Effect of the Molecular Structure Change of a Matrix Polymer (Nylon 6) on the Deformation of Dispersed Phase (a Thermotropic Liquid Crystalline Polymer) Droplets in Shear Flow

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ABSTRACT: In this work, we investigated the effect of a change in the molecular structure and ensuing molar mass change of a matrix polymer (polyamide 6, Ny 6) on droplet deformation of a dispersed thermotropic liquid crystalline polymer (TLCP, a poly(ester amide)) in shear flow. This study focuses on a total capillary number (the sum of the shear capillary number and the elasticity capillary number) and the viscosity ratio between the TLCP and Ny 6, for the morphological development and mechanical performance of TLCP/Ny 6 blends. In contrast to Ny 6, which has a lower melt viscosity than the TLCP melt, a modified Ny 6 (m-Ny 6) with ca. 2 orders higher melt viscosity than that of Ny 6 at a shear rate of 1 s⁻¹ was found to facilitate the deformation of the TLCP phase. A total capillary number was defined to characterize the viscoelasticity effect on droplet deformation in the blend system. The first normal stress difference obtained from the viscosity curve using Steller’s method was used for the evaluation of the elasticity capillary number. The total capillary number for the Ny 6 blend was far less than the critical capillary number and was insufficient for the dispersed TLCP droplets to be deformed. The shear capillary number of the m-Ny 6 blend was greater than the critical capillary number but was still insufficient for droplet deformation into fibril shapes. The total capillary number, including the elastic capillary number, was sufficiently greater than the critical capillary number for deformation of the dispersed TLCP droplets. Morphological observations and a comparison with the theoretical work confirmed the importance of the viscoelasticity of the melt in the immiscible Ny 6/TLCP blends for in situ composite fabrication in shear flow. Both the high viscosity and the first normal stress difference of m-Ny 6 promote the deformation and fibrillation of the dispersed TLCP droplets.

INTRODUCTION

Thermotropic liquid crystal polymers (TLCPs) have been extensively studied as blend additives because they can satisfy the rheological (low melt viscosity) and mechanical (high modulus and strength) properties required for various applications.1−7 One of the requirements is the ability to form in situ composites (blends of TLCPs and thermoplastics), which are useful because they can solve some of the problems commonly encountered in the conventional processing of fiber-reinforced composites and also have the potential to provide a sustainable route to fiber-reinforced composites.5−7 These useful properties are attributed to the spontaneous molecular orientation of TLCPs during the processing to form a fibril morphology with a high degree of orientation.1−4 The morphological development of the TLCP phase in thermoplastic matrices is critical for the performance of the resultant in situ composites.5−11 Although numerous studies on the TLCP blends and in situ composites prepared with commercially available thermoplastics have been reported, there were few studies on the fabrication of in situ composites in shear flow.1−5 Once an elongational force is applied to the two-phase systems of TLCPs, deformation and fibrillation of the TLCP phase can readily occur because the elongational flow field stabilizes elongated droplets, independent of the viscosity ratio.12−15 In processes where the shear flow dominates, such as injection molding or extrusion, TLCP particle deformation is not as straightforward.8−11,16 Fibrils of the TLCP phase are usually formed in the extruder near the die exit with an orientation of the flow direction because of the extensional forces.12 However, in pure shear flow (a weak flow), not all immiscible thermoplastic/TLCP

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blend pairs can generate in situ composites. If the viscosity of the matrix phase is lower than that of the dispersed phase (TLCP), the TLCP phase cannot be deformed into a fibrillar structure.\textsuperscript{7–11,13–15} When a sufficient amount of the minor TLCP phase (at least 10%) is present in the blend and internal or external drawing is applied, i.e., when there is a high flow rate through the entrance to the capillary rheometer or drawing is performed beyond the die exit, the minor TLCP phase of lower viscosity becomes deformed and/or elongated into fibrils, irrespective of the viscosity ratio.\textsuperscript{9–11}

Several critical factors affect the deformation of the dispersed TLCP phase under the shear flow such as the applied shear stress, viscosity ratio, and the interfacial tension.\textsuperscript{10–16} Numerous studies have shown that these rheological factors influence the deformation of the dispersed phase, particularly the ratio of the viscosities of the dispersed phase and the matrix polymer as well as the elasticity effect.\textsuperscript{17–22} Kirchberger and Münstedt have recently surveyed previous studies of droplet deformation.\textsuperscript{23} Over the past 2 decades, we have continuously sought for a feasible method for easily deforming a TLCP phase dispersed in a matrix with a viscosity lower than that of the TLCP phase.\textsuperscript{8–13} In principle, such a deformation is possible if the interfacial tension is sufficiently low that the capillary number (i.e., a ratio of the shear stress to the interfacial tension) becomes larger than the critical capillary number (see the discussion of Figure 3).\textsuperscript{20–22}

