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Reactive compatibilization of PA6/LDPE blends with an ethylene–acrylic acid copolymer and a low molar mass bis-oxazoline

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Abstract

A sample of polyamide-6 (PA) was blended with low density polyethylene (LDPE) in the 80/20 wt/wt ratio, either without and with 2 phr of an ethylene–acrylic acid copolymer (EAA), Which was known to behave as a compatibilizer precursor, and the effect of the addition of small amounts (0.2 or 0.35 phr) of a fourth component, 2,2′-(1,3-phenylene)-bis(2-oxazoline) (PBO), was investigated. The reactions of PBO with EAA, PA and their blends were studied by recording as a function of time the torque applied to the blending apparatuses and by studying the solubility behavior of the products in formic acid. The PALDPE blends were prepared in a co-rotating twin screw extruder and were characterized by Molau tests, differential scanning calorimetry, scanning electron microscopy, rheology, and determination of the ultimate mechanical properties, including impact tests. The results indicate that the effectiveness of EAA as a compatibilizer precursor is considerably enhanced when PBO is added into the blends. It is thought that the reactions of PBO with the free carboxyl groups of EAA and with the amine or carboxyl end groups of PA run, at least in part, toward the formation of PA-*g*-EAA copolymers acting as the true compatibilizers for these blends.

Keywords: PA/LDPE blends; Reactive compatibilization; Oxazoline

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1. Introduction

Blends of polyolefins (POs) with condensation polymers (PCs) are extremely interesting not only from a scientific point of view but also for their possible practical applications [1–10]. However, since the components of these blends are highly incompatible, a compatibilization step is needed in order to obtain materials with properties suited to practical applications [11,12]. Among the different POs/PCs blends, those of polyethylene (PE) with polyamide-6 (PA) are particularly appealing, as it would be very interesting to combine the high impact resistance of PE with the mechanical strength and the barrier properties of PA.

In previous works [13,14] some of us investigated the efficacy of ethylene–acrylic acid copolymers (EAA) for the reactive compatibilization of the blends of PA with low density polyethylene (LDPE). These copolymers were actually found to behave as effective compatibilizer precursors (CPs) as it was demonstrated that they give rise, during blending, to slow acidolysis reactions with the amide bonds of PA to yield EAA-*g*-PA copolymers. The addition of only 1–2 phr EAA was found to improve considerably the dispersion of the minor phase droplets and to inhibit their coalescence [13]. However, the addition of 2 phr EAA into these blends, carried out during their preparation in a single screw extruder, led to a modest improvement of the mechanical properties of the produced ribbons [14].

With the aim of exalting the compatibilizing efficiency of EAA by increasing the rate of the grafting reactions, we investigated the effect of the addition, into the 75/25/2PA/LDPE/EAA blends, of a bis-oxazoline compound, as the fourth component. Oxazoline derivatives have been shown to be highly reactive toward a number of functional groups, including carboxyl and amine [15]. Thus, we selected 2,2′-(1,3-phenylene)-bis(2-oxazoline) (PBO), which had already been used for the chemical modification of POs, to increase their stiffness, and of polyamides, to

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improve their water resistance and impact properties [16, 17]. When PBO is added into the blend of PA, LDPE and EAA in the proportions indicated above, it is obviously possible that it reacts exclusively with the end groups of PA, or, alternatively, with the carboxyl groups of EAA. If so, the effect on blend compatibility would clearly be negligible, if any. However, since PBO might probably have a tendency to migrate to the interface between the phases, at least a fraction of the PBO molecules can also be expected to react with the carboxyl groups of EAA, through one of the oxazoline rings, and with the amine (or carboxyl) end groups of PA, through the other, as indicated in the scheme below, thus forming a chemical link between the PA grafts and the EAA backbones.

In this work, the reactions between PBO and the different blends components have been qualitatively assessed and their effect on the morphology and the rheological and mechanical properties of PA/LDPE/EAA blends produced by extrusion has been investigated.

