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Composites from Functionalized Polyolefins and Silica

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Summary: The effect of diethyl maleate (DEM) units grafted to the polyolefins on the compatibility with inorganic fillers has been investigated. Ethylene-propylene rubber functionalized with DEM (EPR-g-DEM) was mixed with silica in different weight ratios using a Brabender mixer (Plastograph), by comparing analogous mixtures prepared starting with unmodified ethylene-propylene-rubber (EPR) and silica. The Torque traces showed that the diethyl maleate grafted on the EPR significantly changed the interfacial interaction between the silica surface and the EPR during the mixing process. Incorporation of silica into either EPR and EPR-g-DEM by mechanical mixing produced a fraction of insoluble by association with the filler (*bound rubber*), as revealed by the solvent extraction technique. Bound rubber evaluations pointed out the major capability of the EPR-g-DEM to interact with the mineral surface. In this case specific interactions involving the carbonyl groups of the functionalized polyolefin and the polar sites on the filler surface have been identified by means of FT-IR spectroscopy. As revealed by SEM observations, these specific interactions at the interface promote the mutual wettability and adhesion of the components in EPR-g-DEM/silica composites.

Introduction

Synthetic elastomers are amorphous with low glass transition temperatures and so the chains are thermally mobile under the temperature conditions used in the rubber industry. For these reasons the mechanical properties which are needed are only obtained by adding appropriate fillers such as carbon black or silica. The reinforcement phenomenon, well known about its effect on the variation of the stress-strain properties of the composites, involves both physical and chemical interactions between the two phases[1,2] (organic and inorganic phases) and depends on the structure and composition of the polymer, on the type of the filler and on the size of the particles[3].

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The interaction between filler and elastomer is clearly revealed by the formation of "bound rubber". Indeed reinforcing carbon black or any other reinforcing filler (silica) when is included can form an insoluble gel with the polymer[1,4]. This behaviour, well known in the case of carbon black as filler, makes a not extractable fraction of the insoluble polymer that seems to play a significant role in the reinforcement[5,6].

In the case of functionalized elastomers (maleated[7] or sulfonated[8] ethylene-propylene-diene terpolymer) it was possible to propose a mechanism of interaction between the functional groups present on the filler particles (OH groups in the case of silica), and the ionic groups present in the polymer in order to explain the increase the hardness, modulus, tear strength, abrasion resistance of the sulfonated elastomer[8].

In this work we report the results obtained by mixing in the melt silica and a functionalized polyolefin with particular reference to study the interactions between the two phases and their effects on the processability, thermal properties, and morphology of the mixes.

Experimental

Materials

Ethylene-propylene rubber (EPR) employed was a commercial product, EPR CO-038, from Enichem Elastomeri (Italy). Its main characteristics are listed in Table 1.

Table 1: Characteristics of EPR CO-038 copolymer

d (g/cm^3)	Mw/Mn	MFI$_{5Kg}$	$[\eta]^a$ (cm^3/g)	ethylene/propylene^b	% of crystallinity
0.865	4.5	0.3	3-3.5	7/3	<5

a: in trichlorobenzeneat 135°C

b: molar ratio

A maleated version of EPR CO-038, hereafter referred as EPR-g-DEM, was prepared by radical functionalization with diethylmaleate (DEM) as monomer and dicumyl peroxide (DCP) as radical initiator. The functionalization reaction was performed in a Brabender mixer (Plastograph) according to the procedure reported in literature[9].

The functionalization degree (FD), as determined by FT-IR spectroscopy[10], was 1.1% by mol.

Croxfield silica was used; kindly supplied by Enichem Elastomeri Italy having particle size, 30 μm; specific surface area, 200 m^2/g; bulk density, 0.18 g/cm^3; total number of OH groups, 2 mmol./g SiO_2.

Diethylmaleate (DEM, Aldrich) was distilled under reduced pressure prior to use. Dicumyl peroxide (Montedison Peroximon DC) was used without further purification. Acetone (Carlo Erba), n-heptane (Carlo Erba), toluene (Carlo Erba) were used as received.

Measurements

The TGA were performed with a Mettler TC11 under nitrogen atmosphere at a standard rate of 20°C/min.

