

## Effect of the Processing History on the Morphology and Properties of the Ternary Blends of Nylon 6, a Thermotropic Liquid Crystalline Polymer, and a Functionalized Polypropylene

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**Abstract :** Properties of ternary blends of nylon 6 (Ny6), a thermotropic liquid crystalline polymer (TLCP, poly(ester amide), 20 wt%) and a maleic anhydride grafted polypropylene (2 wt%) (MAPP) were studied under various processing conditions. TLCP was pre-blended with MAPP first and then the binary one blended again with Ny6. The processing temperature of the second mixing was varied. Thermal properties show the partial miscibility of the ternary blend. The morphology of the TLCP phase in the first blending shows mostly in the fibril bundle shape, but varies between droplets and oriented fibrils after the second processing. Some of TLCP phase lost the fibril morphology during the second processing stage. The morphology variation invokes the change in tensile properties. Low extrusion temperature (270°C) provides more fibril shapes, which are associated with less deformation in the second stage. The processing temperature effect was more evident when the draw ratio was high. High drawing was applicable due to the stabilizing action of the compatibilizer

### Introduction

The use of thermotropic liquid crystalline polymers (TLCPs) in blends with other thermoplastics is quite attractive for many reasons.<sup>1-14</sup> One of these is that, under appropriate conditions, two-phase polymer blends containing a TLCP can be processed in such a way that the dispersed TLCP domains can be deformed into fibril shapes that reinforce the matrix upon solidification, leading to so-called in situ composites.<sup>1-5</sup> However, not all TLCP blends can produce self-reinforced (in situ) composites. Some thermoplastics having lower melt viscosities than that of TLCP at the processing temperature can not deform TLCP droplets even with strong drawing.<sup>7-11</sup> Dispersed droplet deformation and the parameters which affect it, can be qualitatively described using the theory of deformation and breakup of isolated droplets,

originally developed by Taylor.<sup>15-22</sup> It is reported that a higher matrix viscosity than that of TLCP's is required to achieve the droplet deformation into fibril shape.<sup>23-26</sup> Generally speaking, polymers produced by condensation reaction, such as polyamides and polyesters, have melt viscosities much lower (sometimes two or three orders) than those of TLCPs at processing temperatures and shear rates.<sup>8,11,14</sup> Hence, it can be easily expected that in situ composite of nylon 6 is hard to obtain, if not impossible, because of the low viscosity of the matrix. La Mantia *et al.* reported that they could not observe any elongated structure of the TLCP (Vectra B 950, VB) phase in nylon 6 matrix even at a very high draw ratio of 100.<sup>22</sup>

Recently we systematically sought for a preparation method of polyamide in situ composites.<sup>14,23-26</sup> What we found is that in situ composites of nylon 6 can be made even for the extrudate from a twin screw extruder when the shear rate is not high and very weak or no drawing is applied, provided a

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polymer is added to the binary blend and it can react with TLCP and nylons to produce a kind of a graft copolymer that acts at the interface between nylons and the TLCP phase.<sup>14,23,25,26</sup> The produced compatibilizer yields not only a reduction in the interfacial tension, but provides better adhesion which invokes effective stress transfer at the interface.<sup>14,24</sup> In the shear flow field, the final shape of the dispersed phase is a dynamic equilibrium between the shear stress and the compatibilizing action.<sup>26</sup> Therefore, efficient stress transfer by improved adhesion at the interface is the only practical way to achieve the deformation of TLCP droplets in the nylon matrix. When the proper amount of the compatibilizer is added, some fine fibrils are formed in the ternary blend system even without strong elongational drawing.<sup>23-26</sup> However, in spite of fibril formation in nylon 6 matrix, the improvement of mechanical properties was not remarkable except when the optimum amount of compatibilizer was added, which was possibly due to the loss of ductility of nylon 6 by the addition of a TLCP and the compatibilizer as well as degradation of the matrix and elastomer phase after blending at high temperature.<sup>14,23</sup> Also, non-uniformity across the surface contributes to the low mechanical properties. Another fact that is attributable to this is the compatibilizing action. Too much compatibilizing activity would produce droplets which are too small to be deformed by shear flow field only. When maleic anhydride grafted EPDM (ethylene-propylene-dien terpolymer) was used as a compatibilizer for nylon 6 and the TLCP blend, the TLCP phase was deformed into microfibril shapes as well as small droplets.<sup>23</sup> Extension was not applicable because of extrudate instability with drawing. We found, however, that addition of a suitable compatibilizer can enhance the stability and thus enable us to apply high drawing for the extrudate of uniform diameter.<sup>25,26</sup> Addition of maleic anhydride grafted polypropylene (MAPP) evidently showed the compatibilizing action at the interface of VB and nylon 6.<sup>26</sup> The balance in the morphological changes was influenced by processing history. In our previous study, we varied die exit temperature.<sup>26</sup> The optimum die exit temperature was found to be 280°C, which is close to TLCP phase (VB) nematic transi-

