Morphology and Rheology of HDPE/LCP Blends Compatibilized by a Novel PE-g-LCP Copolymer

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ABSTRACT: A novel graft copolymer (PE-g-LCP) consisting of polyethylene (PE) backbones and liquid crystalline polymer (LCP) branches was synthesized via reactive blending of an acrylic acid-functionalized PE (Escor 5000 by Exxon) with a semiflexible LCP (SBH 1 : 1 : 2 by Eniricerche S.p.A.). The crude reactive blending product (COP) was shown by investigation of the fractions soluble in boiling toluene and xylene and of the residue to contain unreacted Escor and SBH, together with the graft copolymer forming the interphase. The compatibilizing activity of COP for PE/SBH blends, compared to that of pure Escor, was investigated using two PE grades. The COP addition into 80/20 PE/SBH blends caused a much stronger reduction of the SBH droplet dimensions and morphology stabilization than did that of pure Escor. The rheological behavior of the samples showed that COP leads to a slight increase of interfacial adhesion in the melt as well and that the effect is more pronounced when lower molar mass PE grade is used as the blend matrix. Melt-spinning tests demonstrated that deformation of the SBH droplets into highly oriented fibrils can be obtained for the blends of lower molar mass PE, compatibilized with small amounts of the novel PE-g-SBH copolymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2069-2077, 1999

Key words: LCP-graft-polyethylene; polyethylene/LCP blends; compatibilization

INTRODUCTION

Recent investigations¹⁻⁸ have dealt with the preparation and the characterization of blends of polypropylene (PP) or polyethylene (PE) with liquid crystalline polymers (LCPs) containing

different commercially available compatibilizers. These studies have shown that maleic anhydride-grafted PP (PPMA) or acrylic acid-functionalized PP (PPAA) can improve the interfacial adhesion in PP/LCP blends, and an enhancement of the tensile modulus, tensile strength, and surface finish was observed.¹⁻⁶ For blends of PE with a semiflexible LCP, compatibilized with two samples of maleic anhydride-grafted PE (PEMA),^{7,8} the enhancement of the mechanical properties was generally modest. Also, in this case, the enhancement of some of the blend properties was attributed to

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the promotion of specific polar interactions between the components.

Reactive compatibilizers containing epoxy groups have also been used for PP/LCP blends.^{9,10} The reaction between the functional groups and the LCP end groups was shown to result in a decrease of the LCP droplet dimensions and an improvement of the impact strength; however, the tensile modulus and the degree of crystallinity of the PP matrix underwent substantial reduction.

The approach of using compatibilizers consisting of graft copolymers made up of segments whose chemical structure is similar⁵ or identical^{8,11–13} to that of the polymers being blended was applied recently to the modification of polyolefin/LCP blends. The compatibilization mechanism involves the migration of the copolymer molecules to the interphase and the penetration of each copolymer segment into a structurally alike phase. The reduction of interfacial energy can cause a reduction of the LCP particle dimensions and a stabilization of the blend morphology.

Previous articles from these laboratories have described the synthesis of compatibilizing copolymers, consisting of PE^{12, 13} or PP¹¹ backbones and LCP grafts. A semiflexible LCP (SBH), synthesized from sebacic acid (*S*), 4,4'-dihydroxybiphenyl (*B*), and 4-hydroxybenzoic acid (*H*) in the mol ratio 1 : 1 : 2,^{14,15} was used for the copolymers' preparation. A functionalized PE sample containing free carboxyl groups, or PPAA, was employed as the substrate for the polyolefin-g-SBH synthesis. The latter was realized either by *in situ* melt polycondensation of the SBH monomers^{11,12} or by reactive blending of the same functionalized PE with preformed SBH.¹³

