

Effect of Grafted PP on the Properties of Thermoplastic Elastomers Based on PP-EPDM Blends

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Introduction

Isotactic poly(propylene) (iPP), while having many valuable properties, is known to have an inadequate frost resistance as well as a high glass transition and crystallization temperature, which underlines its rigidity and brittleness at low temperatures.^[1,2] Since PP is a nonpolar polymer, it blends poorly with polar plasticizers and also with polar polymers, which are quite popular at present. The plastification of PP by blending with rubbers, in particular ethylene propylene copolymers and terpolymers (EPM and EPDM, respectively), was found to be highly effective. These blends are commonly referred to as ther-

moplastic polyolefin elastomers (TPOs). They belong to a class of materials that combines the good processing characteristics of thermoplastics at elevated temperatures^[3-5] with the physical properties of conventional elastomers at service temperatures,^[6,7] playing an increasingly important role in the polymer industry. Recently, our research group has carried out a complete characterization of this type of systems.^[8-11] The most utilized TPOs at industrial level are those constituted of PP-EPDM blends. In fact, EPDM is considered to be one of the most effective impact modifiers for PP^[12-15] because of its high impact strength over a wide temperature range.

The elastomeric phase is added to PP with the main objective of improving its flexibility and properties at low temperatures. However, with rubber inclusion, certain mechanical properties, such as stiffness and hardness,^[16, 17] are inevitably reduced, therefore limiting the application field of these materials. For this reason and in order to overcome these limitations, the preparation of thermoplastic elastomers with functionalized poly(propylene) as polymeric matrix should give rise to a better dispersion between both polymeric phases, and then, it could be possible that a more homogeneous and cocontinuous structure will be obtained.

It is well known that the modification of polymers constitutes one of the most interesting processes recently applied to the preparation of new materials. In the last few years, several studies have been reported on the modification of polymeric materials, especially polyolefins, in order to improve the properties and stabilities of the final products. The grafting of polar monomers onto PP via free radical reactions has gained wide industrial application and attracted scientific interest. The most studied modification of PP is that with maleic anhydride,^[18–21] which is performed either in solution,^[22, 23] in the solid state^[24, 25] or in the PP melt.^[9, 26, 27] Other polar monomers, such as unsaturated carboxyl derivatives and vinylic or acrylic substances, containing more than one functionality, have also been investigated.^[23, 28–30] In the present study, PP was modified with itaconic acid derivatives, in particular monomethyl itaconate (MMI) and dimethyl itaconate (DMI), in the melt at 190 °C by using 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (Lupersol 101). In a previous work carried out in our laboratories, it was demonstrated that PP can be functionalized with itaconic acid in a homogeneous medium with short reaction times at reaction temperatures as high as 190 °C and with reproducible proportions of incorporated monomer.

The aim of this work was to evaluate the performance of grafted PP with two itaconic acid derivatives, MMI and/or DMI, as components of blends with elastomers. With this purpose, different thermoplastic elastomers based on blends of modified poly(propylene) and ethylene-propylene diene rubber (50/50) were prepared and their properties were investigated. A comparative study of blends processed with unmodified PP was also carried out.

Experimental Part

Materials and Preparation of the Blends

Poly(propylene) (PP) (melt flow index 6.0 at 230 °C and density 0.905 g · cm⁻³), generously supplied by Montell under the trade name C30G, and ethylene propylene diene terpolymer rubber (EPDM) with 5-ethylidene-2-norbornene (ENB) as a termonomer (68% ethylene content and density 0.86 g · cm⁻³), supplied by Bayer under the trade name BUNA EP

