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# Morphological stability of postconsumer PET/HDPE blends

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## Summary

The morphological stability and the mechanical properties of postconsumer polyethylene terephthalate (PET) and high density polyethylene (HDPE), at different composition with and without compatibilizer were investigated. The blends were prepared in an internal mixer and in a twin screw-extruder at different stretching ratio.

For uncompatibilized blends, (previously prepared by extrusion), the particle size of the dispersed phase increases after being reprocessed in an internal mixer. However, in the case of compatibilized blend the particle size remains constant. Consequently, the compatibilizer reduces interfacial mobility, coalescence effects and stabilizes the morphology. The mechanical properties are also modified by the presence of the compatibilizer, mainly the elongation at break.

## Introduction

The interrelation between processing, morphology and physical properties of polymeric blends has had a lot of attention lately. The processing parameters that affect the blend morphology are shear stress, shear rate, mixing time and screw speed [1].

Frequently, immiscible polymer blends display poor mechanical properties compared with the properties of the raw materials, besides of showing unstable morphology [2]. That kind of blends shows unfavorable interaction at a molecular level, which can lead to the presence of high interfacial tension on the melt. This interaction makes more difficult the dispersion of the components during the mixing process. Such interactions also cause the unstability of the morphology, besides poor interfacial adhesion. These limitations can be overcomed by means of the compatibilization, using copolymers that act like interfacial agents [2].

Blends of PET with polyolefins have been the topic of several studies [2,3,4]. For example, Akkapeddi *et al* [3], studied the morphology and mechanical properties of PET/HDPE blends compatibilized with a ethylene-glycidyl methacrylate copolymer. They reported an important improvement on hardness and heat resistance for the compatibilized blends. Traugott *et al* [5] observed that the triblock copolymer (Kraton G-1652) adhered fairly well to PET/HDPE interphase. On the other hand, they showed that some mechanical properties of compatibilized blends, such as ductility, depended on the orientation in inyection molded specimens.

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Berger *et al* [6], working on the cold drawing of PET/HDPE blends, found that the samples of the stretched blends exhibited a metallic luster on the surface, which was attributed to the formation of a highly uniform fiber-hole structure. Subramanian [7], studied the compounding of PET with low modulus polymers in order to improve its hardness, but without a decrement on its permeability. He found that by adding EMAA (ethylene-methacrylic acid) copolymers to PET, its hardness was significatively increased and that the permeability properties to hydrocarbons and organic were good.

In this study we propose to extend the polymer blend application to post-consumer materials to obtain blends with good processability properties and an attractive combination of properties.

## Experimental

### *Materials*

The high density polyethylene (HDPE) and the polyethylene terephthalate (PET) used in this study were obtained from scraps of beverage bottles. They were originally prepared, in the case of PET, using a Eastapak 9663 from Eastman Chemical Co. with an intrinsic viscosity of 0.8 dl/g. The HDPE was Paxon AD60-007 from Polymer Co. with a medium molecular weight homopolymer and a MFI=0.7 g/10 min. These materials were washed, dried and milled before processing. The compatibilizer agent used in this study was Kraton G-1652 provided by Shell, which is a SEBS triblock copolymer containing 70 %w of a random copolymer of hydrogenated ethylene-1 butene, and 30 %w of styrene.

### ***Mixing***

The blending of the materials was performed in a HAAKE Rheomix 600 internal mixer using the roller blade geometry. During this stage, the total volume of the mixture was kept constant. The operational conditions were: chamber temperature of 250 °C, rotor speed of 40 RPM, and blending time of 7 minutes. Torque vs. time data was obtained and the specific mechanical energy input was calculated.

Mixtures of 10, 20, 30, 40, 50, 60, 70, 80 and 90 %vol. of PET in HDPE with and without interfacial agent were compounded. The amount of Kraton added to the blend corresponded to 10 %w based on the minor phase in each case. The blends were carried out in two steps. First the copolymer was mixed with the major phase, and then the minor phase was incorporated. There were no significant changes on the constant torque values or on the blend morphology with a change on the order of addition of the mixture components.

