Compatibilization of Polyethylene/Polyamide 6 Blends with Oxazoline-Functionalized Polyethylene and Styrene Ethylene/Butylene Styrene Copolymer (SEBS)

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ABSTRACT: Study was made of the compatibilization of polyethylene/polyamide 6 (PE/PA6) blends with a ricinoloxazoline maleinate grafted polyethylene and styrene ethylene/butylene styrene copolymer. The blends were prepared in a twin-screw midiextruder, and the specimens for mechanical tests were injection molded with a mini-injection molding machine. The effect of compatibilizing on the mechanical properties and the morphology of the blends was studied. The toughness and ductility of the blends were substantially improved as a result of the compatibilization. Simultaneously, the strength and stiffness were slightly reduced. Morphological studies showed that the particle size was reduced and the adhesion of the dispersed phase to the matrix was improved by the compatibilization. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1443–1450, 1999

Key words: oxazoline; compatibilization; polyethylene/polyamide 6 blend; reactive extrusion

INTRODUCTION

There is an ever-growing demand for low-cost production of polymeric materials with a desirable combination of properties. Polymer blends provide a good solution for the needs of industry. Blending has been done for years to improve the performance of commodity and engineering plastics and to ensure for them wider applications.[1,2]

The reasons for blending polyolefins with engineering plastics are, on the one hand, to improve particular properties of the engineering plastics (e.g., toughness, moisture absorption, or processability) and, on the other, to improve the performance of the polyolefins (rigidity, thermal stability, and barrier properties to oxygen and solvents).[3,4] Polyamide 6 is a polymer of great industrial importance, but its end uses are limited by its poor toughness, particularly below the glass transition temperature, poor dimensional stability due to high moisture pickup, and poor processability. Low-density polyethylene (PE-LD) is tough, flexible, and insensitive to moisture.[4]

The performance of polyamide 6 (PA6) can be improved by blending it with a low-modulus PE, which, in dispersed form, acts as an effective stress concentrator and enhances both crazing and shear yielding in the PA6 matrix. Since crazing and shear yielding absorb large amounts of energy, the resultant blend exhibits superior resistance to crack propagation under impact conditions.[5]

Multilayer systems of PE and PA have been widely used for the packaging of agricultural, chemical, and industrial products containing organic solvents. Although PE offers low cost, high moisture barrier properties and ease of processing, it is highly permeable to organic solvents,

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which then act as swelling agents. The problem is overcome by incorporating PA as a barrier layer.[6]

Owing to their lack of polarity, polyolefins are immiscible with engineering plastics, such as polyesters and polyamides. Unfavorable interactions at the molecular level lead to high interfacial tension and make the melt mixing of the components difficult. This leads to an unstable morphology and poor interfacial adhesion, and the end result is blends with mechanical properties inferior to what would be expected by the additive mixing rule.

A common way to improve the properties of immiscible blends is to add block or graft copolymers. The copolymer compatibilizers are assumed to locate at the interface of the blend components, where they improve the blend morphology by decreasing the particle size and increasing the adhesion between the phases. The compatibilization effect is based on the ability of the compatibilizers to react or to be miscible with the blend components.[7,8]

Graft copolymers have been widely used as compatibilizers in blends of polyolefins and polyamides. The most common compatibilizers are polyolefins grafted with maleic anhydride or carboxylic acids.[2] Raval et al.[4] achieved compatibility in PE-LD/PA6 blends by using PE-LD grafted with butyl acrylate (PE-*g*-BuA) as an interfacial agent. The improvement in toughness was attributed to the formation of a PE/PA6 graft copolymer during melt mixing. Raval et al.[5] also observed that the impact properties of a PE-LD/PA6 blend can be significantly improved, and the water absorption of the blend clearly reduced, by the addition of butyl acrylate-*co*-maleic anhydride grafted PE-LD[PE-*g*-(BuA-*co*-MA)]. In studies on the compatibilization of PE-LD/PA6 with an ethylene/butyl acrylate/maleic anhydride terpolymer and an ethylene/vinyl acetate copolymer grafted with maleic anhydride, Beltrame et al.[9] found that the degree of crystallinity of both PA and PE decreased when the compatibilizer content was increased from 0 to 10 wt %. They also studied the effect of compatibilization on the interfacial tension in the blend and noted that the interfacial tension decreased substantially with addition of ethylene/butyl acrylate/maleic anhydride and to some extent with an ethylene/vinyl acetate copolymer. Armat and Moet[10] used a styrene ethylene/butylene styrene copolymer grafted with maleic anhydride (SEBS-*g*-MA) to compatibilize a blend of PE-LD and PA6 at the blend composition of 75/25. They found that SEBS-*g*-MA coupled the phases of the blend through a microbridging mechanism. They also observed that incorporating SEBS-*g*-MA in excess of 10 wt % reduced the elongation at break, while smaller amounts of the compatibilizer increased the elongation value. Likewise, Chandramouli and Jabarin[6] obtained significantly improved compatibility with the use of a SEBS-*g*-MA copolymer as a compatibilizer for a PE/PA blend.

