Microwave-Induced Devulcanization for Poly(ethylene–propylene–diene) Recycling

Alberto Bani, Giovanni Polacco, Giuseppe Gallone

Department of Chemical Engineering, University of Pisa, Largo Lucio Lazzarino, 2-56122 Pisa, Italy

ABSTRACT: The production of high quantities of end-of-life rubbers is an environmental problem of growing importance. Because of their crosslinked nature, such rubbers cannot be easily reprocessed, and actually, they are mainly wasted or reused after a simple mechanical grinding. In this study, a microwave (MW)-induced thermal treatment at temperatures above 300°C was proposed to obtain partial devulcanization of a poly(ethylene–132#propylene–diene) (EPDM) rubber filled with carbon black. The use of MWs showed to be a very fast and simple technique, which allowed the production of a treated rubber with a relatively low degree of crosslinking, a slight revulcanization ability, and suitability for reuse in conjunction with virgin rubber. Preliminary mechanical characterization, performed on the revulcanized samples, indicated that the virgin and treated rubber were able to establish a good interface adhesion, which led to performances better than those of similar materials where the recycled part was made of ground untreated EPDM. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2904–2911, 2011

Key words: mechanical properties; recycling; vulcanization

INTRODUCTION

Since it was introduced to the market of synthetic rubbers in 1963, poly(ethylene–propylene–diene) (EPDM) M class has found application in automotive (profiles, hoses, and seals), building and construction, cable and wire insulation, and appliances for a wide variety of molded articles. Differently from general-purpose elastomers such as natural rubber, styrene–butadiene, rubber and butadiene rubber, EPDM production is still growing quite constantly.[1] In fact, part of this growth is due to the progressive replacement of the aforementioned rubbers with EPDM itself because of its better chemical and thermal resistance. Moreover, EPDM has good electrical properties, little moisture adsorption, excellent resistance to weathering and chemicals, a good compression set, and a very good dynamic fatigue resistance.[1]

Like other rubbers, EPDM is used in a crosslinked form, and therefore, it has the disadvantages of difficult recycling, and reprocessing is not directly applicable. Vulcanized rubbers, if not wasted, are usually ground and then used in this form or burned to produce energy. However, recent norms strongly limit the latter solution, and end-of-life rubbers are becoming an environmental problem, such as in the case of tires, which are produced in huge amounts. For these reasons, there is a growing interest in the development of devulcanization processes able to produce a virginlike material, but until now there have been no solutions conveniently applicable on a large scale, and most end-of-life rubbers are destined for disposal in dumps. The most studied ways for devulcanization are based on thermal[2] or mechanothermal[3–7] treatments, with the high temperature being of fundamental importance for inducing the rupture of the interchain bonds. In this context, microwave (MW) technology may offer some advantages, with respect to conventional thermal treatments, such as noncontact heating, volumetric heating, material selectivity, and fast startup. When the MWs pass into the rubber compound, the electric field established inside it determines changes in the molecular motions (rotations and vibrations) and polarizations of the molecules; this induces molecular frictions and a subsequent heating of the material. However, the heating efficiency depends on the material composition because the response to MWs is strongly influenced by the dielectric properties.[8] In particular, because of its very low polar character, EPDM is scarcely responsive to the electromagnetic fields. Nevertheless, for an end-of-life treatment with MWs, the widespread use of carbon black (CB) as a conventional filler to improve the mechanical properties has the additional advantage of a strong effect on the electrical behavior of rubber. If the temperature is high enough, the chemical bonds may become

TABLE I
EB Formulation

		Ingredient	Quantity (phr)
EB	EPDM	Dutral 4038	100
	CB	N660	40
	VS	Sulfur	2
		TBBS	2
		Stearic acid	1
		ZnO	2

unstable, and a partial devulcanization can take place.[8,9] Of course, it is difficult to set the process to have a selective effect on interchain bonds, and the final goal is to find the right operating conditions to prevalently break the sulfur–sulfur or carbon–sulfur bonds without a massive degradation of the polymer chains.

In this study, the effects induced by MWs on the total sulfur content and crosslink density of EPDM rubber were investigated. Moreover, blends obtained by the mixture of virgin and recycled EPDM were prepared and subjected to mechanical characterization.

