

Recycling of Postconsumer Poly(ethylene terephthalate) and High-Density Polyethylene by Compatibilized Blending

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ABSTRACT: Two ways of recovering the properties of the scrap plastics poly(ethylene terephthalate) (PET) and high-density polyethylene (HDPE) were analyzed: (1) blending incompletely segregated polymers with a compatibilizer and (2) blending nonsegregated polymers with a small amount (2 pph) of another compatibilizer. The advancement of the compatibilization reaction in a twin-screw extruder depended on the residence time and intensity of mixing according to melt viscosity measurements and scanning electron microscopy observations. The acceptable mechanical properties for systems with different PET contents were obtained in blends compatibilized with ethylene-glycidyl methacrylate (EGMA) and styrene-ethylene-butylene-styrene grafted with maleic anhydride. For a blend with 75% PET and 25% HDPE, the optimum content of EGMA was determined to be about 4 pph, and a film was produced with

this composition. Admixtures present in recycled HDPE migrated to PET during blending and accelerated the hydrolysis of PET. As a result of migration, differences in the mechanical properties of the blends were observed, depending on the brand of recycled HDPE used. EGMA was also successfully used for the improvement of mechanical properties of a nonsegregated mixture based on PET. Tensile properties of two compatibilized PET-rich and HDPE-rich commingled scraps indicated the possibility of using these blends for film extrusion, with potential applications in the packaging of technical products. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1473–1485, 2002

Key words: polyethylene (PE); recycling; blends; compatibilization

INTRODUCTION

The improvement of the properties of recycled plastics may be achieved in various ways. One of the possibilities is more effective segregation, which is either time- or cost-consuming and never fully complete. Another way is the preparation of a blend from roughly segregated polymers. Because most polymer pairs are immiscible, the use of compatibilizers is necessary.

During the last several years, numerous publications have dealt with the compatibilization and mixing processes of blends from virgin plastics. Many are focused on blends of poly(ethylene terephthalate) (PET) and polyolefins [mainly high-density polyethylene (HDPE)] because these materials are widely used and are also available in large amounts for potential reprocessing from plastic waste. A review by Xanthos and Dagli¹ of compatibilization routes and systems

summarizes the results of studies up to the end of the 1980s. It is evident from the literature for PET/polyethylene (PE) blends that the most promising route is the addition of a compatibilizer with reactive groups: maleic anhydride (MA) or glycidyl methacrylate (GMA).² Pietrasanta et al.³ pointed out the possibility of compatibilization of the HDPE/PET system by polyolefins functionalized with GMA directly in the injection-molding machine. The mechanical properties of directly injected blends with 5 wt % compatibilizer were comparable to those of previously extruded and then injected samples; however, the results do not seem to be satisfactory. This is probably due to the large sizes and high-shape anisotropy of the inclusions in the blend prepared directly by injection and not by blending. Dagli and Kamdar⁴ discussed the influence of the protocol of component addition on the reactive compatibilization of HDPE/PET blends with ethylene-glycidyl methacrylate (EGMA). The best properties were achieved when the reactive polymer was mixed initially with the nonpolar component of the blend; that is, EGMA was blended first with HDPE and then with PET. Satisfactory results were also obtained when all components were blended together in the extruder.

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A second effective compatibilizer for the PET/EGMA system is a block copolymer of styrene-ethylene-butylene-styrene grafted with maleic anhydride (SEBS-*g*-MA). For a 75% HDPE/25% PET system with 5 pph SEBS-*g*-MA, an elongation to break was obtained even larger than that for pure PE (440 vs 300%).⁵ Dimitrova et al.⁶ used synthesized ethylene-vinyl acetate (EVA) and ethylene-vinyl alcohol (EVOH) based copolyesters for PET/HDPE (80 wt % PET and 5 wt % copolyester) and observed the changes in the morphology and the improvement in the mechanical properties; however, they were less significant than for the related blend with SEBS-*g*-MA. SEBS, not even grafted by MA, was more effective than an EPDM elastomer, as tested by Traugott et al.⁷

Grafted copolymers, prepared from ozonized HDPE, were synthesized by Boutevin et al.⁸ and used for the improvement of the properties of a PET/HDPE blend. Most effective were polyethylene-*g*-maleic anhydride (PE-*g*-MA) and polyethylene-*g*-glycidyl methacrylate (PE-*g*-GMA); however, the blends with the composition 60% HDPE/40% PET and 5% copolymer showed an elongation to break only at 10%. It must be mentioned here that the elongation to break, together with the notched impact strength, is a good indicator of the effectiveness of the compatibilizer, except that it is very sensitive to the PET crystallinity. Any comparison between elongations to break for samples described in different articles is meaningless unless they were prepared in the same way.

The effectiveness of polypropylene-*g*-maleic anhydride (PP-*g*-MA), linear low-density polyethylene-*g*-maleic anhydride (LLDPE-*g*-MA), and SEBS-*g*-MA as compatibilizers for PET/polypropylene (PP) blends was studied by Papadopoulou and Kalfoglou.⁹ The high elongations to break of these blends indicated that SEBS-*g*-MA performed the best. The blends with 15% SEBS-*g*-MA and different contents of PET and PP were ductile, with elongations to break of 360–720%.

Decreasing the interfacial tension in blends seems to be necessary for the improvement of blend properties. The influence of 12 compatibilizers on the interfacial tension of a PE/PET system was examined by Ihm and White.¹⁰ They found similar effectiveness on interfacial tension with the block copolymer poly(butylene terephthalate)-*block*-polyethylene (PBT-*b*-PE), SEBS-*g*-MA, and high-density polyethylene-*g*-maleic anhydride (HDPE-*g*-MA).

The aforementioned articles concern blends of virgin polymers. The reports about the properties of recycled polymers are less numerous. Akkapeddi et al.¹¹ examined the activity of EGMA in blends of recycled PET with recycled HDPE and other virgin polyolefins. The noncompatibilized blend with 50% PET was extremely brittle, with an elongation to break of 2% at a stress of 25 MPa. A relatively high concentration of EGMA (10%) was necessary to obtain acceptable me-

chanical properties in this system, with an elongation to break of 55% and an increase in the absorbed energy in an Izod impact test from 16 to 134 J/m.

Xanthos et al.¹² analyzed the composition of a plastic recycling stream from American cities. The mixture of waste plastics (57% polyolefins and 25% PET) was compounded in a twin-screw extruder, and samples were characterized. Different copolymers were added as compatibilizers. A better dispersion of components and some improvement in the mechanical properties were reached when a styrenic block copolymer or SEBS-*g*-MA was added; however, the samples with 10 wt % elastomer in the tensile tests showed an elongation to break of only about 10–24%.

The data presented in the literature do not give a ready answer to which compatibilization procedure is best for recycled polymers. The number of compositions studied is too small for decisive conclusions. However, the results concerning blends of virgin polymers cannot be directly used because they depend on the properties of used polymers, such as the degree of degradation (lower intrinsic viscosity of PET), and because they often contain quite large amounts of impurities and admixtures of other polymers.

