

Behavior of Poly(ethylene-co-olefin) Polymers as Elastomeric Materials

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ABSTRACT: The properties of two new ethylene- α -olefin copolymers, namely, ethylene-1-hexene copolymer (EHC) and ethylene-1-octadecene copolymers (EOC), synthesized via metallocene catalysts were evaluated. The copolymerization was carried out in an autoclave reactor with Et(Indenyl)₂ZrCl₂/methylaluminoxane as a catalyst system. These single-site catalysts (metallocene type) allow one to obtain very homogeneous copolymers with excellent control of the molecular weight distribution and proportion of comonomer incorporation. So, copolymers with 18 mol % comonomer in the case of EHC and 12 mol % for EOC were shaped, and activities around 100,000 kg of polymer mol⁻¹ of Zr bar⁻¹ h⁻¹ were reached. The properties of these co-

polymers were compared with other commercial elastomers, such as ethylene-propylene copolymers synthesized by Ziegler-Natta catalysts and an ethylene-octene copolymer obtained via metallocene catalysts. The results show that these new copolymers, in particular, EOC, had excellent elastomeric properties. Furthermore, they had a relatively low viscosity, which implied a good response during processing. Moreover, the effectiveness of these copolymers as impact modifiers for polyolefins was also studied. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3008–3015, 2004

Key words: metallocene catalysts; elastomers; blends

INTRODUCTION

Because of new metallocene catalysts, the plastics business is facing one of its most significant periods of innovation in decades, the beginning of an era of custom-made commodity plastics with high-tech properties.¹ In this field, the homopolymers and copolymers of ethylene with long-chain α -olefins obtained via these metallocene catalysts are one of the most important commercial materials; they have been characterized by their major production and consumption in the last few years because of many new different applications.² Few materials can match the versatility and economy of modern polyethylene and polypropylene (PP); therefore, these are the largest selling plastics.^{3,4}

The average plastic is a mixture of polymer chains and structures whose properties are hard to predict and which demand many compromises in their uses. In contrast to the conventional multisite Ziegler-Natta

catalysts, metallocene-based catalysts allow for a higher degree of comonomer incorporation, whereas the uniform reactivity allows the synthesis of very uniform homopolymers and copolymers.⁵ In fact, the presence of an aromatic planar ring, steric and electronic effects, and the bridge group that restricts the mobility of the metallocene play an important role in the control of stereochemistry, molecular mass, and the incorporation of α -olefin comonomers.^{6–8}

In our research laboratories, we have been studying the copolymerization of ethylene with different α -olefins, particularly 1-hexene and 1-octadecene, with a series of metallocene catalysts; the catalytic system Et(Indenyl)₂ZrCl₂/methylaluminoxane (MAO) is the one that permits high catalytic activity, good incorporation of the comonomer, and high molecular weight. For ethylene-1-hexene copolymer (EHC) and ethylene-1-octadecene copolymer (EOC), we have reached activities around 100,000 kg of polymer mol⁻¹ of Zr bar⁻¹ h⁻¹ under optimal conditions (pressure = 2 bar; agitation (ω) = 600 rpm; mole no. of catalyst (n) = 3.7×10^{-7} mol of Zr; Al/Zr = 6000) with control over the intrinsic properties such as comonomer incorporation. With regard to the properties of the obtained polymer, both the thermal and mechanical properties can be well controlled, according to the comonomer incorporated to the main chain. So, in this study we produced polymers with the properties of elastomeric materials. These copolymers were produced with EHC with 18

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TABLE I
Characteristics of the Copolymers

Material	Manufacturer	Designation	Melt flow index (g/10 min)	Mooney viscosity ML 1+4 at 125°C ^a	Ethylene content (%)
PP	Repsol	PP 050	6.0		
EPR 404	Exxon Mobil	Vistalon 404		23.4	45
EPR 504	Exxon Mobil	Vistalon 504		26.9	60
EPR 805	Exxon Mobil	Vistalon 805		32.1	78
Engage 8550 (PEE)	DuPont Dow Elastomers	Engage 8550		6.5	86.2
EHC				3.4	81.9
EOC				2.6	87.9

^a Measured in our laboratories according to ASTM D 1646.

mol % comonomer incorporated and with EOC with 12 mol % comonomer incorporated.