### *Extrusion*

Ribbons containing 10, 20 and 30 %vol. of PET in HDPE with and without compatibilizer were obtained in a LEISTRITZ twin screw extruder. The corrotating screws have a L/D ratio of 25. The extruder was operated at 250 °C in the last zone and the speed of the screws was set at 100 rpm; so the extrusion speed ($V_E$) was maintained constant at 100 cm/min. The ribbon getting out from the 6.5 cm. slit die with an adjustable gap was immersed in a cooling water bath and then taken up ($V_R$) by a system of a roll and a plane surface. This stretching system was set at different speeds to control the stretching ratio of the extrudate ($V_R/V_E$). The blends were processed with four different stretching ratio (1.0, 1.4, 2.0 and 2.7). The ribbons obtained were used to analyze the longitudinal morphology of the alloys and also to investigate their mechanical properties. On the other hand, a portion of each one of these mixtures was milled and reprocessed in the internal mixer (HAAKE), with the objective of analyzing their morphological stability based on the kind of processing the blend undergoes.

### *Morphological Analysis*

The blends obtained from the mixing chamber and the extruder were fractured in the transverse and longitudinal directions under liquid nitrogen, and a thin golden layer was deposited on the fracture area. Micrographs of the samples were obtained using a scanning electron microscope (JEOL JSM 5400 LV). For the transverse images, which presents drop-matrix morphology, the size of the dispersed domains from SEM photomicrographs was analyzed. An average of 200 measurements from each sample were taken and the average number ($D_n$) and volume ($D_v$) diameters were obtained.

### *Mechanical Tests*

Tensile mechanical tests were carried out in a universal mechanical tester (UNITED). The test specimens were prepared by cutting the extruded ribbons using type IV of the ASTM standard D 638.

### *Rheological Analysis*

The Reometrics ARES was used to measure the complex viscosity ($\eta^*$) as a function of frequency ($\omega$) at 250 °C of the HDPE and PET (Figure 1).The experiments were carried out in the dynamic mode in parallel-plate geometry (gap 1.5 mm) at a strain of 10%.

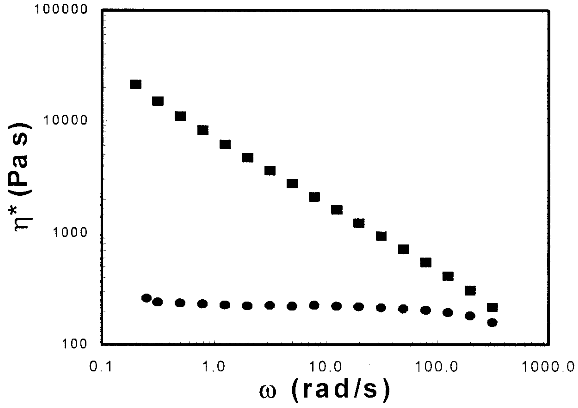


Figure 1. Curves of $\eta^*$ versus $\omega$ for (■) HDPE and (•) PET at 250 $^0$C.

## Results and Discussion

### *Torque and Mixing Energy*

To study the effect of the triblock copolymer on the rheological properties of the PET/HDPE recycled blends, a small quantity of Kraton (10 w% based on the minor phase) was added. Previous works [5,8] have demonstrated that this copolymer is a good compatibilizer for this system. The constant torque of the uncompatibilized blends as a function of the composition (Figure 2), diminishes with the composition. These results are similar to those obtained by Chen and Lai [9], who processed virgin PET/HDPE blends. Their results showed that the minimal constant torque value was obtained when the composition of the mixture was 50/50 vol%. However, in this study the minimal constant torque value was obtained when the composition was 80 vol% PET for compatibilized blend (Figure 2). Gianotta *et al* [10] attribute this minimal values to possible degradation of PET. The constant torque values of the blends without compatibilizer are below the ones obtained by a direct mixing rule, which is characteristic of immiscible polymer blends [11, 12].

The addition of Kraton to the blends caused a decrement of the constant torque values with respect to the uncompatibilized blends (Figure 2). This decrement is due to the fact that the Kraton acts as a high molecular weight plasticizer and increases the free volume between molecules of PET and HDPE [9]. This behavior has been observed by other authors [6,9]. Chen and Lai [9] found that at certain compatibilizer concentrations for a PET/HDPE blends, the viscosity of the blend showed negative deviations from the simple mixing rule. In this study the constant torque values are close to those calculated with the inverse mixing rule (Figure 2).

In Figure 3, the specific mechanical energy as a function of blend composition is shown. The compatibilizer addition decreased the energy requirement by 25%. According with these results, it is possible to reduce the manufacturing costs if adequate processing conditions are selected [7].

