

Effect of the Viscosity Ratio on the Morphology and Properties of PET/HDPE Blends with and Without Compatibilization

Souad Mbarek,^{1,2} Mohamed Jaziri,² Yvan Chalamet,¹ Christian Carrot¹

¹Université de Lyon, Lyon, F-69003, CNRS UMR 5223 Ingénierie des Matériaux Polymères, Université de Saint-Etienne, Saint Etienne, F-42023, France

²Laboratoire Eau-Energie-Environnement Ecole Nationale d'Ingénieurs de Sfax, Université de Sfax, Sfax 3038, Tunisia

Revised 6 March 2009; accepted 2 January 2010

DOI 10.1002/app.32050

Published online 29 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The influence of the molecular weight of polyethylene on the morphology and mechanical properties of blends of high-density polyethylene (HDPE) dispersed as droplets in a poly(ethylene terephthalate) (PET) matrix at various compositions was investigated. The difference of morphologies can be easily explained by the influence of the molecular weight on the viscosity ratio and therefore, on the critical capillary number. The compatibilizing efficiency of copolymers containing glycidyl methacrylate groups was also addressed in relation to their nature, the protocol for their drying and the molecular weight of the HDPE phase. The increase of adhesion

between PET and HDPE was found to have a larger influence on tensile properties than the reduction of interfacial tension. The amount of compatibilizer needed for adhesion improvement depends on the interfacial area that is defined by both the interfacial tension and viscosity ratio of the components. A qualitative relation between the optimum amount of compatibilizer and the critical capillary number can be written. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1683–1694, 2010

Key words: blends; molecular weight distribution; polyethylene; poly(ethylene terephthalate)

INTRODUCTION

As in most of cases, simple blending of poly(ethylene terephthalate) (PET) and high-density polyethylene (HDPE) results in a material having poor mechanical properties because of the lack of compatibility between the polymers. However, because of its chemical structure, PET can interact readily with polar polymers or through hydrogen bonding. It has also the capability of reacting with other species through chain ends. Thus, the compatibilization of PET and PE can be obtained by in situ reaction of functionalized polymers or functional compatibilizers. The mostly used functional groups are maleic anhydride (MA), acrylic acids (AA), or acrylic esters. They can be grafted onto olefinic polymers such as polypropylene (PP), polyethylene (PE), olefinic copolymers, or styrene-ethylene-butene block

copolymers (SEBS). Various compatibilizations of PET and PE blends with maleic anhydride grafted polyolefins (PE-g-MA, PP-g-MA, EVA-g-MA, EPR-g-MA),^{1–4} maleic anhydride grafted styrene-ethylene-butene-styrene copolymer (SEBS-g-MA),^{4–6} maleic anhydride grafted ethylene-methacrylic acid copolymer (E-MeA-g-MA),⁶ alkyl acrylate, or alkyl methacrylate or glycidyl methacrylate grafted PE³ have been reported. On the other hand, monomers bearing the functional groups can also be copolymerized with the olefinic monomers. Random copolymers of ethylene and methacrylic acid (E-MeA),⁷ ethylene and acrylic acid (E-AA),^{4,8} ethylene and glycidyl methacrylate (E-GMA),^{4,6,9–11} ethylene, ethyl acrylate, and glycidyl methacrylate (E-EA-GMA),^{6,11,12} ethylene, butyl acrylate, and glycidyl methacrylate (E-BA-GMA),¹³ ethylene, ethyl acrylate, and maleic anhydride (E-EA-MA)¹² are widely used.

These compatibilizers do not show similar activity with regards to compatibilization of blends of aromatic polyesters (PET or PBT) and PE. Especially, copolymers containing glycidyl methacrylate are the most efficient species.^{6,10,12} There are many reasons for that. At first, glycidyl methacrylate is more reactive than maleic anhydride towards hydroxyl groups. Second, it can react with both carboxyl and hydroxyl end groups, while MA reacts only with

Correspondence to: C. Carrot (Carrot@univ-st-etienne.fr).

Contract grant sponsors: MIRA project (Rhône-Alpes Region, France), Franco-Tunisian CMCU cooperation project.

TABLE I
Molecular Weight Data of the Polyethylenes

HDPE	M_w (g/mol)	Polydispersity
PE53K	53000	5.5
PE90K	90000	4.6
PE150K	150000	12

hydroxyl ends. At last, the esterification reaction is reversible at high temperature.

This generally results in a more pronounced emulsifying effect of GMA modified polyolefins leading to very small dispersed particles without coalescence. Strong interfacial bonding is also reported. Consecutively, during mechanical tests, the PE particles undergo plastic deformation without de-bonding providing a strong toughening effect.

The effect of the concentration of the polymers has been widely studied by most of the authors. The mode and order of introduction of the components have been also investigated. In particular, though the GMA compatibilizing species can be added during injection molding,¹¹ it is generally recognized that the best properties are generally obtained through extrusion and especially if the compatibilizer is premixed with PE in comparison to one-step mixing.^{4,10} The reason for that is a preferred localization of the compatibilizer at the interface between PET and PE with a limited loss of compatilizer into the PET matrix.

However, very few articles^{1,13} addressed the effect of the rheology of the dispersed phase in competition with the influence of the compatibilizer on interfacial tension and adhesion. In this article, we investigated the effect of the molecular weight, and therefore of the melt rheology, of the PE phase on the morphology and tensile properties of PET-PE blends with and without addition of olefinic compatibilizers containing GMA groups.

MATERIALS AND EXPERIMENTS

Materials

The materials investigated are PET as the matrix and HDPE as the dispersed phase. Three high density polyethylenes (PE53K, PE90K, and PE150K) synthesized by a classical Ziegler-Natta process and having various molecular weights were used in this work. They were chosen for their large differences in molecular weight distribution. The weight average molecular weight increases from PE53K to PE150K. The molecular weight data are indicated in Table I.

For compatibilization purpose, some random copolymers of ethylene and glycidyl methacrylate (E-GMA), Lotader AX8840, or ethylene, acrylic ester, and glycidyl methacrylate (E-EA-GMA), Lotader

AX8900, from Arkema were used. The copolymers have a glycidyl methacrylate content of 8 mol %. The content of acrylic ester in the E-EA-GMA copolymer is 24 mol %.

Processing of PET-HDPE blends

PET and HDPE with and without compatibilizer were melt blended in a co-rotating intermeshing twin-screw extruder (Cleextral BC 21, diameter 25 mm, centerline distance 21 mm, length to diameter ratio $L/D = 36$). The screw profile was built with the following screw elements: 33/150, 25/100, 16/50, KB25/6.25/75, CF25/25, 16/100, 33/100, 25/100, KB25/6.25/75, CF25/25, 16/100 where x/y indicates direct flighted screw with pitch x and length y , CFx/y indicates counter-flighted screw with pitch x and length y and $KBx/z/y$ indicates kneading block with stagerring angle x° , thickness of individual element z and total length y . The temperature was increased from the feeding zone until the die with nine regulation zones with 100 mm length: 50, 150, 180, 255, 260, 260, 260, 260, 260°C. The melting of PET can only be obtained at 252°C, therefore 260°C is the lowest limit for the processing temperature. In the metering zone and the die, the temperature was 260°C to ensure the minimum degradation of the components. A screw rotation speed of 100–110 rpm, at a throughput of 4–5 kg h⁻¹, was used ensuring the best compromise between the mixing intensity and a mean residence time of 5 min as measured by a colorimetric tracer. At the die exit, the polymer was cooled in water and pelletized.

Prior to extrusion and unless a different protocol is mentioned, PET and HDPE were dried under vacuum during 24 h at 120°C, whereas the compatibilizer was dried under vacuum 24 h at 60°C. The dried materials were tumble-blended and fed into the hopper of the extruder. For comparison purposes, the neat polymers have also been processed in the same conditions.