Detailed characterization of the crude copolymers showed that they contain both unreacted polymers and graft copolymers of different composition, forming the interphase.^{16,17} An investigation of the compatibilizing activity of these products for PE/SBH blends⁸ demonstrated that they do, in fact, improve the interfacial adhesion of the two phases both in the melt and in the solid state and make the blend morphology considerably more stable. However, a fairly modest enhancement of the mechanical properties was concurrently observed, and this was attributed to the relatively short PE segments separating the SBH grafts of the copolymers. In other words, these short PE sequences were thought to be unable to grant sufficient penetration into the PE matrix, while the long SBH branches became completely

mixed with the LCP phase of the blend. In this work, therefore, we tried to synthesize copolymers with better compatibilizing efficiency,¹⁸ using a higher molar mass functionalized PE (Escor 5000, by Exxon, USA) as the raw material. The preparation of the PE-g-SBH copolymers was carried out via reactive blending because the melt viscosity of Escor was exceedingly high for a direct *in situ* polycondensation with the SBH monomers. The compatibilizing activity of the reactive blends for the PE/SBH blends was then assessed by morphological, thermal, and rheological analyses of the latter materials.

EXPERIMENTAL

Materials

Two grades of high-density polyethylene (HDPE), kindly provided by Solvay S.A. (Rosignano, Italy), were used for the blend preparations: an injection-molding-grade material (A-1100) with a melt flow index (MFI) equal to 11 dg/min (230°C; 2.16 kg) and an extrusion-grade material (Eltex 4002) with an MFI = 2 dg/min. The LCP, referred to as SBH, was a copolyester of *S*, *B*, and *H*, in the mol ratio 1:1:2, developed by Eniricerche S.p.A. (San Donato Milanese, Italy),¹⁴ whose characterization has been detailed elsewhere.¹⁵ The inherent viscosity of SBH, measured in pentafluorophenol at 60°C, with a concentration of 0.1 g/dL, was 1.01 dL/g. The temperature of melting of SBH is 230°C, and the temperature of crystallization, 217°C.¹⁵ An acrylic acid-functionalized PE, Escor 5000, produced by Exxon, was used as a substrate for the preparation of the graft copolymers. Escor 5000 contains 6% w/w AA branches and its MFI is equal to 8 dg/min.

Procedures

The synthesis of the PE-g-SBH copolymer was made by reactive blending. Escor and SBH, in a 50/50 w/w ratio, were charged to a 30-mL mixing bowl of a Brabender Plastograph and blended 30 min at 240°C and 100 rpm, under a nitrogen blanket. Ti(O—Bu)₄ was used as the transesterification catalyst. To prevent crosslinking, a small amount of antioxidant (Irganox) was added to the mixture. The reactive blend was indicated as COP. A physical blend of Escor and SBH of similar composition (MIX) was also prepared, in the absence of a catalyst, with a mixing time of 6 min. The polymers were dried at least 12 h at 110°C under a vacuum before blending. The blends were milled, washed with acetone, and dried.

Blends of HDPE, SBH, and the compatibilizer (if any) were prepared in a similar way (at 240°C, with a mixing time of 6 min). Either the reactive blend (COP) or pure Escor were used as compatibilizers for the ternary blends. The composition of the latter was designed so as to reach a total SBH content, calculated as the sum of the weighed amount of neat SBH plus that contained in the COP (if any), equal to 20% w/w. The amount of the added compatibilizer was 4 or 10 phr.

The MFI of the polymers were measured according to ASTM method D1328. Extractions of COP and MIX with boiling toluene and xylene were performed in Kumagawa devices as described elsewhere.^{11–13} Infrared (IR) spectra of the polymers, the blends, and their fractions were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Thin films prepared by hot molding were used. Differential scanning calorimetry (DSC) measurements were carried out under nitrogen, with a heating/cooling rate of 10°C/min, on a Perkin-Elmer DSC-4 apparatus. Scanning electron microscopy (SEM) observations were made using a JEOL T300 microscope. The samples were fractured in liquid nitrogen, and the fracture surfaces were coated with gold.

