Poly(ethylene-graft-ethylene oxide) (PE-PEO) and Poly(ethylene-co-acrylic acid) (PEAA) as Compatibilizers in Blends of LDPE and Polyamide-6

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ABSTRACT: In a blend of two immiscible polymers a controlled morphology can be obtained by adding a block or graft copolymer as compatibilizer. In the present work blends of low-density polyethylene (PE) and polyamide-6 (PA-6) were prepared by melt mixing the polymers in a co-rotating, intermeshing twin-screw extruder. Poly(ethylene-graft-polyethylene oxide) (PE-PEO), synthesized from poly(ethylene-co-acrylic acid) (PEAA) (backbone) and poly(ethylene oxide) monomethyl ether (MPEO) (grafts), was added as compatibilizer. As a comparison, the unmodified backbone polymer, PEAA, was used. The morphology of the blends was studied by scanning electron microscopy (SEM). Melting and crystallization behavior of the blends was investigated by differential scanning calorimetry (DSC) and mechanical properties by tensile testing. The compatibilizing mechanisms were different for the two copolymers, and generated two different blend morphologies. Addition of PE-PEO gave a material with small, well-dispersed PA-spheres having good adhesion to the PE matrix, whereas PEAA generated a morphology characterized by small PA-spheres agglomerated to larger structures. Both compatibilized PE/PA blends had much improved mechanical properties compared with the uncompatibilized blend, with elongation at break (ε_b) increasing up to 200%. Addition of compatibilizer to the PE/PA blends stabilized the morphology towards coalescence and significantly reduced the size of the dispersed phase domains, from an average diameter of 20 μm in the unmodified PE/PA blend to approximately 1 μm in the compatibilized blends. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2416–2424, 2000

Key words: PE/PA-6 blends; PEO-graft copolymers; compatibilization; morphology; crystallization

INTRODUCTION

By blending different polymers, new materials with a desirable combination of properties can be developed.[1] Most polymers are incompatible and on mixing they generally form multiphase morphologies. The structures obtained are usually unstable, and the mechanical properties of the blends are poor because of lack of adhesion between the phases. However, the morphology and the properties of the blend can be controlled by introduction of a third component, a compatibilizer, to the blend. The compatibilizer is usually a block or graft copolymer,[2–4] which is interfacially active and adsorbs at the interface between the matrix and the dispersed phase,
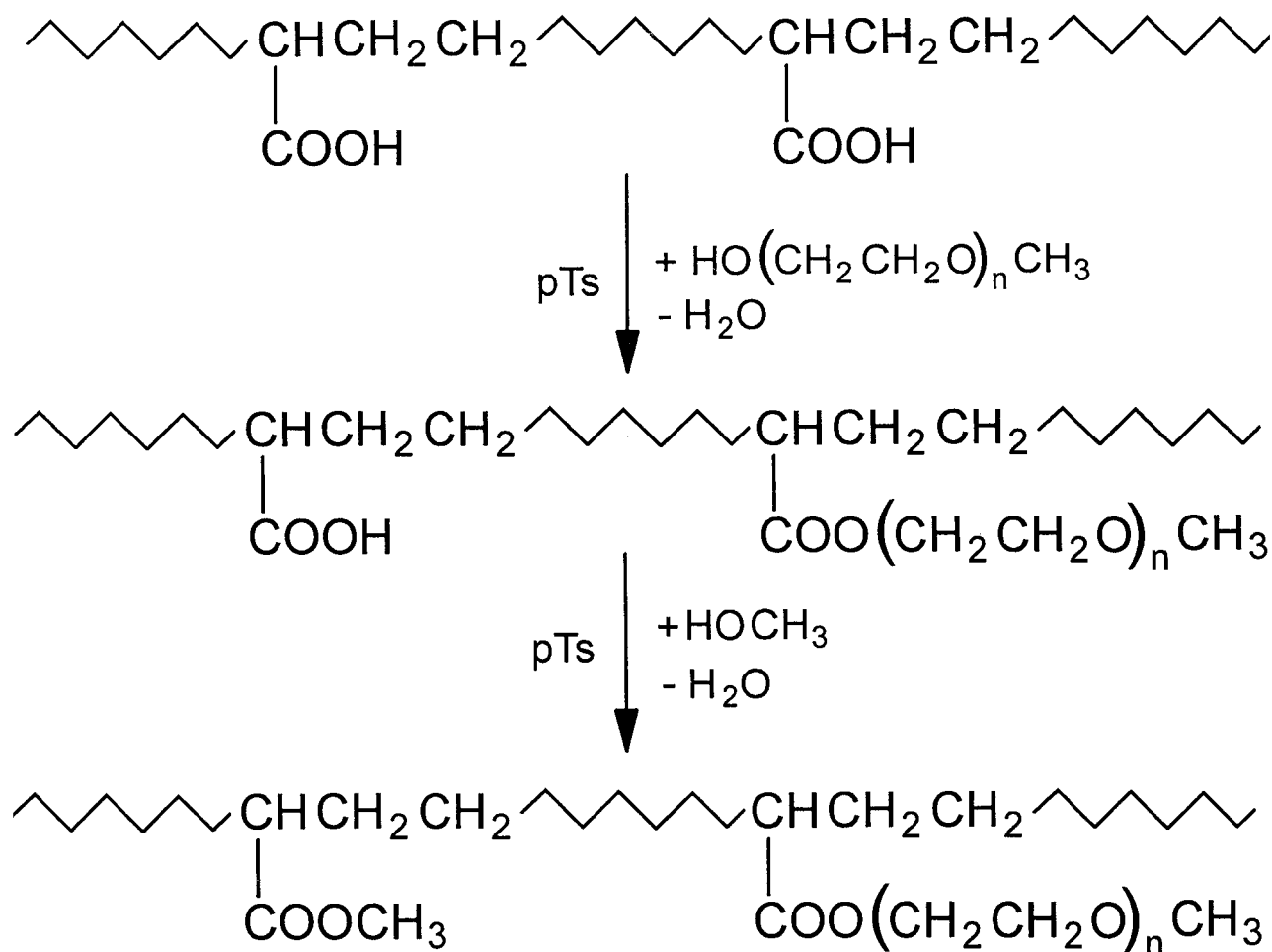
Scheme 1