After drying under vacuum for 24 h at 120°C, the pellets were injection-molded in the shape of ISO1/2 test bars with a Babyplast 610 injection molding machine using barrel temperatures of 252, 260, and 260°C. The mold temperature was 60°C, the injection pressure was 950 bars, with same holding pressure (not adjustable in this type of machine) and the injection rate was 0.77 cm³/s. The injection lasts 2 s while the holding time was 14 s.

Scanning electron microscopy

The morphology of the blends was investigated using a scanning electron microscope (SEM Philips XL 30) on molded bars. The samples were fractured at liquid nitrogen temperature. The fracture surfaces

were perpendicular to the mold filling direction of the injection-molded bars. They were observed after a gold coating under an accelerating voltage of 20 kV. The pictures were processed using the ImageJ software to obtain the size distribution of particles and the average size of the dispersed PE domains. The sizes were measured on the 2D pictures without correction for the 3D effect.

Infra-red spectroscopy

To assess the efficiency of the reaction between the GMA groups of the copolymers and the PET, 18 mg of E-GMA was deposited on a thin film of PET at 110°C. At this temperature, no reaction is expected. The resulting film was analyzed by Fourier Transform Infra-Red transmission spectroscopy in a Nicolet Nexus device. The film was heated at 240°C for 5 min without melting the PET film and a new analysis was performed on the film.

Peeling tests

To assess the efficiency of the reaction between the GMA groups of the copolymers, peeling tests were performed at room temperature on sandwiches of PET with E-GMA using an Adamel Lhomargy DY22 with crosshead speed of 5 mm/min. Test specimens consisted of PET bars (10 mm × 4 mm × 80 mm) and E-GMA films with dimensions (10 mm × 0.8 mm × 80 mm). Adhesion between PET sample and E-GMA film was obtained after heating at 120°C under vacuum for increasing times. Bonding was limited to one half of the PET bars to obtain a contact area of 40 mm × 10 mm. The results of peeling tests are the average of five measurements.

Mechanical tests

Tensile tests were performed on an Adamel Lhomargy DY22 machine at room temperature using injection-molded dumbbell specimens (ISO1/2) in accordance with the NF T 51-034 standards. Crosshead speed was 10 mm/min. All the reported results are the average of at least ten measurements.

Unnotched Charpy impact tests were performed at room temperature (23°C) and low temperature (-23°C) on injection molded bars using a CEA Resil Impactor machine.

Rheology of the neat polymers

The rheology of the neat molten polymers has been measured by dynamic oscillatory measurements in the melt. Measurements on PET were performed in a Rheometrics SR5000 system using parallel plate geometry ($D = 25$ mm, $gap = 1$ mm) in the linear vis-

coelastic domain (stress lower than 1000 Pa) for frequencies ranging from 100 to 0.1 rad/s under nitrogen atmosphere at 260°C. PET was dried under vacuum 24 h at 120°C prior to analysis. To avoid polymer degradation in the parallel-plate rheometer, samples were kept in a nitrogen chamber at 160°C for 20 min. Then temperature was raised from 160 to 260°C at 10°C/min and leveled off at 260°C for 5 min before analysis.

The rheology of the neat HDPE was measured by dynamic oscillatory measurements in the melt at various temperatures from 160°C until 200°C. Measurements were performed in a Rheometrics ARES system using parallel plate geometry (diameter = 25 mm, gap = 2 mm) for frequencies ranging from 100 to 0.01 rad/s. Master curves were built to calculate the activation energy which was found to be 28 kJ mol⁻¹ for HDPE. Finally, the melt viscosity was calculated at 260°C which was the temperature of blending.

RESULTS AND DISCUSSION

Effect of HDPE concentration on the morphology and mechanical properties of PET/HDPE blends

The SEM micrographs of Figure 1 show the morphologies of blends containing between 5 and 20 wt % of PE53K. For these compositions, HDPE is dispersed within the PET matrix. The photographs show morphologies that are typical of immiscible blends. The dispersed phases are generally coarse and irregular in size because of the immiscibility of PET and PE. Indeed, the interfacial tension between HDPE and PET is high. It has been measured by Ihm and White by various methods¹⁴ and the value of 10 mN/m has been reported at 270°C. The particle sizes are given in Table II and they increase almost linearly with the concentration of HDPE. The tensile properties indicated in Table II do not show significant differences with the original properties of PET within the uncertainties of the measurements. In particular, the strain at break remains very low in the order of 10%. Nevertheless, impact properties are slightly improved by the addition of HDPE.

This is mainly related to the lack of adhesion between the PE droplets and the matrix. This lack of adhesion is also responsible for de-bonding that is observed on the SEM micrographs as cavities are left by HDPE particles that have been extracted during the fracture.

Effect of HDPE molecular weight on the morphology of PET/HDPE blends

The 85/15 composition was used to test the influence of the HDPE molecular weight on the morphology

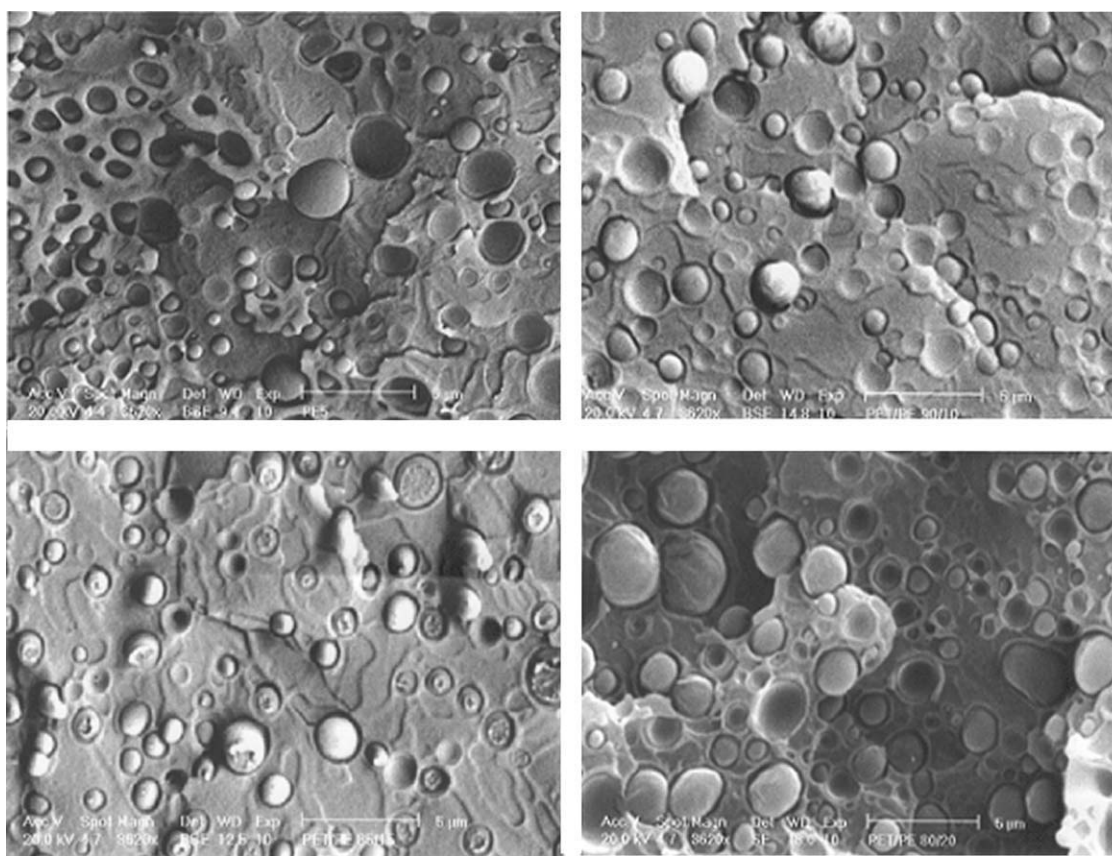


Figure 1 SEM pictures (X3620) of blends PET/PE53K with composition (in wt %) 95/5, 90/10, 85/15, and 80/20, from left to right and top to bottom.

and tensile properties. The micrographs of blends with PE53K, PE90K, and PE150K are shown on Figure 2 at the same magnification. In the same conditions of blending, the final blend morphology is clearly connected with the HDPE molecular weight. Indeed, the lower the molecular weight, the finer the dispersion of the HDPE phase in the blend. The size of the domains is given in Table III.