The viscosity curves of the pure polymers and blends were determined using a capillary viscometer (Rheovis 2100, Ceast, Italy). The tests were carried out at 240°C, with a die of 1 mm diameter and L/D = 40. The Rabinowitch correction was applied to all experimental data.

Some blend specimens were melt spun by manually drawing the filament extruded from the viscometer die and immediately quenching it in an ice bath. The draw ratio (DR) was evaluated as the ratio of the cross sections of the die and the fiber.

RESULTS AND DISCUSSION

Reactive Blending of Escor and SBH

The formation of a PE-g-SBH copolymer via reactive blending of Escor and SBH can occur by the reaction of the carboxyl groups of Escor with the hydroxyl end groups, if any, and the ester bonds of SBH. As it is known that SBH is not soluble in most common solvents,¹⁵ the reactive blending product (COP) was fractionated with boiling tol-



Figure 1 (Curve 1) IR spectra of Escor, (curve 5) SBH, and the fractions of COP: (curve 2) soluble in toluene; (curve 3) soluble in xylene; (curve 4) insoluble.

uene and xylene, which are good solvents for PE, and the presence of SBH segments in the soluble fractions, as well as that of PE in the residue, was taken as evidence that the graft copolymer had been obtained. In fact, as is shown in Figure 1, the IR spectra of the toluene- and xylene-soluble frac-



Figure 2 SEM micrographs of the fracture surfaces of (a) physical blend Escor/SBH 50/50 w/w (MIX) and (b) reactive blend Escor/SBH 50/50 w/w (COP).

tions of COP display absorption bands ascribable to the SBH component, while the spectrum of the insoluble fraction indicates that a considerable number of Escor segments are present in this fraction. On the contrary, the IR spectra of the same fractions of the Escor/SBH mechanical blend (MIX) are practically coincident with those of the corresponding pure polymers.

The morphology of COP, compared to that of the mechanical blend (MIX), provides further evidence in favor of the presence of the PE-g-SBH copolymer in this material (Fig. 2). In fact, the SEM micrograph of the mechanical blend shown in Figure 2 is typical for a biphasic material made up of two incompatible phases: The SBH dispersed phase appears in the form of droplets of $2-30 \mu m$, with no adhesion to the matrix. On the contrary, the reactive blend (COP), though being also biphasic, is clearly characterized by strong interfacial adhesion, meaning that there must be a graft copolymer acting as a compatibilizer for the two phases. Taking into account that it is not possible to obtain these IR and DSC results for COP, MIX, and their fractions if only hydrogen bonding between AA and ester groups of SBH exists, we consider the morphology of the reactive blend COP as further confirmation for the presence of a graft copolymer at the interphase.

A comparison of the temperatures and the enthalpies of the thermal transitions of pure Escor and of the mechanical blend (MIX), shown in Table I, shows that the thermal behavior of Escor is practically unaffected by simple blending with SBH. The fusion/crystallization enthalpies of the Escor phase of the blend are in perfect agreement with the values calculated for the blend composition. Thus, the data in Table I indicate that the toluene-soluble fraction of the blend is practically pure Escor and that almost no Escor is contained in the residue.

Sample	First Heating		First Cooling		Second Heating	
	T_m (°C)	ΔH_m (cal/g)	T_c (°C)	ΔH_c (cal/g)	T_m (°C)	ΔH_m (cal/g)
Escor	103.7	21.6	85.3	22.1	102.5	21.9
MIX	102.8	10.9	86.7	9.3	101.2	9.9
Soluble in toluene	103.9	22.9	88.8	19.2	103.1	19.8
Insoluble	_	_	_	_	_	
COP	94.3	8.2	72.1	8.2	88.9	7.9
Soluble in toluene	106.6	21.0	92.7	21.1	105.3	20.1
Soluble in xylene	106.9	18.3	82.9	16.0	97.6	15.6
Insoluble	100.1	8.0	65.1	5.0	82.2	4.9

Table I DSC Characteristics of Escor and of the PE Phase of MIX, COP, and Their Fractions