We have studied the behaviors of blends of nylons with some immiscible TLCPs and have found that when an extensional flow is applied during the processing, the TLCPs can be elongated into a fibril shape oriented in the flow direction.\textsuperscript{9–11,24} In the absence of this extensional component, however, only spherical domains were observed.\textsuperscript{8–11,24} Although strong drawing after the die exit can somewhat deform the dispersed droplets, this approach is not readily applicable to nylon blends because of their drawing instability.\textsuperscript{23–25} These difficulties also arise with other polymers synthesized via polycondensation, such as polyamides or polyesters, which exhibit peculiar rheological properties that differ dramatically from those of other polymers synthesized via free-radical polymerizations, i.e., they have a broad Newtonian viscosity plateau over a wide range of shear rates as well as a rather low melt viscosity.\textsuperscript{26} Hence, elongating the blend extrudate with stable dimensions and smooth surfaces is not easily feasible.

We have recently reported success in producing Ny 6 with a high melt viscosity by varying its structure and/or performing an anionic polymerization with reactive extrusion.\textsuperscript{26–29} Even though the molar mass of the modified polymer was less than twice that of neat Ny 6, its melt viscosity was more than 200 times greater than that of Ny 6.\textsuperscript{26} We attributed these properties to the presence of a branching structure.\textsuperscript{27–29}

Because its melt viscosity at low shear rates is 2 orders higher than that of neat Ny 6, it can exert high shear stress on the TLCP droplets to initiate the droplet deformation in shear flow.

The aim of the present study is to demonstrate the importance of the viscoelasticity of the matrix polymer for the deformation of dispersed droplets in the shear flow. To elucidate the influence of critical parameters on the deformation and fibrillation of the TLCP phase in shear flow, we investigated the effect of a change in the molecular structure of the Ny 6 matrix phase in a binary blend of Ny 6 and a TLCP (Vectra B950 (VB)) without a compatibilizer on the morphological development. We demonstrate the feasibility of the TLCP phase deformation in two different nylon 6 polymers having different molecular structures; one has branching on its backbone, which induces dramatically different rheological properties. Both the viscosity ratio and the blend elasticity were taken into account using Steller’s method.\textsuperscript{30} Because the first normal stress difference is much larger than the shear stress in shear flow, it critically affects droplet deformation. Our morphological observations confirm that the TLCP droplets can be deformed without drawing or the addition of a compatibilizer once the melt viscosity of the matrix phase is sufficiently high to provide high shear stress and elasticity as well as a small viscosity ratio.

### Results and Discussion

Figure 1 shows the transitions in the two blends (Ny 6/VB and modified Ny 6 (m-Ny 6)/VB), as obtained using a dynamic mechanical thermal analyzer (DMTA). Two distinct peaks are observed: one is associated with the Ny 6 glass transition at 70 °C and the other at 148 °C due to the VB, in good agreement with our previous results.\textsuperscript{10} The tan δ peak of m-Ny 6 appears at 72 °C. These results indicate that Ny 6 and m-Ny 6 are both immiscible with VB. The heat of melting for m-Ny 6 (31.25 J/g) is slightly lower than that of Ny 6 (33.76 J/g) because of its different structure.\textsuperscript{26}

The flow properties of the blended and neat materials were investigated at 260 and 290 °C. The viscosity–shear rate relationships for the pure components and the blends are shown in Figure 2a. As described in our previous study,\textsuperscript{30} the m-Ny 6 melt exhibits a strong shear-thinning behavior due to molecular structural changes (generation of branched molecules), whereas the Ny 6 melt shows a typical Newtonian fluid behavior. At 290 °C and a shear rate of 1 s\textsuperscript{−1}, the m-Ny 6

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**Figure 1.** Normalized tan δ versus temperature for (a) Ny 6+VB and (b)m-Ny 6+VB.
exhibits a viscosity of almost 2 orders of magnitude greater than that of Ny 6 and 1 order of magnitude greater than that of VB (Figure 2b). The extrudate speed was set to fix the draw ratio of the measured extrudate diameter to the die diameter to 1. The viscosities of the two blends (Ny 6/VB and m-Ny 6/VB) are lower than those of the neat polymers (Figure 2b), which illustrates the viscosity reduction of the blend by mixing with the TLCP and demonstrates its great ability as a processing aid.\textsuperscript{26–29} Ny 6 and the Ny 6 blend exhibit Newtonian fluid behavior, whereas m-Ny 6 exhibits a strong shear-thinning behavior at high shear rates because of the branching structure.\textsuperscript{26–29} At the shear rate of 1 s\textsuperscript{-1}, the m-Ny 6 blend exhibits a melt viscosity almost 40 times higher than that of the VB, whereas the unmodified Ny 6 exhibits a melt viscosity lower than that of the VB (Figure 2b).