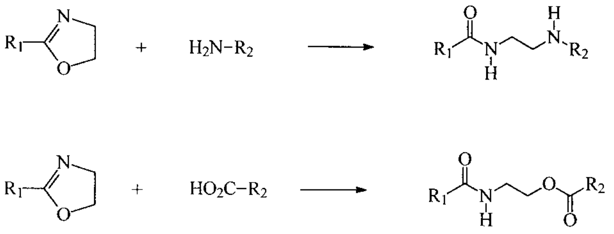

Figure 1 Reaction of oxazoline with the amino and carboxyl end groups of PA.

In this work, oxazoline grafted PE and SEBS were used as compatibilizers in PE/PA6 blends. The oxazoline group is of interest because it can react with the amino and carboxyl end groups in the PA6, as shown in Figure 1.

EXPERIMENTAL

Materials

The PE used as a blend component was a low-density PE, LE 1804, supplied by Borealis Polymers. According to the manufacturer, it has a melt flow rate of 2.1 g/10 min (2.16 kg, 190°C). The aliphatic PA6 was a medium-viscosity extrusion grade for films of enhanced clarity, Ultramid B4F, supplied by BASF. PE (PE_c) and styrene ethylene/butylene styrene copolymer (SEBS) grafted with ricinoloxazoline maleinate were used as compatibilizers. The compatibilizers were produced in our own laboratory by melt free radical grafting as previously reported.[11] PE, LE 7518 (Borealis Polymers), and SEBS, Kraton G-1652 (Shell), were used as base materials for the grafting and as references for the compatibilizers.

Blending and Injection Molding

The blend compositions studied were PE/PA6 80/20, 60/40, 40/60, and 20/80. The amount of the compatibilizer (10 wt %) was subtracted equally from the two phases. The PA6 and the compatibilizers were dried overnight at 80 and 60°C, respectively, in a dehumidifying dryer before blend-

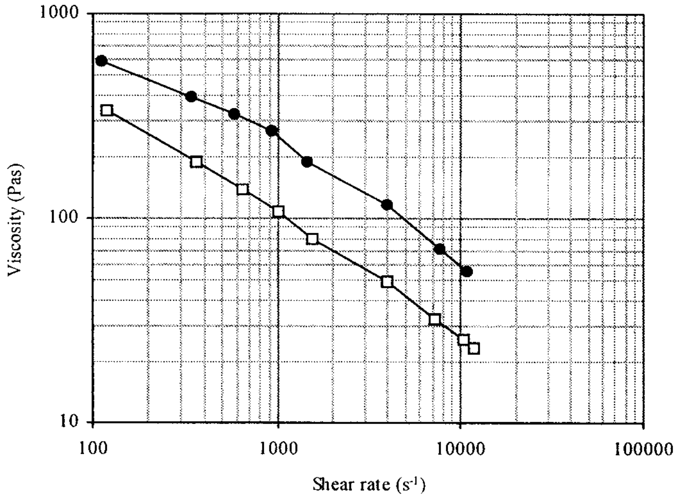

Figure 2 Viscosities of the blend components, (□) PE and (●) PA6, versus shear rate at 250°C measured with a capillary rheometer.

ing. The blends were prepared with a corotating twin-screw midiextruder (DSM, capacity = 16 cm^3, screw length L = 150 mm) under nitrogen atmosphere. The screw speed was 50 rpm during filling and 65 rpm during mixing. The mixing time was 3 min, after which the blend was injection molded with a mini-injection molding machine (DSM) into tensile and impact test specimens. The blending and injection molding temperature was 250°C, and the temperature of the mold was 40°C.