thus controlling and stabilizing the blend morphology, and increasing the adhesion between the phases.

Much work has been reported on blends of polyamides with polyethylene.[5–10] In most systems investigated the matrix material is polyamide-6 (PA-6) with a dispersed phase of polyethylene (PE), which improves the impact properties of PA-6. In PE films a dispersed PA-6 phase can improve the resistance to oxygen permeation, which is of great interest for the use of PE in barrier films.[10] PE and PA-6 are incompatible and will form a phase-separated unstable morphology when blended. To stabilize the PE/PA-6 blends many different compatibilizers have been used. In many studies compatibilizers such as copolymers or adducts of maleic anhydride[6,8,11] or different acrylates such as polyethylene-graft butylacrylate[9] or polyethylene-metacrylic acid isobutyl acrylate terpolymer[5] are used.

In the present work we studied blends of low-density PE and PA-6 with PE as the matrix. We have for several years studied the preparation and interfacial properties of poly(ethylene oxide) (PEO) graft copolymers, and recently we reported on the preparation and properties of poly(ethylene-graft-ethylene oxide) (PE-PEO).[12] This graft copolymer was used in the present work as compatibilizer for the PE/PA-6 blends. The PE-PEO graft copolymer was prepared by coupling of poly(ethylene-co-acrylic acid) (PEAA) backbone with poly(ethylene oxide) monomethyl ether (MPEO) by esterification, as shown in Scheme 1. The compatibilizing effect of PE-PEO was compared with that of the unmodified backbone polymer, PEAA. The blends were prepared by melt mixing in a co-rotating, intermeshing twin-screw extruder, and in all blends PE was the matrix phase at a weight ratio between PE and PA-6 of 70 : 30.

Table I   Barrel Set Temperatures Used for Temperature Zones 1–10 of the Extruder

Blend	Set Temperatures for Barrel Zones 1–10 (°C)					
	1	2	3	4–6	7–8	9–10
PE/PA	50	220	230	250	260	250
PE/PA/4% PE-PEO	35	230	250	250	260	250
PE/PA/4% PEAA	35	230	250	250	260	250