The adjustment of the ratio between the measured extrudate diameter and the die diameter to a value of 1 means that no extrudate swelling occurs. The extrudate surfaces are fairly smooth with no surface roughness under these processing conditions, implying that the extrudate surfaces are stable.\textsuperscript{13} The final shape of the dispersed TLCP phase is determined by the dynamic equilibrium between the stresses exerted by the matrix polymer on the droplet (shear stress and normal stress) and the resisting force of the droplet (the interfacial tension and the normal stress of the droplet).\textsuperscript{2, 6, 11} The balance of the forces that act on the droplet can be simply expressed using the following equation

\[ \tau_{\text{xy}} + N_1^\text{n} = \Gamma / r + N_1^\text{f} \]  

\[ \eta_{m} \dot{\gamma} + (N_1^\text{m} - N_1^\text{l}) = \Gamma / r \]  

where \( \tau_{\text{xy}} \) is the shear stress of the matrix polymer (\( = \eta_{m} \dot{\gamma} \)), \( N_1^\text{n} \) is the normal stress (this is the same as the first normal stress difference in the shear flow) of the matrix, \( \Gamma \) is the interfacial tension, \( N_1^\text{m} \) is the first normal stress difference of the droplet, and \( r \) is the radius of the droplet.\textsuperscript{11} Thus, we can define the capillary number as follows

\[ \text{Ca} = \eta_{m} \dot{\gamma} / (\Gamma / r) + (N_1^\text{m} - N_1^\text{l}) / (\Gamma / r) = \text{Ca}_S + \text{Ca}_E \]  

To judge the importance of the fluid’s elastic effect on droplet deformation, we need the first normal stress value, which is not easy to measure for polymer blends in the molten state. Wagner\textsuperscript{31} showed that the relationship between the first normal stress function and the viscosity function in the steady shear flow can be expressed as

\[ N_i(\dot{\gamma}) = \frac{1}{m} \dot{\gamma} \frac{d\eta(\dot{\gamma})}{d\dot{\gamma}} \]  

(4)

where \( m \) is a material parameter associated with the strain dependence of the memory function. Steller recently proposed a new method for calculating the first normal stress difference function from a generalized viscosity function in a shear flow, which enables the first normal stress difference to be determined from the flow curves.\textsuperscript{30} After fitting the viscosity data to the Carreau model (eq 5) with the Cox–Merz rule and applying the Wagner model, Steller obtained eq 6

\[ \frac{\eta}{\eta_0} = [1 + (\lambda \dot{\gamma})^{n-1/2}]^{n/2} \]  

(5)

\[ N_i \tau = 14(1 - n)/(1 + on) \]  

(6)

where \( \tau \) is the shear stress, \( \lambda \) is the characteristic relaxation time, \( n \) is the parameter of the power-law index in the Carreau model, and \( \dot{\gamma} \) is the shear rate. In our previous study, the following \( n \) values were determined as \( n = 0.16 \) (Ny 6) and 0.42 (m-Ny 6).\textsuperscript{20}

The first normal stress difference of the TLCP phase is subtle because of its unusual behavior at low shear rates.\textsuperscript{32, 33} A steady negative value has sometimes been reported for the first normal stress difference of thermotropic polymers.\textsuperscript{34} At low shear rates, the value of the first normal stress difference is not comparable to the shear stress of the matrix; we can therefore neglect the first normal stress difference of the TLCP droplet.\textsuperscript{32–35} In the present study, however, as an initial guess, we assume that the first normal stress difference of the VB follows the Steller equation (eq 6), although the validity of this assumption requires further study in the future. The shear stress at a shear rate of 1 s\textsuperscript{-1} is the same as the viscosity. The melt viscosity of m-Ny 6, Ny 6, and VB is 33 000, 330, and 850 Pa·s, respectively (Figure 2b). The value of the Carreau parameter (\( n \)) for VB was evaluated to be 0.35 after fitting the experimental data.