Characterization

Since PA6 is highly sensitive to moisture, the injection molded samples were dried for 16 h at 80°C in a dehumidifying dryer before mechanical testing. Tensile properties were characterized with an Instron 4204 testing machine with a test speed of 2 mm/min and with specimen type 1BA according to the standard ISO 527-1993(E). Charpy impact tests of the unnotched and notched specimens with dimensions of 4 × 6 × 50 mm were made with a Zwick 5102 pendulum-type testing machine according to ISO 179-1993(E).

The melt viscosities of neat polymers were measured with a Göttfert Rheograph 2002 capillary viscosimeter over a shear rate range from 100 to 10 000 s^{-1}. The measuring temperature was 250°C, and a die with a length to diameter ratio (L/D) of 30/1 was used. All measurements include Rabinowitsch correction, but Bagley correction was not made.

The morphology of the blends was characterized with a JEOL JSM-840A scanning electron microscope (SEM) from the fracture surfaces of cryogenically fractured tensile test specimens. The specimens were fractured both parallel and perpendicular to the injection direction and coated with a thin layer of gold.

RESULTS AND DISCUSSION

Rheology

The melt viscosities of neat PE and PA6 were measured to evaluate the viscosity ratio of the components under the blending conditions. According to Hietaoja et al.[12] and Heino et al.,[13] the compatibility of the blend components is better when their viscosities under the blending conditions are very similar. The viscosities of the blend components are shown in Figure 2.

The viscosity ratio of PA6 to PE was about 2 at all shear rates tested, which means that the viscosities of the blend components were not very close to each other and the uncompatibilized blends would be expected to exhibit poor morphology. Because PE is of lower viscosity than is PA, the dispersion of the particles should be finer in the blends where PE forms the dispersed phase. It is also well known that the blend component with the lower viscosity tends to form the continuous phase. One may anticipate, therefore, that the phase inversion point lies at a PA6 fraction of more than 50 wt %.

Mechanical Properties

The tensile modulus, stress at 5% offset strain, elongation at break, and Charpy impact strength

Table I Tensile Modulus (E), Stress at 5% Offset Strain ($\sigma_{5\%}$), Elongation at Break (ε_b), and Charpy Impact Strength of Unnotched and Notched Specimens of Uncompatibilized and Compatibilized PE/PA6 Blends

Blend	Blend Composition (wt %)	E (MPa)	$\sigma_{5\%}$ (MPa)	ε_b (%)	Charpy Impact Strength (kJ/m^2)	
					Unnotched	Notched
PE/PA6	100/0	58 (3)	9.1 (0.6)	119 (12)	*NB*	*NB*
	80/20	189 (18)	12.3 (0.6)	91 (7)	*NB*	10.6 *P* (3.3)
	60/40	354 (14)	18.3 (0.8)	22 (4)	13.6 (1.2)	7.9 *P* (2.1)
	40/60	631 (12)	29.2 (0.9)	12 (2)	26.3 *P* (9.1)	26.6 *P* (8.9)
	20/80	975 (53)	48.0 (1.9)	76 (59)	*NB*	13.2 (2.2)
	0/100	1234 (36)	58.7 (1.0)	318 (45)	*NB*	6.1 (0.6)
PE/PA6/PE$_c$-*g*-OXA	75/15/10	79 (6)	8.6 (0.2)	121 (7)	*NB*	*NB*
	55/35/10	304 (14)	17.5 (0.6)	62 (10)	*NB*	9.8 *H* (1.2)
	35/55/10	612 (14)	30.9 (0.9)	51 (11)	*NB*	24.1 *P* (10.8)
	15/75/10	883 (22)	41.9 (0.5)	446 (20)	*NB*	23.2 (3.7)
PE/PA6/SEBS-*g*-OXA	75/15/10	54 (6)	7.7 (0.3)	143 (8)	*NB*	*NB*
	55/35/10	264 (15)	15.0 (0.5)	73 (11)	*NB*	35.2 *P* (4.1)
	35/55/10	547 (13)	27.7 (0.6)	83 (22)	*NB*	64.2 *P* (24.0)
	15/75/10	801 (46)	37.4 (0.4)	424 (32)	*NB*	52.1 *P* (18.3)
PE/PA6/PE$_c$	75/15/10	171 (10)	11.7 (0.3)	110 (9)	*NB*	17.8 *P* (3.5)
	55/35/10	352 (10)	18.6 (0.5)	40 (15)	17.7 (3.0)	7.0 *P* (0.6)
	35/55/10	596 (8)	28.2 (0.9)	53 (23)	38.0 *P* (18.0)	15.3 *P* (7.4)
	15/75/10	967 (19)	44.1 (0.9)	69 (22)	*NB*	11.7 (1.8)
PE/PA6/SEBS	75/15/10	135 (6)	10.6 (0.2)	114 (8)	*NB*	35.1 *P* (1.5)
	55/35/10	300 (12)	16.9 (0.3)	62 (12)	*NB*	13.2 *P* (2.8)
	35/55/10	579 (3)	28.1 (0.3)	44 (6)	65.4 *P* (15.3)	25.7 *P* (8.1)
	15/75/10	854 (26)	40.8 (0.4)	41 (6)	116.5 *P* (15.9)	12.5 (1.7)