The FT-IR spectra of soluble polymeric products were run with a Perkin-Elmer model 1330 spectrophotometer.

The FT-IR spectra of polyolefin/silica mixtures and residues were recorded with a Perkin-Elmer FT-IR 1760-X Spectrometer.

The scanning electron microscopy (SEM) micrographs were obtained from microtomed surfaces using a scanning electron microscope Jeol JSM mod T-300.

Preparation of samples

Details of the formulation for the different mixtures EPR/silica and EPR-g-DEM/silica are given in Table 2.

The mixtures were prepared in a Brabender mixer (Plastograph) with a rotor speed of 50 rpm and the mixer chamber set at 180°C. In order to have reproducible compounding conditions, EPR and EPR-g-DEM were mixed with silica according to the following procedure: initially, the polyolefin was melted in the mixer for 2 min under nitrogen atmosphere; next, silica was added to it and mixed for another 6 min to ensure uniform mixing of the ingredients. The neat polymers were also processed under the same conditions for 8 min.

The samples recovered from the Brabender were sequentially extracted with boiling acetone and n-heptane; when this last extraction left a residue toluene was also used.

Results and Discussion

Brabender mixing

Both unmodified EPR (run S1-S5) and EPR containing 1 mol% of grafted with diethylmaleate (EPR-g-DEM run FS3-FS5) were melt-mixed with silica in different compositions, as shown in Table 2. The torque *vs* time was measured during mechanical mixing for all performed experiments.

Table 2: Formulation of different mixtures and results of solvent extractions

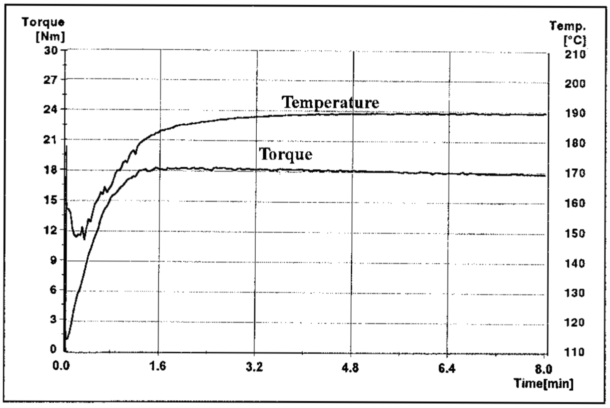
Run	load[a]	acetone soluble[b]	n-heptane soluble[b]	toluene soluble[b]	residue[c]
S0	0	1.0	99.0	-	-
S1	2	1.1	97.8	0.4	0.7
S2	5	1.1	96.2	0.9	1.8
S3	10	0.9	91.7	1.5	5.9
S4	20	0.9	86.0	4.1	9.0
S5	30	0.9	83.0	3.6	12.5
FS0	0	0.4	99.6	-	-
FS3	10	0.6	92.5	2.5	4.4
FS4	20	0.7	76.7	8.4	14.2
FS5	30	0.7	74.4	7.5	17.4

a: part of silica with respect to 100 part of polyolefin

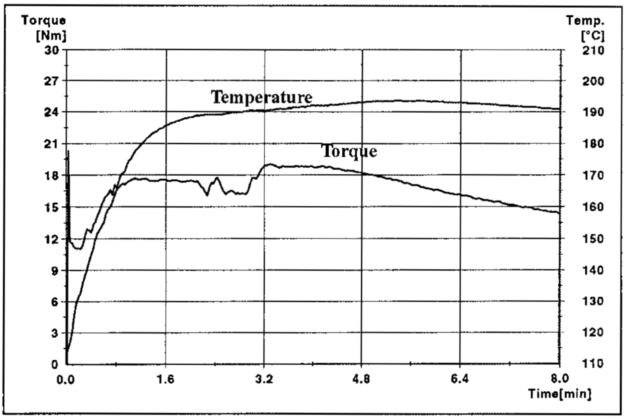
b: wt% extracted with acetone, n-heptane, toluene to respect to 100 parts of composite

