# Use of Oxazoline Functionalized Polyolefins and Elastomers as Compatibilizers for Thermoplastic Blends

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Received 12 January 1998; accepted 6 March 1998

ABSTRACT: Oxazoline functionalized polypropylene, polyethylene, ethylene propylene copolymer (E/P), and styrene ethylene/butylene styrene copolymer (SEBS) were studied as compatibilizers in blends of polyolefins with polyesters and polyamides. The blends investigated were polypropylene/polyamide 6, polypropylene/polybutylene terephtalate, and polyethylene/polyamide 6, with engineering thermoplastic contents of 30 wt %. The blends were prepared in a twin-screw midiextruder, and injection molded with a mini-injection molding machine. The effect of compatibilization substantially improved the toughness of all tested blends. Their strength and stiffness remained at the level of the binary blends when polypropylene or polyethylene based compatibilizers were used, but slightly decreased with other compatibilizers. Morphological studies showed that the particle size was reduced, and the adhesion of the dispersed phase to the matrix improved by compatibilization. The effect of unfunctionalized polyethylene, polypropylene, E/P, and SEBS was also studied to compare the compatibilizers with them. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1923–1930, 1998

Key words: oxazoline; polymer blend; compatibilization; reactive extrusion

## **INTRODUCTION**

Blending thermoplastics is a useful and relatively cost-effective way to produce new materials with desired property combinations. Polyolefins have good moisture stability, processability, and low cost. Engineering plastics, on the other hand, can improve the thermal and mechanical properties of the blend. However, most thermoplastic blends are immiscible, and thus, exhibit poor properties. Unfavorable interactions at the molecular level lead to high interfacial tension and make the melt mixing of the components difficult. This also leads to unstable morphology and poor interfacial adhesion, which are the main causes for inferior mechanical properties of the blends. To increase the compatibility of the blend components, pre-formed block or graft copolymers are often used. The copolymer compatibilizers are expected to locate at the interface of the blend components, where they improve the blend morphology: decrease the particle size, and increase the adhesion between the discrete polymer phases. The compatibilization effect is based on the ability of the compatibilizers to react or to be miscible with the blend components.<sup>1,2</sup>

Polyolefins, which are nonpolar, are immiscible with polyamides and polyesters. The same applies for unfunctionalized elastomers like ethylene propylene rubber (EPR) and styrene ethylene/ butylene styrene copolymer (SEBS). Grafting polyolefins with functional monomers yields reactive polymers that are suitable compatibilizers for polyolefin-based blends. SEBS, ungrafted or grafted, has also been found to be an effective impact modifier in these blends.<sup>3-5</sup>

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Journal of Applied Polymer Science, Vol. 70, 1923-1930 (1998)

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

Compatibilization of binary blends by reactive extrusion has been studied by several research groups.<sup>6,7</sup> The most frequently used functional monomers in free radical grafting are maleic anhydride and glycidyl methacrylate. In this work, a long-chain monomer containing an oxazoline group has been used. Long-chain oxazolines have been reported to be less toxic than maleic anhydride and glycidyl methacrylate.<sup>8,9</sup> Oxazoline grafted polymers are suitable compatibilizers because the oxazoline group reacts with carboxyl and amino end groups of engineering plastics, as shown in Figure 1.<sup>10–12</sup> Oxazoline is reactive with other functional groups as well; an overview of its reactions can be found in literature.<sup>13</sup>

Novel ricinoloxazoline maleinate grafted polyethylene, ethylene propylene copolymer, and styrene ethylene/butylene styrene copolymer were prepared and used as compatibilizers in blends of polyolefins with polyesters and polyamides. The blend properties were studied in terms of morphology and mechanical properties: tensile strength and modulus and Charpy impact strength for both notched and unnotched specimens.

