Polymer Blends Based on Polyolefin Elastomer and Polypropylene

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ABSTRACT: A new family of homogeneous polyolefin polymers that exhibit unique molecular and rheological properties designated polyolefin elastomers (POEs) are characterized by a narrow molecular weight and high degrees of comonomer distribution. Because these copolymers are often elastomeric in nature, one of the uses for these materials is as impact properties improver for brittle polymers such as polypropylene at low temperatures. In this work a study was carried out about the effectiveness of the polyethylene elastomer (POE) as an impact modifier for polypropylene in relation to the traditional modifier EPDM. In this study the flow properties of of the POE/PP and EPDM/PP blends were also evaluated. The blends were analyzed by solid-state ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectroscopy, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). The results showed that PEE/PP and EPDM/PP blends present a similar crystalline behavior, which resulted in a similar mechanical performance of the blends, on the composition analyzed. It was also verified that the POE/PP blend presents lower torque values than the EPDM/PP blend, which indicates a better processability when POE is used as an impact modifier. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2005–2014, 1997

Key words: polymer blends; polyolefin elastomer; polypropylene

INTRODUCTION

Since 1980 an increasing utilization of polymer blends and alloys of thermoplastic materials have been observed. The main reason for that is the favorable economy.[1]

The development of materials with a full set of desired properties is not an easy task. Frequently, a new spectrum of material properties can be achieved by producing a blend with the convenient selection of components. In recent years, elastomeric rubber–plastic blends have become technologically interesting for use as thermoplastic elastomers. These materials exhibit some of the physical properties of conventional elastomers at service temperatures and are processable at elevated temperatures.[2,3]

Polypropylene (PP) is a thermoplastic with a number of desirable properties that makes it a versatile material. However, the poor impact properties, especially at low temperatures, limit some of its applications. To achieve better properties, impact modifiers have been added to PP. Among the impact modifiers commonly used for PP, ethylene–propyl-

Table I Characteristics of Polymers Samples Used

Material	PP	PEE	EPDM
Manufacturer	Polibrasil S.A.	Dow Chemical	Nitriflex
Designation	KM 6100	EG 8100	EP 57C
Density at 23°C (g/cm³)[a]	0.917	0.887	0.874
Hardness (Shore A)[b]	73.6	60.0	46.2
Melt index (g/10 min)[c]	2.1	2.0	—
Mooney viscosity ML 1 + 3 φ 100°C[d]	—	42.1	99.0

[a] Measured in our laboratory by ASTM D792.
[b] Measured in our laboratory by ASTM D2240.
[c] Measured in CENPES/PETROBRÁS laboratory by ASTM D1238.
[d] Measured in Nitriflex laboratory by ASTM D1646.

ene–diene terpolymers (EPDM) have been considered the most effective ones.[4,5]

Recent catalyst developments in polyolefin synthesis allowed the control of molecular weight distribution and the proportion of comonomer incorporation. Those emerging catalyst systems, termed single-site catalysts (metallocene type), allow polymer producers to make a much more well-defined molecule by enabling the incorporation of long comonomer chains.[6] 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.[7]

One family of these new polymers produced by Dow Chemical, known as ENGAGE polyolefin elastomers (POEs), has been commercialized. Engage POEs (>20 wt % octene comonomer) have distinctive properties when compared with elastomeric materials currently available, due to the long chain branching. POEs are aimed for competing with thermoplastic olefin impact modifiers, like EPDM.[8,9]

According to the manufacturer, POEs can compete against ethylene–propylene–diene terpolymers (EPDM) in the production of polypropylene-based blends because of their pellet form, which allows for faster mixing and expanded handling and compounding option.[10]

