Compatibilization of Nylon 6/Liquid Crystalline Polymer Blends with Three Types of Compatibilizers

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ABSTRACT: Polyblends of nylon 6 and liquid crystalline polymer (LCP) (Vectra A 950) are immiscible and highly incompatible, with resultant poor interfacial adhesion, large phase domains, and poor mechanical properties. In the present work, compatibilizing strategies are put forward for blends containing nylon and LCP. Effects of three types of compatibilizers, including ionomer Zn–sulfonated polystyrene (SPS), reactive copolymer styrene–maleic anhydride (SMA), functional grafted copolymers—polypropylene grafted glycidyl methacrylate (PP-g-GMA) and polypropylene grafted maleic anhydride (PP-g-MAH)—are studied in the aspects of morphology and dynamic mechanical behavior. The addition of compatibilizers decreases the domain size of the dispersed phase and results in improved interfacial adhesion between LCP and matrix. The compatibilization mechanism is discussed by way of diffuse reflectance Fourier transform spectroscopy (DRIFT), showing the reaction between compatibilizers and matrix nylon 6. Mechanical properties are improved by good interfacial adhesion. The contribution of SMA to mechanical properties is more obvious than that of Zn-SPS and grafted PPs used. The blending procedure is correlated with the improvement of mechanical properties by the addition of compatibilizer. Two-step blending is demonstrated as an optimum method to obtain composites with better mechanical properties as a result of a greater chance for LCP to contact the compatibilizer. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1452–1461, 2003

Key words: LCPs; nylon; blends; compatibilization

INTRODUCTION

Polymer blending is, in principle, one of the easiest and most flexible methods to obtain new polymer materials due to the effectively reduced cost and combined properties of neat component polymers for engineering purposes. Among the polymer blends, *in situ* composites containing a thermotropic liquid crystalline polymer (LCP) is one group of particular attractive materials, owing to their specific rheological and mechanical performance.[1–13] LCP can be processed and molded to structural parts of different shapes by means of conventional processing techniques for thermoplastics such as extrusion and injection molding. Due to the rigidity of molecular chains of LCPs, injection-molded parts of pure LCPs usually show strong anisotropy, evidenced by higher strength, and modulus along the flow direction and weak lateral adhesion transverse to the flow direction. LCPs are usually blended with other thermoplastics to reduce the anisotropy of the final products and widen their application areas. LCP tends to form fibrous structure in the shear or elongational field, due to its rigid rod-like macromolecular chain. Given the inherent strength and stiffness of the thermotropic LCP, these fibrous inclusions would then act as reinforcement, much like "meltable chopped glass fibers."

However, most thermoplastics are immiscible with LCPs, so is nylon 6 with an aromatic copolyester Vectra A950. The interfacial tension between the two polymers is extremely high because of the difference of molecular structure. In practice, the properties of polymer/LCP blends fall far short of expectations with respect to the rule of mixture. This short fall is largely the result of poor interfacial adhesion between the dispersed microfibrillar LCP phase and the thermoplastic matrix phase, which limits the wide application of *in situ* composites. So in recent years, more and more attention has been paid to the compatibilization in *in situ* composites. The compatibilization in *in situ* composites can be accomplished by introducing interactions between the two phases, including specific interactions, hydrogen bonding, chemical interaction, or a combination of these. Detailed methods of compatibilization of composites containing LCPs have been reviewed by He and his co-worker.[14]

In recent years, more attention has been focused on reactive compatibilization of immiscible polymer blends giving rise to *in situ* generation of copolymers. This is a very fast, easy and cost effective approach. The basic principle underlying reactive compatibiliza-

tion is that by making use of the functionalities present in one or more polymers, which can form graft or block copolymers *in situ* during melt processing. These *in situ* formed copolymers act as compatibilizers by reducing the interfacial tension and increasing the adhesion between the phases, and thereby allowing a finer dispersion and a more stable morphology. Many grafted copolymers with functional groups, offering specific interaction and/or chemical reaction with component polymers, have been used as compatibilizers.[15–26] Seo reported the compatibilization of ethylene–propylene–diene grafted maleic anhydride terpolymer (EPDM-g-MAH) in nylon/LCP and poly(butylene terephthalate) (PBT)/LCP blends.[19–25] It was shown that a fine fibril structure of LCP could be developed by a shear flow in a thermoplastic matrix, even though the viscosity of the matrix was lower than the dispersed LCP. It was believed that some chemical reactions between MAH groups and functional groups of the LCP were responsible for the compatibilization. Baird et al.[26–28] used a functionalized polypropylene, PP-g-MAH, as a compatibilizer for *in situ* composites based on polypropylene reinforced by different thermotropic LCPs such as Vectra A950, B950, and Rodrun LC-3000. They reported that the addition of PP-g-MAH resulted in a finer and uniform distribution of the dispersed LCP fibrils. As a consequence, a significant enhancement in both tensile modulus and strength was achieved. They suggested that compatibilization was realized by introducing some specific interactions such as hydrogen bonding. Chang et al.[29] used ethylene–glycidyl methacrylate copolymer (EGMA) as a reactive compatibilizer for PP and LCP (Vectra A 900). They reported that the compatibilized PP/LCP blends showed finer dispersed LCP domains and tended to shift the LCP fibrous structure near the skin region of the uncompatibilized blends into the droplet domains. Further, the PP crystallinity in the compatibilized PP/LCP blends was lower than that of the corresponding uncompatibilized blends. They believed this was due to the interference in the PP crystallization by the *in situ* formed EGMA-g-LCP copolymers. Zhang et al.[30] used maleic anhydride grafted polysulfone (PSF) to compatibilize PSF/LCP blends. The diffuse reflectance spectra (DRS)–Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) investigations showed that some chemical reactions had occurred between PSF-g-MAH and LCP components. The improvement of compatibility was also confirmed by dynamic mechanical (DMA) and thermogravimetric (TGA) analysis. Morphological observation showed that the addition of compatibilizer significantly reduced the size of the dispersed LCP phase.