T 6470P, were used in this study. Itaconic acid was purchased from Aldrich. Monomethyl itaconate (MMI) and dimethyl itaconate (DMI) were synthesized by esterification of itaconic acid with methanol and their purity was checked by ¹H NMR spectroscopy. 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (Lupersol 101) from Akzo was used as radical initiator. This organic peroxide has a half-life of 36 s at 190 °C. PP was functionalized in the melt by grafting with itaconic acid derivatives using a Brabender plasticorder. The optimum conditions for the grafting reaction were 190 °C, 75 rpm and 6 min. The modified PP samples were extracted, using methanol in the case of MMI and chloroform in the case of DMI, in a Soxhlet for 24 h in order to eliminate unreacted monomers or possible homopolymers that may form during the grafting reactions. The characterization of grafted PP was performed according to the procedure described by Yazdani-Pedram et al.^[31]

In the samples denominated as unmodified blends (*b*-PP), PP was passed through the Brabender plasticorder in the presence of all components except the itaconates prior to mixing with the elastomer.

Melt-blended specimens were prepared in a Haake Rheomix 90 internal mixer, equipped with high-shear roller-type rotors. The temperature of the mixing chamber was set to 170 °C and the blending time was 10 min. The rotor speed was set to 60 rpm. Immediately after the completion of mixing, the materials were compression-molded for 15 min at 180 °C into 0.2 mm thick plaques before testing.

Measurements

The evidence of grafting as well as its extent, expressed as weight percent of grafting, was determined by FT-IR spectroscopy. FT-IR spectra were recorded on a Bruker IFS-28 spectrometer from 4000 to 400 cm⁻¹. Films of 600 μm thickness from PP and grafted samples were obtained by compression molding between steel plates covered with thin aluminum sheets at 190 °C for 1 min.

The molecular weights of PP and the functionalized PP samples were determined by dilute solution viscosity measurements using decalin as solvent at 135 °C. An Ubbelohde dilution type viscometer was used. The viscometer was checked for kinetic energy correction by measuring the flow time for water at 20, 25, 30, 35, and 40 °C before use. The concentrations of the polymer solutions were recalculated at 135 °C by considering the volume correction factor for decalin at 135 °C and by using the relation $C = 100M/1.07V$, where M is the mass of the polymer, V is the solvent volume in ml at 25 °C and 1.07 is the volume correction factor. The intrinsic viscosity values $[\eta]$ of the samples were determined by the single point method, and the viscosity-average molecular weights were calculated by employing the Kuhn-Mark-Houwink-Sakurada relation ($[\eta] = KM^a$) for PP in decalin with $a = 0.80$ and $K = 1.1 \cdot 10^{-4}$ dl/g.

Torque versus time curves were recorded during the processing of the material in the Haake Rheomix 90. The melt flow index was determined using a CFR 91 according to ASTM D-1238.

The rheological measurements were performed using a Rheometric Scientific ARES N2 dynamic mechanical spec-

trometer with parallel plate geometry. Tests were carried out in the dynamic frequency mode at 190 °C. The rheological properties were determined as a function of angular deformation speed in the range from 0.015 to 20 Hz. The strain amplitude was kept constant at 5%. The dynamic mechanical properties of the solid polymer were determined with the same instrument at a frequency of 5 Hz and the temperature programs were run from -100 °C to 50 °C under a sinusoidal strain controlled at a heating rate of 2 °C/min in a flow of nitrogen. The oscillating dynamic strains amounted to 0.15%.

Tensile measurements were performed according to ASTM D-638 M at room temperature on an Instron dynamometer, model 4301. Tests were carried out at a crosshead speed of 5 mm/min until a deformation of 20% and 50 mm/min at break, and the tensile properties (Young's modulus, strength and elongation at break) were determined. All the results were the average of at least five measurements.

Thermal analysis experiments were carried out on a Perkin Elmer Pyris 1 differential scanning calorimetry (DSC) instrument coupled with an intercooler in isothermal and dynamic modes. For isothermal measurements, samples of about 8 mg were melted at 200 °C for 10 min in order to eliminate any thermal history of the material; then, they were cooled to the crystallization temperature, T_c , and kept at this temperature during the necessary time to complete the crystallization of the matrix. Four crystallization temperatures were examined in a range between 125 and 132 °C. Dynamic DSC scans were performed at a heating and cooling rate of 10 °C/min in a temperature program from -50 to 200 °C.

