

Melt grafting of itaconic acid and its derivatives onto an ethylene-propylene copolymer

J. Bruna ^{a,b}, M. Yazdani-Pedram ^{a,*}, R. Quijada ^b, J.L. Valentín ^c,
M.A. López-Manchado ^c

^a *Facultad de Ciencias Químicas y Farmacéuticas y Centro para la Investigación Interdisciplinaria Avanzada en Ciencia de los Materiales, Universidad de Chile, Casilla 233, Santiago, Chile*

^b *Facultad de Ciencias Físicas y Matemáticas y Centro para la Investigación Interdisciplinaria Avanzada en Ciencia de los Materiales, Universidad de Chile, Casilla 2777, Santiago, Chile*

^c *Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva, 3, 28006-Madrid, Spain*

Abstract

An ethylene-propylene copolymer (EPR) was functionalized in the melt by grafting with itaconic acid and its mono- and di-methyl esters by using dicumyl peroxide as radical initiator. Grafting reactions were carried out in a Brabender-Plasticorder at 180 °C under a nitrogen flow at a speed of 75 rpm for 6 min. Fourier transform infrared spectroscopy (FTIR) was used to confirm the existence of grafted monomers. The absorption bands characteristic of each monomer grafted were observed in the FTIR spectrum of the modified EPR and were taken as evidence of grafting.

The percentage of grafting attained was also followed by FTIR analysis, where the amount of monomer incorporated in EPR was estimated from a calibration curve established for the monomers used in this work. The degree of grafting obtained was 1.1% by weight of EPR for itaconic acid, 1.2% for monomethyl itaconate and 2.5% for dimethyl itaconate. Rheological and contact angle measurements indicate that the polarity of EPR is increased by grafting reaction.

Keywords: Ethylene-propylene copolymer; Free radical grafting; Itaconic acid; Monomethyl itaconate; Dimethyl itaconate

* Corresponding author. Tel.: +56 2 678 2855; fax: +56 2 678 2868.

E-mail address: mypedram@gmail.com (M. Yazdani-Pedram).

1. Introduction

The modification of polyolefins such as polypropylene [1–13] and an olefinic elastomer such as random copolymer of ethylene and propylene

(EPR) [14–25] with the aim of introducing polar functional groups into their non-polar olefinic chain has been the subject of intense research work during recent years. The most widely used method for the functionalization of polyolefins is to graft monomers that contain polar functional groups such as oxazoline [17,18], maleic anhydride [1–4,9–12,19,25], itaconic acid and its derivatives [5–7], alkyl maleates [1,8,9,14,24], maleimides [1,13], acrylic and methacrylic acids [1,2], glycidyl methacrylate [15,16,21], allyl(3-isocyanate-4-tolyl) carbamate [22,23], a functional monomer prepared from reaction of 2-hydroxyethyl methacrylate with isophorone diisocyanate [20], etc.

The functionalized polyolefins have found application as compatibilizers in blends of polyolefins with polar polymers, where specific interactions between the blend components have shown to improve the interfacial adhesion and compatibility of the blend components [17,22,26–30].

Polymer blending is a route widely used for the preparation of advanced materials with specific properties. An important example at industrial level is constituted by thermoplastic polyolefin elastomers (TPOs) based on blends of a thermoplastic and an elastomer. Although these polymers have a similar chemical structure, melt mixing leads to a two-phase system because polymers are thermodynamically immiscible. Consequently, the resulting material exhibits high interfacial tension with unstable morphology and poor and undesirable mechanical properties because of unfavorable interactions at the molecular level. Several methods to improve the phase adhesion between two immiscible polymers have been developed. One of these methods is by adding functionalized polymers containing polar groups as compatibilizers to the blend in order to promote phase mixing through specific interactions at the phase boundary.

However, the potential use of itaconic acid, a vinyl monomer containing two carboxylic groups, and its derivatives has been investigated recently by our group as polar monomers in grafting reactions onto polypropylene and polyethylene [5–7]. These reactions were carried out either in solution or in the melt phase, through free radical grafting, with the aim of using them as compatibilizing agents in blends of PP with polar polymers [27–30].

The application of itaconic acid can be considered important because of its carboxylic bifunctionality and due to the fact that itaconic acid is produced from non-oil based renewable natural resource, i.e., by large scale fermentation of molasses, a by-product from sugar industry. The structure of itaconic acid and its mono- and dimethyl esters are shown in Scheme 1.

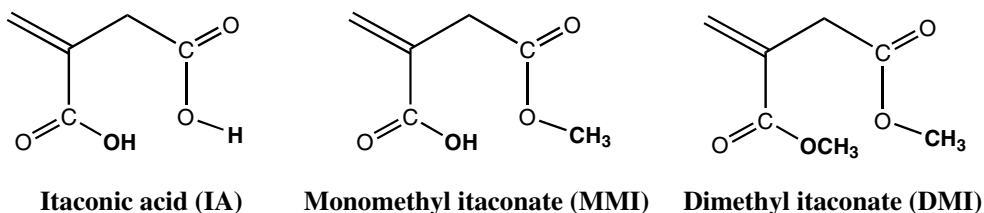
In this study, an ethylene-propylene random copolymer (EPR) was functionalized by melt grafting process using itaconic acid (IA) and its derivatives namely, monomethyl itaconate (MMI) and dimethyl itaconate (DMI).

