TLCP Ternary Blends for *In Situ* Composites: *In Situ* Compatibilizer

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ABSTRACT: It is experimentally shown that an *in situ* compatibilizer for the thermotropic liquid crystalline polymer blend can be generated in the extrusion process and that the compatibilizing action by the maleic anhydride-attached ethylene–propylene–diene terpolymer (MA–EPDM) in the blend of nylon46 and a thermotropic liquid crystalline polymer (polyesteramide) is due to the graft copolymer produced by the chemical reactions between the MA group of EPDM and functional groups of nylon46 and polyesteramide. This is apparent from the ^{1}H-NMR spectra and TGA thermograms. Produced compatibilizers act at the interface to enable better adhesion, better stress transfer, and, hence, deformation of the dispersed phase into fine fibril shape even when the viscosity of the matrix is lower than that of the dispersed phase and the draw ratio is quite low (ca. 1.6). © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1589–1595, 1998

Key words: chemical reaction; MA-grafted EPDM; polyesteramide; ternary blend; thermotropic liquid crystalline polymer blend

INTRODUCTION

There have been innumerable studies of *in situ* composites and thermotropic liquid crystalline polymer (TLCP) blends with commercial thermoplastics.[1–3] To obtain a self-reinforcing fibril structure, the rheological properties of TLCP blends should be carefully controlled. Not all TLCP blends with commercial thermoplastics can produce *in situ* composites. Fibrils of the TLCP phase are formed after the die exit as a result of the extensional force in the flow direction. For special engineering plastics such as polyetherimide, polyarylates, polyphenylene sulfide, or polymers produced by radical polymerization that can retain high viscosities at a high processing temperature (at least higher than the crystal–nematic transition temperature), extension is readily applicable. On the other hand, the viscosities of polymers produced by condensation, such as polyamides and polyesters, rapidly decrease with temperature and are two or three orders lower than those of TLCPs at the processing temperature and shear rates. Hence, extension is not readily applicable to these polymers, whereas it is definitely needed to produce *in situ* composites. Following Taylor's theory, at least qualitatively, La Mantia and Valenza studied the morphologies of TLCP blends which were determined by the particular viscosity ratios.[4] They insisted that large TLCP particles are formed when the viscosity of TLCP is much greater than that of the matrices; the fibrillation morphology occurs only when the viscosity of the thermoplastic matrix is much greater than that of TLCPs. Following their argument, it is expected that fine dispersion and

fibril formation of TLCP will be very difficult in polyamides and polyester matrices, two of the most widely used engineering plastics, because of their low viscosities at the processing temperature and shear rates. The lack of miscibility between TLCPs and these matrices also invokes poor adhesion at the interface, poor dispersion of TLCP droplets, and deterioration of some mechanical properties.

Most of the thermoplastics studied thus far are immiscible or incompatible with TLCPs.[5] The reinforcing effect is less than that obtained from the miscible system. One way to provide compatibility in *in situ* composites is to add a compatibilizer.[6] Ternary blends present an attractive approach to the development of reinforced systems. Compatibilizing agents are generally block or graft copolymers possessing segments with chemical structures or solubility parameters that are similar to those of the polymers being blended.[6] Acting as polymeric surfactants, they reduce the interfacial tension, thus promoting interfacial adhesion and inducing more uniform and finer dispersion of the TLCP phase. Compatibilization of thermoplastic blends with TLCPs was attempted very recently.[6–9]

Recently, we experimentally showed that a fine fibril structure of a TLCP can be developed in a shear flow field of a thermotropic matrix even though the viscosity of the matrix is lower than that of the TLCP.[7,9,10] This is believed to result from the *in situ* compatibilizing action of a maleic anhydride-grafted elastomer (ethylene–propylene–diene terpolymer; MA–EPDM). In our earlier works, we ascribed the compatibilizing action to the compatibilizer produced in the blending process by the chemical reaction between the MA groups and some (end) functional groups of TLCP.[7,9,10] This conclusion was based on the experimental results of FT Raman spectroscopy and differential scanning calorimetry measurements. On the other hand, others insisted, based on their infrared spectroscopy data, that the interaction was the result of secondary interaction such as a hydrogen bonding between the MA group and the TLCP.[8] This different point of view merits further detailed investigation, since the compatibilizing effect would be different for each different action. This is also a key factor in understanding the ternary system's reinforcement and improvement of its mechanical properties. Here, we clarify the issue based on ^{1}H-NMR spectrum and TGA analyses.

EXPERIMENTAL

The materials are all commercial polymers: an aromatic liquid crystalline polyesteramide, Vectra B950 (Hoechst Celanese Co., U.S.A.), a maleic anhydride-grafted ethylene–propylene–diene terpolymer (MA–EPDM, Royaltuf 465 from Uniroyal Chemical Co., U.S.A.), and a nylon46 (C2000NS, Teijin Co., Japan). Nylon46 was used as the matrix for the blend. The pellets of the nylon46 and Vectra B (VB) 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.[7] 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 ratios (DR), defined as the diameter at the die exit to far downstream. A high draw ratio was not applicable because of the instability of the 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.