In order to analyze the morphology of the composites, fracture surfaces of the compression-molded specimen were sputtered with gold and observed with a Jeol T-330A scanning electron microscope (SEM).

Results and Discussion

Evidence of Grafting

The existence of grafted MMI and DMI in PP was confirmed by FT-IR spectroscopy. Figure 1 shows the FT-IR spectrum of PP grafted with DMI. The absorption band observed at 1744 cm^{-1} is due to the carboxyl group of the ester linkage of DMI and confirms the incorporation of this monomer into PP chains. The intensity of this band was compared with that of the methyl group from PP centered at 1167 cm^{-1} . The 1744 cm^{-1} /1167 cm^{-1} band ratio was defined as the carbonyl index (IcE). This can be considered as a measure of the extent of monomer grafting in PP, either as single units and/or poly(dimethyl itaconate) chains.

The extent of grafting was converted into the incorporated weight percent (% of grafting) of the monomer by using a calibration curve obtained from FT-IR analysis of the physical mixtures of PP with different amounts of DMI. These mixtures were obtained by melt mixing of PP and DMI in a Brabender mixing chamber at 190 °C under nitrogen for 6 min.

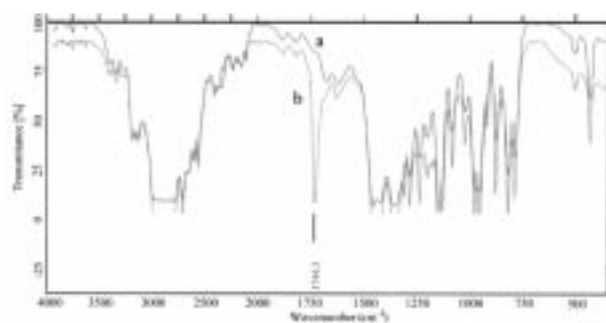


Figure 1. FT-IR spectrum of: a) unmodified PP and b) DMI-functionalized PP.

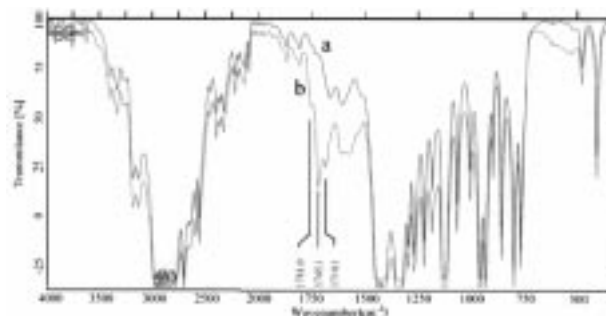


Figure 2. FT-IR spectrum of: a) unmodified PP and b) MMI-functionalized PP.

It was confirmed that the relative intensity of this band increases with increasing initial concentration of DMI used in the grafting reaction. The percentage of grafting can then be calculated using the following relation:

$$\% \text{ of grafting} = 0.393 IcE \quad (1)$$

In the case of MMI-modified PP, the FT-IR spectrum showed three absorption bands in the carbonyl region that are absent in the spectrum of unmodified PP (Figure 2). The absorption bands at 1710 cm^{-1} and 1745 cm^{-1} are due to stretching vibrations of the carbonyl groups of the ester and the carboxylic acid of the monomer, respectively. The third absorption band centered at 1781 cm^{-1} was assigned to a carbonyl group from a five-membered anhydride ring. The sum of the intensities of the absorption bands at 1710 cm^{-1} and 1745 cm^{-1} was compared with that of the methyl group from PP centered at 1167 cm^{-1} , and the carbonyl index ($Ic_{\text{monoester}}$) corresponding to the incorporation of the monomer as monoester was calculated. Similarly, the intensity of the absorption band at 1781 cm^{-1} was compared with that of the methyl group from PP centered at 1167 cm^{-1} . This band ratio was defined as the carbonyl index (IcA) corresponding to the incorporation of the monomer in its cyclic anhydride form. In order 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. In a similar manner as in the case of

Table 1. Values of MW and percentage of grafting for functionalized PP samples.