The importance of specific interactions in achieving miscibility in polymer blends is well recognized. Interaction between an ionomer and a polar polymer can induce miscibility or improve compatibility. Ionic groups can cause several interactions with polar groups, including dipole–dipole, ion–dipole, ion–ion, and hydrogen bond. By using DSC and DMA, Dutta and co-workers[31] observed that Zn-SPS was miscible with LCP Vectra A950. Zn-SPS was shown to be an effective compatibilizer for blends of LCP with PA66 and polycarbonate. Zn-SPS was miscible with PA66 because of strong intermolecular attractive interactions between the sulfonate and amide group, while the ionomer was miscible with polycarbonate (PC) and the LCP, respectively, because of intramolecular repulsive interactions along the ionomer molecules. With tools of differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and FTIR, He et al.[32,33] found that SPS and its four salts were miscible with a copolyester of *p*-hydrobenzoic acid and poly(ethylene terephthalate), although their molecular structures and the rigidity of their molecular chains differed greatly from each other. And SPS was partially miscible with PSF, PC, and LCP. As a result, ternary blends of LCP/SPS/PSF, LCP/SPS/PC, and LCP/SPS/PEI had enhanced mechanical properties with acceptable processabilities.

Until now, though many researches on compatibilizers have been applied in *in situ* composites, only one compatibilizer was used in a specific system at one time and the effect of compatibilization was discussed accordingly. In fact, for one blend system, compatibility improvement can be achieved by several methods. For example, ionomers usually provide specific interactions, while reactive copolymers often provide functionalized groups, which can react with two components in a binary blend, and nonreactive compatibilizers usually possess segments structurally similar to or miscible with the blend constituents and act like an emulsifier at the interface in the blends. In the present work, three types of compatibilizers, including an ionomer (zinc salt of lightly sulfonated polystyrene, Zn-SPS), a reactive copolymer (styrene–maleic anhydride copolymer, SMA) and two functional grafted copolymers (polypropylene grafted glycidyl methacrylate, PP-g-GMA, and polypropylene grafted maleic anhydride, PP-g-MAH) are used in nylon 6/LCP *in situ* composites.

Compatibilization effects of these four compatibilizers are compared in the aspects of thermal behavior and morphology. The compatibilization mechanism is discussed and compatibilization effect is evaluated by mechanical tests.

EXPERIMENTAL

Materials

Polyamide 6, a widely used engineering plastic, was chosen as matrix polymer, with commercial trademark Akulon F138E, kindly supplied by DSM, The Netherlands. LCP was Vectra A950 from Hoechst

Celanese, a wholly aromatic copolyester of 73 mol % *p*-hydroxybenzoate (HBA), and 27 mol % 2,6-hydroxynaphthanoate (HNA), hereafter simply referred as LCP. Four compatibilizers were Zn-SPS, SMA, PP-g-GMA, and PP-g-MAH, as described in the previous section.

Zn-SPS was synthesized in our laboratory by the following procedure. PS was PS 666D ($\overline{M}_w$ = 243,000, measured by gel permeation chromatography) obtained from Yanshan Petrochemical Co., Beijing, China. The SPS was prepared by sulfonating PS with acetyl sulfate in a dichloroethane solution, by following the procedure of Makowski and colleagues.[34] This method has relatively little effect on the polymer backbone and the molecular weight, and results in a random placement of sulfonic acid groups at the *para* position on the phenyl ring of PS. The sulfonation level was 3.4 mol % measured by element analysis. The zinc salt was prepared by neutralizing the solution of SPS with a methanol solution containing an excess zinc acetate. The salt was precipitated, filtered, washed, and dried. The zinc salt was referred to as Zn-SPS. A copolymer of styrene-*co*-maleic anhydride (SMA) was obtained from Shanghai Petrochemical Institute, Shanghai, China. The percentage of MAH was 18%. PP 2401 was used as a precursor for PP-g-GMA, obtained from Yanshan Petrochemical Co., Beijing, China. Initiator dicumyl peroxide (DCP) was dissolved in acetone, mixed with glycidyl methacrylate (GMA), styrene, and PP in a container. The use of small amount of styrene was to reduce PP chain scission and enhance grafting efficiency. The materials were put in a vacuum oven at room temperature to remove the acetone. The dried mixture of PP, DCP, GMA, and styrene was mixed at 190°C for 5 min in a HAAKE Rheomix 600 with the rotator speed at 50 rpm. The grafted copolymer was referred to as PP-g-GMA. PP-g-MAH was obtained from Haier Kehua Co., China. The graft ratio was reported about 1%.

Blending and injection molding

All the materials were carefully dried at 90°C under vacuum for at least 24 h, and then blended by using a CS-194 Mini-Max Extruder (CSI Company, USA) at a rotor speed of 120 rpm. The rotor temperature and head temperature were set at 280°C. The residence time was about 25 s. The extrudates were cooled in air and pelletized.

Cylindrical dumbbell samples with an overall length of 22 mm and a diameter of the narrow section of 1.58 mm were injection molded at 280°C by using a CS-183 Mini-Max Moulder (CSI Company, USA).

Dynamic mechanical analysis

DMA of the injection-molded plaques (15 × 5 × 2 mm) was performed with a Perkin-Elmer DMA-7

from 10 to 150°C. All measurements were conducted in the dual cantilever mode at a fixed frequency of 1 Hz and a heating rate of 5°C/min.