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 single cantilever clamping geometry in the tensile mode was used. Thermogravimetric analysis (TGA) was carried out with a DuPont TGA 960 equipped with a DuPont 2000 data analyzer. The TGA experiments were performed in a dynamic mode at 10°C/min up to 700°C, which covers the temperature range of the degradation process of the materials. ^{1}H-NMR measurements were carried out on a Varian-600 instrument at 600 MHz. CDCl$_3$ was used as a solvent for solutions of the neat polymers and the blend.

RESULTS AND DISCUSSION

Prior to the analysis of the ternary blends, binary blends of nylon46 and VB were studied. The glass transition temperature, T_g, was evaluated as the maximum of tan δ in the DMTA thermograms. The T_g of nylon46 is 78°C and that of VB is 145°C.

Figure 1 (a) Normalized tan δ versus temperature for homopolymers and a binary blend (nylon46 : VB = 75 : 25): (□) Nylon46; (○) Vectra B950; (◆) binary blend. (b) Normalized tan δ versus temperature for binary and ternary blends (nylon46 : VB : MA–EPDM = 73 : 25 : 2): (◆) binary blend; (□) ternary blend.

The maximum of tan δ from the DMTA is shown in Figure 1. The lack of change of the T_g indicates that they are immiscible with each other. The maximum of tan δ of the ternary blends, including 2% of MA–EPDM, is also shown in Figure 1. The T_g of nylon46 and VB shifted toward each other. The shift in the T_g indicates that nylon46 and VB become more compatible in the ternary blend. Depending on the amount of MA–EPDM, the elastomer forms its own separate phase and/or concentrates at the interface between nylon46 and TLCP.[7]

Degradation tests preformed by TGA further confirm the compatibility of the blends. These tests also allow the possibility of analyzing the effect of the interaction between MA–EPDM and

VB during the degradation reaction. The results of the TGA analysis are presented in Figure 2. Nylon46 degradation shows a peak at 424°C. A peak in VB degradation appears at about 493°C. The degradation behavior of the nylon46/VB/EPDM(68/25/7 wt %) ternary blend is characterized by a major peak of the weight loss derivative signal at 421°C with a small shoulder from nylon46 [Fig. 2(c)]. On the other hand, when the test is conducted on the binary blend of nylon46/VB (75/25 wt %), a double peak characteristic of two different reactions is obtained [Fig. 2(d)]. Another peak at 490°C is ascribed to that from the VB. The presence of only one peak in the degradation of the ternary blend shows the uniformity of the blend composition due to the improved compatibility of both polymers.[11] If the interaction between MA–EPDM and VB is solely the result of hydrogen bonding as others insist,[8] the binary blend should exhibit similar degradation behavior. However, the existence of the peak from VB manifests that there are other interactions beside the hydrogen bonding that induces the compatibility between the nylon46 and VB.

The NMR spectra recorded for the binary blend of MA–EPDM and VB in a 50 : 50 weight ratio is shown in Figure 3. For clarity, we show only the characteristic range of aromatic hydrogens. VB is nonsoluble in $CDCl_3$. No peaks other than one from the solvent is observable between 7 and 8 ppm for the VB spectrum. This is also true for the MA–EPDM solution. On the other hand, the blend solution shows many peaks in this range. They agree with those calculated peak positions for VB. This shows that some kind of graft copolymers were formed and dissolved in $CDCl_3$. To be dissolved in $CDCl_3$, the mol fraction of VB in the graft copolymer would be low because VB itself does not dissolve. Since there is no aromatic moiety in the neat MA–EPDM polymer, we must believe that some grafting reactions have occurred. It may be conjectured that the reacted VB moiety would be from the VB formed by thermal depolymerization. However, the binary blending of VB and MA–EPDM was performed at 300°C. As shown in Figure 2(b), VB is not thermally depolymerized at all. Hence, it should be from VB chains.

In our previous study,[10] we suggested that the chemical reactions would be possible between MA–EPDM and VB shown in Scheme 1 and Scheme 2. Reaction 2 (Scheme 2) is more probable since a more vigorous reaction occurs between amines and MA. However, its exact mechanism

Figure 2 TGA thermograms of (a) nylon46 neat polymer, (b) VB neat polymer, (c) ternary blend of nylon46/VB/MA–EPDM (68 : 25 : 7), and (d) binary mixture (nylon46/VB = 75 : 25). Straight lines are weight-change curves and dashed lines are the derivative curves of the weight change with respect to temperature.

cannot be ascertained here because the amide and ester group positions overlap with those of the VB moiety.