In our earlier articles,^{13,14} scrap plastics from Polish and Italian sources were studied. Eight selected polymers, including four types of PET and four types of PE [low-density polyethylene (LDPE), HDPE, and a mixture], were characterized by the following techniques: differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy, scanning electron microscopy (SEM), thermogravimetry, and oxidation induction time (for polyolefins). Mechanical properties were characterized with tensile and Izod tests. From an analysis of the compositions of the recyclates, it was concluded that in all materials analyzed, inclusions of other polymers were present, independent of the claimed purity. The level of admixtures, including poly(vinyl chloride) (PVC), depended strongly on the source of the polymers and varied between 50 ppm and 15%. SEM observations showed that in those scraped polymers, the admixture of other polymers was phase-separated. The most PET-degrading residues were found to be sugar, caramel, glue from labels, and PVC. For recycled polyolefins, the most authoritative parameters are the oxidation induction time and mechanical ultimate properties, which detect the presence of microgels and degradation. Usually, the elongation to break and the capacity for plastic deformation were lower for recyclates than for typical virgin polymers, and some of the analyzed polyolefins showed an oxidation induction time below 4 min, which indicates the loss of activity of antioxidants and stabilizers. Besides the admixture of other polymers, impurities such as soil, cellulose from labels, glue residue, and caramel were detected in the recyclates. The effect of admixtures included the loss of tough-

TABLE I
List of Examined Materials

Polymer/name	Source	Comments
PET Rilal	Replastic Co., Italy	IV = 0.75; M_n = 21,400, M_w = 43,800; flakes from beverage bottles
PET Hanex	GTX Hanex Plastics, Poland	IV = 0.74; ground PET, flakes from beverage bottles
PET Ekogeminex	Ekogeminex Co., Poland	Ground polymer from beverage bottles; flakes
PET PTM3	Replastic Co., Italy	Commingled scraps; 85–90% PET, 10–15% polyolefins; mixed flakes
HDPE Rilae	Replastic Co., Italy	3% PP present; OIT = 3.9 min, pellets
HDPE Ekogeminex	Ekogeminex Co., Poland	2% PP present; OIT = 7.7 min, pellets
PO PEM	Replastic Co., Italy	Commingled scraps; 90–95% PE and PP, 10–5% PET. OIT = 2.2 min; mixed flakes

IV = intrinsic viscosity; M_n = number-average molecular weight; M_w = weight-average molecular weight; OIT = oxidation induction time.

ness always, the loss of impact resistance, often the loss of color, and worse or imperfect processability.

The goal of this work was to develop an effective method of compatibilized blending for typical systems of recycled and scrap commingled polymers from municipal waste. Because PET and polyolefins are the most popular recyclates, our attention was focused on these two groups. Compatibilized blending should restore a combination of those beneficial physical (mainly mechanical) properties that are unique for each blend component, thereby avoiding thorough segregation of commingled scrap polymers. The representative scrap commingled polymers PET and polyolefins were chosen from leading Italian and Polish suppliers.

Two approaches for blend preparation were selected: the addition of a commercial compatibilizer to a mixture of segregated polymers and the addition of a commercial compatibilizer to poorly segregated polymers containing admixtures of 5–25% of other polymers. The influence of additives present in scrap polymers on the properties of blends was judged on the basis of the application of polyolefin scraps of different origins and, therefore, different impurities.

EXPERIMENTAL

Materials

Table I shows the polymers that were selected for the studies. PET Rilal (Replastic Co., Milano, Italy) showed the best properties among the polyesters studied in our earlier work,¹³ whereas HDPE Rilae (Replastic) and HDPE Ekogeminex (Ekogeminex Co., Lodz, Poland) were the best among polyolefins.¹⁴ These polymers were used for blend preparation. PET PTM3 and PO PEM were, in fact, mixtures containing 10–15% polyolefins for PTM3 and 90–95% polyolefins and 5–10% PET for PEM, so we investigated the possibility of improving their properties by adding a compatibilizer.

The following compatibilizers were tested as potentially useful for the systems studied: EGMA copolymer [Bondfast 2C, Sumitomo, Japan, weight-average molecular weight = 240 K, 8 wt % GMA, and Lotader AX8840, Elf-Atochem Paris, 8 wt % GMA, mass-flow index (MFI) = 5 g/10 min at 190°C for 325 g, melting point = 109°C], SEBS-*g*-MA (PAB 192, Shell Development Co., Emeryville, CA, equivalent to FG 1901, 1.7 wt % MA), HDPE-*g*-MA (Polybond 3009, Uniroyal, 4 wt % MA), poly(ethylene-*co*-acrylic acid) (E-AA; Escor 5000, Exxon, Zwijndrecht, Belgium, 6 wt % AA), PE-*g*-MA (Fusabond P, DuPont, Wilmington, DE, 1 wt % MA), polypropylene-*g*-acrylic acid (PP-*g*-AA; Polybond 1001, BP Chemicals, Baytown, TX, 6 wt % acrylic acid), and EPR-*g*-MA (Fusabond N, DuPont, 1 wt % MA).

Methods

The efficiency of the aforementioned compatibilizers was checked by the preparation of selected PET/HDPE blends with the recycled PET Hanex and the virgin HDPE Eltex (Solway, Antwerpen/Lillo, Belgium). The 75/25 and 25/75 blends (by weight), with 5 wt % of each compatibilizer, were prepared with a Brabender W50E (Duisburg, Germany) measuring mixer. The torque as a function of time during blending was taken as evidence of the reaction rate and effectiveness. On this basis and the SEM observations of phase dispersion, we have concluded that the best potential compatibilizers for application to PET/HDPE blending are EGMA, SEBS-*g*-MA, and HDPE-*g*-MA. All of them show some affinity toward HDPE, and they have chemical groups that are able to react with PET.

Based on the PET Rilal, the HDPE Ekogeminex, and the HDPE Rilae, with SEBS-*g*-MA, EGMA, and HDPE-*g*-MA as compatibilizers, a series of blends were prepared. The composition of the blends was based on the following scheme: the base components (PET and

TABLE II
Composition of Blends Prepared by Mapre Extruder

Blend	Composition ^a (wt %/wt %/pph)	Processing speed (rpm)
PET/HDPE Ekogeminex/SEBS-g-MA	75/25/0, 2, or 5	500
PET/HDPE Ekogeminex/SEBS-g-MA	25/75/0, 2, or 5	500
PET/HDPE Rilae/SEBS-g-MA	75/25/0, 5, or 10	250
PET/HDPE Rilae/SEBS-g-MA	25/75/0, 5, or 10	250
PET/HDPE Rilae/SEBS-g-MA	75/25/5	500
PET/HDPE Rilae/SEBS-g-MA	25/75/5	500
PET/HDPE Rilae/EGMA	75/25/0, 5, or 10	250
PET/HDPE Rilae/EGMA	25/75/0, 3, or 5	250
PET/HDPE Rilae/HDPE-g-MA	75/25/10	250
PET/HDPE Rilae/HDPE-g-MA	25/75/10	250

^a The description 75/25/0, 5, or 10 means that to the total mass of blend with composition 75 wt % PET and 25 wt % HDPE was added 0, 5, or 10 pph compatibilizer.

HDPE) were in the proportion 75/25 or 25/75, and the compatibilizer was added in the amount of 0, 2, 3, 5, or 10 pph of the total weight of the blend. The prepared compositions are specified in Table II. All materials were carefully dried before blending (PET, 4 h at 170°C; HDPE, 2 h at 105°C; SEBS-g-MA, 2 h at 80°C; and EGMA, 2 h at 105°C). The drying conditions were determined on the basis of several tests, and the drying time and temperature were restricted on the basis of the DSC and thermogravimetry data.

The Mapre DS 40 (Leige, Belgium) corotating, intermeshing, twin-screw extruder ($L/D = 33$) was used for the preparation of blends. All components, still hot after drying, were fed into the extruder. The blending was performed at 120, 235, 240, 240, 250, 255, and 260°C at the respective heating zones of the extruder, whereas the die temperature was maintained at 270°C. The residence time was 42 or 80 s for a screw rotation speed of 500 or 250 rpm, respectively. The blends were extruded into a water bath and then pelletized.

The results of mechanical tests for the prepared blends (discussed later) suggested the need for optimization of the quantities of EGMA in the blend. For this goal, additional 75/25 PET/HDPE Rilae blends with 2.5, 4, and 10 pph EGMA were blended in a laboratory twin-screw, nonintermeshing, corotating extruder ($L/D = 33$, $D = 25$ mm; two venting zones); the treats were air-cooled, pelletized, and sealed in air-tight bags. The materials were blended at 270°C with an extruder residence time of 7 min. The blends were then injection-molded to deliver samples for mechanical tests.