Scanning electron microscope

In order to conduct a comparison of the dimension of the dispersed phases in different blends, the samples for SEM observation were prepared by following procedure: The extrudates from CS-194 were molten in a cup kept at 280°C for 2.5 min, then the melt was spooned out. Since no shear stress was exerted during melting and spooning, LCP phase in the sample was in the form of spheres. From the size and size distribution of the dispersed droplets and interfacial cohesive state in uncompatibilized and compatibilized composites, the compatibilization effect could be compared qualitatively. The samples were immersed and broken in liquid nitrogen and surface coated with gold. The fracture surface of the blends was observed with a Hitachi S-530 scanning electron microscope.

Diffuse reflectance FTIR spectroscopy

Samples of binary blends for diffuse reflectance FTIR spectroscopy (DRIFT) measurements were melt blended at 280°C in a CS-183 molder. The compounds were subjected to extraction with selective solvent to remove unreacted compatibilizer. The procedure of extraction must be carried out with time long enough for removing all unreacted compatibilizers. For grafted PP, the extraction with dimethylbenzene lasted for 48 h. For Zn-SPS and SMA, the extraction with toluene and acetone, respectively, lasted for 24 h. The remnant after extraction was put in an oven at vacuum at 80°C for several days to remove the solvent. Film samples were obtained by pouring the remnant on aluminum foil kept at certain temperature and spreading the remnant into the form of film in 2 s. For the remnant containing nylon 6, the aluminum foil was heated to 230°C. For remnant containing LCP, the foil was heated to 280°C. The films on foil substrate were used for DRIFT characterization. DRIFT characterization was performed with a Perkin-Elmer FTIR 2000 spectrophotometer; 32 scans were signal-averaged with a resolution of 1 cm^{-1}.

Mechanical tests

Tensile strength and modulus of the dumbbell samples were measured with a universal tensile tester, Instron 1122. The tests were carried out at a crosshead speed of 5 mm/min. The average of at least five tests was reported. The relative humidity at test was about 36%.
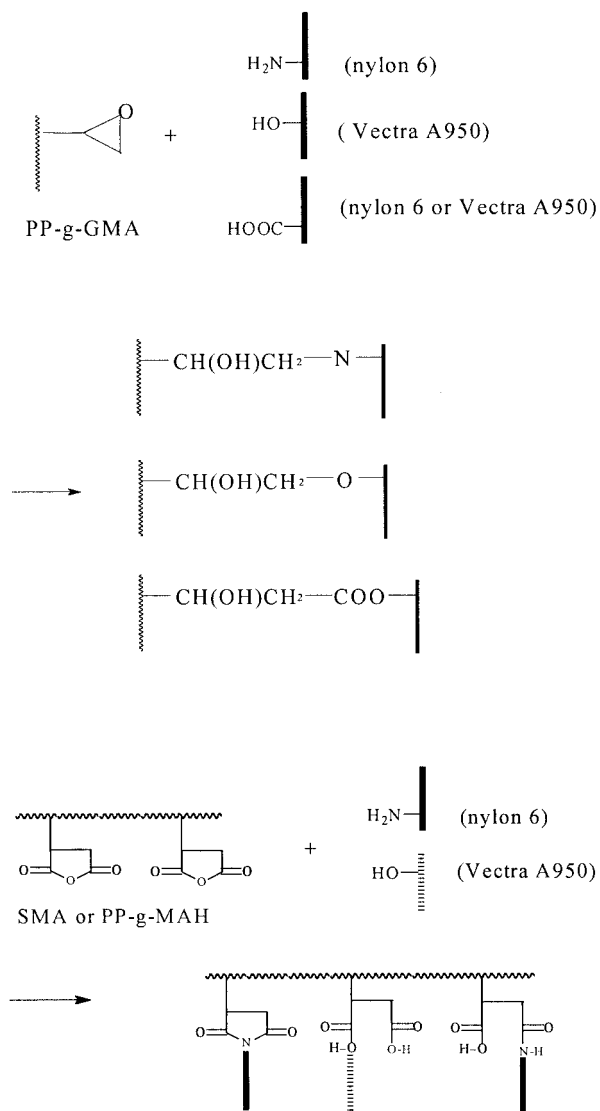
Figure 1 Possible reactions between compatibilizers and nylon 6 and LCP.

RESULTS AND DISCUSSION

Compatibilization design

Reactive functional compatibilizers are suitable for nylon 6/LCP blends due to the fact that nylon 6 has inherent chemical functional groups capable of reacting with other functional groups such as carboxy, anhydride, and epoxy. LCP (Vectra A950) has carboxylic acid and hydroxyl end groups, which may react with different functional groups to form various compatibilizer-g-LCP copolymers *in situ* at the interface during melt processing. The possible reactions are shown in Figure 1. Baird et al.[28] investigated the possibility of compatibilization for ternary blends of PP/PP-g-MAH/LCPs (Vectra A 950, Vectra B 950, LC 3000). On the basis of their FTIR analysis, they have concluded that hydrogen bonding between maleic anhydride and LCP is the mechanism leading to the compatibilization. So, two possible mechanisms may

be included: the occurrence of a chemical reaction, or an interaction such as hydrogen bonding.

Specific physical interaction of ionomer is involved in the present compatibilization design. It has been established that the choice of metal ions significantly affects the miscibility between component polymers. Transition metal ions such as Zn^{2+} and Mn^{2+} produce stronger miscibility than alkali metal ions such as Na^+ and Li^+.[35] Lightly sulfonated polystyrene containing a Zn^{2+} ion is selected as a compatibilizer in the present study. Spectroscopic analyses have revealed the specific interaction between Zn^{2+} and the amide nitrogen atom.[36] Amide hydrogen atoms of the polyamide are also involved in hydrogen bonding with the sulfonate groups of the ionomer.[37] The amide nitrogen atom is considered to participate in the specific interaction through electron migration from the nitrogen atom to the metal ion via the carbonyl group.