The interfacial tension between Ny 6 and VB was evaluated using the harmonic equation
were adapted with ref 23. Copyright 2010 AIP.) CaS is the shear capillary number and CaE is the elasticity capillary number. Scanning electron microscope (SEM) micrographs of the fractured surface of binary blends of (b) Ny 6+VB and (c) m-Ny 6+VB. The scale bar is 5 µm.

\[
\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p}
\]

where \(\gamma_1\) and \(\gamma_2\) are the surface tensions of phases 1 and 2, respectively, \(\gamma_1^d\) and \(\gamma_2^d\) are the dispersion components, and \(\gamma_1^p\) and \(\gamma_2^p\) are the polarization components of the surface tensions of the two phases.\(^\text{34-40}\) Evaluating the surface tension of the TLCP phase is quite cumbersome, especially near the transition region in the processing window.\(^\text{37,39}\) The temperature-induced variation in the surface tension of the TLCP melt has a positive gradient, (i.e., it increases as the temperature increases to the nematic–isotropic temperature), in contrast to the general surface tension behavior of other thermoplastics.\(^\text{40,41}\) Even though the temperature dependence of the surface tension of VB is somewhat ambiguous,\(^\text{37,42}\) Lee and Denn calculated \(\gamma_1\) at 300 °C to be 41.1 mN/m, with \(\gamma_1^d = 26\) mN/m and \(\gamma_1^p = 15.1\) mN/m.\(^\text{41}\) Although some different data have been reported for the polarization component of VB, we used Lee and Denn’s results because they give more realistic interfacial tension values for blends of VB and thermoplastic polymers.\(^\text{41,42}\) The surface tension of Ny 6 at 230 °C has been reported to be 37.19 mN/m for \(\gamma_2^d\), 35 mN/m for \(\gamma_2^d\), and 2.2 mN/m for \(\gamma_2^p\).\(^\text{30}\) By considering the temperature dependence, we estimated the corresponding surface energies at the processing temperature (290 °C) to be 36.7, 34.5, and 2.2 mN/m for the surface tension \(\gamma_1\), \(\gamma_1^d\), and \(\gamma_1^p\) respectively.\(^\text{36,40}\) The interfacial tension between the VB and Ny 6 was then calculated to be 6.4 mN/m at 290 °C. O’Donnell and Baird calculated the interfacial tension between VB 950 and polypropylene to be 5.1 mN/m.\(^\text{35}\) Because the absolute values of the interfacial tension, which were predicted using the harmonic mean equation, strongly depend on the surface tensions of the pure polymers,\(^\text{36,45}\) we cannot compare the interfacial tensions of different polymer pairs. Nevertheless, the interfacial tension value of 6.4 mN/m is close to that of the VB 950/PP pair if we exclude the polarization part for the VB/Ny 6 pair.

The capillary number needs to be greater than the critical capillary number, \(C_{\text{acritical}}\). When the capillary number of the droplets in the shear flow is greater than the \(C_{\text{acritical}}\), the shear stress deforms the droplet.\(^\text{20,26}\) By contrast, if the Ca is smaller than the \(C_{\text{acritical}}\), the hydrodynamic forces are no longer able to deform the droplets (Figure 3). If they are equal, then breaking of the deformed droplets can occur.\(^\text{19,20}\) The \(C_{\text{acritical}}\) in different flow fields have been experimentally determined as a function of the viscosity ratio, \(\lambda = \eta_1 / \eta_m\), where \(\eta_1\) is the viscosity of the minor phase and \(\eta_m\) is the viscosity of the matrix phase (Figure 3).\(^\text{19,20}\) Utracki et al. described the behavior of a droplet in a matrix polymer depending on the reduced capillary number, \(C_{\text{a}} = C / C_{\text{acritical}}\).\(^\text{46}\) Four regions were separated depending on the \(C_{\text{a}}\) value: (1) for \(0.1 > C_{\text{a}}\), droplets do not deform, (2) for \(0.1 > C_{\text{a}} < 1\) droplets deform, but they do not break, (3) for \(1 > C_{\text{a}} < 4\) droplets deform and then split into two primary droplets, and (4) for \(C_{\text{a}} > 4\) droplets deform into stable filaments.\(^\text{24}\)

The first normal stress difference was calculated using Steller’s method (eq 6); the \(N_1/r\) values for Ny 6, m-Ny 6, and VB were found to be 6, 2.3, and 2.93, respectively. On the basis of the SEM morphology, the average radius of the dispersed TLCP droplets was estimated from the SEM micrographs to be 0.5 ± 0.2 µm for the Ny 6 blend. Hence, the shear stress capillary number \(C_{\text{acritical}}\) for the Ny 6 blend at a shear rate of 1 s\(^{-1}\) was found to be 330 Pa·s × 1 s\(^{-1}\) × 0.5 µm/(6.4 mN/m) = 0.025 and the capillary number of the first normal stress difference \(C_{\text{a}}\) was estimated to be \((6 × 330 − 2.93 × 550) \text{ Pa·s × 1 s}^{-1} × 0.5 \text{ µm}/(6.4 \text{ mN/m}) = 0.029\) with a total capillary number \(C_{\text{a}}\) for Ny 6 of 0.054. In contrast, the average radius of droplets was estimated to be 0.5 ± 0.1 µm for the m-Ny 6 blend, the \(C_{\text{a}}\) for the m-Ny 6 melt at a shear rate of 1 s\(^{-1}\) was found to be 3300 Pa·s × 1 s\(^{-1}\) × 0.5 µm/(6.4 mN/m) = 2.58, and the \(C_{\text{a}}\) was calculated to be \((2.3 × 33000 − 2.93 × 550) \text{ Pa·s × 1 s}^{-1} × 0.5 \text{ µm}/(6.4 \text{ mN/m}) = 5.8\); thus, the total \(C_{\text{a}}\) for m-Ny 6 is 8.38, which is approximately 155 times greater than that for neat Ny 6.