As expected, the thermal behavior of the reactive blend of equal composition (COP), and of its fractions, differs in many aspects from that of the mechanical blend. The most evident difference is that the insoluble fraction contains a considerable amount of the crystallizable PE component, and this can only be explained through the chemical bonding of the PE chains to the SBH fragments. Another important difference is that the enthalpies and the temperatures associated with the fusion/crystallization of the Escor phase are appreciably reduced on going from the toluene-soluble to the xylene-soluble and to the insoluble fraction. An appreciable reduction of T_c is observed along the series, thus showing that the rate of crystallization of the Escor phase is progressively decreased, possibly due to the reduced mobility of PE crystallizable segments bonded to SBH grafts, whose content increases concurrently.

The above results demonstrate that during the reactive blending of Escor and SBH some PE-g-SBH copolymer is formed. The product consists of unreacted pure components and of PE-g-SBH copolymer molecules whose composition changes with the number of Escor carboxyl groups entering the transesterification and/or with the length of SBH grafts. Depending on the relative content of Escor and SBH, the solubility behavior of the copolymers may be intermediate between those of the pure polymers. Thus, a PE-rich copolymer will be found, together with pure Escor, in the toluene-soluble fraction, whereas the SBH-rich copolymer molecules will remain in the residue. In the bulk product of reactive blending, the unaltered polymers form separated phases with strong interfacial adhesion caused by the copolymer molecules giving rise to the interphase. It may be expected, therefore, that this material behaves as a compatibilizer for the HDPE/SBH blends.

Compatibilization of HDPE/SBH Blends by COP and by Pure Escor

The compatibility of Escor with the two types of HDPE (A1100 and Eltex) used for the preparation of the HDPE/SBH blends was investigated by studying the morphology of the binary blends (75/25 w/w) by SEM. The micrographs (Fig. 3) demonstrate that Escor is not miscible with HDPE, whatever the grade. However, the two phases display very strong interfacial adhesion, and the dimensions of the Escor droplets are



Figure 3 SEM micrograph of the fracture surface of 75/25 A1100/Escor blend.

smaller (up to 0.5 μ m) when dispersed in an Eltex matrix (not shown) and slightly larger (0.5–3.0 μ m) in the blend with A1100 (Fig. 3).

The compatibilizing activity of the reactive blend (COP) for the HDPE/SBH blends was evaluated by an investigation of the effect of the addition of this material, as well as that of pure Escor, on the morphology, the thermal properties, the rheological behavior, and the melt spinning of these blends. The SEM micrographs of the fracture surfaces of the A1100/SBH 80/20 blends without and with compatibilizers are shown in Figure 4. It is clearly visible that the uncompatibilized blend [Fig. 4(a)] consists of two highly incompatible phases, with the LCP forming the dispersed phase. The latter appears in the form of poorly elongated droplets of 2–30 μ m, with no adhesion to the matrix. The morphology of the blend practically does not vary as a result of the addition of different amounts of pure Escor [Fig. 4(b)], whereas profound changes are observed in the presence of COP [Fig. 4(c)]. The A1100/COP/ SBH blends with compositions 78/4/18 [Fig. 4(c)] and 75/10/15 w/w/w are also biphasic, but are clearly characterized by strong interfacial adhesion. Moreover, the average dimension of the SBH-dispersed particles decreases strongly upon addition of 4 wt % COP [compare Fig. 4(a,c)] and increases very slightly when the compatibilizer content is increased to 10 wt %.

When HDPE with a higher molar mass (Eltex) is used as the matrix, the morphology of the binary blend demonstrates very poor LCP dispersion and complete lack of adhesion [Fig. 5(a)]. This is probably due to the large difference between the melt viscosity of Eltex and SBH. The addition of 4 or 10% Escor to this blend fails to improve the phase dispersion and the interfacial adhesion. The latter characteristics are drasti-



Figure 4 SEM micrographs of the fracture surfaces of (a) 80/20 A1100/SBH blend, (b) the same, with 4% Escor, and (c) the same, with 4% COP.