c: wt% residue of toluene extraction to respect to 100 parts of composite

Figure 1a shows the torque trace for the unmodified EPR treated in Brabender without silica (run **S0**). It can be seen that at first the torque increases rapidly with time corresponding to the introduction of the polyolefin in the mixer; then it stays almost constant up to the end of the Brabender processing, thus suggesting that degradation to short chains or even chain extension, and/or cross-linking reaction, are minor processes. A typical Brabender Plastograph curve of the run with EPR and silica (run **S3,** but the behaviour is the same for all loading of the silica) is shown in figure 1b. The addition of silica to EPR after 2 min produces an increase of the torque measured due to the viscosity build-up associated to the incorporation of rigid particles in the molten matrix. The torque reaches a maximum and then decreases slowly as a result of degradation of the polymer.



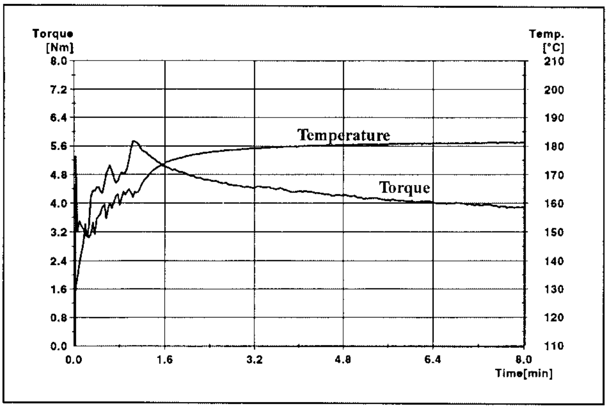
(a)



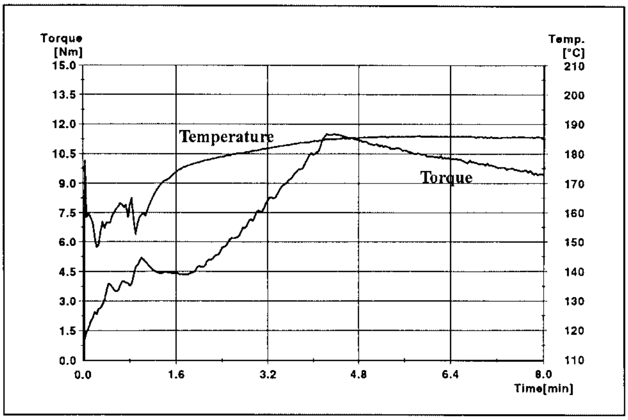
(b)

Figure 1:Torque/temperature traces for the runs **S0** (a) and **S3** (b)

By comparison, the Brabender Plastograph traces referred to the neat EPR-g-DEM (run **FS0**) and the EPR-g-DEM compound containing 20 parts per hundred parts of silica (phr) (run **FS4**) are reported in figure 2. In the case of the virgin EPR-g-DEM (figure 2a), after the rapid increase associated with the introduction of the polyolefin in the mixer chamber, the torque decreases gradually owing to the slight degradation of the polymer. In the case of the silica-filled system (figure 2b) it is observed that the torque registers a sharp increase upon addition of filler to the EPR-g-DEM.



(a)



(b)

Figure 2: Torque/temperature traces for the runs **FS0** (a) and **FS4** (b)

This increase, which corresponds again to the viscosity build-up associated to the incorporation of rigid particles in the matrix, is more pronounced than that observed for silica-filled EPR systems, probably due to the stronger interfacial interaction between filler and polymer.

In order to compare EPR and EPR-g-DEM with respect to the rheological behaviour during Brabender mixing, we have calculated the torque increase ($\Delta\tau$), defined as follows:

$$\Delta\tau = \tau_{max} - \tau_{2min}$$

where τ_{max} is the maximum torque value during the mechanical mixing, τ_{2min} is the torque value after of 2 min, i.e. immediately before the addition of filler. As expected, (figure 3) the quantity $\Delta\tau$ increases sequentially with increasing silica loading. This trend is verified both for the silica-filled EPR and for the silica-filled EPR-g-DEM systems, but $\Delta\tau$ is significantly higher at all loading for the latter. From the above comparison, it is evident that diethylmaleate modification results in an increase in the torque required to disperse mineral particles throughout the matrix and to oppose the extra-viscosity due to their presence.