The goal of this study was to analyze the properties of these new copolymers as compared with elastomeric materials currently available, such as ethylene-propylene copolymers (EPRs) synthesized via Ziegler–Natta catalysts and ethylene–octene copolymers (PEEs) obtained with metallocene catalysts. Furthermore, we attempted to study the effectiveness of these new poly(ethylene- α -olefins), EHC and EOC, as impact modifiers for PP and to evaluate the possibility of their use as substitutes for conventional impact modifiers.

EXPERIMENTAL

Materials

Commercially available grades of the polymers PP, EPR (EPR 404, EPR 504, and EPR 805), and PEE (Engage 8550) were used in this study. Their technical specifications are listed in Table I. We purified commercial toluene by refluxing it over metallic sodium, with benzophenone as the indicator. We purified the 1-octadecene comonomer (Aldrich, Madrid, Spain) by distilling it over metallic sodium. Polymerization-grade ethylene was deoxygenated and dried by passage through columns of BASF R3-11 catalyst and 0.4-nm molecular sieves (Sao Paulo, Brazil). Commercial MAO and the catalyst *rac*-Et(Ind)₂ZrCl₂, from Witco (Bergkamen, Germany) and Boulder Scientific Co., were used without further refinement. All of the manipulations were carried out in an inert nitrogen atmosphere. All of the vulcanization system ingredients, oxide zinc, perkadox 14-40 [di-(2-*tert*-butylperoxyisopropyl)benzene], and the peroxide activator, were used as received without further purification.

Copolymerization

All of the copolymerizations were carried out in a 1-L autoclave reactor (Parr, Illinois) with toluene as the

solvent at a reaction temperature of 60°C. The reagents were introduced into the reactor in following order: toluene, comonomer, MAO, and the required amount of catalyst solution. The reaction mixture was degassed, and then, ethylene was introduced until a pressure of 2 bar was reached. After 30 min, polymerization was stopped by the addition of a 2 vol % HCl/methanol solution, and then, the polymer was recovered by filtration. It was washed first with a HCl/methanol solution and then with acetone to remove all of the unreactive comonomer; finally, it was dried.

Preparation of the materials

Rubber compoundings were prepared by mixture on an open two-roll mill (friction ration = 1:1.4) at room temperature. The compounding recipes are given in Table II. Curing times were previously determined with a Monsanto moving die rheometer (MDR 2000; Swidon, England, UK). The compounds were then compression-molded with an electrically heated hydraulic press (Gumix, Barcelona, Spain) at 170°C to their respective optimum cure times (t_{95}' s; Table III). Specimens were mechanically cut out from the vulcanized plaques.

PP–elastomer blends, PP–EPR 404, PP–EPR 504, PP–EPR 805, PP–PEE, PP–EHC, and PP–EOC with a 30 wt % of elastomer phase were processed in a Haake Rheomix 600 internal mixer equipped with high-shear roller-type rotors (Akron, OH). The temperature of the mixing chamber was set to 190°C, and the blending time was 10 min. The rotor speed was set to 60 rpm.

TABLE II
Recipes of the Rubber Compounds

Copolymer	100
Zinc oxide	2
Perkadox 14–40	5
Activator OC	1

TABLE III
Curing Characteristics of the Materials at 170°C

	t_{s2} (min)	t_{50} (min)	t_{95} (min)	CRI (min^{-1})	S_{max} (dNm)	S_{min} (dNm)	ΔS (dNm)
EPR 404	2.20	2.83	21.05	5.32	5.47	0.54	4.93
EPR 504	1.10	2.39	18.19	5.84	11.56	0.59	10.97
EPR 805	0.81	1.80	15.46	6.83	17.64	0.94	16.70
PEE	1.70	3.74	18.78	5.76	12.93	0.13	12.80
EHC	2.80	5.41	20.95	5.52	8.14	0.10	8.04
EOC	2.85	5.65	21.55	5.43	6.87	0.08	6.79

Immediately after the completion of mixing, the materials were compression-molded for 15 min at 190°C into 0.2 mm thick plaques before testing.