EXPERIMENTAL

Materials

PEAA Escor 5110 from Exxon Chemical, Norden AB, Göteborg, Sweden containing 11 wt % acrylic acid units was used for preparation of the PE-PEO graft copolymer, and as additive. Low-density polyethylene LD SC 7641 from Dow (density 0.9235 g/cm3) and Ultramid B4 polyamide-6 from BASF AG, Ludwigshafen, Germany were used as blend components. The graft copolymer containing PEO side chains on a PE backbone (PE-PEO) was prepared by coupling of PEAA and MPEO (MW = 2000) by esterification. PEAA and MPEO were allowed to react in o-xylene at 140°C under N_2 in the presence of p-toluenesulfonic acid as catalyst. After the reaction was finished, methanol was added in excess to esterify residual acid groups. Details of the synthesis were given previously.[12]

Blend Preparation

Blends of PE and PA-6 containing 0 and 4 wt % graft copolymer or 4% PEAA were prepared in a Berstorff ZE 25 × 43D twin-screw extruder with co-rotating, intermeshing screws at a screw speed of 200 rpm. The screws had length to diameter ratio (L/D) of 43. The barrel zones of the extruder were set at the temperatures given in Table I. The blends were extruded through a ribbon die and the extrudates cooled in a water bath and then dried at ambient temperature. The weight ratio of PE to PA-6 was 70 : 30 in all cases.

Morphological Characterization

The morphology of the blends was studied by scanning electron microscopy (SEM), using an ISI 100A instrument operating at 15 kV. The samples for SEM analysis were prepared by cryo fracturing the blends after extrusion at liquid nitrogen temperature. Pieces of the blends were fractured parallel and perpendicular to the extrusion direction. All samples were sputter coated with 20 nm of Au before analysis. To study the thermal stability of the morphology, the blends were also examined after heat treatment. Pieces of the blends were treated at 250°C for 12 min, cooled to room temperature, and then cryo fractured.

The fibrous PA-6 phase present in the uncompatibilized PE/PA-6 blend was studied by dissolving the PE matrix in boiling o-xylene. The remaining PA-6 phase was then transferred to SEM holders and sputter coated as above.

To obtain information on the adhesion between the matrix and the dispersed phase, the fracture surfaces of the test bars after tensile testing were studied by SEM after sputter coating as above.

Thermal Characterization

The thermal properties of the blends were investigated by differential scanning calorimetry (DSC) using a Mettler DSC30 STARe system with a low-temperature cell. The samples, 10–15 mg, were sealed in 40 μL Al crucibles. The samples were first heated up from 25°C to 300°C, cooled down to 0°C, and then reheated up to 300°C. Temperature scan rates were in all cases 10°C/min.

Mechanical Testing

Test bars for tensile testing were punched out from 1.2-mm thick plates, which were compression molded from pelletized blend material at 170°C. At this temperature the morphology of the PA-6 phase was not affected. The tensile properties of the specimens were evaluated according to ISO R527 using a JJ Instruments T30K tensile tester at a cross-head speed of 10 mm/min. The results reported are mean values of 12 measured specimens for each material.
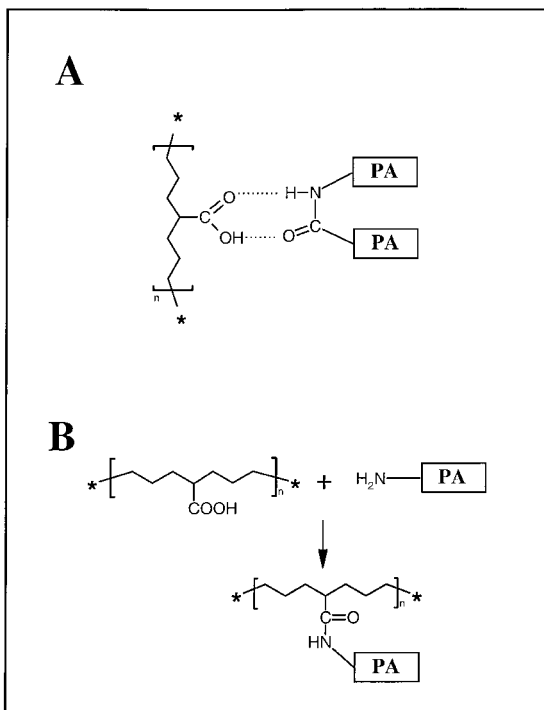
Figure 1 Possible interactions between poly(ethylene-co-acrylic acid) (PEAA) and polyamide-6 (PA-6). A, hydrogen bonding; B, grafting.

