Use of Monomethyl Itaconate Grafted Poly(propylene) (PP) and Ethylene Propylene Rubber (EPR) as Compatibilizers for PP/EPR Blends

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Introduction

Poly(propylene) (PP) is a semi-crystalline, thermoplastic polyolefin that offers a very attractive combination of physical and mechanical properties at a relatively low cost. This makes it a versatile material with a continuously increasing number of applications. However, in some cases, not all the characteristics of this material are suitable for common service conditions. For instance, PP exhibits poor low-temperature, impact resistance because of its high transition temperature and high crystallinity.[1,2] To overcome these limitations, impact modifiers have been added to PP and, among them, ethylene propylene random copolymers (EPR) and ethylene propylene diene terpolymers (EPDM), are the most common and effective ones[3–6] due to their high impact strength over a wide range of temperatures. In fact, the rubber modification of PP can lead to a material with improved impact strength and environmental stress-cracking resistance.[7]

It is assumed that, when the rubbery phase forms highly dispersed small particles, it behaves as an effective stress concentrator and enhances resistance to crack propagation

in the matrix. These blends commonly referred to as TPOs, thermoplastic polyolefin elastomers, have gained considerable scientific and commercial interest in the last two decades. Although these polymers have a similar chemical structure, the elastomer is not compatible with polyolefins and as a consequence, the elastomeric phase exists as separate small particles in the continuous thermoplastic matrix.[8] Unfavorable interactions at the molecular level give rise to high interfacial tension and impede the melt mixing of the components. Moreover, the incompatibility of these blends cause an unstable morphology and a poor interface adhesion, which are the main causes of poor and undesirable mechanical properties of the blends.

To improve the compatibility of the blend components, functionalization is often used. Hence, the modification of polymeric materials, in particular, polyolefins, by the incorporation of functional monomers with the main objective of obtaining advanced materials with improved technological properties has gained wide industrial application and attracted scientific interest during recent years. Several polar monomers, such as oxazoline,[9] mercapto,[10] cyanate ester,[11,12] maleic anhydride,[13,14] alkyl maleates,[15,16] and itaconic acid and its derivatives,[17–19] have been investigated. Among them, the most studied modification of polyolefins are those with maleic anhydride and alkyl maleates which is performed either in solution, in the solid state, or in the melt phase. In the present study, both poly(propylene) (PP) and ethylene propylene random copolymers (EPR) were modified with an itaconic acid derivative, namely, monomethyl itaconate (MMI), in the melt at 190 °C by using 2,5-dimethyl-2,5-bis(*tert*-butylperoxy) hexane (Lupersol 101) and dicumyl peroxide as radical initiators.

The aim of this study is to evaluate the effect of grafting of a polar monomer, such as MMI, on PP and EPR, via free radical reaction on the processability, morphology, and properties of the thermoplastic blends.

Experimental Part

Materials

Isotactic poly(propylene) (iPP) (MFI: 2.9 $dg \cdot min^{-1}$ at 190 °C, 5 kg, density: 0.905 $g \cdot cm^{-3}$) supplied by Repsol Química, S.A. under the trade name of Isplen PP-050 and the ethylene-propylene random copolymer (EPR) (59% poly-(propylene) content and a Mooney viscosity ML $(1+4)$ at 125 °C: 44) supplied by EniChem under the trade name Dutral CO 054 were used in this study. Itaconic acid was purchased from Aldrich. Monomethyl itaconate (MMI) was synthesized by the esterification of itaconic acid with methanol; their purity was checked by ^{1}H NMR spectroscopy. 2,5-Dimethyl-2,5-bis(*tert*-butylperoxy) hexane (Lupersol 101) and dicumyl peroxide were purchased from Akzo and used as radical initiators for the functionalization of PP and EPR, respectively.

Grafting Reactions

PP and EPR were functionalized in the melt by grafting with MMI using a Brabender Plasticorder. The reaction scheme proposed for the grafting process is shown in Figure 1. The type of polymer used in a grafting reaction is expected to affect the nature of the side reactions. It is well-known that poly(propylene) primarily undergoes β-chain scission (via the tertiary macroalkyl radicals), leading to a reduction in the molar mass and viscosity of the polymer. On the other hand, polyethylene predominantly undergoes cross-linking reactions (through the secondary macroalkyl radicals) during the melting process, resulting in an increase in the molar mass and viscosity of the polymer. In the case of an ethylene-propylene random copolymer with both ethylene and propylene components, these two side reactions can occur during the radical grafting process. In our case, EPR cross-linking was confirmed by extraction in hot toluene. The unmodified polymer is completely soluble under these conditions, whereas MMI-grafted EPR gave a gel content of approximately 20%. The polymer to be grafted was mixed with a predetermined amount of the monomer using an initial monomer concentration of 3 phr in the case of PP and 5 phr in the case of EPR and an initiator concentration of 1.0 phr in both cases, before melt mixing at 190 °C. At the end of reaction, the product was dissolved in hot xylene and precipitated with acetone. The unreacted monomer, initiator, and possible homopolymer, which eventually form during the grafting reaction, were separated from the grafted polymer by exhaustive extraction of the sample with methanol in a Soxhlet for 24 h.[19] The extracted samples were dried under reduced pressure before analysis.

Evidence of grafting, as well as its extent, expressed as weight percent of grafting, was obtained by FTIR spectroscopy.[19]

Blend Preparation

The PP/EPR blends with two compositions, 70/30 and 30/70 and the corresponding pure homopolymers, were prepared by melt mixing in a roll mill at 190 °C. The blending time was about 20 min. Immediately after mixing, the material was cut into pellets and dried overnight at 60 °C in a vented oven. The blends were then injection-molded in a Margarit M50/125 model injection molding machine to prepare dog bone specimens. The nominal dimensions of the specimens were $150 \times 10 \times 4$ mm. The temperatures in the three zones of injection molding machine were 210, 220, and 230 °C, respectively. A mold temperature of 60 °C, and an injection pressure of 40 $kg \cdot cm^{-2}$ were used. The period of time for the packing and cooling states were 20 and 30 s, respectively. In all cases, the proportion of grafted polymer was 10% by weight. For preparation of blends without modified polymer, i.e., without using grafted polymer as compatibilizer, both polymers were previously passed through the roll-mill in the presence of corresponding peroxide before melt blending.

