Use of EPDMSDD as Compatibilizer Agent for EPDM/EPDMR Blends: Rheologic, Mechanical, and Morphologic Properties

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ABSTRACT: Around the world, concern is growing about the amount of waste rubber going into landfills. Policymakers are encouraging researchers to find innovative ways to recycle this waste. In this study, as part of an effort to recycle waste rubber (EPDMR) as filler in compositions of EPDM, we prepare a terpolymer of ethylene–propylene–diene with 1-dodecanethiol (EPDMSDD). We use it as a compatibilizing agent to improve adhesion and incorporation of the residue (EPDMR) in EPDM/EPDMR blends. We synthesize and characterize EPDMSDD through ^{13}C-NMR and FTIR spectroscopy. We evaluate the effect of the compatibilizer EPDMSDD using vulcanization parameters, such as optimum cure time, scorch time, and torque. To evaluate its effect on the interaction between EPDMSDD/EPDMR, we carried out mechanical tests of samples with and without EPDMSDD. Our findings show that the tensile strength and elongation increased with the addition of EPDMSDD, indicating a better interaction between EPDMR/EPDM. Tear strength also increased with the presence of EPDMSDD, particularly for the amount of 70 and 80 phr of EPDMR. This suggests a good adhesion between the phases in high amounts of waste. The micrographs of the mixtures revealed that the addition of EPDMSDD improved the dispersion of the EPDMR in the EPDM phase. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 948–955, 2011

Key words: compatibility; interfaces; waste; recycling; rubber

INTRODUCTION

One of the most important polymers used by automotive industries is EPDM rubber. It possesses special mechanical and thermal properties and has good processing.[1] EPDM is widely used by the automobile industry to produce bumpers, weather stripping, and for many other applications. This manufacturing process as well as the disposal of postconsumer products, scrap especially, produce a considerable amount of waste rubber. Governments over the last decade have grown increasingly concerned about the amount of rubber residues. When compared to human lives, the rubber decomposes over a long time. This high decomposition time and the environmental problems these materials cause have prompted governments to call for new technologies that can recycle these materials.

Rubbers often contains mineral fillers such as carbon black and silica, curing agents and other additives, materials having considerable commercial value.[2,3] For these reasons, researchers around the world are intensifying the search for appropriate technologies to recycle waste rubber.[4,6]

Several processes are currently used to recycle rubber. These include microwave, mechanical, cryogenic-mechanical, ultrasonic, thermomechanic, and "pan" methods.[7–10] All of these processes involve either the partial or complete thermal degradation of vulcanized rubber. If we are to maintain the rubber's original properties, we must preserve, during and after the recycling process, the elastomer's carbon–carbon bonds. To ensure this we must apply only enough thermal energy so as to break the sulfur-sulfur bonds and carbon-sulfur links. Most recycling processes, however, use heat and shear, making it difficult to control the material's thermal degradation. As a
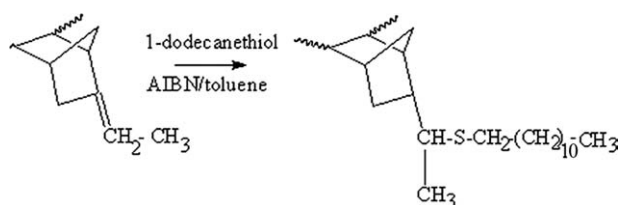
Figure 1 Reaction of the modification of EPDM with 1-dodecanethiol.

result, recycled rubber almost always has lower physical properties than virgin rubber.[11–14]

One way of overcoming this problem is to reduce how much rubber waste is used as filler in virgin rubber.[15–18] The literature shows that when we add ground rubber as filler the result is often a substantial deterioration in the physical properties of the composites. The deterioration is due to a lack of interfacial interaction between the particles of rubber waste and rubber matrix, mainly reclaiming a high concentration of waste.[19–22]

In practice, adding waste as filler to virgin rubber results in immiscible mixes. To improve the miscibility or dispersion between phases we can use a compatibilizer agent. Such an agent promotes a specific interaction between the filler and rubber. Researchers have used the compatibilization technique to improve the mechanical and thermal properties of immiscible blends.[23–25] The compatibility can be promoted by using block copolymers or graft copolymer. These reduce the interfacial tension, thus providing a better contact between the phases of polymers.[26] In recent work, researchers compatibilized blends of NBR/EVA using EVA modified with mercapto acid. The researchers observed an improvement in physical properties.[27]

In this study, we prepared ethylidenenorbonene terpolymer ethylene-propylene modified with dodecanethiol 1 (EPDMSDD). We used it as a compatibilizing agent to increase the interaction between the waste EPDMR and virgin EPDMR.

