Morphology and Mechanical Properties of Extruded Ribbons of LDPE/PA6 Blends Compatibilized with an Ethylene-Acrylic Acid Copolymer

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Summary: Two grades of low density polyethylene (LDPE) were blended with polyamide-6 (PA) in the 75/25 and 25/75 wt/wt ratios and shaped into ribbons with a Brabender single screw extruder. An ethylene-acrylic acid copolymer (EAA) was used in the 2 phr concentration as a compatibilizer precursor (CP). The morphology of the ribbons and its evolution during high temperature annealing were investigated by scanning electron microscopy (SEM). The results confirmed that EAA does actually behave as a reactive compatibilizer for the LDPE/PA blends. In fact, in the presence of EAA, the interfacial adhesion is improved, the dispersion of the minor phase particles is enhanced and their tendency toward fibrillation is increased, especially for the blends with the higher molar mass LDPE grade. The mechanical properties of the latter blends were found to be considerably enhanced by the addition of EAA, whereas the improvement was relatively modest for the blends with the lower molar mass LDPE. The fracture properties of double end notched samples of the ribbons prepared with the blends containing the lower molar mass LDPE grade were also studied. It was shown that, despite of the increased interfacial adhesion caused by the presence of EAA, the latter plays a measurable positive effect on the fracture properties only for the blends with LDPE as the matrix.

Keywords: blends, impact resistance, low density polyethylene, mechanical properties, morphology, polyamide-6

Introduction

The preparation of compatibilized blends of polyolefins with condensation polymers has attracted considerable attention during the last few decades not only because of its scientific implications, but also in view of the interesting practical applications of these blends.[1-10] In particular, the compatibilization of blends of polyethylene (PE) with polyamide-6 (PA), carried out by the

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addition of compatibilizer precursors (CPs) consisting of polyolefins containing maleic anhydride, acrylic acid, oxazoline, or other functional groups capable of reacting with PA to form PA-*g*-CP copolymers has been the object of a considerable number of scientific publications.[3-10]

In a previous work,[11] some of us made a detailed investigation of the effectiveness of ethylene-acrylic acid copolymers (EAA) as CPs for the reactive blending of low density polyethylene (LDPE) with PA. It was shown that EAA form immiscible, yet highly compatible, blends with LDPE, and give rise to relatively slow acidolysis reactions, when blended with PA, yielding EAA-*g*-PA copolymers. The scanning electron microscopy (SEM) investigation of the ternary LDPE/PA/EAA blends showed that the addition of 1-2 phr EAA enhances considerably the dispersion of the minor phase droplets, prevents their coalescence during subsequent annealing and/or reprocessing operations and increases interfacial adhesion. It was also found that no further improvement of these properties could be obtained by the use of higher proportions of these compatibilizers. The compatibilizing efficiency of the EAA copolymers was shown to be particularly prominent for the LDPE/PA blends containing an LDPE grade with a melt viscosity considerably higher than that of the PA.

In the present work, blends of PA with two grades of LDPE, with 75/25 and 25/75 wt/wt compositions, were shaped into ribbons with a Brabender single screw extruder. An EAA copolymer (Escor 5001, with 6.2 wt% acrylic acid) was used as a CP in the 2 phr concentration which was shown by previous morphological studies to produce optimum results. The morphology of the ribbons and its evolution during high temperature annealing were investigated by SEM. The ultimate mechanical properties of specimens cut out from the ribbons in the flow direction, were studied. The fracture resistance of double end notched (DEN) ribbon samples was also investigated. The results of the mechanical characterizations were discussed with reference to the morphology of the samples and to the effect of the EAA reactive compatibilizer.

Experimental

Two grades of LDPE, kindly provided by Polimeri Europa, were used: Riblene FF20 with a melt flow index (MFI) equal to 0.8 g/10 min and d = 921 Kg/m^3, referred to herein as LD08, and Riblene FC30 (LD03) with MFI = 0.27 g/10 min and d = 922 Kg/m^3. The polyamide-6 (PA) sample was kindly supplied by Snia Tecnopolimeri; its intrinsic viscosity in formic acid (85%) was

1.45 dL/g and the contents of amine and carboxyl end groups were 34 and 35 meq/Kg, respectively. The EAA sample, Escor 5001 by Exxon-Mobil Chemical Mediterranea, was an ethylene-acrylic acid copolymer with 6.2 wt % acrylic acid and MFI = 2.0 g/10 min.