tion temperature. Lower die exit temperature did not provide more fibril formation and neither did higher temperature. The resulting properties reflect the effect of different processing conditions in the extruding die. In the present paper, as a part of continuous research to search for an optimum condition for the preparation of the polyamide in situ composites, we report experimental results of ternary blends of a high melting TLCP (Vectra B 950 (VB)) with nylon 6 and a maleic anhydride grafted polypropylene (MAPP) as a compatibilizing agent under different processing histories. We investigate the effect of the mixing step and the effect of the blending condition in the second stage to see if there is any variation of the morphology and the compatibilizing action.

## Experimental

The material employed in this study was a copolyesteramide of 6-hydroxy-2-naphthoic acid (60%), terephthalic acid(20%), and aminophenol (20%), commercially known as Vectra B950 (VB) manufactured by Celanese Hoechst (U.S.A.). The material was supplied in the form of pellets. This material has been used and characterized by many researchers.<sup>4,10,11,14,22-26</sup> Nylon 6 was supplied by Kolon Co. (KN111, Korea). Nylon 6 and Vectra B950 are immiscible.<sup>23</sup> The maleic anhydride grafted polypropylene (MAPP) used as a compatibilizer was obtained from Honam Petroleum Co. (Korea). Its maleic anhydride content is known to be ca. 1%. In this study, 2 wt% of MAPP was used because excessive amount of the compatibilizer caused coalescence and coagulation of dispersed phase and also formed a separate phase.<sup>14,23</sup>

The pellets of nylon 6 and VB were dried in a vacuum oven at 120°C and MAPP was dried at 100°C for at least 24 hrs before use. TLCP content was maintained at 20 wt%, around which content the composite showed a maximum fibril aspect ratio.<sup>2,6,27</sup> Dried VB and MAPP were blended first to see the effect of pre-blending. VB has a much higher viscosity than that of nylon 6 and fewer free amine end groups to react with the anhydride group of MAPP.<sup>25</sup> Pre-blending was done to provide more chance of reaction for VB with MAPP. They were put in a container before

blending. Blending was carried out in a 42 mm Brabender twin screw extruder (AEV651) equipped with a pulling unit. In the first processing, the extrusion temperatures of the transporting zone/melting zone/die were set as 290, 290, 280°C. After the extrudates were pelletized, the pellets were dried at 100°C in a vacuum oven for 24 hrs. Dried pellets and nylon 6 chips were mixed in a container and then blended again. The second blending was carried out in the same twin screw extruder. Temperatures of transporting zone/melting zone/die were set the same and varied as 270, 280, 290°C, because the nematic transition temperature of VB is ca 283°C. Differential scanning calorimetry (DSC) studies of thermal properties were performed on a Du Pont 910 d.s.c. controlled by a 9900 thermal analyzer. The heating rate was 10°C/min, the cooling rate was 10°C/min, and the materials were scanned from 25 to 350°C. Thermograms were repeated at least twice, using different samples to verify the reproducibility. A Du Pont 2000 thermal analyzer with a thermogravimetric analyzer (TGA) was used to check the stability of the polymers at the processing temperatures. Dynamic mechanical thermal analysis (DMTA) of the blends was carried out with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model 2) at the frequency of 1 Hz. A clamping geometry in the tensile mode was used.