The aim of this study is to evaluate the effect of reaction conditions and structure of a polar monomer (IA, MMI and DMI) on the extent of grafting onto EPR, via free radical reaction in the melt phase. The extent of grafting was estimated by using Fourier transform infrared spectroscopy (FTIR). Rheological, polarity and adhesive properties of the grafted samples are also evaluated.

2. Experimental

2.1. Materials

Ethylene-propylene random copolymer (EPR) (59% polypropylene content and a Mooney vis-



Scheme 1. Structures of itaconic acid, monomethyl itaconate and dimethyl itaconate.

cosity ML (1 + 4) at 125 °C: 44) was kindly supplied by EniChem, under the trade name Dutral CO-054. Itaconic acid was purchased from Aldrich. MMI and dimethyl itaconate were synthesized by esterification of itaconic acid with methanol and their purity was checked by ¹H NMR spectroscopy. The details for their synthesis are described in a previous works [6,7]. Dicumyl peroxide was purchased from Akzo-Nobel Corp. and recrystallized from anhydrous ethanol before use.

2.2. Grafting reactions

EPR was functionalized with IA and its derivatives, MMI and DMI with dicumyl peroxide as initiator in a reactive melt polymer processing by using a mixer Brabender plasticorder. The type of polymer used in a grafting reaction is expected to affect the nature of side reactions. It is well known that polypropylene undergoes primarily β -chain scission, via the tertiary macroalkyl radicals, leading to reduction in the molar mass and viscosity of the polymer. On the other hand, polyethylene undergoes predominantly crosslinking reactions (through the secondary macroalkyl radicals) during melt processing, resulting in an increase in molar mass and viscosity of the polymer [1,2]. In the case of an ethylene-propylene random copolymer consisting of both, ethylene and propylene components, the two side reactions can occur during the radical grafting process. In our case, an evidence of EPR crosslinking was obtained from measurements of the extent of insoluble gel determined by extraction in hot xylene for 8 h. Note that the unmodified polymer is completely soluble under these conditions, whereas grafted EPR with DMI gave 23% gel content, EPR grafted with MMI gave 17% gel content while EPR grafted with IA was completely soluble.

Grafting reactions were carried out by mixing predetermined amounts of monomer and initiator before melt mixing at 180 °C under nitrogen. At the end of reaction the product was dissolved in hot toluene and was precipitated into acetone. The unreacted monomer, initiator and possible homopolymer that could eventually form during

the grafting reaction was separated from grafted polymer by exhaustive extraction of the sample with methanol for IA and MMI and with chloroform for DMI in a Soxhlet for 24 h as previously described [27]. The extracted samples were dried under reduced pressure before their analysis.

2.3. Characterization

The evidence of grafting as well as an estimation of its extent, expressed as weight percent of grafting, was determined by FTIR spectroscopy of the grafted EPR samples after removing of non-reacted monomer, initiator and homopolymer but without separation of gel fraction in all cases. FTIR spectra were recorded on a Bruker IFS-28 spectrometer from 4000 to 400 cm^{-1} with an average of 16 scans at 4 cm^{-1} resolution and 1 cm^{-1} sensitivity. Films of 100 μm thickness from 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 Rheometric Scientific ARES N2 with parallel plate geometry. Tests were carried out in dynamic frequency modes at 190 °C. The samples were melted and plate shaped. Disks of approximately 25 mm in diameter and 1 mm thickness were used for the rheological measurements. Dynamic shear properties were determined as a function of angular speed of deformation in the range 0.1 to 500 rad/s. The amplitude strain was maintained constant at 5%.

Advancing contact angles were measured at 23 ± 2 °C and at a relative humidity of $50 \pm 5\%$ on a optical contact meter model Krüss G10 equipped with a 61041 video. Distilled water, diiodomethane and ethylene glycol were employed. Contact angles were obtained by placing the tip of the syringe near the sample surface and depressing the syringe to produce a constant drop volume of about 2 μl . Three drops per sample and 60 readings per each drop were carried out with 1 s settling time. For each sample, the average value together with their standard deviation were calculated and reported in this study.

3. Results and discussion

3.1. Evidence of grafting

The existence of grafted IA, MMI or DMI in EPR was confirmed by FTIR spectroscopy [6].