Sample	Grafted monomer	Percentage of grafting wt.-%	MW g/mol
v -PP			170 000
b -PP 1			150 000
b -PP 2			88 000
PP- g -DMI 1	DMI	0.5 ± 0.05	124 000
PP- g -DMI 2	DMI	1.4 ± 0.1	55 000
PP- g -MMI 1	MMI	0.5 ± 0.05	140 000
PP- g -MMI 2	MMI	1.4 ± 0.1	70 000

DMI, the total percentage of MMI grafted in the form of both monoester and anhydride can be determined by using the following relation:

$$\% \text{ of grafting} = 0.554 I_{c_{\text{monoester}}} + 0.339 I_{cA} \quad (2)$$

Two samples of PP grafted with different amounts of either DMI or MMI were used in this work. The percentage of grafting as well as the viscosity-average molecular weights of virgin PP (v -PP), PP treated with Lupersol 101 in the absence of monomer and passed through the Brabender plasticorder (b -PP), and functionalized PP samples with either DMI or MMI are shown in Table 1.

Rheological Studies

The flow properties of the materials studied in the molten state were analyzed by melt index, torque curves, and rheology. Torque values obtained during mixing in the internal mixer as a function of the monomer concentration are represented in Figure 3. It is well known that the torque value in the plateau region obtained after stabilization characterizes the viscous nature of the material in the molten state. The results clearly show that the functionalization of PP gives rise to a decrease of the torque value of the blend, which indicates a better processability. In addition, a slight decrease is observed as the amount of monomer incorporated in PP is increased.

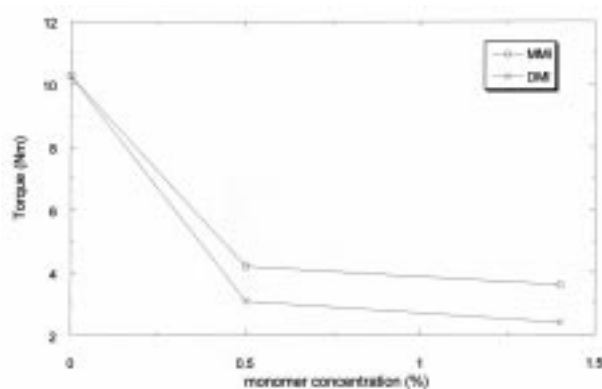


Figure 3. Total torque as a function of the monomer concentration.

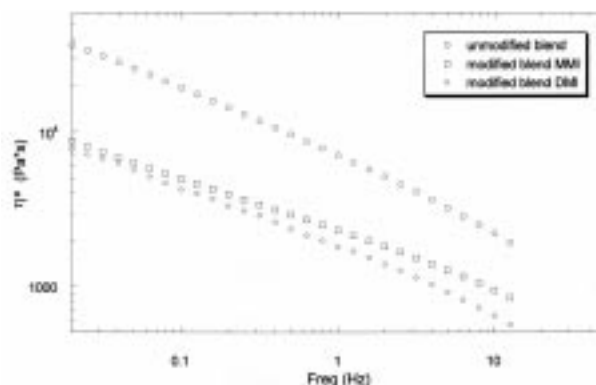


Figure 4. Variation of complex viscosity with angular frequency at 190°C for different blends studied.