Characterization

The amount of comonomer incorporated was estimated by ^{13}C -NMR spectroscopy (Fig. 1). Measurements were performed at 80°C on a Varian XL-200 or XL-300 spectrometer (Harbor City, CA). The samples were dissolved in *o*-dichlorobenzene. Benzene- d_4 (20%) was used as an internal lock, and chromium(III) triacetylacetonate was used as a paramagnetic substance to reduce the relaxation time. The intrinsic viscosities were determined in decahydronaphthalene (decalin) at 135°C with a Viscomatic-sofica viscometer (Houston, TX).

Tensile stress-strain properties were measured at room temperature on a Instron dynamometer (model 4301) (Buckinghamshire, UK) according to ISO 37-1977 for rubber compounds and ASTM D 638M for the PP-elastomer blends. Tests were carried out at a crosshead speed of 500 mm/min for rubber compounds and, for PP-elastomer blends, 5 mm/min until a deformation of 20% was reached and then at 50 mm/min at break. Compression set measurements were performed according to ISO 815-1972 for 24 h at 70°C with 25% compression. Rebound resilience measurements were carried out on a Schob pendulum (Oberdischingen, Germany) according to ISO 4662-1978. Shore hardness was measured with a Bareiss Rockwell tester (Oberdischingen, Germany) according to ASTM D 2240. The tension sets under constant elongation were calculated according to ISO 2285 for 24 h at room temperature.

Impact experiments were carried out according to ASTM D 256 (v-notched) at room temperature in an Izod pendulum Ceast mod. Resil 25 (New York), with an impact speed of 3.48 ms^{-1} recording the maximum force and the energy to fracture. The notches were prepared in a Ceast electrical notching apparatus at 20% of the thickness, and the angle of the V side grooves was 45°. Impact strength was expressed in terms of the energy absorbed per meter of notch. Impact properties were the average of at least seven

measurements. The rheological measurements were performed with a Rheometric Scientific ARES N2 dynamic mechanical spectrometer (Althengstett, Germany) with parallel plate geometry. Tests were carried out in dynamic frequency modes at 190°C. Dynamic shear properties were determined as a function of angular frequency in the range 0.1–500 rad/s. The amplitude strain was maintained at 5%.

To analyze the morphology of the blends, the impact fractured surface of several samples were observed in a Philips XL30 ESSEM scanning electron microscope (Eindhoven, The Netherlands). Fracture surfaces of the test specimens were sputtered with gold before observation in the scanning electron microscopy (SEM) chamber.

RESULTS AND DISCUSSION

Characterization of the copolymers

Processing characteristics

The curing characteristics, expressed in terms of the cure times, including scorch time (t_{s2}), t_{50} , and t_{95} , and torque values, maximum torque (S_{max}) and minimum torque (S_{min}), respectively, and change in torque (ΔS), measured as $S_{\text{max}} - S_{\text{min}}$, for the studied materials are given in Table III. t_{s2} is the time taken for the S_{min} value to increase by two units. It is a measure of the premature vulcanization of the material. The results indicate that the new copolymers of 4 poly(ethylene- α -olefins), in particular, EOC, exhibited better scorch safety. For the EPR family, t_{s2} became shorter with increasing ethylene content in the copolymer. So, EPR 805 showed the minimum t_{s2} . t_{95} is the vulcanization time required to obtain optimum physical properties. t_{95} decreased with increasing ethylene content in the copolymer in the EPR commercial series. In addition, the t_{95} values of the new copolymers EHC and EOC were similar to that of EPR with a low ethylene content (EPR 404). The cure rate index (CRI) is a measure of the fast curing nature of the rubber compounds and is calculated by the following equation:

$$\text{CRI} = 100 / (t_{90} - t_{s2}) \quad (1)$$

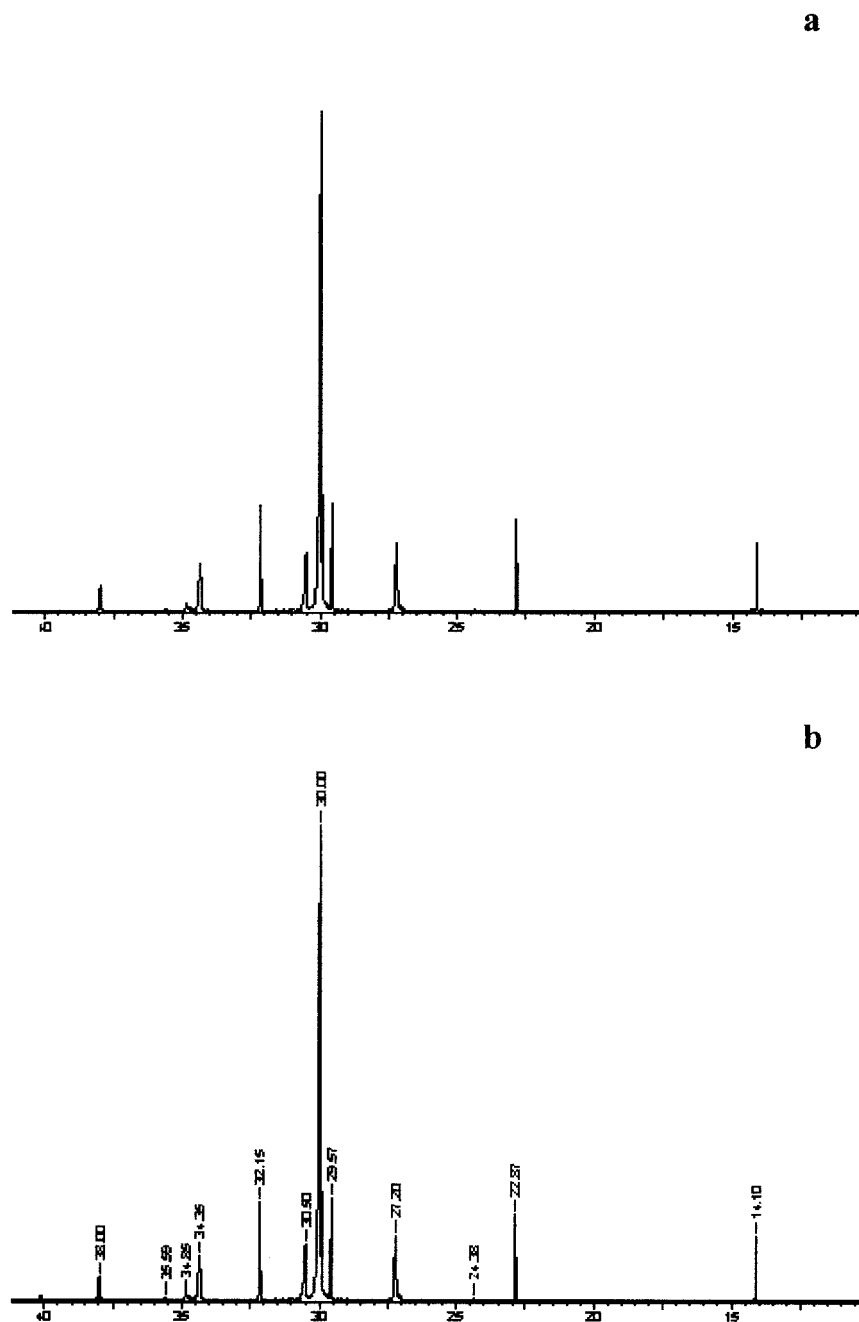


Figure 1 ^{13}C -NMR spectroscopy.

The CRI values of the rubber compounds are expressed in Table III. In EPR family, EPR 805 had the highest CRI values and decreased as the ethylene content in the copolymer decreased. The CRI values of the new copolymers were closer to those of PEE and EPR 404.

S_{\min} in the rheocurves is an index of the viscosity and indicates the extent of the mastication. As shown in Table III, a lower viscosity for EHC and EOC was expected. These results were in concordance with the measurements of Mooney viscosity reported in Table I. Com-

pared with commercial PEE and EPRs, EHC and EOC showed lower Mooney viscosities. This suggests that the new copolymers, in particular, EOC, could be processed with a evident economic advantage. In addition, it was easily observed that for the EPR family, S_{\min} increased with increasing ethylene content, which indicated greater processing difficulty for EPR 805. The S_{\max} in the elastograph was a measure of the crosslinking density. EPR 805 showed the maximum crosslinking density, which gradually decreased as the ethylene content in the copolymer decreased.