Figure 3 also shows the microstructures of the fractured surfaces of the blends with two different Ny 6 matrices. The micrograph of the Ny 6 blend shows that most droplets have a spherical shape, in accord with the above explanation, because the total capillary number is 0.054, which is far less than the critical capillary number at the viscosity ratio of 1.86. Consequently, VB droplets cannot be effectively deformed in
a shear flow field. However, the m-Ny 6 blend resulted in a lot of deformed fibril shapes or nodular ellipsoids, even if no drawing was applied. If only the Caₙ (≈ 2.58) for the m-Ny 6 blend is considered, few droplets may have deformed because it is slightly larger than the Ca* at the viscosity ratio of 0.02. According to Utracki et al., theoretical criteria, this Caₙ value (2.58/1.2 = 2.18) corresponds to region 3 (1 < Ca* < 4), where droplets deform and then split into two primary droplets. After the Caₙ is taken into account, the total Ca is far above the Ca*critical and the Ca* (≈ 8.38/1.2 ≅ 6.98) corresponds to region 4, where droplets deform into stable filaments. This morphological outcome is in agreement with the theoretical prediction of Utracki et al.21

Nevertheless, not all of the dispersed TLCP droplets were deformed. Though the high viscosity of m-Ny 6 and the ensuing high normal stress difference are expected to be sufficient to deform the TLCP droplets, deformation of all droplets is not guaranteed. Numerous small droplets are not deformed but rather rotate because the Ca of the small droplet is smaller than the Ca*critical for deformation.21 To deform the small droplets in the shear flow, either a higher viscosity matrix or a compatibilizer must be used to reduce interfacial tension and ensure good adhesion at the interface for efficient stress transfer.21,22 Higher shear rates and a lower viscosity ratio tend to coalesce the small particles, which will help the deformation of the droplets.22

Although the use of the m-Ny 6 blend produced numerous fibril shapes or deformed droplets, its mechanical performance was not better than that of Ny 6 (Figure 4). Since stable strand extrusion was possible, tensile properties were evaluated directly using extruded strands having a constant diameter. The modulus of the blend was much higher than that of Ny 6 because of the reinforcing effect from the dispersed TLCP phase, but the elongation was seriously decreased due to the weak adhesion at the interface of the blend.21 Given that the mechanical properties of m-Ny 6 are superior to those of Ny 6, the lower-than-expected mechanical performance of the m-Ny 6/VB blend is due to the incompatibility with the matrix polymer and the incomplete transformation of the VB phase into a fibrous morphology.9,10,27–29 Possible hydrogen bonding interactions between the amide groups of the VB and m-Ny 6 may not be sufficiently strong to ensure good adhesion at the interface and large elongation.6,8,10 Hence, good interfacial adhesion is paramount to the deformation of the dispersed TLCP phase as well as to the mechanical performance of the composite.8–15

■ CONCLUSIONS

We investigated the effect of melt viscoelasticity on the equilibrium morphology of TLCP droplets dispersed in two different nylons (Ny 6 and m-Ny 6). Although its molar mass is less than twice that of Ny 6, m-Ny 6 has a much higher melt viscosity than Ny 6 because of molecular structure changes (branched molecules).26 The elastic capillary number was calculated using the first normal stress difference, which was obtained by Steller’s method based on the Carreau viscosity model and Wagner’s equation. The total capillary number, which is the sum of the shear capillary number (Caₙ) and the elasticity capillary number (Caₑ), for the VB/Ny 6 blend was not sufficiently large to deform the VB droplets according to the criterion of Utracki et al., though the Caₑ value of the Ny 6/VB blend was greater than the Caₙ.22 Even though the Caₙ of the m-Ny 6/VB blend was greater than the critical capillary number, it was not large enough to produce a fibrillar morphology according to the criterion of Utacki et al. When the elastic capillary number of the blend is taken into account, the total capillary number is far greater than the critical capillary number at the corresponding viscosity ratio and the total critical capillary number corresponds to a region where droplets deform into stable filaments in the shear flow. The morphological observation of the blends is in accordance with the capillary number criterion. The observations reveal that the Ny 6/VB blend mostly contains spherical droplets without much deformation, whereas the m-Ny 6/VB blend contains numerous fibrils and nodular ellipsoids, even without drawing. These results confirm the importance of the matrix viscoelasticity for deformation of the dispersed droplets in shear flow. Although the m-Ny 6/VB blend meets the criterion for droplet deformation and the morphology accordingly shows fine fibrils and/or nodular ellipsoids, no significant improvement was observed in the mechanical properties over those of the Ny 6/VB blends due to poor adhesion at the interface and incomplete fibrillation in shear flow.