These results were further confirmed by rheological studies. The variation of the complex viscosity, η^* , as a function of the angular frequency for unmodified PP-EPDM blend and blends prepared with PP grafted with MMI and DMI, respectively, at 190°C is presented in Figure 4. From these results, it can be concluded that the grafting reaction on PP chains gives rise to a significant decrease of the matrix viscosity, which is more evident for incorporated dimethyl itaconate than for incorporated monomethyl itaconate. Moreover, the viscosity gradually decreases as the monomer concentration increases. The viscosities of the materials studied at a frequency of 1 Hz are presented in Table 2.

The zero-viscosities were also calculated by fitting the rheological data to the equation proposed by Ellis,^[32] which is based on the Cross model:^[33]

$$\eta = \frac{\eta_0}{(1 + (K\omega)^m)} \quad (3)$$

η_0 represents the zero-shear viscosity, ω is the angular frequency, K is a constant with the dimension of time, and m is a dimensionless constant. The results obtained are summarized in Table 2. As expected, the zero-shear viscosity of the blends prepared with functionalized poly(propylene) decreases relative to the unmodified blend. The results of the rheological analysis can be understood by the fact that the grafting reaction produces a β scission of PP chains, giving rise to a diminution of the molecular weight. Moreover, the degradation process is proportional to the amount of monomer incorporated during the grafting reaction.

Melt flow index values (MFI) of the different materials were also determined, and the results are reported in Table 2. It becomes clear that the functionalization of PP increases the MFI value, which is still more evident when dimethyl itaconate is used as functional monomer. It can also be seen that the MFI values regularly increase as the amount of monomer incorporated in PP increases. The melt flow index is a measure of the ability of the material

Table 2. Rheological parameters of the materials studied.

Property	Unmodified blend	Modified blend			
		Monomethyl itaconate		Dimethyl itaconate	
		0.5%	1.4%	0.5%	1.4%
Torque value/(N · m)	10.3	4.2	3.6	3.1	2.4
Melt index/(g/10 min)	1.1	15	21	24	33
Viscosity/(Pa · s)	7 118.6	2 308.1	1 913.2	1 793.5	1 688.6
Zero viscosity/(Pa · s)	43 000	13 100	11 800	11 350	9 900

Table 3. Dynamic mechanical properties of the PP-EPDM blends studied.

PP-EPDM in%	EPDM			PP		
	T_g °C	$\tan \delta$	G' Pa	T_g °C	$\tan \delta$	G' Pa
50/50	-36.7	0.094	$5.30 \cdot 10^8$	6.8	0.071	$2.53 \cdot 10^8$
50/50 M1	-35.6	0.092	$7.25 \cdot 10^8$	6.4	0.064	$2.65 \cdot 10^8$
50/50 M2	-34.1	0.095	$8.97 \cdot 10^8$	6.3	0.066	$2.97 \cdot 10^8$
50/50 D1	-34.9	0.098	$8.32 \cdot 10^8$	6.0	0.062	$2.96 \cdot 10^8$
50/50 D2	-32.7	0.097	$1.05 \cdot 10^9$	6.2	0.068	$3.37 \cdot 10^8$

to flow, and thus, grafted PP has a higher flow speed in the molten state, which indicates a lower viscosity of the material. Consequently, these results are in agreement with those previously obtained by torque analysis and rheological studies and provide a further confirmation of the higher facility of processing of the blends prepared with modified PP, which is probably due to the degradation process of the polymeric matrix chains.

Dynamic Mechanical Analysis

The dynamic mechanical properties of the different materials were studied over a wide temperature range (-100 to 50 °C). The obtained results are shown in Table 3. On the one hand, it can be observed that the presence of two loss peaks, corresponding to those of their constituents, reveals the immiscibility of this type of systems. On the other hand, it could be demonstrated that the grafting reaction hardly changes the position of the peak corresponding to the glass transition temperature (T_g) of PP, however, a shift of the T_g of elastomers to higher temperatures was observed. These results seem to indicate that the incorporation of both monomers favors the interaction between the elastomeric and polymeric phases.