Thus, the aim of this work is to evaluate the effectiveness of the new polyethylene elastomer (PEE) as an impact modifier for polypropylene and verify if this new polymer can replace the conventional impact modifier—EPDM.
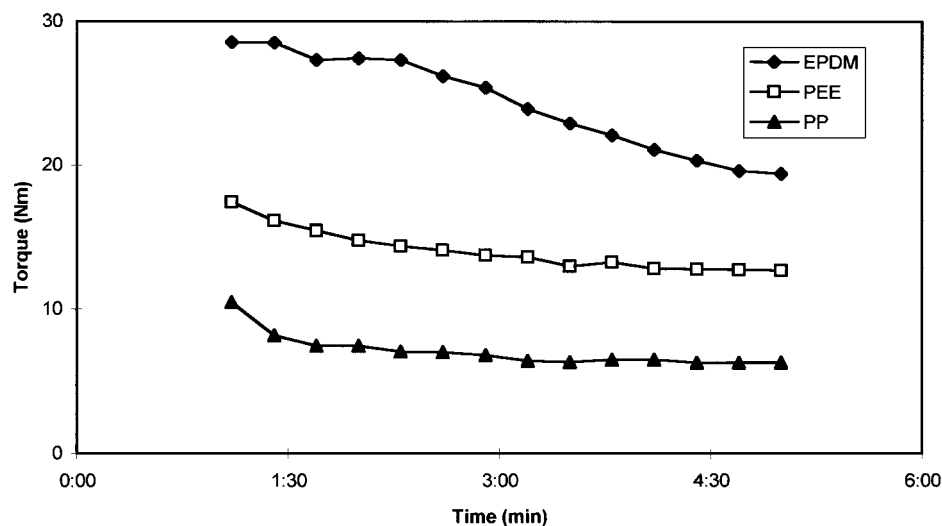

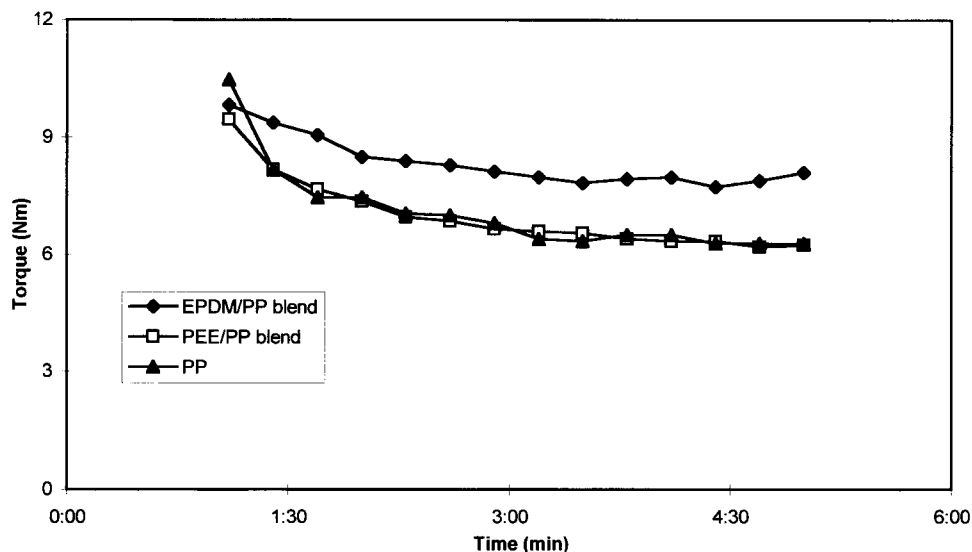
Figure 1 Torque curves of EPDM, PEE, and PP.

Figure 2 Torque curves of the EPDM/PP blend, the PEE/PP blend, and PP.

EXPERIMENTAL

Materials and Blend Preparation

Commercially available grades of the polymers polypropylene (PP), ethylene–octene copolymer (PEE), and ethylene–propylene–diene terpolymer (EPDM) with 5-ethylidene-2-norbornene (ENB) as a termonomer were used. The material specifications are listed in Table I.