Characterization

The evidence of grafting as well as its extent, expressed as weight percent of grafting, was determined by FTIR

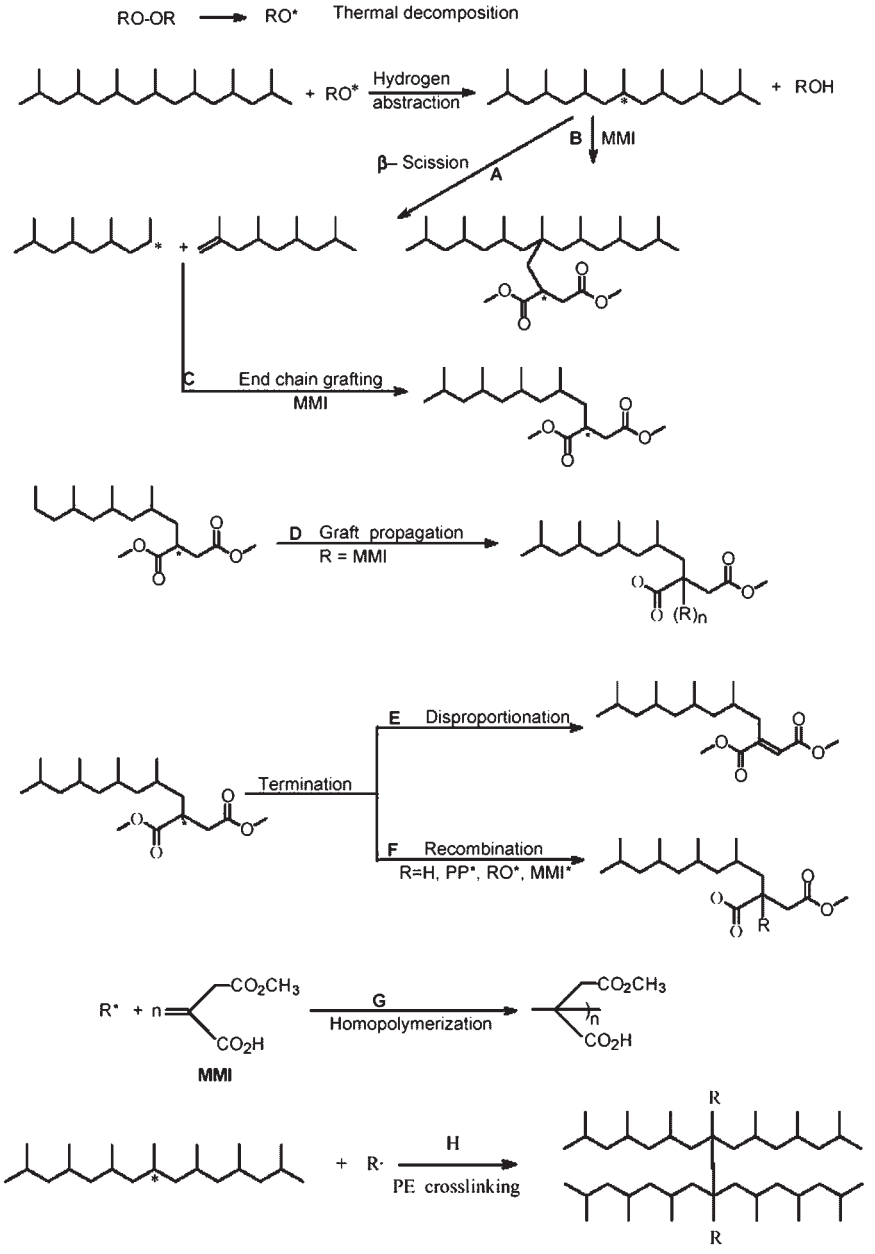

Figure 1. Reaction scheme for grafting of monomethyl itaconate on PP or EPR.

spectroscopy. The FTIR spectra were recorded on a Bruker IFS-28 spectrometer from 4 000 to 400 cm^{-1}. Films of 600 μm thickness of unmodified polymers and grafted samples were obtained by compression molding between steel plates covered with thin aluminum sheets at 180 °C for 1 min.

The rheological measurements were performed using a Rheometrics mechanical spectrometer, RMS, Model 605 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 of 0.1 to 500 $rad \cdot s^{-1}$. An amplitude strain of 5% was maintained.

Dynamic mechanical properties of the solid polymer were determined using a dynamic mechanical thermoanalyzer Metravib Model Mark 03. The nominal dimensions of the specimens were $25 \times 10 \times 6$ mm. Test were carried out in torsion deformation mode at a frequency of 5 Hz, and the temperature programs were run from −140 to 40 °C at a heating rate of 2 $°C \cdot min^{-1}$ under a controlled sinusoidal strain in a flow of nitrogen.

Thermal analysis experiments were performed using a Mettler Toledo differential scanning calorimeter Model DSC 822. Crystallization tests were carried out under nonisothermal conditions. Samples of about 8 mg were melted at 200 °C for 10 min, to eliminate any previous thermal history of the material. They were then cooled down −50 °C at 10 $°C \cdot min^{-1}$, to determine the crystallization temperature, T_c. The sample

was heated again to 200 °C at 10 °C · min^{-1} to obtain the melting point, T_m, and melting enthalpy, ΔH_m. T_c and T_m are defined as the temperature, at which the respective endothermic and exothermic maxima are observed.

