Oxazoline Functionalization of Polyethylenes and Their Blends with Polyamides and Polyesters

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Summary: The compatibilization of blends of polyamide-6 (PA6) with linear low density polyethylene (LLDPE) and of poly(ethylene terephthalate) (PET) with high density polyethylene (HDPE), by functionalization of the polyethylenes with oxazoline groups was investigated. Chemical modification of LLDPE and HDPE was carried out by melt free radical grafting with ricinoloxazoline maleinate. Blends preparation was made either with a two-steps procedure comprising functionalization and blending, and in a single step in which the chemical modification of polyethylene with the oxazoline monomer was realized *in situ*, during blending. The characterization of the products was carried out by FTIR spectroscopy and scanning electron microscopy (SEM). The rheological and mechanical properties of the blends were also investigated. The results show that functionalization of the polyethylenes can be achieved by melt blending with ricinoloxazoline maleinate even in the absence of free radical initiators. The compatibilization of the blends enhances the dispersion of the minor phase significantly, increases the melt viscosity, and improves the mechanical properties. The one-step preparation of the compatibilized blends was also found to be effective, and is thought to be even more promising in view of commercial application.

Introduction

Blending commercial polymers to produce new materials with targeted properties is one of the most popular topics of modern polymer research and practice. The aim is obviously that of promoting a synergism among the immiscible polymers forming the blend, so as to achieve a net property gain with respect to those of the components. This normally requires the use of appropriate compatibilizers that help improve the otherwise weak interfacial adhesion and reduce the morphological instability of the straight blends[1-5)].

For the commercially interesting blends of polyolefins with polyamides and polyesters, compatibility is so poor that the use of appropriate strategies leading to reduction of

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interfacial tension, enhancement of dispersion of the minor phase, and improvement of adhesion and morphological stability, becomes mandatory. During the last years, it has been shown that such blends can be efficiently compatibilized if appropriate functional groups, e.g. those derived from maleic anhydride, acrylic acid, glycidyl methacrylate, etc., are grafted onto the polyolefin chain so that hydrogen bonds, or even covalent bonds, can form between the two polymers at the blending stage[6-11]. Recently, the well known reactivity of the oxazoline ring toward a number of functional groups, such as carboxyl, amine, phenol, mercaptan, etc.[12], has been exploited for the production of oxazoline modified polymers that can thereafter be blended reactively with polymers containing such groups[13-26]. In particular, polyethylene was successfully functionalized by melt grafting with oxazoline monomers, such as isopropenyloxazoline and ricinoloxazoline maleinate, in the presence of peroxide initiators, and was then used for the preparation of compatible blends with polar polymers[22-26].

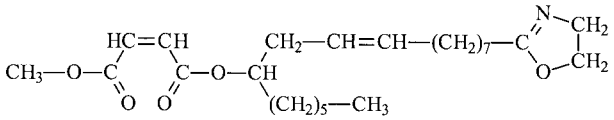
In this work, two polyethylene samples, linear low density polyethylene, referred to herein as LLD, and high density polyethylene (HD) were functionalized by free radical melt grafting with ricinoloxazoline maleinate in the absence of initiators and the modified products (LLDm and HDm) were used to produce compatible blends with polyamide-6 (PA6) and poly(ethylene terephthalate) (PET), respectively. The possibility of functionalizing the polyethylenes and blending them with the polar polymers in one step was also investigated.

Experimental

Materials

The polyethylenes were a film blowing grade of LLDPE (Clearflex FG306U, Polimeri Europa, Italy), with d = 928 Kg/m^3 and MFI = 1.0 dg/min (190°C; 2.16 Kg), and a HDPE sample (Eraclene MP94, Polimeri Europa), with d = 960 Kg/m^3 and MFI = 7.0 dg/min. The polyamide-6 (PA6) was a commercial sample, ASN-27S, provided by Rhodia, having a density d = 1,112 Kg/m^3. Poly(ethylene terephthalate) (PET) was a bottle grade sample (P82, Shell), with i.v. = 0.82 g/dL.

The oxazoline monomer, ricinoloxazoline maleinate (Loxamid V-EP 85/15, Henkel), was used as received. The structure of this monomer, referred to herein as OXA, is shown below.



Dicumyl peroxide (dcp), by Elf Atochem Italia, was used in some of the experiments carried out for optimizing the grafting conditions. The half life of dcp at 180°C is about 60 s.