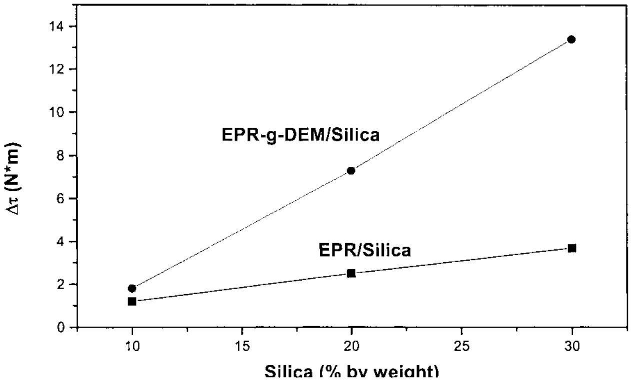


Figure 3: Behaviour of $\Delta\tau$ parameter with silica loading

Solubility of composites

The modification of EPR by diethyl maleate grafting was also found to have an influence on the solvent extraction behaviour of composites. At the end of the Brabender processing, the samples were all sequentially extracted with boiling acetone, n-heptane and toluene in that order and the residue was collected when present.

The amount of the acetone-soluble fraction (Table 2) is always less than 2 wt% of the whole material; thus indicating that in any case degradation to short chains (PM≈ 1000) is a minor process during mechanical mixing. Furthermore, the amount of material extracted with acetone is approximately independent of the filler content.

According to the original solubility of the used polymers, n-heptane was expected to dissolve exhaustively the polyolefin component of the composite systems. Indeed the unfilled polyolefins (samples **S0** and **FS0**) were completely extractable with the first two solvents at the end of the Brabender processing. In the case of the silica-filled systems (samples **S3-S5** and **FS3-FS5**) the amount of the n-heptane-soluble fraction decreases with increasing silica loading according to the expected trend. The material unextracted with n-heptane consists of a fraction extractable with boiling toluene and of an insoluble residue.

Although the EPR and EPR-g-DEM composites with silica exhibit a similar behaviour in respect to the solvent extraction, both the toluene-soluble fractions and the toluene-insoluble residues are larger for EPR-g-DEM/silica mixtures (FS3-FS5) in particular evident at high loading of silica (20 and 30 % by weight).

FT-IR analysis

The IR spectra of the fractions extracted with n-heptane for the samples **S4** and **S5** (see figure 4) show a strong absorption band around 1100 cm^{-1} which is ascribed to the Si-O stretching. The evidence of the presence of silica in the heptane soluble fraction is provided by FT-IR characterisation of the residues to solvent extraction. The IR spectra of such residues, (a typical example is reported in figure 5), show bands attributable to both the ethylene-propylene copolymer (2922, 2852, 1464, 1376 and 722 cm^{-1}) and the silica (1104 and 805 cm^{-1}). This demonstrates that when silica is incorporated into EPR by mechanical mixing, a part of polyolefin becomes insoluble.

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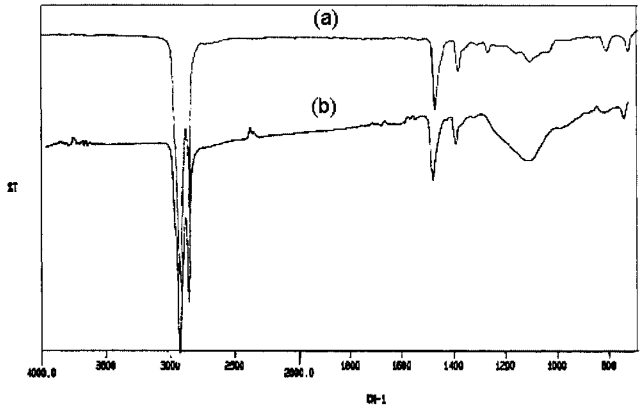