2. Experimental

2.1. Materials

The PE sample used for the preparation of the blends was a LDPE grade (Riblene FC30) kindly supplied by Polimeri Europa, Italy. The melt flow index, measured at 190 °C and 2.16 kg, was 0.27 dg/min and the density at room temperature was 922 kg/m^3. The PA sample was provided by Snia Tecnopolimeri; its intrinsic viscosity, measured in formic acid 45 dl/g and the contents of amine and carboxyl end groups were 34 and 35 mequiv./kg, respectively. The EAA, Escor 5001, was kindly supplied by Exxon-Mobil Chemical Mediterranea. Its melt flow index, measured at 190 °C and 2.16 kg, was 2.0 dg/min and the acrylic acid content was 6.2 wt%.

The oxazoline modifier, 2,2′-(1,3-phenylene)-bis(2-oxazoline) (PBO), was purchased from Adeka Palmarole, France, and used as received.

2.2. Blends preparation

Before use, all the polymers were accurately dried: the LDPE and the EAA, at 70 °C under vacuum for 12 h, and the PA in a ventilation oven overnight, at 100 °C, and under vacuum for 4 h, at 120 °C.

Preliminary experiments were carried out in a Brabender Plasticorder, equipped with a static mixer of 50 ml capacity, and in a Haake Minilab Rheomex mod. CTWS mixer/twin screw extruder, both allowing to record the torque vs. time curves, in order to get an insight into the reactions involving functional groups of PA, the carboxyl groups of EAA, and the oxazoline rings of PBO. To this end, 0.35 phr PBO were added into molten PA or EAA, and 80/20 PA/EAA blends, with and without 0.35 phr PBO, were prepared. A temperature of 240 °C and a rotor speed of 30 rpm was used in the Brabender, whereas a flat temperature profile of 240–240–240 °C and a speed of 240 rpm was employed in the Minilab apparatus.

The PA/LDPE blends, both with and without 2 phr EAA and 0.2 or 0.35 phr PBO, with a 80/20 wt/wt composition in a OMC, Italy, co-rotating twin screw extruder. The thermal profile was 140–200–240–240–240–240–220 °C and the speed 40 rpm.

The relatively low die temperature and screw speed allowed to work with a residence time of about 4 min, which should be sufficient for the grafting reactions to occur to a reasonable extent.

2.3. Characterizations

Rheological measurements were performed using a Rheometrics RDAII parallel plate rheometer. Before testing, the samples were accurately dried as illustrated above.

Scanning electron microscopy (SEM) observations of the surfaces produced by fracturing the samples under liquid nitrogen and coating them with gold were made with Jeol JSM-5600 LV and Jeol T300 microscopes.

Tensile test were performed with an Instron mod. 4443 on samples of $10 \times 100 \times 0.7\ \text{mm}^3$ cut off from compression molded sheets prepared at 240 °C with a Carver laboratory press. According to ASTM D882, the cross-head speed was held at 1 mm/min for the first 120 s and was than rapidly raised to 50 mm/min until breaking occurred. Before the tensile tests, all the samples were humidified according to ASTM D570 by immersion in water at 90 °C for 0.7 h, followed by 4 days storage at 23 °C in an atmosphere at 50% RH. The results reported in the present work are the average of at least 10 tests. Their maximum deviation was ±5%.

Impact tests were performed at room temperature with a CEAST (Italy) Izod pendulum equipped with a 7.5 J hammer. The samples (70 mm long, 12.7 mm wide, 2.54 mm thick) were prepared by injection molding by the use of a laboratory injection-molding machine (Ray Ran, Italy). The results reported in this work are the average of at least 10 tests, with a maximum scatter of ±7%.

Molau tests [18,19] were performed by stirring about 500 mg of the blends in 125 ml of 85% formic acid, storing the test tubes for 24 h, and measuring the turbidity of the solutions with a HANNA turbidimeter mod. HI93703.

Calorimetry measurements were performed under nitrogen flow, with a DSC7 Perkin Elmer differential scanning calorimeter, on dried samples of 5–8 mg, using a scanning rate of 10 °C/min.

