Mechanical, Rheological, Thermal, and Morphological Properties of Blends Based on Poly(propylene)/Poly(propylene-co-1-octene)/Poly(ethylene-co-1-octene)

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ABSTRACT: The effect of addition of propylene copolymer, produced by metallocene catalysts, on the mechanical, rheological, and morphological properties of blends based on poly(propylene) (PP) and ethylene–1-octene copolymer (EOC) was evaluated. It was observed that the addition of 2 wt % propylene–1-octene copolymer (POC) improved the impact strength of the EOC/PP blends. The rheological analysis indicated that the addition of propylene copolymer produced materials with improved processability. Thermal and morphological analysis showed that the POC acts as a compatibilizer on the EOC/PP blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1690–1695, 2003

Key words: poly(propylene) (PP); metallocene catalysts; copolymerization; blends

INTRODUCTION

Poly(propylene) (PP) is a semicrystalline polymer with very good mechanical and thermal properties, but its toughness, and in particular its notched toughness, is not sufficient for PP to be used as an engineering plastic.[1,2] In the past two decades, much attention has been paid to blends of isotactic poly(propylene) (i-PP) and olefin elastomers, such as ethylene–propylene random copolymer (EPR) and ethylene–propylene–diene terpolymers (EPDM), for the sake of both scientific interest and commercial utility. EPR/PP and EPDM/PP blends have been investigated with the aim of improving impact behavior. A lot of effort is still being made to further improve the mechanical properties and morphology of these blends and to expand their applicability.[4–7]

Recent developments in catalysts for olefin polymerization have allowed the control of molecular weight distribution and the proportion and distribution of comonomer incorporation. Those emerging catalyst systems, termed single-site catalysts (metallocene type) allow polymer producers to make a more well-defined molecule by enabling the incorporation of long comonomer chains. The metallocene catalysts are having a tremendous impact on the polyolefin industry. In contrast with the conventional heterogeneous Ziegler–Natta catalysts (multisite), the single-site catalyst leads to a higher degree of comonomer incorporation, while the uniform reactivity allows the synthesis of very homogeneous copolymers. One family of these new polymers, known as polyethylene elastomer (EOC) has been commercialized. These copolymers, containing >20 wt % octene, have distinctive properties compared with elastomeric materials currently available because the long-chain branching EOCs compete with thermoplastic olefin impact modifiers, such as EPDM.[8–11]

Metallocene ethylene–higher α-olefin copolymers, which are already one of the most important commercial products in the polyolefins market, have been widely studied in recent years.[12–15] However, not much has been published on propylene–higher α-olefin copolymers.[16–20] Thus, the aim of this work was to evaluate the EOC/PP blend properties and to verify the effect of the addition of the new propylene–1-octene copolymer (POC) produced with a heterogeneous metallocene catalyst in our laboratory.

EXPERIMENTAL

Materials

Commercially available grades of poly(propylene) (PP) and ethylene–octene copolymer (EOC) were used. The characteristics and specifications of PP and EOC used in this work are shown in Table I.

TABLE I
Characteristics of Commercial Polymer Samples

Material	PP	EOC
Manufacturer	POLIBRASIL RESINAS	DOW CHEMICAL
Designation	KM 6100	EG 8100
Density at 23°C $(g/cm^3)^a$	0.917	0.887
Melt index $(g/10 min)^b$	2.1	2.0
M_w^c	430,000	313,000
M_w/M_n^c	9.2	2.0

[a] Measured in IMA laboratory by ASTM D792.
[b] Measured in CENPES/PETROBRAS laboratory by ASTM D1238.
[c] Measured in Nitriflex laboratory by ASTM D 1646.

Polymerization grade propylene was supplied by Polibrasil and further purified by passing through 4-Å molecular sieves and copper catalyst columns to remove residual water and oxygen. Commercial toluene was kindly donated by Shell and treated by passing through 4-Å molecular sieves, refluxing with sodium, and distilling immediately before use. 1-Octene (97% purity) was acquired from Sigma-Aldrich and further purified by refluxing with calcium hydride and distilling prior to use. Metallocene catalyst [rac-Me$_2$Si(2-ethyl, 4-phenyl, 1-indenyl)$_2$ZrCl$_2$] was donated by Boulder Scientific, with a purity >98 wt % of the racemic isomer [determined by proton nuclear magnetic resonance spectroscopy (^{1}H NMR)], and used as received. Methylaluminoxane (MAO; cocatalyst) in toluene (10 wt/vol %) was kindly donated by Witco GmbH and used as received.