The virgin polymers and PP blends were processed in a Haake Rheomix 600 internal mixer, equipped with a pair of high shear roller-type rotors. For the PEE/PP and EPDM/PP blends, with a 30 wt % of elastomer phase, the temperature of the mixing chamber was set at 200°C and the blending time was 5 min. The rotor rate was set at 70 rpm. The rheological behavior of the blends was evaluated on the basis of recorded torque versus time.

Measurements

The torque versus time curves were obtained during the processing of the pure polymers and the PP blends in the Haake Rheomix 600 internal mixer.
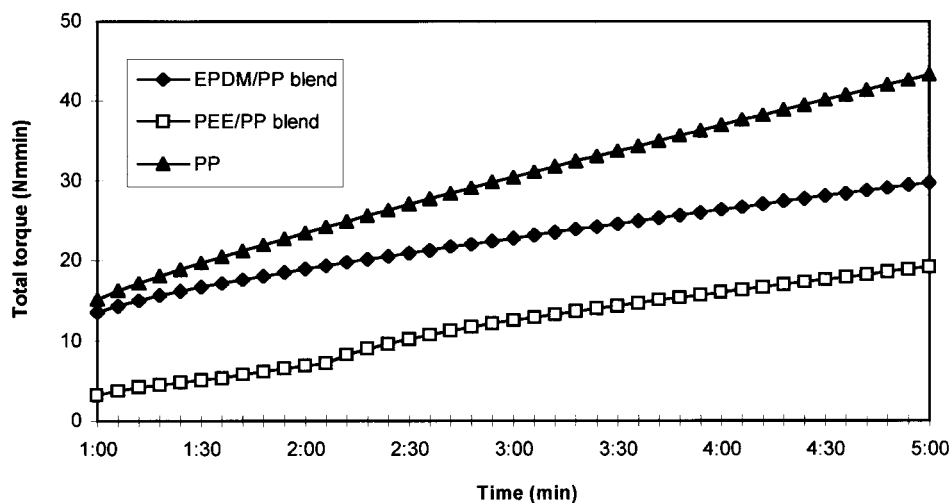

Figure 3 Total torque curves of the EPDM/PP blend, the PEE/PP blend, and PP.

Table II   Melt Flow Index of PP and PP Blends

Material	MFI (g/10 min)
PP	2.1 ± 0.5
PEE/PP	2.0 ± 0
EPDM/PP	1.3 ± 0

The melt flow index of virgin polymers and polypropylene blends were determined using an EMIC IFT 315 instrument according to ASTM D1238.

The tensile tests were conducted at room temperature (25°C and 55% RH) using samples obtained by compression molding on an INSTRON Tester (Model 4204), according to ASTM D882, at a strain rate of 50 cm/min.

Impact strength was measured according to ASTM D256 (V-notched) on an Impact Tester Microtest at different temperatures. All results were the average of at least seven measurements.