We investigated the compatibilizer effect of the EPDMSDD by examining the rheological and mechanical properties of the EPDMR/EPDM blends.

EXPERIMENTAL

Materials

The ethylene propylene ethylidenenorbonene rubber (EPDM 65) was supplied by DSM Brazil S.A. The rubber had the following properties: average molecular (M_n) = 150,000, Mooney viscosity (ML1 + 4 at 100°C) = 77, (60/40) Ethylene/propylene proportions.

Ethylene propylene ethylidenenorbonene rubber waste (EPDMR) comes from the automotive industry. The EPDM-R waste was triturated in a knife

mill. It was then sieved in different particle sizes, ranging from 0.252 to 0.358 mm.

Functionalization of EPDM

Ethylene propylene ethylidenenorbonene modified by 1-dodecanethiol (EPDMSDD) was prepared through a reaction between EPDM (65) and 1-dodecanethiol in toluene solution at 70°C for 3 h, over a nitrogen atmosphere, Figure 1.

Characterization

To evaluate the graft reaction (EPDMSDD), the ^{13}C NMR spectra in solution were recorded at 200 MHz, Bruker DRX 200. The material was dissolved in CDCl$_3$. Chemical shifts are given relative to TMS as the internal standard.

FTIR spectra analyses were also used to identify the EPDMSDD modified. Infrared spectra were carried out on KBr pellets using a Perkin–Elmer 1600 spectrophotometer.

The titration technique was also used to evaluate the 1-dodecanethiol residual. The moles of 1-dodecanethiol reacted with EPDM were determined by difference of concentration of 1-dodecanethiol in solution after 3 h of reaction. The concentration of residual 1-dodecanethiol was determined by alkali titration using 0.00496N sodium hydroxide in methanol. The grafting percentage (G) was calculated according to eq. (1):

$$X = \frac{M_{io} - M_i}{M_{io}} \qquad (1)$$

Where M_{io} is the initial moles of 1-dodecanethiol and M_i is the final moles of 1-dodecanethiol after reaction. The conversion of reaction (X) was 90%.

Preparation of EPDM/EPDMR blends

EPDM/EPDMR blends were prepared using a two-roll mill at 70°C and 50 rpm. An overall mixing time of 20 min was established to offer a better dispersion of the ingredients. The basic formulation of compositions was in phr (phr = part for 100 parts of Rubber) (100): EPDM, (5) Zinc Oxide, (1) Stearic acid, (2) Sulfur, (1) 2, 2'-dithiobisbezothiazole, (MBTS), (1) tetramethylthiuram disulphide (TMTD). Rubber waste (EPDMR) varying between 5 and 80 phr and, for compatibilized compositions, 5 phr of EPDMSDD was used.

Rheometric testing

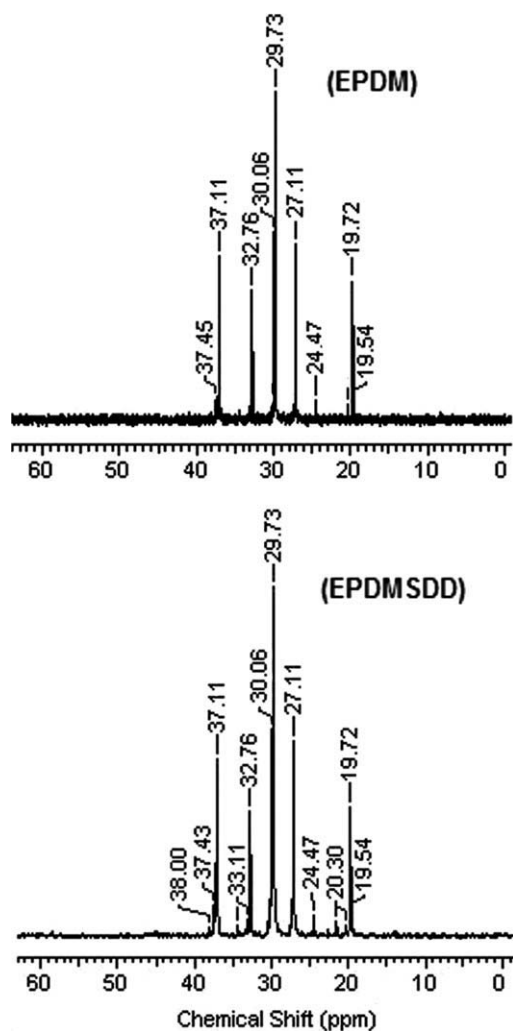The vulcanization parameters of the mixes were measured on an oscillating disk rheometer (ODR)