The FTIR spectrum of the grafted EPR with IA (EPR-g-IA) showed two absorption bands in the carbonyl region that are absent in the spectrum of unmodified EPR (Fig. 1). The absorption band at 1712 cm^{-1} is due to stretching vibrations of the carbonyl groups of the carboxylic acid of the monomer. The second absorption band centered at 1770 cm^{-1} could be due to a carbonyl absorption band coming from the monomer grafted as anhydride which could form during the grafting reaction. The formation of anhydrides through dehydration/de-esterification reactions of monoesters of itaconic acid has been reported by Cowie and his co-workers in their thermal stability studies of the corresponding poly-monoesters [31,32]. They came to the conclusion that the dehydration/de-esterification reactions were either inter- or intramolecular in nature.

The ratio of the sum of the intensities of the absorption bands at 1712 cm^{-1} (A_{1712}) and 1770 cm^{-1} (A_{1770}) to the intensity of the absorption band at 720 cm^{-1} (A_{720}), corresponding to the out of plane bending vibration of CH_2 of the EPR backbone, allows to determine the carbonyl index $I_{\text{C}_{\text{acid+anhydride}}}$ ($I_{\text{C}} = \frac{A_{1712}+A_{1770}}{A_{720}}$). This can be con-

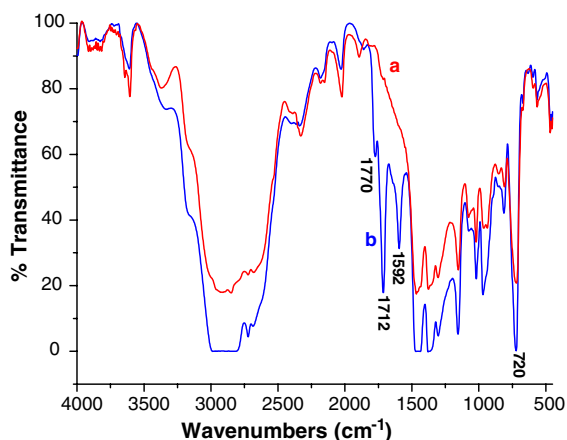


Fig. 1. FTIR spectrum of: (a) EPR and (b) EPR grafted with IA.

sidered as a measure of the extent of grafting of the monomer in EPR in its both acid and anhydride form. The extent of grafting was converted into the incorporated weight percent (G_{IA} in wt%) of the monomer by using a calibration curve obtained from FTIR analysis of the physical mixtures of EPR with different amounts of IA as shown in Fig. 2. These mixtures were prepared by melt mixing of EPR and IA in a Brabender mixing chamber at $180\text{ }^{\circ}\text{C}$ under nitrogen stream for 6 min.

The percentage of IA grafted onto EPR can be estimated by using the following relation:

$$G_{\text{IA}}(\text{wt}\%) = \frac{I_{\text{C}}}{0.3012}. \quad (1)$$

An additional absorption band centered at 1592 cm^{-1} was identified by close examination of the FTIR spectrum of the functionalized EPR with IA and also MMI. This band is absent in the FTIR spectrum of the unmodified EPR. The relative intensity of this band increases with increasing the initial monomer concentration used in the grafting reaction. Although we have no clear explanation at this stage, it could be attributed to a product generated from decomposition of the monomer. This decomposition product seems to be linked to EPR chains since it was not possible to remove it by the extraction procedure used in this work.

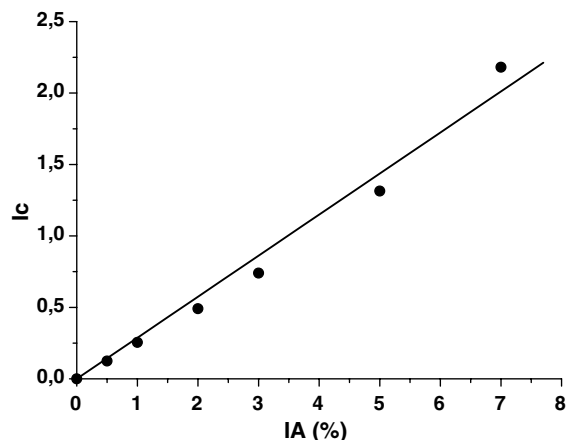


Fig. 2. FTIR calibration curve for determining the weight percentage of grafted IA onto EPR.

It should be noted that FTIR spectra shown in this work are not those spectra used for the estimation of the percentage of grafting but they reflect only qualitatively the grafting.

In the case of grafting with MMI (EPR-g-MMI), the FTIR spectrum of the modified EPR with this monomer also showed two absorption bands in the carbonyl region that are absent in the spectrum of unmodified EPR (Fig. 3). The absorption band at 1727 cm^{-1} is due to the stretching vibration of the ester carbonyl groups of the monomer. The second absorption band appears as a shoulder at 1770 cm^{-1} . This band was assigned to a carbonyl group from a five member-anhydride ring.