Table 4. Tensile properties of the materials analyzed.

Property	Unmodified blend	Modified blend			
		Monomethyl itaconate		Dimethyl itaconate	
		0.5%	1.4%	0.5%	1.4%
Young's modulus/MPa	150	177	193	188	202
Maximum strength/MPa	12.7	8.7	9.1	8.9	9.0
Deformation at break/%	542	40	32	44	35

This observation was verified by measurements of the storage modulus, where a noticeable increase was observed when the polymer matrix is modified. Furthermore, it is worth noting that these effects are more sensitive when dimethyl itaconate is incorporated in the chemical structure of the polymeric matrix.

Tensile Properties

In order to evaluate the effect of the PP grafting reaction on the mechanical properties of PP-EPDM blends and to compare both monomers (MMI and DMI), the tensile properties were analyzed, and the results are summarized in Table 4. On the basis of these results, it was found that the grafting reaction gives rise to a more rigid and tenacious material, showing consequently a significant improvement of the tensile properties, such as Young's modulus and strength at low deformations, as well as a considerable decrease of the deformation at material break. This behavior regularly changes as the monomer percentage used in the grafting reaction is increased. Furthermore, it is of interest to note a more significant effect when PP is modified with dimethyl itaconate. These results agree well with those obtained by dynamic mechanical analysis, which strongly support the assumption that the incorporation of both monomers in the PP chain promotes the interaction between both polymeric phases, giving rise to a more rigid and more stable structure.

Crystallization Studies

The effects of the elastomers on the crystalline structure and crystallization kinetics of PP were investigated in a previous work.^[9] It was demonstrated that the incorporation of the elastomer alters the crystalline structure of the

Table 5. Crystallization parameters of the materials studied.

Property	Unmodified blend with <i>b</i> -PP	Unmodified blend with PP of IMW ^{b)}	Modified blend			
			Monomethyl itaconate		Dimethyl itaconate	
			0.5%	1.4%	0.5%	1.4%
$\tau_{1/2}/s$	213	200	50.4	78.6	93.9	188.4
n	2.61	2.46	2.54	2.60	2.50	2.63
K_n	$2.63 \cdot 10^{-2}$	$3.53 \cdot 10^{-2}$	$1.08 \cdot 10^0$	$3.43 \cdot 10^{-1}$	$2.26 \cdot 10^{-1}$	$3.42 \cdot 10^{-2}$
$T_c/^\circ C$	117.2	119.5	123.8	122.2	121.6	121.2
$T_m/^\circ C$	161.9	161.4	160.9	156.6	159.2	156.9
$\Delta H/(J/g)^{a)}$	46.1	46.6	45.1	46.6	50.5	47.5
$X_c/\%$	22.1	22.3	21.6	22.3	24.2	22.7

a) $\Delta H(PP)$ (100% crystalline) = 209 J/g.

b) IMW = low molecular weight.

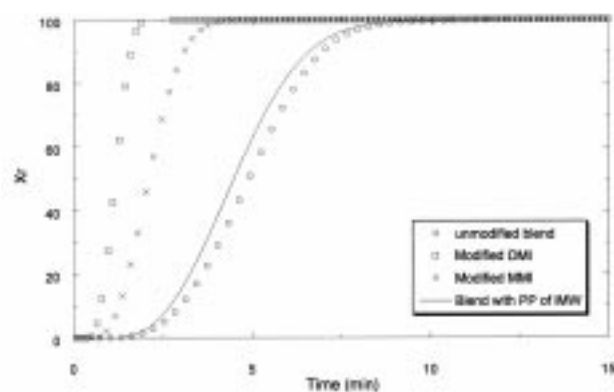


Figure 5. Degree of crystallization of unmodified and MMI- and DMI-modified PP-EPDM blends at 130°C. Comparative study with a PP sample of low molecular weight.