■ EXPERIMENTAL SECTION

An aromatic liquid crystalline poly(ester amide), Vectra B950 (VB), which is a copolymer based on 6-hydroxy-2 naphthoic acid (60%), terephthalic acid (20%), and aminophenol (20%) produced by Hoechst Celanese Co. was used as the TLCP. It has a high nematic transition temperature of 283 °C. Neat Ny 6 resin (KN 171 from Kolon Co. (Korea)) and modified Ny 6 (m-Ny 6) obtained with the procedure developed in our previous study were used as the matrix polymer.26 The method we used to prepare the high viscosity Ny 6 (m-Ny 6) consists of a simple reactive extrusion process in the presence of a linking agent. The molar mass of m-Ny 6 was increased by reacting it with a linking agent in a twin-screw extruder, which first results in linear connections between two Ny 6 chains that double its molar mass, and then later generates 3- and/or 4-armed polymers in a controllable manner.26

The pellets of neat Ny 6 or m-Ny 6 and Vectra B were dried in a vacuum oven at 60 and 120 °C, respectively, for at least 24 h before use. The TLCP content was maintained at 20 wt % because the fibril aspect ratio of the composite passes through a maximum near this content.13 Dried pellets of VB, and modified Ny 6 (m-Ny 6) or Ny 6 were mixed in a container before blending in the extruder. The VB/Ny 6 (or m-Ny 6) mixture was blended in a twin-screw extruder (PRISM) at a screw rotation speed that could be varied to control the shear

![Figure 4. Mechanical properties (tensile modulus and tensile strength) of extruded strands.](image-url)
rate. Extrude drawing was not performed. The extrusion temperatures of the feeding zone/transporting zone/melting zone/die were set at 140/290/290 °C, respectively. All of the extrudates were found to have the same smooth shape (cylindrical rods) as the nylon 6 extrudates, which implies that no structural variations such as gelation (or cross-linking) occur during the processing. 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 tensile mode was used.

The rheological properties were measured at 290 °C with a UDS200 (Physica, Germany) rheometer on which a 25 mm diameter cone and plate were mounted. The frequency range was set at 0.1–500 rad/s, and the applied strain was 5%. Before the measurement, the samples were prepared with a compression molder at 280 °C. The measurements were carried out under a nitrogen atmosphere. Rheological measurement was also carried out using a capillary viscometer RH7 (Rosand, England) at 290 °C. The capillary was 1 mm in diameter and had a length to diameter ratio of 32.

Scanning electron microscopy (SEM) observations of the composite samples were performed on a JEOL JSM7600F model. Fractured surfaces of the blends were prepared by a 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. Testing of the gold in an SPI sputter coater. The morphology was determined using an Instron Universal Testing Machine (model 4204) at a frequency of 1 Hz. A single cantilever clamping geometry in the tensile mode was used.

REFERENCES

1. Donald, A.; Windle, A.; Hanna, S. Processing and Applications of Structural Liquid Crystalline Polymers. In Liquid Crystalline Polymers; Cambridge University Press: Cambridge, 2006; Chapter 6, Vol. 2006, pp 439–503.

2. de Kort, G. W.; Rastogi, S.; Wiles, C. Controlling processing, morphology, and mechanical performance in blends of polyactide and thermotropic polyesters. Macromolecules 2019, 52, 6005–6017.

3. Liquid Crystalline Polymers: Processing and Applications; Thakur, V. K.; Kessler, M. R., Eds.; Springer International: Switzerland, 2015; Vol. 2, 69–102.

4. Mossety-Leszcak, B.; Wlodarska, M. Liquid Crystalline Organic Compounds and Polymers as Materials of the XXI century: From Synthesis To Applications; Iwan, A.; Schab-Balcerzak, E., Eds.; Transworld Research Network: Kerala, India, 2011; pp 129–152.

