary blend fibers: (●) draw ratio = 4; (○) draw ratio = 6.

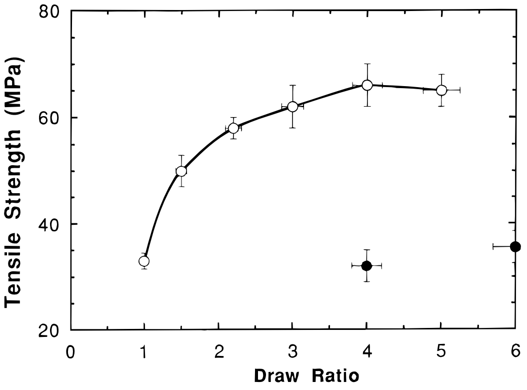


Figure 15. Tensile strength vs draw ratio (DR) for nylon 46/VB/MA-EPDM (60:25:15) ternary blend fibers. Filled symbols are for binary blends.

How much amine end group remains in VB is not detectable from IR analysis because of the overlapping of the amine peak with the hydroxyl peak, but the existence of the hydroxyl group can be clearly seen at

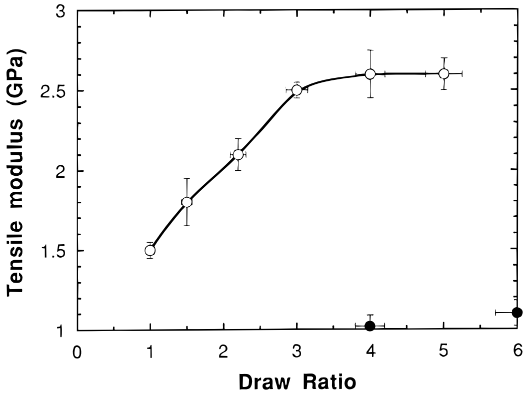


Figure 16. Tensile modulus vs draw ratio (DR) for nylon 46/VB/MA-EPDM (60:25:15) ternary blend fibers. Filled symbols are for binary blends.

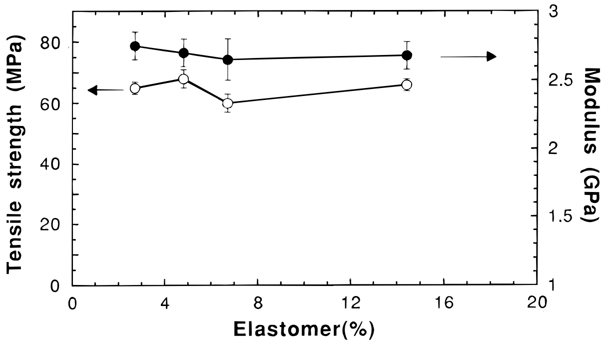


Figure 17. Tensile strength and tensile modulus of nylon 46/VB/MA-EPDM ternary blend fibers vs MA-EPDM content. The draw ratio was 4. The VB content was fixed as 25%.

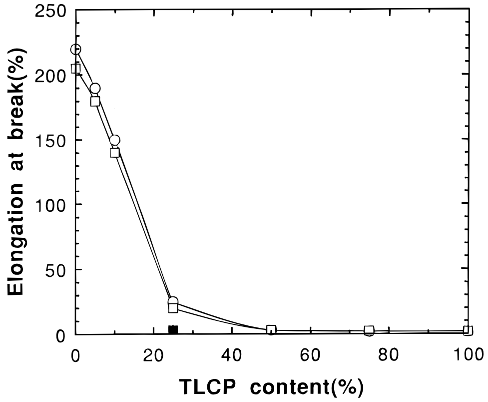


Figure 18. Elongation at break for binary and ternary blends. Open symbols are for binary blends (○, draw ratio 4; (□, draw ratio 6) and filled symbols are for ternary blends (■, draw ratio 4; ◆ = draw ratio 5).