It is worth mentioning that data were obtained from fractures of molded bars. Injection molding was necessary to obtain the proper samples for mechanical testing and to discuss the relation between the morphology and the mechanical properties. However, such post-blending operation can change

the morphology of the blends. On one hand, this could be due to rupture processes during the filling phase of the molding especially during the plastication and flow through the nozzle and runners. On the other hand, during the holding and packing phase, coalescence could take place. Even though, micrographs on extrudates and on molded samples show very similar morphologies. Table III also shows the comparison between the areas of the PE domains as measured on both types of samples. The difference is slight and it can be considered that injection molding conditions were sufficiently soft to avoid significant distortion of the morphology. This is particularly true considering the static

TABLE II
Average Size of the PE Domains, Tensile and Impact Properties in Blends of PET with Various Amounts of PE53K

PET (wt %)	PE53K (wt %)	Average size (μm^2)	Tensile modulus (MPa)	Strength at break (MPa)	Elongation at break (%)	Charpy impact unnotched, 23°C/-23°C (kJ/m^2)
100	0	–	2490 ± 20	64 ± 3	9 ± 1	16 ± 2/11 ± 1
95	5	1.1 ± 0.1	2500 ± 40	40 ± 1	33 ± 10	51 ± 5/35 ± 3
90	10	1.3 ± 0.1	2410 ± 20	50 ± 10	12 ± 2	53 ± 4/36 ± 3
85	15	1.4 ± 0.1	2400 ± 20	50 ± 10	12 ± 2	55 ± 4/32 ± 3
80	20	1.7 ± 0.1	2250 ± 20	40 ± 9	17 ± 10	48 ± 4/34 ± 3
0	100	–	1150 ± 30	15 ± 1	1100 ± 200	NB/NB

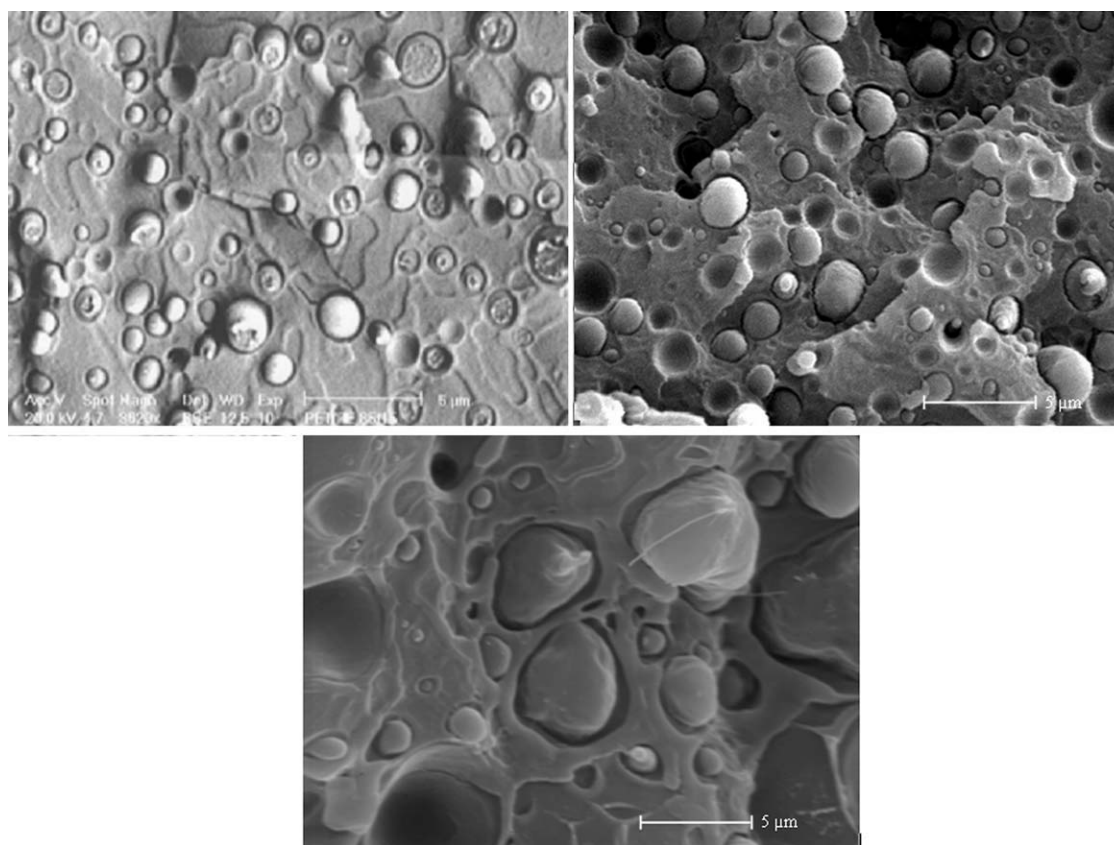


Figure 2 SEM pictures ($\times 3620$) of blends PET/HDPE with composition 85/15 varying the molecular weight of HDPE : 53,000 g/mol, 90,000 g/mol, and 150,000 g/mol (from left to right and top to bottom).

plasticating unit of the injection molding machine that was used in this study. On the other hand, at low concentration of PE such as those of this study, the coalescence is not favored. Therefore, on the basis of the results of Table III, the analysis was conducted on the injection molded samples to get the simultaneous correlation with mechanical properties.

The dependency of the size of the dispersed domains on the molecular weight is a direct consequence of the effect of the later on the melt viscosity. The flow curves of the various PE are presented on Figure 3 at $T = 260^\circ\text{C}$ in comparison with the flow curve of PET. Curves for HDPE have been previously shifted according to time-temperature superposition. The Cox-Merz rule was assumed to be valid, and therefore data are presented in terms of shear rate and shear viscosity. PE53K, PE90K, and PE150K have increasing viscosities. This is the primary reason for the finest dispersion of PE53K in PET and of the coarser domains of PE150K. At the processing temperature of 260°C , the calculation of the shear rates in the extruder was performed by means of a simulation package based on the work of Potente et al.¹⁵ The average shear rates in each screw zone following the first counter-flighted section, where melting was achieved, are 33, 38, 35, 35, 35, 45, 33 s^{-1} with a peak in the second counter-flighted

screw. The overall average value is 35 s^{-1} . This value can also be well approximated assuming a Couette flow with the dimensions of the extruder (25 mm of diameter and 4 mm of gap) and the speed of rotation of 100 rpm. In these conditions, the droplet to matrix viscosity ratio is close to 4.1 for PE150K, while it is 1.5 for PE90K, and 0.3 for the less viscous PE53K.