In order to quantify the amount of MMI incorporated in EPR, a calibration curve was also established by mixing different amounts of the monomer with EPR. These physical mixtures of MMI and EPR were prepared following the same procedure used in the case of IA, as was described earlier. The intensity of the sum of the absorption bands at 1727 and 1770 cm^{-1} was compared with that of EPR at 720 cm^{-1} . This band ratio was defined as the carbonyl index $I_{C_{\text{monoester+anhydride}}}$, corresponding to the incorporation of the monomer into EPR in its both acid and anhydride form. The $I_{C_{\text{monoester+anhydride}}}$ values were converted into the incorporated weight percent (G_{MMI} wt%) of the monomer by using a calibra-

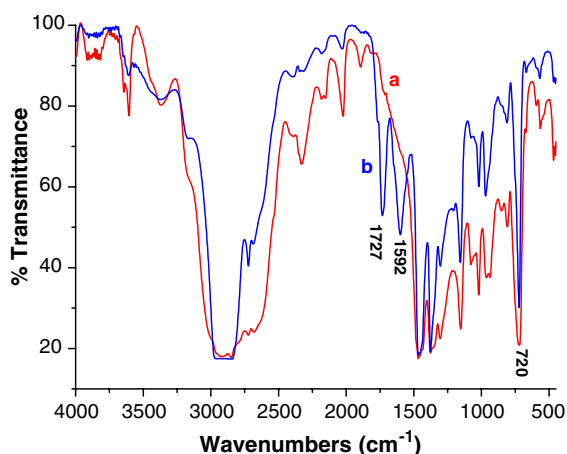


Fig. 3. FTIR spectrum of: (a) EPR and (b) EPR grafted with MMI.

tion curve obtained from FTIR analysis of the physical mixtures of EPR with different amounts of MMI as shown in Fig. 4. The percentage of grafting of MMI onto EPR can be estimated by using the relation:

$$G_{\text{MMI}}(\text{wt}\%) = \frac{I_C}{0.3214}. \quad (2)$$

Fig. 5 shows the FTIR spectra of EPR grafted with DMI (EPR-g-DMI), where an absorption band in the carbonyl region that is absent in the spectrum of unmodified EPR can be detected. The absorption band at 1727 cm^{-1} is due to carbonyl stretching vibrations of the ester groups of the monomer. The ratio of the intensity of the peak at 1727 cm^{-1} (A_{1727}) corresponding to carbonyl group of EPR-g-DMI to the absorbance of the methylene group at 720 cm^{-1} (A_{720}), corresponding to CH_2 of the EPR backbone allows to determine carbonyl index (I_C). This can be considered as a measure of the extent of grafting of the monomer in EPR either as single units and or poly (dimethyl itaconate) chains.

The extent of grafting was converted into the incorporated weight percent (G_{DMI} in wt%) of the monomer by using a calibration curve obtained from FTIR analysis of the physical mixtures of EPR with different amounts of DMI as shown in Fig. 6. The mixtures of DMI and EPR were prepared following the same procedure

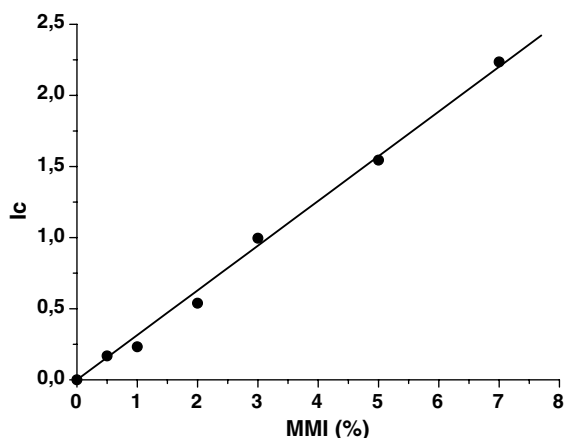


Fig. 4. FTIR calibration curve for determining the weight percentage of grafted MMI onto EPR.

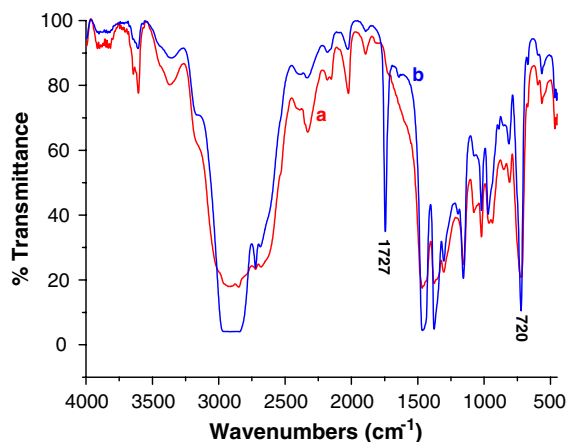


Fig. 5. FTIR spectrum of: (a) EPR and (b) EPR grafted with DMI.

