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Deformation of thermotropic liquid crystalline polymer droplets dispersed in a polyamide

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SUMMARY: The deformation of dispersed droplets of a thermotropic liquid crystalline polymer in a polyamide (nylon 6) matrix was studied by morphological observation. An immiscible binary blend and compatibilized ternary blends were studied. For the uncompatibilized blend, the morphology of the blends was that of a typical immiscible blend showing poor adhesion and no deformation of the dispersed phase. For the compatibilized blend, deformation of the dispersed TLCP phase was observed even if the viscosity of the matrix was lower than that of the TLCP phase. Compatibilizer addition improved the interfacial adhesion, hence enabled TLCP droplets to be deformed. A simple mechanism for the deformation of TLCP droplets was presented considering characteristic rheological properties of the TLCP melt.

Introduction

Thermotropic liquid crystalline polymers (TLCPs) have been intensively investigated as “blend additives” because of the admirable qualities imparted to a given host resin, including impressive rheological (low melt viscosity) and mechanical (high modulus and strength) properties which are ascribed to their spontaneous molecular orientation1,2). Upon melting, TLCPs give rise to highly organized liquid phases (mesophases), which tend to spontaneously pack parallel one to 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 the so-called in-situ composites. These have attracted a great deal of interest because they can solve some problems that arise during the processing of conventional fiber-reinforced composites1). Thus, the morphology development of the TLCP phase in thermoplastic matrices is decisively important since it affects the final product performance. Consequently, it is important to understand how the break-up phenomenon of the dispersed TLCP droplet proceeds in thermoplastic polymer melts.

In polymer blend research, the drop break-up phenomena have been extensively studied for Newtonian fluids and viscoelastic fluids3-6). Although for TLCP droplets, there have been innumerable experimental studies about their morphological development, theoretical analysis has seldom been done due to their anomalous rheological properties such as negative first

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normal stress difference and extrudate shrinkage rather than swelling[7-9]. For a Newtonian droplet in the immiscible blend, the deformation is possible in pure extensional flow at all viscosity ratios, but it is impossible in pure shear flow if the viscosity ratio of the droplet to matrix phase is above 4[10]. Hence, it is easy to predict that the deformation of a TLCP droplet would be very difficult in polyamide melts, one of the most widely used engineering plastics, because of their immiscibility with TLCPs and their viscosities lower than those of TLCPs at the processing temperature and shear rate[11,12]. Previous studies showed that no deformation of TLCP droplets occurred at all in pure shear flow in spite of high shear rates[13,14]. Micrographs of the binary blends showed that the TLCP was present in a droplet structure and few droplet deformations into elongated shapes could be observed, even with the high draw ratio of 100[14]. In another study, just a few deformations of TLCP droplets (polyester, Vectra A 950) in nylon 6 could be observed if the shear rate was very high (2700 s^{-1}), where the viscosity of the TLCP approaches that of nylon 6 (the ratio was about 4) [15].

Interfacial adhesion is quite poor between nylon 6 and the TLCP phase due to the immiscibility. One of the well-known techniques frequently used in polymer industry to provide compatibility and thus to improve the interfacial adhesion is the addition of a compatibilizer acting at the interface reducing the interfacial tension and improving the interfacial adhesion, which can transfer the applied stress more easily to the dispersed TLCP phase[16]. In this study, we investigate the mechanism of the TLCP droplet deformation in the nylon 6 matrix and the effect of the addition of a compatibilizer.

Experimental

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.). Nylon 6 was supplied by Kolon Co. (KN171, Korea). Nylon 6 and Vectra B950 are immiscible. 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.-%. Maleic-anhydride-grafted polypropylene (MA-PP) was obtained from Honam Petroleum Co. (Korea), its maleic anhydride content being 1 %. In this study, 2 wt.-% of compatibilizer was used because excessive amounts of compatibilizer caused coalescence and coagulation of the dispersed phase and also formed a separate phase[12,17].