Figure 4 shows the correlation between the viscosity ratio and the square root of the mean area of the droplets. Actually, within the same conditions of shear and with the same interfacial tension, these dimensions should be strictly correlated with the critical capillary number Ca^* and not with the viscosity ratio. Indeed, the minimum characteristic

TABLE III
Average Size of the PE Domains in Blends of PET Containing 15 wt % of HDPE with Various Molecular Weights

HDPE molecular weight (g/mol)	Number average area on injection molded bars (μm^2)	Number average area on extrudates (μm^2)
53000	1.4 ± 0.1	1.8 ± 0.2
90000	2.2 ± 0.1	2.4 ± 0.2
150000	8.2 ± 0.5	9.0 ± 0.5

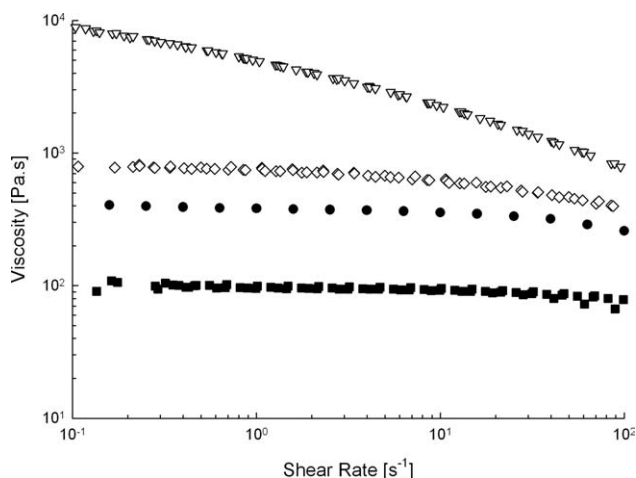


Figure 3 Viscosity of PET (■), PE53K (●), PE90K (◇), and PE150K (▽) at $T = 260^\circ\text{C}$.

dimension R^* that can be achieved during blending can be calculated from the comparison between the capillary number and the critical capillary number. Reduction of size can only be achieved provided that $Ca > k Ca^*$. k is a constant, generally between 1 and 4, defining whether the capillary number is high enough to induce breakup rather than deformation of the droplets,¹⁶ thus at equilibrium:

$$R^* = k \frac{Ca^*(\sqrt{\Pi_{\dot{\gamma}}})\sigma}{\eta_m \Pi_{\dot{\gamma}}} \quad (1)$$

Where $Ca^*(\sqrt{\Pi_{\dot{\gamma}}})$ is a critical capillary number depending on the second invariant of the rate of strain tensor,

$\Pi_{\dot{\gamma}}$ is the second invariant of the rate of strain tensor,

η_m is the matrix viscosity,

σ is the interfacial tension,

R^* is a characteristic dimension of the dispersed phase.

On Figure 4, the variation of the critical dimension R^* as a function of the viscosity ratio, with a critical capillary number calculated in shear and in extension from the equations proposed by de Bruijn,¹⁷ is also reported for comparison purpose. The calculation was performed assuming $\eta_m = 400$ Pa.s, $\sigma = 10$ mN/m, a shear rate of 35 s⁻¹ and $k = 4$. The curves are similar to those proposed by Grace.¹⁸ The comparison shows that, as expected, in the extruder, the flow has a complex kinematics. From Figure 4, it can only be asserted that the flow is not pure shear since theoretically, for viscosity ratios larger than 4, the droplets could not be broken, therefore PE150K would not be dispersed into PET. The flow is obviously not purely extensional since for the viscosity ratio under investigation, the capillary number would be nearly constant. According to Wu,¹⁴ the number average dimension of dispersed phase

blends obtained in a twin screw extruder is related to the viscosity ratio by a power law with exponent 0.8 when the viscosity ratio is above unity and exponent -0.8 when the viscosity ratio is below unity.

Consequences of these morphologies on the specific process of fractionated crystallization of HDPE within the droplets have been reported and discussed elsewhere.^{19,20} Anyway, it has been shown that even if the process and temperatures of crystallization or HDPE are changed, the global crystal content of HDPE remains unchanged. Crystallization of PET is not affected by the process within the range of concentration under investigation.

Effect of GMA-based compatibilizers on the morphology and mechanical properties of PET/HDPE blends

GMA-containing olefinic copolymers (GMA-PO) act as compatibilizers by reaction between the epoxy groups with the hydroxy and carboxy ends of the PET. The evidence of this reaction between PET and PE is demonstrated on Figure 5. This figure presents the FTIR spectra of the E-GMA and PET and of composite films of PET and E-GMA obtained either in temperature conditions (110°C) that prevent the reaction or in conditions at which the reaction is susceptible to occur (240°C). The region of the typical bands of the epoxy groups was addressed, and the attention was focused on the band at 910 cm⁻¹ which is not present in the PET film. For the unreacted films, the band is present, though it is convoluted with typical bands of PET. After heating at 240°C during 5 min, which is close to the residence time in the extruder, the band has significantly decreased indicating significant reaction. The evidence of a reaction at low temperature was also

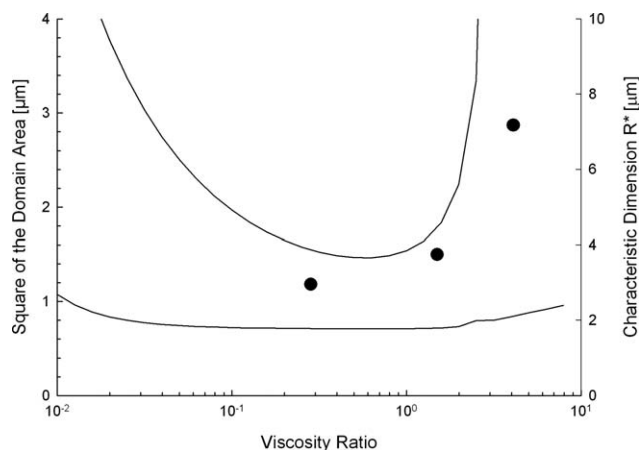


Figure 4 Size of the domains versus viscosity ratio between HDPE and PET. The characteristic dimension R^* that can be calculated from the critical capillary number in shear (upper curve) and extension (lower curve) is plotted on the right axis.

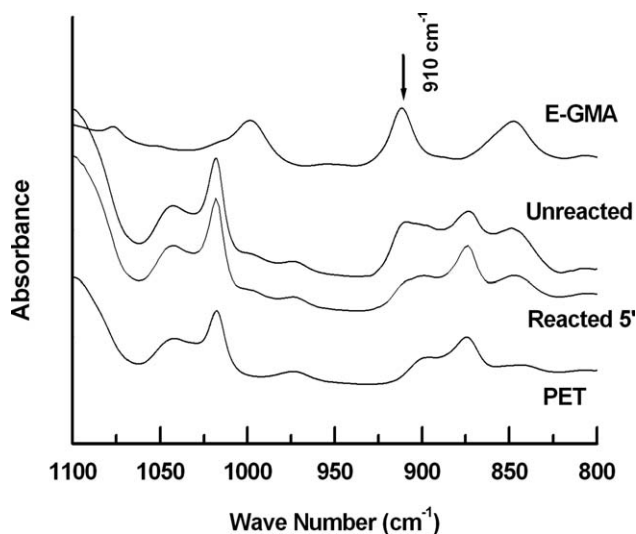


Figure 5 FT-IR spectra of films of PET, E-GMA, and unreacted or reacted composite films of E-GMA and PET. In the unreacted case, PET and E-GMA in close contact were heated at 110°C while in the reacted 5' case, they were heated during 5 min at 240°C.

demonstrated on Figure 6 that reports the peeling force observed during peeling tests carried out on bilayers sandwiches of PET with E-GMA. The peeling strength clearly increases with the reaction time at 120°C. However at such a low temperature, considerably longer reaction times are needed.