Dynamic mechanical analysis

Detecting T_gs is one of the most effective methods for characterizing the miscibility in blends. DMA curves of neat resins and ternary blends are shown in Figure 2. The T_gs of pure nylon 6 and LCP are 60.7 and 109.6°C, respectively. The T_g of nylon 6 in nylon 6/LCP 80/20 blends (curve 2a) is ca. 60.2°C, showing no significant shift compared with that of pure nylon 6. This means that nylon 6 is completely immiscible with LCP. T_gs of LCP in these blends studied are not clear due to the rigidity of LCP chain and insufficient content in the blends. However, compatibility improvement can be demonstrated by the T_gs' shift of nylon 6. When compatibilizers are added, the T_gs of nylon 6 are shifted to higher temperatures with an increase of about 6°C. It is known that if the compatibility in the system is improved, T_gs of the compo-
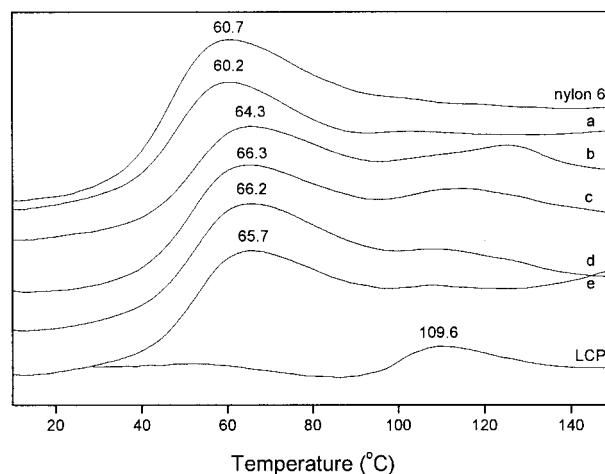

Figure 2 DMA curves of nylon6/LCP/compatibilizer 80/20/5. (a) Nylon 6/LCP, (b) nylon 6/LCP/SPS, (c) nylon 6/LCP/PP-g-GMA, (d) nylon 6/LCP/PP-g-MAH, and (e) nylon 6/LCP/SMA.
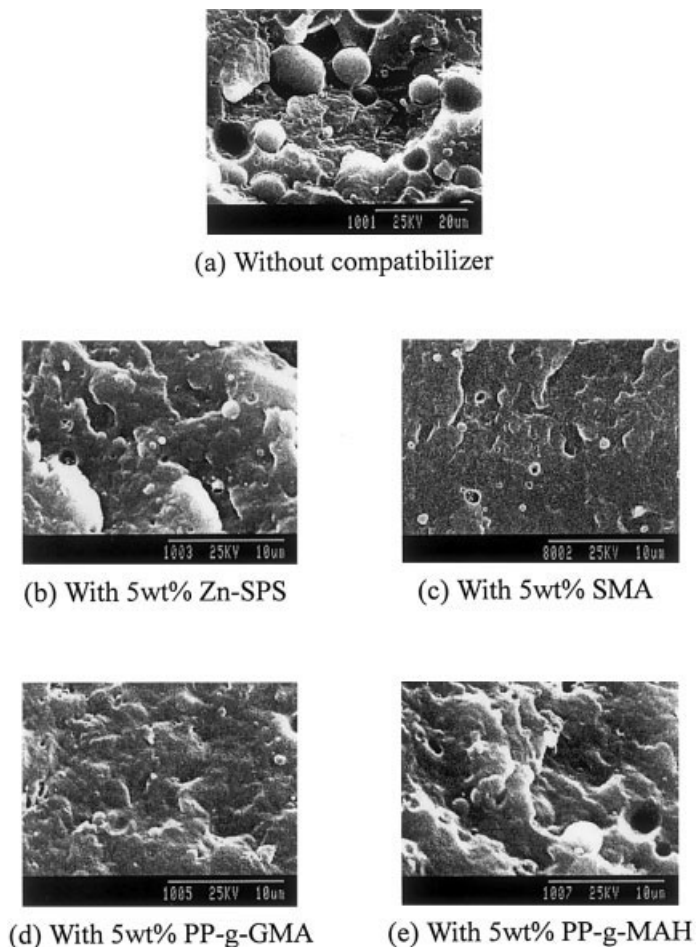
(a) Without compatibilizer

(b) With 5wt% Zn-SPS

(c) With 5wt% SMA

(d) With 5wt% PP-g-GMA

(e) With 5wt% PP-g-MAH

Figure 3 SEM photos of unmodified and modified nylon 6/LCP 93/7 blends.

nents will shift inward to each other. If the two components are completely miscible, the T_g of the blend can be calculated from empirical Fox equation:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

where w_i is the weight fraction of component i and T_{gi} is the glass transition temperature of component i. The shift of T_gs from 60.7°C of nylon 6 to 64–66°C of these four compatibilized systems indicates probable interaction between nylon 6 and LCP at the presence of these compatibilizers.

Morphology

SEM micrography is the most convenient approach to differentiate the morphologies between the compatibilized and the uncompatibilized blends. The incompatible blends possess higher interfacial tension and usually result in coarser morphology than that of the corresponding compatibilized blends. Figure 3 shows the SEM micrographs of nylon 6/LCP 93/7 series blends.

Figure 3(a) provides direct evidence that phase separation occurred in a binary nylon 6/LCP 93/7 blend.

