

# Preparation and Characterization of Blends of High Density Polyethylene and Poly(ethylene-co-1-octene) Elastomer

MARIA JOSÉ O. C. GUIMARÃES,<sup>1,2</sup> FERNANDA M. B. COUTINHO,<sup>1,3</sup> MARISA C. G. ROCHA,<sup>4</sup>  
MARIA ELIZABETH F. GARCIA<sup>5</sup>

<sup>1</sup> Instituto de Macromoléculas Professora Eloisa Mano, UFRJ, P.O. Box 68525, 21945-970, Rio de Janeiro, RJ, Brazil

<sup>2</sup> Escola de Química/Departamento de Processos Orgânicos, UFRJ, Rio de Janeiro, RJ, Brazil

<sup>3</sup> Departamento de Processos Industriais/IQ, UERJ, Rio de Janeiro, RJ, Brazil

<sup>4</sup> Instituto Politécnico/UERJ, Nova Friburgo Rio de Janeiro, RJ, Brazil

<sup>5</sup> Programa de Engenharia Química/COPPE, UFRJ, Rio de Janeiro, RJ, Brazil

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**ABSTRACT:** Mechanical, thermal, and morphological properties of blends of high density polyethylene and poly(ethylene-co-1-octene) (PEO) were evaluated. The blends were prepared in a single screw extruder at 230°C and 50 rpm with volume fraction of elastomer varying in the range from 0.05 to 0.8. Factors such as chemical similarity and melt viscosity favor the interdiffusion process of phases, resulting in better interfacial adhesion. A synergistic effect on the strength at break and elongation at break for a particular range of blend composition was observed. Blends with a volume fraction of PEO higher than 5% presented a super tough behavior at room temperature. Thermal analysis showed that there is a certain degree of interaction between high density polyethylene and PEO. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1991–1995, 2001

**Key words:** polymer blends; polyolefin elastomer; HDPE; properties

## INTRODUCTION

The individual members of polyethylene family offer a broad spectrum of structures, properties, and applications. This spectrum can be broadened by blending these polyethylenes with other polymers, chemical additives, inorganic fillers, or reinforcing fibers. These blends are of commercial interest, and both theoretical research and prac-

tical development are currently very active.<sup>1,2</sup> Moreover, with the development of catalysts based on specific metallocenes, ethylene polymers with a narrow polydispersity index and homogeneous  $\alpha$ -olefin comonomer distribution in the polymer chain have been produced.<sup>3,4</sup> This new class of polyethylenes, modified by the nature of the long chain branchings and the arrangement of the short chain branchings in the macromolecule, when blended with polyolefins produce materials easily processable and with tailored properties for specific purposes such as automotive and medical applications.<sup>5–12</sup> According to the manufacturer, the ethylene/ $\alpha$ -olefin copolymers can compete against conventional elastomers in the produc-

Correspondence to: F. M. B. Coutinho (fern@ima.ufrj.br).  
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tion of polyolefin-based blends because, being a thermoplastic elastomer, it is produced in the pellet form, which allows for faster mixing and wider handling and compounding options.<sup>13</sup> Several researchers have studied the properties of blends of high density polyethylene (HDPE) with conventional rubbers or elastomeric materials such as natural rubber,<sup>13–16</sup> polyisoprene,<sup>17</sup> polyisobutylene,<sup>18,19</sup> and EPDM.<sup>20–23</sup> However, the literature relative to the study of properties of blends based on HDPE and polyolefin elastomers produced by metallocene technology is still scarce.<sup>5–7,24</sup> Therefore, in this work, a systematic study was performed to investigate HDPE-based blends containing poly(ethylene-co-1-octene) elastomer (PEO), produced by metallocene technology, as the second component. The influence of PEO content on the mechanical, thermal, and morphological properties of those blends was evaluated.

## EXPERIMENTAL

### Material and Blend Preparation

HDPE ( $M_w = 285,700$ , MFI = 0.93 g/10 min) and PEO (ENGAGE 8100, with 24 wt % of octene,  $M_w = 323,000$ , MFI = 1.0 g/10 min) were donated by Polialden (Brazil) and Dow Chemical (USA), respectively. A Wortex single screw extruder, model H210, was used to prepare the binary blends (HDPE/PEO) by melt blending. The screw speed was set at 50 rpm and the temperature profile in the extruder from the feed to the metering zone was set at 230°C. The extrudate in the form of narrow sheets was quenched in cold water. The PEO proportion was varied from 5 to 80 wt %.