polymeric matrix, changing the number and average size of the spherulites. The effects of the grafting reaction with monomethyl and dimethyl itaconate on the crystallization characteristics of PP were then investigated in isothermal and dynamic modes by differential scanning calorimetry (DSC). The representation of the degree of crystallization as a function of time (Figure 5) shows that the rates of crystallization of the functionalized blends are higher than those of the unmodified blends, which is reflected in a notable decrease of the half-time of crystallization. It is important to emphasize that the grafting reaction gives rise to a reduction of the molecular weight of iPP, and this fact influences the crystallization kinetics enormously. Therefore, and in order to evaluate the real effect of the grafted monomers, a comparative study with a PP sample of similar molecular weight was also carried out. It can be observed that the crystallization kinetics of PP increases as the molecular weight decreases. However, the crystallization rate of the functionalized samples is always higher. According to these results, it can be argued that the functional polar monomers used in this work act as effective nucleating agents for PP, favoring the crystallization of the semicrystalline polymer. This behavior could be explained by the fact that a higher

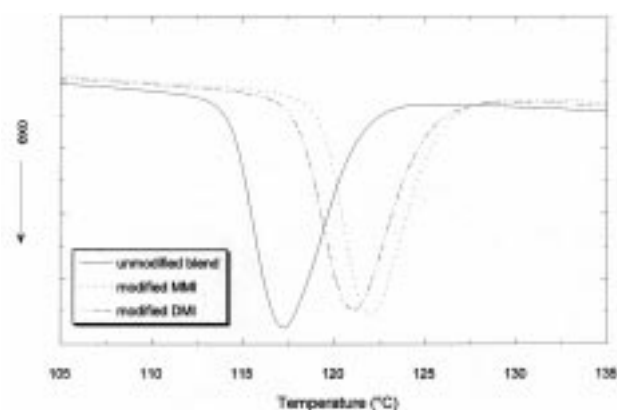


Figure 6. Nonisothermal crystallization thermograms of the blends studied.

number of nuclei are present during the crystallization process. In this case, monomethyl itaconate is the more effective monomer in promoting crystallization of PP. Furthermore, it is important to notice that a decrease of the crystallization rate is observed as the monomer concentration is increased.

The effect of the grafting reaction on the crystallization of iPP was also analyzed by nonisothermal experiments. The results showed that the crystallization peak temperature increases when the monomers are incorporated in the chemical structure of the polymer. As shown in Figure 6, the increment of the crystallization peak temperature is higher for the blends with MMI-modified PP, with the crystallization dynamic thermograms recorded at a cooling rate of 10°C/min. The observed dynamic crystallization behavior confirms the results obtained in isothermal tests, indicating a strong nucleation ability of the monomers used for the crystallization kinetics of PP. Regarding the effect of the grafting reaction on the melting temperature, no substantial differences were detected, while a small tendency to increase the total amount of crystallinity with monomer incorporation was observed. Crystallization parameters obtained in both isothermal and dynamic modes are shown in Table 5.

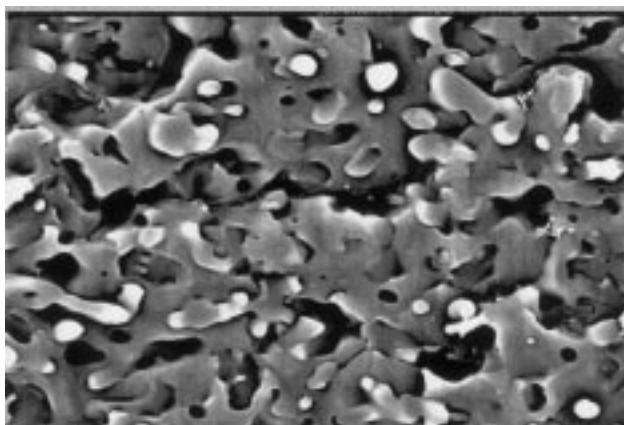


Figure 7. Fracture surface of unmodified PP-EPDM blend.