This sample has a distinct two-phase morphology, i.e., a continuous nylon 6 phase with a dispersed LCP phase. The LCP particles in the form of spheres have diameters in the range of 1–10 μm and most of them have diameters larger than 5 μm. All the spheres and holes have smooth surfaces, indicating poor interfacial adhesion between LCP and nylon 6 phases. However, with the addition of compatibilizers, the morphology of fractured surface changes dramatically. The photos in Figures 3(b–e) show that the sizes of the dispersed LCP phase are much smaller than those in Figure 3(a). With each of the four compatibilizers in the nylon 6/LCP 93/7 blends, the domain size of the minor LCP phase decreases significantly due to the reduced interfacial tension. Many particles have their diameters smaller than 1 μm, in a narrow range of diameter distribution. In addition, the dispersion is less visible and the dispersed particles are very well embedded in the matrix. From these phenomena, it is evident that Zn-SPS, SMA, PP-g-GMA, and PP-g-MAH show considerable compatibilizing effect in nylon 6/LCP composites by reducing interfacial tension, resulting in finer phase domains and improving interfacial adhesion between LCP and matrix nylon 6.[38]
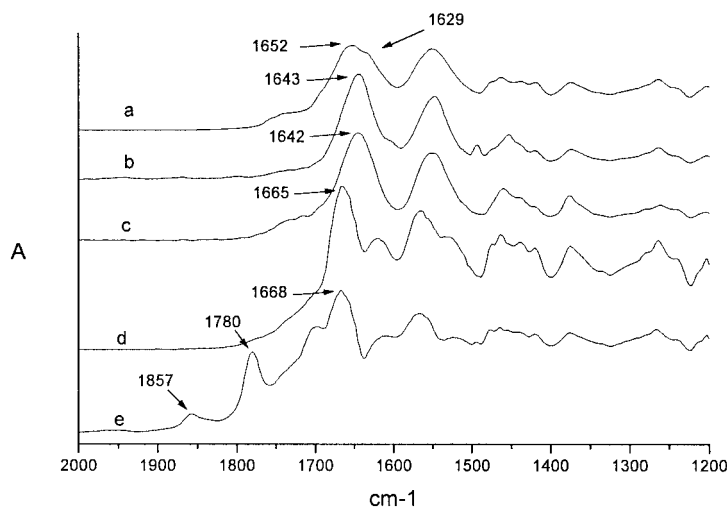
Figure 4 DRIFT spectra of nylon 6 in nylon 6/compatibilizer blends after compatibilizers are extracted. (a) Nylon 6, (b) nylon 6/Zn-SPS 20/80, (c) nylon 6/PP-g-GMA 20/80, (d) nylon 6/PP-g-MAH 20/80, and (e) nylon 6/SMA 20/80.

It is well established that the phase morphology of immiscible polymer blends can be controlled by the addition or *in situ* formation of compatibilizers, which act as interfacial agents. The addition of a properly selected compatibilizer to an immiscible binary blend should (1) reduce the interfacial energy between the phases, (2) permit finer dispersion during melt mixing, (3) provide stability against gross segregation, and (4) result in improved interfacial adhesion,[39] so that enhance mechanical properties.

Diffuse reflectance FTIR spectroscopy

Figure 4 compares DRIFT absorption spectra of neat nylon 6 and nylon 6/compatibilizer blends after the extraction of compatibilizers. Curve 4a represents neat nylon 6 having a peak of stretching vibration of C=O ($\nu_{C=O}$) at 1652 cm^{-1} and bending vibration of N—H (σ_{N-H}) at 1629 cm^{-1}. Compared with that of the neat nylon 6, no new peaks are detected for nylon 6/Zn-SPS (curve 4b), due to the fact that the compatibilization by Zn-SPS is a result of specific interactions. The area and shape of the characteristic peaks for nylon 6 blends containing PP-g-GMA (curve 4c) and PP-g-MAH (curve 4d) are similar to those for neat nylon 6 (curve 4a). The results are expected, since grafted PPs have low grafting ratios by the melt grafting process. This indicates that, if chemical reaction takes place during melt blending, its extent is small. The low concentration of grafted PP reacted with nylon 6 could not be detected by DRIFT, although compatibilization effect has been demonstrated by mechanical tests and morphology discussed in other sections of this paper. However, for nylon 6/PP-g-MAH (curve 4d), an absorption peak of σ_{N-H} in amide shifts to higher wave number of 1665 cm^{-1}. It can be deduced that although the reaction between nylon 6 and PP-g-MAH can not be detected, hydrogen bonding formed in the system

is detected. As can be seen in curve 4e, the characteristic absorption bands of SMA at 1857 and 1780 cm^{-1}, corresponding to carbonyl resonance by the maleic anhydride group, are detected clearly in nylon 6/SMA blends after the extraction of SMA. These new peaks observed indicate that the expected reaction between SMA and nylon 6 to form SMA-g-nylon 6 copolymers indeed occur through the maleic anhydride/amide reaction. The characteristic peak of amide shifted to 1668 cm^{-1} is also observed. It indicates that compatibility improvement in nylon 6/SMA is the result of both chemical reaction and hydrogen bonding.

Figure 5 represents the DRIFT absorption spectra of LCP/compatibilizer blends after the extraction of compatibilizer, and of neat LCP as well. Neat LCP has a smooth absorption spectrum in the range from 4000 to 2000 cm^{-1}. However, for other four samples of remaining LCP, new peaks are observed within this range, although the compatibilizers have been extracted. It is well known that DRIFT is more sensitive in the high wavenumber region. These new peaks indicate some reactions or interactions between LCP and compatibilizers. However, they are not informative enough for the assignment of groups involved in these reactions.