Two commingled scraps, PTM3 and PEM, produced by Replastic (see Table I) as side products of PET and HDPE segregation, were also used for compatibilized blending. Both materials are claimed by the producer to be useless for further processing and are burned or landfilled. The aim of this part of the work was to determine the possibility of improving the properties

of poorly or nonsegregated plastics. On the basis of the previous experiments, two compatibilizers were selected: EGMA for PTM3 and HDPE-g-MA for PEM. Two compositions were prepared with a laboratory corotating, twin-screw, nonintermeshing extruder: PTM3 with 2 wt % EGMA and PEM with 2 wt % HDPE-g-MA. The materials before blending were dried at 105°C for 12 h. The materials were blended at 270°C with an extruder residence time of 7 min.

Prepared blends were characterized by the techniques described next.

Thermal properties were analyzed with a TA 2100 differential scanning calorimeter (TA Instruments, New Castle, DE). The samples were heated to 270°C and then cooled to 20°C at a heating/cooling rate of 10°/min. The thermooxidative stability of the recyclates and blends was measured by the determination of the oxidation induction time (according to the EN 728 standard) with the TA 2100 DSC apparatus, with the nitrogen changed to the oxygen flow through the measuring cell. Fracture surfaces of averaged specimens were studied with a JEOL T300 (Jeol Ltd., Alrishima, Tokyo), scanning electron microscope. The samples for SEM were broken in liquid nitrogen after 15–20 min of freezing. The flow rates of thermoplastics (e.g., MFI) were studied with an extrusion plastometer at 265°C and with an applied weight of 2.16 kg along with other parameters according to ASTM Standard D 1238-95. For these studies, dry pellets (4 h at 100°C) were used. Samples for tensile testing were prepared via injection molding to a form according to standards for specimens for the tensile testing of plastics. A Battenfeld 30-g injection-molding machine was used. Mechanical properties of the blends were studied with an Instron tensile testing machine ($v = 50\%/min$). At least five samples of each blend were tested. The impact strength was determined in Izod tests with Resil 5.5 (Ceast, Torino, Italy), an instrumented impact hammer. Notched type A samples were used.

TABLE III
Values of the MFI (265°C, 2.16 kg)

Sample	Composition (wt %/wt %/pph)	MFI (g/10 min)
PET (before extrusion)	100	25.3
PET (after extrusion)	100	44.4
HDPE Rilae	100	0.6
HDPE Rilae	100	0.2 ^a
HDPE Ekogeminex	100	0.8
HDPE Ekogeminex	100	0.2 ^a
EGMA	100	10.3
PET/HDPE Rilae	75/25/0	31.0
PET/HDPE Rilae/SEBS-g-MA	75/25/5	26.6
PET/HDPE Rilae/SEBS-g-MA	75/25/10	16.5
PET/HDPE Rilae/EGMA	75/25/5	5.5
PET/HDPE Rilae/EGMA	75/25/10	7.5
PET/HDPE Rilae/HDPE-g-MA	75/25/10	20.2
PET/HDPE Ekogeminex	75/25/0	50.1
PET/HDPE Ekogeminex/SEBS-g-MA	75/25/2	26.1
PET/HDPE Ekogeminex/SEBS-g-MA	75/25/5	27.0
PET/HDPE Rilae	25/75/0	1.4
PET/HDPE Rilae/SEBS-g-MA	25/75/5	1.0
PET/HDPE Rilae/SEBS-g-MA	25/75/10	0.8
PET/HDPE Rilae/EGMA	25/75/10	0.8
PET/HDPE Rilae/EGMA	25/75/3	0.3
PET/HDPE Rilae/EGMA	25/75/5	0.3
PET/HDPE Rilae/HDPE-g-MA	25/75/10	0.8
PET/HDPE Ekogeminex	25/75/0	3.4
PET/HDPE Ekogeminex/SEBS-g-MA	25/75/2	2.3
PET/HDPE Ekogeminex/SEBS-g-MA	25/75/5	1.2

^a Measured at 190°C, weight = 2.16 kg.

RESULTS

Compatibilized blends from segregated scrap plastics

The blending process on the Mapre twin-screw extruder was flawless, and the extrudates were bubble-free, with smooth surfaces. The injection molding of all blends was easy, and injection-molded samples were smooth and were characterized by proper sizes and shapes. The MFI measurements indicated large differences between the viscosities of noncompatibilized and compatibilized blends (Table III). The blends with the HDPE Ekogeminex had MFIs higher than the blends with the HDPE Rilae, despite the similar flow properties of the two PEs. Apparently, the additives present in Ekogeminex more effectively degraded PET than those present in Rilae. The addition of the SEBS-g-MA compatibilizer stabilized the changes in the MFI caused by the impurities. All blends with compatibilizers showed lower MFI values than the blends without compatibilizers, and the decrease depended on the compatibilizer used: the most viscous blends were those with EGMA, the less viscous were those with HDPE-g-MA, and the least viscous were those with SEBS-g-MA. A nearly constant MFI level was observed when 5 wt % or more of EGMA was applied for a blend with a PET matrix and when 3 wt % or more was applied for an HDPE matrix. This suggests that at

these concentrations, the optimum of the reaction with the compatibilizer had been reached. The increase in the residence time in the extruder with decreasing screw rotation speed during processing resulted in slightly lower values of MFI because of prolonged and more effective compatibilization. For example, for the 75%/25%/5 pph PET/HDPE Rilae/SEBS-g-MA composition, the MFI was 26.6 g/10 min for the blend prepared with the extruder screw rotation speed of 500 rpm (residence time = 42 s) but 21.7 g/10 min for the blend prepared at 250 rpm (residence time = 80 s).

The thermal stability of the blends was studied with PET/HDPE Ekogeminex/SEBS-g-MA blends (Table IV). A slow decrease in the oxidation induction time with increasing content of the compatibilizer was ob-

TABLE IV
Oxidation Induction Time for Selected PET/HDPE Ekogeminex/SEBS-g-MA Blends

Composition (wt %/wt %/pph)	Oxidation induction time (min)
0/100/0	7.7
75/25/0	6.7
75/25/2	6.4
75/25/5	5.9
25/75/0	8.3
25/75/5	6.2