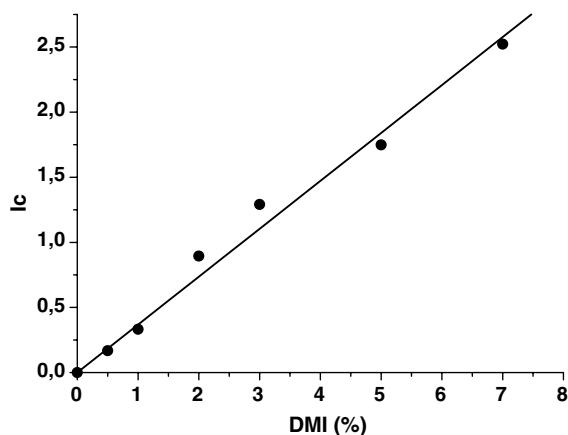


Fig. 6. FTIR calibration curve for determining the weight percentage of grafted DMI onto EPR.

previously described. Therefore, an estimation of the percentage of DMI grafted onto EPR can be obtained by using the following relation:

$$G_{\text{DMI}}(\text{wt}\%) = \frac{I_c}{0.3581}. \quad (3)$$

3.2. Effect of reaction variables on grafting

The effect of monomer and initiator concentration on the extent of grafting attained as a function of the monomer has been evaluated (Figs. 7–9). As shown in Fig. 7 it can be deduced that the amount

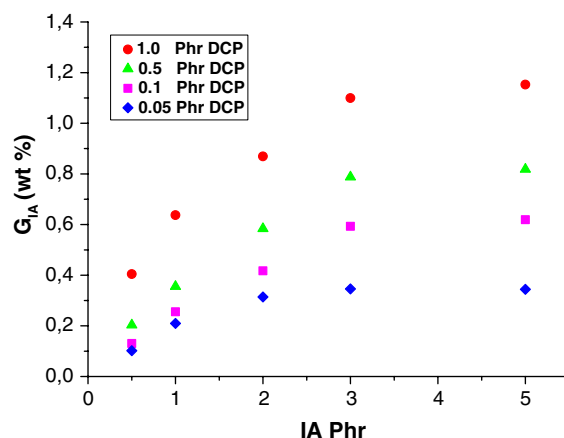


Fig. 7. Variation of the percentage of grafting of IA (G_{IA} – wt%) onto EPR as function of monomer and initiator concentrations.

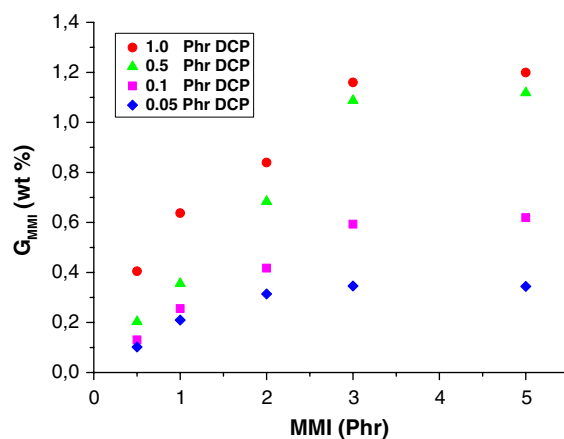


Fig. 8. Variation of the percentage of grafting of MMI (G_{MMI} – wt%) in EPR as function of monomer and initiator concentrations.

of IA incorporated in EPR increases with IA monomer concentration for a determined amount of the initiator initially used in the grafting reaction. A maximum grafting percentage of 1.2 wt% of EPR is attained when the concentration of IA is around 3 wt%. It is of interest to note that a further increase of the amount of IA hardly vary the grafting percentage. This behavior is expected since at higher monomer concentrations, more monomer is available for grafting onto a determined number of active sites that can be generated by a fixed amount of the initiator used initially in

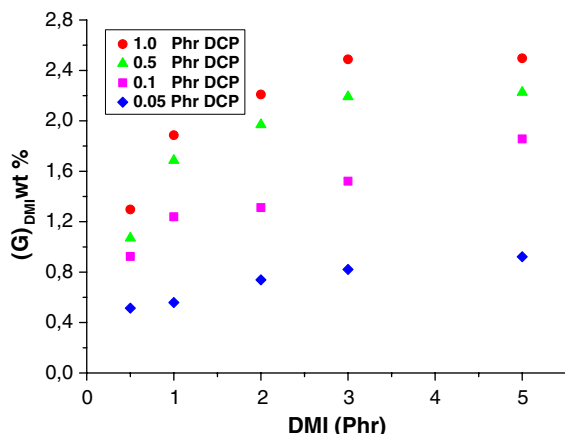


Fig. 9. Variation of the percentage of grafting of DMI (G_{DMI} – wt%) onto EPR as function of monomer and initiator concentrations.

the reaction. It is evident that the percentage of grafting does not increase by a further increase in the amount of monomer beyond 3 phr. This can be explained by considering that more monomer would be available for homopolymerization of the monomer.

Similar grafting percentages (approximately 1.2 wt%) are obtained when MMI is used as monomer (Fig. 8). However, a sensible increase of the grafting percentage is attained in the case of DMI reaching a maximum of 2.4% (Fig. 9). This can be explained in terms of the difference of polarity between monomers. DMI is the less polar monomer than MMI and IA, consequently its solubility in the EPR is increased. Therefore, most grafting takes place as consequence of higher affinity of DMI monomer with the EPR polymer backbone.