3. Results and discussion

The occurrence and the extent of the chemical interactions taking place between PA, EAA and PBO were qualitatively assessed either by recording as a function of time the torque applied to the Brabender mixer or the Minilab apparatus while blending these components, as described in Section 2, and by comparing the solubility behavior of some of the products.

The torque vs. time curves shown in Fig. 1, recorded during some of the experiments carried out in the Brabender mixer, exemplify the results. In these experiments, the appropriate amount of EAA or PA was introduced in the mixer bowl, preheated to 240 °C, and was kneaded for 5–10 min until temperature and torque became constant. Then, the second component was added at $t = 0$, and the third, if any, at $t = 6$ min.

Curve (a) shows the behavior of the torque applied to molten EAA after addition of 0.35 phr PBO. It can be observed that the viscosity of the molten polymer increased rapidly by about three times as a result of the reactions of PBO with the carboxyl groups of EAA. Considering that under the shear rate conditions prevailing in the experiment the slope of the log–log plot describing the effect of molecular weight on melt viscosity was shown to be close to 2.5–3 [20], the torque behavior illustrated by curve (a) in Fig. 1 indicates that the molar mass of EAA became about 1.5 times higher as a result of the addition of 0.35 phr PBO. It should be emphasized that, in the investigated system (EAA with 0.35 phr PBO), the number of carboxyl groups equivalents was about 35 times that of the oxazoline rings and the probability that the second ring of a PBO molecule reacted with another carboxyl of the same EAA macromolecule, with negligible effect on the viscosity of the mixture, was fairly high.

The experiment illustrated by curve (b) was carried out by the addition of 0.35 phr PBO into PA. In this case, chain extension due to reaction of the oxazoline rings of PBO with the carboxyl or amine end groups of PA is the only expected effect. With the concentrations of reagents used in the experiment (PA with 0.35 phr PBO), the number average molar mass of PA could be expected to increase from the initial value of about 29,000 to the final level of about 54,500, and the torque to become approximately five times higher after completion of the reaction. The experimental result shows that the rate of viscosity increase is rather low, as it might be expected considering the low concentration of the end groups of PA, and that the reaction extent after 30 min blending.

The torque changes recorded when PA is added with EAA, in the 80/20 proportion, are illustrated by curve (c). Notice that the stationary torque measured while blending pure PA, before addition of the second component, was lower than that measured in the previous experiment because the amount of PA was smaller. As already discussed in a previous work [13], the gradual torque following the addition of EAA is thought to result from the slow formation of PA-*g*-EAA copolymers at the interface, and the resulting increased adhesion between the molten phases.

Finally, curve (d) shows that a pronounced acceleration of the blend thickening results from the addition, at $t = 6$ min, of 0.35 phr PBO, into the 80/20 PA/WA