Mechanical tests

Compared with most isotropic polymers, LCPs possess outstanding mechanical properties due to their rigid rod-like backbones. However, in almost all the *in situ* composites, tensile modulus is improved by the addition of an LCP, while the tensile strength varies from system to system. In many cases, mechanical properties (especially strength and toughness along the transverse direction of injection-molded parts) are low for blends of thermoplastics and LCPs, due to poor interfacial adhesion between these two phases.
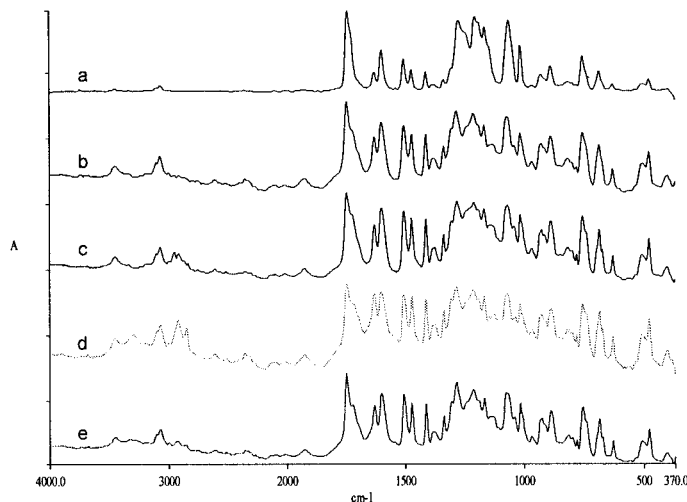
Figure 5 DRIFT spectra of LCP in LCP/compatibilizers blends after compatibilizers are extracted. (a) LCP, (b) LCP/Zn-SPS 20/80, (c) LCP/PP-g-GMA 20/80, (d) LCP/PP-g-MAH 20/80, and (e) LCP/SMA 20/80.

Compatibilization of *in situ* composites can strengthen the reinforcing effect of LCP fibrils through increasing interfacial adhesion between the matrix and the reinforcement.

The mechanical properties of unmodified and modified nylon 6 composites containing 7 and 20 wt % LCP are shown in Figure 6. For nylon 6/LCP 93/7, the addition of four compatibilizers enhances the tensile strength [Fig. 6(a)]. Herein, the addition of 1 wt % Zn-SPS increases the tensile strength from 66.4 to 78.7 MPa, an increase of 19%. The increases of tensile strength for blends with 5 wt % compatibilizers added are not as significant as those with 1 wt % compatibilizers, except with SMA. The addition of 5 wt % SMA increases tensile strength from 66.4 to 94.2 MPa, an increase of 42%.

Figure 6(b) is a plot of Young's modulus vs compatibilizers. It has a similar trend as exhibited in Figure 6(a). For nylon 6/LCP 93/7 system, the addition of 1 wt % Zn-SPS, PP-g-GMA, and PP-g-MAH has a similar effect, i.e., increasing Young's modulus by about 40%. While the addition of 5 wt % SMA increases Young's modulus significantly from 642 to 1294 MPa, an increase of 102%.

Figure 6(c) shows the elongation at break of blends vs compatibilizers. For nylon 6/LCP 93/7 system, the addition of both 1 and 5 wt % compatibilizers increases the elongation at break. In the case of blends containing 1 wt % Zn-SPS, the elongation at break is enhanced about 7 times, and in blends containing 5 wt % SMA, the elongation at break is increased twofold. For nylon 6/LCP 80/20 system, the addition of four compatibilizers almost does not change elongation at break, although it increases both tensile strength and Young's modulus.

The bars in Figure 6 represent the standard deviations of mechanical properties. Since samples used are small in size, voids and defects in samples will result

in large deviation of measured values. However, the deviation does not affect the trend of the change caused by the addition of compatibilizers. For system of nylon 6/LCP/compatibilizer 93/7/5, the minus deviation of tensile strength of blends with SMA is still higher than the plus deviation of blends with other compatibilizers.