Mechanical characterization was also carried out by tensile testing and impact measurements. Tensile testing was performed at room temperature on a Instron dynamometer, Model 4301, according to ASTM D 638M. Tests were carried out at a cross-head speed of 5 mm · min^{-1} until a deformation of 20% and then at a speed of 50 mm · min^{-1} at break. Impact experiments were carried out according to ASTM D-256 (v-notched) at −60 °C in an Izod pendulum Ceast mod. Resil 25 with an impact speed of 3.48 ms^{-1}. 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°. The impact strength is expressed in terms of the energy absorbed per meter of notch. All mechanical properties were the average of at least seven measurements.

The blends morphology was characterized by scanning electron microscopy (SEM) by using a Tesla BS 343 A scanning electron microscope. Micrographs were obtained after the extraction of the EPR phase from the surface of cryogenically fractured samples using toluene at 70 °C for 8 h. Fracture surfaces of test specimens were sputtered with gold before to be observed in the SEM.

Results and Discussion

Evidence of Grafting

The existence of grafted MMI in PP as well as EPR was confirmed by FTIR spectroscopy.[19] Figure 2 shows the FTIR spectra of PP and PP grafted with MMI (PPgMMI). In the case of MMI-modified PP, the FTIR spectrum showed three absorption bands in the carbonyl region that are absent in the spectrum of unmodified PP. The absorption bands at 1 710 and 1 745 cm^{-1} can be attributed to the stretching vibrations of the carbonyl groups of the ester and the carboxylic acid of the monomer, respectively. The third absorption band centered at 1 781 cm^{-1} was assigned to a carbonyl group from a five-membered anhydride ring. The sum of the intensities of the absorption bands at 1 710 and 1 745 cm^{-1} was compared with that of the band for the methyl group from PP centered at 1 167 cm^{-1}, and the carbonyl index ($I_{Cmonoester}$) calculated corresponds to the incorporation of the monomer as a monoester. Similarly, the intensity of the absorption band at 1 781 cm^{-1} was compared with that of the methyl group from PP centered at 1 167 cm^{-1}. This band ratio was defined as the carbonyl index (I_CA) corresponding to the incorporation of the monomer in its cyclic anhydride form. To quantify the contribution of MMI grafted in its cyclic form, the commercial anhydride, 2-dodecene-1-yl-succinic anhydride (DSA), was used as model compound to establish a calibration curve. The total percentage of MMI grafted in the form of both the monoester and anhydride can be determined by using the following relation:

$$\%\text{grafting} = 0.554 I_{Cmonoester} + 0.339 I_C A \quad (1)$$

Therefore, a degree of grafting of 1.5% by weight was obtained for PP.

Similarly, in the case of EPR grafted with MMI (EPRgMMI) (Figure 3), the intensity of the carbonyl absorption band from grafted MMI at 1 739 cm^{-1} was compared with the absorption band at 730 cm^{-1} from EPR. The 1 739/730 cm^{-1} band ratio was defined as the carbonyl index (I_C). A calibration curve was also constructed in this case as was described for the PP. The percentage of grafting of MMI onto EPR can be estimated by using the relation:

$$\%\text{grafting} = {}^{I_C}/_{0.3214} \quad (2)$$

Thus, a degree of grafting of 1.2% by weight was obtained for EPR.

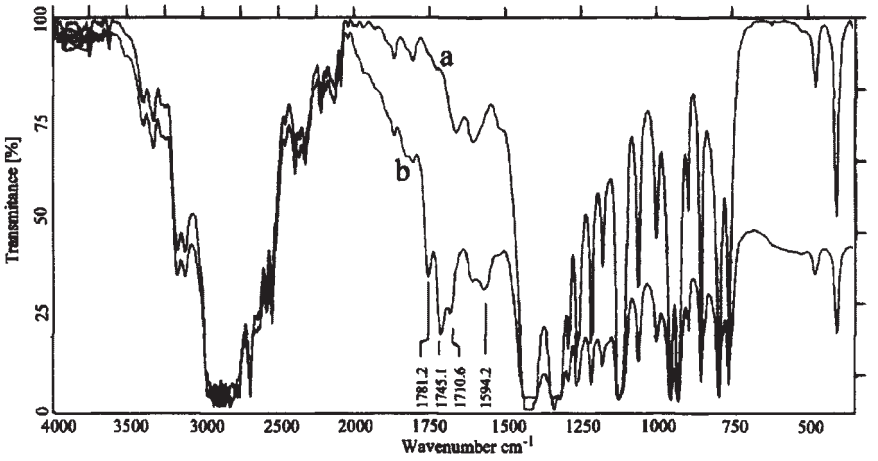

Figure 2. FTIR spectrum of a) PP and b) grafted PP with MMI.

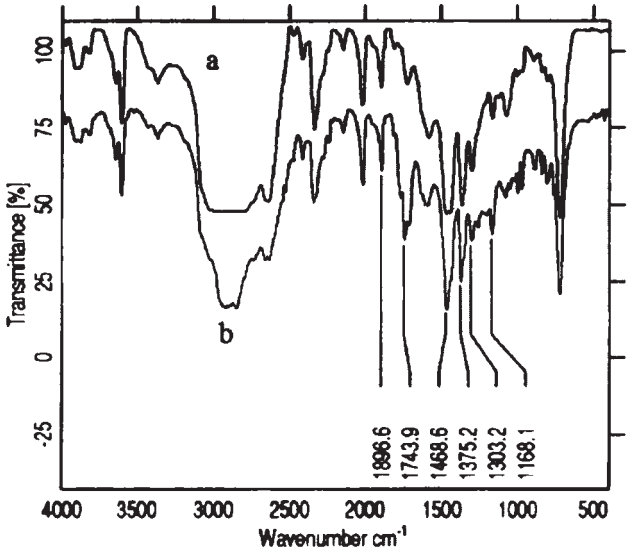

Figure 3. FTIR spectrum of a) EPR and b) grafted EPR with MMI.