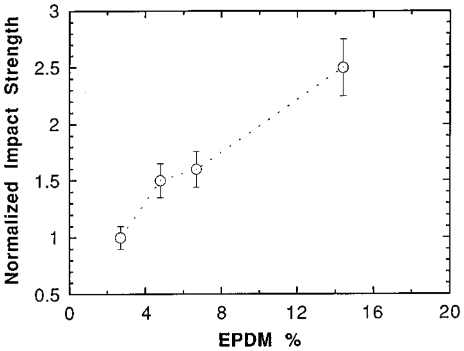


Figure 19. Impact strength vs elastomer content for nylon 46/VB/MA-EPDM ternary blend fibers. It was normalized to that of the binary blend. The VB content was fixed as 25%. The dotted line is the guide for eyes.

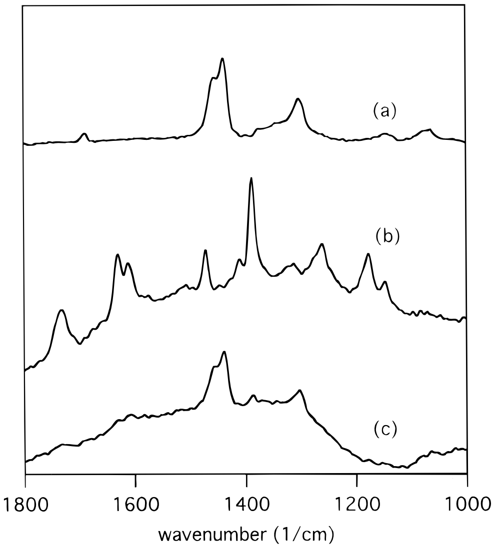


Figure 20. FT Raman spectra of (a) MA-EPDM, (b) VB, and (c) the extracts.

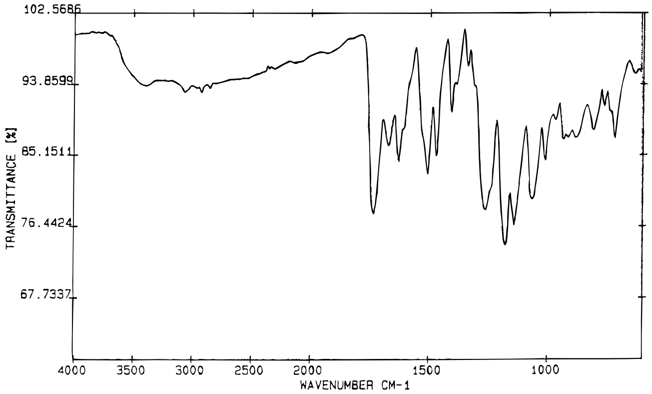


Figure 21. FT IR spectrum of VB virgin resin.

3300 cm^{-1} (Figure 21). Also, the ester moiety in VB can give a reaction such as acidolysis with the maleic anhydride group. Though this reaction usually requires catalysts for speed, remnant catalysis in VB can promote it. If the compatibilizing action occurrs solely because of hydrogen bonding, the binary blend of nylon 46 and VB, both of which have strong hydrogen bonding, should be compatible. As already seen in the properties and morphologies of binary blends, they are not compatible. Little interaction can be observed between VB and nylon 46. It is also conceivable that hydrogen bonding can take part in the compatibilizing interaction, but we believe that some reactions between MA-EPDM and VB occur and that the products act as a compatibilizer. The amine end group of VB and nylon 46 competitively react with the anhydride group of EPDM (Scheme 1) to form a kind of (comb shape) block copolymer having different branches which will act as the compatibilizer at the interface (Figure 1). Though we do not have quantitative data for the chemical reaction occurring in the ternary blend, it proceeds very well. Grafted TLCP can form its own domain. This can be seen from the polarized micrographs of binary blend extracts from the Soxhlet apparatus. Since the elastomer phase is opaque, it was sheared between the micro slide glasses to make it thin and transparent. The existence of TLCP's own domain is evident in Figure 22. The existence of the TLCP domain can also be checked by a DSC thermogram. Figure 23 shows a thermogram of the extracts.