EXPERIMENTAL

Materials

The base of all the materials studied was an uncured, green EPDM blend (EB) composed by EPDM Dutral 4038 (Polimeri Europa, Ferrara, Italy), a vulcanization system (VS) consisting of milled sulfur (Siarkopol, Grzybów, Poland), zinc oxide (Grillo Zinkoxid GmbH, Goslar, Germany), stearic acid (Fluka, Seeize, Germany), *n-tert*-butyl-2-benzothiazol sulfenamide (TBBS) Vulkacit NZ/EG-C (Bayer, Leverkusen, Germany), and CB N660 as the filler (Klean Carbon, Vancouver, B.C., Canada). Toluene, *n*-heptane (Carlo Erba, Milano, Italy), 2-propanethiol, 1-hexanethiol, and piperidine (Sigma-Aldrich, Milano, Italy) were used as received.

Rubber compounding

EB compounded stock was mixed in a Banbury mixer (Farrel corporation, Ansonia, CT, USA) with a chamber fill factor of 0.7. Two-stage mixing was selected for the EB compound. In the first, nonproductive stage, the initial conditions were heating at 100°C and mixing at 100 rpm. The polymer was introduced into the chamber first, and after 2 min, the filler was added. After 7 min of total mixing time, the material was discharged. In the subsequent productive stage, the initial conditions were heating at 100°C and mixing at 50 rpm. The rubber was introduced into the chamber first, and after 2 min, all of the chemicals (sulfur, curatives, and curing

promoters) were added. After 5 min of total mixing time, the material was discharged. The compounded stock was sheeted at 2.5-mm thickness on a two-roll mill (Brabender GmbH, Duisburg, Germany) between the two stages and before curing. The formulation of the EB compound is summarized in Table I.

Processing

Vulcanization

EB was vulcanized in a Carver laboratory press (Menomonee Falls, WIS, USA) at 195°C for 5 min. After the obtained material [vulcanized EB (VEB)] was taken out of the mold, it was immediately quenched into melting ice to prevent further curing. After vulcanization, the rubber was mechanically crumbled into small pieces with an average size of 2–3 mm.

MW treatment

The VEB was treated in a MW oven model BP-211/50 from Microwave Research and Applications, Inc. (Laurel, MD, USA). To set the appropriate operating conditions, preliminary MW treatments were performed on batches of 40 g of crumbled rubber kept in a glass flask. During the MW irradiation, the temperature of the rubber was monitored by means of an optical fiber probe. Larger amounts of microwave-treated rubber (TR) were then obtained from a second set of MW treatments, which were performed on 400-g batches inside a Pyrex reactor. Sample holders were thermally insulated by means of a MW transparent, ceramic fibrous insulator (Duraboard by Unifrax Italia, Saronno, Italy) jacket.

Sample preparation

Both TR and untreated VEB were cryomilled with a Fritsch miller (Fritsch Gmbh, Koblenz, Germany) before any further use. Then, they were properly formulated and processed to give the samples used for the investigations reported hereafter.

It was immediately apparent that TR could not be considered a virginlike material because it was only partially soluble in toluene; nevertheless, some preliminary tests showed that after mixing with VS, TR could be successfully subjected to revulcanization. The TR + VS (prepared with the same rubber/VS ratio reported in Table I) was, therefore, mixed with EB to prepare a material with a partial content of recycled rubber. However, because TR was not completely devulcanized, there arose the question of how much of the VS could be effectively incorporated into it, with the excess part available as additional VS for EB. To better understand this point, TR and EB were also mixed without further addition of
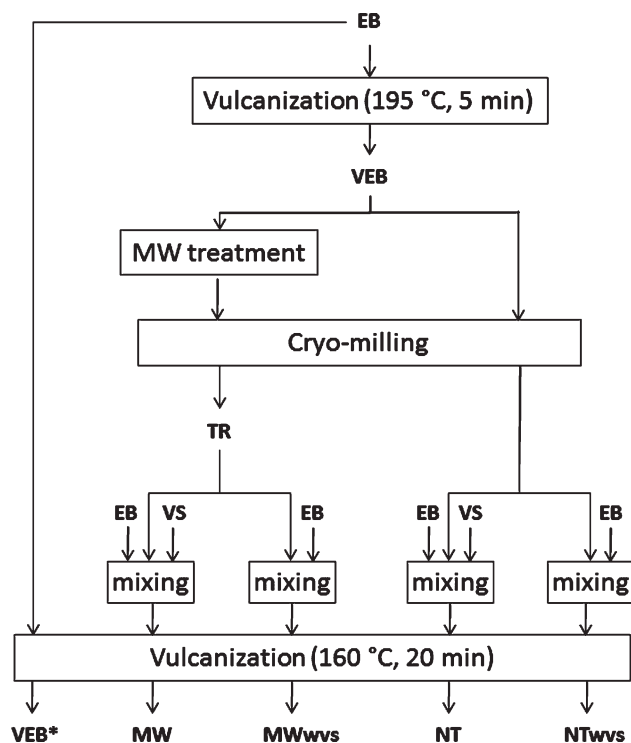
Figure 1 Scheme of sample preparation.