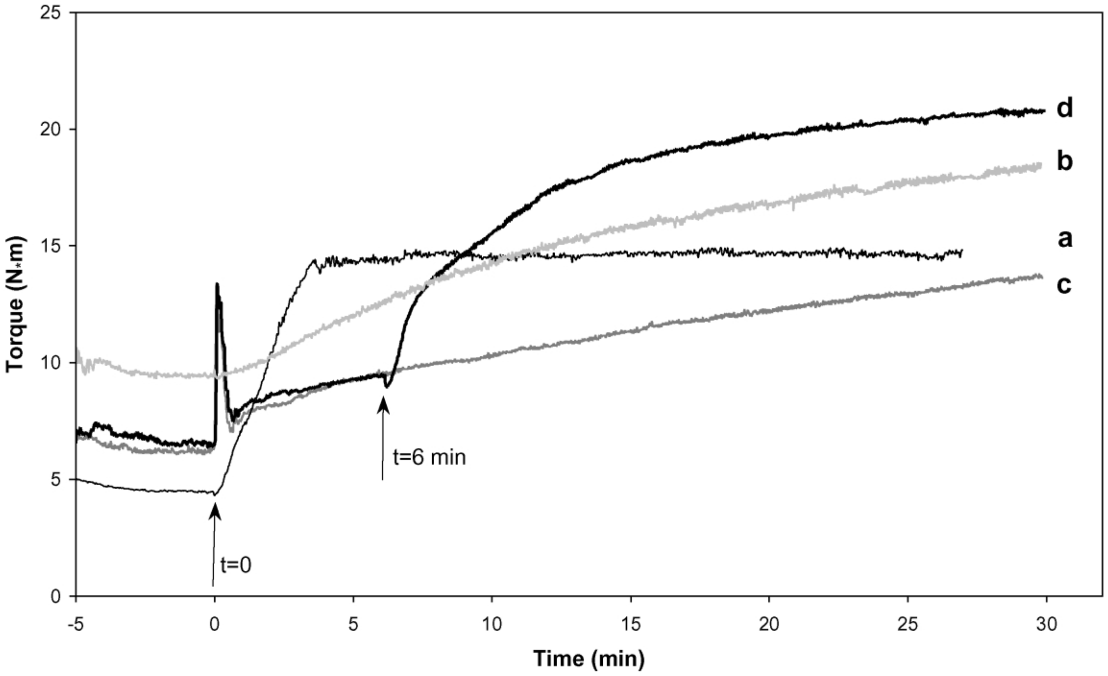


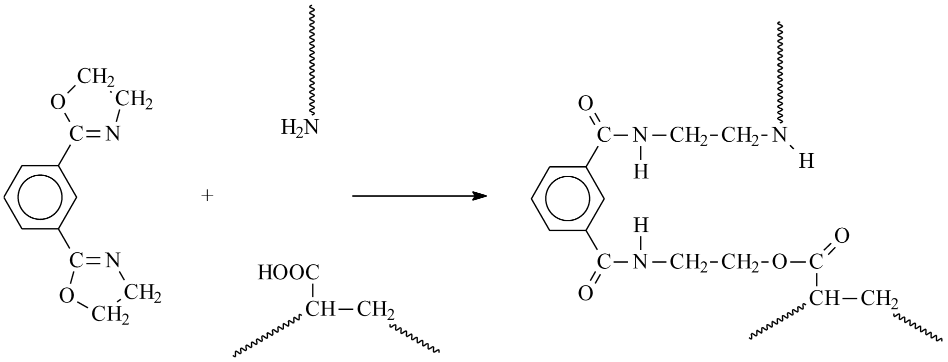
Fig. 1. Torque vs. time curves recorded while blending: (a) EAA with 0.35 phr PBO (added at time $t = 0$); (b) PA with 0.35 phr PBO (added at time $t = 0$); (c) PA with EAA (added at time $t = 0$), in the 80/20 wt/wt ratio; (d) PA with EAA (added at time $t = 0$), in the 80/20 wt/wt ratio, and with 0.35 phr PBO (added at time $t = 6$ mm).

blend. This effect practically ends after 10 min and the subsequent viscosity increase follows a trend similar to that of the PA/EAA blend considered before (curve c).

The results shown in Fig. 1 cannot obviously be taken as a definite evidence in favor of the occurrence of reactions such as those shown in Scheme 1. In fact, although the fairly rapid increase in viscosity following the addition of PBO into the PA/EAA blend cannot be ascribed to the chemical interaction of PBO with PA only, because this would be much slower, it might probably be explained through the reaction of PBO with the EAA phase only. However, that this is not so was definitely demonstrated by formic acid treatment of the PA/EAA blends obtained as the products of the two experiments illustrated by curves (c) and (d). Samples of the two blends were stirred for several hours in 85% formic acid until fairly stable suspensions or colloidal solutions were obtained, Prolonged centrifugation of the suspension formed by the binary blend prepared in the absence of PBO yielded a turbid colloidal solution on which a layer of insoluble particles floated. This was carefully separated and diluted with fresh formic acid. The new suspension was again stirred for several hours and centrifuged. This treatment was repeated four times and an insoluble fraction amounting to 4.1% of the initial sample was finally recovered by vacuum drying. Thus, the insoluble fraction that could be separated by this treatment was only 20.5% of the formic acid insoluble material (EAA) contained in the blend. The same treatment was applied in a previous work [13] to the 80/20 PA/EAA blend prepared by 4 min blending and led to separation of an insoluble fraction amounting to 53% of the EAA component. These results are in fair agreement and demonstrate the amount of PA-*g*-EAA copolymer formed by reactive blending increases gradually with time. On the contrary, when the procedure was applied to the 80/20/0.35 PA/EAA/PBO blend, no separation of a supernatant layer of insoluble droplets could be observed, even after longer centrifugation times. This result provides qualitative, yet definite, demonstration that formation of the compatibilizing graft copolymers is appreciably enhanced in the presence of PBO.