NB, nonbreak (hammer: 4 J); *P*, partial break; *H*, hinge break.

of unnotched and notched specimens of the blends are shown in Table I. Because neat PE and the blends with high PE concentration did not exhibit a yield maximum, the stress was measured at 5% offset strain.

Neat PE was very tough. Neither the unnotched nor the notched specimens broke during the impact tests. However, the tensile tests showed neat PE to exhibit very poor strength and stiffness. Neat PA6, on the other hand, exhibited good impact strength for unnotched specimens, but when the specimen already was defective, the crack continued through the sample very easily, as was indicated by the impact values for the notched specimens. Comparison of the uncompatibilized blends of different composition showed that the strength and stiffness clearly increased with the PA6 content. This was not the case for the toughness of these blends: The impact strength of both the notched and unnotched specimens exhibited the lowest value at the PE/PA6 compositions of 60/40 and 40/60.

Compatibilization with oxazoline functionalized PE$_c$ or SEBS increased the toughness of the blends substantially, despite the high viscosity ratio of the blend components. All unnotched specimens of the compatibilized blends withstood the impact test without breaking, even those of PE/PA6 compositions 60/40 and 40/60 (Fig. 3). The impact strength of the notched specimens was also significantly increased by compatibilization, as illustrated in Figure 4. Here, SEBS-*g*-OXA seemed to give even better results than those of PE$_c$-*g*-OXA. Unfortunately, the tensile strength and modulus decreased slightly when the toughness was improved.

Comparative tests were made with unmodified PE$_c$ and SEBS to clarify the effect of the

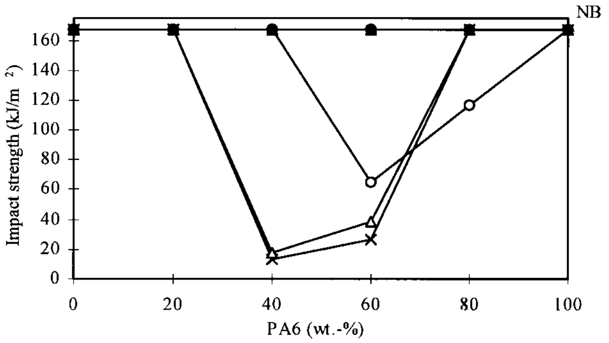

Figure 3 Charpy impact strength of unnotched specimens of (×) binary and ternary PE/PA6 blends. The third component added was (▲) PE_c-*g*-OXA, (●) SEBS-*g*-OXA, (△) PE_c, or (○) SEBS. The x-axis denotes the PA6 fraction of PE/PA6 excluding the compatibilizer.

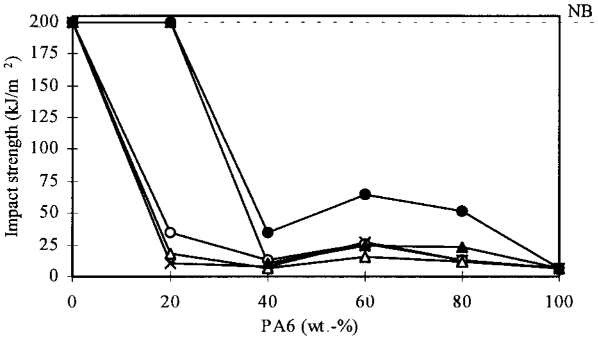

Figure 4 Charpy impact strength of notched specimens of (×) binary and ternary PE/PA6 blends. The third component added was (▲) PE_c-*g*-OXA, (●) SEBS-*g*-OXA, (△) PE_c, or (○) SEBS. The x-axis denotes the PA6 fraction of PE/PA6 excluding the compatibilizer.