Before use, all the polymers were accurately dried under vacuum for 12 h at 70°C (for the LDPE and the EAA samples) or 120°C (for the PA). The ribbons were extruded from a rectangular die (width 100 mm, thickness 1 mm) using a Brabender single screw extruder, at 240°C and 50 rpm. The residence time was about 2 min. The molten ribbons were taken on a device, consisting of a moving tape and an air cooled metal roll, that cooled the ribbon and drew it with a stretching ratio equal to 6 (calculated as the ratio of the die section to the section of the ribbon).

Scanning electron microscopy (SEM) observations of the surfaces produced by fracturing the ribbons under liquid nitrogen, either parallel and perpendicular to the flow direction, and coated with gold were made with JEOL JSM-5600 LV or Jeol T300 microscopes. Annealing experiments were made by heating ribbon samples in a nitrogen atmosphere at 240°C for different times.

Tensile tests were carried out with an Instron Mod. 4443 using samples of 10×100×0.6 mm cut out of the ribbons in the flow direction. All the samples were held in the laboratory atmosphere (T ≈ 25°C, r.u. ≈ 70%) for a week before testing. The barrel speed was held at 1 mm/min for 2 min and was then increased to 50 mm/min; the clamps distance was 30 mm.

The fracture properties were studied on DEN (double end notched) samples of the ribbons of 75/25 and 25/75 LD08/PA blends, without and with 2 phr EAA. The width of the samples was of ca. 45 mm and the ligament, i.e., the width between notches, was varied between 3 and 25 mm. The employed deformation speed was 500 mm/min.

Results and Discussion

Examples of the micrographs taken by SEM on the fracture surfaces of ribbons prepared from uncompatibilized 75/25 and 25/75 LD08/PA and LD03/PA blends are shown in Figure 1. It is clearly observed that fairly long fibrils, together with smaller, poorly elongated droplets are present in the blends containing LD08. The particles dimensions are somewhat smaller for the blends with PA as the minor phase (Figure 1a). For the blends with a LD03 matrix (Figure 1c), the PA particles are much larger and show practically no fibrillation. On the other hand, the 25/75 LD03/PA blend has distinctly lamellar morphology (Figure 1d). Notice that the viscosity of LD08

is close to that of PA, at the processing temperature, whereas that of LD03 is considerably higher. The micrographs in Figure 1 demonstrate that dispersion and fibrillation of the minor phase is only granted, under the employed extrusion conditions, if the viscosity ratio of the two phases is appropriate. However, practically no interfacial adhesion is obtained in the absence of a CP.

The SEM micrographs of the corresponding blends containing 2 phr EAA are shown in Figure 2. It is clearly observed that the morphology of the ribbons prepared from LD08 is only slightly improved, as far as the dimensions and the geometry of the minor phase particles are concerned, although the interfacial adhesion is enhanced. On the contrary, for the LD03 blends, the effect of the EAA addition is very strong: the size of the minor phase particles is reduced dramatically and their shape is also changed profoundly, as fibrillation is now evident. Clearly, the interactions brought about by the EAA-*g*-PA copolymers formed at the interface are such as to lower interfacial tension considerably and to allow fibrillation of the dispersed particles, despite of the difference of viscosity of the two phases. The latter effect is particularly evident for the 25/75 LD03/PA blend (cf. Figure 2d).