Figure 5 SEM micrographs of the fracture surfaces of (a) 80/20 Eltex/SBH blend and (b) the same, with 4% COP.

cally improved, on the contrary, when COP is used as the compatibilizer, as is clearly visible in Figure 5(b). The SBH particles are now very fine and show good penetration in the matrix, meaning that the PE-g-SBH copolymer does actually behave as a compatibilizer for these blends. This is due mainly to the strong affinity between SBH grafts of the COP and SBH domains of the blends (SBH grafts can penetrate into the SBH domains), while between Eltex and the PE segments of COP, only good compatibility exists. It is noteworthy that the optimal concentration of COP is of about 4%, whereas, at 10%, the compatibilization effect decreases slightly. This behavior is typical for many compatibilizing agents.

The temperatures and the enthalpies of fusion/ crystallization of the PE phase of the HDPE/SBH blends, detected by DSC, do not change appreciably in the presence of compatibilizers. This result



Figure 6 Viscosity curves of the 80/20 A1100/SBH blends with 4% of compatibilizing agents at 240°C.

indicates that the PE matrix preserves the characteristics of its phase transitions in the compatibilized blends.

The study of the rheological behavior of the pure components of the blends, namely, A1100, Eltex, Escor, and SBH, published elsewhere,^{7,8,19} shows that the viscosity of Eltex is higher than that of A1100, that Escor displays a lower viscosity than that of the two HDPE samples, and that SBH has the lowest viscosity in the whole shear rate range. The melt viscosity of the binary (50/50 w/w) blends A1100/Escor and Eltex/Escor is intermediate between the values for the pure components.

The rheological behavior of COP is very interesting because its melt viscosity is higher than that of either pure component (Escor and SBH). This finding is interpreted in terms of a kind of structured morphology in the molten state, which can be due either to the presence of crosslinked material or to strong interfacial adhesion between the two phases. The first possibility was ruled out by experiments in which the SBH chains of COP were alcoholized with boiling ethanol in the presence of sodium hydroxide and the residue, after acidification, washing with water, and drying, was found to be soluble in toluene. Thus, the rheological behavior of COP is another strong confirmation that a PE-g-SBH copolymer is actually present in the Escor/SBH reactive blends.

The viscosity curves of the 80/20 A1100/SBH blends, without and with a compatibilizer, are presented in Figure 6. It may be noted that the addition of SBH to A1100 lowers the viscosity of the latter, as has been shown previously.⁸ The analysis of the curves in Figure 6 demonstrates that the addition of 4 wt % Escor or COP into this binary blend increases slightly the viscosity in the lower shear rate range. This increase, which is just a little higher for COP, is an indication that the adhesion between the blend components is improved in the presence of the compatibilizers.⁸ It should noted that the slight increase of the viscosity in the presence of COP is a repeatable experimental fact.⁸ At higher shear rates, however, the compatibilizers seem to lower the blends' viscosity, thus showing that the effect of the interfacial adhesion forces disappears when strong stresses act on the interphase.

The corresponding viscosity curves for the blends with an Eltex matrix are shown in Figure 7. Again, the viscosity of the blend Eltex/SBH 80/20 is lower than that of pure Eltex in the whole shear rate range investigated. Here, the low



Figure 7 Viscosity curves of the 80/20 Eltex/SBH blends with 4% of compatibilizing agents at 240°C.

shear viscosity enhancement due to the compatibilizers is less evident.

