

Effect of Heterophasic or Random PP Copolymer on the Compatibility Mechanism between EVA and PP Copolymers

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ABSTRACT: Compatibility mechanisms between EVA and PP copolymers (C-PP) blends have been studied as a function of the type of copolymer, using a heterophasic PP copolymer (PP-EP) and a random PP copolymer (PP-*r*-EP), with similar ethylene content. The morphology and thermal and mechanical properties of PP/EVA blends with different levels of EVA containing 28% vinyl acetate (VA) were determined. The obtained results indicated compatibility for both systems showing interactions at the amorphous interfaces; however, this interaction was higher for the PP-*r*-EP/EVA, which showed a single glass transition temperature and changes in the PP crystalline fraction

(changes in the fusion temperature and in the diffraction patterns). The evolution of the morphology from isolated spherical domains (20% EVA) to elongated shapes (40% EVA) was related to the observed changes in thermal and mechanical properties. The impact strength and deformation properties showed significant improvement with increasing EVA content above 40% where the highest values of elongation for the PP-*r*-EP and of impact strength for the PP-EP were obtained. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2290–2297, 2009

Key words: PP-EP/EVA; blends; compatibility

INTRODUCTION

Polymer blending, rather than synthesis of new polymer, has become one of the most interesting means to obtain new materials with specific properties.¹ Some properties can be combined by blending different polymers together, and some properties can even be improved in comparison to individual components. Miscibility and compatibility in polymer blends are directly related to the final properties of polymer blends.^{2,3} Miscibility is generally obtained in polymers with molecular affinity between the blend components, however only a few polymers have this affinity. The enhancement of properties in a polymer blend is usually called compatibility, which is associated with a stable morphology, polymer affinity and ease of mixing.^{4,5}

Among the wide variety of polymer blend systems, blends of PP with elastomeric materials have been widely studied with the main aim of enhancement of impact strength. A particularly interesting blend is PP/EVA because of the ready availability of

these materials, principally as recycled materials. These blends, considered as immiscible, have been widely studied to elucidate the compatibility mechanisms.^{6–12} Gupta et al.,⁷ have studied the morphology, rheology and mechanical properties of PP/EVA blends, finding that the impact strength was enhanced with higher than 30% EVA content, and that the impact strength was also a function of the VA (9, 12, and 19%) content of EVA which was related to the reported morphologies. An increase on the mechanical properties of blends of iPP and EVA, when polypropylene grafted maleic anhydride (PPgMA) and hydroxylated EVA (EVAOH), were used as compatibilizers, has been reported.¹³ The impact properties of EVA/iPP systems was improved when calcium carbonate was included as a reinforcement.¹⁴ It has been reported ternary blends of PP, EVA and carbon black (CB)¹⁵ in which an increase in dynamic modulus and viscosity was observed when the concentration of EVA/CB increased and when multiple passes in the extruder was performed. This was attributed to a decreased the phase size of these blends. Blom et al.¹⁶ found that at low contents of EVA (1–6%) the impact strength and the puncture resistance of PP/EVA (28 y 33% de VA) blends were significantly increased. The increase in mechanical properties was attributed to three factors: the elastomeric nature of the modifier, the interfacial adhesion between EVA and PP

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and the size and distribution of the EVA phase. McEvoy and Krause¹⁷ studied these blends and proposed that the difference in crystallinity between polymers favored an interfacial mechanical interlocking of the elastomer phase into the PP phase enhancing the impact strength of the blend. Other studies have been focused on chemical modification of PP^{6,18} and EVA¹⁰ trying to enhance the interfacial interactions between them, achieving in some cases a partial miscibility. Several methods have been reported to prepare polymer blends including solution mixing, mechanical mixing and *in situ* polymerization.^{19–21} The greatest interest has been focused on mechanical mixing^{22–24} because this is generally considered more economical, more flexible for formulation, and involves compounding and fabrication facilities commonly used in commercial practice.

In our research group, different studies on this type of blend have been performed. In one study of PP/EVA blends¹¹ the compatibility of the system at contents of EVA (28% of VA) above 40% was reported where a T_g shift and an enhancement of the impact strength and elongation at break was observed. This was attributed to the morphology evolution and to the interaction between amorphous interfaces. Other recent studies²⁵ were conducted using heterophasic copolymers (PP-EP) with different ethylene content (5–24%) in blends with EVA (28% of VA) in which an amorphous compatible phase with a single T_g was reported. In this study, two morphological transitions were observed. The first one occurred at an 80/20 ratio where the morphology changed from spherical voids to interconnected voids and a second transition occurred at a 60/40 ratio where the morphology changed from interconnected voids to fibrous crystals. These morphological changes occurred simultaneously with the enhancement of the system compatibility, indicated by the trend of the blend to develop a single T_g , and with the increase in elongation at break, and in a lesser manner, with the increase in impact strength.