### **EXPERIMENTAL**

#### Materials

The graft copolymers were produced in our own laboratory as previously reported.<sup>14</sup> The degree of grafting was 1.9 wt % for PP<sub>c</sub>-g-OXA, 1.0 wt % for

	Blend				Charpy Impact Strength (kJ/m <sup>2</sup> )	
Blend	Composition (wt %)	E (MPa)	$\sigma$ (MPa)	$\varepsilon_b~(\%)$	Unnotched	Notched
PP <sub>1</sub> /PA6	70/30	923 (19)	37.8 (0.6)	19 (5)	20.1 (2.0)	3.2(0.3)
PP <sub>1</sub> /PA6/PP <sub>c</sub>	60/30/10	929 (16)	37.1(0.4)	36 (6)	17.4(2.3)	4.3(0.5)
PP <sub>1</sub> /PA6/SEBS	60/30/10	903 (19)	36.0 (0.4)	16 (3)	21.5(1.7)	2.3(0.3)
PP <sub>1</sub> /PA6/E/P	60/30/10	760(13)	33.8 (0.6)	24(4)	20.0 (1.8)	3.9(0.5)
PP <sub>1</sub> /PA6/PP <sub>c</sub> -g-OXA	60/30/10	1018 (20)	39.3 (1.1)	50 (6)	37.4 (8.7)	2.2(0.2)
PP <sub>1</sub> /PA6/SEBS-g-OXA	60/30/10	755(41)	32.5(0.9)	377(99)	NB	3.6 (0.6)
PP <sub>1</sub> /PA6/E/P-g-OXA	60/30/10	738 (60)	34.8 (0.8)	331 (102)	NB	4.6 (0.4)
PE/PA6	70/30	313(12)	20.3 (0.6)	55(11)	$42.5 \text{ H}^{a}(12.2)$	6.6 (0.7)
PE/PA6/PE <sub>c</sub>	60/30/10	320 (9)	20.0 (0.7)	38(5)	22.1 H (4.0)	6.4H(1.6)
PE/PA6/SEBS	60/30/10	293 (11)	20.4 (1.0)	55(4)	NB	11.4H(2.7)
PE/PA6/E/P	60/30/10	273(19)	15.6(0.7)	30 (8)	21.1 H (4.1)	10.9H (1.3)
PE/PA6/PE <sub>c</sub> -g-OXA	60/30/10	180 (8)	15.9(1.2)	57 (6)	NB	26.1P (4.2)
PE/PA6/SEBS-g-OXA	60/30/10	233(13)	20.4 (0.8)	75(8)	NB	25.2P (4.9)
PE/PA6/E/P-g-OXA	60/30/10	188 (20)	13.7(1.9)	44(5)	NB	7.2H(0.7)
PP <sub>2</sub> /PBT	70/30	845(17)	33.3(0.4)	$>\!500$	59.1 (18.0)	3.5(0.7)
PP <sub>2</sub> /PBT/PP <sub>c</sub>	60/30/10	886 (8)	32.2(0.5)	> 500	55.4 (16.1)	4.9 (0.8)
PP <sub>2</sub> /PBT/SEBS	60/30/10	715(26)	28.5(0.4)	$>\!500$	NB	6.0(2.1)
PP <sub>2</sub> /PBT/E/P	60/30/10	725(20)	29.4 (0.8)	$>\!500$	NB	4.9 (0.7)
PP <sub>2</sub> /PBT/PP <sub>c</sub> -g-OXA	60/30/10	836 (19)	31.3 (0.6)	$>\!500$	NB	3.8 (0.3)
PP <sub>2</sub> /PBT/SEBS-g-OXA	60/30/10	679(22)	28.1(0.1)	$>\!500$	NB	7.9 (0.8)
PP <sub>2</sub> /PBT/E/P-g-OXA	60/30/10	661 (14)	28.9(0.2)	$>\!500$	NB	7.2(0.5)

Table I Tensile Modulus (*E*), Tensile Strength ( $\sigma$ ), Elongation at Break ( $\varepsilon_b$ ), and Charpy Impact Strength for Unnotched and Notched Specimens of the PP<sub>1</sub>/PA6, PE/PA6, and PP<sub>2</sub>/PBT Blends

NB = nonbreak, P = partial break and H = hinge break.

<sup>a</sup> Two of the samples were NB.