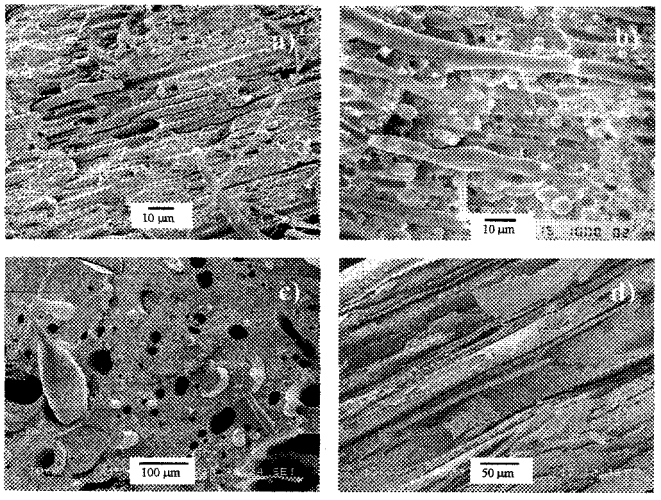

Fig. 1. SEM micrographs of the fracture surfaces of ribbons prepared from uncompatibilized blends: a) 75/25 LD08/PA; b) 25/75 LD08/PA; c) 75/25 LD03/PA; d) 25/75 LD03/PA.

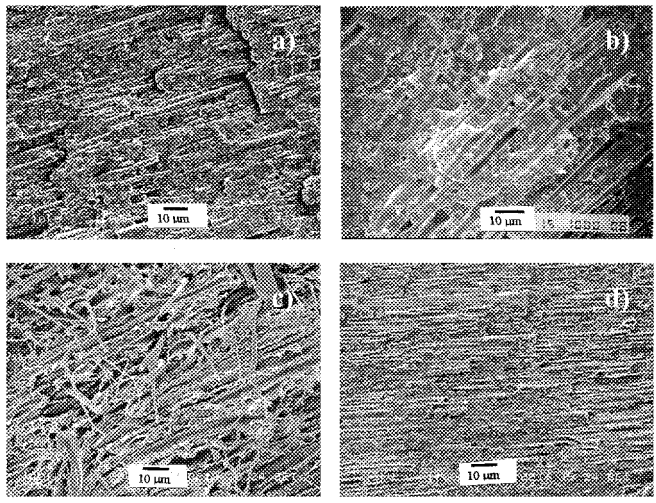

Fig. 2. SEM micrographs of the fracture surfaces of ribbons prepared from blends compatibilized with 2 phr EAA: a) 75/25 LD08/PA; b) 25/75 LD08/PA; c) 75/25 LD03/PA; d) 25/75 LD03/PA.

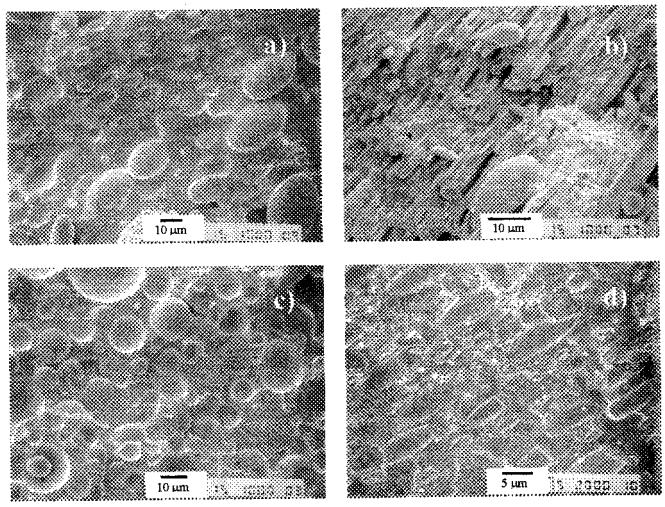

Fig. 3. SEM micrographs of the fracture surfaces of ribbons prepared from 75/25 (a, b) and 25/75 (c, d) LD08/PA blends, without (a, c) and with (b, d) 2 phr EAA, annealed at 235°C for 15 min (a, b, c) and 60 min (d).