Figure 4: IR spectra of n-heptane soluble fractions: (a) run S4, (b) run S5

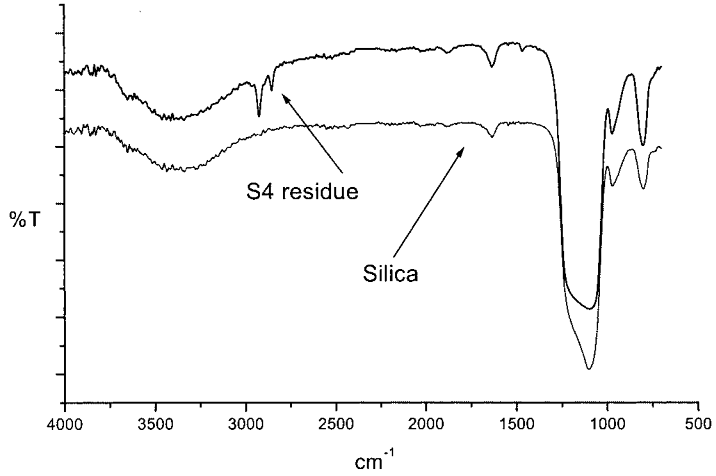

Figure 5: IR spectra of silica and insoluble residue of run S4

The insoluble component has been regarded to be an adsorbed fraction of the elastomer, which is either physically or chemically bonded to the surface of the filler and can not be removed by solvent in silica filled poly-olefins[11].

The amount of polyolefin rendered insoluble by association with filler, hereafter referred as bound rubber (BR) in analogy to similar nomenclature found in the rubber literature, was determined by thermogravimetric analysis of the residues to solvent extractions. It is seen (figure 6) that the bound rubber increases sequentially with increasing silica loading and therefore, in the case of an uniform dispersion of the filler, with the increasing the total surface. In the case of EPR/silica composites the amount of insoluble polyolefin formed during Brabender mixing is small at all loading examined, presumably owing to the weak interaction between the unmodified EPR (apolar) and the silica surface (polar).

For the EPR-g-DEM/silica mixtures the mass balance shows that the amount of material extracted with n-heptane is much less than that for the EPR/silica mixes, thus suggesting a larger extent of insolubilization of polyolefin chains on the silica surface. The TGA data obtained reveals that the organic content in the residues to solvent extraction is larger than that found for the analogous EPR/silica residues. Comparison of bound rubber values of EPR/silica and EPR-g-DEM/silica mixtures (figure 6) shows that the modification with diethyl-maleate of EPR increases the amount of bound rubber at all loading.

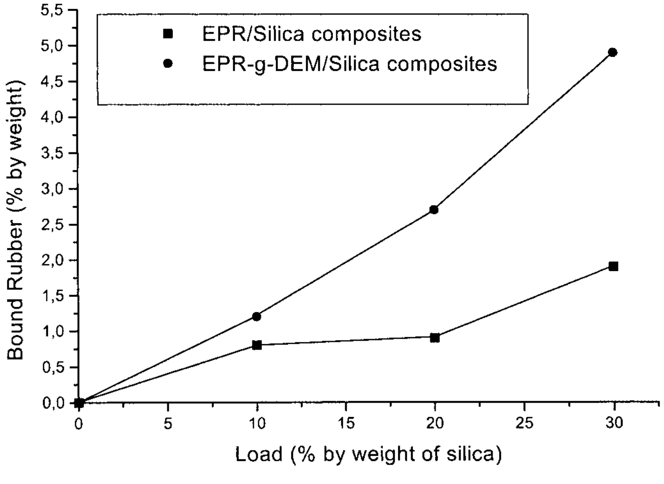

Figure 6: Bound Rubber of EPR/Silica and EPR-g-DEM/Silica composites

This is certainly due to the major capability of the polyolefin chains grafted with diethylmaleate to interact with the mineral surface.

The FT-IR microspectroscopy has provided a substantial contribution to understand, at the molecular level, the specific interaction that occurs at the interface between the ester groups and the active sites on the silica surface. The band associated with the stretching vibration of C=O in the ester groups of attached maleate units was used. Figure 7 shows the carbonyl-stretching region of both unfilled and silica-filled EPR-g-DEM samples (mixes **FS0** and **FS4**). The carbonyl stretch of the former sample has a single well-defined band centred at 1737 cm^{-1}, whereas the composite shows an additional band at 1712 cm^{-1} which is assigned to a carbonyl that is hydrogen bound to silica surface.