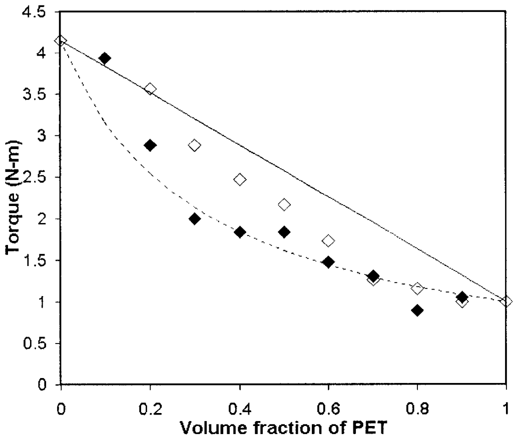


**Figure 2**. Constant torque (after seven minutes) as a function of PET volume fraction. PET/HDPE blends with (◆) and without (◇) compatibilizer. Simple mixing rule (—) and inverse mixing rule (---).

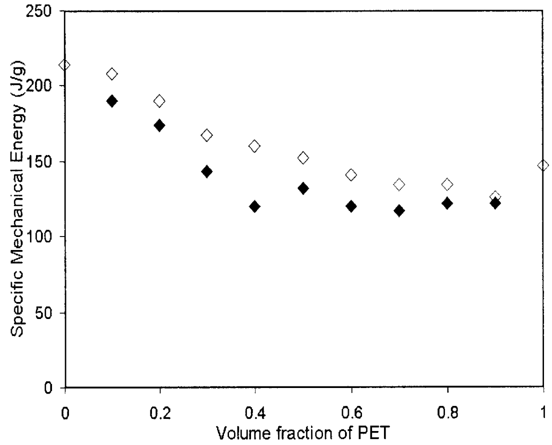
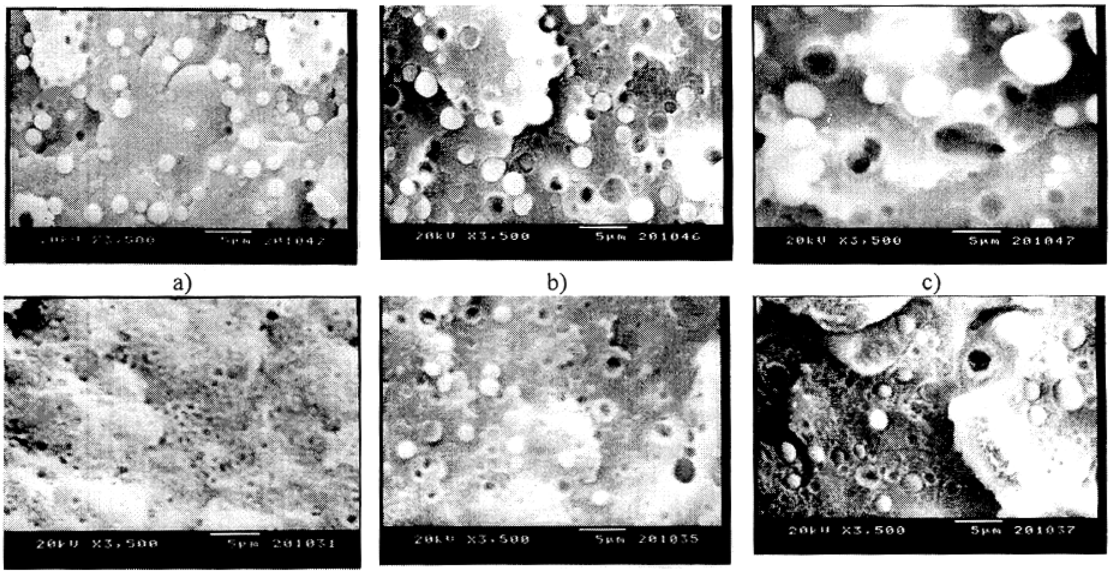


**Figure 3**. Specific mechanical energy of blends versus composition. PET/HDPE blends with (◆) and without (◇) compatibilizer.