Annealing experiments were carried out as described in the experimental section to investigate the effect of the presence of the EAA copolymer on the morphology changes due to loss of orientation and coalescence of the dispersed particles. The SEM micrographs shown in Figure 3 illustrate the behavior of the blends based on LD08. A comparison with the micrographs of unannealed ribbons shown in Figures 1 and 2 demonstrate that the speed of shape relaxation is considerably smaller for the compatibilized blends. In fact, nearly spherical droplets of the minor phase are already seen, for the blends without EAA, after 15 min annealing (Figures 3a and 3c), whereas only partial shape relaxation takes place for the compatibilized blends, even after 60 min. Also, the size of the dispersed particles remains smaller when the EAA copolymer is present. Similar annealing experiments were also carried out for the 25/75 LD03/PA blends, and the results are illustrated by the micrographs in Figure 4. It is clearly seen that very important morphological rearrangements take place in these blends upon annealing. Either the lamellar structure of the uncompatibilized blend (Figure 1d) and the fibrillar morphology of that containing EAA (Figure 2d) change gradually into those shown in Figure 4, which are typical for unoriented blends. The changes are much faster for the blend without EAA (Figure 4a), where LD03 spherical droplets are already seen after 25 min annealing, whereas much longer annealing times are needed to get the same result for the compatibilized blend (Figure 4b). Moreover, as it was expected on the basis of the results of previous studies,[11] a comparison of the two micrographs in Figure 4 demonstrates that the morphology is much coarser for the annealed blend without EAA, thus confirming that the addition of this CP at the mixing stage leads to a considerable reduction of interfacial tension in the LDPE/PA blends.

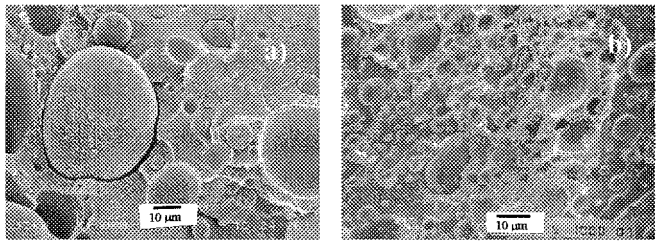

Fig. 4. SEM micrographs of the fracture surfaces of ribbons prepared from 25/75 LD03/PA blends, without (a) and with (b) 2 phr EAA, annealed at 235°C for 25 min (a) and 120 min (b).

The results of the tensile tests carried out on samples of the ribbons are shown in Table 1.

Table 1. Tensile mechanical properties of the ribbons.

Composition	E MPa	σ_b MPa	ε_b %
LD08/PA/EAA 75/25/0	193	21.9	370
75/25/2	190	20.0	395
25/75/0	295	49.4	310
25/75/2	292	51.1	330
LD03/PA/EAA 75/25/0	143	23.0	339
75/25/2	178	27.8	384
25/75/0	229	38.3	297
25/75/2	293	53.7	334

It can be seen that, in the absence of reactive compatibilizer, the elastic modulus E of the blends based on LD03 is lower than that of the blends containing LD08, for both compositions. This can probably be explained on the basis of the morphology of the former blends, shown in Figure 1, that are more irregular and practically void of oriented fibrils. The addition of 2 phr EAA brings about an improvement of the mechanical properties which is rather modest for the LD08/PA blends and appreciable for the LD03/PA blends. It is interesting that the properties of the compatibilized blends are nearly independent of the molar mass of the LDPE component, whereas they are critically influenced by the morphology. In fact, as it is clearly seen in Figure 2, the addition of EAA makes the LD03 blends of either composition attain a pronounced degree of orientation and fibrillation of the minor phase, so that their morphology becomes similar to that of the corresponding LD08 blends. This similarity is evidently paralleled by the similarity of the tensile properties. For the samples with fibrillar morphology, the improvement of mechanical properties, in particular the elongation at break, caused by the addition of EAA is generally small, as it is probably influenced scarcely by the increased interfacial adhesion and is mainly ascribable to the enhancement of dispersion and the reduction of size of the minor phase.

The technique normally used for measuring the essential work of fracture was employed to investigate the fracture behavior of samples of the LD08/PA ribbons, which were shown by SEM to posses fibrillar morphology even in the uncompatibilized state. The results are illustrated in Figure 5, where the specific work of fracture, measured as the ratio of the area under the stress-strain curve to the fractured area, is plotted as a function of the resistant width (ligament).