Figure 2 13C NMR of (A) EPDM and (B) EPDMSDD.

Monsanto at 160°C and 1 arc degree, according to the ASTM D-2084-84 method. After the mixing process, the blends were vulcanized, up to the optimum cure time, in a hydraulic press at 160°C and 15 MPa.

Mechanical testing

Stress-strain properties and tear strength were measured in an EMIC Universal Testing Machine; model DL2000, according to ASTM D412 and D624, respectively. The crosshead speed used was 50 mm min^{-1}.

RESULTS AND DISCUSSION

^{13}C NMR feature and FTIR spectroscopy

The solution ^{13}C NMR spectrum of EPDM and EPDMSDD is shown in Figure 2(a,b), respectively. The signals at 19.9–37.3 ppm correspond to the methylene, methine, and methyl carbon units of the

main-chain of EPDM. The solution ^{13}C NMR spectrum of the EPDMSDD is similar to the spectrum of EPDM rubber. Signals at 20.30 and 33.11 ppm, however, are not present in the ^{13}C NMR of EPDM, Figure 2. Grott et al. recently used ^{13}C NMR 75 Hz to determine the composition of EPDM/PP blends with extender oil and talcum filler.[28] According to these authors, the ^{13}C NMR EPDM spectrum is considerably complex. Peak assignments were made by comparing with the isotactic propylene spectra reported by Carmen et al. and Randall.[29,30] For ^{13}C NMR spectrum of EPDM/PP, the signals at 14.0, 22.8, and 32.1 ppm were attributed to the response of the butyl chain-end of the oil because these signals are not present in the EPDM spectrum. Comparing the results obtained by Grott et al. with the results observed in this work, we concluded that the respective signals 20.30 and 33.11 ppm are due to the presence of dodecanyl chain-end of the EPDMSDD. A similar observation was also made by Winters.[28]

Figure 3(a,b) show the infrared spectra in the 500–4000 cm^{-1} region for EPDM and EPDMSDD, respectively. In Figure 3(a), absorption bands can be observed in 700, 716, and 755 cm^{-1}, which correspond to the $(CH_2)_n$ in the main-chain of EPDM. It can be observed that these three bands have disappeared for EPDMSDD, resulting in only one absorption band at 720 cm^{-1}. The results suggest the grafting of 1-dodecanethiol onto EPDM. Two intense absorption bands at 1374 and 1460 cm^{-1} can also be seen in Figure 2, which correspond to the methylene groups ($\delta(CH_3)$) symmetric stretching bands. The EPDMSDD spectrum is evidence of an overlapping of bands between 1600 and 1733cm^{-1} range. Absorption bands at regions 2720 and 2021 cm^{-1} can be assigned to grafted 1-dodecanethiol. This is because the 1-dodecanethiol exhibits an intense absorption in
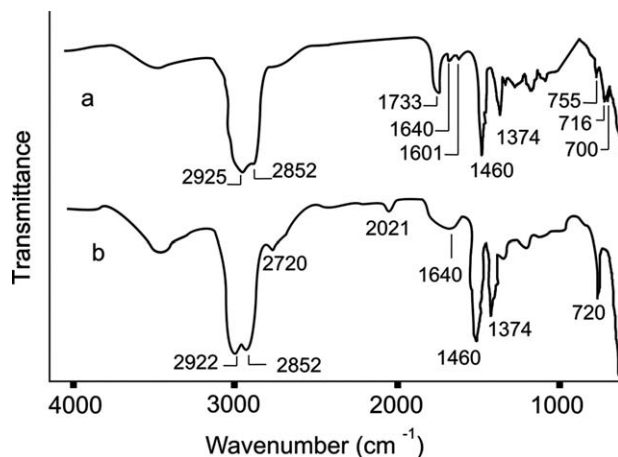