The solvents used for the purification of the crude products of grafting, xylene and acetone, were commercial materials and were used as received.

Techniques

The apparatuses used for the grafting reactions and the blends preparations were a batch mixer (Brabender Plasticorder, mod. PLE 330), equipped with a mixing chamber of 50 mL, and a co-rotating twin screw extruder (APV, mod. MP2000).

The two-steps procedure employed for the preparation of the PA6/LLD/LLDm and PET/HD/HDm blends consisted of the polyolefin grafting reaction, with 6 pph OXA, and the blend preparation. The former operation was normally carried out in the batch mixer at 180°C and 64 rpm for 7 min. In a few cases, however, the twin screw extruder was used (residence time ≈ 2 min). The product of grafting was purified by dissolution in boiling xylene, filtration of the hot solution through a brass gauze to separate the gel fraction, and precipitation into a threefold excess of acetone under vigorous stirring. The precipitated polymer was then separated from the solvent mixture, washed with fresh acetone and dried at 70°C for 12 h, and then at 80°C under vacuum for at least 10 h. The gel fraction eventually retained on the wire gauze was washed with acetone, dried and weighed. The grafting conditions indicated above were optimized as detailed elsewhere[27] by varying the temperature in the 180-200°C range, the speed of the mixer's rotors between 32 and 128 rpm, and the mixing time between 3 and 30 min. The addition of dcp as a radical initiator (0.3 pph) was found to lead to appreciable crosslinking (gel fraction of 10-48%) unless the minimum mixing time was used. The blends preparation was made either in the batch mixer or in the twin screw extruder. The temperature was 240°C for the PA6 blends and 270°C for the PET ones.

In the one-step procedure, that was employed only for the preparation of compatibilized PA6/LLD blends, the two polymers and OXA were fed together to the batch mixer or to the twin screw extruder, and blended at 240°C. The temperature profile and the screw types used for the extruder were selected as described elsewhere[27].

The content of oxazoline rings in the grafted products was evaluated qualitatively through FTIR spectroscopy of purified polymer films. For the preparation of the latter a polymer sample was placed between two aluminum foils and compressed in a laboratory press at 180°C. After cooling, aluminum was dissolved by treatment with a sodium hydroxide solution and the film was washed with distilled water and dried. FTIR analysis was made with a Perkin Elmer Spectrum 2000 apparatus.

Blends morphology was studied with a Philips mod. 501 scanning electron microscope (SEM).

The thermal properties of all the materials were determined by differential scanning calorimetry (DSC), with a Perkin Elmer DSC-7 apparatus.

Rheological measurements were carried out on a Rheometrics RDAII Dynamic Solid Analyzer with the parallel plate configuration. The samples used for the tests were cut out of compression molded sheets. The mechanical properties of the investigated materials were measured with an Instron apparatus mod. 1122 using samples of 10×100×~2 mm cut out of compression molded sheets prepared with a Carver laboratory press at 180°C. Impact strength measurements were made with an Izod pendulum with a 2N head on samples of 70×12.7×2.54 mm (ASTM D256).

Results and Discussion

Virgin LLD and HD samples were completely soluble in boiling xylene. Almost complete solubility, as judged by the absence of gel particles left on the wire gauze when the hot xylene solution was filtered, was also observed for samples treated in the mixer, either with and without OXA, in the absence of dcp. Only with mixing times of 30 min, a small amount of gel (less than 2%) was occasionally found. On the contrary, in the presence of dcp, gelification was considerable and increased with mixing time (about 50% after 30 min), either with and without OXA. This suggests that crosslinking is probably caused by the formation of polyethylene macroradicals. Although this aspect was not studied in detail in this work, it is supposed that grafting of OXA onto PE occurs with essentially the same mechanism, with and without dcp.

The FTIR spectrum of OXA displays two characteristic peaks at 1725 and 1670 cm^{-1}, with $I_{1725}/I_{1670} \approx 1.45$, that were assigned to the stretching vibration of the >C=O bonds of the ester groups of OXA and, respectively, to a complex mode involving >C=N- stretching and

oxazoline ring bending. These peaks have always been used in previous studies[13-26] to calculate the OXA content of modified polyolefins.