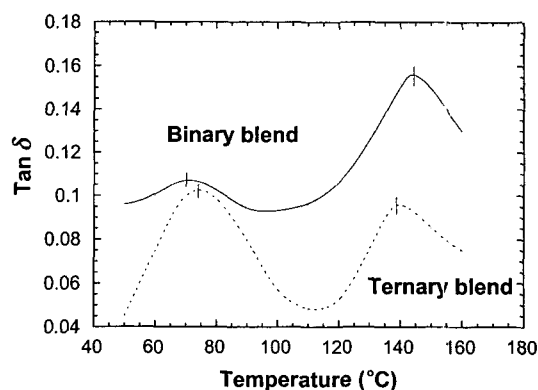
Scanning electron microscope (SEM) observations of the composite samples were performed on a Hitachi S-2500 model. The samples fractured in liquid nitrogen were coated with gold to provide electrical conductivity.

Rheological measurements were carried out using a capillary viscometer RH7 (Rosand, England) at 290°C. The capillary had 1 mm diameter and the length to diameter ratio of 32.

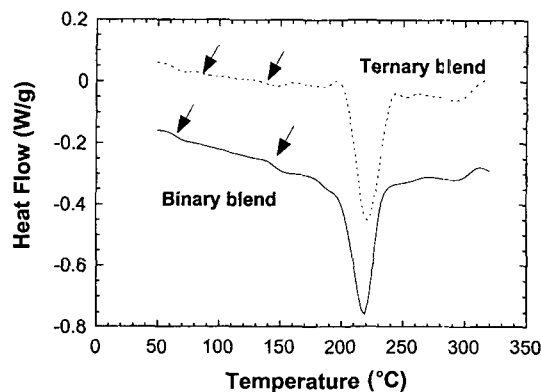
Testing of the mechanical properties of the blends was performed using an Instron Universal Testing Machine (model 4204) at a constant temperature. A gauge length of 30 mm and a crosshead speed of 10 mm/min were used. All the reported results are averages of at least 7 measurements.

## Results

**Thermal Properties.** Transitions of the binary



**Figure 1.** Normalized  $\tan\delta$  versus temperature for binary and ternary blends.



**Figure 2.** D.s.c. thermograms of binary and ternary blends.

blends and ternary blends as resolved by DMTA are shown in Figure 1. The change in  $\tan\delta$  with varying temperature is shown. In the binary blend, two distinct  $\tan\delta$  peaks associated with the glass transition of nylon 6 and VB are located at 68 and 143°C, respectively. Two distinct glass transition temperatures ( $T_g$ ) indicate that they are immiscible. The higher and lower  $\tan\delta$  peaks in the ternary blend shift toward each other. The ternary blend extruded at 280°C shows the peak temperature at 74 and 138°C, which are in exact agreement with our previous measurement.<sup>26</sup> The shift of  $T_g$  means that nylon 6 and VB becomes compatible in the ternary blend. DSC results confirm the shift of the glass transition temperature of the ternary blend (Figure 2). The heat of crystallization and crystallization temperature of the ter-

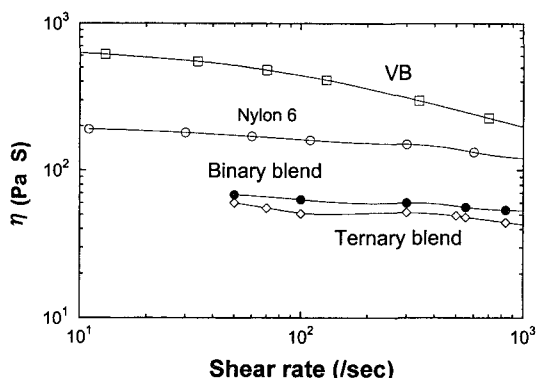
nary blends were slightly changed compared to that of single step mixing, however, thermal behavior looks almost the same.

**Flow Properties.** The flow properties of blended and neat materials have been investigated at 290°C using a capillary rheometer. Corrections for end pressure loss (Bagley) and departure from Newtonian flow (Rabinowitsch) have been applied. Viscosity-shear rate relationship for the pure components and the blends are shown in Figure 3. These results are in good agreement with our previous results.<sup>25</sup> The viscosities of the binary and ternary blends are lower than those of the neat polymers, indicating a synergistic effect of reducing the viscosity of the TLCP composite and its great ability as a processing aid. Nylon 6 and the blend follow Newtonian fluid behavior, while VB shows shear thinning at high shear rates.