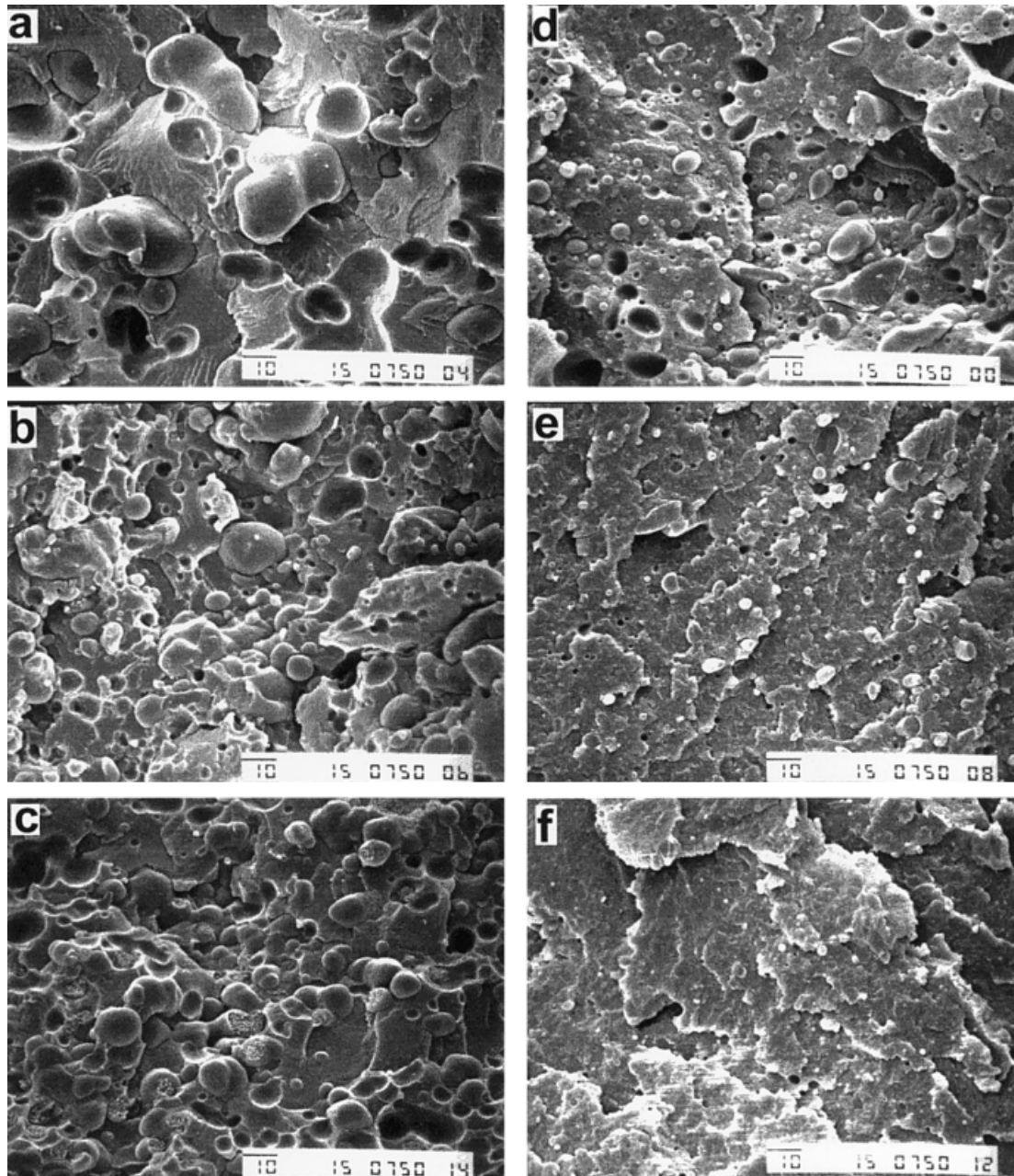


Figure 1 Fracture surfaces of the blends with the HDPE Ekogeminex as observed with SEM. The PET/HDPE/SEBS-g-MA compositions were (a) 75 wt %/25 wt %/0 pph, (b) 75 wt %/25 wt %/2 pph, (c) 75 wt %/25 wt %/5 pph, (d) 25 wt %/75 wt %/0 pph, (e) 25 wt %/75 wt %/2 pph, and (f) 25 wt %/75 wt %/5 pph.

served; however, the stability of HDPE was roughly maintained inside the blend. The measurements for these and other selected blends showed that in all cases acceptable values of the oxidation induction time were obtained, all above 5 min.

The morphologies of the blends were studied by SEM, and exemplary micrographs are presented in Figure 1 for the blends with the HDPE Ekogeminex and in Figure 2 for the blends with the HDPE Rilae. In the noncompatibilized 75%/25% PET/HDPE Ekogeminex blend, the size of the HDPE inclusions was 10–15 μm . Poor adhesion of HDPE inclusions to the PET matrix

could be seen. The addition of the compatibilizer caused a decrease in the inclusion size and an increase in bonding to the matrix. In the blend with 5 pph SEBS-g-MA, the inclusion size was reduced to approximately 5 μm .

In the noncompatibilized 25%/75% PET/HDPE Ekogeminex blend, the minor component PET showed finer dispersion, and the inclusions were 3–5 μm . Also, the adhesion was poor. The addition of SEBS-g-MA reduced the inclusion size to 1 μm for the blend with the composition 25%/75%/5 pph.

The noncompatibilized 75%/25% PET/HDPE Rilae blend showed slightly better HDPE dispersion than

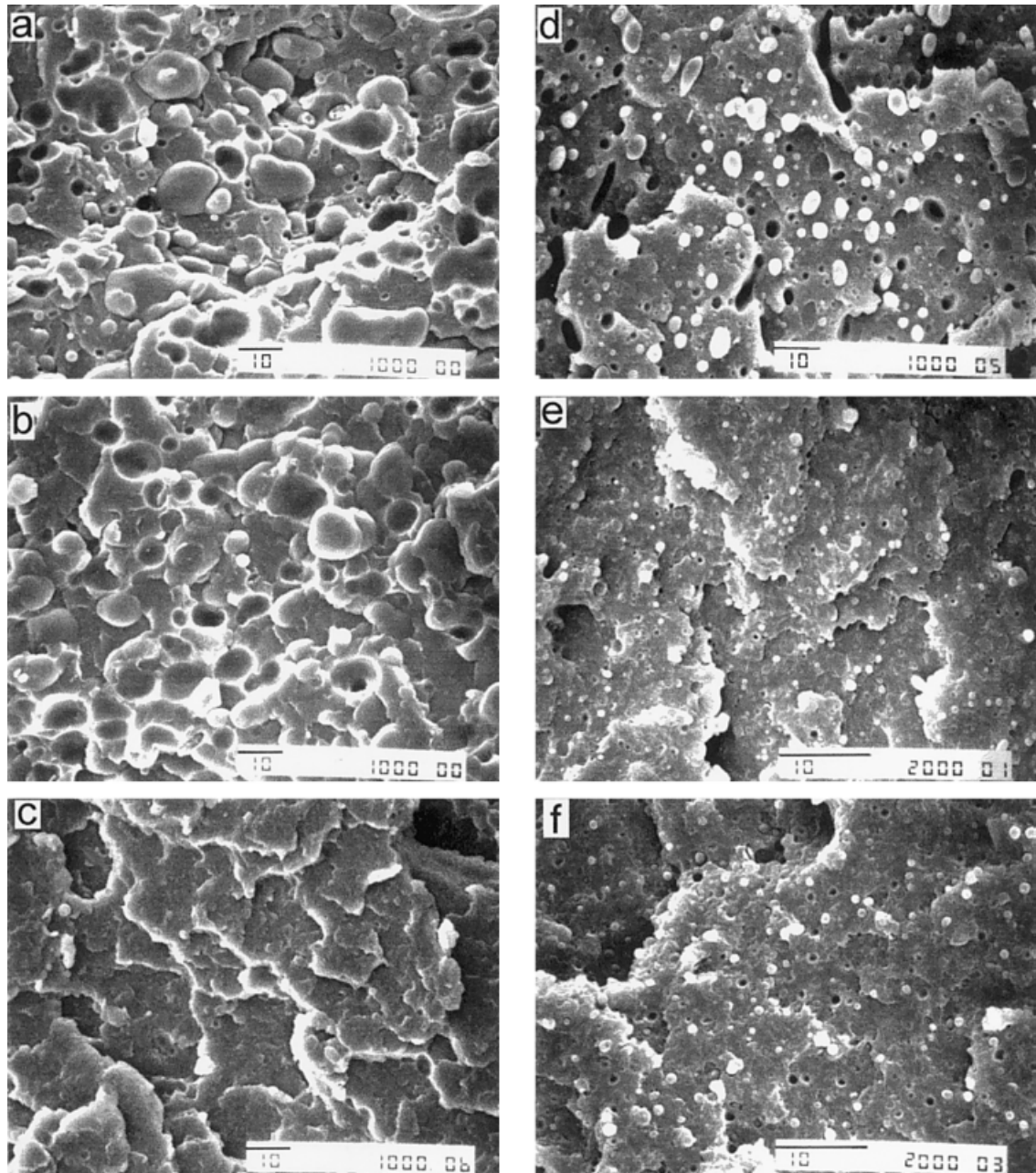


Figure 2 Fracture surfaces of the blends with the HDPE Rilae as observed with SEM: (a) 75 wt %/25 wt % PET/HDPE, (b) 75 wt %/25 wt %/10 pph PET/HDPE/SEBS-*g*-MA, (c) 75 wt %/25 wt %/10 pph PET/HDPE/EGMA, (d) 25 wt %/75 wt % PET/HDPE, (e) 25 wt %/75 wt %/10 pph PET/HDPE/SEBS-*g*-MA, and (f) 25 wt %/75 wt %/5 pph PET/HDPE/EGMA.

the blend with Ekogeminex; however, the average size of the inclusions was still around 10 μm . (cf. Figs. 1 and 2). The addition of 10 pph SEBS-*g*-MA only slightly reduced the average size. Much more effective was EGMA; when applied in the amount of 5 or 10 pph, it changed the dispersion of HDPE in the matrix to less than 1 μm (Fig. 2).