Typical FTIR spectra of LLD and LLDm are shown in Fig. 1, whereas the spectra of the corresponding HD samples are reported in Fig. 2. In order to exclude that traces of monomeric OXA could have remained in the films of modified polymers, double purification of the samples by xylene dissolution and acetone precipitation was performed before FTIR analysis. Previous studies on the functionalization of polypropylene with ricinoloxazoline maleinate[17] showed that grafting takes place predominantly through the much more reactive double bond of the maleic group. On the basis of literature data on oxazoline grafting onto polypropylene[17, 20], the content of oxazoline rings in LLDm and HDm was estimated to be about 1.5 wt %. It should be observed that all grafted samples prepared by us had I_{1725}/I_{1670} always higher than 1.45, especially for mixing times of 15 or 30 min. This may be explained considering that additional carboxyl groups can form, under the grafting conditions used by us, as a result of oxidation.

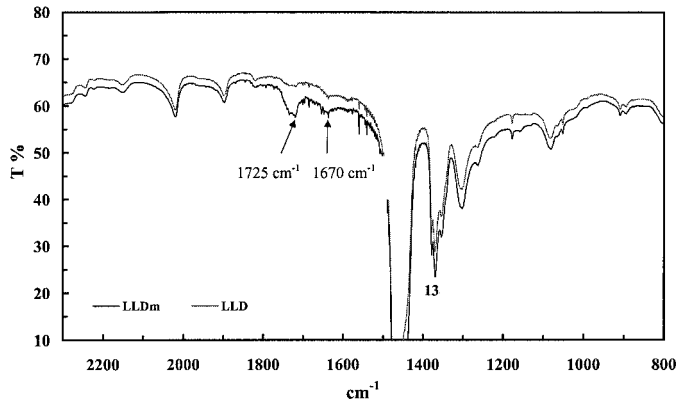


Fig. 1: FTIR spectra of LLD and LLDm.

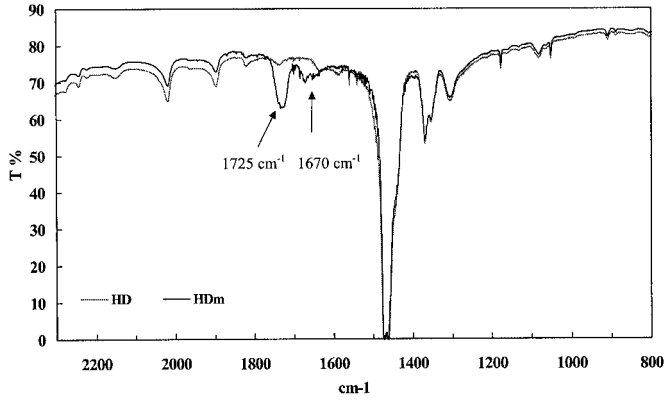


Fig. 2: FTIR spectra of HD and HDm.

The PA6/LLD and PET/HD blends discussed in this paper are shown in Tables 1 and 2, together with their preparation conditions. The blends composition was always equal to 80/20, where the second figure indicates the overall mass content of PE, either functionalized or not. The blends will be referred to, in the following, either by their number (1st column in Tables 1 and 2) or by their composition (2nd column). The additional italic letter *M* or *E* is sometimes used to indicate that blend preparation was carried out in the batch mixer or in the twin screw extruder, respectively. When OXA is indicated among the blend components (3rd column of Table 1) functionalization and blending were performed with the one-step procedure.

Table 1. PA6/LLD/LLDm blends, and their preparation conditions.

Blend	Composition PA6/LLD/LLDm	Blending[a] (components)	LLD Premixing	LLD Functionalization[a]	LLDm Purification
1	80/20/0	*M* (PA6-LLD)	-	-	-
2	80/20/0	*M* (PA6-LLD)	Yes	-	-
3	80/20/0	*E* (PA6-LLD)	-	-	-
4	80/15/5	*M* (PA6-LLD-LLDm)	Yes	*M*	Yes
5	80/0/20	*M* (PA6-LLDm)	-	*M*	Yes
6	80/0/20	*M* (PA6-LLD-OXA)	-	-	-
7[b]	80/0/20	*M* (PA6-LLD-OXA)	-	-	-
8	80/0/20	*M* (PA6-LLDm)	-	*M*	-
9	80/0/20	*E* (PA6-LLDm)	-	*M*	Yes
10	80/0/20	*E* (PA6-LLDm)	-	*E*	Yes
11	80/0/20	*E* (PA6-LLD-OXA)	-	-	-

[a] *M* = batch mixer; *E* = twin screw extruder
[a] Blending carried out at 128 rpm

Table 2. PET/HD/HDm blends, and their preparation conditions.