The above qualitative conclusion was confirmed by a comparison of the characteristics of the PA/LDPE blends prepared in the twin screw extruder. The picture shown in Fig. 2 displays the appearance of the four test tubes in which the Molau tests were carried out for the 80/20 PA/LDPE blends without and with EAA (2 phr) and PBO (0.2 or 0.35 phr). The binary blend with no EAA gave, after stirring with formic acid and 24 h settling in a test tube, a clean separation of an almost transparent solution of PA (turbidity lower than 300 FTU) from the upper layer of LDPE particles, as shown in Fig. 2c. It should be noted that the solution in tube (c) is not perfectly clear probably because a small amount of PA–LDPE copolymer may have been produced through stress induced reactions caused by melt blending [21]. The turbidity (about 600 FTU) measured for test tube (d) in which the 80/20/2 PA/LDPE/EAA blend was treated with formic acid is considerably higher and confirms that grafting reactions take place in these systems [13]. The addition of 0.2 or 0.35 phr PBO into this ternary blend brings about a strong additional increase of turbidity (above 1000 FTU), as demonstrated by the photographs of test tubes (a) and (b). This demonstrates that a larger amount of PA-*g*-EAA copolymer is produced, also in the ternary PA/LDPE/EAA blends, in the presence of PBO.

The thermal properties of pure components and blends, measured on a second heating scan carried out at 10 °C/mm, are collected in Table 1. As already pointed out in a previous paper [13], the temperatures and the enthalpies of fusion of the two main components are little affected by blending. Also, the addition of 2 phr EAA does not cause important alterations in the thermal behavior of the blends having the composition considered in this work. Only for the blends with PA as the minor phase, compatibilization was shown to lead to profound changes in the crystallization mechanism of PA; in fact, when the PA droplets become very small, their number may exceed that of the heterogeneous nuclei and a fractionated crystallization of PA is observed [13, 22–27]. From the data in Table 1, however, a measurable and consistent reduction of the degree of crystallinity of the PA phase is observed for the blends containing PBO. This may be tentatively ascribed to an increased content of PA-*g*-EAA copolymers which, as demonstrated by their tendency to form colloidal solutions in formic acid, may be partially miscible with the PA phase. Thus, the calorimetric



Scheme 1.

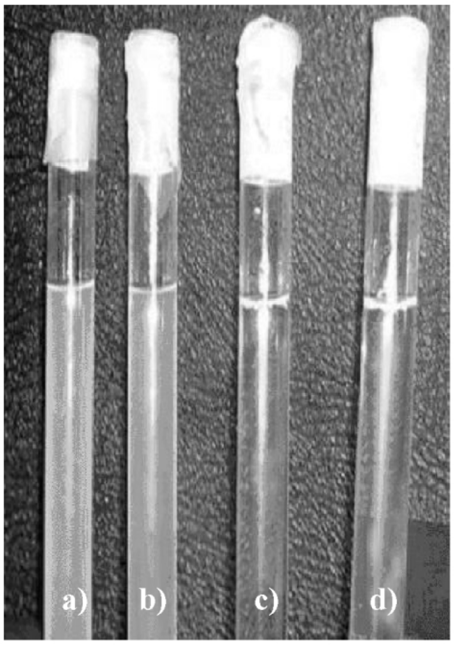


Fig. 2. Picture of the test tubes used for the Molau tests carried out on the PA/LDPE/EAA/PBO blends with composition: (a) 80/20/2/0.2; (b) 80/20/2/0.35; (c) 80/20/0/0; (d) 80/20/2/0.

characterization of the PA/LDPE blends provides another circumstantial evidence in favor of a synergic effect of PBO in the grafting reactions leading to the formations of the compatibilizing PA–EAA copolymers.