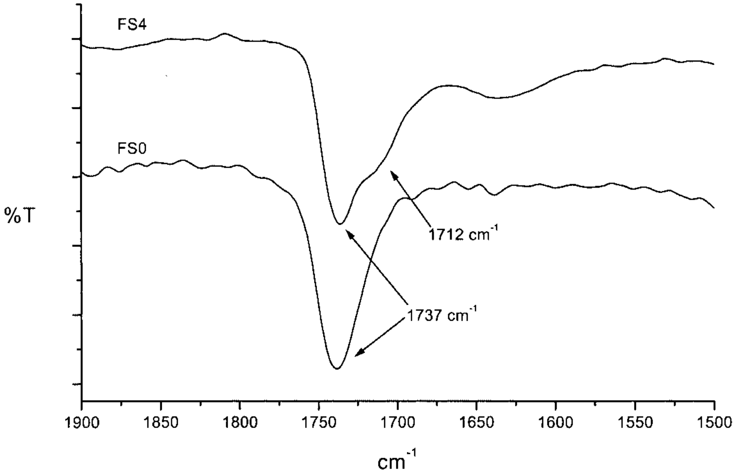

Figure 7: IR spectra of carbonyl region of FS0 and FS4 runs

A similar phenomenon has been reported for composites of PVAc obtained by polymerization of tetraethoxysilane (TEOS)[12] in the presence of PVAc, where it is observed a band centred at 1737 cm^{-1} due to the free carbonyl and an additional band at 1711 cm^{-1}, which is attributed to a hydrogen-bound carbonyl. The IR evidence for both free and hydrogen-bound carbonyls indicates that in the composites only a portion of the polyolefin chains interacts with the silica through the grafted ester groups. Two distinct microarea of the mix **FS4** with different silica content, show that the band at ca. 1712 cm $^{-1}$ is stronger in the microarea with the higher silica content (figure 8). The fraction of hydrogen-bound carbonyls is the associated with the presence of an interfacial region where the polymer chains interact strongly with the siliceous phase. The examination of the carbonyl stretching region for the residue to toluene extraction obtained for mix **FS4** (see figure 9) reveals only the peak centred at 1712 cm^{-1}. This supports our suggestion that the specific interactions involving the carbonyl groups of grafted maleate units play an important role on the formation of the unextractable polyolefin existing at the silica surface.