Catalyst heterogenization

Silica was dried and partially dehydroxylated at 400°C for 5 h, under nitrogen flow, and then treated with MAO (10 wt/vol % in toluene) for 12 h, under nitrogen atmosphere. The MAO-treated silica was filtered and washed with toluene to remove excess MAO. A metallocene solution was added to the MAO-treated silica and stirred for 3 h at room temperature. The catalyst was filtered and washed with toluene, dried under vacuum, and analyzed by inductively coupled plasma spectroscopy (ICP) to determine Al and Zr contents. The heterogeneous catalyst used in this work has a Zr content of 0.15 wt % and an Al content of 11.0 wt %.

Polymerization

The poly(propylene-co-1-octene) was produced in batches in a Büchi pressure reactor using 6 μmol of dimethylsilylene-bridged bis-indenylzirconocenes [Me$_2$Si(2-ethyl, 4-phenyl, 1-indenyl)$_2$ZrCl$_2$] supported on MAO-treated silica, which was prepared according to the procedure already described. Additional external MAO was employed (molar ratio of Al/Zr = 500). Tol-

uene (600 mL) was used as diluent. Pressure and temperature were set at 2 bar and 55°C, respectively. The concentration of 1-octene in the feed was set at 14 mol % to produce the copolymer. The properties of the propylene–octene copolymer (POC) produced in the laboratory are shown in Table II.

Blend preparation

The virgin polymers and PP blends, EOC/PP and EOC/POC/PP, were melt blended in a HAAKE Rheomix 600 internal mixer. The EOC/PP and EOC/POC/PP blends contained 30 and 28 wt % (plus 2 wt % of POC) elastomeric phase, respectively, the temperature of the mixing chamber was set at 190°C, the blending time was 5 min, and the rotor rate was set at 70 rpm.

Measurements

Rheological behavior

The viscosities of the polymers were measured over a low shear rate range (ω = 0.1–100 rad/s) on a cone-plate type rheometer (Rheometrics Dynamic Stress rheometer – SR 200) at 200°C.

Morphology evaluation

The morphology of the blends was examined in a Zeiss scanning electron microscope (SEM; model DSM-960). Samples that had been cryogenically fractured in liquid nitrogen were etched with heptane at 25°C for 7 days to extract the elastomer phase. The

TABLE II
Properties of Propylene–Octene Copolymer (POC)

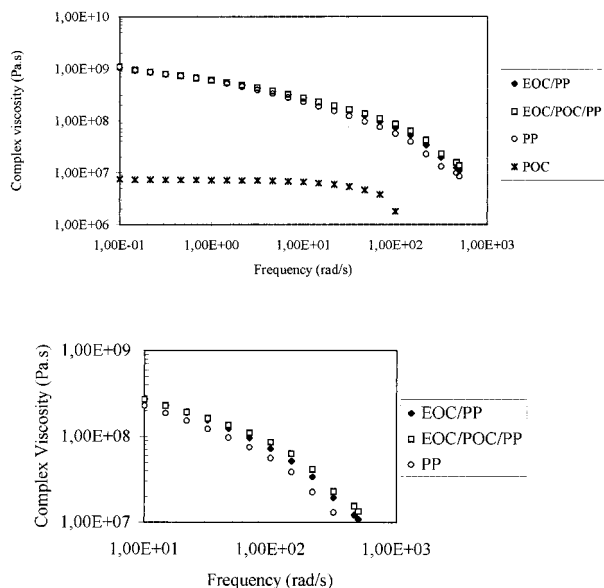| Property	Value
M_w	170,000
M_w/M_n	2.1
wt % of comonomer	17
Density (g/cm^3)	0.882

Figure 1 Complex viscosity, η^*, versus frequency for PP, POC, EOC/PP, and EOC/POC/PP.

samples were then dried and finally gold coated prior to their installation in the SEM chamber.

Impact strength evaluation

Impact strength was measured according to ASTM D256 (V-notched) on an Impact Tester Microtest at two different temperatures (-20 and 25°C).

Dynamic mechanic thermal analysis (DMTA)

A dynamic mechanic thermal analyzer (DMTA MK III) was used to determine tan δ of EOC, PP, and EOC/PP and EOC/POC/PP blends over the temperature range $-80–70°$C at a constant frequency of 1 Hz and a heating rate of $2°$C/min. The dimensions of the samples specimens were as follows: length, 24 mm; width, 9 mm; and thickness, ~2.0 mm.