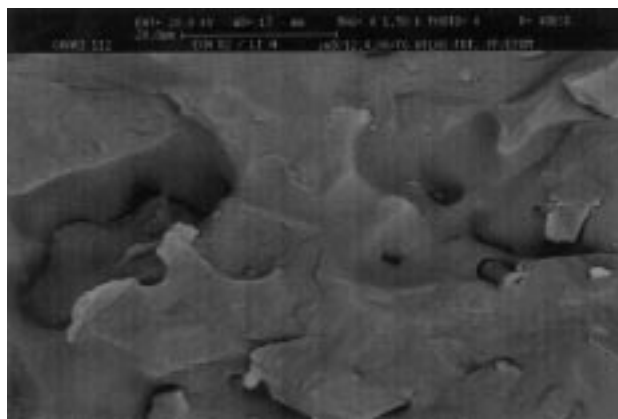


Figure 9. Fracture surface of the blend prepared with DMI-modified PP.

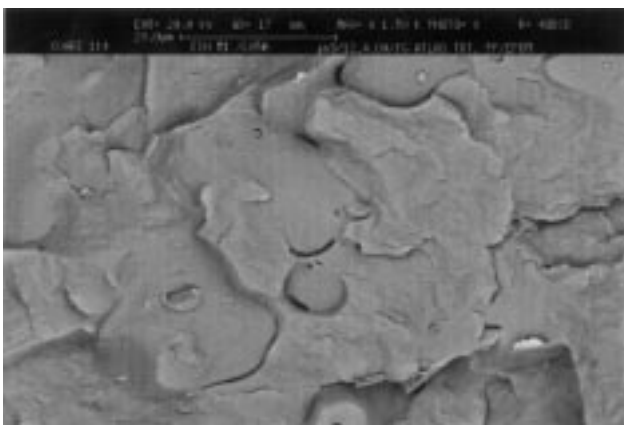


Figure 8. Fracture surface of the blend prepared with MMI-modified PP.

Morphological Studies

In order to characterize the morphology of the blends and to study the relationship with their properties, a morphological study was carried out by scanning electron microscopy (SEM). Micrographs of the impact fracture surfaces of unmodified PP and PP modified with MMI and DMI blends are shown in Figure 7–9. The results of the morphological study are in accordance with the analyzed properties, where it is possible to observe a better dispersion between both phases when the blends are prepared with functionalized PP. From Figure 7 it can be easily observed that the blends of unmodified PP and EPDM form an immiscible system, with two cocontinuous phases clearly separated. However, the PP grafting reaction with itaconate acid derivatives gives rise to a better dispersion between both polymeric phases, showing a more stable structure, as can be observed in Figure 8 and 9. This feature permits to explain the better properties of the blends prepared with modified PP with respect to those with unmodified PP.

Conclusions

The effects of the poly(propylene) grafting reaction on the properties of thermoplastic elastomers based on PP-EPDM blends were evaluated in the present work. PP was functionalized with two itaconic acid derivatives, monomethyl and dimethyl itaconate (MMI and DMI, respectively), at two different initial monomer concentrations (0.5 and 1.4 wt.-%).

The study of the flow properties carried out by torque measurements, melt index and rheological analysis showed that the blends prepared with modified PP have a better processability, showing a lower viscosity, with this effect being more significant when PP is modified with DMI. Dynamic mechanical analysis and tensile properties revealed that the grafting reaction promotes the interaction between both polymeric phases, giving rise to a more rigid structure. Furthermore, it was observed that the functional polar monomers not only act as compatibilizers but also behave as nucleating agents for PP crystallization, showing a substantial decrease of the half-time of crystallization, which could be attributed to the presence of a higher number of nuclei during the crystallization process. These results are in agreement with the observations carried out by scanning electron microscopy (SEM), where a better interaction between both polymeric phases is observed when PP is functionalized.

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