The extrudate did not show any noticeable swelling at all. In our previous study, we already revealed that the average ratio of measured extrudate diameter to die diameter at different die temperature showed almost no extrudate swell when no drawing was applied.<sup>26</sup> Extrudates of this study also show no surface roughness under the processing conditions. The regularity of the filament surface was conserved during the extrusion process. The irregularity of the surface prevented the application of high drawing ratio and extrudate quality was not improved by lowering the extrusion temperature,<sup>23</sup> but current extrudates all showed clean and smooth surfaces. Hence draw-

ing could be easily applied. Lower processing temperature than 270°C raised, however, some problems. The extrudates processed at 260°C caused surface irregularity which prevents high drawing.

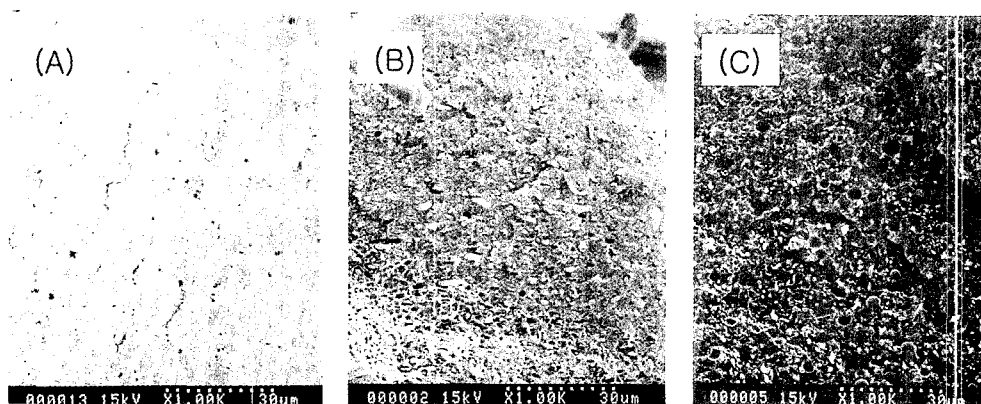
**Morphology.** SEM micrographs manifest the microstructure of the fractured surfaces of the blend extrudates prepared under various extrusion conditions. Figure 4 shows the fractured surface of a VB/MAPP binary blend. TLCP exists as fibril bundles and lamellae shapes. Figure 5 shows the morphology of the ternary blends at different second extrusion temperatures at a low draw ratio of ca. 1.8~2. In spite of weak drawing, the TLCP, which is present at 20%, existed as fine and coarse fibrils, ellipsoids, and some droplets distributed in the nylon 6 matrix. Less fibrils or deformed shapes were obtained when processed at higher temperatures of 280 and 290°C. Since the VB phases are in the form of fibril bundles after the first stage, we expected those to be kept during the second extrusion. However, it appears that some part of them were deformed possibly by higher temperature in the extruder due to thermal dissipation. When the temperature goes over the transition temperature, it is just like a single stage extrusion. In our previous study, the die exit temperature of 280°C was reported to be the optimum temperature for more uniform and fibril



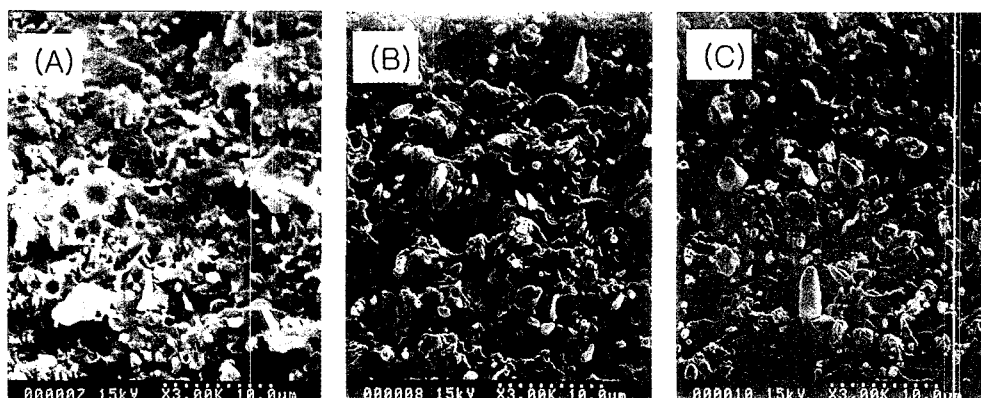
**Figure 3.** Viscosity-shear rate relationship of (○) nylon 6, (□) VB, (●) binary and (◇) ternary blends at 290°C.