During reactive extrusion of PET/HDPE/GMA-PO blends, the compatibilizer may locate at the interface. Ideally, the olefinic segments are expected to be partially miscible with HDPE while the active epoxy groups (GMA) may react with the hydroxy and carboxy ends of the PET matrix. The in situ formation of PET-PE copolymers reduces the interfacial tension and above all suppresses coalescence. The

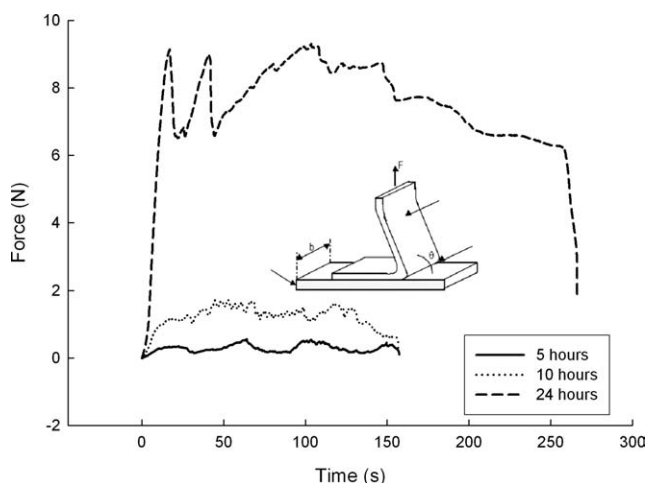


Figure 6 Peeling force observed during the peeling test of sandwiches of PET and E-GMA (geometry is indicated on the figure).

copolymer is also expected to act as an emulsifier reducing the size of the dispersed phase and also by providing adhesion between the phases. Further evidence of the efficient bonding between the phases can be directly seen on SEM pictures with large magnification where fibrils connecting the matrix and the dispersed phase are clearly observed for example on Figure 7 for blend PET/PE53K/E-GMA having 85/12/3 composition.

Figure 8 shows the morphology of blends containing 80 or 90 wt % of PET and PE53K with GMA-PO copolymers either of the E-GMA or E-EA-GMA type. The ratio of the amount of GMA containing copolymers to the amount of PE53K is kept constant (1/3) in all blends. In all cases, there is a clear reduction of the size of the dispersed phase as shown by the values indicated in Table IV. As previously shown, the size of the dispersed domains increases with the amount of PE. But the most remarkable feature is probably the large difference of efficiency of the GMA containing copolymers with regard to the elongation at break. Though in all cases the addition of the copolymers has a positive effect on this tensile property, the E-GMA copolymer provides a tenfold increase of the elongation at break while the later is only increased by a factor of three in the case of the E-EA-GMA copolymer. Other values of the tensile properties, especially those related to elasticity, remain quite unchanged. This indicates that the adhesion may be sufficient with both compatibilizers when low strains are involved, however at larger strain, the E-EA-GMA compatibilizer fails into providing sufficient adhesion to avoid de-bonding. This is due to the lower miscibility of the E-EA segments with the HDPE in comparison to the ethylene segments of E-GMA. Figure 8 shows a large difference of adhesion using one copolymer or the other. In the case of the E-EA-GMA copolymer a clear interface is

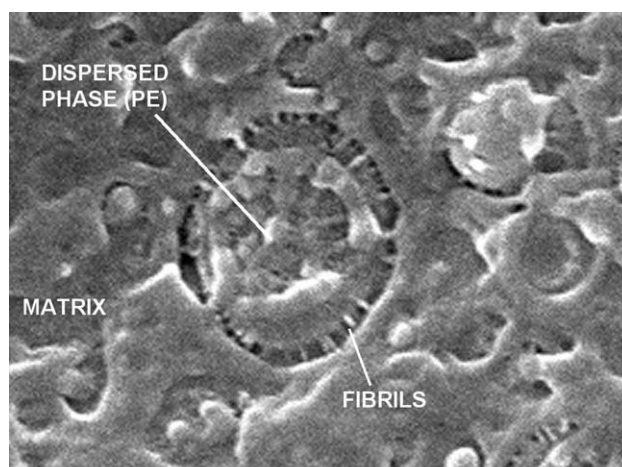


Figure 7 SEM Picture of blend PET/PE53K/E-GMA 85/12/3 (×18000).

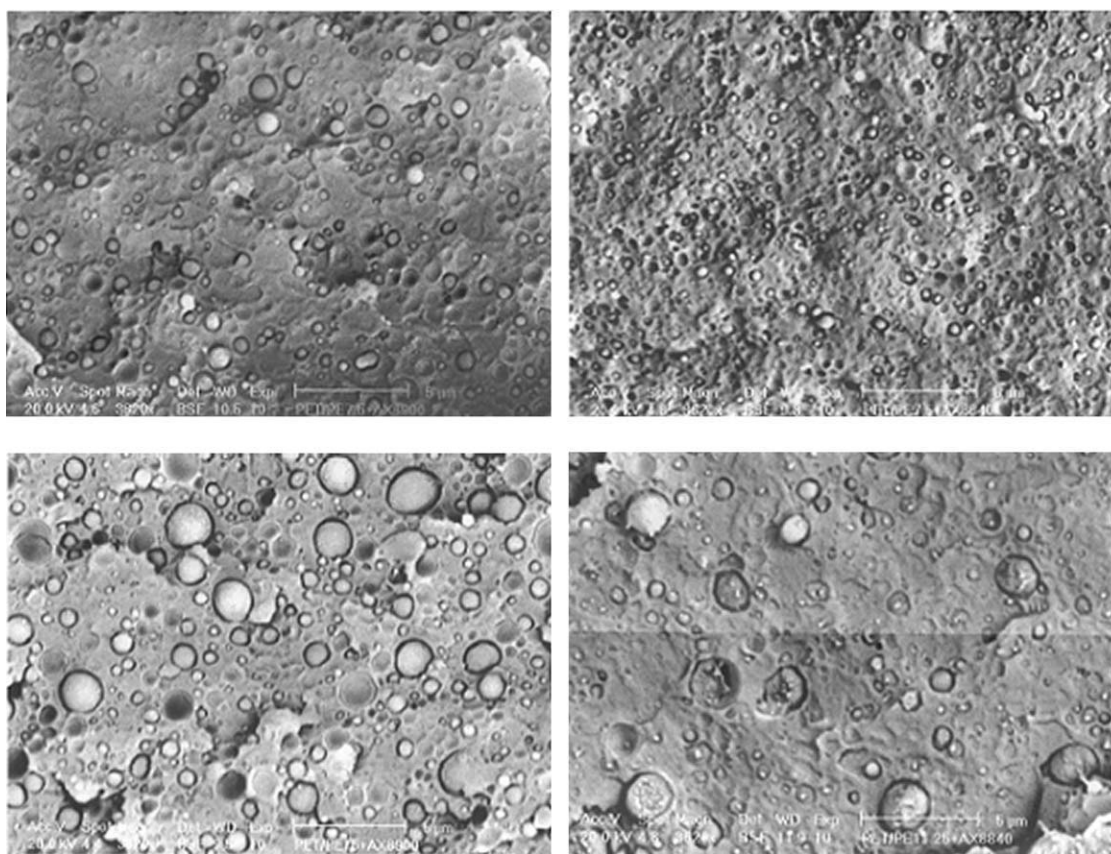


Figure 8 SEM pictures ($\times 3620$) of blends PET/PE53K with composition 90/7.5/2.5 (top) and 80/15/5 (bottom) using E-EA-GMA (left) or E-GMA (right) as compatibilizers.

still observable while the fracture sometimes goes through the particles in the case of the E-GMA copolymer with composition 80/15/5. Also, on Figure 8, for blend with composition 80/15/5 with E-EA-GMA as compatibilizer, a shell of E-EA-GMA copolymer can even be observed on the boundary of the remaining hole left by a PE droplet that has been removed during the fracture. The copolymer reacts with PET but is de-bonded from the PE phase because of a lack of miscibility. This is not the case for the E-GMA compatibilizer for which miscibility and adhesion are achieved so that the crack even

propagates inside the PE particle without de-bonding as evidenced on Figure 8. The issue of the difference of miscibility of the E-GMA and E-EA-GMA copolymers with HDPE has already been addressed by Pietrasanta et al.¹¹ In their study, binary blends of HDPE with 5 wt % of E-GMA copolymer show a single phase while two-phase systems were observed with terpolymers, the immiscibility being enhanced by large ester contents. This was especially true in the case of E-EA-GMA Lotader AX8900 for which observation of sticks of terpolymer with no adhesion with the matrix of HDPE were reported.