*Morphology*

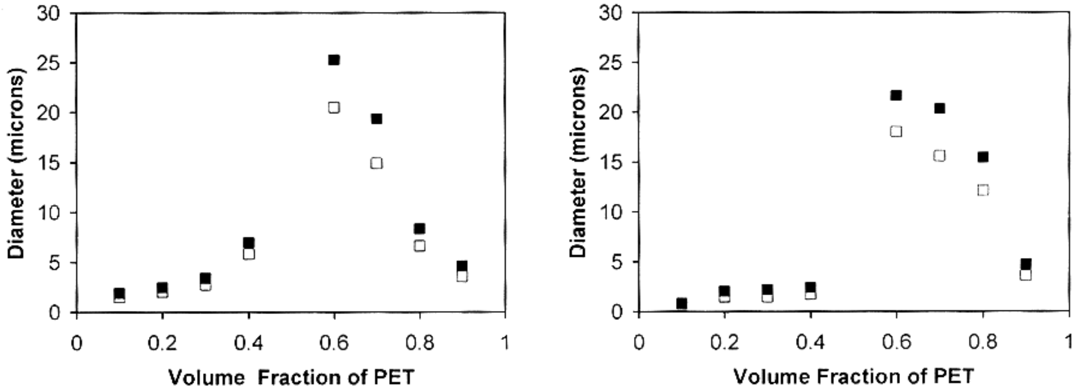
The morphology of mixtures PET/HDPE recycled with and without compatibilizer has been studied. Figure 4 shows the photomicrographs of uncompatibilized and compatibilized blends (10, 20 and 30 vol% PET). The images show a particle matrix morphology and a decrease of the particle size for compatibilized blends is observed (Figure 4 d, f, g). Figure 5 shows the particle size of the dispersed phase as a function of the blend composition. When the PET is the dispersed phase, the particle size shows a relatively little increment with PET composition. However when the HDPE is the dispersed phase, the drop sizes were much higher than PET's (up to 3 times higher). This can be explained if we take into account that the viscosity ratio ($\eta_d/\eta_m$ or torque ratio $TQ_d/TQ_m$) is low (0.25) when PET is the dispersed phase and particle disintegration is



a) b) c)

d) f) g

**Figure 4.** Scanning electron micrographs of fractures surfaces of uncompatibilized blends with (a) 10% of PET, (b) 20% of PET, (c) 30% of PET and compatibilized blends with (d) 10% of PET, (e) 20% of PET, (f) 30% of PET.



a) b)

**Figure 5.** Particle size of the dispersed phase as a function of the blend composition for (a) uncompatibilized and (b) compatibilized blends. Average number, $D_n$ (□) and volume, $D_v$ (■) diameters.

the process that governs the particle size blends. At higher viscosity ratios (4.0) when HDPE is the dispersed phase, the droplet breakup process becomes much slower and consequently starts to dominate droplet size. Under such conditions, the droplet size increases with viscosity ratio and changes only slightly with concentration [8]. The addition of the compatibilizer agent decreases the droplet size by 45% for $D_n$ and by 35% for $D_v$ (Figure 5 b). This tendency has been observed in many systems compatibilized with block copolymers [3,8,9]. These results suggest that interphase tension between polymers diminished with the presence of the triblock copolymer, because specific interfacial area is directly proportional to the ratio shear stress/interphase tension [13,14]. In this case, the size of the dispersed phase diminished because the coalescence phenomena decreased [7,15,16]. The interfacial tension reduction promotes the droplet breakup [17] by the presence of repulsive forces between particles, which are induced by the presence of the interfacial agent [18]. It is been found that the interfacial activity of this copolymer improves the adhesion between phases [5].

*Morphological Stability*

When coalescence of dispersed phase particles is reduced, it is also possible to stabilize the blend morphology [4,8,10]. Figure 6 shows the number average diameter of droplets as a function of blend composition with and without compatibilizer, and also as a function of processing device. The compatibilized samples showed just a little change on the droplet size when they are reprocessed on the mixing chamber, compared with the size of the particles of the mixtures obtained from the twin screw extruder. Nevertheless the increment of the droplet diameter of the blends without Kraton is significant, which demonstrate that the copolymer addition diminished substantially the sensibility of the dispersed phase size to the kind of processing the blend undergoes. Similar results have been obtained for PA6/HDPE/Surlyn systems [15] and for PE/PS/Kraton systems [10] in an annealing process. Willis *et al* [1] demonstrated that the presence of an interfacial agent diminishes the effect of the screw speed and the material throughput (residence time) on the blend morphology. The morphological stability showed broadens the applicability possibilities of this system to plastic recycling since it is advisable that the achieved morphology does not change when the polymeric mixture or alloy is processed to obtain an end use product.