The morphology of the blends was examined in a JEOL scanning electron microscope (SEM), model JSM-5300. Samples were cryogenically fractured in liquid nitrogen and etched with hep-
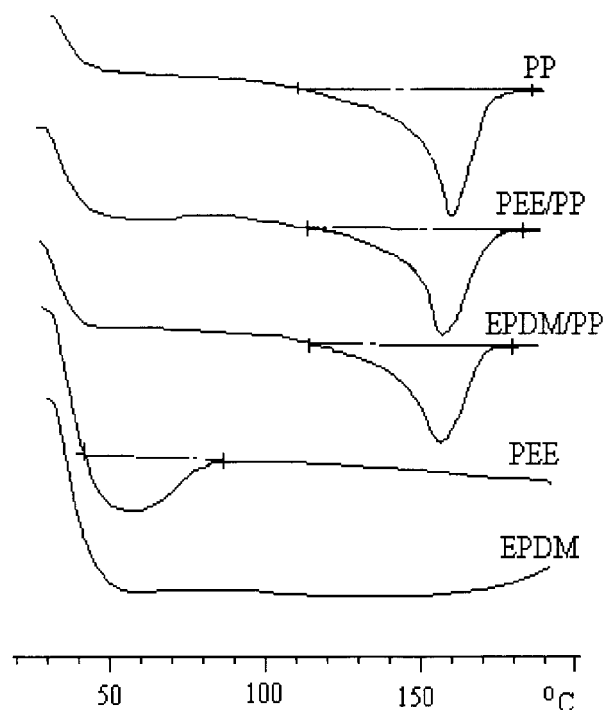
Figure 4   Melting behavior of the pure polymers and PP blends.
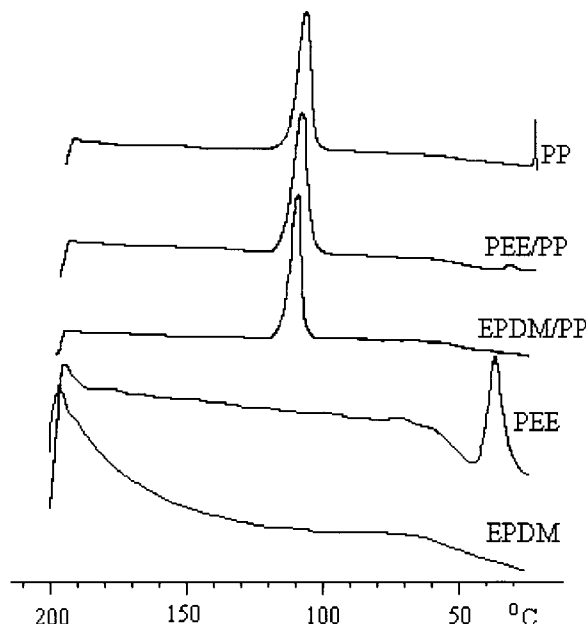
Figure 5   Crystallization behavior of the pure polymers and PP blends.

tane at 25°C to extract the elastomer phase for 5 days and then dried for about 3 h at 80°C under vacuum, followed by gold coating prior to their installation in the SEM chamber.

A Perkin–Elmer DSC-7 apparatus was used to determine the glass transition temperature (T_g) of the virgin polymers and blends. DSC tests were run at a heating rate of 10°C min^{-1} and cooling rate of 80°C min^{-1}. The melting and recrystallization behavior of the pure polymers and PP blends was also analyzed on an Perkin–Elmer DSC-7 instrument at a heating rate of 10°C min^{-1} and cooling rate of 10°C min^{-1}.

Spin-lattice relaxation times in the rotating frame, $T_{1\rho}^{H}$ s were determined from the intensity attenuation of carbon-13 peaks with increasing contact time. All NMR spectra were obtained on a Varian VXR 300 spectrometer operating at 299.6

Table III   Crystallinity (wt %) of PP and PP Blends

Sample	ΔH_r (J/g)	Crystallinity (wt %)
PP	90.0	43
PEE/PP	60.9	29
EPDM/PP	63.0	30

Table IV   Glass Transition Temperature of PP and PP Blends

Material	T_{g1} (°C)	T_{g2} (°C)
PP	−5	—
PEE	−47	—
EPDM	−42	—
PEE/PP	−54	−3
EPDM/PP	−47	−5

MHz and 75.4 MHz for ^{1}H and ^{13}C, respectively. All experiments were carried out at ambient probe temperature and were performed using gated high-power decoupling. Zirconium oxide rotor of 7 mm diameter with Kel-F caps were used to acquire the NMR spectra at rates of 4 kHz. Carbon-13 spectra are referred to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm). The ^{13}C-NMR were carried out in the crosspolarization mode with magic-angle spinning (CP/MAS) and CP/MAS with variable contact time. A range of contact time was stablished as 200 ms to 8000 ms.

RESULTS AND DISCUSSION

Rheological Behavior

Torque Versus Time Analysis

According to previous studies, it is possible to correlate torque data to viscosity of non-Newtonian materials.[11]

Figures 1 and 2 show the rheological behavior of the virgin polymers (PP, EPDM, and PEE) and blends (PEE/PP and EPDM/PP), respectively, on the basis of recorded torque versus time. The torque value in the plateau region, termed "stable torque" characterizes the viscous nature of the melt.