5. HE, J.; ZHANG, J. Thermotropic Liquid Crystal Polymers: Thin Polymerization, Characterization, Blends, and Applications; Chug, T. S., Ed.; Technomic Publishing Co. Inc: Lancaster, PA, 2001; Chapter 7, pp 183–218.

6. La Mantia, F. P. Thermotropic Liquid Crystal Polymer Blends; La Mantia, F. R., Ed.; Technomic Publishing: Lancaster, PA, 1993; pp 59–156.

7. Oh, K. H.; Kim, H.; Seo, Y. Liquid Crystalline Polymers; Mittal, V., Ed.; Central West Publishing: Orange (Australia), 2018; Chapter 6, pp 181–204.

8. Seo, Y.; Hong, S. M.; Kim, K. U. 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). Macromolecules 1997, 30, 2978–2988.

9. Seo, Y.; Kim, B.; Kim, K. U. Structure development during flow of ternary blends of a polyamide (Nylon 46), a thermotropic liquid crystalline polymer (poly(ester amide)) and a functionalized polypropylene. Polymer 1999, 40, 4483–4492.

10. Seo, Y.; Kim, B.; Kwak, S.; Kim, K. U.; Kim, J. Morphology and properties of compatibilized ternary blends (nylon 6/a thermotropic liquid crystalline polymer/a functionalized polypropylene) processed under different conditions. Polymer 1999, 40, 4441–4450.

11. Seo, Y. Deformation of thermotropic liquid crystalline polymer droplets dispersed in a polyamide. Macromol. Symp. 1999, 147, 201–208.

12. Seo, Y.; Hwang, S. S.; Hong, S. M.; Park, T. S.; Kim, K. U. Effect of die geometry on the structural development of a thermotropic liquid crystalline polymer in a thermoplastic elastomer matrix. Polym. Eng. Sci. 1995, 35, 1621–1628.

13. Lee, S. M.; Hong, S. M.; Seo, Y.; Park, T. S.; Hwang, S. S.; Kim, K. U.; Lee, J. Characterization and processing of blends of poly(ether imide) with thermotropic liquid crystalline polymer. Polymer 1994, 35, 519–531.

14. Seo, Y.; Hong, S. M.; Hwang, S. S.; Park, T. S.; Kim, K. U.; Lee, S. M.; Lee, J. Compatibilizing effect of a poly(ester imide) on the properties of the blends of poly(ether imide) and a thermotropic liquid crystalline polymer: 1. Compatibilizer synthesis and thermal and rheological properties of the in situ composite system. Polymer 1995, 36, 516–524.

15. Seo, Y.; Hong, S. M.; Hwang, S. S.; Park, T. S.; Kim, K. U.; Lee, S. M.; Lee, J. Compatibilizing effect of a poly(ester imide) on the properties of the blends of poly(ether imide) and a thermotropic liquid crystalline polymer: 2. Morphology and mechanical properties of the in situ composite system. Polymer 1995, 36, 525–534.

16. Seo, Y. Liquid Crystalline Polymer Composites-Preparation and Properties. In Handbook of Engineering Polymeric Materials; Cheremisinoff, N. P., Ed.; Marcel Dekker: New York, 1997; Chapter 38, pp 585–600.

17. Gao, P.; Mckley, M. R.; Zhao, D. F. The deformation and break-up of thermotropic co-polyester droplets in a molten polypropylene matrix subjecting to oscillatory simple shear and entry. J. Non-Newtonian Fluid Mech. 1999, 80, 199–216.
(18) Kernick, W.; Wagner, N. J. The role of liquid-crystalline polymer rheology on the evolving morphology of immiscible blends containing liquid-crystalline polymers. *J. Rheol.* **1999**, *43*, 521–550.

(19) Heino, M. T.; Hietaja, P. T.; Vainio, T. P.; Seppälä, J. V. Effect of viscosity ratio and processing conditions on the morphology of blends of liquid crystalline polymer and polypropylene”. *J. Appl. Polym. Sci.* **1994**, *51*, 259–270.

(20) Grace, H. P. Dispersion phenomena in high viscosity immiscible fluid systems and application of static mixers as dispersion devices in such systems. *Chem. Eng. Commun.* **1982**, *14*, 225–277.

(21) Huneault, M. A.; Shi, H.; Utracki, L. A. Development of polymer blend morphology during compounding in a twin-screw extruder. Part IV: A new computational model With coalescence. *Polym. Eng. Sci.* **1995**, *35*, 115–127.

(22) Delaby, J.; Ernst, B.; Germain, Y.; Muller, R. Droplet deformation in polymer blends during uniaxial elongational flow: influence of viscosity ratio for large capillary numbers. *J. Rheol.* **1994**, *38*, 1705–1720.