The morphology of the blends is illustrated by the SEM micrographs shown in Fig. 3. The binary 80/20 PN/LDPE blend with no compatibilizing agent displays very coarse morphology with poor dispersion of the droplet size and no interfacial adhesion. As it was also shown in a previous work [13], the addition of 2 phr EAA to this blend leads to a strong improvement of both the interfacial adhesion, as demonstrated by some of the marks (indicated by arrows) that were left by the LDPE droplets on the PA matrix, and the minor phase dispersion (notice the higher magnification of the relevant micrograph in Fig. 3). The addition of 0.2 or 0.35 phr PBO into the ternary 80/20/2 PA/LDPE/EAA blends brings about a considerably further improvement of compatibility. In fact, the two phases of the blend become practically indistinguishable already after addition of 0.2 phr PBO, and no strong morphological effect is found when the amount of this additive is increased to 0.35 phr. It should be emphasized that the ratio between the equivalents of oxazoline rings of PBO and carboxyl groups of EAA is equal to about 0.84 and 1.46 in the two cases. Even with the lower amount of added PBO it seems highly unlikely that the oxazoline rings are only consumed by reaction with the carboxyl groups of EAA. It is more reasonable to assume that, in both cases, a considerable number of the PBO molecules react with both the end groups of PA and the carboxyl groups of EAA to produce the graft copolymers, as indicated in Scheme 1.

Table 1
Thermal properties of the pure components and of the blends

Blends composition (PA/LDPE/EAA/PBO)	PA phase		LDPE phase	
	T_m (°C)	ΔH_m[a] (J/g)	T_m (°C)	ΔH_m[a] (J/g)
0/100/0/0	–	–	110.4	87.4
100/0/0/0	219.4	67.7	–	–
80/20/0/0	220.1	65.2	110.8	85.4
80/20/2/0	219.6	62.5	110.6	81.5
80/20/2/0.2	219.4	57.3	110.0	86.9
80/20/2/0.35	219.5	55.0	110.2	92.0

[a] Figures normalized to the amount of the relevant phase.

The results of the rheological measurements carried out on the blends are shown in Fig. 4, where their viscosity curves are plotted as a function of frequency together with those of the pure components. As expected, the viscosity curve of PA shows a fairly wide Newtonian region, whereas that of pure LDPE displays a pronounced shear-thinning behavior. The blends also display a non-Newtonian trend, but the slope of their viscosity curves is lower. At low frequencies, they are less viscous than LDPE and more viscous than PA, whereas at high frequencies their viscosity is close to that of PA and considerably higher than that of LDPE Among the blends, those containing PBO are considerably more viscous, the viscosity increasing with an increase of the PBO concentration, and their non-Newtonian behavior is more pronounced. At intermediate frequencies, the viscosity of these blends is considerably higher than that of both the components and the uncompatibilized blend. An increase of both the viscosity and the non-Newtonian behavior is typical for compatibilized blends [28–31]. The rheological characterization clearly indicates that the addition of PBO promotes the compatibilization of the two phases of these blends by enhancing the formation of PA-*g*-EAA copolymers, according to Scheme 1.