3.3. Rheological properties

The variation of the apparent viscosity, η as a function of shear rate, $\dot{\gamma}$, at 180 °C for neat EPR and grafted EPR with IA, MMI and DMI is shown in Fig. 10. It is observed that in all the cases, the viscosity decreases with the shear rate and increases with the grafting reaction. This effect is more evident when MMI and DMI are used as monomers. Thus, at $\dot{\gamma} = 1 \text{ s}^{-1}$, the viscosity value goes from 8799 Pa s for neat EPR to 18,475 Pa s

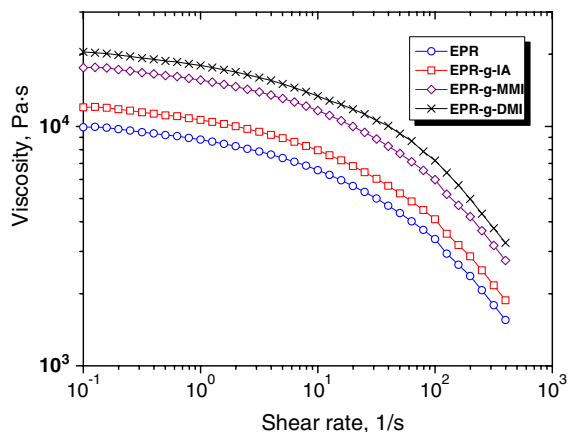


Fig. 10. Variation of complex viscosity with angular frequency at 180 °C for EPR and EPR grafted with IA, MMI and DMI.

for EPR-g-DMI and EPR-g-MMI, while EPR-g-MMI shows a value of 15,599 Pa s and EPR-g-IA 10,647 Pa s. This increase of the viscosity can be attributed to the stronger interaction among the EPR macromolecular chains induced by the grafted functional groups. This leads to the formation of entanglements, physical and chemical crosslinking. All monomers exhibit tendency to form hydrogen and covalent bonds. The relative reactivity of the ester groups is higher than carboxylic acid in nucleophilic addition-elimination reaction such as esterification or trans-esterification reactions. Consequently, the formation of covalent bonds has the following order: DMI > MMI > IA, whereas the tendency to form hydrogen bonds will be: IA > MMI > DMI. The viscosity measurements indicated that the formation of covalent bands is predominant in relation to hydrogen bonds.

The rheological parameters of the analyzed materials were calculated by fitting the rheological data to the equation proposed by Ellis which is based on the Cross model [33,34]:

$$\eta = \frac{\eta_0}{(1 + (K\omega)^m)}, \quad (4)$$

where η_0 represents the zero-shear viscosity, ω the angular frequency, K is a constant with the dimension of time and m is a dimensionless constant. The fitted parameters of the proposed models are summarized in Table 1. A strong increase of

Table 1
Rheological parameters of pristine EPR and EPR grafted with IA, MMI and DMI

	η at 1 rad/s (Pa s)	Ellis model		
		η_0 (Pa s)	K (s)	m
EPR	8799	10,209	0.036	0.57
EPR-g-IA	10,647	12,353	0.037	0.57
EPR-g-MMI	15,599	18,097	0.037	0.56
EPR-g-DMI	17,939	20,540	0.039	0.54

zero-shear viscosity values was observed for grafted EPR. In particular, this effect was more evident when DMI was used as monomer. This indicates that the EPR modified with DMI has a higher crosslinking density and hence a higher viscosity.

3.4. Contact-angle measurements

Advancing contact angle measurements were carried out in order to evaluate the polar character of modified EPR and the results are reported in Table 2. The surface energy and its components of the samples were determined from contact angle measurements using the Lifshitz-van der Waals (LW) method also known as acid–base (AB) approach or van Oss, Good, and Chaudhury method [35,36]. The theory behind this method of estimating the solid surface free energy and its components has been extensively described in the literature. Van Oss et al. [35,36] divided the surface tension into different components, i.e., the Lifshitz-van der Waals (LW), acid (+) and base (−) components.

$$\gamma_i = \gamma_i^{\text{LW}} + \gamma_i^{\text{AB}} = \gamma_i^{\text{LW}} + 2\sqrt{\gamma_i^+ \gamma_i^-}, \quad (5)$$

where, i denotes either the solid or liquid phase and the acid–base component (γ_i^{AB}) takes into account the electron-donor (γ_i^-) and electron-acceptor

(γ_i^+) interactions of the polar component of the surface tension of the liquid and solid. Young–Dupré equation has been usually given for solid–liquid systems [37],

$$\frac{1 + \cos \vartheta}{2} \gamma_L = \sqrt{\gamma_S^{\text{LW}} \gamma_L^{\text{LW}}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_L^+ \gamma_S^-}, \quad (6)$$

where ϑ is the contact angle measured through the tangent of the drop and γ_L is the surface tension of the liquid. The three components of the surface free energy of the solid, γ_S^{LW} , γ_S^+ and γ_S^- can be determined from contact angle measurements. Liquids chosen to obtain the three γ component values of the solid samples were distilled water, diiodomethane and ethylene glycol. It is deduced that for all the samples, the contact angle values are higher for water, followed by those of ethylene glycol and diiodomethane.