In this work we report a comparative study between blends of PP copolymers; heterophasic (PP-EP) and random (PP-*r*-EP) with EVA (28% of VA). The main goal of this work was to elucidate the morphologic effects on the compatibility mechanisms of these types of blends, as a function of the type of PP copolymer (heterophasic and random) and its influence on the mechanical properties.

EXPERIMENTAL

Materials and blend preparation

Two commercial PP copolymers from Profax were used. A heterophasic (PP-EP) with 5 wt % of ethyl-

ene, MFI = 7 dg/min, and a random (PP-*r*-EP) with 3.5 wt % of ethylene, MFI = 11 dg/min. The poly (ethylene vinyl acetate) (EVA) was from Exxon and contained 28% VA and had a MFI of 6.3 dg/min.

PP/EVA blends with EVA concentrations of 10, 20, 40, 60, and 70 wt % were prepared in a twin screw W and P ZSK-30 extruder, operating at 300 rpm with feed-die temperature profile of 180, 190, 190, 190, and 200°C. The screw configuration used in the ZSK-30, directly affects the residence time and the shearing exerted upon the sample. The screw configuration used, has two kneading sections of 28 mm. It has a reverse conveying section of 10 mm; and has a normal conveying section. Injection molded ASTM samples for mechanical property evaluation were prepared using a Battenfeld BA 750 CDK injection molding machine.

Techniques and methods

The real ethylene content was determined in the PP copolymers (PP-EP and PP-*r*-EP) using an Infrared spectrometer FTIR Nicolet 550 4 cm⁻¹ of resolution and 30 scans. A calibration curve was obtained through iPP/LLDPE blends prepared in solution with xylene at 125°C and coprecipitated with methanol according to a previously reported method.¹² The film thickness was 40 μm. Taking as a reference the absorbance bands at 720 (LLDPE) and 974 cm⁻¹ (i-PP), the FTIR spectra were obtained for the PP copolymers to determine the ethylene content.

Thermal traces of heating and cooling cycles were obtained from references and blends in a MDSC2920 TA Instrument calorimeter, at a heating/cooling rate of 10°C/min, in a flux of nitrogen of 50 mL/min. Aluminum pans were used as sample holders and the heating/cooling temperature range was 0–188°C. An isothermal step at 188°C for 5 min was included to homogenize the thermal history of the blend. The 188°C limit was the reported equilibrium melting temperature of iPP.²⁶

The dynamic mechanical properties of the blends were determined using a DMA analyser (DMA TA Instrument 983). Injection molded probes were used for this purpose and the heating rate was 3°C/min, with an amplitude of 0.4 mm, a frequency of 1 Hz and a temperature range between -70 and 40°C.

X-ray diffraction patterns were obtained in a Siemens D-500 diffractometer. Samples with an average thickness of 0.95 mm were heated at 188°C for 10 min and then cooled at 10°C/min in a Mettler FP90 hot stage. Diffraction patterns were collected within the 2θ range 8–30° at a scanning rate of 0.4°/min using a filament intensity of 25 mA and a voltage of 35 kV.

The morphology of the blends was observed by scanning electron microscopy (SEM) in a Top Con

510 microscope. Prepared samples were cryogenically fractured in liquid Nitrogen for 4 h, at a temperature quite lower than the polymers T_g , to avoid the shear during sample preparation. The fractured samples from injection molding were then extracted with toluene at 40°C and observed in the central part of the sample. A thin layer of Au/Pd alloy was used to enhance the electronic conduction of the samples. Micrographs were obtained using a tilting angle of 30° and a working distance of 8 mm, 15 kV and 3000×.

Izod impact strength was determined in a Custom Scientific Instrument 137 C tester according to ASTM D256-93 method at -35°C. Tensile strength and elongation were obtained in a universal Instron machine (United CCF-45) using type V samples according to the ASTM D-638 method.

RESULTS AND DISCUSSION

FTIR has been a widely used technique in studies of blends. Other authors have measured the ethylene content on the PP copolymer by FT and Raman spectroscopy.²⁷ Using FTIR the final content of ethylene on the PP copolymers was determined comparing the absorbance A_{720}/A_{974} ratios (related with the absorbance bands of ethylene and polypropylene respectively), according to a previous reported method.¹² The obtained ethylene contents were 5 wt % for the heterophasic copolymer (PP-EP) and 3.5 wt % for the random copolymer (PP-*r*-EP).