Blending and measurements Pellets of nylon 6 and VB were dried in a vacuum oven at 120 °C and MA-PP and MA-EPDM were dried in a vacuum oven at 100 and 60 °C, respectively, for at least 24 h before use. The TLCP content was maintained at 20 wt.-%. They were premixed in a container before blending. Blending was carried out in a 42-mm Brabender twin-screw extruder (AEV651). The extrusion temperatures of the feeding zone/transporting zone/melting zone/die were set as 140/290/290/290 °C, respectively. Differential scanning calorimetry (DSC) studies of thermal properties were performed on a Du Pont 910 DSC controlled by a 9900 thermal analyzer. Both the heating and the cooling rates were 10 °C/min, and the materials were scanned from 25 to 350 °C. Every thermogram was repeated at least twice, using different samples to verify the reproducibility. 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 microscopy (SEM) observations of composite samples were performed on a Hitachi S-2500 model. The samples fractured in the liquid nitrogen were coated with gold to provide electrical conductance. Rheological measurements were carried out using a capillary viscometer RH7 (Rosand, England) at 290 °C. The capillary was 1 mm in diameter and the length-to-diameter ratio was 32. Testing of 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 seven measurements.

Results and Discussion

Addition of MA-grafted PP and EPDM to the binary blend brings about two effects. The first is a chemical reaction between maleic anhydride group and amino groups of nylon 6 and VB to form a kind of graft copolymer. The other is providing an interaction such as hydrogen bonding. We speculate that both effects (hydrogen bonding and graft copolymer interaction) may contribute to the compatibilizing action. According to our Raman spectra analysis, Soxhlet extracts of ternary blends show traces of aromatic and ester peaks whereas no such peaks were observed with the binary blend extracts18). This shows some chemical reactions occurring between maleic anhydride group and VB. We proposed some possible reactions19). The produced graft copolymers act as compatibilizers at the interface.

Thermal properties reveal the change in the nature of the blend with an addition of the compatibilizer. Transitions of the binary and ternary blends as resolved by DMTA are shown in Fig. 1. In the binary blend, two distinct maximum tan δ peaks show that VB and nylon 6 are immiscible. These two peaks shift to each other in the ternary blend, which means that they become more compatible. This is also checked by DSC measurements (Fig. 2). Two glass transition temperatures (T_gs) and two melting endotherms evidently show that they are immiscible in the binary blend. The difference between the two T_gs becomes smaller with an addition of the compatibilizer.

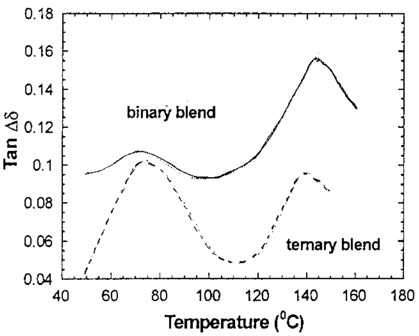

Fig. 1 Normalized tan Δδ versus temperature for binary blend (nylon 6/VB) and ternary blend (nylon 6/VB/MA-PP)

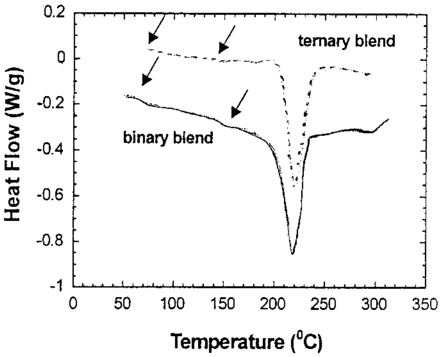

Fig. 2 DSC thermograms of binary blend (nylon 6/VB) (—) and ternary blend (nylon 6/VB/MA-PP) (- - - -)

The morphologies of the binary (nylon 6/VB) and ternary (nylon 6/VB/compatibilizer) blends are shown in Figs. 3 and 4.

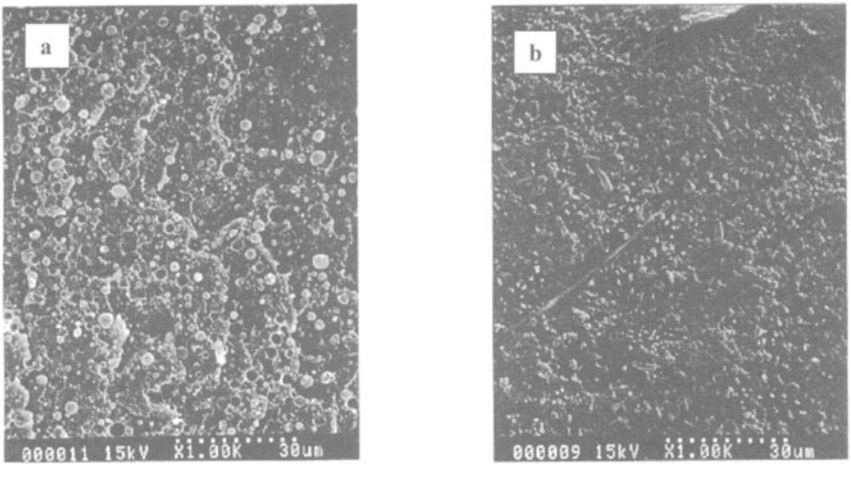

Fig. 3 SEM photographs of fractured surfaces: (a) binary blend (nylon 6/VB), (b) ternary blend (nylon 6/VB/MA-PP)