addition of an elastic material and of the reaction between oxazoline and PA6 end groups on the macroscopic properties. It was clear that the functionalized copolymers were better impact modifiers than were their unfunctionalized counterparts. As anticipated, the addition of ungrafted PE_c did not affect the mechanical properties beyond what would be expected with a 5 wt % increase in the fraction of polyethylene in the blend. As can be seen in Table I, when neat SEBS was added, an effect typical for elastomers was observed: The tensile strength and modulus of the blends decreased, while the toughness was improved. Relative to neat PE_c and SEBS, the addition of grafted polymers to blends caused the tensile strength and stiffness to decrease a bit more. The impact strength, on the other hand, was significantly higher for the compatibilized blends.

The elongation at break was clearly higher for neat PE and even more so for neat PA than for the binary blends. When a compatibilizer was added, the elongation at break improved over the whole composition range. This result is consistent with the findings of Raval et al.[4] They speculated that the large size of the dispersed particles of binary blends may hinder drawing of the matrix, causing premature rupture of the material and thus lowering the elongation value. The compatibilized blends have a finer morphology and the compatibilizers are assumed to be located at the blend interface, where they help to decrease the high stress concentrations around the dispersed particles by local plastic deformation. In our study, the improvement in the elongation at break was most significant for the compatibilized blends of the PE/PA6 composition 20/80 (Fig. 5). These blends exhibited an even higher elongation value than that of neat PA6.

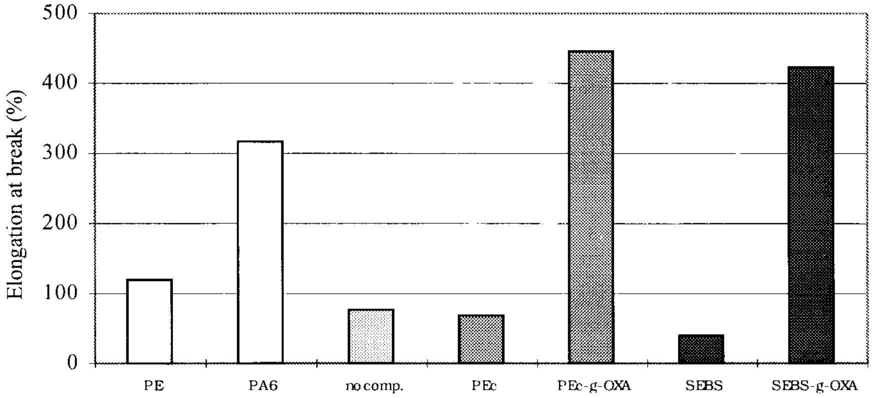

Figure 5 Elongation at break for the (white bars) neat blend components and (gray bars) PE/PA6 blends of composition 20/80.