**Figure 4.** SEM photographs of fractured surfaces of VB/MAPP binary blend at the draw ratio of ca. 1.



**Figure 5.** SEM photographs of fractured surfaces of ternary blends at the processing temperature of (a) 270 °C, (b) 280 °C, and (c) 290 °C, respectively. Draw ratio was about 1.8.



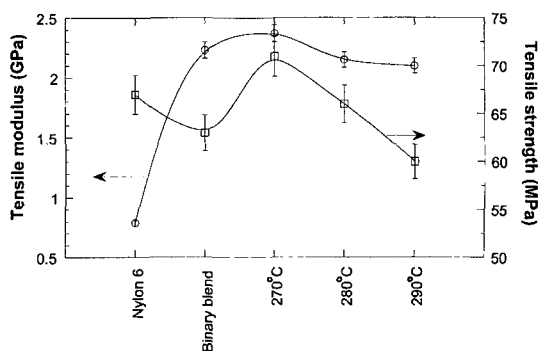
**Figure 6.** SEM photographs of fractured surfaces of ternary blends at the die temperature of 270 °C; (a) Draw ratio of 1.8, (b) Draw ratio of 4.4, and (c) Draw ratio of 6.8.

shapes.<sup>26</sup> Hence, the morphology at 280 °C looks better than that of 290 °C.

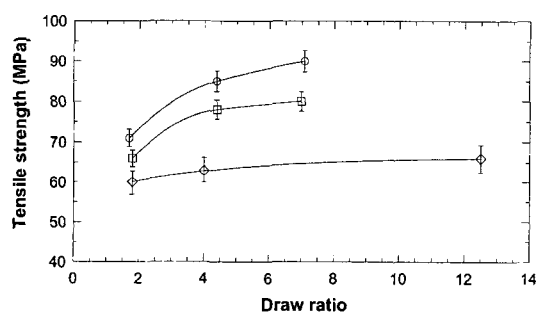
The effect of the draw ratio on the blend microstructure is demonstrated in Figure 6. The texture of the samples reveal the presence of dispersed TLCP phases. These deformed phases range in diameter up to a maximum of 2  $\mu\text{m}$ , but small domains of fibril shape predominate. Comparison of Figure 5 and 6 reveal that textured droplets of TLCP are more abundant in highly drawn samples. Though the temperature of 270 °C is below its crystalline-nematic transition temperature of VB, high drawing enables the deformation of TLCP phase. It has been studied and shown in some detail that the supercooling behavior of TLCP allows the possibility of processing TLCP below its actual melting point once it is in molten state.<sup>15,17</sup>

The micrographs shown in Figure 5 and 6 clearly demonstrate the influence of elongational flow on the development and refinement of TLCP fibrils, by the compatibilizer inducing better adhesion and dispersion.

**Tensile Properties.** Tensile modulus and strength for the ternary blend extrudates are shown in Figure 7. The sensitivity of tensile properties to extrusion temperature is significant especially at the high drawing ratio. Higher tensile modulus for the extrudate of 270 °C extrusion temperature is consistent with the fractured surface morphology. We believe that the difference is due to the temperature effect on the fluid properties. At the processing temperature of 270 °C, more VB phase keeps its shape, hence they work as the reinforcing filler while the compatibilizer at the interface



**Figure 7.** Tensile modulus ( $\circ$ ) and tensile strength ( $\square$ ) for binary and ternary blends. Draw ratio was ca. 1.8. Lines are guides for the eyes. Error bars represent one standard deviation.