The dispersion of the HDPE Rilae in the 25%/75% PET/HDPE Rilae blend was reduced to 1 μm with the addition of 10 pph SEBS-*g*-MA or 5 pph EGMA. The third compatibilizer, HDPE-*g*-MA, applied at 10 pph, was not effective in the improvement of the dispersion

in both PET- and HDPE-rich systems; the sizes of the inclusions were similar to those in noncompatibilized blends.

The results of tensile tests for injection-molded samples of the blends with SEBS-*g*-MA are presented in Figure 3. The noncompatibilized PET/HDPE blends were characterized by poor tensile properties. The composition with the HDPE Ekogeminex showed the worst mechanical properties. This was the result of the presence of additives and impurities in this brand of HDPE, which migrated to PET during blending and caused its hydrolysis. The conclusion was confirmed

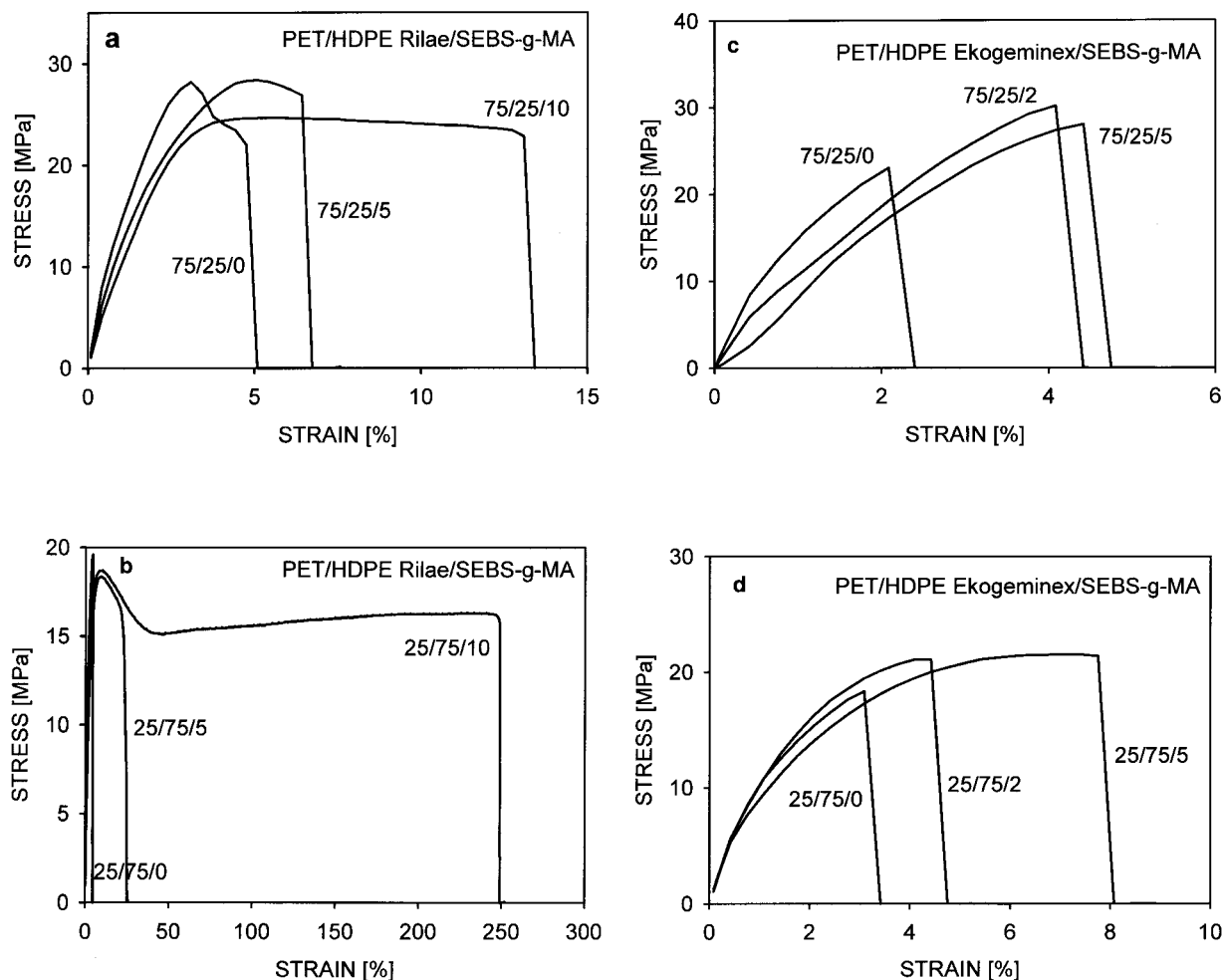


Figure 3 Stress-strain curves for the blends with the SEBS-g-MA compatibilizer. The 75/25/5 composition in this and following figures indicates 75 wt %/25 wt %/5 pph compatibilizer.

by the higher MFI of this composition in comparison to that of the composition with the HDPE Rilae. The positive effect of the compatibilizer on the mechanical properties was visible for all these blends. The elongation at break and the stress at break increased with increased SEBS-g-MA content. The yield and short region of plastic deformation were reached in the PET-rich blend. The blend with HDPE as a continuous phase could be more easily deformed plastically. The yield occurred at nearly 19 MPa and 10% strain. After the yield was reached, a neck was formed that propagated over the whole gauge length of the samples (elongation to break = 250%). This value of the elongation to break was larger than that for noncompatibilized blends (5%) and was also larger than that for pure recycled components, 70% PET and 100% Rilae. The yield stress slowly decreased with the SEBS-g-MA content. PET-rich blends with Ekogeminex [Fig. 3(c,d)] were less compliant for modification, and only in the composition 25%/75%/5 pph was the yield reached before the break.

The effect of increasing the rotation speed of screws of the extruder from 250 to 500 rpm (shorter

residence time and decreased intensity of mixing) on mechanical properties is presented in Figure 4(a, b) for the PET/HDPE Rilae blends with 5 pph SEBS-g-MA. For both PET-rich and HDPE-rich blends, the elongation to break decreased and the yield stress slightly increased when the rotation speed was increased from 250 to 500 rpm. It follows that the residence time was more important for the advance of the compatibilization reaction than the intensity of mixing.