TABLE IV
Average Size of the PE Domains, Tensile and Impact Properties in Blends Containing Various Amounts of PE53K and GMA-based Compatibilizers (the Ratio GMA-PO/HDPE is Kept Constant and Equal to 3)

PET (wt %)	PE53K (wt %)	Compatibilizer	Average size (μm^2)	Tensile modulus (MPa)	Strength at break (MPa)	Elongation at break (%)	Charpy impact unnotched, 23°C/-23°C (kJ/m^2)
90	10	none	1.3 ± 0.1	2410 ± 20	50 ± 10	12 ± 2	$53 \pm 4/36 \pm 3$
90	7.5	E-GMA	0.4 ± 0.1	2200 ± 30	61 ± 1	120 ± 10	NB/NB
90	7.5	E-EA-GMA	1.0 ± 0.2	2110 ± 30	62 ± 2	32 ± 7	$96 \pm 9/95 \pm 7$
80	20	none	1.7 ± 0.1	2250 ± 20	40 ± 9	17 ± 10	$48 \pm 4/34 \pm 3$
80	15	E-GMA	1.2 ± 0.1	2000 ± 30	48 ± 2	100 ± 20	NB/NB
80	15	E-EA-GMA	1.5 ± 0.2	1920 ± 30	52 ± 1	29 ± 2	$110 \pm 20/87 \pm 9$

TABLE V
Tensile Properties of Blend PET/PE53K/E-GMA with
Composition 85/11.25/3.75

Protocol	Tensile modulus (MPa)	Strength at break (MPa)	Elongation at break (%)
One step	2180 ± 20	32 ± 2	200 ± 50
Two steps	1900 ± 40	46 ± 4	540 ± 20

Nevertheless, because of immiscibility with HDPE and preferential location as a shell around the HDPE particles as indicated on Figure 8, the copolymer acts efficiently to prevent coalescence during the processing of the blends insuring small dispersed particles. Even though, this is not sufficient for the improvement of ultimate mechanical properties if adhesion is weak. Impact properties given in Table IV confirm the superior effect of E-GMA since the specimens are never broken even at low temperatures while E-EA-GMA has only a limited toughening effect.

Effect of the drying protocol of the E-GMA compatibilizer on the tensile properties of PET/HDPE/E-GMA blends

Among the parameters that increase the efficiency of the compatibilizer, reactivity with PET and miscibility with PE are prerequisites. However, the location of the compatibilizer at the interface between PET and PE is also very important as will be demonstrated hereafter. Blends of 85 wt % of PET with PE53K in presence of 3.75 wt % of E-GMA were prepared according to two different protocols. These protocols differ mainly by the methods used to perform the unavoidable drying of the pellets prior to extrusion. Drying is always necessary to prevent the hydrolysis of PET during extrusion. In the first type of blend (named "one step"), all the pellets were tumble-blended together and dried during 24 h under vacuum at 120°C

above the melting point of E-GMA before extrusion. For the second type of blend (named "two steps"), first, only the PET and the HDPE were blended together and dried during 24 h under vacuum at 120°C. E-GMA was dried separately at 60°C below its melting point. In a second step, the dried pellets were tumble-blended together before extrusion. The resulting tensile properties, indicated in Table V, show considerable difference as far as elongation at break is concerned. Also the SEM pictures of Figure 9 indicate that a more homogeneous dispersion is obtained with the "two steps" protocol, whereas for the "one step" preparation, small and large particles coexist. Also, for the "two-steps" blend, no holes were left during the fracture while the pictures show significant de-bonding of large particles in the other case. Selective removal of the PE with 1,2,4-trichloro benzene at high temperature fails to remove the grafted layer of E-GMA at the phase boundaries in the "two-steps" blend as can be seen on Figure 9. The chemical stability of the E-GMA has been checked by FTIR spectroscopy before and after drying at 120°C. The large difference of efficiency of the compatibilizer is directly connected to interactions that are created between PET and E-GMA during the drying stage in the "one-step" protocol, especially since the E-GMA is in the molten state at 120°C. The reactivity of E-GMA and PET has been clearly demonstrated by the peeling tests in Figure 6. The E-GMA that has already reacted with PET and that is grafted onto PET cannot migrate towards the interface with the HDPE particles during the mixing stage in the extruder and therefore will be dispersed as separated micells within the PET matrix. On the contrary, when the compatibilizer is added separately, due to the driving force related to immiscibility, it would preferably locate at the interface with the HDPE before any reaction takes place, inducing true and efficient compatibilization.

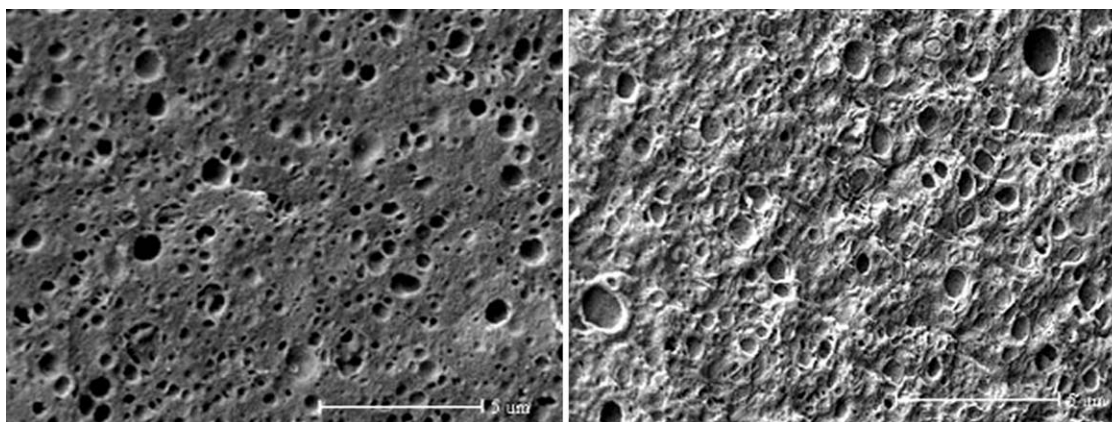


Figure 9 Etched surfaces ($\times 3620$) of blends PET/PE53K/E-GMA using one-step (left) and two-steps (right) protocols.