It should be noted that FTIR spectrum shown hear are not the spectra used for the estimation of the percentage of grafting and reflect only qualitatively the grafting.

Rheological Properties

The flow properties of the materials studied in the molten state were analyzed by rheological studies. The change in the complex viscosity (η^*) as a function of the angular frequency for the PP/EPR blends at different compositions is shown in Figure 4. It can be easily observed that the complex viscosity of all the samples gradually decreases with increasing angular frequency, indicating a typical pseudoplastic behavior for these materials (shear thinning). The pseudoplastic nature comes from a random-oriented and highly entangled state of the polymer chains, which, on application of high shear rates, get disentangled in the orientation of the force and become oriented resulting in a reduction of viscosity.[20]

On the other hand, the blend viscosity increases with the rubber content due to the higher viscosity of the rubbery component. The viscosity of the blends lies between those of the pure homopolymers. An increase in viscosity on incorporation of rubber phase has been reported for several systems.[21,22] However, this increment is nonlinear, and the experimental values taken at a frequency of 1 rad $\cdot$ s^{-1} are lower than those predicted by the linear additive rule of ideal blends, which is represented by the straight line shown in Figure 5. This negative deviation in viscosity is due to the heterogeneous nature of the components and can be associated with the incompatibility of PP/EPR blends. It is obvious that in polymer blends, the viscosity not only depends on the characteristics of the components, but also is influenced by additional factors, such as the miscibility of the system, morphology, and the changes it introduces to the interfacial interactions.[23,24] This is because, in polymer blends, there is an interlayer slip along with orientation and disentanglement on the application of shear stress. Thus, when shear stress is applied to a blend, it undergoes an elongational flow. When the interface is strong, deformation of the dispersed phase is effectively transferred to the continuous phase. In the case of incompatible blends, characterized by a sharp interface and poor interaction between both polymeric phases, an interlayer slip[25] between phases occurs and consequently, the viscosity of the system decreases. It can also be observed that the viscosity increases slightly up to a 30% EPR content followed by a strong increase at higher EPR content.

To evaluate the effect of grafting reaction with MMI on the rheological properties of the polymers, the variation of the viscosity of the binary blends, PP with 10% PPgMMI and EPR with 10% EPRgMMI, was analyzed. As shown in Figure 4, a slight increase in the polymer viscosity, in both cases, with the addition of the grafted polymer is observed. It is of interest to point out that this increase in viscosity is

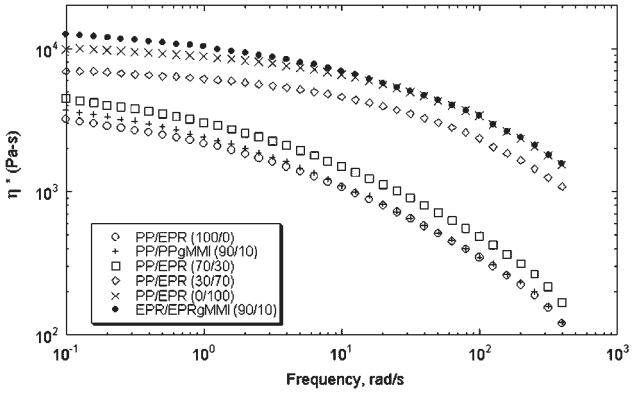

Figure 4. Change in complex viscosity with angular frequency at 180 °C for different PP/EPR blends.

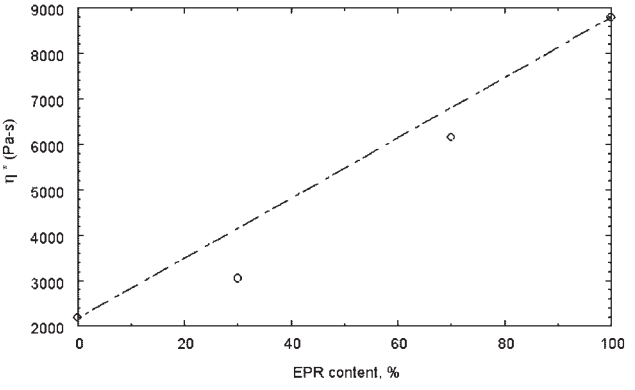

Figure 5. Change in complex viscosity at a frequency of 1 rad $\cdot$ s^{-1} as a function of rubber content at 180 °C.

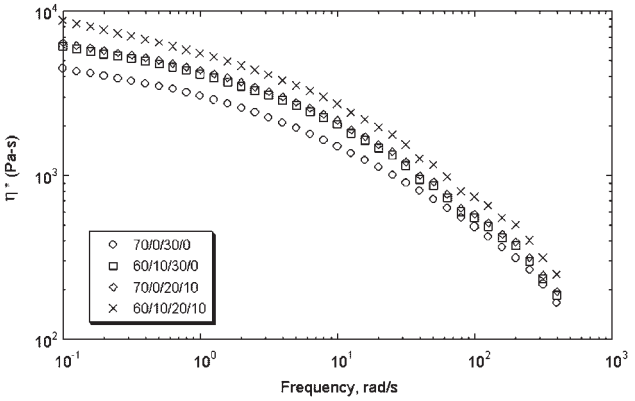

Figure 6. Change in complex viscosity with angular frequency at 180 °C for unmodified and MMI-functionalized PP/EPR (70/30) blends.

only significant at lower frequencies. That is, with increasing angular frequency, the viscosity difference between the blends is practically negligible.