RESULT AND DISCUSSION

In a heterogeneous polymer blend the interfacial interactions between the components determine the blend morphology and the adhesion between the phases. It can be expected that mechanical blending of PE and PA-6 gives rise to a very unstable morphology because of the large dissimilarity of the two polymers. PE is a pure hydrocarbon polymer with low polarity, whereas PA-6, because of its amide linkages, is polar and hydrogen bonding. The interfacial energy should consequently be high and the state of mixing should be very sensitive to changes in shearing rates at temperatures where both polymers are in the melt state.

The interfacial energy can be decreased by adding a surface active component to the blend, for example an amphiphilic polymer, as a compatibilizer. However, in order to positively contribute to the adhesion between the phases the amphiphile should show a strong interaction with both components of the blend. By employing a block or graft copolymer containing polymer segments miscible with each phase this requirement can be fulfilled. We have previously shown that styrene/

ethylene oxide graft copolymers can be successfully used as compatibilizers for polystyrene/PA-6 blends,[13] and that PEO strongly interacts with the PA-6 phase by means of hydrogen bonding between the amide groups and the ether oxygens in the PEO grafts.[13–15]

In the present study we have investigated morphology, thermal properties, and mechanical properties of compatibilized and uncompatibilized blends of low-density PE and PA-6. These two copolymers will act as compatibilizers in the PE/PA-6 blends by different mechanisms. In a blend containing PEAA, the carboxylic acid groups in the copolymer may interact with the amino end groups in polyamide either by hydrogen bonding (Fig. 1A) or by an amidation reaction (Fig. 1B), which would generate a PA-6 grafted copolymer during melt mixing at high temperature.[4,16,17] Both PEAA and the PA-6 grafted copolymers would have strong self-association and show affinity to both PE and PA-6. In the blend containing the PE-PEO graft copolymer, the ether oxygens of PEO grafts may act as hydrogen bond acceptors and interact with amide N—H hydrogens (Fig. 2). These interactions will induce partial miscibility of PEO with PA-6, as reported by Jannasch and Wesslén[13] and Coleman and coworkers.[14,15] The PE backbone of the graft copolymer should be miscible with the PE matrix.

Blend Morphology

The blends were prepared by melt mixing of PE, PA-6, and the compatibilizer in a twin-screw extruder at 250°C. The extrudate was rapidly cooled by water. The morphology of the different blends was investigated by SEM on freeze-fractured specimens. Directly after extrusion the PA-6 phase in the uncompatibilized PE/PA-6 blend was
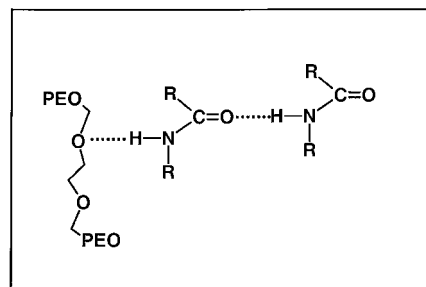
Figure 2 Hydrogen bonding in poly(ethylene oxide) (PEO) and polyamide-6 (PA-6), inducing partial miscibility of PEO in PA-6.
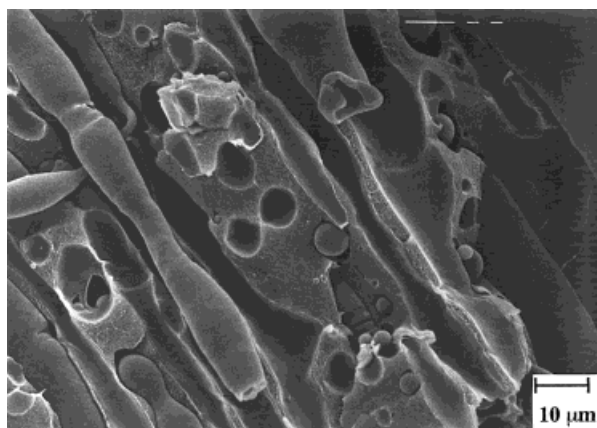
(a)
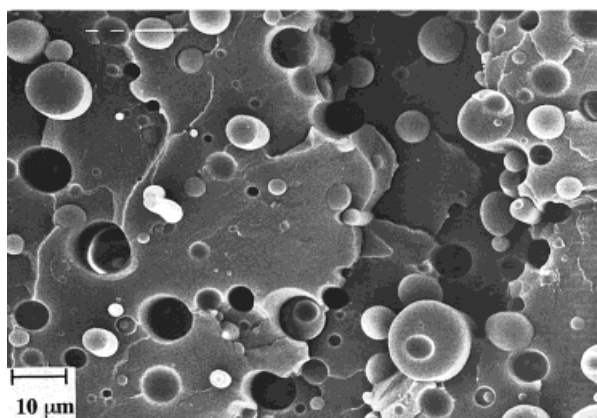
(b)