TABLE IV
Mechanical Properties of the Elastomers

	EPR 404	EPR 504	EPR 805	PEE	EHC	EOC
50% strength (MPa)	0.21	0.38	0.78	1.0	0.24	0.22
100% strength (MPa)	0.31	0.50	1.1	2.1	0.4	0.37
300% strength (MPa)	0.56	—	—	—	1.0	0.63
Maximum strength (MPa)	0.58	0.62	1.7	3.8	1.1	0.69
Elongation at break (%)	326	189	224	292	308	343
Shore A hardness	32.1	45.8	78.1	82.8	42.1	36.6
Resilience	49.5	59.5	57.5	40	51.5	54.5
Compression set (%)	6.5	11.3	17.4	28.6	6.9	6.7
Tension set at elongation site (%)	11.0	23.2	58.6	41.9	11.5	9.2

In addition, ΔS values indicated an important reduction of processing energy consumption for the new copolymers. In fact, EHC and EOC showed similar values to the corresponding EPRs with low ethylene contents (EPR 404 and EPR 504). Both EHC and EOC, although containing high ethylene percentages (82 and 88%, respectively), presented better processing conditions when compared to their EPR 805 and Engage 8550 counterparts.

Mechanical properties

The mechanical characterization of pristine copolymers was also evaluated, and the results are reported in Table IV. As expected, the thermoplastic character of EPR was higher when the ethylene content in the copolymer was higher. So, EPR 805 had the highest tensile strength, modulus at different elongations, and hardness values, which decreased with increasing ethylene content in the copolymer. However, this improvement of stiffness was inevitably accompanied by a clear reduction in the elastic behavior of the material. That is, a considerable decrease in the resilience and elongation set and a marked increase in the compression set with increasing ethylene content in the copolymer were observed.

Likewise, the thermoplastic character of new EHC and EOC was markedly lower compared to their counterparts EPR and PEE. That is, a considerable decrease in the tensile strength and modulus and hardness was observed. Nevertheless, EHC and EOC showed better elastomeric properties, which was reflected by a sensible increase in the resilience and tension set at constant elongation and a clear decrease in the compression set. This was particularly evident in the case of EOC, probably because of the higher long-chain branching. It is also of interest to point out that the mechanical properties of the new copolymers were similar to those of EPR with low ethylene contents (EPR 404 and 504).

Characterization of PP-elastomer blends

As has been widely mentioned in the literature,^{9–13} one of the more important industrial applications of

these copolymers is as impact modifiers of polyolefins. To evaluate the effectiveness of the new EHC and EOC as impact modifiers for PP, several PP-elastomer blends were prepared. Rheological analysis and mechanical characterization (tensile and impact properties) of the blends were carried out. SEM micrographs were also used to determinate the state of dispersion of the two blend systems and the rubber particle size.

Rheological behavior

The flow properties of the materials studied in the molten state were analyzed by rheological studies. The variation of the complex viscosity (η^*) as a function of the angular frequency for the PP-elastomer blends is shown in Figure 2. It was easily observed that the η^* of all samples gradually decreased with increasing angular frequency, indicating a typical pseudoplastic behavior of these materials (shear thinning). The pseudoplastic nature was given from random oriented and highly entangled state of the polymer chains, which on application of high shear rates, got disentangled in the orientation of the force and became oriented, resulting in a reduction in the viscosity.¹⁴ The viscosity of the PP-EPR blends gradually increased as the ethylene content in the copolymer increased. Thus, the PP-EPR 805 blend showed the highest viscosity. It is important to note that the viscosity of the blends containing new copolymers, EHC and EOC, was lower than those containing PEE or EPR 805. These results supported an indication that a better response of the blend during processing should be expected when the new copolymers are used as PP impact modifiers. In this case, EOC was the most effective.

Mechanical characterization

Mechanical characterization of the PP-elastomer blends was also carried out, and the results are reported in Table V. As expected, the addition of the rubbery phase to the PP matrix resulted in a decrease in the maximum stress and Young's tensile modulus