It can be seen (Fig. 1) that the polyethylene elastomer (PEE) has a lower value of torque than EPDM. This behavior means that PEE has a better response during processing than EPDM. It also indicates that the PEE melt viscosity, at the shear rate and temperature employed, is closer to the PP viscosity.

The torque versus time curves of PEE/PP and EPDM/PP blends (Fig. 2) show that the PEE/PP blend presents lower torque values than the EPDM/PP blend. These results indicate that a better processability of the blend should be expected when the polyethylene elastomer is used as a PP impact modifier.

The area under the curve result of the plot total torque versus time gives the energy consumption during the blend preparation. Figure 3 shows that the energy consumption of the PEE/PP blend is lower in comparison with the EPDM/PP blend, which is an advantage in terms of processability for the PEE/PP blend. This behavior is confirmed by the MFI analysis.
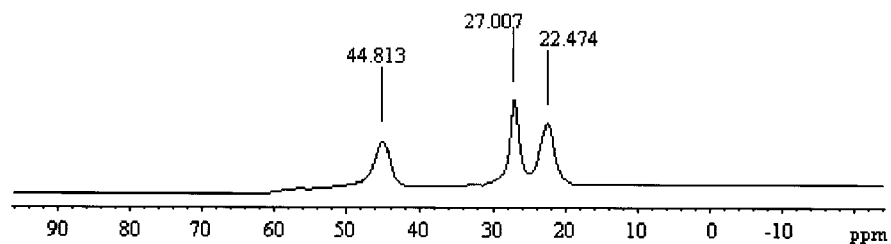
MFI Analysis

MFI is a measure of the fluidity of the molten polymers.[12] Table II shows that the PEE/PP blend presents a higher melt flow index (higher flow rate in the molten state). An increase of MFI, which means a reduction of viscosity, indicates a more significant improvement on the flow properties compared with the EPDM/PP blends.

Differential Scanning Calorimetry (DSC)
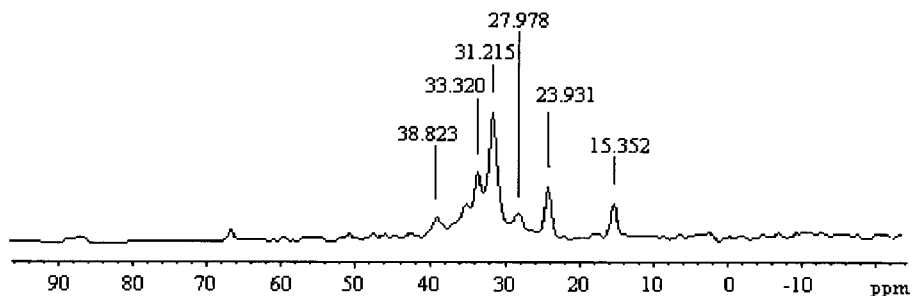
The mechanical properties of PP are determined by its crystalline structure. Any changes in that structure will result in a change of properties, so

Table V   Proton Spin-Lattice Relaxation in the Rotating Frame of PP, EPDM, PEE, and PP Blends
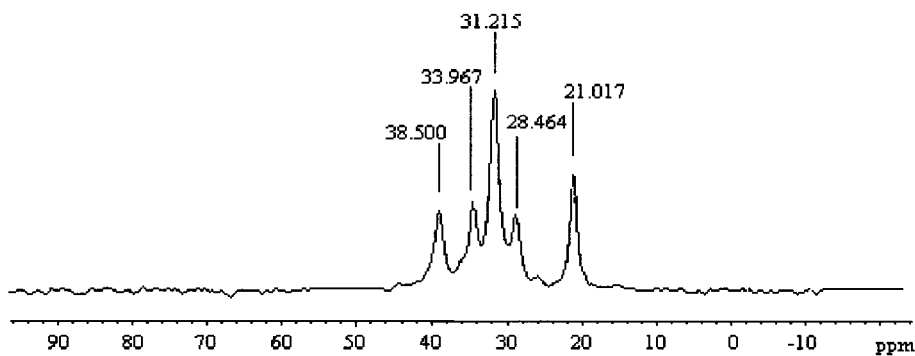
Chemical Shift δ (ppm)	$T_{1\rho}^{H}$ (ms)				
	PP	EPDM	PEE	PEE/PP	EPDM/PP
44.6	2.5	—	—	2.7	2.6
38.3	—	6.2	—	—	—
33.4	—	50.3	1.1	1.5	—
31.2	—	5.2	—	—	8.5
26.8	2.6	—	—	2.7	2.6
22.3	2.3	—	—	2.5	2.3