RESULTS AND DISCUSSION

Rheological behavior

In a general way, high-shear sensitivity is desired for materials processing. High viscosity at low shear rates (e.g., 0.1 s^{-1}) provides high melt strength, whereas low viscosity at high shear rates (e.g., 100 s^{-1}) improves the melt processability.[21] The dependence of the logarithm of the value of the complex viscosity value (η^*) on the logarithm of investigated frequencies for the pure polymers, PP and POC, and for the blends, EOC/PP and EOC/POC/PP, is shown in Figure 1. As shown in the whole range of explored frequency, PP, EOC/PP, and EOC/POC/PP exhibit an accentuated decrease in the viscosity value with in-

creasing frequency; that is, these systems are pseudo-plastic melts. It also should be noted that for the propylene copolymer POC, the non-Newtonian flow only starts at larger shear rate; that is, this new material exhibit a wider range of Newtonian flow behavior in the experimental conditions analyzed in this work. Among the analyzed materials, EOC/POC/PP blend tends to present the highest viscosity values as the frequency increases. This behavior is better observed in the lower, magnified graph in Figure 1.

According to the literature,[22] all viscoelastic materials behave more or less solid-like (elastic) and liquid-like (viscous) depending on the rate at which they are deformed. This behavior is related to the fact that strained macromolecules tend to pull back to their original conformation. The dynamic storage modulus, G', is related to the elastic behavior of the material and may be considered as the amount of the energy stored. The dynamic loss modulus, G'', represents the amount of energy dissipated. The dependence of G' and G'' on the frequency is a measure of the relative motion of all molecules in the bulk and can give important information about the flow behavior of melts.

The dependence of the storage modulus, G', on the investigated frequencies of PP, POC, and EOC/PP and EOC/POC/PP blends is shown in Figure 2. A magnification of the elastic behavior of PP and blends at the high frequency range is shown in the lower graph in Figure 2. PP, EOC/PP, and EOC/POC/PP, at low frequencies, present similar G' values. However, at high frequencies, the EOC/POC/PP blend shows a tendency to present higher G' values, as may be observed in the lower graph of Figure 2. Considering that G' is related to the energy stored, the latter finding indicates that the EOC/PP blend with the addition
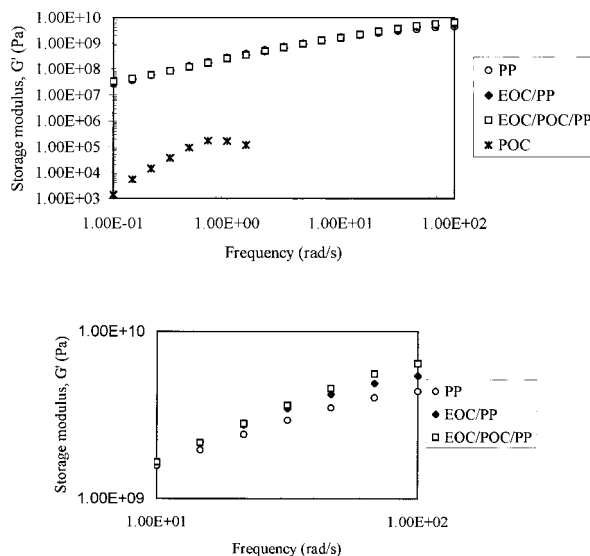

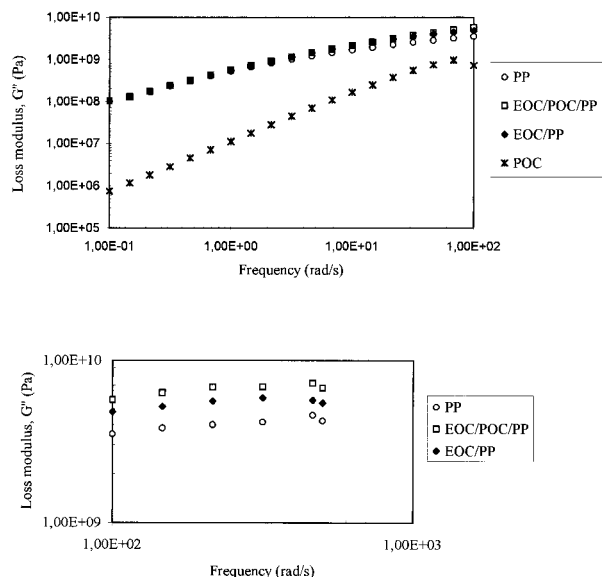**Figure 2** Storage modulus, G', versus frequency for PP, POC, EOC/PP, and EOC/POC/PP.