Blend	Composition PET/HD/HDm	Blending[a] (components)	HD Functionalization[a]	HDm Purification
12	80/20/0	*M* (PET-HD)	-	-
13	80/15/5	*M* (PET-HD-HDm)	*M*	Yes
14	80/0/20	*M* (PET-HDm)	*M*	Yes

[a] *M* = batch mixer

Uncompatibilized blends 1 and 2 (PA6/LLD/LLDm, 80/20/0) differ from one another for the premixing stage of LLD employed in the preparation of blend 2. The characterization of

these blends showed that premixing of polyethylene has no appreciable effect on any of the blend properties. Thus, LLD premixing was generally omitted thereafter.

The effect of compatibilization on the morphology of PA6/LLD blends was studied by SEM. The SEM micrographs of some representative PA6/LLD/LLDm blends are shown in Fig. 3. Blend 1 (Fig. 3a) displays clearly biphasic morphology. The LLD minor phase consists of spherical droplets of 1-8 μm that have practically no adherence to the PA6 matrix. Using the extruder for preparing the blend (cf. blend 3 in Table 1) did not change the morphology of this uncompatibilzed blend appreciably. Considerable improvement of both minor phase dispersion and interfacial adhesion was instead observed when one fourth of the LLD phase was replaced with LLDm. This is demonstrated by the micrograph in Fig. 3b: the PE droplets show much smaller dimensions and some of them, indicated by arrows, appear fractured. Complete replacement of LLD with LLDm leads to stronger morphological changes, as shown in Fig. 3c.

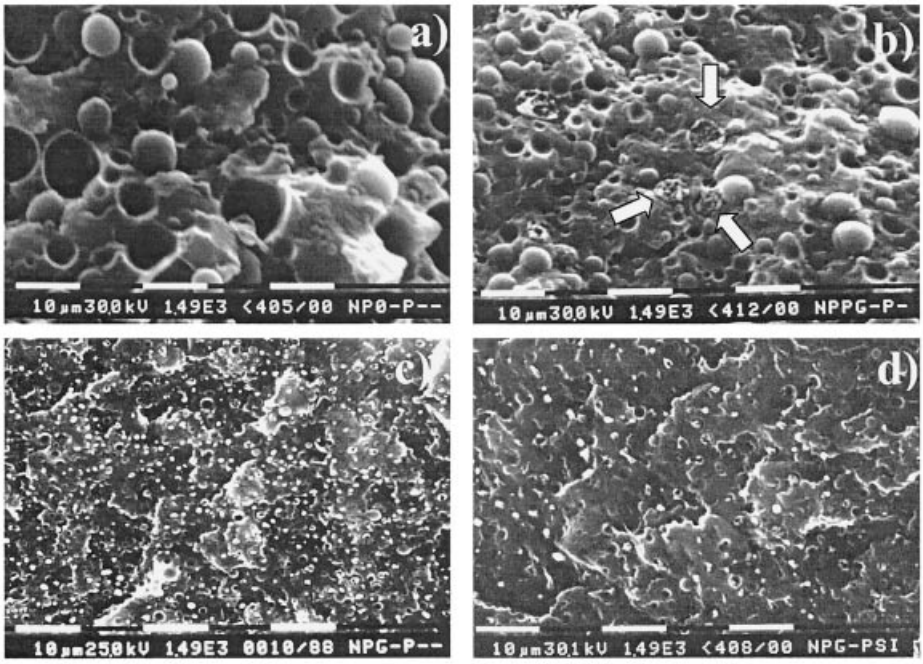


Fig. 3: SEM micrographs of PA6/LLD/LLDm blends (cf. Table 1): a) 80/20/0 (blend 1); b) 80/15/5 (blend 4); c) 80/0/20 (blend 5); d) 80/0/20 (blend 6).