27.007   22.474

44.813

90   80   70   60   50   40   30   20   10   0   -10   ppm

(a)

27.978

31.215

33.320   23.931

38.823   15.352

90   80   70   60   50   40   30   20   10   0   -10   ppm

(b)

31.215

33.967

21.017

38.500   28.464

90   80   70   60   50   40   30   20   10   0   -10   ppm

(c)

**Figure 6** ^{13}C-NMR/CP/MAS spectra of (a) PP, (b) PPE, and (c) EPDM.

it is essential to determine the effect of elastomer blending on the crystalline structure as well as on the melting and crystallization behavior of PP.[12-14]

The evaluation of the effect of elastomer addition on the crystallization of polypropylene is complicated because of the sensitivity of the PP morphology to the temperature of crystallization. The conventional and most widely occurring crystal structure of PP is a monoclinic, denominated α
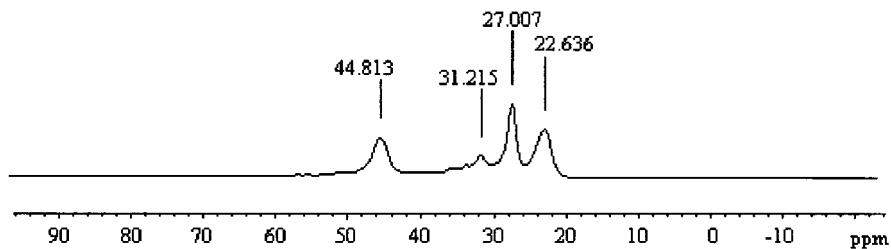
(a)
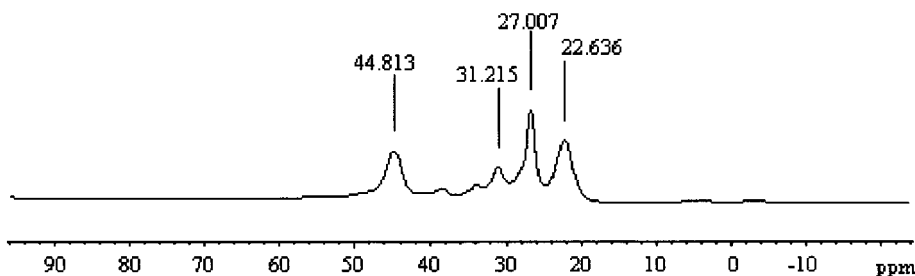
(b)

Figure 7 ^{13}C-NMR/CP/MAS spectra of (a) the PPE/PP blend and (b) the EPDM/ PP blend.

form. It is also observed that occasionally PP can crystallize in a hexagonal or β form.[12]

The primary variable affecting crystallinity in PEE and EPDM is the organization of ethylene sequences and can be represented by an ortho-rhombic unit cell as for polyethylene.[15]

DSC cooling and heating curves illustrating melting and recrystallization behavior of the pure polymers and PP blends are shown in Figures 4 and 5, respectively. Both blends show broad melt-ing behavior, which is probably related to changes on the distribution of PP crystal morphology when elastomers are added. The melt temperatures of pure PP, PEE/PP, and EPDM/PP blends occur at about 160°C, as shown in Figure 4. No melting peak was detected in the EPDM curve, character-izing its amorphous nature. However, a deflection can be observed in the PEE melting curve at about 60°C, indicating a certain degree of crystallinity.