Figure 2 Charpy impact strength for unnotched specimens of the PP<sub>1</sub>/PA6 blends.

 $PE_c$ -g-OXA, 1.4 wt % for E/P-g-OXA, and 1.4 wt % for SEBS-g-OXA. The blend components used were PE L 420 C, PP VC12 33B (PP<sub>1</sub>) with polyamide 6, and VB19 50K (PP<sub>2</sub>) with polybutylene terephtalate. The polyolefins were supplied by Borealis Polymers. The polybutylene terephtalate (PBT) used was Grilpet XE 3060, supplied by EMS Chemie, and the polyamides were Ultramid B3S for PP<sub>1</sub>/PA6 blends and Ultramid B4F for PE/PA6 blends, both supplied by BASF. The references for the compatibilizers were PP<sub>c</sub> Valtec CL 101D and E/P Hifax CA 10A supplied by Montell, PE<sub>c</sub> LE7518 supplied by Borealis Polymers, and SEBS Kraton G-1652 supplied by Shell. These have been used as matrix materials for the grafted copolymers.

#### **Blending and Injection Molding**

The blend components were dried in a dehumidifying dryer before blending according to the recommendations of the manufacturers. The blend compositions were 60 wt % polyolefin, 30 wt % engineering polymer, and 10 wt % third component for ternary blends, and 70/30 wt % for binary blends. The blends were prepared with a corotating twin-screw midiextruder (DSM, capacity = 16 cm<sup>3</sup>, 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

Because polyamide is highly sensitive to moisture, the injection molded samples containing polyamide were dried for 16 h at 80°C in a dehu-



Figure 3 Tensile strength (bars) and tensile modulus (points) of the PP<sub>1</sub>/PA6 blends.



Figure 4 Charpy impact strength for unnotched specimens of the PE/PA6 blends.

midifying dryer before mechanical testing. The other samples were conditioned for 3 days at 23°C and 50% relative humidity. 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 unnotched and notched specimens with dimensions of  $4 \times 6 \times 50$  mm were made with a Zwick 5102 pendulum-type testing machine according to ISO 179-1993(E).

The morphology of the blends was characterized with a JEOL JSM-840A scanning electron microscope (SEM) from the fracture surfaces of cryogenically fractured impact test specimens coated with a thin layer of gold.

## **RESULTS AND DISCUSSION**

#### **Mechanical Properties**

Mechanical properties of the blends are characterized by tensile modulus, tensile strength, elongation at break, and Charpy impact strength of unnotched and notched specimens (Table I). For the PP<sub>1</sub>/PA blend, all compatibilizers increased the Charpy impact strength of unnotched specimens (Fig. 2) and the elongation at break. The unnotched specimens of the blends compatibilized with SEBS-g-OXA and E/P-g-OXA did not fail at all, and the impact strength for notched specimens was also slightly improved. With PPc-g-OXA the increase in toughness was not as pronounced, but due to improved tensile modulus and strength, better balance between all the tested properties was achieved (Fig. 3). Similar effects, that is, improvement in toughness at the expense of strength and stiffness with SEBS- and PE-based compatibilizers, but not with PP-based ones, have been observed in earlier studies, also.4,5,15

For the PE/PA6 blends, Charpy impact strength for both unnotched and notched specimens increased considerably due to compatibilization, as shown in Figures 4 and 5. The unnotched specimens did not fail at all, and the notched ones were



Figure 5 Charpy impact strength for notched specimens of the PE/PA6 blends.



Figure 6 Charpy impact strength for unnotched specimens of the PP<sub>2</sub>/PBT blends.

only partially broken when SEBS-g-OXA or  $PE_c$ -g-OXA was used. The tensile modulus and strength of the blends generally decreased when a compatibilizer was added. The same trend has been observed using maleinated polyethylene as compatibilizer.<sup>16</sup> SEBS-g-OXA, however, retained the strength achieved with an uncompatibilized blend, and the stiffness was considerably better than with other compatibilizers.