The rheological properties for unmodified and modified PP/EPR (70/30) and (30/70) blends were measured and the results are presented in Figure 6 and 7, respectively. It can be seen that the viscosity of the blend containing small amounts of functionalized polymers increases as compared to unmodified blends, revealing their higher viscosity at a particular angular frequency. This effect is larger for the blends containing both polymeric phases grafted with MMI. Similar results on the effect of the compatibilization in the viscosity of immiscible polymer blends have been reported in the literature.[26–28] The increase in viscosity indicates that there is less slippage at the interface as a result of the addition of compatibilizers. These results may be explained by behavior of the monomethyl itaconate-grafted polymers as effective compatibilizers, inducing a strong interaction between the two phases. This offers more resistance to flow and results in a higher viscosity. It also gives rise to a reduction in the interfacial tension and an increase

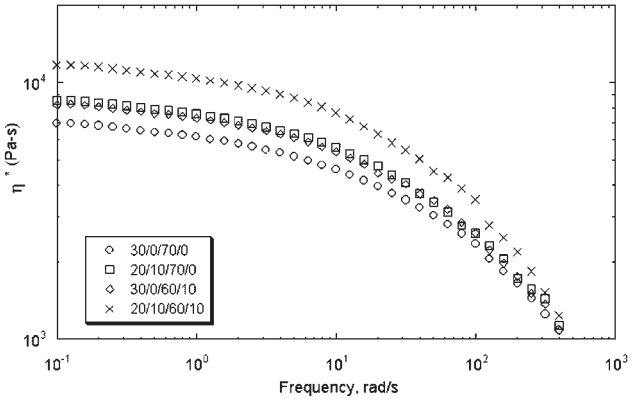

Figure 7. Change in complex viscosity with angular frequency at 180 °C for unmodified and MMI-functionalized PP/EPR (30/70) blends.

in interfacial adhesion.[29] In addition, the effect of grafted polymers on the viscosity of PP/EPR blends is more noticeable in the low shear rate region. The viscosity of the blend in the high shear rate region hardly varies with the addition of grafted polymers to the blend.

George et al.[30] reported that the viscosity of a polymer blend depends on different factors, such as the miscibility of the system, morphology, interfacial adhesion, and interface layer thickness (compatible domain). So, the compatibilizer located in the interface will lead to an increase in interfacial thickness, and consequently, an effective stress transfer between the dispersed phase and the continuous phase, and an increase in interfacial adhesion is observed. This gives rise to a reduction in the interlayer slip and thus, the viscosity increases.

As can be observed by SEM micrographs, the size of the dispersed EPR phase in the compatibilized 70/30 blends decreases, the viscosity increases. This effect is more sensible in the blend where both grafted polymers were used as compatibilizers. The decrease in domain size upon the addition of grafted polymers to PP/EPR blends indicates that the interfacial adhesion between both polymeric phases increases as the interfacial tension decreases. Similar results have been observed by several authors.[9,30,31]

Mechanical Characterization

Mechanical properties of PP/EPR blends were characterized by tensile modulus and strength, elongation at break, and Izod impact strength measurements. As was expected, the mechanical characterization shows a strong influence of the composition on the properties studied (Table 1). Therefore, the tensile modulus and strength decrease with increasing EPR amount in the blend. In addition, the impact strength was logically increased by the incorporation of EPR, indicating the function of elastomer as an impact modifier of polyolefins. This can be explained by a highly deformed, rubbery phase during the impact test, which thus, absorbs a part of the impact energy. The deformed rubbery domains cause the so-called shear yielding, which is considered to be the main mechanism of impact toughness of polyolefin-elastomer blends at service temperatures.

On the other hand, it is of interest to point out that the blends containing grafted polymers show a higher toughness without a reduction in strength and stiffness. In fact, even a slight increase in tensile modulus and strength was observed on compatibilization. Moreover, a pronounced increase in the deformation at the break of the material is observed. This statement is well-demonstrated when both polymeric phases are modified with MMI. An explanation of these results is the improved interfacial adhesion between both polymeric phases as well as size reduction and fine dispersion of rubber particles into the continuous polyolefin matrix, which influence the compatibilization mechanism. It is assumed that a decrease in the rubber

Table 1. Mechanical properties of PP/EPR blends.

PP/PPgMMI/EPR/EPRgMMI	Young's modulus	Max. strength	Def. at break	Impact strength
	MPa	MPa	%	$J \cdot m^{-1}$
100/0/0/0	$1\,050 \pm 48.3$	29.5 ± 0.6	256 ± 22	38 ± 3.2
70/0/30/0	407 ± 9.3	21.1 ± 0.3	789 ± 85	266 ± 15.4
60/10/30/0	410 ± 13.3	18.9 ± 0.4	884 ± 78	346 ± 21.2
70/0/20/10	415 ± 4.7	23.9 ± 0.5	$> 1\,000$	381 ± 23.5
60/10/20/10	$429 \pm 8.$	22.8 ± 0.4	$> 1\,000$	425 ± 26.4
30/0/70/0	51 ± 2.0	6.2 ± 0.2	416 ± 31	NB[a)]
20/10/70/0	58 ± 4.3	5.6 ± 0.1	484 ± 28	NB
30-0-60-10	55 ± 4.6	6.1 ± 0.2	598 ± 45	NB
20/10/60/10	67 ± 2.2	5.8 ± 0.1	680 ± 44	NB
0/0/100/0	5.4 ± 0.4	1.8 ± 0.1	562 ± 38	NB

[a)] N.B.: not broken.

particle size is strongly related to the enhancement of the impact strength of the material. It can be concluded that in the presence of the compatibilizer, a better balance of all the tested properties is achieved. A similar trend has been observed by Vocke et al.[9] using oxazoline-functionalized polyolefins as compatibilizers for thermoplastic blends.