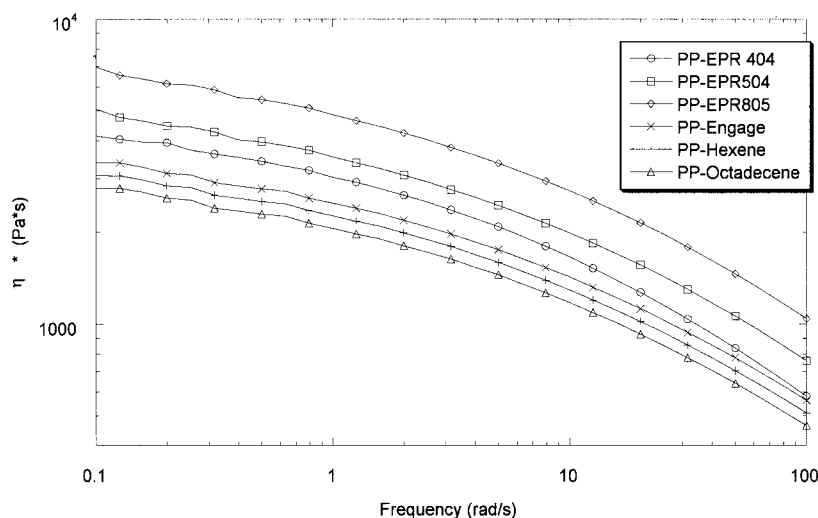


Figure 2 Variation of η^* with angular frequency at 180°C for all of the materials.

and in an increase in toughness. These data can be viewed as the result of the decrease in the crystallinity of the blends in relation to pristine PP. In general, polymer blends have large interfacial tensions and poor interfacial adhesions and, thus, exhibit poor mechanical properties relative to the composition of their constituents.¹⁵

These behaviors were largely dependent on the ethylene content in the copolymer. So, the tensile properties of the PP-EPR blend increased as the ethylene percentage in the copolymer increased. Thus, the PP-EPR 805 blend presented a higher Young's modulus and tensile strength, whereas the deformation at break of the material decreased. In addition, the blends containing Engage 8550 (PEE) showed higher modulus and strength values than those prepared with the new copolymers. Nevertheless, the deformation at break was higher for those blends containing EOC and EHC as the elastomeric phase. Moreover, although there was a high ethylene content in the new copolymers, the tensile properties of PP-EOC and PP-EHC blends were similar to those of the PP-EPR 404 blend.

The notched Izod impact strength of elastomer-modified PP blends are also reported in Table V. The

TABLE V
Mechanical Properties of the PP-Elastomer Blends

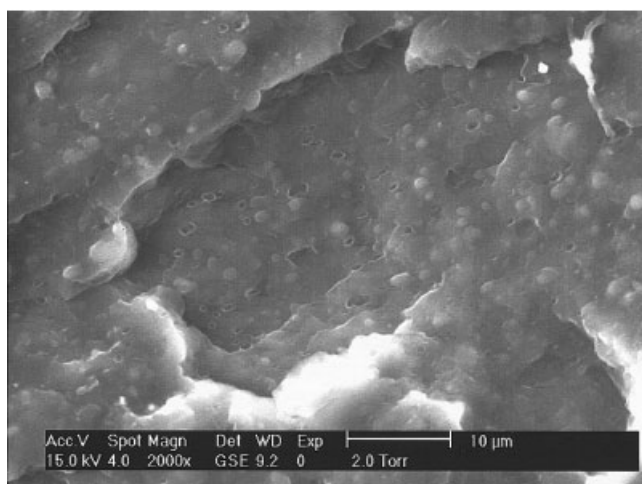
	Young's modulus (MPa)	Maximum strength (MPa)	Deformation at break (%)	Impact strength (J/m)
PP	1050	29.5	256	38
PP-EPR 404	521	13.8	280	115
PP-EPR 504	636	14.6	36	97
PP-EPR 805	700	16.2	7.6	70
PP-PEE	790	19.3	17.0	140
PP-EHC	662	15.3	115	124
PP-EOC	565	16.2	250	135

impact test is commonly accepted as a measure of the toughness of a material. The PP impact strength markedly increased in all of the cases with the addition of the elastomers, indicating their function as impact modifiers for polyolefins. This can be explained by the fact that the rubbery phase was highly deformed during the impact test and, thus, absorbed a part of impact energy. The rubber domains deformed because the shear yielded; this is considered the main mechanism of impact toughness of polyolefin-elastomer blends at the service temperatures.¹⁶⁻¹⁸ In the EPR family, the capability of these elastomers as impact modifiers for PP decreased with the ethylene content in the copolymer. Thus, the PP-EPR 404 blend showed the highest impact strength. In addition, the impact strengths of the blends prepared with the copolymers of poly(ethylene-co-olefins) were higher than those of the PP-EPR blends. These results allow for the possibility of using these new copolymers as substitutes for conventional impact modifiers, such as EPR.