The LLDm droplets of blend 5 are less than 1 μm in diameter and are uniformly dispersed within the PA6 matrix. A comparison of the micrographs in Fig.s 3a and 3c demonstrates clearly that oxazoline functionalization of LLD greatly improves the compatibility of the polyolefin with PA6. The use of LLDm as a compatibilizer for PA6/LLD blends is also effective, but leads to much slighter improvement of the minor phase dispersion (Fig. 3b). Despite of this, the observed increase of interfacial adhesion might equally lead to enhanced mechanical properties. It should be pointed out, however, that final aim of this work was to assess the possibility of carrying out the *in situ* compatibilization of PA6/LLD blends by the direct addition of OXA, together with the blend components, in the blending apparatus: either a batch mixer or a twin screw extruder. In this case, opening of the OXA rings by reaction with the carboxyl end groups of PA6 would probably be faster than grafting onto the PE chain. At any rate, oxazoline functionalization would clearly be expected to involve the whole amount of LLD, so that the product should actually be treated as a PA6/LLDm blend, and compared with the two-steps blend of Fig. 3c. The morphology of the one-step blend 6 is shown in Fig. 3d.

The minor phase particles of this blend appear well dispersed within the matrix polymer. Their dimensions are in the 2-4 μm range and are, therefore, considerably smaller than those of both blends 1 and 4, though being slightly larger than those of the blend with 20% LLDm. The latter observation suggests that functionalization is probably less effective when carried out *in situ*, either because of partial OXA evaporation (the temperature used in the one-step procedure is much higher than that used for LLD grafting), or because OXA reacts with the PA6 functionalities before being grafted. At any rate, as judged from microscope observation, the compatibilization obtained in the one-step operation appears good. Blend 7 (cf. Table 1) was prepared using higher shear rates (mixing at 128 rpm). No appreciable morphological difference was observed, however, with respect to blend 6. As it is shown in Table 1, in order to study the effect of the preliminary LLDm purification, blend 8 was prepared using the crude product of LLD grafting: again, no significant difference was observed with respect to the corresponding blend 5. Blends 9, 10 and 11 were prepared with the twin screw extruder (cf. Table 1). SEM investigation of these blends showed that the dimensions of the dispersed particles are slightly larger than those of the corresponding blends prepared in the mixer, probably due to a shorter residence time. However, the conclusions of the morphological study of these blends with reference to the effect of compatibilization and preparation procedure are in excellent agreement with those mentioned above for the blends prepared in the batch mixer.

SEM investigation of the PET/HD/HDm blends (cf. Table 2) demonstrated that oxazoline functionalization of the polyolefin leads to effective compatibilization of these blends, too. The SEM micrographs recorded for the PET-based blends are shown in Fig. 4. The morphology of the binary blend 12, illustrated in Fig. 4a, is characterized by poor dispersion, with droplet dimensions in the 1-12 μm range, and practically no adhesion. Partial replacement of HD with 5% HDm (blend 13) lowers particle size to about one third and greatly improves interfacial adhesion (Fig. 4b). In fact, practically all the minor phase droplets appear fractured. Examination of the micrographs of blends 4 and 13 (Fig.s 3b and 4b) indicates that compatibilization was more effective for the latter. This can be tentatively explained on the basis of one, or both, of the following possibilities: i) the reactivity of PET toward oxazoline is higher than that of PA6; ii) the content of oxazoline rings is higher in HDm than in LLDm.

The highest level of compatibilization was obviously obtained when PET was blended with HDm only (blend 14). As it is shown in Fig. 4c, the size of the majority of the HDm droplets is in the 0.1-0.5 μm range, although some larger particles (1-3 μm) can also be seen. Despite of this, the morphology of blend 14 closely resembles that of blend 5 based on PA6 (Fig. 3c).