The thermal behavior of PP random copolymer (PP-*r*-EP) and PP heterophasic copolymer (PP-EP) is shown in Figure 1. It can be seen that the PP-EP showed a melting temperature at 165°C showing a sharp melting point peak of the main melting endotherm, associated with iPP, and a slight second endotherm close to 120°C associated with the ethylene content present in the heterophasic copolymer. The intensity of this transition increases with the increase of the ethylene in the heterophasic copolymers as was discussed in previous works.^{12,25} Impact polypropylene has been reported as a blend of three components; iPP, noncrystalline ethylene propylene rubber (EPR), and an spectrum of crystallisable EP copolymers in which a major component is an ethylene rich copolymer. This second endotherm at 120°C could be associated to the ethylene rich sequences on the heterophasic copolymer.²⁸ The melting point found for the random copolymer was 153°C showing a double melting behavior. This difference in the melting point between the two types of copolymers, which have similar ethylene content, is attributed to how the EP copolymer is attached to the main chain. In the heterophasic copolymer, it is attached mostly at the ends of the chain or forming independent structures, according to its sequential

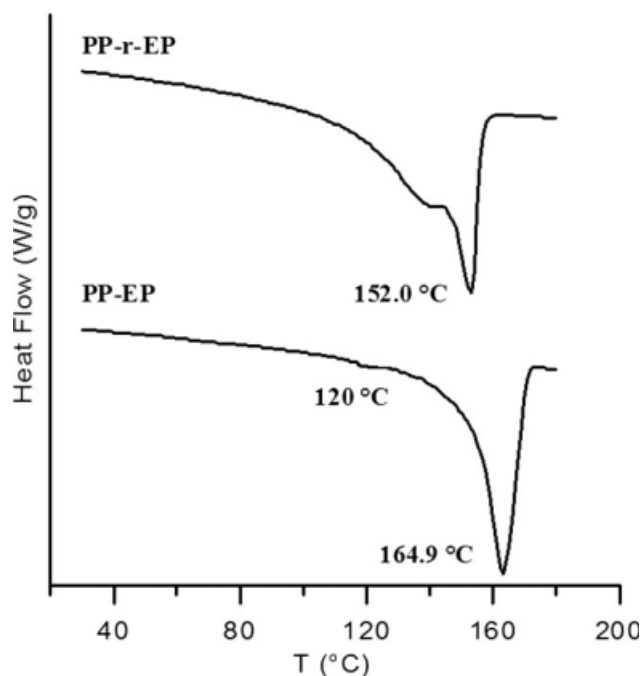


Figure 1 DSC heating traces of heterophasic PP-EP and random PP-*r*-EP copolymers. The melting points are shown.

synthesis process,^{28–30} whereas the random copolymer has the EP sequences included into the main iPP polymer chain.³¹ Therefore, during crystallization, there would be a tendency of such sequences to be rejected from the growing PP crystals, indicating the formation of defective PP crystals with lower density.^{32,33} This would be reflected in the depression of the melting temperature and in the degree of crystallinity. According to Karger-Kocsis³¹ for each 1 wt % of ethylene content in the random PP copolymers, the copolymer melting temperature is decreased by 3°C. On the other hand, in the heterophasic PP copolymers, the crystallizing EP chains have practically no effect on the PP crystallization process.²⁸

Figure 2 shows the thermal behavior of the PP-EP/EVA blends, where the PP melting temperature in both copolymers is shown as a function of the EVA content in the blend. Vivek et al.³⁴ reported a decrement on the melting point of the PP in PP/PS blends, as the composition of the amorphous polymer decreases. It was attributed to interactions that may occur between the glassy polymer and the crystalline part of the semi crystalline polymer. In Figure 2, a melting point depression with as low as 20% EVA in both copolymers can be observed. This depression is more pronounced for the PP-*r*-EP, being of 7°C (from 153 to 146°C). For PP-EP, the highest depression on melting temperature was achieved at 60% of EVA, being of near 2°C. The gradual depression on the melting temperature of

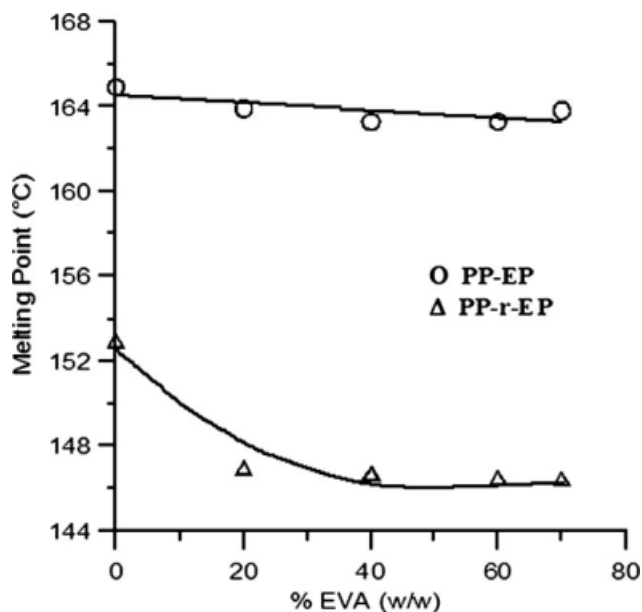


Figure 2 Melting point for the PP-EP/EVA and PP-r-EP/EVA blends as a function of EVA content.