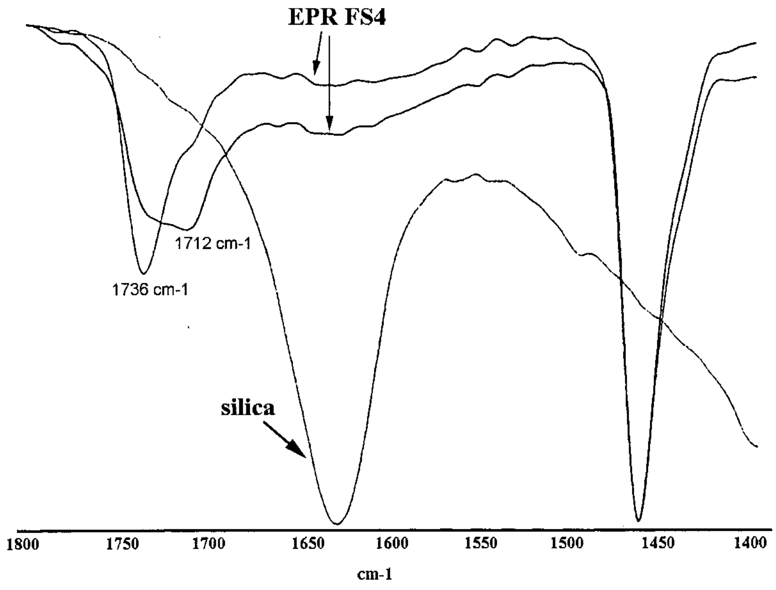

Figure 8: IR spectra of different microarea of FS4 sample

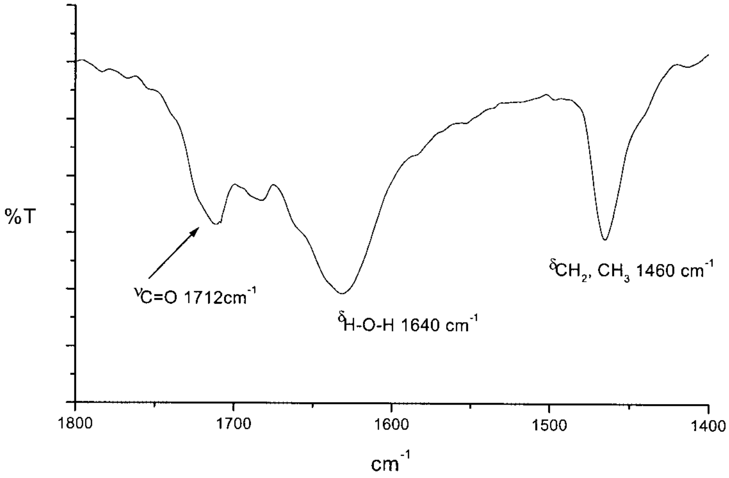

Figure 9: IR spectrum of the FS4 residue

SEM analysis

According to the FT-IR results, diethylmaleate modification of the EPR was expected to enhance the compatibility with silica filler. Thus it was worthwhile to check the influence of such interaction on the morphology of the mixtures.

The micrographs of the mixtures EPR/silica (see as example the micrograph of **S4** run in the figure 10a) show composites with a very large heterogenity: silica particle agglomerates are present (figure 10b) with size larger than 10 micron dispersed in the polyolefin matrix; this denotes the poor interfacial interactions between the filler and the organic phase.

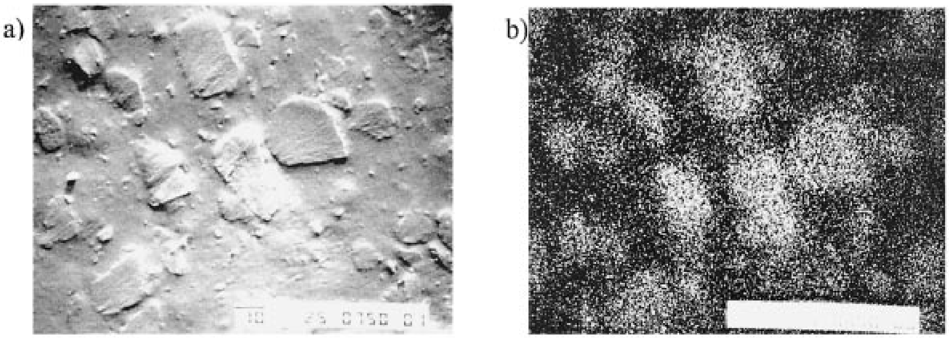

Figure 10: SEM micrograph of EPR S4 sample

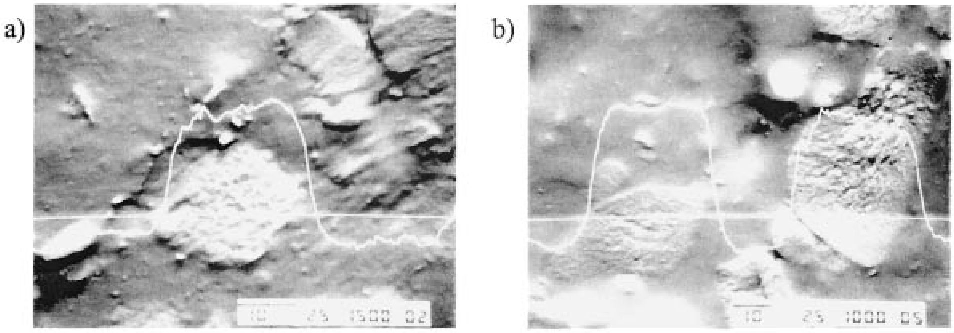

Figure 11: SEM micrograph of S4 (a) sample and FS4 (b)