The ultimate mechanical properties of the pure components and the blends: modulus (E), tensile stress (TS) and elongation at break (EB) are collected in Table 2. The pure components display a ductile behavior. EAA and LDPE show a relatively low value of E and TS and a higher value of EB. For the binary blend, the elongation at break is lower than that of the neat components. Moreover, the modulus

Table 2
Mechanical properties of the pure materials and of the blends

Blends composition (PA/LDPE/EAA/PBO)	E (MPa)	TS (MPa)	EB (%)
0/100/0/0	174	11	600
100/0/0/0	300	60	335
0/0/100/0	134	17	530
80/20/0/0	235	22	190
80/20/2/0	250	34	260
80/20/2/0.2	255	37	265
80/20/2/0.35	261	38	275

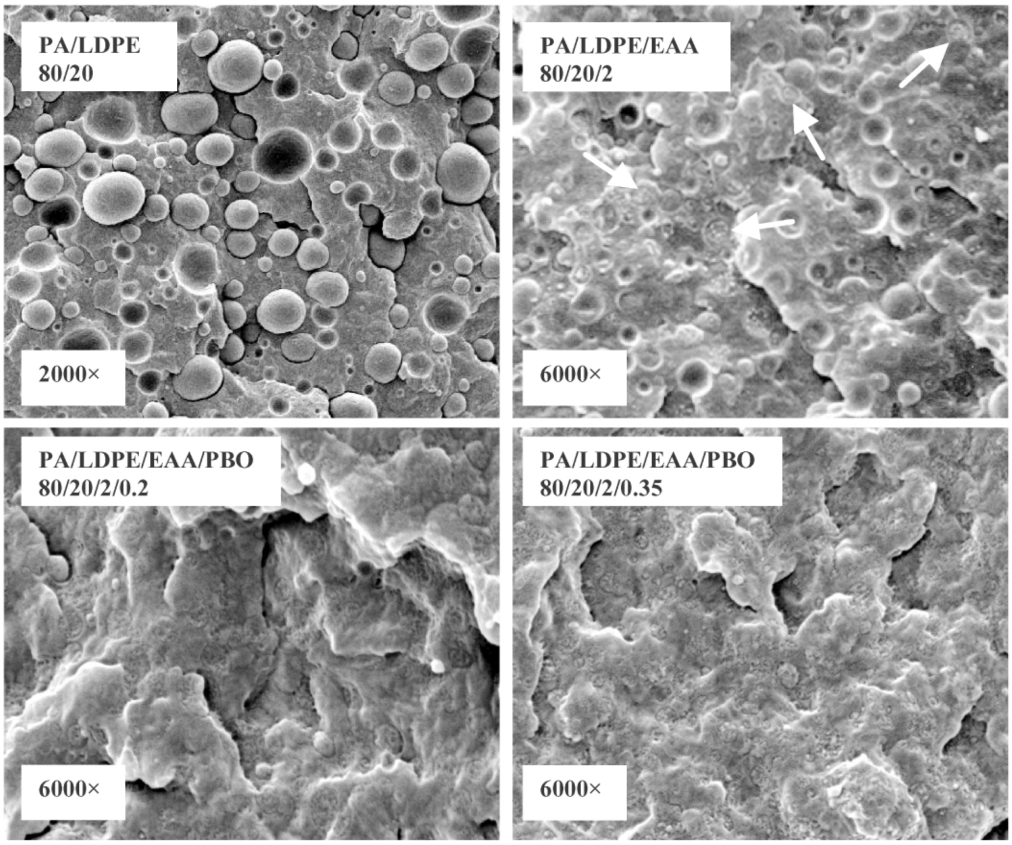


Fig. 3. Scanning electron micrographs of the 80/20 PA/LDPE blends without and with EAA and PBO.

and the tensile stress are intermediate but lower than those expected on the basis of an additive rule. These features are typical for incompatible blends and agree with the rheological and morphological results reported above. The situation is different if EAA is added. All three mechanical properties are improved considerably, especially tensile strength and elongation at break. The addition of PBO causes an additional improvement. Moreover, as found for the rheological properties, an increase of the PBO concentration from 0.2 to 0.35 phr enhances the mechanical properties further. With respect to the uncompatibilized PA/LDPE blend, the modulus of the quaternary blends is 10% higher, the tensile stress is increased by over 65% and the elongation at break by about 40%. The results of the