Dynamic Mechanical Analysis

The dynamic mechanical properties of PP/EPR blends were studied over a wide temperature range ($-80\,^{\circ}C$ to $40\,^{\circ}C$) and the results are reported in Table 2. These measurements provide a useful means of studying the miscibility of polymer blends. Figure 8 shows the storage modulus of the PP/EPR blends with different rubber contents. It is observed that by increasing the percentage of the elastomer in the blend, the storage modulus decreases, which correlates with the elastomer function as the impact modifier of the polyolefin matrix. As is reported in Table 2, all the blends have two glass transition temperatures, corresponding to those of the pure homopolymers. The first one is detected approximately at $-40\,^{\circ}C$, corresponding to the glass transition temperature of EPR. Another loss-peak maximum is around $5\,^{\circ}C$ and can be assigned to the glass transition temperature of the amorphous region of PP. These results indicate the formation of a two-phase system with a limited degree of miscibility of its components, as described in the rheological analysis. Figure 9 shows the loss factor ($\tan\delta$) curves of unmodified and modified PP/EPR (70/30) blend. It can be seen that the grafting reaction gives rise to an increase in the height of the $\tan\delta$ traces of both components of the blend, which is related to a better behavior as an impact modifier. It is well-assumed that an increase in the intensity of $\tan\delta$ peak correlates with an increase in the impact strength of the blends; in other words, an increase of viscoelastic energy dissipation of the blends is accompanied by an increase in their impact strength.[32,33] A similar trend was observed for the PP/EPR 30/70 blends. On the other hand, the peak corresponding to the glass transition temperature of PP is shifted to higher temperatures (about $3-4\,^{\circ}C$) with grafted polymers, whereas no significant changes in T_g of the EPR

Table 2. Dynamic mechanical analysis for unmodified and MMI-modified PP/EPR blends.

PP/PPgMMI/EPR/EPRgMMI	PP			EPR		
	$\tan\delta$	T_g	G' at T_g	$\tan\delta$	T_g	G' at T_g
		°C	Pa		°C	Pa
100/0/0/0	0.0345	5.7	1.57×10^9	–	–	–
90/10/0/0	0.0378	5.9	1.45×10^9	–	–	–
70/0/30/0	0.0437	7.8	7.23×10^8	0.0331	−55.1	1.46×10^9
60/10/30/0	0.0635	8.9	8.04×10^8	0.0492	−53.8	1.62×10^9
70/0/20/10	0.0639	10.3	8.56×10^8	0.0468	−56.2	1.70×10^9
60/10/20/10	0.0649	10.1	7.68×10^8	0.0554	−54.2	1.66×10^9
30/0/70/0	0.0784	7.1	1.90×10^7	0.0970	−43.9	2.18×10^8
20/10/70/0	0.0807	7.9	2.01×10^7	0.111	−42.8	2.35×10^8
30/0/60/10	0.0798	7.8	1.95×10^7	0.095	−43.9	2.31×10^8
20/10/60/10	0.0808	8.6	2.08×10^7	0.185	−42.6	2.45×10^8
0/0/100/0	–	–	–	0.3470	−40.3	1.46×10^8
0/0/90/10	–	–	–	0.3540	−39.9	1.49×10^8

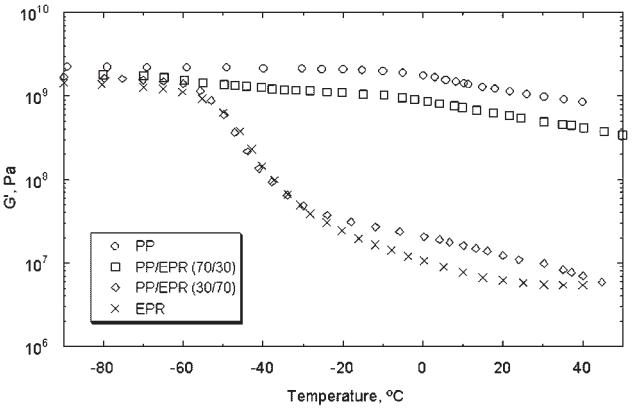

Figure 8. Storage modulus of PP/EPR blends with different rubber content.

component are observed by compatibilization. As can be seen in Table 2, the addition of PPgMMI to PP and EPRgMMI to EPR hardly influence the T_g of the corresponding processed polymers.

The incorporation of the elastomeric phase increases the T_g of PP due to the effect of EPR domains on the segmental mobility of PP. On the other hand, it can be observed that an increase in PP content in the blend gradually reduces the intensity and magnitude of the EPR peak; a displacement of the peak to lower temperatures is also observed (from −40.3 for pure EPR to −43.9 for 30/70 PP/EPR blend and −55.1 °C for 70/30 PP/EPR blend). This behavior was explained by Da Silva et al.,[34] who considered that the elastomer has a higher thermal expansion coefficient than the PP matrix. The cooling of the blend then gives rise to a negative hydrostatic pressure that acts on the elastomeric particles, and thus the thermal tensions generated can be responsible for the decrease in the EPR phase glass transition temperature. Moreover, this peak shift of EPR suggests that an interpenetration between the noncrystalline portion of PP and the interface of EPR exists, indicating that the two components have a certain degree of miscibility. It is interesting to note that this effect is more pronounced when both functionalized polymers are added to the blend. This seems to indicate that the grafted polymers favor the miscibility between the components of the blend and supports a further indication of enhanced interfacial adhesion between both polymeric phases by addition of monomethyl itaconate-grafted PP and EPR. This leads to greater restrictions on the segmental mobility of PP chains. These results agree with the mechanical properties and rheological analysis discussed above.