By comparing the SEM micrograph of the **S4** and **FS4** composites (figure 11a and 11b) we can see that the grafting of DEM onto polyolefin backbone does not change substantially the morphology of the mixture and the dimension of the silica agglomerates. Indeed the used mixing procedure probably does not allow a finer breakdown of silica. Even if it is not possible to observe an alteration in the dispersion between the two phases, the micrographs with larger amount of enlargements of the two samples (**S4** and **FS4**, figure 12a and 12b) show a better adhesion of the silica particles to the matrix, when the polyolefin matrix is modified by the ester groups. In this case the domains of the inorganic filler have borders and surfaces not defined and clean, thus suggesting a good wettability of the silica by the functionalized polyolefin.

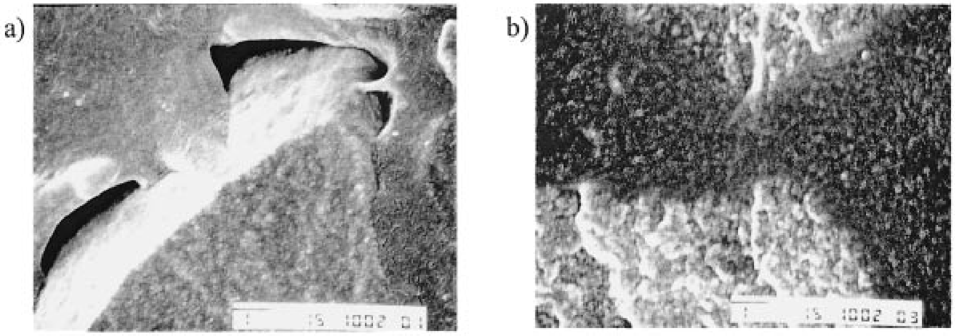

Figure 12: SEM micrograph of S4 (a) and FS4 (b) samples (larger amount of enlargement)

From the above results we can observe that the functionalized polyolefin shows a better ability to adhere to the mineral surface than the unmodified polyolefin.

Conclusions

The mixing of the functionalized polyolefin with silica provides composites where the inorganic phase (silica) and the organic phase (EPR) strongly interact as shown by the results obtained from selective solvent extractions, FT-IR, TGA and SEM analysis. The carbonyl groups inserted onto backbone of the polyolefin presumably give rise to the formation of hydrogen bonds with the O-H groups on the silica surface: these interactions increase the amount of "bound rubber", the decomposition temperature of the composites and the adhesion at the interface between polyolefin and silica especially at high loading of inorganic filler.

From the above results, it can be inferred that the polyolefin-filler interaction in the case of silica-filled EPR-g-DEM is of two types: (1) the interaction between the filler particles and the apolar segments of the polymer backbone, which is similar to the interaction occurring in the EPR/silica composites; and (2) the interaction between the ester groups of the polymer and the polar sites (hydroxyl groups) present on the silica surface, which is responsible of the increased amount of "bound rubber". Several investigations[11] have evidenced that polyolefins (PP, PE and EP) functionalized with diethylmaleate give rise to intermolecular interactions with groups of more polar polymers through a hydrogen bond involving the carbonyl of the ester groups in the side chains. Hence, it is believed that in the composites here reported the polymer-filler interaction due to ester groups can be of hydrogen-bonded type involving the carbonyl groups of the side chains, as depicted in figure 13.

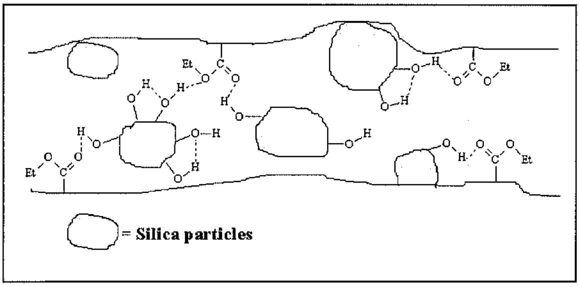

Figure 13: Schematic representation of interaction between silica surface and ester groups inserted onto polyolefin

Acknowledgement

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