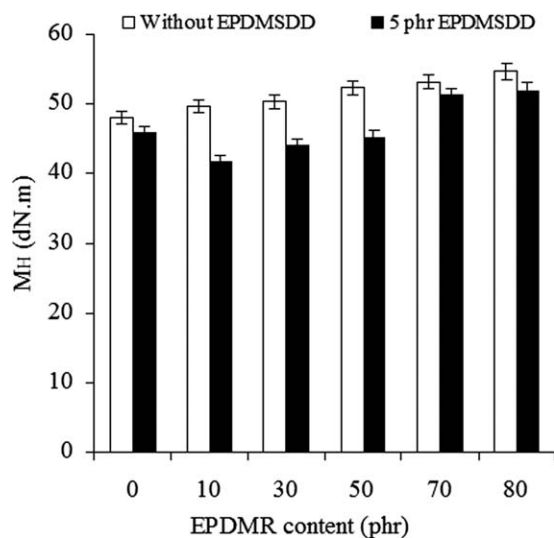**Figure 3** FTIR spectrum: (A) EPDM and (B) EPDMSDD.

Figure 4 Effect of EPDMSDD and EPDMR loading on the maximum torque (MH) of EPDM composition.

$2924–2700$ cm^{-1}, due to CH$_2$ symmetric and anti-symmetric stretching bands.[28,29]

Rheometric properties

We investigated the vulcanization parameters to better understand the effect of adding EPMDSDD and of the amount of EPDMR on the curing process of EPDM formulations. For uncompatibilized mixes, as illustrated in Figure 4, the maximum torque values increased with the EPDMR content. Maximum torque represents the cure state of rubber; it is proportional to the crosslink formations. Consequently, this result suggests that the formation of crosslinks in the EPDM changes as the amount of EPDMR increases. The EPDM residue contains in its original formulation many ingredients, such as accelerators, sulfur, and carbon black. Sulfur and accelerators present in the EPDMR can migrate from the EPDMR to the EPDM matrix, increasing the crosslink and torque maximum. The rates of diffusion of the sulfur and accelerators are proportional to the concentration gradient of ingredients between the two phases. We can find in the literature studies on the curative diffusion in blends of dissimilar elastomers.[31–33]

Conversely, the amount of carbon black increases as the EPDMR loading increases. Also, according to Payne, carbon black, due to its rigid nature and special morphology, promotes interesting changes in the rheological behavior of rubber. Thus, carbon black also promotes a good adhesion between rubber phases and increases the maximum torque.[34]

For compatibilized mixes, the maximum torque does not change significantly for mixtures without EPDMR. The maximum torque was significantly reduced, however, with the addition of 10 phr of EPDMR. For compatibilized mixes, at low EPDMR content, the viscosity and maximum torque were reduced due to the preferential interaction between EPDMSDD and EPDMR residue. This can be explained by the emulsifying effect of EPDMSDD. This preferential interaction decreases the formation of aggregates, reducing the maximum torque. When the amount of EPDMR increases, the interaction between EPDMR-EPDMR particles are favored, increasing the viscosity and torque.

At higher concentrations of EPDMR, filler loading outweighs the effect of compatibilization promoted by EPDSDD, reducing the difference between the minimum and maximum torque rheometer. Why does this happen? When the amount of EPDMR increases, more layers of carbon black are formed, covering the entire sample surface. Thus, aggregates of carbon black are in contact, preferably, with the rotor charge of torque.

Figure 5 shows the effect of both EPDMR and EPDMSDD on the minimum torque (M_L). Carbon black present in waste reduces the flow in the melt process. Its structures are strongly connected and not easily destroyed during processing. Consequently, an increase in the minimum torque is observed.