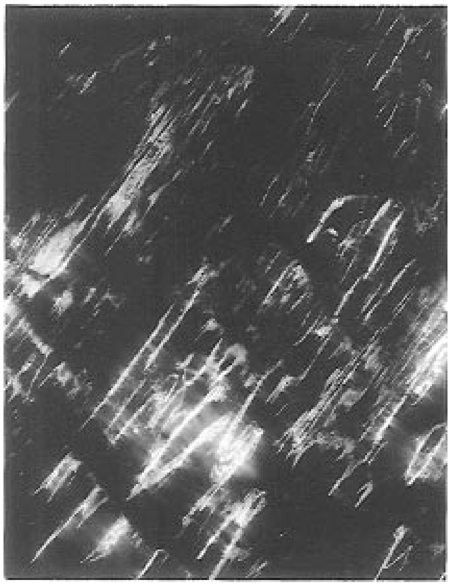


Figure 22. Crossed polarization photomicrgraphs of the extract from MA-EPDM/VB binary blend.

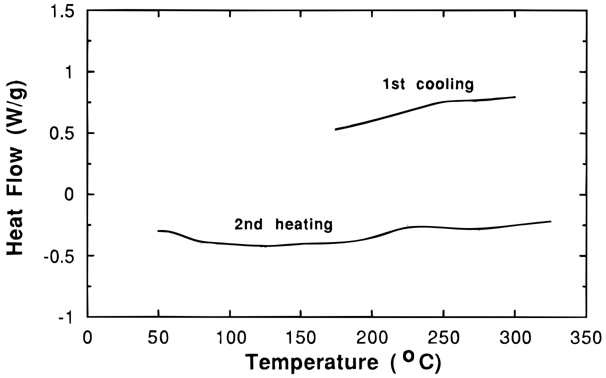


Figure 23. DSC thermograms of extracts from MA-EPDM/VB binary blend.

A broad endotherm around 280 °C exists, which is close to the nematic transition temperature of VB. Upon cooling, a small crystallization exotherm appears at around 247 °C, which is close to the crystallization temperature of VB. From all these experimental results, we believe a chemical reaction between VB and MA-EPDM happens to form graft copolymers. More detailed research should be conducted to verify the chemical structure. This will be reported in the future.

Summary

The addition of MA-EPDM to a nylon 46/VB blend induces enhanced adhesion, finer dispersion of the TLCP phase, and, hence, reduced interfacial tension, which are characteristics of compatibilized blends. The addition of MA-EPDM to the nylon 46 and VB leads to significant mechanical property improvements over the binary blend owing to better adhesion and fibrillation of VB in nylon 46, which has a much lower viscosity than VB. Using the functionalized elastomer (MA-EPDM), impact strength as well as tensile properties were improved. However, the addition of 15 wt % elastomer does not change the brittle nature of the binary blend. Thus, tensile elongation was reduced. Drawing the extrudates (application of elongation) easily deforms more TLCP droplets into the fibril structure, even at low draw ratio, and hence leads to more improved mechanical properties. A monotonous increase in mechanical properties with limited draw ratio was observed, but they soon reached a plateau value.

The significance of this study is that the addition of MA-EPDM not only reduced the size of TLCP phase but also caused the fibrous structure to be formed without elongation that induces the reinforcement of the matrix. The possibility of fibril structure formation without elongation in the nylon matrix was experimentally verified in this study and can be applied to other thermoplastics whose matrix viscosity is lower than that of the dispersed phase or whose melt strength is relatively weak for applying the post-drawing process.

On the basis of the mechanical properties, morphological observations, and FT Raman spectrum, it is believed that some chemical reactions occur between MA-EPDM and VB. Noncompatibility between nylon 46 and VB supports the idea that hydrogen bonding is not the sole cause of the compatibilization. Further studies addressing the chemical reaction between MA-EPDM and VB and the effect of maleic anhydride grafted amount are underway. They will be reported in the future.

Acknowledgment. This work was supported by the Korea Institute of Science and Technology (KIST) under Grant No. 2E14183. Special thanks go to Jun Yup Lee and Myung Kyu Han for their help with experiments.

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MA961343D