**Figure 8.** Tensile strength of ternary blends vs draw ratio. Processing temperatures were ( $\circ$ ) 270°C, ( $\square$ ) 280°C, and ( $\diamond$ ) 290°C. Lines are guides for the eyes. Error bars represent one standard deviation.

improves the adhesion. As we mentioned above, at 280°C which is close to the nematic transition temperature of VB, the temperature in the extruder would be over 280°C due to the thermal dissipation. Thus, previously generated fibril shapes are lost in the extruder. Then it would be the same as the single extrusion. We already reported that die exit temperature of 280°C was the optimum temperature.<sup>26</sup> The mechanical properties are, therefore, better than that processed at 290°C. The effect of the extrusion temperature, hence the processing effect, is manifest even when the extrudates were extended. Figure 8 shows the effect of the draw ratio, which is defined as the ratio of die diameter to that of the produced strand. The influence of the draw ratio on the tensile modulus is attributed to modification of the TLCP phase.

The overall tensile properties of the ternary blends are similar to those found in our previous study,<sup>26</sup> but show a definite increase with draw ratio. Tensile strength at the high draw ratio for the extrudates processed at 270°C shows the highest value, while those processed at 290°C have the worst properties. Such a high tensile strength value of 90 MPa was not obtained before.<sup>26</sup> Drawing of the ternary blend was possible because of consistent surface regularity and stability provided by MAPP, which was not achievable when maleic anhydride grafted EPDM was used as a compatibilizer.<sup>23,28</sup>

## Discussion

Compatibilizing action by addition of MA-PP can be ascribed to two possible mechanisms<sup>31</sup>; the occurrence of a reaction, or an interaction such as hydrogen bonding. Recently O'Donnell and Baird<sup>32</sup> investigated the possibility of these two mechanisms for ternary blends of polypropylene/maleic anhydride grafted polypropylene/TLCPs (Vectra A 950, Vectra B950, LC 3000). Based on their i.r. 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  $\text{cm}^{-1}$ . 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-PP should be compared with that of MA-PP. We investigated this by preparing a binary blend of VB and MAPP (50:50 ratio) under the same processing conditions.<sup>25,26</sup> Then, using the soxhlet extractor with boiling dichlorobenzene, we extracted the soluble part. The Raman spectra of the extract showed characteristic peaks of aromatic and ester at 1380, 1620 and 1742  $\text{cm}^{-1}$  (Figure 9 of ref. 26) which can not be seen in MA-PP spectrum. This means that VB moiety is included in the extracts. Since VB is not soluble in dichlorobenzene, we believe that some reactions occurred to produce some kind of graft copolymers. Recently we pro-

posed some reactions occurring between the maleic anhydride group and the end groups of nylon 6 or VB.<sup>25</sup> It is well known that maleic anhydride can react with the amine end group of nylons. Hydroxyl end groups can also react with the maleic anhydride to produce graft copolymers. How much amine end group remains in VB is not detectable from i.r. analysis because of the overlapping of the amine peak with the hydroxyl peak, but the existence of the hydroxyl group could be clearly seen at  $3300\text{ cm}^{-1}$  (Figure 21 of ref. 14). Also, ester moiety in VB can react with the maleic anhydride group. Though this reaction usually requires catalysts for speed, remnant catalyst in VB can promote it. It may be conjectured that reacted VB moiety would be from the low molecular weight VB produced by thermal depolymerization. However, TGA thermogram of the TLCP (VB) didn't show any signs of thermal degradation until the temperature reached  $350^\circ\text{C}$ .<sup>25</sup> If the compatibilizing action occurs solely because of hydrogen bonding, the binary blend of nylon 6 and VB, both of which have strong hydrogen bonding, should be compatible. As already seen in the properties and morphologies of the binary blend, they are not compatible.<sup>23</sup> Little interaction can be observed between VB and nylon 6. The amine end group of VB and nylon 6 would react with the anhydride group of MA-PP to form a kind of (comb shape) block copolymer having different branches which will act as the compatibilizer at the interface.

Thermal properties and microstructure reveal the change of the nature of TLCP/nylon 6 blend with the addition of MAPP. The shift in  $T_g$  of nylon 6 and TLCP in the ternary blends toward each other, reflecting the partial miscibility, is consistent with previous studies that reported changes in the glass transition temperature of TLCP and polyamides (nylon 46<sup>14</sup>, nylon 66<sup>24</sup>, and nylon 6<sup>23,26</sup>) with the addition of a compatibilizer. It was desired that deformed TLCP phase keep its shape in the second processing, hence produce the reinforced composites. However, depending on the processing temperature, fractured surfaces show the existence of TLCP as fine and coarse fibrils as well as ellipsoids and droplets in the nylon 6 matrix after the second processing when the draw ratio is