According to Paul and Barlow, if we add properly selected compatibilizers to binary immiscible blends we can expect a reduction in the interfacial energy of the phases.[35] This reduction permits a finer dispersion during the mixing processes. Several studies have investigated in detail the efficiency of the reactive and nonreactive compatibilization.
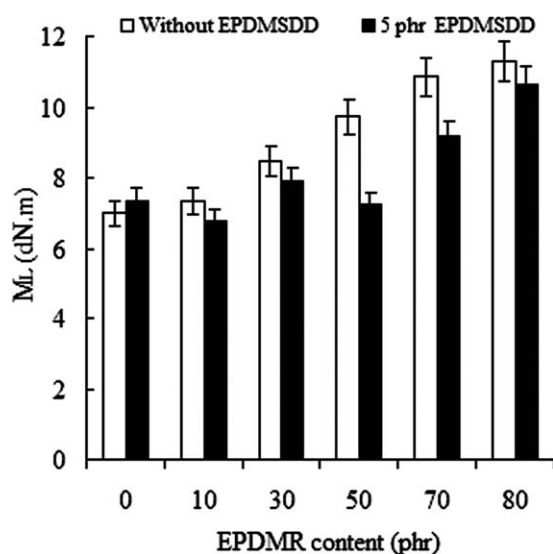

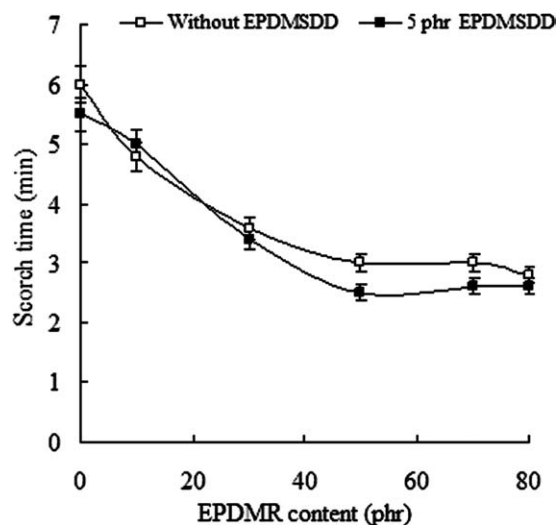**Figure 5** Variation of minimum torque (ML) as a function of the EPDMR content.

Figure 6 Variation of Scorch time as a function of the EPDMR content.

Figure 8 Tensile Strength behavior as a function of the EPDMR content.

The high degree of physical interactions between dodecanyl chains and carbon black can increase rubber-filler interaction and improve filler dispersion. We can explain this result by the emulsifying action of EPDMSDD during the mastication process in the roll-mill. Thus, as shown in Figure 4, a decrease of minimum torque was observed.

In the mixing process, an important parameter for safety control is scorch time. The variation of scorch time with the EPDMR content is shown in Figure 6. Scorch time decreases as EPDMR content increases and displays similar values between 10 and 30 wt % of the EPDMR. Scorch time is decreased by compatibilization in the range of 30–80 wt % of EPDMR. We can attribute this result to the emulsifying effect of the graft EPDMSDD and to the catalytic effect of
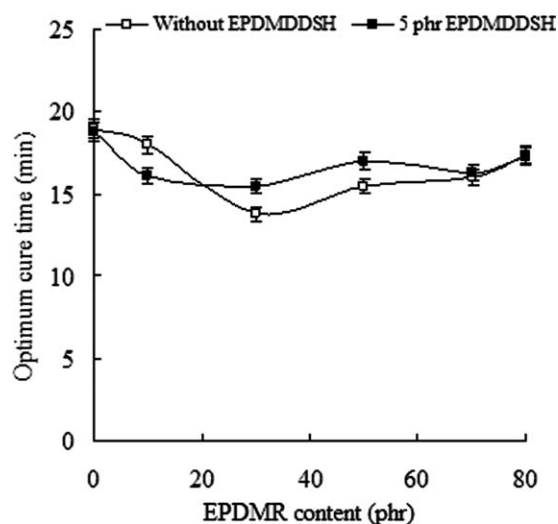
carbon black in the mixes. Similar results were observed with ENR50/SMRL blends containing carbon black.[34]

The optimum cure time results of compatibilized and uncompatibilized EPDM compositions are illustrated in Figure 7. At lower concentrations of EPDMR, the optimum cure time of compatibilized mixes was lower than the uncompatibilized mixes. Optimum cure varies slightly in the range of 10–80 wt % of EPDMR. However, the highest differences were observed between 20 and 70 wt % of EPDMR, where the addition of EPDMSDD increased the optimum cure time.