### Mechanical Properties

The tensile properties were measured with an Instron 4204 universal mechanical testing machine at room temperature (25°C and 55% relative humidity), at a crosshead speed of 50 cm/min, according to ASTM D882, and the samples were obtained from the extrudate sheets. The impact strength was measured in a Ceast impact tester at the V-notched Izod mode, according to ASTM-D256, and the specimens were produced by injection molding. The values of the mechanical properties for each sample set (each blend composition) were determined as averages of seven (tensile) and six (Izod) specimens.

### Thermal Analysis

The melting and recrystallization behaviors of the pure polymers and their blends were determined by using a Perkin-Elmer differential scanning calorimeter (DSC-7). Each blend was cycled twice through its heating profile to eliminate the effects of its previous thermal history. The samples (10 mg) were scanned up to 150°C at a scanning rate of 10°C/min, annealed for 5 min, and cooled to 0°C at a scanning rate of 10°C/min under nitrogen atmosphere and then subjected to a second heating cycle at identical conditions. Melting temperatures and heats of fusion (both during the second heating) and crystallization temperatures (second cooling) were determined. Crystallinity measurements were relative to the heat of fusion of pure polyethylene crystal (293 J/g). Thermogravimetric analyses were performed in a DTA-TGA Perkin-Elmer using 10 mg of sample, a heating rate of 10°C/min, and a nitrogen flow of 100 mL/min. The measurements of the dynamic mechanical properties were made by using a dynamic mechanical thermal analyser—dynamic mechanical thermal analysis (DMTA) MK III (software release 5.41; Rheometric Scientific Ltd.). Bars measuring approximately  $25 \times 9 \times 2.0$  mm were used as specimens for DMTA analysis. The loss tangent ( $\tan \delta$ ) was measured in the temperature range from -140 to 5°C, at a constant frequency of 1 Hz and a scanning rate of 2°C/min.

### Scanning Electron Micrograph

The morphology of the blend was examined in a JEOL scanning electron microscope (SEM), model JSM-5300. The sample was cryogenically fractured (perpendicular to the extrusion direction) in liquid nitrogen, and etched with xylene for 20 s to extract the elastomeric phase. The fractured surface was then sputter coated with a thin coat of gold/palladium alloy before SEM observation. The operation voltage of the microscope was set at 15 KV.

## RESULTS AND DISCUSSION

Table I shows the results of tensile tests of the blends of HDPE and PEO. An increase was observed on the strength at break and elongation at break for blends with elastomer volume fraction in the range of 30 to 50%, indicating the existence of a good interfacial adhesion between HDPE and

**Table I Mechanical Properties of HDPE, PEO, and HDPE/PEO Blends**

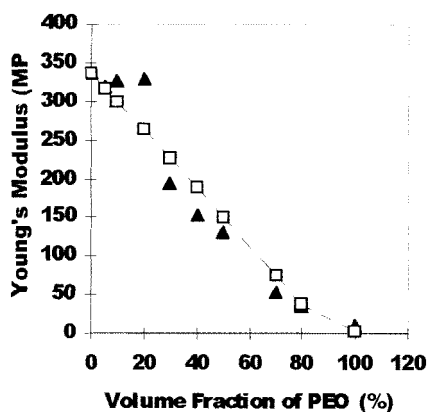
| PEO (wt %) | Strength at Break (MPa) | Elongation (%) | Young's Modulus (MPa) | Impact Energy (J/m) |
|------------|-------------------------|----------------|-----------------------|---------------------|
| 0          | 13 ± 0.5                | 219 ± 30       | 338 ± 45              | 297 ± 20            |
| 5          | 16 ± 1                  | 455 ± 54       | 319 ± 27              | 457 ± 21            |
| 10         | 17 ± 1                  | 775 ± 32       | 327 ± 24              | <sup>a</sup>        |
| 20         | 18 ± 1                  | 898 ± 26       | 330 ± 45              | <sup>a</sup>        |
| 30         | 26 ± 1                  | 1308 ± 13      | 193 ± 22              | <sup>a</sup>        |
| 40         | 25 ± 1                  | 1322 ± 15      | 153 ± 15              | <sup>a</sup>        |
| 50         | 23 ± 1                  | 1326 ± 10      | 131 ± 10              | <sup>a</sup>        |
| 70         | 15 ± 1                  | 1110 ± 69      | 52 ± 6                | <sup>a</sup>        |
| 80         | 13 ± 1                  | 1034 ± 55      | 35 ± 3                | <sup>a</sup>        |
| 100        | 9 ± 2                   | 1021 ± 22      | 11 ± 1                | <sup>a</sup>        |

<sup>a</sup> It did not break under the conditions used in the tests.