The calculated surface energy components and the total surface energies are also reported in Table 2.

The contact angles obtained in diiodomethane, where the LW components of the surface energy dominate, were different for EPR and grafted EPR. It can be seen from Table 2 that the LW surface energy component of pristine EPR is lower than those of the grafted EPR.

In this sense, it is important to remark that the use of polar liquids to measure the polar component of the surface tension of a solid only allows to obtain the excess of electron acceptor (γ^+) or electro donor (γ^-) values of a dry surface. This excess γ^- is the only polar entity that can be measured via the contact angle approach, or dry solid surfaces. It is also the only γ^- by which the solid can interact with other polar entities, solid or liquid. When both γ^+ and γ^- values are found for a solid surface, it is caused by the existence of water molecules on the surface of the solid,

Table 2
Contact angle measurements, surface energy components of pristine EPR and grafted EPR with IA, MMI and DMI

Sample	EPR	EPR-g-IA	EPR-g-MMI	EPR-g-DMI
$\theta_{\text{water}} (^{\circ})$	84.7 ± 0.5	82.9 ± 0.4	83.8 ± 0.2	84.6 ± 0.4
$\theta_{\text{ethylene glycol}} (^{\circ})$	65.9 ± 0.4	67.9 ± 0.5	65.3 ± 0.4	69.8 ± 0.4
$\theta_{\text{diiodomethane}} (^{\circ})$	63.9 ± 0.5	59.4 ± 0.3	63.0 ± 0.5	60.6 ± 0.2
$\gamma_{\text{total}} \approx \gamma^{\text{LW}}$ (mJ/m ²)	26.3	28.9	26.9	28.2
γ^+ (mJ/m ²)	0.1	0	0.1	0
γ^- (mJ/m ²)	7.4	10.1	7.6	10.1

because only in polar liquids both components can coexist. Therefore, the surface tension can be defined as $\gamma_L = \gamma^{LW}$. The value of the surface tension presented the following order: EPR < EPR-g-MMI < EPR-g-DMI < EPR-g-IA.

As shown in Table 2, the electron-donor (γ_s^-) contribution is greater for grafted EPR. These results are in agreement with the contact angle values measured with ethylene glycol. It is a liquid with high electron donor component of surface energy ($\gamma^- = 47 \text{ mJ/m}^2$; $\gamma^+ = 1.92 \text{ mJ/m}^2$), hence polar repulsion and contact angle is increased.

This indicates that the polarity of the polymer is increased by grafting reaction. It is well known that an increase of the polar component of the surface tension increases the energy of adhesion between the polar liquid and the surface of the solid and, in consequence the contact angle is decreased. This behavior was observed when a polar liquid such as water is used as solvent as shown in Table 2. In this case, the contact angle decreases in the following order: EPR > EPR-g-DMI > EPR-g-MMI > EPR-g-IA.

The grafting reaction gives rise to an increment of the polarity and increase of the surface tension. This fact is particularly important from a thermodynamic point of view for the preparation of polymer blends, since the driving force of the incompatibility of a blend is the difference in surface energies, both in the intensity and nature, among the polymers comprising the blend.

4. Conclusions

It is concluded from this study that IA, MMI and DMI could be successfully grafted onto EPR in the melt phase. The relative polarity of these monomers determine the extent of grafting attained where higher percentage of grafting was obtained for DMI, a less polar monomer. This was attributed to higher solubility of DMI in the EPR melt compared with those of IA and MMI. Moreover, the extent of grafting depends on the initial concentration of the monomer and initiator in all cases, where an optimum grafting was established for each monomer studied. Contact angle measurements indicated that the polarity of EPR is increased by grafting

reaction. Grafted EPR could be used as a potential compatibilizer for polyolefin/elastomer blends. Rheological measurements revealed the strong increase of zero-shear viscosity values for grafted EPR. In particular, this effect was more evident when DMI was used as monomer. This indicates that the EPR modified with DMI has a higher cross-linking density and hence a higher viscosity.

Moreover, by considering that grafted EPR can be used as compatibilizer in polymer blends, where the second component of the blend could be a polar polymer, MMI modified EPR and, particularly IA modified EPR would be certainly a better compatibilizer than DMI functionalized EPR since a more effective interaction between the blend components could occur.

Acknowledgments

The authors acknowledge the financial support of CONICYT, Projects FONDECYT 1040927, FONDAF 11980002 and Ministerio de Ciencia y Tecnología (Spain) for the concession of a Ramón y Cajal contract to Dr. López-Manchado.