We can attribute the oscillation observed in the results of the optimum cure time to competitive mechanisms that may occur during the curing reaction. In this system, carbon black and other agents are present as well as the compatibilizer EPDMSDD, with its acidic nature. As EPDMR increases, the mass ratio EPDMR : EPDMSDD increases. This may be affecting the dispersion of curing agents and the mixture as well as the interfacial interaction—affecting all rheometer parameters differently.

Figure 7 Variation of optimum time as a function of the EPDMR content.

Mechanical properties

Figure 8 shows the effect of adding EPDMR and EPDMSDD on the tensile strength property of the EPDM mixes. Aside from 50 phr EPDMR composition, the tensile strength increases, for both uncompatibilized and compatibilized mixes, with the addition of EPDMR. We can attribute this result to the reinforcement effect of carbon black as filler in rubber compositions. In general, the best results for tensile strength were observed with compatibilized mixes. If we obtain a good superficial adhesion of
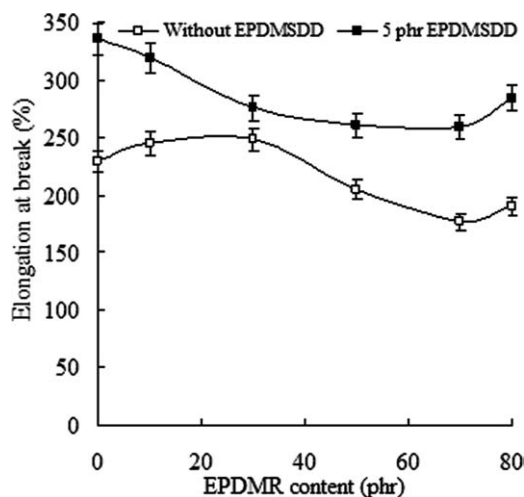
Figure 9 Elongation at break behavior as a function of the EPDMR content.

Figure 11 Shows the results related to extraction experiments.

the carbon black in the EPDM matrix, then we can expect an improvement in the mechanical properties.

The elongation at break decreases as EPDMR content increases, see Figure 9. The absence of a good interaction between EPDMR-carbon black particles and EPDM matrix does not permit an adequate stress transfer across the material. Consequently, elongation is decreased. We observed, however, an interesting result for compatibilized mixes for elongation at break. As shown in Figure 9, with the addition of 5 phr of EPDMSDD higher elongation values were obtained. The physical contact between carbon black and the EPDMSDD is sufficiently stronger to permit the transfer of energy between the materials, avoiding premature ruptures. The
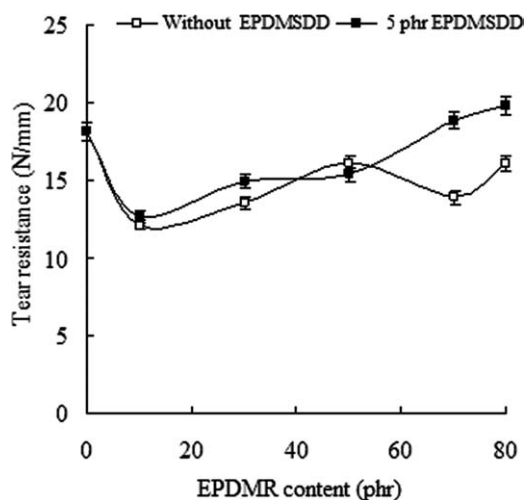
conservation of energy can be maintained during mechanical analysis and higher deformation is obtained. Concerning the tensile properties, this result also indicates that EPDMSDD gives better combination stress–strain at break.

The effects of the EPDMSDD and EPDMR content on the tear resistance are shown in Figure 10. Compatibilized and uncompatibilized mixes show a similar behavior of tear strength in the range of 10 to 50 wt % of EPDMR. After this composition, the addition of EPDMSDD content improved the tear strength. For this reason, in practical formulation, oil is often used to improve both the processability of the mix and the dispersion of the carbon black. Carbon black dispersion favors the chemisorption of polymer, resulting in a stronger interaction and reinforcement effect. Returning to the discussion of this work, in the range of 50–80 wt % of EPDMR, the compatibilized compositions presented the highest values of tear strength. The probability of interaction between carbon black particles and the EPDM increases with the EPDMR content. The addition of the EPDMSDD as a compatibilizing agent reduces the interfacial tension, improving the physical contact between the EPDM and carbon black (EPDMR). To improve the mechanical properties, however, it is necessary to have an optimum amount of carbon black.