low (Figure 5 and 6). This is partly attributable to the phase transition of VB. Even though the extrusion temperature is  $280^\circ\text{C}$  which is close to the melting point of VB, the temperature in the extruder would be over  $280^\circ\text{C}$  due to the thermal dissipation. Thus previously generated VB fibril shapes are lost in the extruder. Then it would be the same as the single extrusion. Hence, the extrudates at  $280^\circ\text{C}$  show better performance than  $290^\circ\text{C}$ . Also there is a possibility of thermal degradation of the nylon 6 matrix after the second processing, but thermo-gravimetric analysis proves that degradation of nylon 6 after the second processing was very slight. Blending of 20 wt% TLCP decreased the viscosity to a value lower than those of the constituent materials. The overall shape of the blend curve follows that of nylon 6. The exact mechanism of viscosity reduction in TLCP blends is not yet completely understood.<sup>10,19,21</sup> According to a relationship proposed by Bye and Miles,<sup>29</sup> the observed flow behavior is consistent with stratification of flow and interfacial slip in the melt. Ternary blends show almost the same viscosity as that of the binary blend because of mixed morphology. The relative amount of viscosity reduction by different processing temperatures was not vivid.

Other blend studies have also shown improvement in tensile properties with decreasing extrusion temperature. In a report by Beery and co-workers,<sup>30</sup> extrusion was undertaken  $15^\circ\text{C}$  below the melting temperature of TLCP. This indicates the possibility that lower temperatures favor improved fibril formation owing to the greater shear stress developed at lower temperatures when TLCPs have low crystallization temperature and high melting temperature. But the high processing temperatures induce rapid cooling, hence rapid solidification and/or increase of the viscosity of TLCP phase rather than providing high shear stress by increased matrix viscosity. Though higher drawing increases the deformation of VB phases, processing temperature effect still dominates.

The presence of fibrils in the microstructure correlates with the increased tensile modulus. This is in accordance with the fractured surface morphology. Results show that fibril formation is favored when a significant level of drawing is applied and previously generated fibril shapes are more pre-

served when processing is undertaken at a temperature lower than the crystal-nematic transition temperature of VB. More deformation of VB phase developed at higher draw ratios results in the increased value of the tensile modulus. The reason why two step mixing was applied here is to hopefully preserve the fibril bundles of VB phase as well as to enhance the reaction between VB and MAPP. In the one step mixing, since the viscosity of nylon 6 (hence fluidity) is much lower than VB and nylon 6 has more reacting amine groups than VB, it is expected that nylon 6 reacts more actively with MAPP than VB. We tried to provide more reaction between VB and MAPP by extruding first the VB and MAPP. Extrudates of VB and MAPP binary blend show fibrils and tape-like fibril shapes of VB. Then we tried to make a reinforced composite by keeping the fibril shape of the processed VB phase, but it was not much successful though it showed a possibility.

## Conclusions

We have investigated the effect of processing conditions on the properties of TLCP ternary blends. Ternary blends show complicated behavior because of their multiphase character depending on the processing condition. Addition of MAPP evidently shows the compatibilizing action at the interface of VB and nylon 6. The state of the dispersed TLCP phase varies between droplet and fibril morphologies. The balance between these structures is influenced by processing history. At the extrusion temperature of 270°C, some of the fibrils generated in the first processing remained. It showed the highest tensile strength value. The another one processed at 280°C did not show the high tensile strength as much as the one processed at 270°C, but it was better than the other processed at 290°C because the optimum die exit temperature is 280°C which is close to the nematic transition temperature. Lower die exit temperature than 270°C did not provide enough stability for high drawing. In the high temperature case (280 and 290°C), fibrils generated in the first step seem to be lost in the extruder because of higher temperature by viscous dissipation. Then it was just the same as the single step process. The

resulting properties reflect the effect of different processing conditions in the second mixing. The difference in tensile properties was not dramatic, when draw ratio was low, but becomes manifest with high draw ratio. The compatibilizer provides the extrudate stability which enables the application of a relatively high draw ratio. This was not obtainable when MA-EPDM was used as a compatibilizer.<sup>23</sup> A high draw ratio presents more oriented fibril shapes which are correlated with increased mechanical properties.

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