References

- [1] G. Moad, *Prog. Polym. Sci.* 24 (1999) 81.
- [2] M. Rätzsch, M. Arnold, E. Borsig, H. Bucka, N. Reichelt, *Prog. Polym. Sci.* 27 (2002) 1195.
- [3] S. Al-Malaika, *Reactive modifiers for polymers*, Chapman & Hall, London, 1996.
- [4] M. Xanthos, *Reactive extrusion*, Oxford University Press, New York, 1992.
- [5] M. Yazdani-Pedram, H. Vega, R. Quijada, *Macromol. Rapid. Commun.* 17 (1996) 577.
- [6] M. Yazdani-Pedram, H. Vega, R. Quijada, *Macromol. Chem. Phys.* 199 (1998) 2495.
- [7] M. Yazdani-Pedram, H. Vega, R. Quijada, *Polymer* 42 (2001) 4751.
- [8] C. Rosales, H. Rojas, R. Perera, A. Sanchez, *J. Macromol. Sci.: Pure Appl. Chem.* A37 (10) (2000) 1227.
- [9] E. Passaglia, S. Ghetti, F. Picchioni, G. Ruggeri, *Polymer* 41 (2000) 4389.
- [10] D. Shi, J. Yang, Z. Yao, Y. Wang, H. Huang, W. Jing, J. Yin, G. Costa, *Polymer* 42 (2001) 5549.
- [11] C. Li, Y. Zhang, Y. Zhang, *Polym. Test.* 22 (2003) 191.
- [12] A. Galia, R. De Gregorio, G. Spadaro, O. Scialdone, G. Filardo, *Macromolecules* 37 (2004) 4580.

- [13] T. Kim, D. Oh, *Polym. Degradat. Stability* 84 (2004) 499.
- [14] R. Greco, G. Maglio, P. Musto, *J. Appl. Polym. Sci.* 33 (1987) 2513.
- [15] X. Zhang, L. Li, Z. Yin, Y. Qi, J. Yin, *J. Appl. Polym. Sci.* 62 (1996) 1933.
- [16] G. Hu, H. Cartier, *J. Appl. Polym. Sci.* 71 (1999) 125.
- [17] C. Vocke, U. Antilla, M. Henio, P. Hietaoja, J. Söpala, *J. Appl. Polym. Sci.* 70 (1998) 1923.
- [18] U. Anttila, C. Vocke, J. Seppala, *J. Appl. Polym. Sci.* 72 (1999) 877.
- [19] A. Machado, J. Covas, M. Van Duin, *Polymer* 42 (8) (2001) 3649.
- [20] J. Jun, J. Park, K. Suh, *J. Appl. Polym. Sci.* 74 (1999) 465.
- [21] S. Al-Malaika, W. Kong, *J. Appl. Polym. Sci.* 79 (2001) 1401.
- [22] Y. Ding, Z. Xin, Y. Gao, J. Yin, G. Costa, *J. Polym. Sci.: Part B: Polym. Phys.* 41 (2003) 387.
- [23] Y. Ding, Z. Xin, Y. Gao, X. Xu, J. Yin, G. Costa, L. Falqui, B. Valenti, *Macromol. Mater. Eng.* 288 (5) (2003) 446.
- [24] E. Passaglia, S. Coiai, M. Aglietto, G. Ruggeri, M. Ruberia, F. Ciardelli, *Macromol. Symp.* 198 (2003) 147.
- [25] M. Zhang, J. Duhamel, M. Van Duin, P. Meessen, *Macromolecules* 37 (2004) 1877.
- [26] Y. He, B. Zhu, Y. Inoue, *Prog. Polym. Sci.* 29 (2004) 1021.
- [27] M.A. López-Manchado, J. Kenny, R. Quijada, M. Yazdani-Pedram, *Macromol. Chem. Phys.* 202 (9) (2001) 1909.
- [28] M.A. López-Manchado, M. Yazdani-Pedram, J. Retuert, R. Quijada, *J. Appl. Polym. Sci.* 89 (8) (2003) 2239.
- [29] M. Yazdani-Pedram, H. Vega, J. Retuert, R. Quijada, *Polym. Eng. & Sci.* 43 (3) (2003) 960.
- [30] M. Yazdani-Pedram, R. Quijada, M.A. López-Manchado, *Macromol. Mater. Eng.* 288 (2003) 875.
- [31] J.M.G. Cowie, *Pure Appl. Chem.* 51 (1979) 2331.
- [32] J.M.G. Cowie, Z. Haq, *Br. Polym. J.* 9 (1977) 246.
- [33] C.J. Carriere, H.C. Silvis, *J. Appl. Polym. Sci.* 66 (1997) 1175.
- [34] M.M. Cross, *J. Colloid. Interface Sci.* 20 (1965) 417.
- [35] C. Van Oss, M. Chaudhury, R. Good, *Adv. Colloid. Interface Sci.* 28 (1987) 35.
- [36] C. Van Oss, M. Chaudhury, R. Good, *Chem. Rev.* 88 (1988) 927.
- [37] R. Giese, C. Van Oss, *Colloid and surface properties of clays and related minerals*, Marcel Dekker, New York, 2002.