PEO. The synergistic effect on the strength at break was not observed for other HDPE/elastomer blends.<sup>13–23</sup> However, a similar behavior in the strength at break of PEO elastomer modified HDPE was also verified by Yousefi et al.<sup>6</sup> The Young's modulus decreased as the concentration of elastomer in the blend increased, as the result of decreasing on the crystallinity of the HDPE matrix. The experimental values for the modulus were compared with the values calculated by using the rule of linear additivity [Eq. (1)]:

$$E_b = E_1\phi_1 + E_2\phi_2 \quad (1)$$

Where  $E_1$  and  $E_2$  are the Young's moduli of HDPE and PEO, respectively, and  $\phi_1$  and  $\phi_2$  are their volume fractions. Figure 1 shows plots of experimental and theoretical values. It can be observed



**Figure 1** Variation of Young's modulus with PEO proportion. The solid line (squares) represents the theoretical values [Eq. (1)], and the triangles represent the experimental values.

that the majority of blends exhibited a negative deviation, except those with volume fraction of 10 and 20% of PEO.

In the tensile test, HDPE and all blends presented some whitening in the necked zone. The whitening of the materials during the deformation process is generally a manifestation of a fine-scale cavitation process<sup>24,25</sup> and suggests that both HDPE and the elastomer can cavitate during the plastic flow under conditions used in the tests.

Table I presents the notched Izod impact energy of the blends measured at room temperature. The blend with 5 wt % of PEO showed an enhancement of 53% in the impact strength in comparison with the pure HDPE. Blends with elastomer proportion higher than 5 wt % exhibited super tough behavior and did not break under the conditions used in the tests. All samples showed whitening near the fracture surface.

Table II shows the thermal properties of the pure polymers and their blends. To ensure the same thermal history for all the blends, the samples were melt annealed for 5 min at 150°C to erase any thermal memory. The incorporation of PEO into HDPE matrix provoked a decrease in the melting temperature and crystallinity as well as a slight increase in the crystallization temperature. The experimental values of crystallinity and heat of fusion of blends are close to those calculated by the rule of linear additivity. The melting behavior of HDPE blends suggests that the crystallites are thinner and connected by a larger concentration of tie molecules, resulting in a change in the lamellar thickness.<sup>26</sup> PEO presented a small melting peak at 127°C and two distinct crystallization peaks at 44°C and 112°C. These different crystallization peaks may be at-

**Table II** Physical Properties of HDPE, PEO, and HDPE/PEO Blends

| PEO (wt %) | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_f$ (J/g) <sup>a</sup> | $\Delta H_f$ (J/g) <sup>b</sup> | $\chi$ (%) <sup>c</sup> | $\chi$ (%) <sup>d</sup> |
|------------|------------|------------|---------------------------------|---------------------------------|-------------------------|-------------------------|
| 0          | 138        | 114        | 205                             | 205                             | 70                      | 70                      |
| 5          | 135        | 116        | 195                             | 200                             | 65                      | 68                      |
| 10         | 136        | 115        | 185                             | 167                             | 63                      | 57                      |
| 20         | 137        | 119        | 165                             | 163                             | 56                      | 56                      |
| 30         | 135        | 116        | 145                             | 149                             | 40                      | 48                      |
| 40         | 137        | 117        | 125                             | 110                             | 42                      | 38                      |
| 50         | 134        | 117        | 105                             | 108                             | 35                      | 36                      |
| 70         | 134        | 116        | 65                              | 54                              | 21                      | 18                      |
| 80         | 134        | 118        | 45                              | 31                              | 14                      | 11                      |
| 100        | 127        | 44/112     | 4.9                             | 4.9                             | —                       | —                       |

<sup>a</sup> Theoretical values of heat of fusion.<sup>b</sup> Experimental values of heat of fusion.<sup>c</sup> Theoretical values of crystallinity.<sup>d</sup> Experimental values of crystallinity.