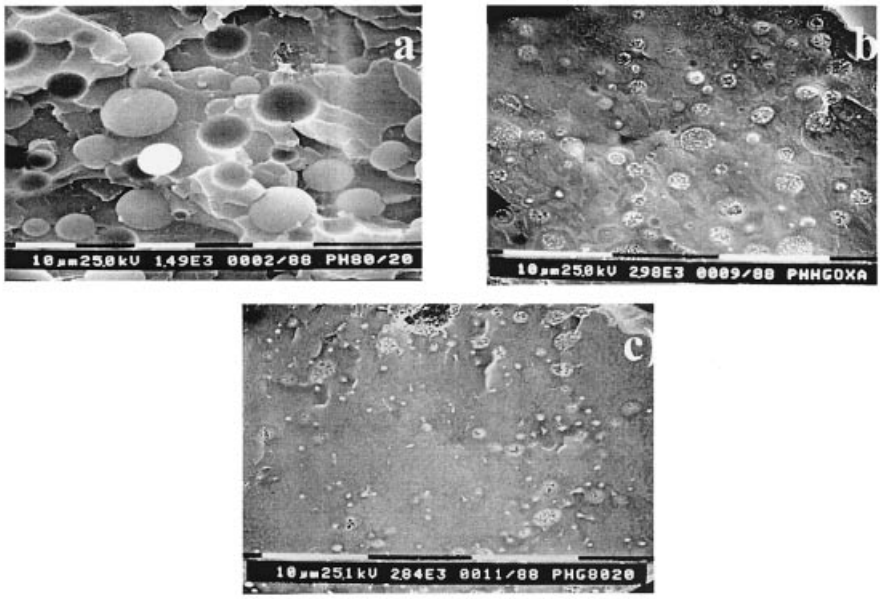


Fig. 4: SEM micrographs of PET/HD/HDm blends (cf. Table 2): a) 80/20/0 (blend 12); b) 80/15/5 (blend 13); c) 80/0/20 (blend 14).

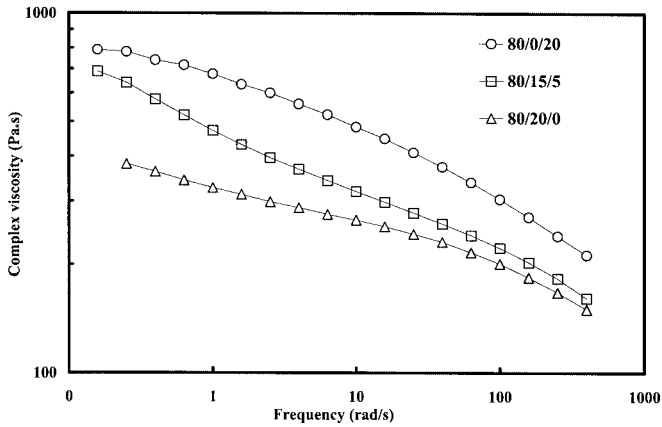


Fig. 5: Rheological behavior of representative PA6/LLD/LLDm blends (cf. Table 1): 80/20/0 (blend 1); 80/15/5 (blend 4); 80/0/20 (blend 5).

The effect of compatibilization on the rheological behavior of the blends has been studied with reference to the PA6/LLD/LLDm blends at 240°C. The viscosity vs. frequency curves of three representative blends are shown in Fig. 5. It is clearly seen that compatibilization results in a considerable increase of melt viscosity in the whole frequency range investigated. This is clearly ascribable to an enhanced contribution of the interfacial interaction of the phases caused by both the improved dispersion of the minor phase droplets and the increased adhesion of the particles to the matrix. As it could be expected on the basis of the morphological investigation described above, the strongest viscosity increase was found for the *M*-80/0/20 PA6/LLD/LLDm blend (blend 5, Table 1), whereas the viscosity curve of the *M*-80/15/5 blend is intermediate. The blend prepared with the one-step procedure in the mixer (blend 6) showed a rheological behavior very similar to that of blend 4, with a slightly higher viscosity. All the other *M*-blends shown in Table 1 displayed viscosity curves intermediate between those of blends 1 and 5. The viscosity of the *E*-blends was slightly higher than that of the corresponding *M*-blends, probably because of the lower blending time that caused lesser degradation of the PA6 matrix, but the general behavior was quite similar. The rheological investigation of the PA6/LLD/LLDm also showed that compatibilization appreciably enhances the shear thinning behavior of these materials. This is further support to the hypothesis that, in the investigated systems, compatibilization is the

result of chemical interactions, between the oxazoline rings of LLDm and the end groups of the polyamide, yielding LLD-b-PA6 copolymers. The latter could in fact give rise to an adherent interphase responsible for the observed rheological effects.

Table 3. Mechanical properties of the PA6/LLD/LLDm blends (cf. Table 1).