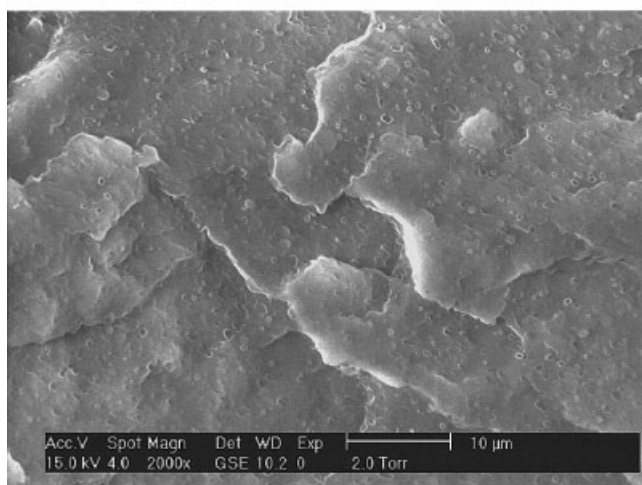
These results find an explanation in terms of the relation of viscosity between the minor phase (elastomer) and the major phase (PP). Thus, when the viscosity of the elastomer was relatively low (PEE, EHC, and EOC), it was possible to obtain blends with smaller rubber particles well dispersed in the continuous matrix. This was more difficult with increasing viscosity of the elastomer. In addition, we assumed that a decrease in the rubber particle size was intimately related with enhancement of the impact strength of the material.¹⁹

Morphological analysis

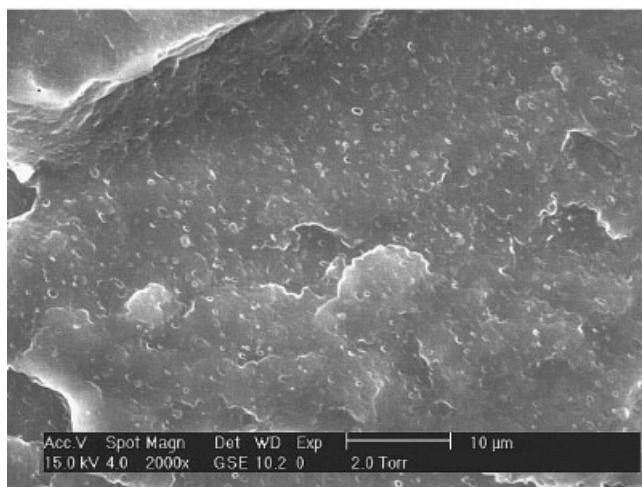
The notched Izod fracture surface of the blends was analyzed with SEM. Figure 3 shows SEM micrographs of the fracture surface of PP-EPR 805, PP-PEE, and



(a)



(b)



(c)

Figure 3 SEM images of the (a) PP-EPR 805, (b) PP-PEE, and (c) PP-EOC blends.

PP-EOC. The micrographs indicate the immiscibility of this type of system, showing clearly two separated phases, where the elastomer formed small particles with the appearance of droplets finely distributed in a continuous matrix of PP. However, the blends prepared with elastomers of lower viscosity, such as PEE and EOC, were much better distributed and more homogeneous compared to those containing EPR 805. The state of dispersion in a heterogeneous blend system is determined by the rheological properties of the constituent component and the processing conditions under which the blends are prepared.²⁰

The results also show that the ethylene- α -olefin copolymers, PEE and EOC, presented a lower rubber particle size in comparison with EPR 805, which may have been, as mentioned previously, due to their lower viscosities. This was particularly evident for EOC. These results demonstrated the good properties of new copolymers as impact modifiers for PP.

CONCLUSIONS

The properties of two new ethylene- α -olefins copolymers synthesized via metallocene catalysts were compared versus other conventional elastomers. The results shown the low viscosity of these new elastomers, which implies a good response during processing and, in consequence, offer significant cost-performance advantages. Also, the effectiveness of the new elastomers as impact modifiers for PP was demonstrated. This can be understood in terms of the low viscosity of the new copolymers, which will allow one to obtain blends with smaller rubber particles. This was corroborated by SEM observations, where it was also observed that the rubber particles were finely dispersed in the PP continuous matrix.

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