the copolymer blends was attributed to the potential enhancement of molecular interactions between the amorphous interfaces of PP-EP/EVA and to the interactions during the PP copolymer crystallization in the blend, according to the results reported before.²⁵ In the same way, a depression on the crystallization enthalpy with increasing the EVA content in the blend was observed for both copolymers. The observed melting point depression for these blends suggests compatibility or partial miscibility, being more noticeable for the PP-r-EP/EVA blend. This variation on the melting temperature (T_m) has been reported in studies of PP/EVA blends^{10,11} and in blends of heterophasic copolymers PP-EP with EVA.¹² In these studies, the authors assigned the melting temperature depression to compatibility or partial miscibility, attributed to interface interactions between blend components. This was corroborated by glass transition studies using DMA.

Dynamic mechanical analysis helps to study polymer/polymer miscibility or compatibility in polymer blends and also measures the glass transition temperatures (T_g) of polymers. Moreover, through DMA we can obtain the storage (dynamic) modulus, loss modulus and damping behavior (internal friction), giving information about the blend behavior and the phase morphology. Figure 3 shows the results of an analysis of the T_g for both copolymers (heterophasic and random) through measurement of the loss modulus (E''). It can be seen in this figure that for PP-r-PP, only one single T_g at 3.3°C was observed, which is a typical behavior of the random copolymers in which only a single T_g of the blend components can be found. On the other hand, the heterophasic co-

polymer developed two glass transitions temperatures, one at 8.8°C and the other around -40°C. Ramirez-Vargas¹² have reported that heterophasic copolymers show two amorphous regions, one T_g associated to iPP around 8°C and other at -50°C corresponding to EP copolymer fraction, this is mainly attributed to the heterophasic nature of this type of polymer blend.

Figure 4 shows the loss modulus (E'') thermograms for the blends of both copolymers. For all the PP-r-EP samples a single T_g is observed which shifts towards lower temperatures as the EVA content in the blend is increased. For the PP-EP samples this T_g shift is seen up to 40% EVA content. This indicates that the random PP copolymer shows more potential enhancement of interaction with EVA in all the studied contents. This higher interaction of EVA with this type of copolymer can be explained by the way in which the random PP copolymers crystallize, rejecting the EP sequences from the growing crystals and forming defective PP crystals. This allows EVA to interact with the excluded sequences filling the crystal imperfections.²⁵ This also could be related to the mechanical linkage reported by McEvoy and Krause,¹⁷ in which during PP crystallization, EVA would penetrate into the PP crystals filling the voids that were generated by changes in density.

The morphologies found in SEM micrographs (Fig. 5) of the neat PP copolymers indicates a morphology of only one phase for the PP-r-EP, as was expected for this type of copolymer³¹; meanwhile for

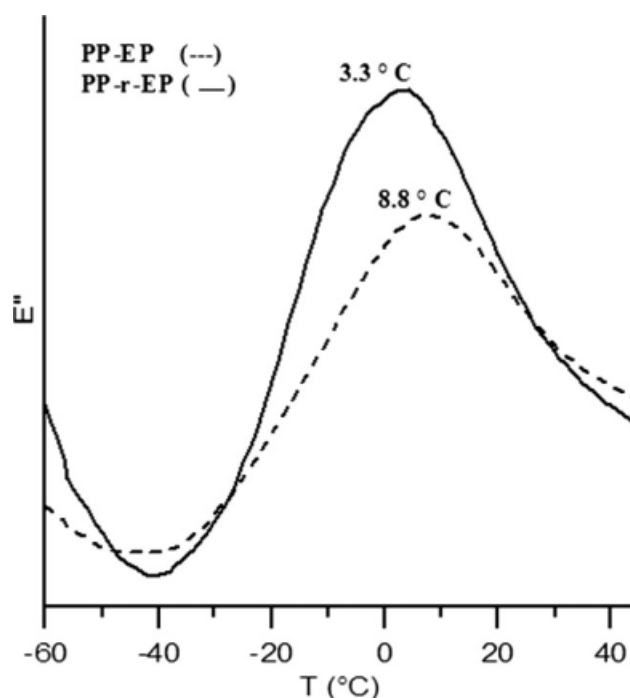


Figure 3 DMA results for heterophasic PP-EP and random PP-r-EP copolymers.