Figure 3   A, PE/PA-6 blend cryo fractured parallel to the flow direction. B, PE/PA-6 blend cryo fractured perpendicular to the flow direction.

present as long and thin fibers with an estimated aspect ratio larger than 100. Small spheres of PA-6 were also present, with diameters ranging from 2 to 10 μm. Figure 3 shows micrographs of samples of the blend fractured parallel and perpendicular to the extrusion direction. It is obvious from Figure 3 that the adhesion between the PE matrix and the PA-6 phase domains was very poor, as expected. The fibers displayed a broad distribution of diameters, ranging from two μm up to 100 μm. The fibrous PA-6 domains could be isolated from the blend by dissolution of the PE matrix phase by boiling o-xylene, and the fiber length distribution estimated. In Figure 4 a micrograph of the isolated PA-6 fibers is shown.

The morphology of the PE/PA-6 blend changed drastically by addition of the compatibilizers. The PA-6 phase morphology was transformed from
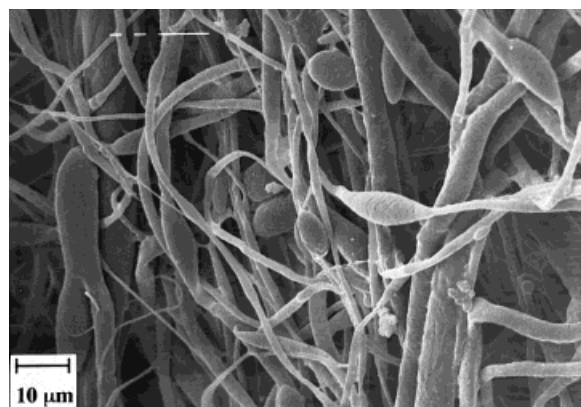

Figure 4   Fibrous PA-6 phase from PE/PA-6 blend after the PE matrix was dissolved with boiling o-xylene.

long fibers to small, almost spherical domains with a much more narrow size distribution. In the blend containing 4% PEAA the PA-6 phase had formed small spheres with an average diameter of 0.9 μm that had agglomerated to larger structures. This is shown in the micrograph in Figure 5. The PEAA compatibilizer seems to adsorb at the PE/PA-6 interface, and extended structures of PA-6 spheres are formed presumably joined together by the PEAA copolymer, which has a strong tendency for self-association through hydrogen bonding at the carboxylic acid groups. Further SEM studies indicated that the agglomerated domains of PA-6 formed a structure similar to an interpenetrating network (IPN) within the PE matrix.

The PE-PEO graft copolymer behaved quite differently from PEAA as compatibilizer for the PE/PA-6 blend. The addition of 4% PE-PEO resulted in well-dispersed spherical PA-6 phase do-
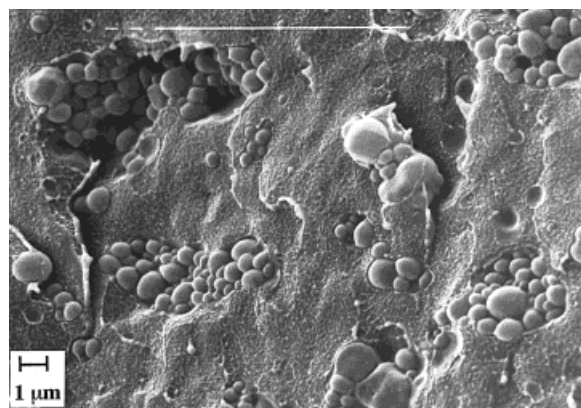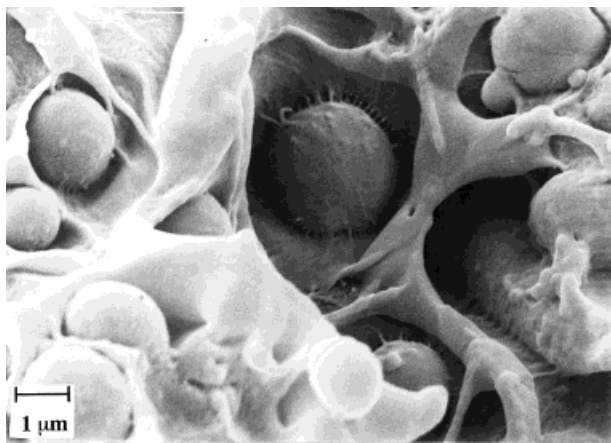