For the PP<sub>2</sub>/PBT blends, Charpy impact strength for unnotched specimens was significantly improved by the compatibilization (Fig. 6). The specimens did not fail at all, unlike the specimens of the uncompatibilized blends. The impact strength for notched specimens also increased using SEBS-g-OXA and E/P-g-OXA, but simultaneously the tensile modulus and strength slightly decreased. When PP-g-OXA was added the tough-





(c)

**Figure 7** SEM micrographs of fracture surfaces of binary blends ( $\times 2000$ ): (a) PP<sub>1</sub>/PA6, (b) PE/PA6, (c) PP<sub>2</sub>/PBT.





**Figure 8** SEM micrographs of fracture surfaces of ternary  $PP_1/PA6$  blends (×2000), the third component being: (a) SEBS, (b) SEBS-g-OXA, (c) E/P, and (d) E/P-g-OXA.

ness was improved without sacrificing the strength and stiffness. Similar effects in PP/PBT blends with an epoxy functionalized polymer have been observed in our earlier studies.<sup>17</sup>

Comparing the ternary blends, a big difference in the compatibilizing effect between functionalized compatibilizers and their unfunctionalized counterparts was observed. When neat  $PP_c$  was added to a blend, no noticeable difference in mechanical properties was observed. Oxazoline functionalized PP<sub>c</sub>, on the other hand, caused a significant improvement in toughness without any reduction in strength or stiffness. In fact, even a slight increase in these properties was discovered for the PP<sub>1</sub>/PA6 blend. When using SEBS and E/P the tensile strength and modulus decreased because of the softness of these materials. When neat materials were used the decrease was less notable than with their functionalized counterparts. The increase in toughness was, however, more pronounced using the oxazoline functionalized polymers because of the predictable reaction at the interface.<sup>5</sup>

#### Morphology

The morphology was coarse for all uncompatibilized blends. The particle size in PA6 blends (2–7  $\mu$ m for PE/PA6 and 3–8  $\mu$ m for PP<sub>1</sub>/PA6) was larger than in PBT blends (1–4  $\mu$ m) (Fig. 7). Adding neat polyolefin—that is PP, PE, or E/P—did not reduce the particle size. Neat SEBS, on the other hand, slightly reduced the particle size in all blends, and when it became small enough, toughness was improved, although no reaction between the phases could have taken place. This was related to the rubber-like nature of the added SEBS.

Addition of oxazoline grafted polymers resulted in much more homogeneous blend morphology (Figs. 8 and 9). The particle size of these blends was generally reduced to less than 1.5  $\mu$ m. The PE/PA6/(E/P-g-OXA) blend formed an exception, exhibiting dispersed particles of 1.5-4  $\mu$ m. This explains the inferior toughness of this blend compared with the other compatibilized PE/PA6 blends. In all compatibilized





**Figure 9** SEM micrographs of fracture surfaces of ternary PE/PA6 and PP<sub>2</sub>/PBT blends (×2000): (a) PE/PA6/PE<sub>c</sub>, (b) PE/PA6/PE<sub>c</sub>-g-OXA, (c) PP<sub>2</sub>/PBT/PP<sub>c</sub>, and (d) PP<sub>2</sub>/PBT/PP<sub>c</sub>-g-OXA.

blends the particles were much better embedded in the matrix than in the uncompatibilized blends. The improved adhesion between the phases was most probably due to the reaction of the oxazoline group with carboxylic acid or amino end groups of polyesters or polyamides. The morphology studies supported the mechanical results: the particle size was reduced, and the adhesion of the dispersed phase to the matrix improved due to compatibilization.