It is clear from these results that some chemical reactions between VB and MA–EPDM have occurred to produce a graft copolymer. If the compatibilizing action occurs solely because of hydrogen bonding, the binary blend of nylon46 and VB, both of which have strong hydrogen bonding, should be compatible. However, they are not compatible at all, as verified in our previous experiments[7] and clearly shown in Figures 1, 2(d), and 4. The amine end groups of nylon46 and VB may react strongly with the MA group to produce a kind of (comb shape) graft copolymer, having different branches which would act as the compatibilizer at the interface.[7,12] They provide good adhesion at the interface and thereby good stress transfer which enables deformation of the dis-

persed TLCP phase into fine fibrils as shown in Figure 4. It is remarkable that fibrils are almost everywhere [Fig. 4(b)], although the draw ratio, defined as the diameter of the strand to that of die exit, is ca. 1.6, while no deformation can be seen in the binary blend in spite of a higher draw ratio of 4 [Fig. 4(a)]. The viscosity of the matrix (nylon46) was much lower than that of VB at the processing condition.[7] The processing shear rate was low (about 40 s^{-1}), where the viscosity of nylon46 is much lower than that of VB. As noted, a viscosity increase from the addition of MA–EPDM can be expected, but lower viscosity of the ternary blend than that of the pure components eliminates this possibility. As we reported in another study,[13] in explaining the occurrence of fibrillation, we can consider elongation at the center line. But the droplet phase does not deform as rapidly as does the continuous phase, when the

[REACTION 1]

Scheme 1

viscosity of the continuous phase is lower than that of dispersed phase. Hence, we can hardly expect any deformation in the dispersed phase.

La Mantia et al.[14] reported that they could not observe any elongated structure of the TLCP (VB) phase in the nylon6 matrix having a similar viscosity to our case at a very high shear rate of 1200 s^{-1}. However, the viscosity of the blend was lower than that of polymer matrix (nylon6), quite similar to the present case.[7,9,15] We believe that the graft copolymers produced in the processing by the chemical reaction between the anhydride group and amine groups of nylon46 and VB act at the interface to promote the improved adhesion at the interface, leading to better stress transfer to the dispersed phase. In the viscous flow field, with the assumption of the absence of an elongational field and a negligible primary normal stress difference (which is not clearly proven yet[16,17]), the

deformation of the dispersed droplets is a balancing process between the shear force imposed by the flow field and the interfacial tension (interfacial stress divided by the curvature of the droplet),[18,19] which are combined into a dimensionless group, the so-called capillary number, N_{Ca}. In the simple shear flow of Newtonian fluids, a dispersed droplet will be elongated if $N_{Ca} > 0.5$, indicating that the ratio of shear stress ($\eta_0\dot{\gamma}$) should be larger than half of the interfacial energy (σ/b), where $\dot{\gamma}$ is the shear rate; σ, the interfacial tension; b, the initial diameter of the droplet; and η_0, the viscosity of the suspending liquid. Until now, most studies of *in situ* composite preparation focused on the impartation of high shear stress to the dispersed phase for deformation. Hence, the easiest way to provide high shear stress is to increase the viscosity of the matrix, which demands the use of special engineering plastics or

[REACTION 2]

Scheme 2

Figure 3 ¹H-NMR spectra in CDCl₃ for a binary blend of VB and MA–EPDM (50 : 50 ratio).

additionally polymerized plastics having high melt viscosity. In spite of the poor adhesion at the interface, high shear stress enables the deformation of the dispersed phase. We can obtain the same effect if we can reduce the interfacial stress by a compatibilizing action. Too much compatibilizing activity will produce droplets too small to be deformed, but a mild compatibilizing action can reduce the interfacial tension slightly, thereby preventing the droplets from breaking up into very small droplets whose capillary number is below the critical value. Also, good adhesion at

the interface is as efficient as high viscosity in providing enough stress to deform the dispersed phase.[9] Without good adhesion and thus good stress transfer by the compatibilizer at the interface, this deformation is not possible at all [Fig. 4(b)].

CONCLUSIONS

The addition of MA–EPDM to the nylon46/VB blend induces enhanced adhesion, finer dispersion of the TLCP phase, and, hence, reduced interfacial tension, which are characteristics of compatibilized blends. The compatibility was observed from DMTA thermograms. It is obvious from the ¹H-NMR spectra and the TGA thermograms that the compatibilizing action between nylon46 and VB is ascribable to the compatibilizer produced by some chemical reactions between the MA groups attached to EPDM and the functional groups of VB rather than hydrogen bonding between VB and MA–EPDM. TGA thermograms also show the compatibility between nylon46 and VB. The compatibility endowed by the produced compatibilizer provides good adhesion at the interface and thereby good stress transfer to induce the deformation of the TLCP phase into fibrils as shown in the SEM photograph. This result has significance in that *in situ* composites can be prepared even when the viscosity of the matrix is lower than that of the dispersed phase and when the draw ratio is quite low.

Figure 4 SEM photographs of fractured surfaces of (a) nylon46/VB binary blend (nylon46 : VB = 75 : 25) at the draw ratio of ca. 4. (b) Nylon46/VB/MA–EPDM ternary blends (nylon46 : VB : MA–EPDM = 73 : 25 : 2) at the draw ratio of ca. 1.6.

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