(23) Kirchberger, A.; Münstedt, H. Droplet deformation under extensional flow in immiscible and partially miscible polymer blends based on poly(styrene-co-acrylonitrile). *J. Rheol.* **2010**, *54*, 687–704.

(24) Seo, Y.; Kim, H.; Kim, Y.; Rhee, H. Effect of a compatibilizer on the structural development of a thermotropic liquid crystalline polymer/polystyrene blend. *Polym. Eng. Sci.* **2002**, *42*, 951–960.

(25) Chiou, Y.; Chang, D.; Chang, F. In situ compatibility of polystyrene and liquid crystalline polymer blends. *Polymer* **1996**, *37*, 5653–5660.

(26) Seo, Y. P.; Seo, Y. Effect of molecular structure change on the melt rheological properties of a polyamide (Nylon 6). *ACS Omega* **2018**, *3*, 16549–16555.

(27) Kim, H.; Oh, K.; Seo, Y. Rheological and mechanical properties of a novel polyamide 6 synthesized by anionic polymerization of ε-Caprolactam in a twin-screw extruder. *Polymer* **2019**, *177*, 196–201.

(28) Oh, K.; Kim, H.; Seo, Y. Effect of diamine addition on structural features and physical properties of polyamide 6 synthesized by anionic ring-opening polymerization of ε-Caprolactam. *ACS Omega* **2019**, *4*, 17117–17124.

(29) Oh, K.; Kim, H.; Seo, Y. Long-living anions could dramatically change the overall physical properties of a polyamide (Nylon 6) synthesized by a novel process. *ACS Omega* **2020**, *5*, 17463–17470.

(30) Steller, R. Determination of the first normal stress difference from viscometric data for shear flows of polymer liquids. *Rheol. Acta* **2016**, *55*, 649–656.

(31) Wagner, M. H. Prediction of primary normal stress difference from shear viscosity data using a single integral constitutive equation. *Rheol. Acta* **1977**, *16*, 43–50.

(32) Gotsis, A. D.; Baird, D. G. Rheological properties of liquid crystalline copolyester melts. II. Comparison of capillary and rotary rheometer results. *J. Rheol.* **1985**, *29*, 539–556.

(33) Baek, S. G.; Magda, J. J.; Larson, R. G. Rheological differences among liquid-crystalline polymers. I. The first and second normal stress differences of PBG solutions. *J. Rheol.* **1993**, *37*, 1201–1224.

(34) Narimissa, E.; Rahman, A.; Gupta, R. K.; Kao, N.; Bhattacharya, S. N. Anomalous first normal stress difference behavior of polymer nanocomposites and liquid crystalline polymer composites. *Polym. Eng. Sci.* **2014**, *54*, 1300–1312.

(35) O’Donnell, H. J.; Baird, D. G. In situ reinforcement of polypropylene with liquid-crystalline polymers: effect of maleic anhydride-grafted polypropylene. *Polymer* **1995**, *36*, 3113–3126.

(36) Son, Y. Measurement of interfacial tension between polyamide-6 and poly(styrene-co-acrylonitrile) by breaking thread method. *Polymer* **2001**, *42*, 1287–1291.

(37) Ma, K.; Chung, T.; Good, R. J. Surface energy of thermotropic liquid crystalline polyesters and polystyramide. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 2327–2337.

(38) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982; p 279.

(39) Ma, K.; Chung, T. Thermotropic Liquid Crystal Polymers: Thin Film Polymerization, Characterization, Blends and Application; Chung, T., Ed.; Technomic Publishing Co. Inc: Lancaster, PA, 2001; Chapter 6, pp 157–182.

(40) Zhang, X.; Liu, J.; Wang, Y.; Wu, W. Effect of polyamide 6 on the morphology and electrical conductivity of carbon black-filled polypropylene composites. *R. Soc. open sci.* **2017**, *4*, 170769.

(41) Lee, H. S.; Denn, M. M. Rheology of a viscoelastic emulsion with a liquid crystalline polymer dispersed phase. *J. Rheol.* **1999**, *43*, 1583–1598.

(42) Graebling, D.; Muller, R.; Paliarne, J. F. Linear viscoelastic behavior of some incompatible polymer blends in the melt. Interpretation of data with a model of emulsion of viscoelastic liquids. *Macromolecules* **1993**, *26*, 320–329.

(43) Zhao, C.; Rondeau, E.; Cooper-White, J. J.; Middelberg, A. P. J. 2012, Microfluidic elucidation of the effects of interfacial rheology on droplet deformation. *Ind. Eng. Chem. Res.* **2012**, *51*, 2021–2029.