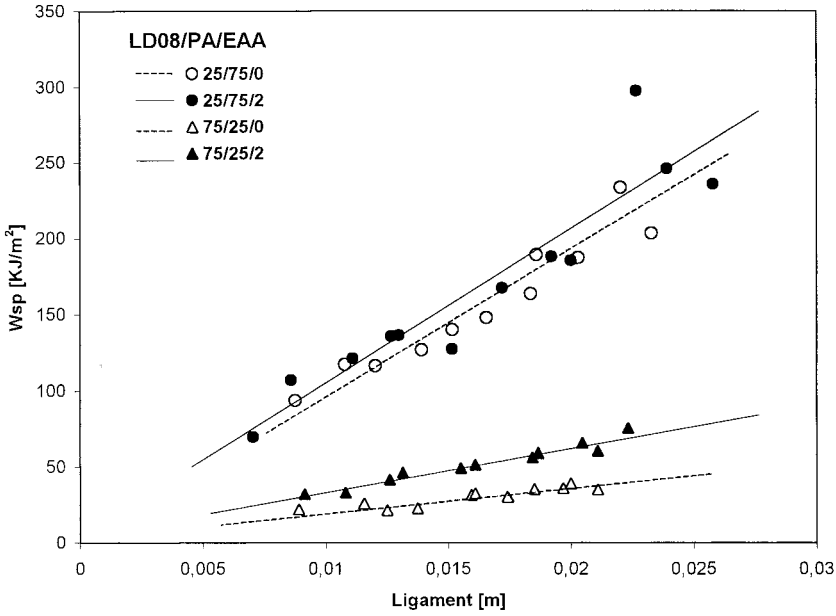

Fig. 5. Specific work of fracture of the LD08/PA/EAA ribbons as a function of the ligament width.

Although the employed measurement conditions (sample shape and deformation speed) were those commonly used for the determination of the essential work of fracture, as the intercept of the straight lines on the Y axis, the latter characteristic could not be determined reliably because the samples were very ductile and the specific work of fracture (Wsp) was mainly due to plastic deformation. However, the results shown in Figure 5 demonstrate that, for the blends with PA as the matrix, Wsp is hardly influenced by the presence of the EAA. Indeed, the experimental points shown in the Figure could practically be interpolated by the same straight line. On the other hand, compatibilization leads to a measurable increase of the work of fracture for the blends with LD08 as the main component, thus showing that the PA-*g*-EAA copolymers formed during blending act more efficiently as interfacial compatibilizers when LDPE forms the matrix. This result is in fair agreement with previous findings. In fact, the results of a former work,[11] in which the

morphology of the same blends, in the undeformed state, was studied, revealed that the enhancement of interfacial adhesion caused by the presence of EAA is more pronounced in the blends with LDPE as the matrix.

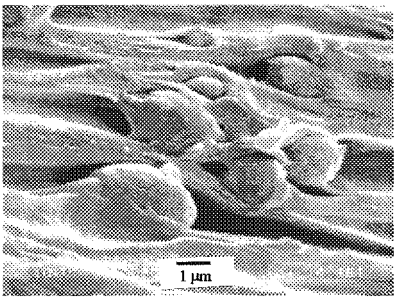

Fig. 6. SEM micrograph showing the morphology of a broken 75/25/2 LD08/PA/EAA ribbon, in the stretched region close to the fracture.

In order to get an experimental evidence of the interfacial adhesion between the LD08 matrix and the dispersed PA droplets, in blends compatibilized by the addition of EAA, the morphology of the stretched region of the broken ribbons used for the fracture experiments was investigated. The micrograph shown in Figure 6 was taken on a 75/25/2 LD08/PA/EAA ribbon. The small PA droplets embedded into the highly deformed LD08 matrix are seen to adhere quite tightly to the latter. No such behavior was displayed in the absence of the EAA reactive compatibilizer.

Conclusions

It has been shown that the morphology of extruded ribbons prepared from 75/25 and 27/75 LD08/PA and LD03/PA blends is appreciably improved if 2 phr of an EAA copolymer is added into them. Indeed, the dispersion of the minor phase droplets, their adhesion to the matrix and their deformation into fibrils were considerably enhanced. These effects have been shown to be particularly prominent for the blends containing the higher molar mass LDPE grade. The mechanical properties of the ribbons are also improved as a result of the addition of the EAA copolymer. The effect is modest for the LD08/PA ribbons, in which a fibrillar morphology is present even in the uncompatibilized state, but becomes appreciable for the LD03/PA samples

whose morphology undergoes major changes when the compatibilizer is present. The determination of the work of fracture of the ribbons has confirmed that good interfacial adhesion between matrix and dispersed particles is obtained as a result of compatibilization, especially for the blends with a LDPE matrix.

Acknowledgment

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