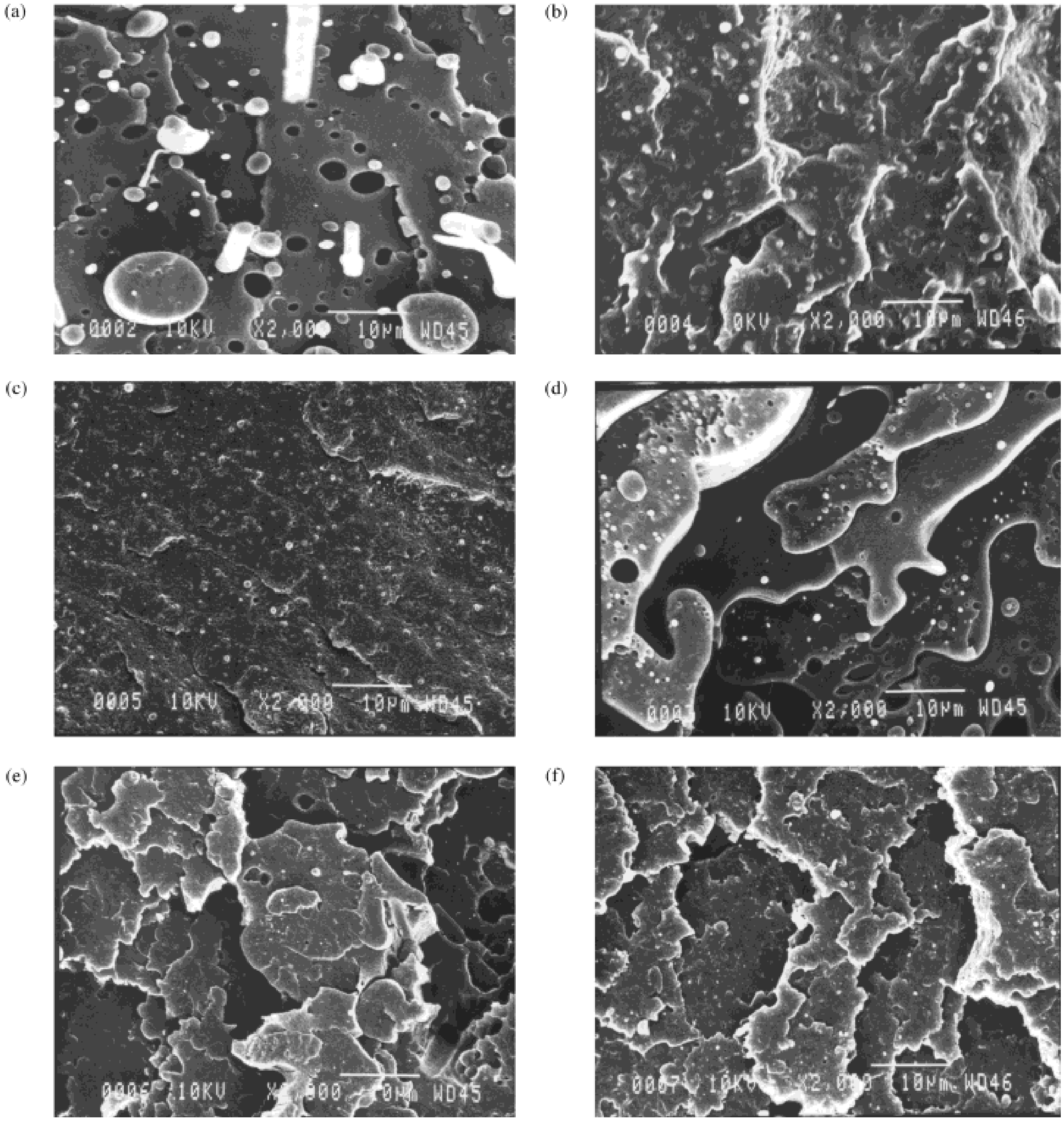

Figure 6 SEM micrographs of fracture surfaces of samples fractured perpendicular to the injection direction of uncompatibilized and compatibilized PE/PA6 blends of compositions 80/20 and 40/60 (×2000): (a) PE/PA6 80/20; (b) PE/PA6/PE$_c$-*g*-OXA 75/15/10; (c) PE/PA6/SEBS-*g*-OXA 75/15/10; (d) PE/PA6 40/60; (e) PE/PA6/PE$_c$-*g*-OXA 35/55/10; (f) PE/PA6/SEBS-*g*-OXA 35/55/10.

Morphology

The binary blends of all compositions tested showed clear visual evidence of the incompatibility between PE and PA6. In the PE/PA6 blends of compositions 80/20 and 60/40, where the PA6 formed the dispersed phase, the dispersion was in the form of rather large fibrils, which varied greatly in size (1–8 and 1–20 μm, respectively). The size of the dispersed PA6 particles increased with the PA6 content. As illustrated in Figures 6(d) and 7(a), the PE/PA6 composition of 40/60 lay near the phase inversion region. The blend seemed to form a cocontinuous structure, with dispersed particles in both phases. In the PE/PA6 blend of composition 20/80, the size of the dispersed PE particles ranged from smaller than 1 to 3 μm. As could be predicted from