The stress-strain curves for injection-molded PET/HDPE Rilae blends with EGMA as a compatibilizer are presented in Figure 5. The compatibilized blends showed improved mechanical properties. For PET-rich blends, the elongation to break increased to 10–12%, together with an increase in the strength from 27 MPa to slightly above 40 MPa for 10 pph EGMA. The compatibilized blends with the HDPE matrix were ductile. The application of 5 pph EGMA to the composition with an HDPE continuous phase increased the elongation to break to 65%. A comparison of the properties of the 25%/75%/5 pph PET/HDPE Rilae blends with EGMA and SEBS-g-MA showed that

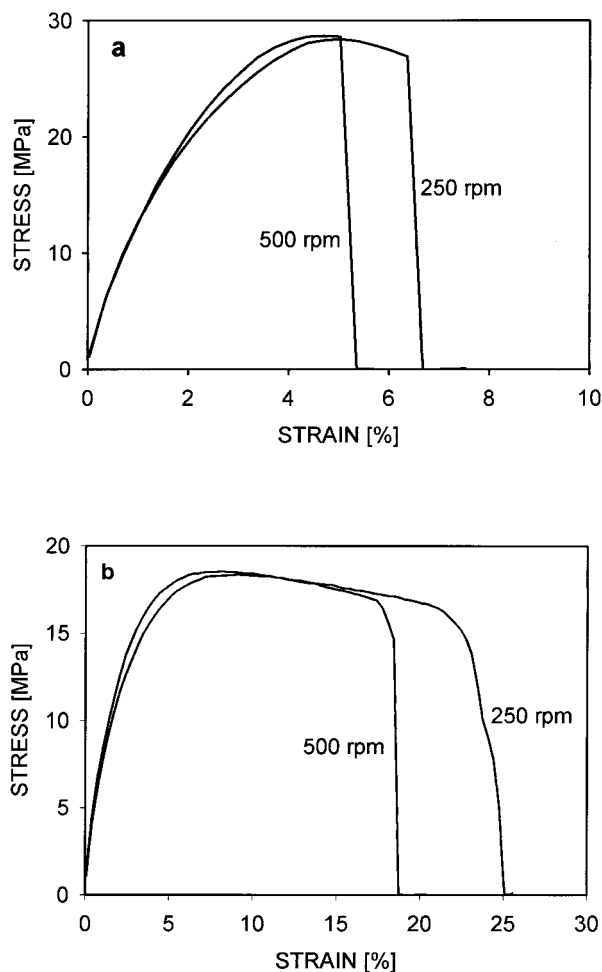


Figure 4 Stress-strain curves for the blends prepared by extrusion with two different rotation speeds of the screws: (a) 75 wt %/25 wt %/5 pph PET/HDPE Rilae/SEBS-g-MA and (b) 25 wt %/75 wt %/5 pph PET/HDPE Rilae/SEBS-g-MA.

EGMA was more effective as the compatibilizer for the PET/HDPE system.

The results of tensile tests of injection-molded samples of the PET/HDPE Rilae blends with 0 and 10 pph HDPE-g-MA are presented in Figure 6(a,b). The blend with the PET matrix was very brittle, and the elongation to break was nearly the same as that for the noncompatibilized blend, whereas the strength increased from 27 to 36 MPa. Also, a small effect of compatibilization was visible in the blend with the composition 25%/75%/10 pph.

The impact strength of the injection-molded samples of the blends was studied with Izod impact test (Figs. 7 and 8). The blends without a compatibilizer showed lower impact strength than the individual components (4.1 kJ/m² for PET, 19.3 kJ/m² for Rilae, and 15.0 kJ/m² for Ekogeminex). The addition of 5 pph SEBS-g-MA was not enough to increase the absorbed energy, and the difference between the two types of HDPE used in the blends was not visible. The

rapid increase in the impact strength was observed with the addition of 10 pph SEBS-g-MA. Very effective for the 25%/75% PET/HDPE Rilae blend was the use of 10 pph SEBS-g-MA. The mean absorbed energy was equal to 14.6 kJ/m², which was 3.5 times more than that for the blend without the compatibilizer.

EGMA, the second compatibilizer applied, added in an amount of 5 pph improved the impact strength more effectively than SEBS-g-MA (Fig. 8). However, a further increase in the EGMA content to 10 pph in the PET-rich blend gave only a small additional increase in the absorbed energy to 6.5 kJ/m². It must be mentioned that all blends prepared with a shorter residence time in the extruder showed a lower increase in the impact strength because of compatibilization.

The results of impact strength measurements of the blends compatibilized with HDPE-g-MA are presented in Figure 8. The 75%/25%/10 pph PET/HDPE Rilae/HDPE-g-MA composition shows an impact strength around 2.5 kJ/m², not improved in comparison to the blend without any compatibilizer. The compatibilized blend with Rilae as a major phase ex-

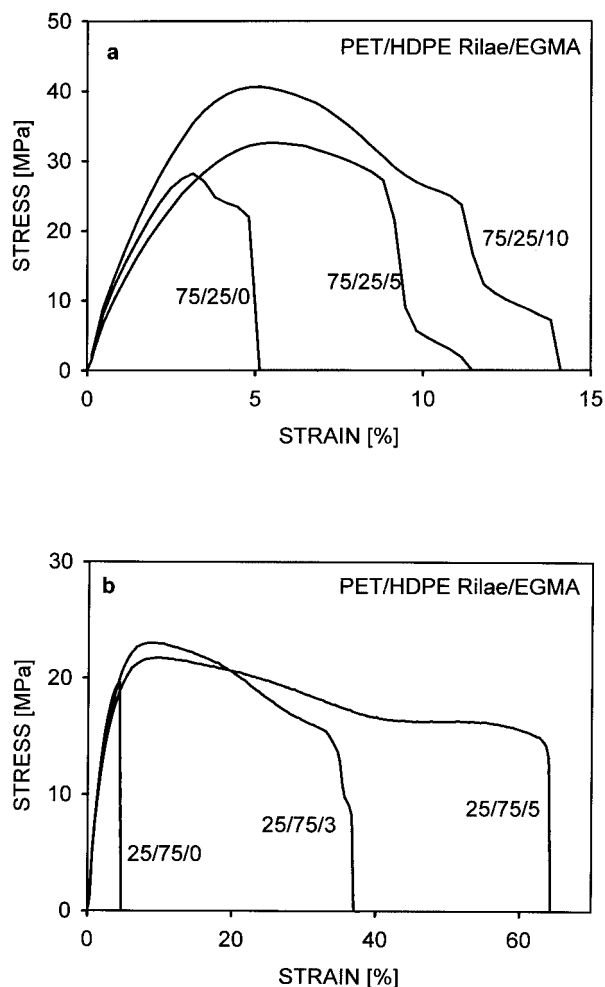


Figure 5 Stress-strain curves for the blends with the EGMA compatibilizer.

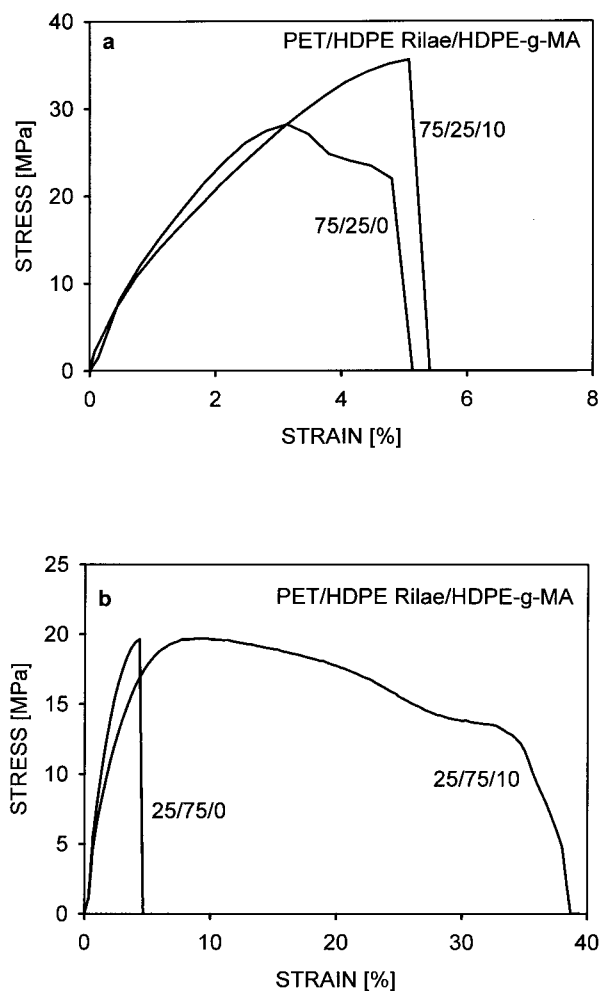


Figure 6 Stress-strain curves for the blends with the HDPE-g-MA compatibilizer.

hibited only slightly improved impact strength in comparison with the 25%/75% PET/HDPE Rilae composition at approximately 4 kJ/m^2 .