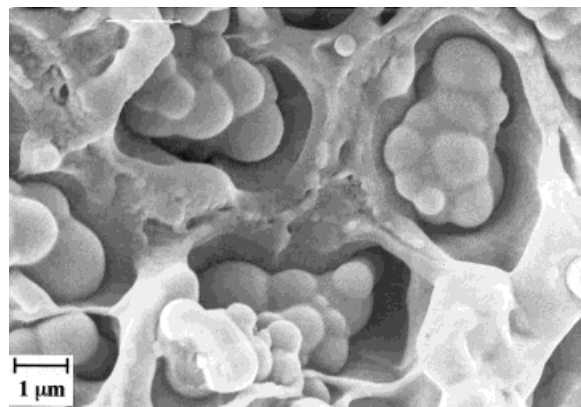**Figure 5**   Cryo fractured blend of PE/PA/4% PEAA.
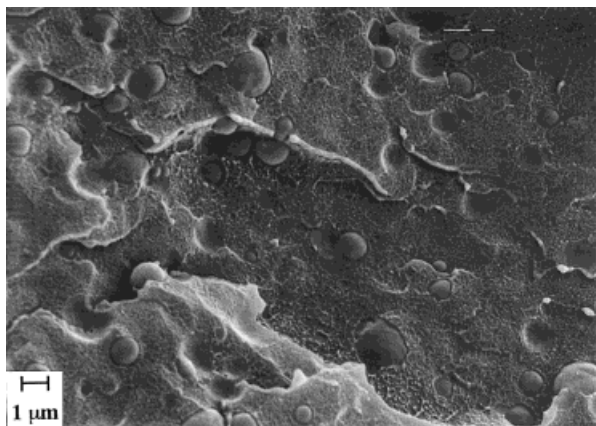
Figure 6   Cryo fractured blend of PE/PA/4% PE-PEO.

Figure 8   Fracture surface of the test bar after tensile testing of the blend containing PEAA.

mains, in contrast to the agglomerated structures of PA-6 found in the PEAA compatibilized blend. The micrograph in Figure 6, showing a freeze-fractured sample, indicates that the adhesion between the PE matrix and the PA-6 domains was better than in the other blends investigated. The PE matrix is partly covering the PA-6 domains, which should be a consequence of stronger adhesion. The dispersed PA-6 phase domains had an average diameter of 1.4 μm.

SEM studies of fracture surfaces obtained after tensile testing at room temperature gave more information regarding the adhesion between the PE matrix and the dispersed PA-6 phase, than did the freeze-fractured surfaces. The micrograph in Figure 7 shows a PA-6 sphere in the PE-PEO graft copolymer compatibilized PE/PA-6 blend at

high magnification. Between the matrix and the dispersed PA-6 phase thin tie fibrils can be seen, which bridges the PA-6 sphere and the PE matrix material together. The fibrils are presumably a result of the compatibilizer being present at the interface. This phenomenon was neither observed in the blend containing PEAA (Fig. 8) nor in the uncompatibilized PE/PA-6 blend, but has previously been reported by Armat and Moet[11] for blends of PA-6 and LDPE compatibilized with a styrene-(ethylene-co-butylene)-styrene   (SEBS) block copolymer functionalized with maleic anhydride.

The stability of a polymer blend at processing conditions is of great importance. Both the uncompatibilized   and   compatibilized   PE/PA-6 blends were heat treated for 12 min in an oven at 250°C, i.e., the processing temperature. At this temperature both the matrix and the dispersed PA-6 phase are in the molten state. In the blends
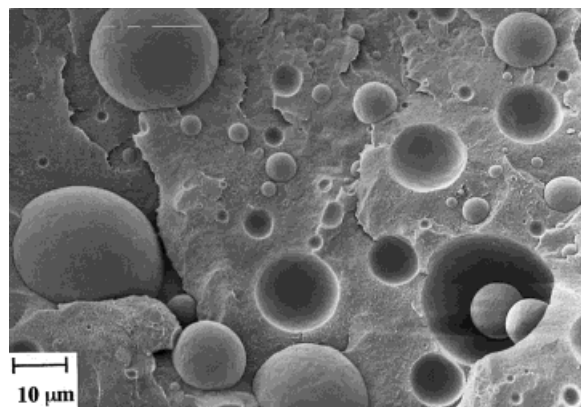

Figure 7   Fracture surface of the test bar after tensile testing of the blend containing PE-PEO. Thin tie fibrils can be seen connecting the PA-6 sphere and the PE matrix.