**Figure 6.** Particle size of the dispersed phase as a function of blend composition, with (♦, •) and without (◇,□) compatibilizer, for different processing device: internal mixer (○, •) and twin screw extruder (◇, ♦).

*Mechanical Properties*

The stress-strain curves of the 10, 20, and 30% vol. of PET with (110, 120, 130) and without (P10, P20, P30) copolymer at different stretching ratios are presented in Figure 6. For uncompatibilized blends the modulus and tensile strength increased with PET concentration, while the elongation at break decreased. These tendencies coincide with the results obtained by Traugott *et al* [5] and by Barlow and Paul [8]. For the case of compatibilized blends, the modulus and the tensile strength do not change sensibly. However, the elongation at break increases significantly [3, 11]. Even though the modulus and tensile strength properties seem to be independent of that variable, the melt stretching ratio produced during processing modified strongly the elongation at break.

Sambaru and Jabarín [4] found that virgin PET/HDPE compatibilized mixtures showed strain hardening upon orientation, whereas the blend without compatibilizer did not strain harden upon orientation. The study presented here confirms these findings and also demonstrates that the elongational flow induced orientation and improves substantially the properties of this recycled blend.

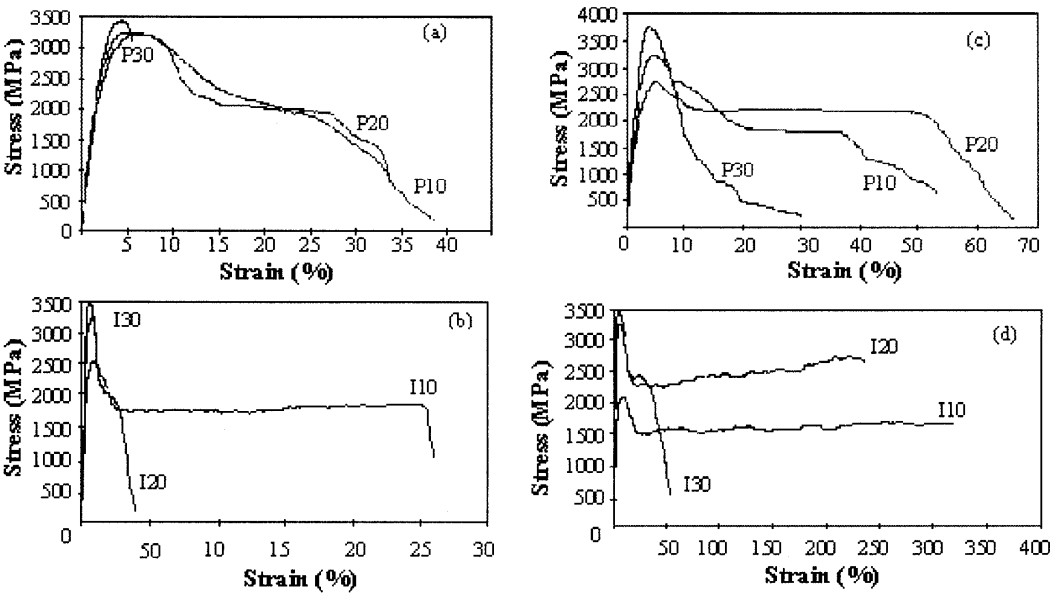


**Figure 7.** Stress-strain curves for different draw ratios (a) and (b) $V_R/V_E = 1.4$, (c) and (d) $V_R/V_E = 2.7$; and at different composition with (I10, I20, I30) and without (P10, P20, P30) compatibilizer.

## Conclusions

It is shown that the addition of an interfacial agent to the postconsumer PET/HDPE blend not only modifies its morphology by inducing the formation of a finer dispersion, but also stabilizes it. The influence of the re-processing for compatibilized blends morphology is negligible. It has been demonstrated that the coalescence phenomenon was reduced drastically. This result is remarkable if we consider the fact that these blends were originally compounded in an efficient mixer (twin screw extruder), and that the second process was carried out in a less effective equipment (that is, the internal mixer). This study has also shown the strong dependence between the elongation at break and the stretching ratio at which the mixtures were prepared. Finally, the presence of Kraton modifies the rheological properties (torque values) of the PET/HDPE recycled blends, in such a way that the specific mechanical energy of mixing diminished significantly. As discussed before, this fact represents an advantage from the processing point of view.

## Acknowledgments

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