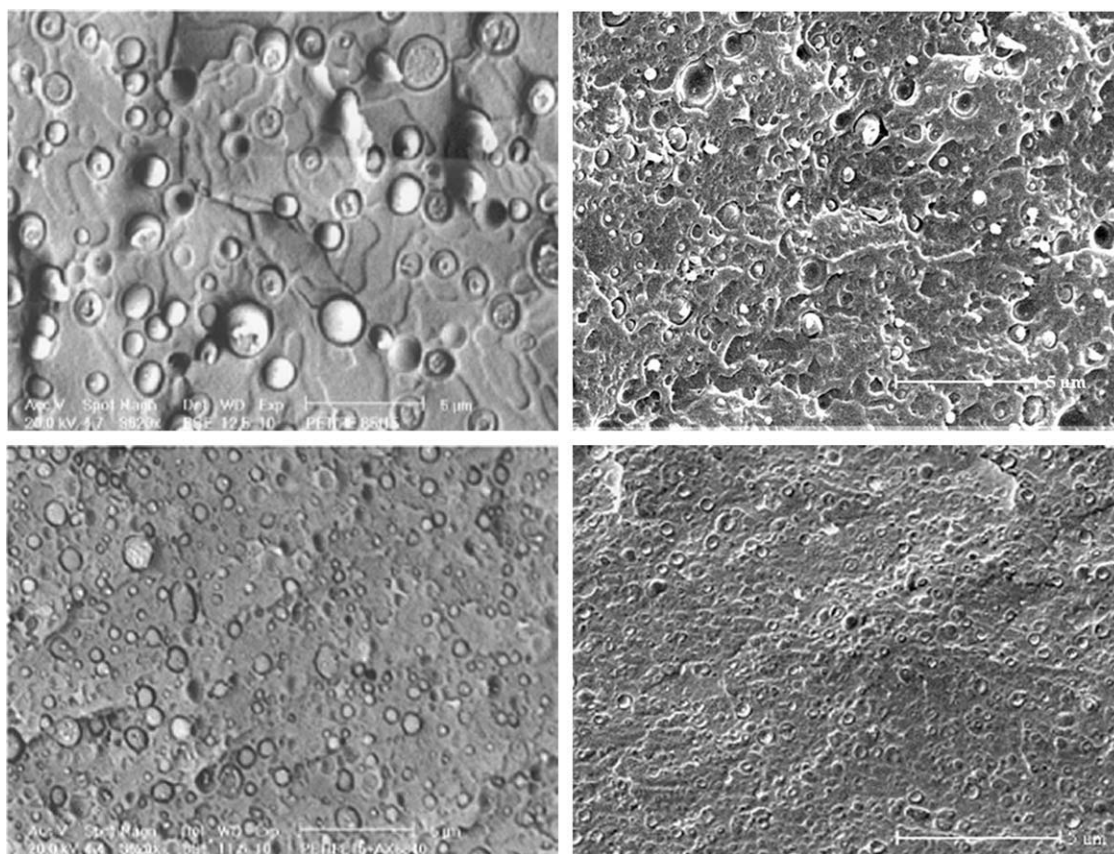


Figure 10 SEM pictures ($\times 3620$) of fractured surfaces of blends containing 85 wt % of PET, PE53K, and increasing amounts of E-GMA compatibilizer: 0, 2.5, 3, 3.75 wt % (from left to right and top to bottom).

Effect of the amount of E-GMA on the morphology of PET/HDPE/E-GMA blends

SEM pictures of Figure 10 show the efficiency of increasing amounts of the E-GMA compatibilizer in the reduction of the interfacial tension and therefore of the mean size of the PE dispersed domains in the case of a blend containing 85 wt % of PET and HDPE with the lowest molecular weight (PE53K). Similar effect are also observed for the HDPE with medium range molecular weight (PE90K).

Effect of the molecular weight of HDPE on the morphology properties of PET/HDPE/E-GMA blends

SEM photographs of blends containing 85 wt % of PET with E-GMA as compatibilizer and HDPE having different molecular weights are shown in Figure 11. Compatibilized blends with only 2.5 wt % of compatibilizer show already well-dispersed HDPE particles inside the PET matrix, with very small size for PE53K and PE90K (0.2 μm to 0.3 μm , respectively). For PE150K, a bimodal distribution of domains is observed with small droplets coexisting with larger ones. The thermal properties and especially the consequences on the fractionated crystallization have been discussed in our previous arti-

cle.^{19,20} It was shown that for the blend containing the high molecular weight PE, the compatibilizer does not induce any change in the thermograms in comparison to the blends with lower molecular weight HDPE where significant fractionated crystallization occurs. This was consistent with the SEM pictures showing little size reduction due to the lowering of the interfacial tension in this later case. Also, for blend with PE150K, the crystallization temperature of PE150K is affected neither by the presence nor by the amount of E-GMA copolymer.

Combined effects of the E-GMA compatibilizer and HDPE molecular weight on the tensile and mechanical properties of PET/HDPE/E-GMA blends.

Table VI gives some characteristics of the samples obtained from tensile and impact testing. The results show the efficiency of the E-GMA as a compatibilizing agent since a large increase of the extension at break and efficient toughening are observed upon addition of E-GMA due to better adhesion between the phases. Other tensile properties such as the tensile strength are not improved because of the poor intrinsic mechanical properties of the E-GMA. Varying the amount of compatibilizer in the blends

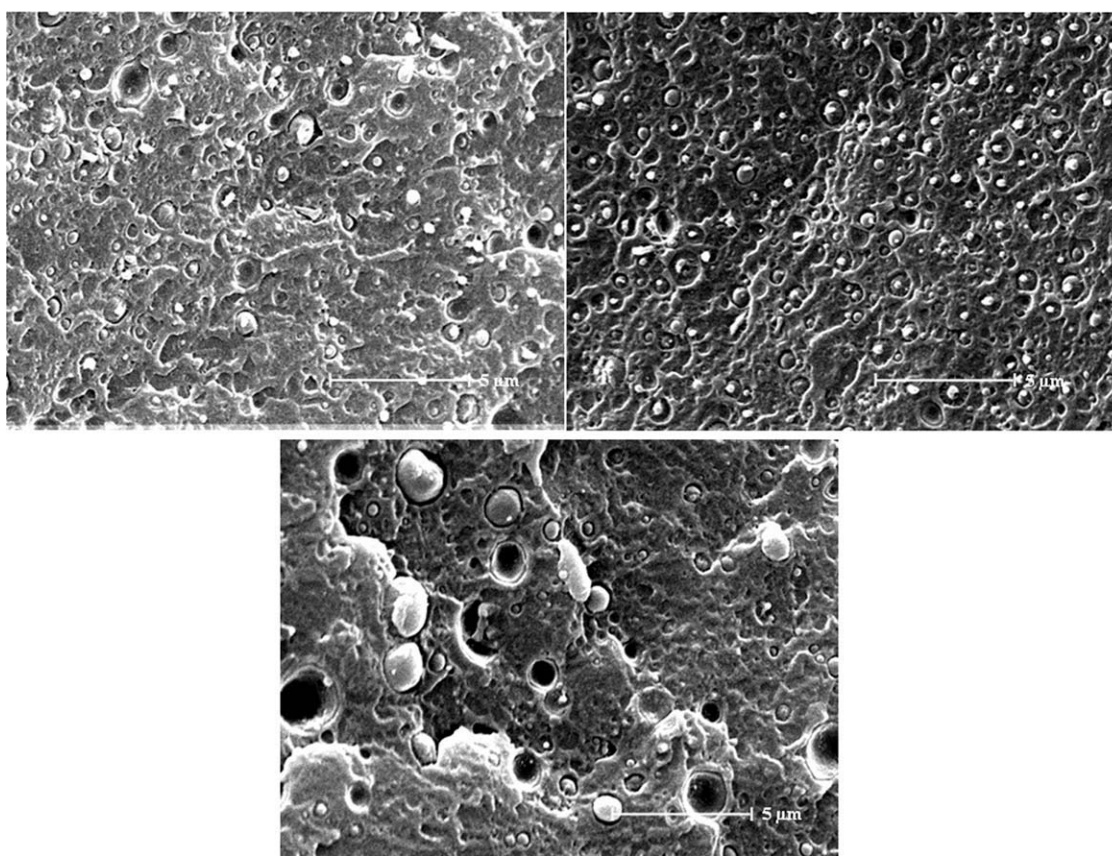


Figure 11 SEM pictures ($\times 3620$) of fractured surfaces of blends containing 85 wt % of PET 2.5 wt % of E-GMA compatibilizer and 12.5 wt % of HDPE with various molecular weights: 53,000 g/mol, 90,000 g/mol, 150,000 g/mol (from left to right and top to bottom).

enables to get similar improvements of the elongation at break whatever the molecular weight of the HDPE. However, the main difference that is observed is essentially related to the amount of compatibilizer that is required for this optimization. The higher the molecular weight of the HDPE, the lower the amount of compatibilizer that is necessary to get the largest elongation at break. This effect is clearly connected to the morphology of the blends but in a complex way.