## **CONCLUSIONS**

Polypropylene, polyethylene, E/P, and SEBS grafted with ricinoloxazoline maleinate were used as compatibilizers for PP<sub>1</sub>/PA6, PE/PA6, and PP<sub>2</sub>/PBT blends. The effect of the compatibilization on the mechanical properties and morphology of the blends was studied. Addition of the grafted polymers was found to im-

prove the Charpy impact strength for unnotched specimens of all blends, but the impact strength for notched specimens was significantly improved only for the PE/PA6 blend. PP<sub>c</sub>g-OXA compatibilized blends retained their strength and stiffness, but with other compatibilizers the blends suffered a slight loss in these properties when the toughness was improved. The toughening was based on a stabilized morphology consisting of a very fine dispersion of the minor phase with droplets well embedded in the matrix. This was most probably 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 carboxylic end groups of polyamides and polyesters. This study proved that oxazoline grafted polyolefins and elastomers act as effective compatibilizers in blends of polyolefins with engineering plastics.

## NOMENCLATURE

E/P = ethylene propylene copolymer

- E/P-g-OXA = oxazoline grafted ethylene propylene copolymer
  - EPR = ethylene propylene rubber
    - H = hinge break
  - NB = non-break
  - P = partial break
  - PA6 = polyamide 6
  - PBT = polybutylene terephtalate
  - PE = polyethylene
  - $PE_c = polyethylene$  used as a matrix material for grafting
- $PE_{c}-g-OXA = oxazoline grafted polyethylene$ 
  - PP = polypropylene
  - $PP_1 = polypropylene$  used as a component in the PP/PA6 blend
  - $PP_2 = polypropylene$  used as a component in the PP/PBT blend
  - $PP_c = polypropylene$  used as a matrix material for grafting
- $PP_c$ -g-OXA = oxazoline grafted polypropylene
  - ref = uncompatibilized reference blend SEBS = styrene ethylene/butylene styrene copolymer
- SEBS-g-OXA = oxazoline grafted styrene ethylene/butylene styrene copolymer

SEM = scanning electron microscopy

### **Symbols**

- E =tensile modulus (MPa)
- $\sigma$  = tensile strength (MPa)
- $\varepsilon_b = \text{elongation at break} (\%)$

## REFERENCES

- N. G. Gaylord, J. Macromol. Sci.-Chem., A26, 1211 (1989).
- 2. M. Xanthos, Polym. Eng. Sci., 28, 1392 (1988).
- M. Heino, J. Kirjava, P. Hietaoja, and J. Seppälä, J. Appl. Polym. Sci., 65, 241 (1997).
- R. Holsti-Miettinen, J. Seppälä, and I. Reima, Polym. Eng. Sci., 32, 868 (1992).
- 5. J. Rösch and R. Mülhaupt, Makromol. Chem., Rapid Commun., 14, 503 (1993).
- 6. S. Datta and D. J. Lohse, *Polymeric Compatibilizers: Uses and Benefits in Polymer Blends*, Carl Hanser Verlag, Munich, 1996.
- 7. M. Xanthos, *Reactive Extrusion: Principles and Practice*, Carl Hanser Verlag, Munich, 1992.
- 8. Henkel KGaA, Loxamid V-EP 8515, Material Safety Data Sheet, Düsseldorf, 1994.
- R. E. Lenga, Ed., *The Sigma-Aldrich Library of Chemical Safety Data*, Sigma-Aldrich Corporation, Milwaukee, WI, 1988.
- T. Vainio, G.-H. Hu, M. Lambla, and J. V. Seppälä, J. Appl. Polym. Sci., 61, 843 (1996).
- T. Vainio, G.-H. Hu, M. Lambla, and J. V. Seppälä, J. Appl. Polym. Sci., 63, 883 (1997).
- P. Hietaoja, M. Heino, T. Vainio, and J. Seppälä, *Polym. Bull.*, **37**, 353 (1996).
- 13. J. A. Frump, Chem. Rev., 71, 483 (1971).
- 14. U. Anttila, C. Vocke, and J. Seppälä, J. Appl. Polym. Sci., in press.
- A. González-Montiel, H. Keskkula, and D. R. Paul, *Polymer*, **36**, 4587 (1995).
- G.-H. Hu, Y.-J. Sun, and M. Lambla, *Polym. Eng. Sci.*, **36**, 676 (1996).
- R. M. Holsti-Miettinen, M. T. Heino, and J. V. Seppälä, J. Appl. Polym. Sci., 57, 573 (1995).