The aforementioned results indicate that EGMA was the most effective compatibilizer for the PET/HDPE blends.

From these results, it follows that the optimum amount of the EGMA compatibilizer for the 75/25 PET/HDPE Rilae blend was below 5 pph, and it depended on the residence time of the blending operation. For optimization of the composition of the blend, the selected compositions with 2, 3, 4, and 5 pph EGMA were prepared on a Brabender internal mixer during 15 min of mixing under nitrogen. The tensile mechanical properties of 1-mm-thick films compression-molded from those blends are summarized in Table V. All blends were ductile, with elongations to break of more than 110%, but the best was the composition with 4 pph EGMA. Morphologies of the blends from Table V were studied with SEM. An increasing amount of the EGMA compatibilizer improved the dispersion; however, the dispersion of HDPE in the sample containing 2 pph EGMA was

coarse, although the adhesion was improved. The micrograph in Figure 9 presents the blend with 4 pph EGMA. A fine dispersion of HDPE was reached for this blend, and the increase in the concentration to 5 pph did not result in a finer distribution of HDPE inclusions.

Thermal (DSC) and dynamical mechanical properties (dynamic mechanical thermal analysis) for these blends subjected to annealing at 90°C for 1 h are discussed in a separate article.¹⁵ The main observations from the DSC data is that with the increase in the EGMA content, the melting peaks for HDPE and PET were shifted to lower temperatures with respect to plain polymers, and the crystallinity of PET and HDPE was reduced in these blends.

It is apparent from the aforementioned data that a possible use of the compatibilized recycled PET/recycled HDPE blends is for films and not for injection-molded articles because the injection-molded samples showed drastically lower toughness than the films.

Compatibilized blends from commingled PET and HDPE scraps

Two compositions from commingled scraps, PTM3 modified with 2 wt % EGMA and PEM modified with 2 wt % HDPE-g-MA, were prepared. The viscous properties were characterized by the MFI: PTM3, containing mainly PET, showed an MFI of about 58 g/10 min that decreased to 47 g/10 min after the addition of EGMA. The increase in viscosity confirmed that the reaction between the compatibilizer and polymers occurred during blending.

The MFI for PEM was 6.6 g/10 min, and its decrease after blending with HDPE-g-MA was only to 6.5 g/10 min.

The thermal properties were studied with DSC. A similarity in the properties of PTM3 and the blend of PTM3 with EGMA was observed. The positions of the melting peaks of the compatibilized blend were shifted only by 1° to a lower temperature, but the crystallinity of PET formed during cooling remained unchanged in comparison with that of PTM3 alone.

The addition of HDPE-g-MA to PEM led to a small increase in the total crystallinity level, as determined from two observed peaks: large and wide for HDPE and LDPE and small for the PP component of PEM. The components in the compatibilized blend melted and crystallized at slightly higher temperatures ($1\text{--}2^\circ$) than those in uncompatibilized PEM.

PTM3 samples without a compatibilizer showed poor tensile mechanical properties [see Fig. 10(a)], whereas PTM3 with the addition of EGMA was able to deform with yielding. A significant increase in the yield stress in the compatibilized blend was also observed from 31–32 MPa to 40–41 MPa for a compatibilized blend, indicating better bonding of polyolefin inclusions to PET.

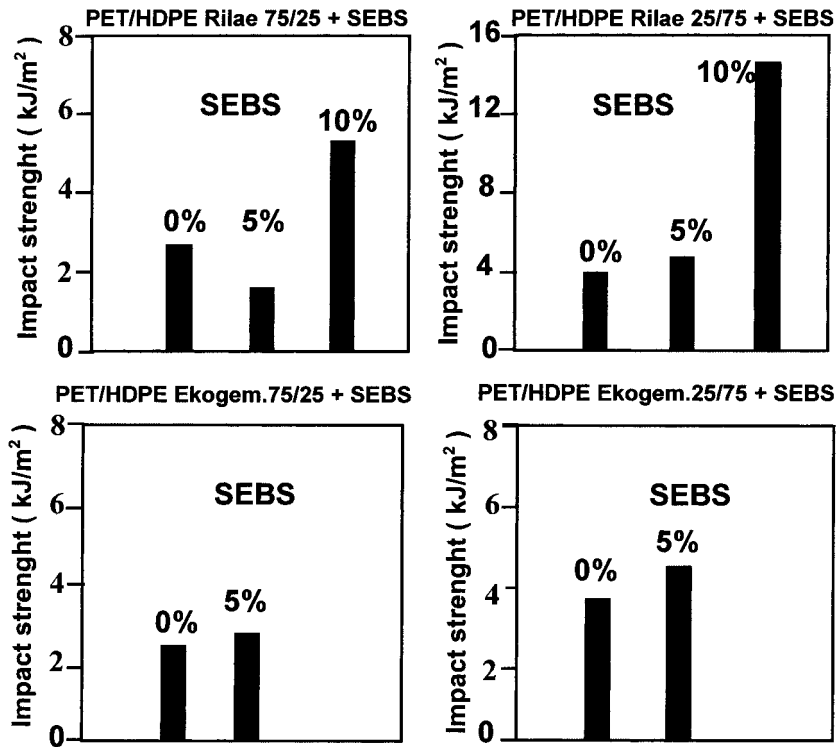


Figure 7 Izod impact strength for the blends compatibilized with SEBS-g-MA.

The samples of PEM [see Fig. 10(b)] showed a yield stress at 14–15 MPa; however, the plastic flow was unstable. The blending of PEM with 2 wt % HDPE-

g-MA appeared to be an effective way of improving its properties: the neck was formed in all studied samples at a stress level of 17–18 MPa and propagated through

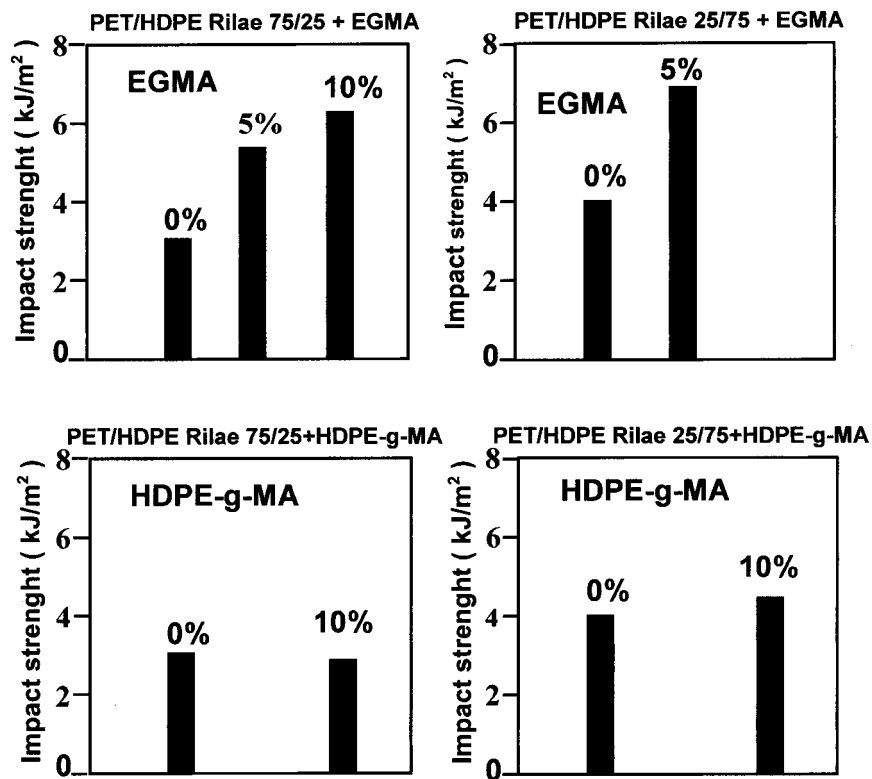


Figure 8 Izod impact strength for the blends compatibilized with EGMA and HDPE-g-MA.