As stated before, the compatibilizer has three main effects: first, reduction of interfacial tension, second, suppression of coalescence and therefore decrease of the droplet size through emulsification and third, the increase of the adhesion between phases. The effects are tightly connected however.

At a first glance, the tensile properties of PET/PE blends seem to be mainly dictated by the adhesion between the matrix and droplets. The amount of

TABLE VI
Tensile and Impact Properties of PET/HDPE/E-GMA Blends at Different (E-GMA/HDPE) Weight Ratio

PET/HDPE	(EGMA /HDPE)	Tensile modulus (MPa)	Strength at break (MPa)	Elongation at break (%)	Charpy impact unnotched, 23°C/-23°C (kJ/m ²)
PET/PE53K	(0/1)	2400 ± 20	55 ± 12	12 ± 2	55 ± 4/32 ± 3
	(1/5)	2250 ± 20	45 ± 3	510 ± 30	NB/NB
	(1/4)	1800 ± 30	42 ± 4	490 ± 80	NB/NB
	(1/3)	1900 ± 20	47 ± 1	550 ± 206	NB/NB
PET/PE90K	(0/1)	2080 ± 30	28 ± 2	70 ± 10	53 ± 7/29 ± 3
	(1/5)	1980 ± 20	39 ± 4	420 ± 60	NB/NB
	(1/4)	2030 ± 30	49 ± 2	600 ± 30	NB/NB
	(1/3)	1950 ± 20	40 ± 2	450 ± 30	NB/NB
PET/PE150K	(0/1)	2080 ± 20	49 ± 1	7 ± 1	28 ± 2/26 ± 2
	(1/5)	2010 ± 30	47 ± 3	580 ± 40	NB/NB
	(1/4)	2080 ± 30	47 ± 3	540 ± 49	NB/NB
	(1/3)	1930 ± 20	41 ± 3	480 ± 50	NB/NB

compatibilizer that is necessary to provide sufficient adhesion depends on the interfacial area. However, the later is also influenced by the emulsification effect that increases the interfacial area. For this reason, the efficiency of high amounts of compatibilizer is clearly questionable in the case of PE150K because the reduction of interfacial tension can not overcome the high value of the critical capillary number related to the high viscosity ratio in eq. (1). In these conditions the reduction of size by emulsification is not efficient. For large particles, only a low amount of compatibilizer (Φ_c) is required to get a complete coverage of the particles according to eq. (2) as stated by Ihm and White et al.¹:

$$\Phi_c \propto \frac{3\Phi}{R} \quad (2)$$

Combining eqs. (1) and (2) gives an approximate relation between the optimal amount of compatibilizer and the critical capillary number assuming that the interfacial tension reduction is effective:

$$\Phi_c \propto \frac{\Phi \eta_m \Pi_{\dot{\gamma}}}{Ca^* (\sqrt{\Pi_{\dot{\gamma}}}) \sigma} \quad (3)$$

The excess of compatibilizer leads to micellization in the matrix phase. This could explain the bimodal distribution of droplets that is observed in 11 since the largest particles are made of HDPE while the smaller ones are composed of compatibilizer.

In the case of PE53K and PE90K, the critical capillary number is smaller, therefore small particles can be obtained and a larger amount of compatibilizer is required for complete coverage and good adhesion.

CONCLUSIONS

The influence of the molecular weight of the polyethylene phase on the morphology and properties of PET/HDPE blends containing between 5 wt % and 20 wt % of PE was investigated. At these compositions, without compatibilizer, HDPE is dispersed as droplets in the PET matrix. The mean size of the PE domains increases with the molecular weight of PE. Differences of morphologies can be easily explained by the influence of the molecular weight of the dispersed phase on the viscosity ratio and therefore on the critical capillary number.

The effect of glycidyl methacrylate containing copolymers and especially of an ethylene-glycidyl methacrylate (E-GMA) copolymer acting as a compatibilizer was also addressed in relation to the molecular weight of the HDPE phase. The increase of adhesion between PET and HDPE was found to have a larger influence on tensile properties than the reduc-

tion of interfacial tension. The amount of compatibilizer needed for adhesion improvement depends on the interfacial area that is defined by both the interfacial tension and viscosity ratio of the components. A qualitative relation between the optimum amount of compatibilizer and the critical capillary ratio can be written for a given PE content.

For very large viscosity ratio, reduction of interfacial tension can not overcome the rheological effects and therefore, large particles of HDPE are observed. In this case, as far as tensile properties are concerned, sufficient adhesion can be obtained with a smaller amount of compatibilizer. An excess of compatibilizer leads to the formation of small E-GMA droplets or micells, co-existing with the large HDPE domains and gives rise to a decrease of the tensile properties.

This clearly show competing effects between the interfacial tension and the rheology of the dispersed phase. The emulsification effect of compatibilizer through interfacial tension reduction is hindered if the viscosity of the dispersed phase is high. Rheology defines the characteristic size of the dispersed domains and only small amounts are required to provide adhesion. On the other hand, if the viscosity of the dispersed phase is low, reduction of size by the emulsification effect is efficient, interfacial tension defines the size of the dispersed domains but good adhesion requires larger amounts of compatibilizer to ensure coverage of the large surface area generated in turn.

References

- Ihm, D. J.; White, J. L. *J Appl Polym Sci* 1996, 60, 1.
- Sambaru, P.; Jabarin, S. A. *Polym Eng Sci* 1993, 33, 827.
- Boutevin, B.; Lusinchi, J. M.; Pietrasanta, Y.; Robin, J. J. *Polym Eng Sci* 1996, 36, 879.
- Pracella, M.; Rolla, L.; Chionna, D.; Galeski, A. *Macromol Chem Phys* 2002, 203, 1473.
- Carte, T. L.; Moet, A. *J Appl Polym Sci* 1993, 48, 611.
- Kalfoglou, N. K.; Skafidas, D. S.; Kallitsis, J. K.; Lambert, J. C.; Van der Stappen, L. *Polymer* 1995, 36, 4453.
- Kalfoglou, N. K.; Skafidas, D. S. *Eur Polym J* 1994, 30, 933.
- Kim, S.; Park, C. E.; An, J. H.; Lee, D.; Kim, J. *Polym J* 1997, 29, 274.
- Akkapeddi, M. K.; Van Buskirk, B.; Mason, C. D.; Chung, S. S.; Swamikannu, X. *Polym Eng Sci* 1995, 35, 72.
- Dagli, S. S.; Kamdar, K. M. *Polym Eng Sci* 1994, 34, 1709.
- Pietrasanta, Y.; Robin, J. J.; Torres, N.; Boutevin, B. *Macromol Chem Phys* 1999, 200, 142.
- Hert, M. *Angew Makromol Chem* 1992, 196, 89.
- Kaci, M.; Benhamida, A.; Cimmino, S.; Silvestre, C.; Carfagna, C. *Macromol Mater Eng* 2005, 290, 987.
- Wu, S. *Polym Eng Sci* 1987, 27, 335.
- Potente, H.; Ansahl, J.; Klarholz, B. *Intern Polym Process* 1994, IX, 11.
- Shi, Z. H.; Utracki, L. A. *Polym Eng Sci* 1992, 32, 1834.
- de Bruijn, R. A. PhD thesis, Eindhoven University of Technology, The Netherlands, 1989.
- Grace, H. P. *Chem Eng Commun* 1982, 14, 225.
- Mbarek, S.; Jaziri, M.; Chalamet, Y.; Elleuch, B.; Carrot, C. *Int J Mat Forming* 2008, 1, 635.
- Mbarek, S.; Jaziri, M.; Chalamet, Y.; Elleuch, B.; Carrot, C. *Int J Mat Forming* 2008, 2, 15.