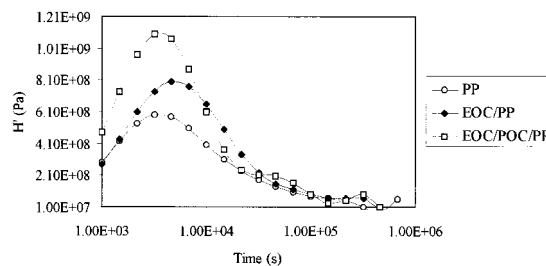**Figure 3** Loss modulus, G'', versus frequency for PP, POC, EOC/PP, and EOC/POC/PP.

Figure 4 Relaxation spectra calculated from the storage moduli G' at 190°C for PP, EOC/PP, and EOC/POC/PP.

increasing the complex viscosity, η^*, and the plateau modulus, G_N.

The relaxation spectra $H(\tau)$ of PP, EOC/PP, and EOC/POC/PP shown in Figure 4 were calculated with eq. 1:[16]

$$G'(\omega) = \sum_{1+1}^{M} H_i \frac{\omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2} \tag{1}$$

where G' is the storage modulus, H_i is the relaxation spectrum, ω is the frequency, and λ is the relaxation time. The results in Figure 4 shows that the EOC/POC/PP blend presents a different relaxation behavior compared with that of the EOC/PP blend. The former material exhibits a more severe shear thinning than EOC/PP blend, and its spectrum falls off rapidly with increasing τ. According to Yamaguchi and coworkers,[24] this behavior suggests that the addition of POC tends to increase the miscibility degree between EOC and PP components. The spectrum of the EOC/PP blend is extended for a longer time that can be associated with phase separation occurrence.

of POC has higher melt elasticity at high frequencies. The tendency to improve this property indicates that the propylene copolymer acts as a compatibilizer in the EOC/PP blend.

The dependence of the loss modulus, G'' on the investigated frequencies for PP, POC, EOC/PP, and EOC/POC/PP is shown in Figure 3. For all examined blends, EOC/POC/PP has higher G'' values than EOC/PP at high frequencies (see magnified graph in Figure 3). Taking into account that the dynamic loss modulus G'' represents the viscous behavior (i.e., the amount of energy dissipated), such a result may indicate that the addition of POC to the binary blend produced a material with higher energy dissipation.

The crossover frequency, ω_c, at which G' and G'' are equivalent is shown in Table III. It is known that the inverse of ω_c can be correlated to the characteristic relaxation time.[23] As the material viscosity increases, $1/\omega_c$ increases and, as a consequence, the relaxation time increases. The values of the complex viscosity at 0.1 rad/s, η^* (0.1), the frequency ω_c at which the storage and loss moduli crossover, and the estimated plateau modulus, G_N, are also shown in Table III. A longer relaxation time was found in the EOC/POC/PP blend, indicating that the addition of POC to the EOC/PP blend affected the viscous behavior by

Morphology evaluation by SEM

It is well known that particle size and dispersion are important factors in attaining optimal material performance. On the other hand, particle size is dependent on the chemical structure of the components and on the differences in rheological behavior. The analysis of the EOC state of dispersion by SEM shows that the minor component segregates as spherically shaped domains (Figure 5). The size of the elastomer domains decreases (Figure 5b) in the blend with POC, the chemical structure of which is more similar to the PP matrix. This result is evidence that POC acted as a compatibilizer in the EOC/PP blend. These results corroborate the rheological data obtained in this work.

Impact strength evaluation

The effect of the addition of POC on the impact property of EOC/PP blend is shown in Table IV. As ex-

TABLE III
Description of Rheology Parameters for EOC/PP and EOC/POC/PP Blends

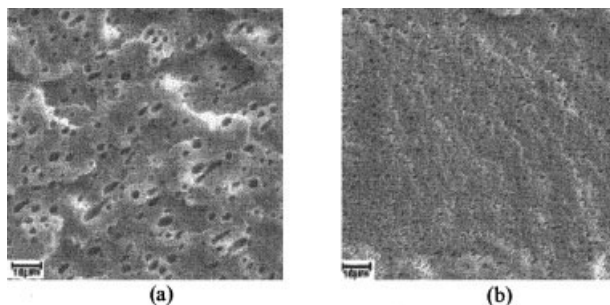| Material	η^* (0.1) (Pa · s)	ω_c (rad/s)	G_N (Pa)
EOC/PP	4.29E+08	31.6	5.18E+09
EOC/POC/PP	1.08E+09	21.5	6.30E+09

Figure 5 SEM micrographs of (a) EOC/PP and (b) EOC/POC/PP samples.

pected, the addition of the polyethylene elastomer, EOC, increased the impact strength of PP at the two different temperatures analyzed. When POC was added, a material with higher impact strength was produced. That behavior corroborate the results obtained by SEM; that is, the EOC/POC/PP blend presents smaller elastomer domains, which are more dispersed on the PP matrix and thus more able to dissipate the impact energy.