In the binary blend, the TLCP domains are mostly spherical and large because of immiscibility, leading to poor dispersion. The ternary blend surface shows a different morphology. The droplet size is noticeably reduced, some droplets being deformed into fibrous shapes. The draw ratio was almost unity, which means that almost no drawing occurred. Since the shear rate was at a low level (about 40 s^{-1}), the viscosity of nylon 6 was much lower than that of VB[16] (Fig. 5). The enlarged fractured surfaces of the binary and ternary blends are shown in Fig. 4. MA-EPDM-added blends show a similar morphology.

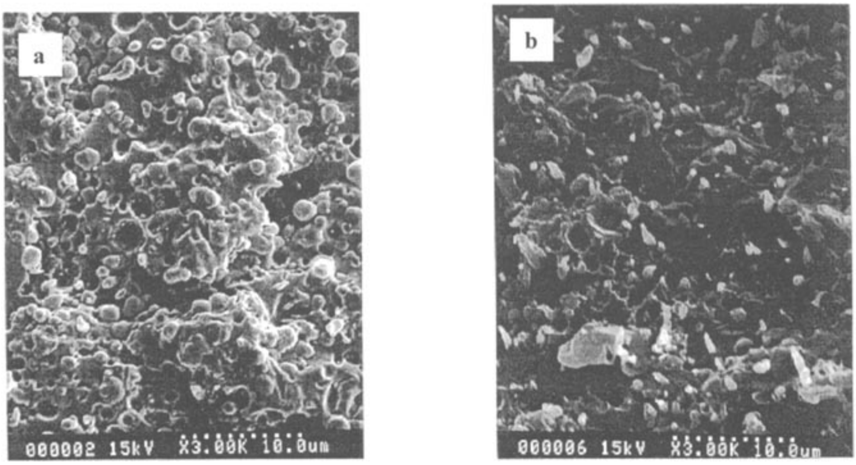

Fig. 4 Enlarged SEM pictures: (a) binary blend (nylon 6/VB), (b) ternary blend (nylon 6/ VB/MA-PP)

Finer dispersion and better adhesion clearly demonstrate the compatibilizer effect. The compatibilizer brings about not only a reduction in the interfacial tension but also a better adhesion, which induces effective stress transfer through the interface. The final shape of the dispersed phase results from a dynamic equilibrium between the force from the matrix (shear stress and the elasticity of the matrix) and the resisting force (elasticity of the droplet and interfacial tension). This can be expressed by the following equations:

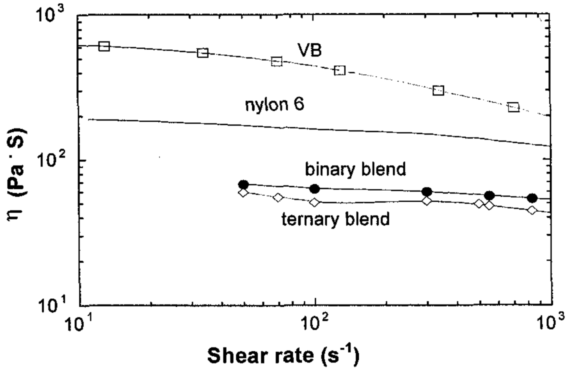

Fig. 5 Viscosity-shear rate relationship of nylon 6, VB, binary blend (nylon 6/VB) and ternary blend (nylon 6/VB/MA-PP)

$$\eta_m\gamma + N_1^m = \Gamma/r + N_1^d \tag{1a}$$

$$\eta_m\gamma + (N_1^m - N_1^d) = \Gamma/r \tag{1b}$$

where η_m is the viscosity of the matrix (nylon 6), γ the shear rate, Γ the interfacial tension, r the radius of the droplet, N_1^m and N_1^d are the first normal stresses of the matrix and droplet. Hence, we can define a new capillary number,