From Figure 6, it is seen that nylon 6/LCP/SMA 93/7/5 has unusual mechanical properties than other blends of different compatibilizers and different compositions. In a comparison of SMA with PP-g-MAH, both of them have the same compatibilization mechanism: providing maleic anhydride group to react with nylon 6 or to form hydrogen bonding. However, the compatibilizing effects are quite different. In system of nylon 6/LCP 93/7, the addition of 5 wt % SMA increases tensile strength from 66.4 to 94.2 MPa, while the addition of PP-g-MAH increases tensile strength to 72.8 MPa. This difference in strength enhancement can be explained by the content of the MAH group, where the percentage of MAH group in SMA is 18% and in PP-g-MAH is 1%. By examining the system of nylon 6/LCP 93/7 as example, nylon 6/LCP/SMA 93/7/5 has 0.86% MAH and nylon 6/LCP/PP-g-MAH 93/7/5 has 0.048% MAH. Blends containing SMA then have more MAH groups to provide reactive site and more chances to form various nylon 6(LCP)-g-compatibilizer copolymer. A larger portion of *in situ* formed graft copolymer during melt processing means better interfacial adhesion and better stress transfer. Comparing nylon 6/LCP/SMA 93/7/1 with 93/7/5, the latter has much better mechanical performance. It can be seen that with increasing SMA content, the compatibility is improved further. Using reactive compatibilizers to improve compatibility between components needs conditions for the occurrence of reactions between them. However, this does not mean that the more the content of reactive
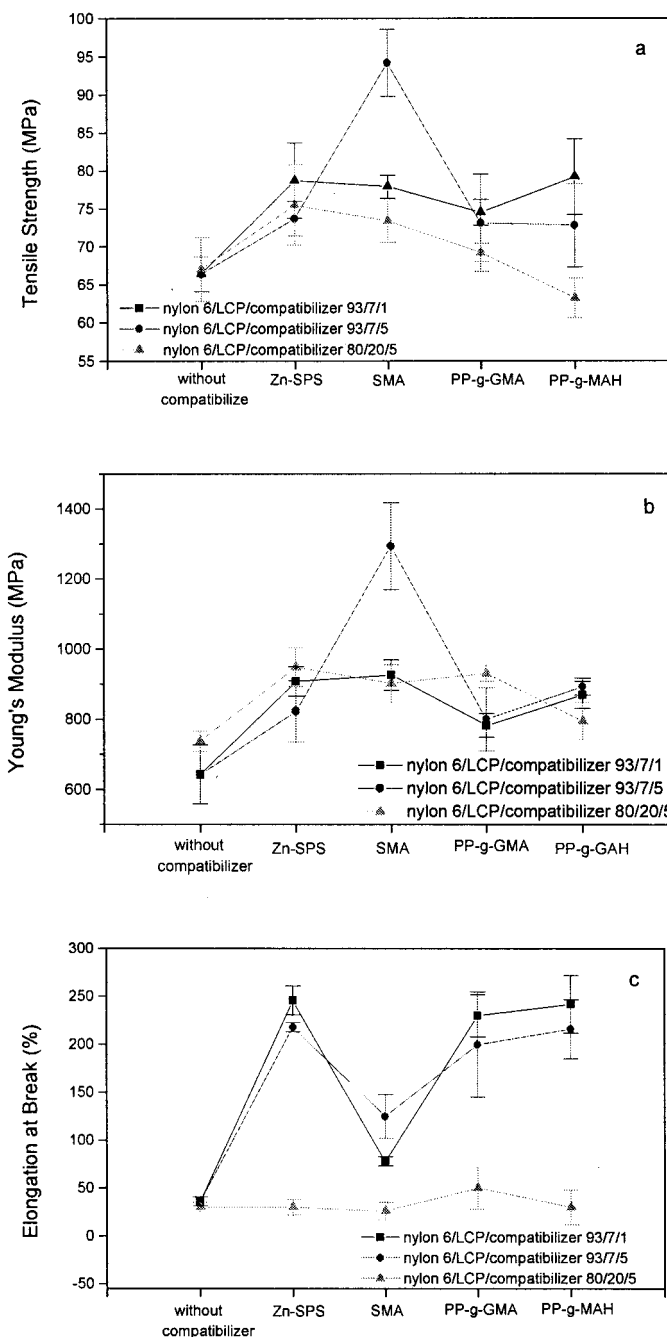
Figure 6 Mechanical properties. (a) Tensile strength, (b) Young's modulus, and (c) elongation at break of nylon 6/LCP *in situ* composites containing compatibilizers.

groups, the better the compatibilization effect. Too large a portion of compatibilizer tends to aggregate and form a third phase with its poor intrinsic mechanical properties[33] and too much *in situ* formed graft copolymer may make the blend crosslinked and result in bad processing property.

SMA has been proven as an effective compatibilizer in several blends, especially with nylons and polyesters as the matrix. Chang et al.[40] used elastomer G1651 as an impact modifier of polyamide-6/poly(phenylene ether) (PA6/PPE) blend. They investigated the compatibilization of SMA in this ternary system. It was

shown that in PA6/PPE/G1651 50/50/20 blend, the addition of 5 phr SMA increased the notched impact strength about 8 times of uncompatibilized blends. Paul et al.[41] reported that the core–shell modifiers could be dispersed in nylon 6 with the aid of SMA. They attributed this enhanced interaction between the rubber and matrix phases to the *in situ* formation of graft copolymers at the interface and improved dispersion in the matrix. As a result, the addition of SMA increased the Izod impact strength dramatically and the yield stress to some extent. Banerjee et al.[42] added SMA in poly(butylene terephthalate)/acrylonitrile–

butadiene–styrene (PBT/ABS) 70/30 (by weight) blends. The compatibilization effect was characterized by tensile strength, interaction parameter, and adhesive strength. When 5 wt % SMA was added, tensile strength increases from 24.8 to 44.0 MPa; interaction parameter increased from −0.06 to 15.32 and adhesive strength from 0.62 to 42.74, indicating better interfacial adhesion at the presence of compatibilizer. Another work in our laboratory showed that SMA could also improve the ability to absorb fracture energy of polycarbonate/LCP blends.[43] All the above-mentioned results show that SMA is an effective compatibilizer for blends containing polyamide and polyester, no matter the dispersed phase is an elastomer or plastic. The present work reveals that SMA can also improve the compatibility between nylon and a rigid chain thermoplastic, LCP.

Blending procedure

From DRIFT results shown in Figures 4 and 5, it can be seen that the reaction between SMA and nylon 6 occurs easily, while the reaction between SMA and LCP is less obvious. The reason is that amide group of nylon 6 is active enough to react easily with anhydride group of SMA. The functional group of LCP is less active and the rigid molecular chain of LCP hinders reactions between LCP and SMA. If SMA is melt blended with nylon 6 and LCP in the same step, LCP may not have enough chance to contact SMA at the interface. So, the blending procedure should be modified to reach optimum compatibilization effect. If SMA is blended with LCP first, followed by blending with nylon 6, LCP will have more chance to contact SMA. In the present work, the effect of two blending procedures has been investigated. One-step blending means that SMA was blended with nylon 6 and LCP at the same time, while two-step blending means SMA was blended with LCP first and then blended with nylon 6.