Figure 9   Cryo fractured PE/PA-6 blend after heat treatment in 250°C for 12 min.

**Table II   Diameters and Standard Deviations of the PA-Spheres in the PE/PA Blends**

Blend	Diameter (μm)	Std Deviation (μm)
PE/PA	21.0	7.0
PE/PA/4% PE-PEO	1.4	0.5
PE/PA/4% PEAA	0.9	0.2

compatibilized with PE-PEO graft copolymer and PEAA the morphology did not change during the heat treatment. For the uncompatibilized PE/PA-6 blend, however, the morphology changed drastically by this treatment. The PA-6 phase structure changed from long fibers to spherical domains as seen in Figure 9. The size distribution ranged from two μm up to 100 μm, with an average diameter of 21 μm. Presumably the long fibers on melting break up to form the small spherical domains observed. The experiments clearly show that both compatibilizers have a stabilizing effect of the morphology of the PE/PA-6 blends.

All data for the dimensions of the PA-6 phase domains for the different blends are given in Table II. The data were obtained by measurements on sets of micrographs of fractured specimens of the different blends. The average diameter of the PA-6 spheres decreased with a factor between 15 to 23 when compatibilizer was added.

Mechanical Properties

As discussed above, the two compatibilizers PE-PEO and PEAA affected the PE/PA-6 blend differently. PE-PEO gave a material having well-dispersed PA-6 spheres in the PE matrix, whereas PEAA gave a network of aggregated PA-6 spheres. The mechanical properties of the blends were tensile tested and compared with those of the uncompatibilized blend. The results
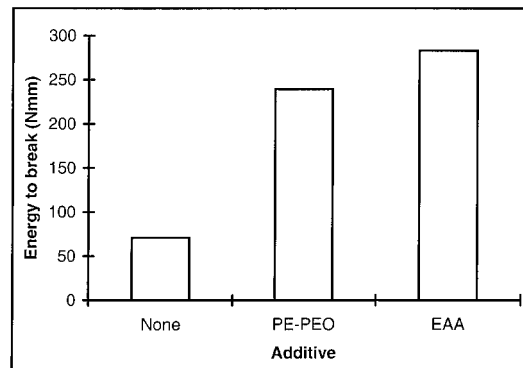
Figure 10   Tensile testing of the blends: energy to break.

from the tensile testing are given in Table III. As seen in Table III both compatibilized blends had improved mechanical properties relative to those of the uncompatibilized blend. The tensile strength (σ_b) increased by 34% and the elongation at break (ε_b) by 170% for the blend containing PE-PEO. For the blend containing PEAA the corresponding values were 48% and 200% respectively. The property mostly improved was the toughness or energy to break, which is defined as the energy required to break the material,[18] and is equal to the area under the stress-strain curve. The increase was 240% for the blend containing PE-PEO and 300% in the blend containing PEAA compared with the uncompatibilized PE/PA-6 blend (Fig. 10). The higher values obtained for the PEAA compatibilized blend may be a result of the extended IPN-like structures of PA-6 spheres, as opposed to the dispersed PA-6 domains in the PE-PEO compatibilized blend.

The pure LDPE material had a tensile modulus of 150 N/mm^2 as compared with 200–270 N/mm^2 for the blends. The maximum tensile strength (σ_{max}) was 10 N/mm^2 and the elongation at maximum was approximately 85%. Due to limitations of the tensile tester the break point was not possible to measure for these samples.

Table III   Mechanical Properties of Blends

Blend	σ (Break) (N/mm^2)	ε (Break) (%)	Energy[a] (N/mm)	Modulus (N/mm^2)
PE/PA	9.1	7	70	270
PE/PA/4% PE-PEO	12.2	19	240	200
PE/PA/4% PEAA	13.5	21	280	260

[a] Energy to break is equal to the area under the stress-strain curve.