$$Ca_{NEW} = \eta_m\gamma / (\Gamma/r) + (N_1^m - N_1^d)/(\Gamma/r) = Ca + Ca_E \tag{2}$$

where $Ca_E = (N_1^m - N_1^d) / (\Gamma/r)$ is the elastic capillary number which is the ratio of the elastic force on the droplet to the interfacial tension. For a normal thermoplastic polymer melt, high shear stress from the matrix is needed to provide more stress for the deformation if the elasticity is not considered. For TLCPs, the first normal stress may show a different behavior than with normal thermoplastics[8,9)]. The first normal stress of the matrix is close to that of VB at the shear rate of this study[20,21)]. Depending on the first normal stress values, the elastic force can be beneficial to droplet deformation. This is an intriguing fact that needs further study in the future. Considering all these facts, the deformation process of a TLCP droplet can be described as follows: (1) without a compatibilizer, the dispersed phase hardly deforms due to the immiscibility of the two phases. Slippage on the surface causes the droplet tumbling in the shear flow[8,22)]; (2) when the compatibilizer is added, it locates at the interface and prevents the droplet from tumbling due to adhesion at the interface[17,18)] (Fig. 4). Better adhesion provides a more effective stress transfer to the droplet, and the difference of the first normal stresses for the matrix and the droplet is beneficial to the droplet deformation depending on their relative values. To conclude, the effect of the compatibilizer is, first, to reduce the interfacial tension and hence to decrease the resisting force, which has the same effect as increasing the capillary number value. Second, it provides efficient stress transfer by better adhesion at the interface. Third, better adhesion prevents the TLCP droplet from tumbling, hence more energy is used for the droplet deformation.

Deformation of the dispersed phase brings about an improvement of mechanical properties. MA-PP addition also brings about the extrudate stability, which enables the drawing of the extrudate with uniform diameter. For the binary blend, extruded strands could not be obtained due to the surface instability. More deformation occurs with the extension.

Figure 6 shows the SEM pictures of the extended ternary blend where more deformed shapes can be seen. Though MA-EPDM-added ternary blend showed a better morphology and finer fibrils, drawing was not applicable owing to the surface instability when extended (possibly due to crosslinking and degradation reactions)[23)].

Fig. 6 SEM photograph of fractured surface when the draw ratio was 4

In spite of the enhanced modulus, tensile strength of the binary blend was lower than that of nylon 6 because of a loss of ductility of the matrix. On the other hand, the ternary blend has a higher modulus and better extension due to better adhesion, and hence better mechanical properties[23)]. Mechanical properties of the ternary blend are enhanced with the draw ratio defined as the diameter of the extrudate to that of the die exit (Fig. 7).

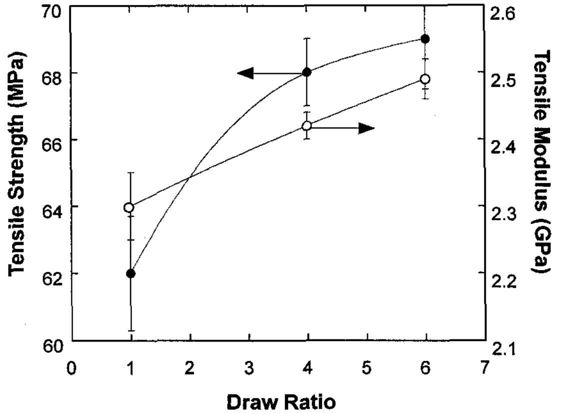

Fig. 7 Tensile properties of ternary blends versus the draw ratio (the line is a guide for eyes)

Conclusions

Deformation mechanism of the TLCP droplet was investigated by the compatibility test and morphological observation. It was revealed that the deformation of TLCP droplets was possible even if the viscosity of the matrix (nylon 6) was lower than that of TCLP melts provided that an appropriate amount of the compatibilizer was added. Addition of the compatibilizer changed the immiscible blend to become more compatible. The compatibilizer reduces the interfacial tension, improves the interfacial adhesion, hence providing more efficient energy transfer, prevents the TLCP droplet from tumbling and enables using more energy for the deformation. The elasticity of the matrix and dispersed phase can be beneficial to the droplet deformation depending on their relative values, which needs further study. Addition of the compatibilizer brought about the extrudate surface stability under extension, hence higher deformation of TLCP droplets. Extended extrudates have enhanced mechanical properties due to the higher deformation. More details will be reported in the future.[18)]

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