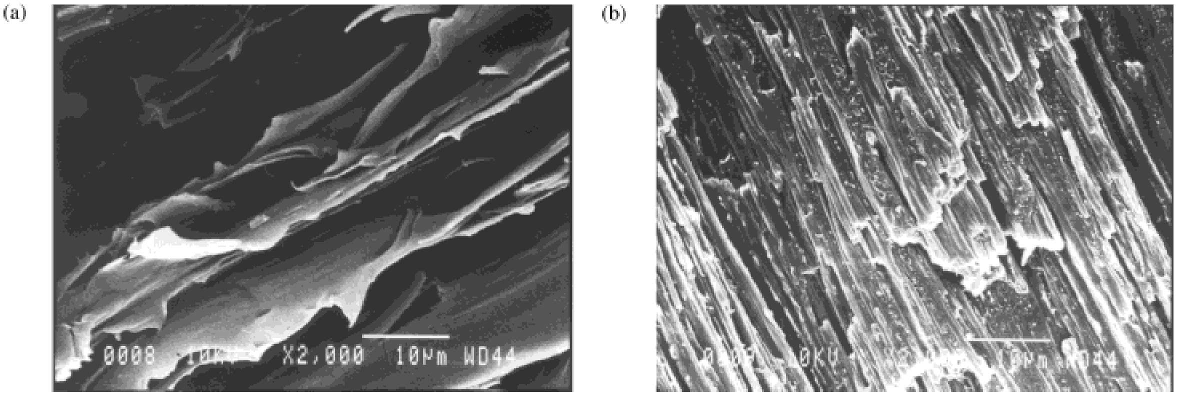

Figure 7 SEM micrographs of fracture surfaces of samples fractured parallel to the injection direction of (a) uncompatibilized and (b) SEBS-*g*-OXA compatibilized PE/PA6 blends of composition 40/60 (×2000).

the viscosity ratio, the dispersed PE particles were clearly smaller than were the dispersed PA6 particles in blends where PE formed the continuous phase.

With the addition of a compatibilizer, the particles of the dispersed phase became more uniform and much reduced in size. The dispersed particles were smaller than 1 μm for all compatibilized blends and much better embedded in the matrix. As depicted in Figure 6, SEBS-*g*-OXA produced even smaller particles than did PE_c-*g*-OXA. It should also be mentioned that the fibrils in the uncompatibilized blends disappeared by compatibilization. The effect of compatibilization was also evident in micrographs of the samples fractured parallel to the injection direction (Fig. 7). The improved adhesion in the compatibilized PE/PA6 40/60 blends is seen in Figure 6 as a rough interphase instead of the smooth one in the uncompatibilized blend.

The addition of neat SEBS reduced the particle size, but not as substantially as did addition of its functionalized counterpart. There was also a clear difference in the size distribution between the compatibilized ternary blends and their uncompatibilized counterparts: The functionalized copolymers produced blends with dispersed particles of highly uniform size.

It is well known that the mechanical properties of a blend are dependent on the size distribution of the particles of the dispersed phase and on the adhesion between the separate phases. Thus, the binary blends having unstabilized morphology exhibited poor impact strength. Addition of a compatibilizer resulted in dispersed particles of uniform and very small size and, consequently, the toughness was significantly increased. This was not the case when neat PE_c or SEBS was added to the blends, which indicates that, in the case of the compatibilizer, a favorable reaction took place between the oxazoline group and the end groups of the PA6.

CONCLUSIONS

A study was made of the compatibilization of blends of PE and PA6 with polyethylene and styrene ethylene/butylene styrene copolymer grafted with ricinoloxazoline maleinate. The effect of the compatibilization on the mechanical properties and morphology of the blends was of interest. Compatibilization was found to significantly improve the impact strength of the blends, but it also caused a slight loss in strength and stiffness. The morphology studies supported the mechanical results: The particle size was reduced and became more uniform and the adhesion of the dispersed phase to the matrix improved due to the compatibilization. These changes most probably were due to the miscibility of the polyolefin part of the compatibilizer with the polyolefin component in the blend and to a reaction between the oxazoline groups in the compatibilizer and the amino and carboxyl end groups of polyamide.

NOMENCLATURE

H	hinge break
NB	nonbreak
L	length
L/*D*	length to diameter ratio

P	partial break
PA	polymide
PA6	polyamide 6
PE	polyethylene
PE_c	polyethylene used as a matrix material for grafting
PE-*g*-BuA	butyl acrylate grafted PE
PE-*g*-(BuA-*co*-MA)	butyl acrylate-*co*-maleic anhydride grafted PE
PE_c-*g*-OXA	oxazoline grafted PE
PE-LD	low-density PE
SEBS	styrene ethylene/butylene styrene copolymer
SEBS-*g*-MA	maleic anhydride grafted styrene ethylene/butylene styrene copolymer
SEBS-*g*-OXA	oxazoline grafted styrene ethylene/butylene styrene copolymer
SEM	scanning electron microscopy

Symbols

E	tensile modulus (MPa)
σ	tensile strength (MPa)
ε_b	elongation at break (%)

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