Sample	Tensile modulus E (MPa)	Tensile strength σ_r (MPa)	Elongation at break ε_r (%)	Impact strength I (KJ/m^2)
LLD	290	19.7	560	n.d.
LLDm	300	17.4	550	n.d.
PA6	1,270	66.0	20.1	n.d.
Blend 1	1,055	43.0	4.8	n.d.
Blend 2	1,055	44.7	4.5	3.2
Blend 3	1,220	29.7	5.2	3.2
Blend 4	1,080	45.7	9.1	6.5
Blend 5	1,270	55.9	7.4	8.8
Blend 6	1,090	46.2	14.9	16.5
Blend 7	1,085	47.4	16.7	17.5
Blend 8	1,120	52.9	8.1	n.d.
Blend 9	1,340	45.2	6.6	5.0
Blend 10	1,610	45.4	12.0	n.d.
Blend 11	1,480	40.4	16.0	8.1

Table 4. Mechanical properties of the PET/HD/HDm blends (cf. Table 2).

Sample	Tensile modulus E (MPa)	Tensile strength σ_r (MPa)	Elongation at break ε_r (%)
HD	770	27.9	630
HDm	710	27.7	520
PET	1,450	41.4	380
Blend 12	1,040	38.3	7.3
Blend 13	1,170	25.1	392
Blend 14	970	24.4	427

The results of the mechanical characterization of the blends are collected in Tables 3 and 4. The data in Table 3 show that using LLDm as the blend component, as in blend 5, causes an increase of about 25% of both modulus and strength, with respect to the corresponding *M*-PA6/LLD binary blends (blends 1 and 2), whereas the elongation at break and the impact

strength increase by approximately 1.5 and 2 times, respectively. It should be observed that the Young modulus of blend 5 is about equal to that of neat PA6, whereas tensile strength and elongation at break remain well below the PA6 values. The blend prepared with unpurified LLDm (blend 8) shows, with respect to blend 5, slightly smaller modulus and slightly larger deformation at break; this result can be explained assuming that residues of unreacted OXA present in LLDm may behave as a plasticizer. The latter interpretation is supported by the finding that the blends prepared in one step (blends 6 and 7) display even higher elongation and impact properties. All other *M*-blends have modulus and strength intermediate between those of blends 1 and 5. The modulus measured for the *E*-blends was found to be higher than that of the corresponding *M*-blends. This might suggest that the *E*-blends possess higher degree of crystallinity, but we couldn't get definite evidence of this from DSC characterizations.

The characterization of the PET/HD/HDm blends (Table 4) confirms that HDm shows much higher compatibility for PET than pure HD. This is particularly evident from a comparison of the elongation at break of blends 12 and 14: in fact the 80/0/20 PET/HD/HDm blend (blend 14) displays ductile failure whereas blend 1 is fragile. The reason why modulus and strength are slightly lowered by the substitution of HD with HDm can probably be a reduction of the degree of crystallinity of the PET phase in the examined samples. The elongation at break of the 80/15/5 PET/HD/HDm blend (blend 13) is indicative of ductile behavior of this material, and confirms that HDm is highly effective even when used in a 5% proportion as a compatibilizing agent in ternary PET/HD/HDm blends.

The results of the mechanical characterization are in good agreement with the conclusions drawn from morphology and rheology investigations, and confirm that oxazoline functionalization of polyethylene appreciably improves the compatibility of this polyolefin with both PA6 and PET.

Conclusions

The present work has shown that functionalization of both LLD and HD can be carried out by melt grafting with an oxazoline monomer (ricinoloxazoline maleinate). Grafting takes place even in the absence of deliberately added free radical initiators, thus minimizing the risk of gelification due to polyethylene crosslinking. Oxazoline functionalization can be accomplished either by blending the monomer and polyethylene in a batch mixer (or extruder) before blending, or, though less effectively, in a single step, in the blending device.

The presence of oxazoline rings grafted onto the polyethylene chain has been shown by SEM investigation to greatly improve the dispersion and the adhesion of the polyolefin phase in blends with polar monomers such as PA6 and PET. The compatibility of oxazoline functionalized polyethylenes with respect to PA6 and PET, and their compatibilizing efficiency toward PA6/LLD or PET/HD blends have also been demonstrated by rheological and mechanical characterizations. The one-step procedure, in which oxazoline functionalization of the polyethylene component and its blending with the polar monomer are carried out in a single operation, is obviously preferred in view of a commercial application. Although the preliminary results obtained in this work by the use of this one-step technique are slightly worse than those of the conventional two-steps procedure, it is thought that further optimization of the process can greatly improve its practical feasibility.

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