Table IV   Melting and Crystallization Temperature and Enthalpy of the PE and PA Phases in the Homopolymers and Blends

	T_m [PE] (°C)	ΔH_m [PE] (J/g)	T_c [PE] (°C)	ΔH_c [PE] (J/g)	T_m [PA] (°C)	ΔH_m [PA] (J/g)	T_c [PA] (°C)	ΔH_c [PA] (J/g)
PE	112	121	94	127	—	—	—	—
PA	—	—	—	—	223	48	167	53
PE/PA	113	114	102	122	223	40	188	46
PE/PA/4% PE-PEO	115	116	100	125	223	49	167	48
PE/PA/4% PEAA	114	118	102	124	222	52	191–120	24

Thermal Characterization

Melting and crystallization temperatures for the blends and the corresponding enthalpies were determined by DSC. The results from these measurements are presented in Table IV. Pure PE and PA-6 show melting endotherms at 112°C and 223°C, respectively, and crystallization exotherms at 94°C and 167°C. In the uncompatibilized PE/PA-6 blend crystallization of the PA-6 phase took place at 188°C, i.e., 21° higher than pure PA-6. It appears as though the presence of the PE phase changes the nucleation rate, and allows crystallization of the PA-6 phase at a higher temperature. For the compatibilized blends the crystallization behavior was more difficult to evaluate. DSC thermograms for crystallization of the blends are shown in Figure 11. In the blend compatibilized with PE-PEO graft copolymer a broad crystallization peak was observed at 167°C, although the rough baseline indicates that crystallization occurred over a broad temperature interval, from 190°C down to about 120°C. In the blend containing PEAA a very small exotherm was observed already at 191°C, but

similarly to the case with the PE-PEO compatibilized blend, crystallization continued down to 120°C. This phenomena is called fractionated or cold crystallization and has been observed previously in blends of PA-6 and polyolefins.[14,16,19–21] The crystallization temperature of polyamides has been shown to be strongly dependent on the size of the polyamide domains. The smaller the domains, the higher the degree of supercooling needed before crystallization takes place. Although crystallization is difficult to evaluate in the compatibilized blends, the melting enthalpy of the PA-6 phase (ΔHm[PA]), was calculated from the PA-6 content in the blends, and found to be similar or slightly higher than that of pure PA-6. The melting temperature of the PA-6 phase was not affected by the blending and was registered at 223°C for the pure materials as well as for all the blends. The crystallization and melting behaviors of the PE phase in the blends were unchanged, except for an increase in the crystallization temperature by 6–8°C compared with that of pure LDPE. This may be an effect of the presence of PA-6 at the interface acting as nucleating sites for the crystallization of the PE phase.
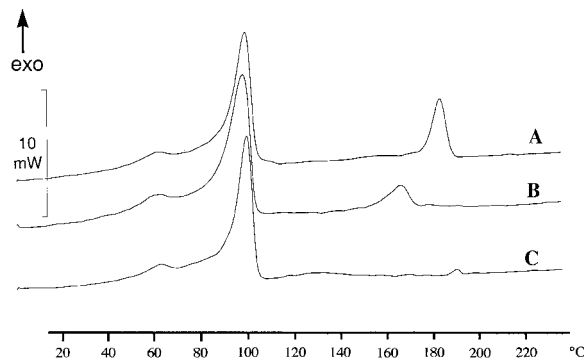
Figure 11 DSC traces for crystallization of the blends. A) PE/PA; B) PE/PA/4% PE-PEO; C) PE/PA/4% PEAA

CONCLUSIONS

Both PE-PEO and PEAA copolymers function as compatibilizers for blends of LDPE and PA-6. The average diameter of the PA-6 domains decreased by a factor between 15 to 23, when compatibilizers were used. The two compatibilizers gave two different morphologies of the PE/PA-6 blends. PEAA gave a blend with PA-6 spheres having an average diameter of 0.9 μm and agglomerated to IPN-like structures in the PE matrix. The graft copolymer PE-PEO gave a material having well-dispersed spherical PA-6 domains, with an average diameter of 1.4 μm. The PA-6 phase showed better adhesion

to the PE matrix in the blend containing the PE-PEO compatibilizer compared with the blend containing PEAA, as shown by fibrils connecting the PE and PA-6 phases. Compatibilization improved the mechanical properties, e.g., toughness and elongation at break (ε_b), of the PE/PA-6 blend.

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