Crystallization Kinetics

The effect of the incorporation of small amounts of grafted polymers into the blend on the crystallization of PP was also analyzed by nonisothermal DSC experiments. Figure 10 shows the dynamic DSC curves obtained for neat PP and unmodified and monomethyl itaconate-modified PP/EPR blends at a cooling rate of $10\,^{\circ}C \cdot min^{-1}$. The dynamic crystallization behavior observed demonstrated the positive effects of the elastomeric phase on the crystallization kinetics of PP. The average values of the absolute degree of crystallinity (χ_c), the crystallization peak temperature (T_c), and the apparent melting temperatures of the crystallized samples (T_m) are summarized in Table 3. It is observed that T_c increases with the incorporation of the elastomer in the blend, confirming the nucleating ability of EPR on the crystallization of PP. The effect of the rubbery phase on the crystallization rate of PP can be attributed to the modification of the PP matrix superstructure by the incorporation of the elastomer. Moreover, the crystallization behavior of PP in the blend has also been attributed to the role of EPDM to selectively extract defective chains from the PP in the molten state.[35] However, with higher percentages of elastomer in the blend (70%), an inversion of the crystallization rate increase is observed, as can be deduced form T_c values reported in Table 3. This can be explained by the balance of two opposite contributions. The results obtained suggest an increase in nucleation at the rubber-matrix interface with the elastomer content, whereas, on the other hand,

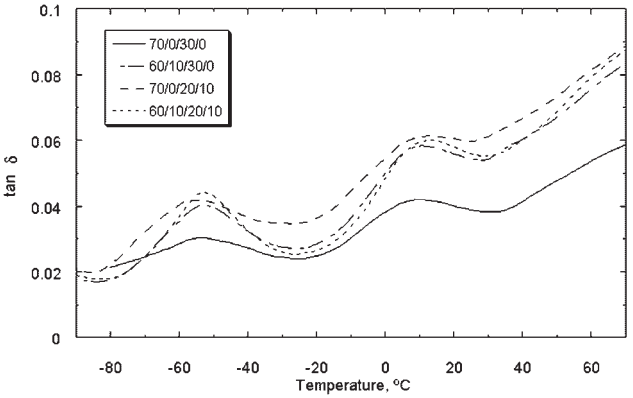

Figure 9. Tan δ traces of unmodified and MMI-modified PP/EPR (70/30) blends.

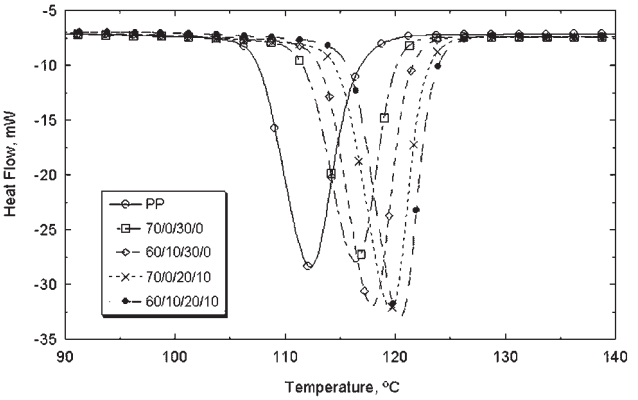

Figure 10. Dynamic crystallization thermograms of unmodified and MMI-functionalized PP/EPR (70/30) blends at $10\,^{\circ}C \cdot min^{-1}$.

Table 3. Crystallization parameters for PP and unmodified and MMI-modified PP/EPR blends.

PP/PPgMMI/EPR/EPRgMMI	T_c	T_m	ΔH_m	Crystallinity
	°C	°C	$W \cdot g^{-1}$	%
100/0/0/0	112.3	159.6	90.30	43.2
90/10/0/0	113.8	159.8	92.45	44.2
70/0/30/0	116.4	160.9	99.78	47.7
60/10/30/0	117.9	160.6	104.96	50.2
70/0/20/10	119.6	160.7	101.37	48.5
60/10/20/10	120.3	159.6	103.98	49.8
30/0/70/0	114.2	160.8	91.42	43.7
20/10/70/0	114.8	161.2	92.77	44.4
30/0/60/10	114.9	161.1	93.93	44.9
20/10/60/10	115.5	161.3	93.00	44.5

the same rubber phase could be responsible of an impingement effect on the spherulitic growth. Similar behavior has been reported for the study of the effects of carbon fibers on the crystallization behavior of different thermoplastic matrix composites.[36]

It is worth noting that a further increase in the maximum of the exothermic peak, T_c, is observed in the blends with grafted polymers, in particular, for the blend containing both grafted polymers. This suggests that the degree of supercooling of blends containing grafted polymers is higher than that of nonfunctionalized blends. It can be assumed that the functional polar monomer used here behaves as an effective nucleating agent for the PP matrix, accelerating the overall crystallization of the semicristalline polymer. That is, by adding grafted polymers, PP spherulites crystallized faster and impinged earlier than that of the nonfunctionalized blends. It is assumed that the overall crystallization rate is controlled by two mechanisms, namely nucleation rate and growth rate. The results obtained indicate that the addition of grafted polymer to PP/EPR blends may increase the nucleation rate by the formation of a higher number of active nuclei during the crystallization process.

The degree of crystallinity of the PP phase, can be estimated using the following equation:[37]

$$\%\text{crystallinity} = \frac{\Delta H_m/(\text{wt.-}\%\ \text{PP})}{\Delta H(100\%\ \text{crystallized PP})} \times 100 \qquad (3)$$

where ΔH_m is the experimental value, which has been normalized to the real content of PP in the blend, and ΔH (100% crystallized PP) is given as 209 $J \cdot g^{-1}$.[38] The obtained results are reported in Table 3. It can be seen that the crystallinity of PP slightly increases in the presence of the elastomer. Moreover, this increase is even clearer when the polymers are functionalized. Jafari et al.[32] demonstrated that the crystallinity is strongly related to the segmental mobility of PP chains. Therefore, an increase in the crystallinity implies a restriction of the mobility of the polymer chains, and consequently, the glass transition of PP is shifted to higher temperatures. These results agree with those obtained by dynamic mechanical analysis (DMA), in which an increase in the T_g of PP was observed.

Furthermore, no significant changes in the melting point of the PP phase were detected in the blends.