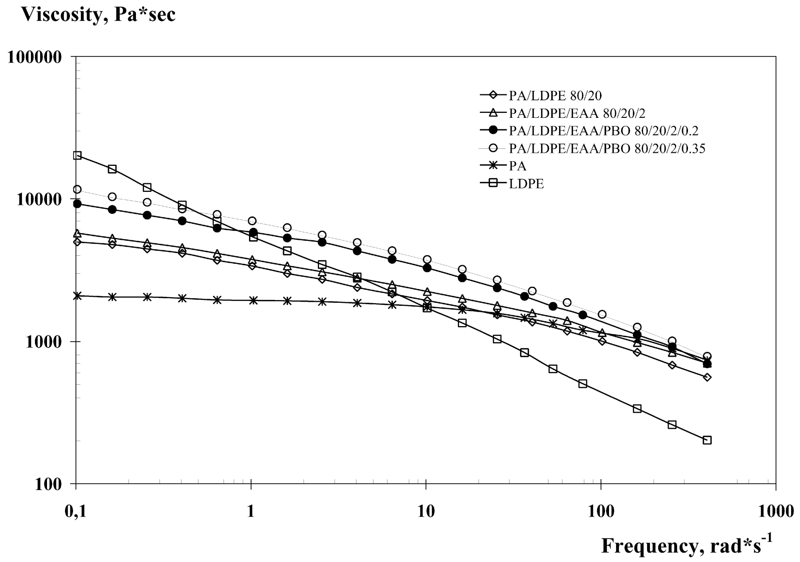


Fig. 4. Viscosity curves PA, LDPE and their 80/20 wt/wt blends, without and with EAA and PBO.

mechanical characterization are in good agreement with all other experimental evidences indicating that PBO does actually help the in situ formation of graft copolymer compatibilizers.

The effectiveness of the compatibilizing system studies in this work was confirmed by an investigation of the impact properties of the binary, ternary and quaternary blends. The results of these tests are reported in Table 3. They show that the addition of EAA into the PA/LDPE blend almost doubles the impact strength, thus confirming that this copolymer does actually behave as a compatibilizer precursor. It is particularly noteworthy, however, that none of the 10 specimens of the quaternary blends investigated was broken under the employed conditions, independent of the concentration of added PBO. This finding provides the most convincing proof of the effectiveness of the compatibilizing procedure studied in this work.

4. Conclusions

EAA had already been shown by a morphological and calorimetric investigation to behave as an effective compatibilizer precursor for PA/LDPE blends [13]. However, the in situ formation of PA-*g*-EAA copolymers was found to be slow and the mechanical properties improvement observed for extruded ribbons of blends containing 2 phr EAA was modest [14]. In this work, the possibility to use a bis-oxazoline compound (PBO) as a promoter for the formation of PA-*g*-EAA copolymers has been investigated.

Although the oxazoline rings of PBO have been shown to react rapidly, under the conditions adopted for the blends preparation, with neat EAA and, more slowly, with neat PA, the characterizations made in this work have definitely shown that, at least in part, they can also give rise to bridging reactions, such as those indicated in Scheme 1, to produced PA-*g*-EAA copolymers. In fact, it was shown that no insoluble fraction could be separated by centrifugation of formic acid suspensions of the binary 80/20 PA/EAA blends, when PBO was added into them. The synergic effect of PBO in the in situ generation of PA-*g*-EAA copolymers was also demonstrated by the increased turbidity of the formic acid suspensions prepared from the 80/20/2 PA/LDPE/EAA blends containing this additive. Moreover, the addition of the bis-oxazoline caused a modest, yet definite, reduction of the degree of crystallinity of the PA phase of these blends. Finally, the morphological analysis, the rheological characterization, the determination of the tensile properties and, more clearly, the impact tests have confirmed that the addition of PBO as the fourth component, even with a concentration of only 0.2 phr, improves considerably the compatibility of the PA/LDPE blends.

Table 3
Impact properties of the blends

Blends composition (PA/LDPE/EAA/PBO)	IS (J/m)
80/20/0/0	400
80/20/2/0	750
80/20/2/0.2	Not broken
80/20/2/0.35	Not broken

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