Dynamic mechanic thermal analysis results

Dynamic mechanic thermal analysis (DMTA) uses low-amplitude sinusoidal stresses to probe various molecular relaxation processes in the polymer at various temperatures. The temperature dependence of tan δ of EOC, PP, and EOC/PP and EOC/POC/PP blends is shown in Figure 6. PP presents a dispersion peak at a temperature ~15°C (Figure 6a), which can be designated as β-relaxation. According to numerous studies, β-relaxation corresponds to the glass–rubber transition temperature (T_g) in the amorphous phase. The EOC sample presents a higher dispersion peak between −50 and −25°C (Figure 6b). This dispersion is attributed to the micro-Brownian motion of amorphous domains; that is the T_g. The results in Figure 6c show that the addition of POC in the POE/PP blend shifted the peak related to the T_g of EOC to higher temperatures and the peak related to the T_g of PP to lower temperature. This result is an indication that the propylene–octene copolymer POC acts as a compatibilizer, confirming the rheological and morphological results obtained in this work.

TABLE IV
Impact Strength of PP, EOC/PP, and EOC/POC/PP

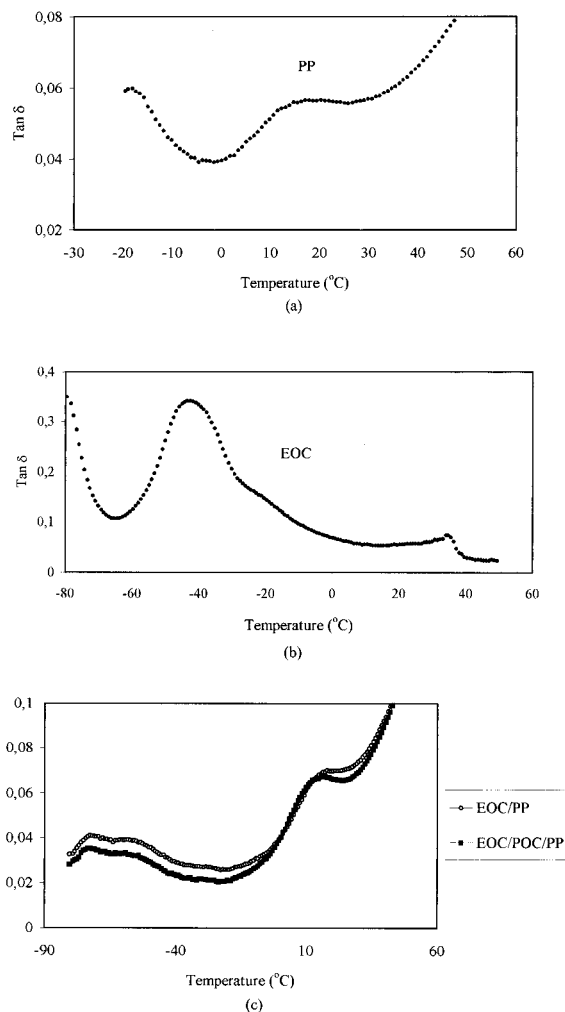| Material	Impact strength (J/m)	
	(J/m)	
	−20°C	25°C
PP	23 ± 3	40 ± 2
EOC/PP	40 ± 4	140 ± 10
EOC/POC/PP	52 ± 7	350 ± 24

Figure 6 Tan δ values of (a) PP, (b) EOC, and (c) EOC/POC/PP.

CONCLUSIONS

The results of a study concerning the effect of addition of a new metallocene propylene copolymer (POC) on the rheological, morphological, mechanical, and thermal properties of EOC/PP blend are reported. In the compositions analyzed, the addition of POC to an EOC/PP blend resulted in a material with higher viscosity and higher impact strength, indicating that POC acts as a compatibilizer in EOC/PP blend. A more detailed compatibility study is in progress to gain a more complete understanding of this subject, and results will be reported in a future paper.

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