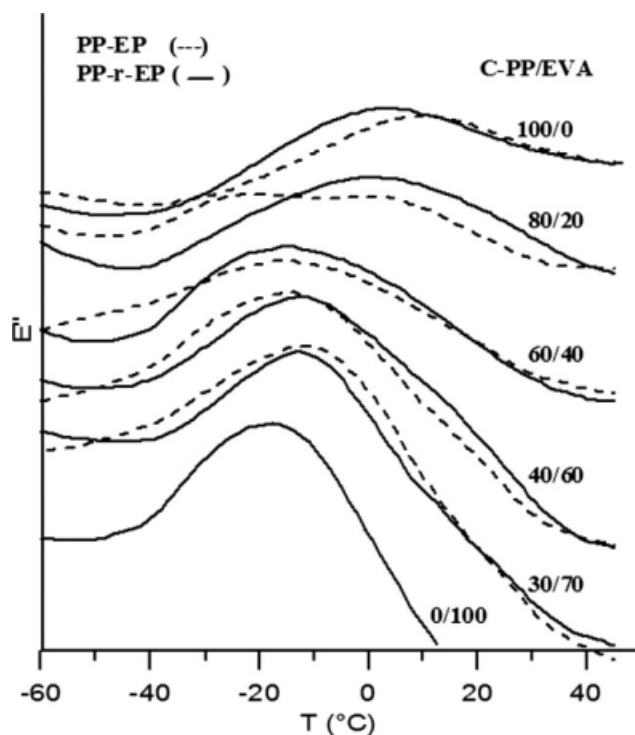


Figure 4 DMA results for the PP-EP/EVA and PP-*r*-EP/EVA blends.

the PP-EP a two phase morphology was observed.^{12,16} The blend micrographs of Figure 6, after extracting EVA with toluene, indicate a two phase morphology at all the studied concentrations, showing changes or morphological transitions from spherical domains at an 80/20 ratio to elongated domains at a 60/40 ratio and to a fibroid structure at 40/60 ratio. This was observed for both PP copolymers. Similar results were obtained in other works for PP homopolymers and heterophasic copolymers.²⁵ However, in this study, when comparing the morphology of both types of copolymers,

smaller and better dispersed domains were found in the random copolymer than in the heterophasic copolymer. This better dispersed morphology could be attributed to the interfacial interactions and to the effectiveness of the shear mixing exerted by the screw configuration used. Similar results were obtained by Maciel et al.,¹³ who found a reduction in particle size of the dispersed EVA phase when a compatibilizer was incorporated to the blend. These smaller and better dispersed domains confirms the higher interaction of the PP-*r*-EP, even at lower EVA content of the blends, previously demonstrated by a single and unique T_g (E'') and by the melting temperature depression observed by DSC.

The WAXD diffraction patterns for PP copolymers are shown in Figure 7. The nonblended patterns clearly indicate differences in the crystalline structures depending on the type of copolymer. In particular, the planes at $2\theta = 17.3$ and 18.7° are sharper in the case of PP-EP. Some reports on PP-poly butadiene rubber blends,³⁵ indicate the formation of β -form crystals influencing the PP mechanical behavior. In our case, it can be seen that both copolymers showed α crystals diffraction planes for isotactic PP. In addition, the PP-EP showed a diffraction plane at $2\theta = 20.05$ corresponding to γ crystals. This crystalline morphology has been reported for random PP copolymers and is attributed to the short sequences of iPP. The intensity of these planes increases with increasing ethylene content in the copolymer.³² For the blends (Fig. 8), EVA in the PP-*r*-EP promoted a reduction of the diffraction plane intensity of the γ crystals at $2\theta = 20.05$ with an EVA content of 20%, until it disappears at an EVA content of 40%. The planes in both copolymers at $2\theta = 21.2$ and 21.9° are convoluted, showing a single peak, attributed to the increasing EVA content on the blend, which shows a characteristic signal at $2\theta = 21.6^\circ$ corresponding to the crystals diffraction plane of ethylene. The other