Morphological Analysis

The fracture surface of the blends after extraction of the EPR phase by using toluene at 70 °C was analyzed by SEM. Figure 11 shows the micrographs of unmodified and MMI-modified PP/EPR (70/30) blends at the same magnification. As is evident from the scanning electron micrographs, the small rubber particles are uniformly distributed in the PP matrix. In addition, the micrographs show that the blends containing grafted polymers have a more homogeneous morphology with a fine and uniform dispersion of rubber particles in the continuous plastic matrix than that of unmodified blends. Moreover, the average size of the dispersed rubber particles was reduced by the addition of monomethyl itaconate-grafted polymers (from 4 μm for unfunctionalized to 0.5–2 μm for the blend containing grafted polymers); this effect is more evident for the blend containing both grafted polymers. Moreover, a higher interphase amount due to smaller particles is obtained as a result of grafting reaction, which correlates with the corresponding increase in the viscosity of the blends discussed above. These results suggest that the grafted monomethyl itaconate have a significant effect on the particle size and possibly, on the interfacial adhesion. This is one of the aspects responsible for the better impact behavior of functionalized blends. Bedia et al.[39] demonstrated that the size of the rubber particles is intimately related to its function as an impact modifier for polyolefins. Thus, a decrease in the rubber particles size correlates with the enhancement of the impact strength of the material. The morphology analysis supports the rheological and mechanical results. By adding grafted polymers, the particle size was reduced, and the adhesion of both polymeric phases was improved.

Conclusions

PP and EPR grafted with monomethyl itaconate (MMI) were used as compatibilizers for PP/EPR blends. The grafting reaction was confirmed by FTIR spectroscopy, by which a degree of grafting of 1.5% by weight for PP and 1.2% by weight for EPR was determined. The compatibilization of these blends was found to increase the viscosity of the system, indicating an increase in interfacial adhesion. The addition of small amounts of grafted polymers improved the toughness and elongation at the break of all blends and retained their strength and stiffness. This effect is particularly evident, when both MMI-grafted PP and EPR were used as blend compatibilizers. The dynamic mechanical analysis show a clear increase in the height of tan δ traces

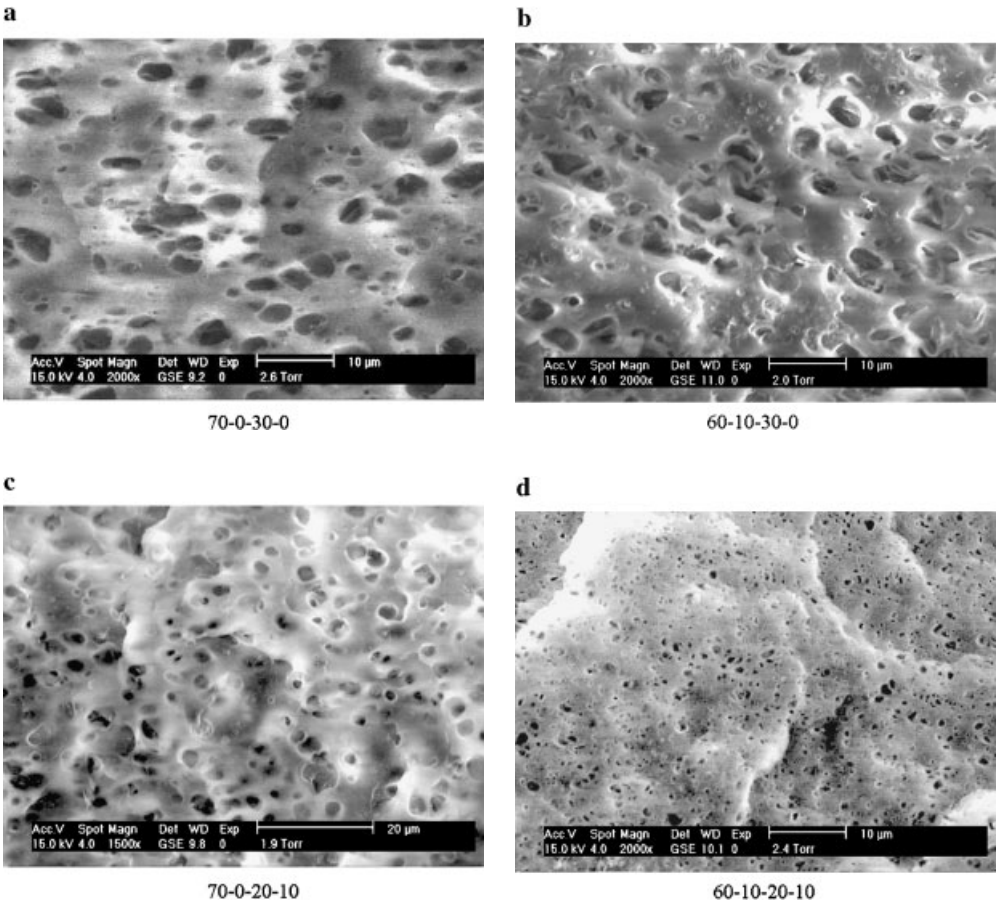

Figure 11. SEM micrographs of PP/EPR (70/30) blends: (a) unmodified blend, (b) PP/PPgMMI/EPR (60/10/30/0) blend, (c) PP/EPR/EPRgMMI (70/0/20/10) blend, and (d) PP/PPgMMI/EPR/EPRgMMI (60/10/20/10) blend.

of both components in the presence of grafted polymers, which further supports the strong indication of its improved behavior as an impact modifier. These results indicate that the monomethyl itaconate-grafted PP and EPR behave as effective compatibilizers in blends of polyolefins and elastomers, reducing the interfacial tension or increasing the interfacial adhesion. The compatibilizing effect of the modified polymers was also confirmed by morphological analysis of the blends, in which a stabilized morphology consisted of smaller droplets of elastomeric phase finely dispersed in the continuous PP matrix.

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