The results of the morphological, calorimetric, and rheological investigations of the ternary blends show that the presence of added COP means an enhancement of interfacial adhesion both in the melt and in the solid state. Pure Escor, on the contrary, displays a negligible compatibilizing effect for these HDPE/LCP blends. Apparently, this functionalized polymer, whose compatibility with HDPE was shown to be good, develops polar interactions with the SBH dispersed phase that are too weak to grant adequate interfacial adhesion. It is also interesting that the compatibilizing effect of both compatibilizers depends on the molar mass of the HDPE matrix and is more pronounced with the lower molar mass PE grade (A1100). This is probably due to a better match of the lengths of the PE chains of the matrix and of the PE sequences present in the PE-g-SBH copolymer molecules of COP. These results are in agreement with those found for HDPE/SBH blends compatibilized with other PE-g-SBH copolymers synthesized previously.¹⁹

To confirm that the addition of COP into the HDPE/SBH blends improves the interfacial interactions between the matrix and the dispersed droplets, melt-spinning experiments were performed and the morphology of the fibers was studied by SEM. As described in the Experimental section, the extruded fibers were manually drawn up to the maximum draw ratio $(\mbox{DR}_{\mbox{max}})$ and were then quenched in ice. The drawability of the two uncompatibilized HDPE/SBH blends was found to be poor (DR_{max} \approx 6-8), as could be expected in view of the scarce adhesion between the components already demonstrated by the morphological investigation. The influence of the compatibilizing agents considered in this work (Escor and COP) on the experimental values of DR_{max} was practically nil for the Eltex/SBH blends. On the contrary, the addition of Escor into the A1100/ SBH blend means an increase of $\ensuremath{\text{DR}}_{\ensuremath{\text{max}}}$ to about 15-18, and that of COP, to about 28-35.

The morphology of the fracture surfaces of the resulting fibers is in fair agreement with the indications obtained from the spinning experiments described above. In fact, the SEM micrograph of the binary 80/20 A1100/SBH blend fiber (not shown) demonstrates that the SBH particles are almost spherical, meaning that they have undergone practically no deformation during the spinning/drawing operation and/or that they have rapidly relaxed back to a spherical geometry be-



Figure 8 SEM micrograph of the fracture surface of the fiber of the 78/4/18 A1100/COP/SBH blend.

fore quenching. In either case, the evidence is in favor of very poor interphase interactions in the molten state of these uncompatibilized blends. The blend compatibilized with pure Escor displays some elongated SBH particles together with a majority of spherical droplets. The morphology of a fiber drawn from the 80/20 A1100/SBH blend compatibilized with COP is, on the contrary, characterized by well-orientated SBH fibrils with a high aspect ratio (Fig. 8). The high extent to which fibrillation has occurred upon spinning this blend is certainly to be ascribed, among other factors, to the favorable viscosity ratio between the two phases (much poorer fibrillation was observed under similar conditions for the corresponding Eltex/SBH blend). However, the most important factor is undoubtedly the enhanced adhesion between A1100 and SBH, which grants the transmission of the deformation forces between the phases and which is due to the compatibilizing efficiency of COP.

CONCLUSIONS

The characterization of the product obtained by the reactive blending of an AA-functionalized PE (Escor) with SBH has demonstrated that this material contains appreciable amounts of PE-g-SBH copolymer molecules. Due to the strong incompatibility between the pure Escor and SBH, the product (COP) is still biphasic. However, the presence of the PE-g-SBH copolymer in the interphase grants fairly strong interfacial adhesion.

The addition of relatively small amounts of COP into binary HDPE/SBH blends was shown to cause a considerable reduction of the dimensions of the SBH particles and an improvement of the adhesion between the phases. A slight enhancement of interfacial adhesion was also shown to take place in the molten state as well. The body of the results accumulated in this study points to a considerable compatibilizing efficiency of this product, which is considerably higher than that of pure Escor and, supposedly, of other commercially available functionalized polyolefins. With respect to the latter compatibilizers, COP has apparently the advantage of a strong affinity with the SBH domains of the blends. The results also confirm previous findings indicating that optimum compatibility between the PE segments of the PE-g-SBH copolymer and the PE matrix is realized when the latter has an appropriate molar mass. Under these conditions, the phase interactions are improved to the extent that the distribution of the dispersed LCP phase and the morphology stability become very good and the extensional flow realized upon drawing an extruded filament of the blend causes pronounced fibrillation of the minor LCP phase.

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