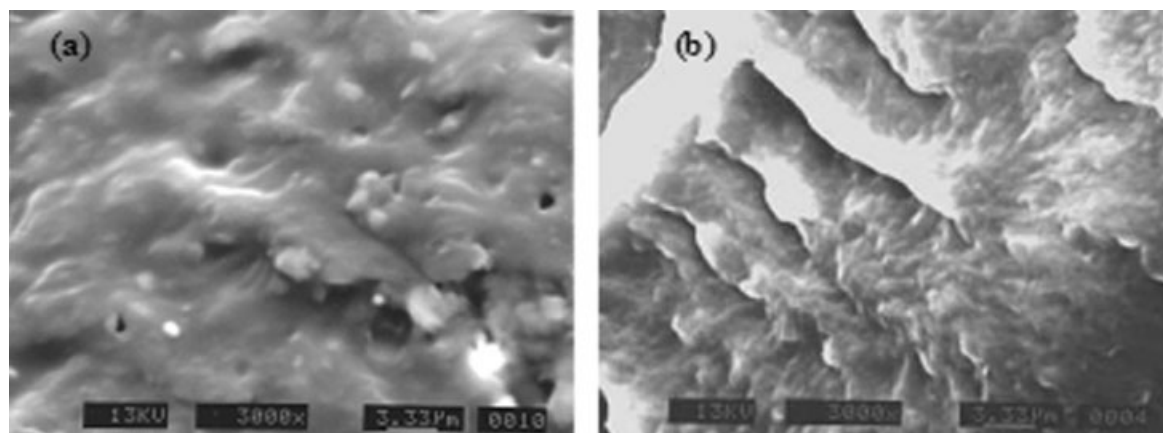


Figure 5 SEM micrographs (3000 \times) of heterophasic PP-EP (a) and random PP-*r*-EP (b) copolymers.

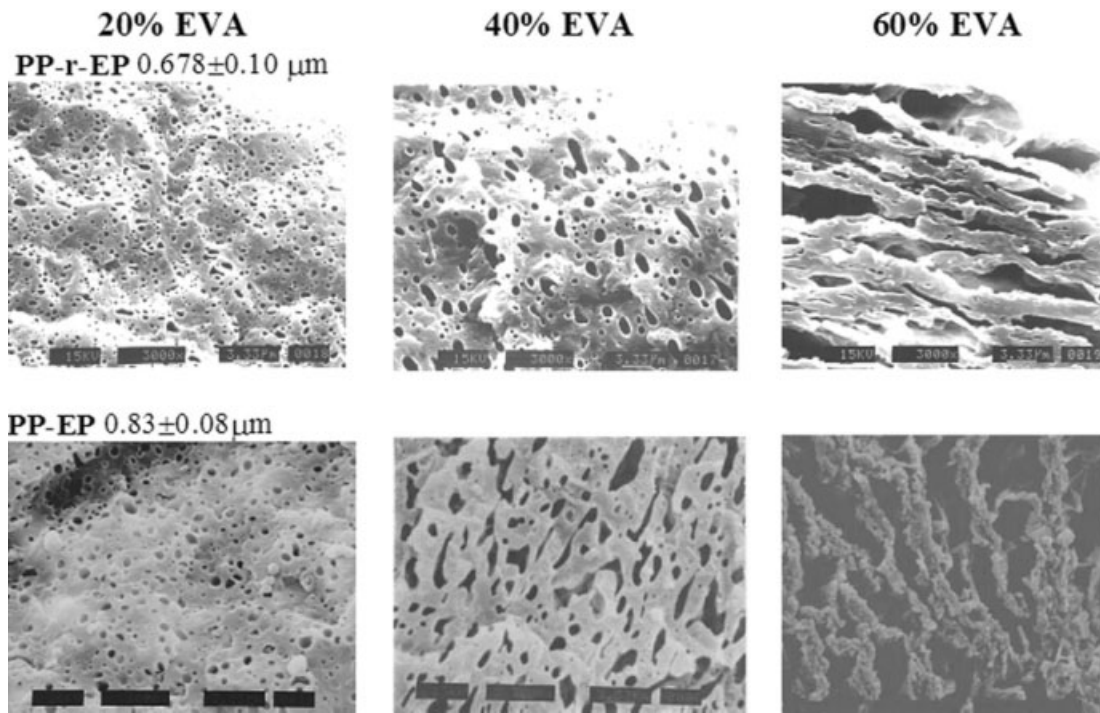


Figure 6 SEM micrographs (3000 \times) of toluene extracted (40 $^{\circ}$ C) for the PP-EP/EVA and PP-r-EP/EVA blends, at 20, 40, and 60% of EVA.

diffraction planes were gradually reduced when the EVA content in the blends was enhanced, this was attributed to an increase of the amorphous character of the blends.