The degree of crystallinity of the PP blends was evaluated by the ratio between the enthalpy of fusion of the blend and the enthalpy of fusion of the perfectly crystalline PP ($\Delta H_{PP} = 209$ J/g).

Table III shows the degree of crystallinity in weight percent of PP and PP blends.

As should be expected, the results show that the blends present lower crystallinity degrees in relation to pure PP. In the composition analyzed, it a difference was not observed between the PEE/ PP and EPDM/PP blend crystallinity.

Figure 5 shows that there is practically no change in the crystallization behavior of the PP matrix when different elastomers were added. The PEE/PP curve shows a peak that appears at about 40°C, indicating the presence of the crystal-line portion of PEE.

In terms of miscibility, blends are described as miscible, semimiscible, or immiscible. Generally speaking, miscible mixtures present strong inter-action between polymers; just one phase and a

Table VI   Mechanical Properties of PP and PP Blends

Material	E (MPa)	σ_b (MPa)	Toughness (MPa)	Impact Strength (J/m)	
				−5°C	23°C
PP	555 ± 5	35 ± 5	5 ± 1	25 ± 5	35 ± 5
PEE/PP	340 ± 35	15 ± 1	60 ± 1	50 ± 5	130 ± 10
EPDM/PP	320 ± 40	15 ± 1	65 ± 5	60 ± 5	140 ± 10

E, Young's modulus; σ_b, stress at break.

single sharp glass transition (T_g) are identified. For semimiscible blends, two values of T_g are detected. Immiscible blends are biphase systems in which the continuous phase is formed by the polymer that is present in higher quantity. These systems present two values of T_g that are similar to those of the two homopolymers.

Analyzing the DSC results listed in Table IV, it can be concluded that in the EPDM/PP blend, PP glass transition temperature was displaced to lower temperatures (from −42 to −47°C). This behavior can be explained by the fact the inclusions of the elastomer present a higher thermal expansion coefficient in relation to the PP matrix. The cooling of the blend results in a negative hydrostatic pressure that acts on the elastomeric particles, and thus thermal tensions that are generated can be responsible for the decrease of the EPDM glass transition temperature. The same behavior can be observed for the PEE/PP blend. The PEE glass transition temperature was displaced from −47 to −54°C. The results of DSC analysis indicate that the EPDM/PP and PEE/PP blends are immiscible on the composition analyzed.

Proton Spin-Lattice Relaxation Time

It is possible to detect, by high resolution, solid-state, pulsed Fourier-transformed (FT) ^{13}C-NMR spectroscopy, the heterogeneous domains in polymer blends and estimate their size because of the existence of a substantial relaxation time difference in the specific carbon between distinguishable regions.[16]

The measurements of proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^{\mathrm{H}}$) make possible the evaluation of blend behavior in terms of sample homogeneity, and consequently give some indication of blend miscibility.[17,18]

Table V exhibits the values of $T_{1\rho}^{\mathrm{H}}$ of the virgin polymers and the PEE/PP and EPDM/PP blends.

Analyzing the value of $T_{1\rho}^{\mathrm{H}}$, it can be concluded that the elastomers addition does not affect the values of $T_{1\rho}^{\mathrm{H}}$ of the PP. This behavior indicates that the polymers are immiscible and a phase separation has occurred. These results are in accordance with DSC analysis.

Figures 6 and 7 show the ^{13}C-NMR spectra obtained by CP/MAS technique for the virgin polymers and PP blends, respectively.

Mechanical Properties

Tensile Strength

Three elements dictate the mechanical properties of polymer blends: crystallinity, morphology, and the interfacial properties. The first one can be estimated from the DSC experiments, the second one from detailed morphological studies, and the last one may be deduced from the mathematical models.