The mechanical properties of resultant samples are illustrated in Figure 7 to show different results of these two procedures. The nylon 6/LCP 93/7 blend has a tensile strength of 66.4 MPa. The addition of 1 wt % SMA by one-step blending increases tensile strength to 77.9 MPa, i.e., an increase of 17%. While the same amount of SMA addition by two-step blending increases the tensile strength to 83.0 MPa, an increase of 25%. Similarly, one-step blending and two-step blending with 5 wt % SMA increase tensile strength to 94.2 and 98.4 MPa, respectively. For nylon 6/LCP 80/20 system, one-step blending and two-step blending with 5 wt % SMA addition increases tensile strength from 67.0 to 73.4 and 78.5 MPa, respectively. The modulus [Fig. 7(b)] and elongation at break [Fig. 7(c)] of compatibilized systems blended in two-step mode are also higher than those of the corresponding uncompatibi-
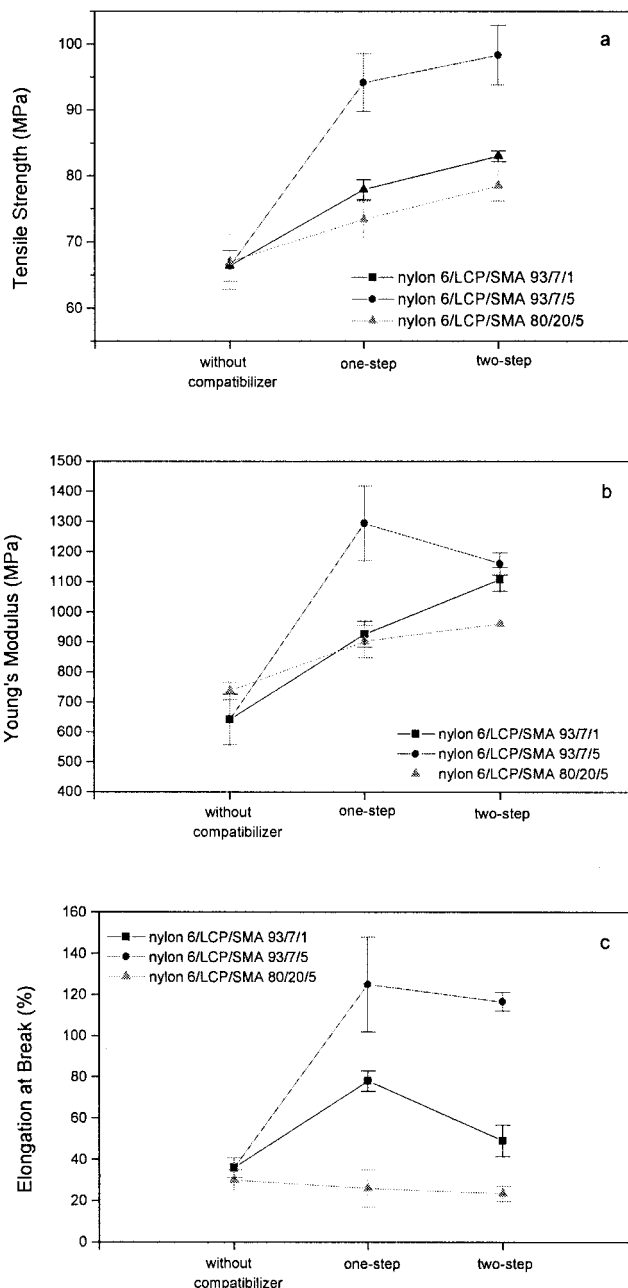

Figure 7 Effect of blending procedure on (a) tensile strength, (b) Young's modulus, and (c) elongation at break of nylon 6/LCP *in situ* composites containing SMA.

lized blends, but the extent of the increase is relatively limited.

The bars in Figure 7 represent the standard deviation of mechanical properties. When SMA is added by two-step blending, the deviation of mechanical tests is smaller, indicating a better reproducibility of sample preparation. It is believed that mixing the compatibilizer with the minor LCP component first makes the former readily available at the interface upon blending with nylon 6. In contrast, if it was first mixed with miscible nylon 6, then its interface concentration would have been diluted, leading to a reduced compatibilization effect.

From the results discussed above, it can be seen that for *in situ* composites containing nylon 6 and LCP, several compatibilizers of different types can be considered to improve the compatibility in the system. For other blends, several strategies can also be considered to enhance the compatibility. An advantage of the capacity of the ionomer to provide specific intermolecular interactions can be taken. This route is usually effective for blends consisting of polar polymers, since specific interactions can exist between ions of ionomers and polar groups of component polymers. For polyblends containing reactive polymers, reactive compatibilizers are among priority choices. Graft copolymers may be produced effectively and conveniently during blending as a result of reactions between the compatibilizer and other two components of the blend. These *in situ* formed copolymers act as compatibilizers at the interface, reduce the interfacial tension and provide good adhesion at the interface. By introducing compatibilizers into the immiscible blends, the compatibility can be improved dramatically, characterized with finer dispersed phase, better interfacial adhesion, and enhanced mechanical properties.

CONCLUSIONS

Blends of nylon 6/Vectra A950 containing three types of compatibilizers, including ionomer Zn-SPS, copolymer SMA, functional grafted copolymer PP-g-GMA, and PP-g-MAH, are prepared by using a mini-type extruder and injection molder. The effect of compatibilization is compared by means of dynamic mechanical analysis and morphology. The addition of 1–5 wt % compatibilizers decreases the domain size and results in improved interfacial adhesion between LCP and nylon 6 matrix. DRIFT spectra reveal chemical reaction and specific interactions between the compatibilizer and nylon 6. Mechanical properties of modified blends are enhanced due to the good adhesion at the interface. Compared with uncompatibilized blend, the addition of SMA in nylon 6/LCP 93/7 blend increases the tensile strength and Young's modulus obviously, an increase of 42 and 102%, respectively. By considering the favored reaction between the compatibilizer and the minor component polymer, a two-step blending procedure was adopted. This blending procedure is demonstrated an optimum method to obtain blends with stronger mechanical properties.

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