Final mechanical properties are frequently correlated with blend compatibility. The obtained mor-

phology for the PP copolymers blends favorably affected the mechanical properties of elongation at break and Izod impact strength, which continuously increased with the EVA content in the blends. These results corroborate the partial miscibility or compatibility of these types of blends. Other authors have¹³

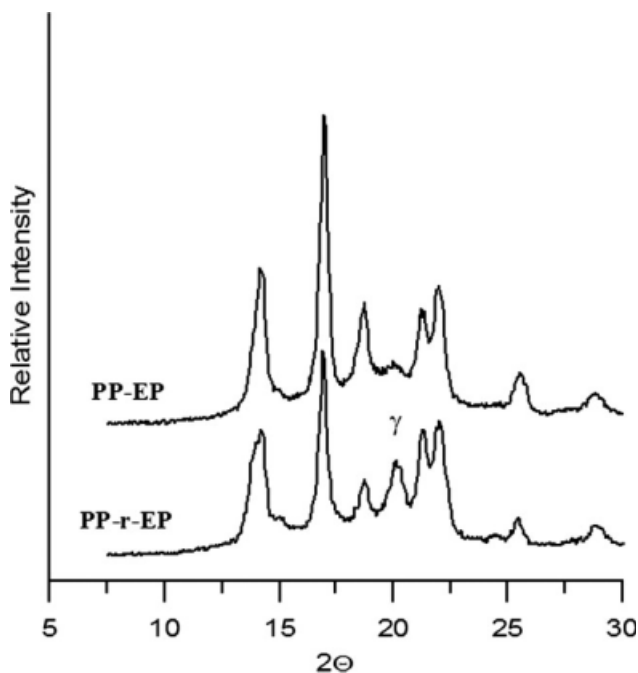


Figure 7 WAXD patterns for heterophasic PP-EP and random PP-r-EP copolymers.

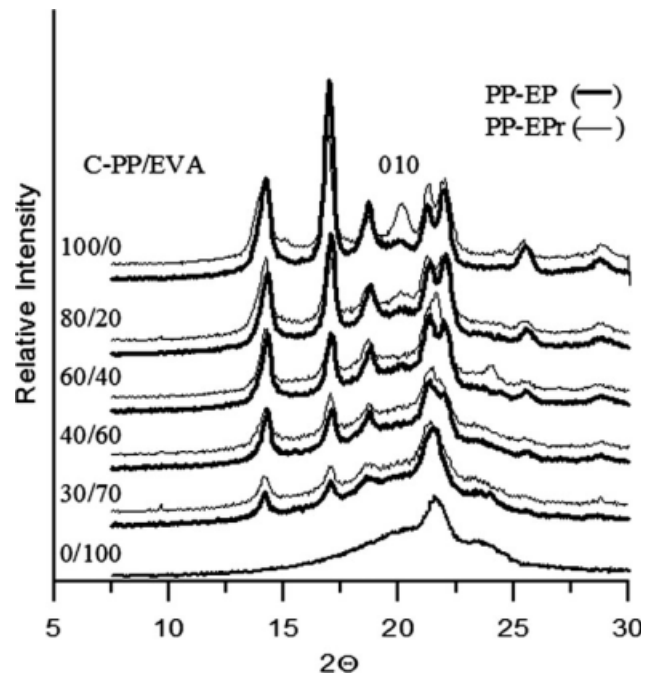


Figure 8 WAXD patterns for the PP-EP/EVA and PP-r-EP/EVA blends, the composition is shown.

reported an enhancement on strain in PP/EVA blends when the EVA content was increased. Elongation at break results is shown in Figure 9 where it can be seen that the PP-*r*-EP showed higher values than the PP-EP for the entire range of compositions studied. Values of up to 400% of elongation were obtained. Similarly, Izod impact strength was increased for both PP copolymers, (Fig. 10), with a more noticeable increase of up to a 40% of EVA, in which a transition from spherical to elongated domains was observed, as was discussed in SEM results (Fig. 6). This mechanical property behavior was also observed by Ramirez-Vargas et al.¹² and Gupta et al.⁷ Maciel et al.¹³ has reported an increase on the impact strength in PP/EVA blends when using PPMA and EVAOH as compatibilizers.

It is reported³⁶ that entanglements between chains in polymer blends is especially important for strong adhesion at the interface. In glassy amorphous polymers, the stress is mainly transferred by entanglements so that the fracture toughness of the interface is negligible until the chains on both sides of the interface are mutually entangled. Thus, the fracture mechanisms changes from chain pullout to chain scission and then finally to crazing.