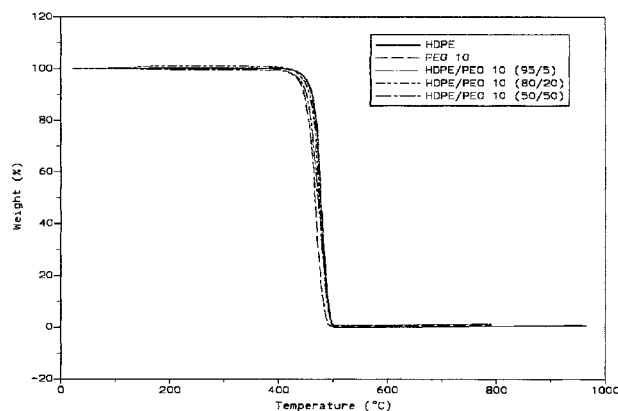
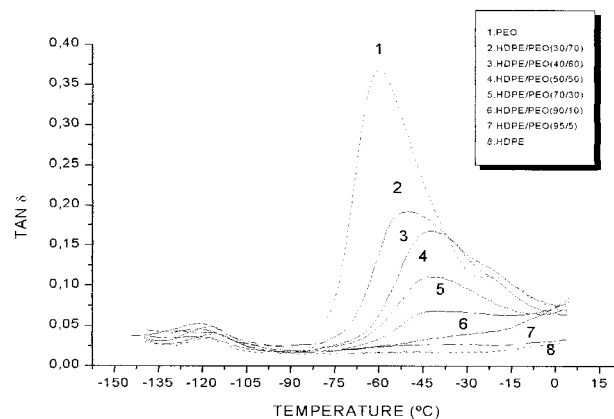
tributed respectively to the long chain branchings (produced by its polymerization process) and to the polymer backbone. The presence of melting and crystallization temperatures in elastomeric metallocene ethylene copolymers such as PEO and their blends can only be observed in special conditions of thermal annealing.<sup>27</sup>

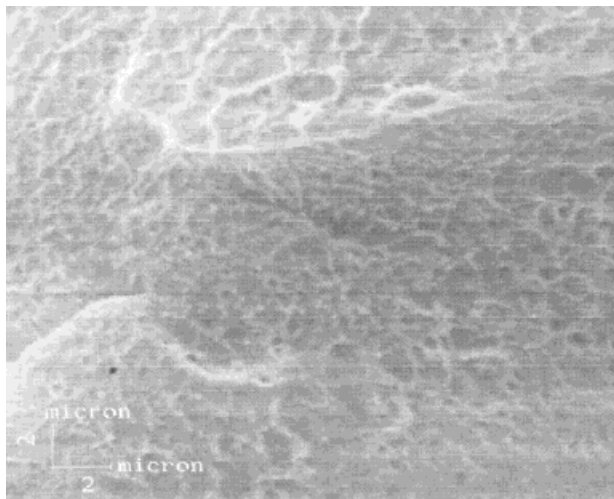
The thermal stability of the blends were evaluated by thermal gravimetric analysis measurements (Fig. 2). The degradation temperature of HDPE was not affected by the presence of PEO. The degradation process occurred in the range of 400 to 500°C.

The temperature dependencies of  $\tan \delta$  of HDPE, PEO, and blends are shown in Figure 3. HDPE and PEO (samples 8 and 1), exhibit  $T_g$  at  $-120^\circ\text{C}$  and  $-58^\circ\text{C}$ , respectively. Their blends presented two distinct  $T_g$ s which are shifted in

relation to the pure components and are located in the temperature range from  $-117$  to  $-121^\circ\text{C}$  and  $-30$  to  $-50^\circ\text{C}$ , respectively. It was observed that the height of the  $\tan \delta$  peak and its shape changed as the PEO content in the blend was increased.  $\tan \delta$  peak height is commonly used as a measure of damping capability of a polymer.<sup>28</sup> These DMTA results indicate that there is a certain degree of interaction between the phases which corroborates the synergistic effect on the strength at break observed in this work.

Figure 4 shows a SEM micrograph of the HDPE/PEO (90:10) blend. It is generally accepted that the morphology of a polymer blend is governed by its rheological characteristics and processing history. For the same processing history, the blend composition and the shear rate used in its preparation determine the blend morphology.<sup>29</sup> SEM analysis

**Figure 2** Thermogravimetric curves of HDPE, PEO, and HDPE/PEO blends.**Figure 3**  $\tan \delta$  curves of HDPE, PEO, and HDPE/PEO blends.



**Figure 4** SEM micrograph of HDPE/PEO (90:10) etched with xylene vapors.

showed that the HDPE/PEO blends exhibit phase separation of components with the dispersed domain, PEO or HDPE, depending on the blend composition. Blends with dispersed elastomer domains were etched with xylene vapors for 20 s to remove the elastomer phase. The etching time was short enough to avoid excessive attack of the HDPE matrix. Because of the similar chemical structure and melt viscosity of HDPE and PEO, which provokes some interdiffusion of domains, the total removal of the elastomeric phase without affecting the HDPE phase was impossible. The SEM micrograph shows that the cavities left by the domains of PEO tend to be filled with swollen HDPE domains, making morphological characterization of these systems difficult.

## CONCLUSIONS

HDPE-based blends with good mechanical properties may be produced by incorporating determined amounts of PEO. Blends with a volume fraction of elastomer higher than 5% exhibited super tough behavior at room temperature. The mechanical, thermal, and morphological analyses showed that some degree of interdiffusion of phases had occurred, resulting in enhancement of compatibility between the phases.

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