Table VI shows that PEE/PP and EPDM/PP blends present similar tensile properties—stress at break (σ_b); Young's modulus (E); and toughness. These results indicate that no significant changes in tensile properties can be related to the similar crystallization behavior of the blends. As expected, the addition of elastomers to PP matrix resulted in a decrease of stress at the break and Young's modulus, and an increase of toughness. These data can be viewed as the result of the lowering on the crystallinity of the blends in relation to pure PP.

Impact Strength

The impact test is commonly accepted as a measure of the toughness of a material. The results
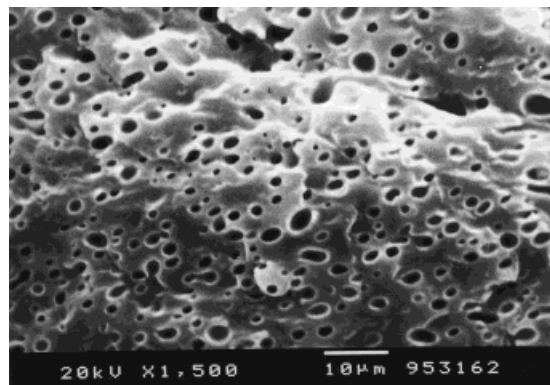
(a)
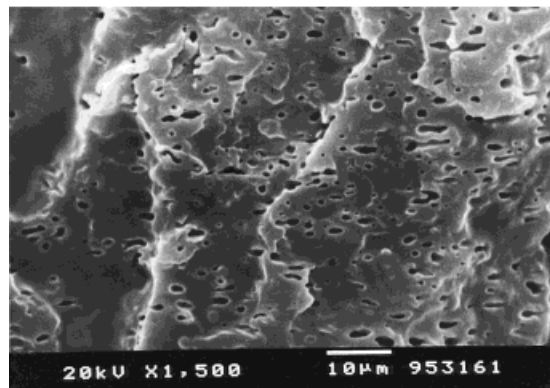
(b)

Figure 8 Scanning electron micrographs of (a) the PPE/PP blend and (b) EPDM/PP.

of the Izod tests provide a comparative basis for estimating the relative shock resistance of polymer materials.

Table VI also presents the values of impact strength at two different temperatures of PP, PEE/PP, and EPDM/PP blends. In the conditions employed in this work, PEE/PP and EPDM/PP blends presented similar impact strength. These results can also be related to the similar crystallinity of the PP blends.

The State of Dispersion of the Blends

It is a well-established fact that the state of dispersion in a heterogeneous polymer blend greatly influences its rheological behavior.[19-23] Therefore, it is meaningless to discuss the rheological behavior of the heterogeneous polymer blends without discussion their state of dispersion. It should be pointed out that the state of dispersion in a het-

erogeneous blend system is determined by the rheological properties of the constituent components, and the processing conditions under which the blends were prepared.

To investigate the state of dispersion of the two blend systems prepared in this work (PEE/PP and EPDM/PP blends), we have examined the two systems with the aid of scanning electron microscopy.

Figure 8 shows representative SEM micrographs of cryogenically fractured surfaces of compression-molded specimens of EPDM/PP and PEE/PP blends.

The SEM micrographs show that PEE and EPDM particles are uniformly distributed in PP matrix. The micrographs also show that PEE domains are much more well distributed and more regular than the EPDM domains. That morphology can be attributed to the similar melt behavior of PP and PEE. These results are in accordance with the results of torque and MFI analysis.

CONCLUSION

It was verified that there is no significant difference in the crystalline behavior between PP blended with PEE or with EPDM. This fact is responsible for the similar mechanical behavior of the blends.

In spite of the fact that the impact efficiency of an elastomer is an important performance property in designing impact resistant thermoplastic blends, the energy consumption cost during the processing must also be considered.

Although the impact strength of PEE/PP blend is slightly lower when compared with the EPDM/PP blend, it is important to consider that PEE offer significant cost-performance advantages over EPDM when used as an impact modifier of PP. A detailed compatibility study is in progress to gain a more complete understanding of this subject, and results will be reported in a future article.

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