It can be said that both copolymers, PP-EP and PP-*r*-EP, enhanced the blend compatibility of the system at up to 40% EVA content. This observed behavior was associated with the morphology transitions, which changed from spherical to elongated domains. However, the mechanical property was influenced by the type of PP copolymer; the elonga-

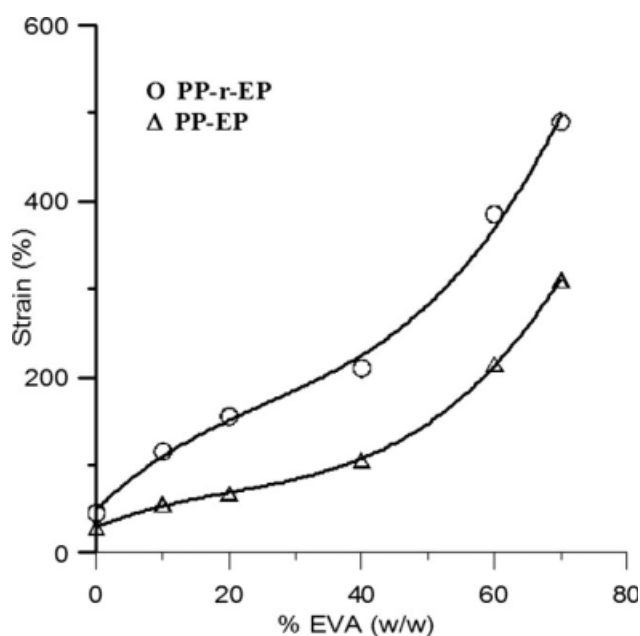


Figure 9 Elongation at break for the PP-EP/EVA and PP-*r*-EP/EVA blends as a function of EVA content.

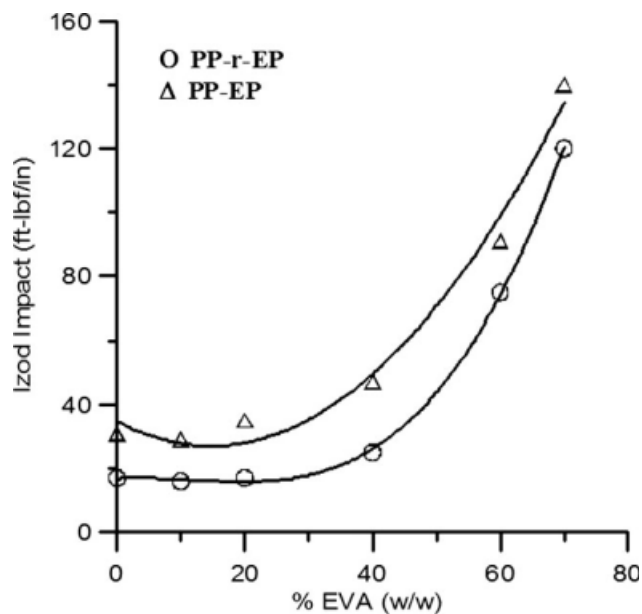


Figure 10 Izod impact results for the PP-EP/EVA and PP-*r*-EP/EVA blends as a function of EVA content.

tion at break was slightly higher for the random copolymer (PP-*r*-EP) while the impact strength was slightly higher for the heterophasic copolymer (PP-EP) which is in agreement with different reported works.^{31,37} This behavior could be explained as follows: the impact strength was higher for the heterophasic copolymer because, besides the EVA content, it has higher elastomeric regions from the EP phase distributed into the PP matrix. This heterophasic copolymer characteristic would enhance the impact strength by transmitting and dissipating this stress into the elastomeric phases of the PP-EP system.^{37,38} On the other hand, elongation at break was higher for the PP-*r*-EP blend over the entire composition range which could be attributed to physical entanglements between the copolymer phases (mostly amorphous) or debonding mechanism between phases that allows a higher molecular sliding and deformation. These mechanisms were proposed by other authors for similar blend systems.³⁹⁻⁴¹

CONCLUSIONS

The study of complex heterophasic and random PP copolymers blended with EVA (PP-EP/EVA and PP-*r*-EP/EVA) has rendered new information regarding the morphology property relationship of these systems. These blends showed interaction mostly in the amorphous regions showing a T_g depression. The random copolymer showed more compatibility, by the increased shift of the E'' (loss modulus) signal for all the blend ratios. On the other hand, slight changes in the melting temperature (T_m depression)

and in the diffraction patterns (elimination of the γ form) of the PP-*r*-EP/EVA blends, indicated interactions between the crystalline interfaces.

Both types of blend systems showed morphological changes or transitions from spherical domains at an 80/20 ratio to elongated domains at 60/40 ratios and to fibroid domains at 40/60 ratios. When comparing the morphology for both PP copolymers, smaller and better dispersed domains were found for the random copolymer than for the heterophasic copolymer. These results corroborate the higher compatibility for PP-*r*-EP/EVA blends at all the studied EVA concentrations.

The developed morphology of the elastomeric phase led to enhanced impact strength and elongation at break for both blended systems. This enhancement was more significant at 40 and 60% EVA concentrations, this behavior was associated with the observed morphology transitions. The mechanical properties were influenced by the type of PP copolymer on the blends.

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