TABLE V
Mechanical Properties of optimized blends with EGMA

Composition PET/HDPE Rilae/EGMA (wt %/wt %/pph)	Yield stress (MPa)	Elongation at yield (%)	Stress at break (MPa)	Elongation to break (%)
75/25/2	27.7 ± 1.8	6.0 ± 0.5	19.2 ± 0.3	110 ± 53
75/25/3	26.4 ± 0.3	6.8 ± 0.5	22.1 ± 2.8	232 ± 190
75/25/4	24.9 ± 0.2	7.1 ± 0.3	22.8 ± 1.5	367 ± 55
75/25/5	23.1 ± 0.7	7.1 ± 0.5	22.1 ± 1.6	340 ± 72

the whole gauge length of all samples tested. The elongation to break was about 350%. The films extruded from compatibilized PEM were smooth but nontransparent, and they assumed a light green-gray color that originated from pigments and fillers present in recycled polyolefins. The mechanical properties of the compatibilized PEM were reasonably good, and the film might find some applications in the packaging of technical articles despite the color.

CONCLUSIONS

An analysis of the composition of recycled PET and recycled polyolefins from Polish and Italian sources has shown that the admixture of other noncompatible polymers is common from 50 ppm to 15 wt %. This suggests that blending should be an inexpensive and useful procedure of recycling such polymers.

Two different approaches to reprocessing PET and HDPE were applied: the compatibilized blending of segregated plastics and the addition of a compatibilizer to poorly segregated plastics. Both methods produced improvements in the mechanical properties with respect to noncompatibilized systems.

Initial studies of the effectiveness of a range of potential compatibilizers for blending PET with HDPE via an internal mixer show that three polymeric compatibilizers are interesting: EGMA, SEBS-g-MA, and

HDPE-g-MA. The application of the compatibilizers improved the mechanical properties of all blends. The noncompatibilized blends were brittle in tensile tests, with very low elongations to break, and the modified blends with EGMA or SEBS-MA were ductile; an increase in the elongation to break to 250% and a strong increase in the absorbed impact energy in Izod impact tests were observed. Samples with high elongation to break showed high impact strength. In both tests, the best results were obtained for the 75%/

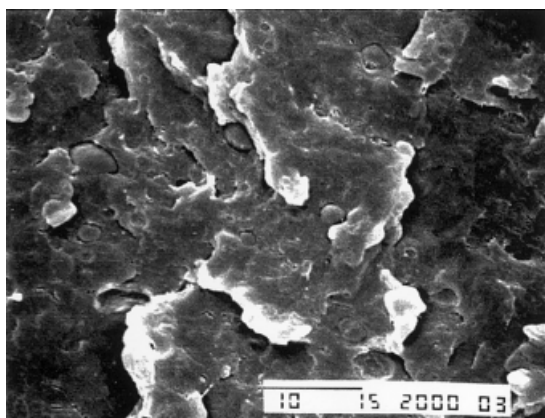


Figure 9 Fracture surfaces of the 75 wt %/25 wt %/4 pph PET/HDPE Rilae/EGMA blend (optimized composition) as seen with SEM.

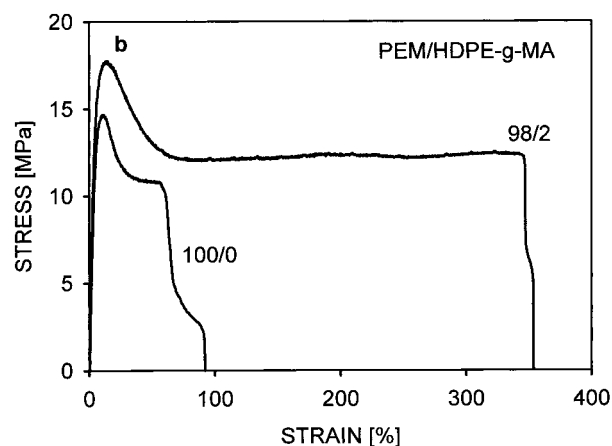
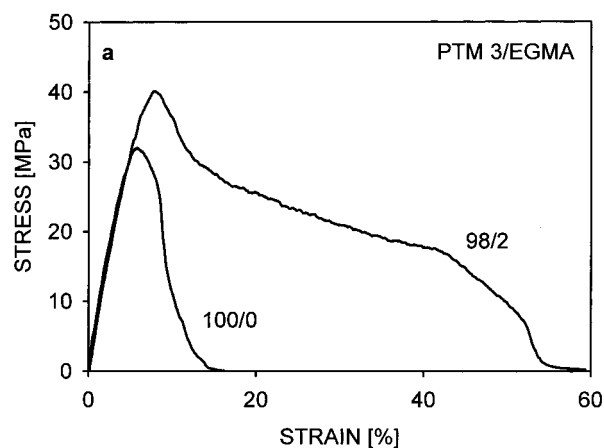


Figure 10 Tensile properties of commingled scraps, (a) PEM and (b) PTM3, before and after modification with compatibilizers.

25%/4 pph PET/HDPE Rilae/EGMA and 25%/75%/10 pph PET/HDPE Rilae/SEBS-g-MA blends.

The observed differences in the properties of the blends of recycled PET with different brands of HDPE, Rilae and Ekogeminex, have their source in the different levels of additives and impurities present. The impurities migrate from HDPE to PET during blending, increasing the rate of PET hydrolysis during processing and resulting in poorer mechanical performance. This observation indicates that the influence of admixtures present in recycled HDPE on the hydrolysis of PET must be checked before blending.

The mechanical properties of the studied blends were strongly related to the phase dispersion. The applied compatibilizers depressed the interfacial tension in the melt and reacted with PET, leading to smaller sizes of the dispersed phase. Morphological observations showed not only a decrease in mean size from 10–15 μm in noncompatibilized blends to 1 μm for some compatibilized compositions but also evidence of increased bonding between main components after the application of SEBS-g-MA or EGMA. It is evident that these compatibilizers locate mainly at interfaces. The increase in the viscosities of compatibilized blends with respect to noncompatibilized blends is the other evidence of reaction during blending. The increase in viscosity partially compensates for the negative influence of hydrolysis.

The third compatibilizer used, HDPE-g-MA, is much less effective for systems with PET as the major component, probably because of encapsulation in the HDPE phase, but it is more effective as a compatibilizer for HDPE-rich blends.

The optimum content of the EGMA compatibilizer for the 75%/25% PET/HDPE Rilae system was found to be about 4 pph. A higher content of EGMA may result in the crosslinking of HDPE and worsen the properties of the blend. A blend with the optimized composition was used for the preparation of films with a laboratory extruder. This technology was then developed further to produce wide films in industry.¹⁶ The anticipated application of such films is in the

packaging of technical goods, as the films are easily thermoformed and welded.

The properties of nonsegregated polymers may be improved by the addition of a properly selected compatibilizer to a previously dried material. Two examples were studied: the addition of 2 pph EGMA to nonsegregated scrap consisting mostly of PET and HDPE (PTM3) and the addition of the same amount of HDPE-g-MA to unsegregated scrap consisting mostly of polyolefins (HDPE, LDPE, and PP) with the addition of PET (PEM). The results of mechanical tests showed significantly improved properties of these commingled, recycled materials after compatibilization. Tensile mechanical properties of compatibilized PTM3 and PEM indicate the possibility of using these blends for film extrusion, with potential applications in the packaging of technical products. The cost evaluated for the blending of recycled PET and HDPE is in favor of EGMA used as a compatibilizer.

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