It can be observed that there is an increase in soluble material proportional to the increase of residue amount. When EPDMSDD was added, however, the amount of soluble material was reduced, Figure 11. This indicates that this interfacial agent improved the adhesion between filler and matrix. This trend combines with the mechanical properties of EPDM compositions. The mechanical properties are directly
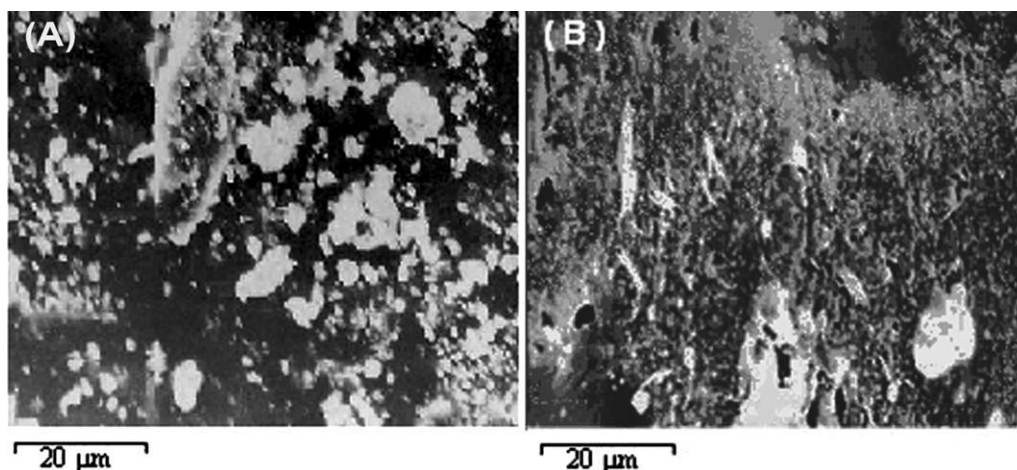

Figure 10 Tear strength behavior as a function of the EPDMR content.

Figure 12 SEM micrographs of EPDM/EPDMR: (A) without EPDMSDD and (B) with 5 phr of EPDMSDD.

related to the adhesion between the filler particles and the backbone chains. The compatibilizing agent also exerts an important influence on the contact between phases because it reduces the interfacial tension, giving a better dispersion and adhesion.

Figure 12 shows the morphology of EPDM mixtures containing EPDMR with and without EPDMSH. The SEM micrographs of the EPDM/EPDMR mixture showed a presence of carbon black on the surface area. The particles appear to be highly aggregated, forming well-defined structures. The addition of 5 phr of EPDMSDD gives a better distribution of the EPDMR particles. The surface area and size distribution of the particles also became uniform, indicating a compatibilizing effect of EPDMSDD. This result suggests that EPDMSDD provides a better interaction between carbon black filler and EPDM.

CONCLUSIONS

The EPDMSDD was successfully prepared and the grafting reaction, through ^{13}C NMR and FTIR analysis, was confirmed. The addition of 5 phr of EPDMSDD exerts an important influence on the processability of the mixture as the maximum and minimum torque show. With an increase of EPDMR, we observed practically no change in the maximum torque. We did observe, however, a substantial increase in minimum torque. When we added 5 phr of EPDMSDD at higher EPDMR compositions, scorch times decreased. As for mechanical tests, adding 5 phr of EPDMSDD as a compatibilizing agent offered the best combination of stress–strain. We attribute this to the better contact between EPDMR rubber particles and graft chains on EPDM matrix. The higher values of tear strength obtained by adding EPDMSDD at higher EPDMR content can also be explained by the dispersive-type force and better

adhesion between the dodecanyl chains and the filler particles EPDMR. SEM analysis also confirmed better adhesion. The presence of EPDMDD permitted the incorporation of a greater amount of EPDMR to the mix, helping to retain its mechanical properties.

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