VS. As described later, the virgin EB was used to obtain the reference material, whereas blends of EB with cryomilled, untreated VEB were also considered for comparison. Thus, four kinds of formulations containing virgin and recycled rubber were prepared for the mechanical characterization: (1) virgin EB and cryomilled TR; (2) virgin EB and cryomilled TR, with this last added with VS in accordance to the formulation in Table I; (3) virgin EB and cryomilled VEB; and (4) virgin EB and cryomilled VEB, with this last added with VS in accordance with the formulation of Table I.

Each compounded stock was mixed in a Banbury mixer with a chamber fill factor of 0.7. A single mixing procedure (100°C and 30 rpm) was chosen for each compound. EB was first introduced into the chamber; then, after 2 min, the recycled material was added, and finally, after 3 min, all chemicals (VS) were added as specified in the experimental recipe. After 7 min of total mixing time, the material was discharged. The compounded stocks were passed on a two-roll mill before curing, sheeted at 2.5-mm thickness, and then vulcanized in a press at 160°C for 20 min. The choice of different curing conditions for the materials with recycled rubber were used with the idea of granting longer times for chain relaxations to occur and improving interactions between the matrix and filler macromolecules. A virgin EB was also vulcanized at 160°C for 20 min (VEB*) and was used as a reference material. A comprehensive scheme of sample prepar-

ation is given in Figure 1. The quantity of recycled material varied from 10 to 50 wt %, but in the following text, only the mechanical properties of mixes with 50% recycled rubber (Table II) are reported.

Characterizations

The operating conditions used for vulcanization were set up after some preliminary tests that were carried out with an oscillating disc sealed rheometer RPA 2000 (Alpha Technologies UK, Heilbronn, Germany) in accordance with ISO 6502. During the measurements, a poly(ethylene terephthalate) film was applied to prevent chamber dirtiness. The mechanical properties were measured during the process, and the duration of the cure was decided on the basis of the time at which the torque leveled off; no reversion phenomena were observed at this point. The time when the torque reached 90% of its equilibrium value was equal to about 5 min at 195°C or 20 min at 160°C and was taken as a reference.

Thermogravimetric analysis (TGA) was performed in a thermobalance from TA Instruments Italia (Milan, Italy) (model Q500). About 10 mg of VEB was heated from room temperature up to 800°C under an N_2 atmosphere at a heating rate of 10°C/min.

The gel content of the samples was determined by gel tests in toluene in accordance with ASTM D 3616-95.

The total sulfur content was measured with a LECO SC-132 sulfur analyzer (LECO Italy, Milan, Italy). Samples of about 100 mg were burned in the presence of an oxygen atmosphere (oxygen purity = 99.95%) at 1350°C.

The crosslink density (v_e) was estimated by a swelling test in n-heptane with the Flory–Rehner equation[10] and the thiol probe method of Campbell.[11] The Flory–Rehner equation, as derived from rubber elasticity theory, is as follows:

$$v_e = \frac{[\chi v_r + \ln(1 - v_r) + v_r]}{V_0(0.5v_r - v_r^{1/3})}$$

where v_r is the equilibrium volume fraction of rubber in the swollen state, χ is the polymer–solvent interaction parameter, and V_0 is the molar volume

TABLE II
Compositions of the Recycled Compounds

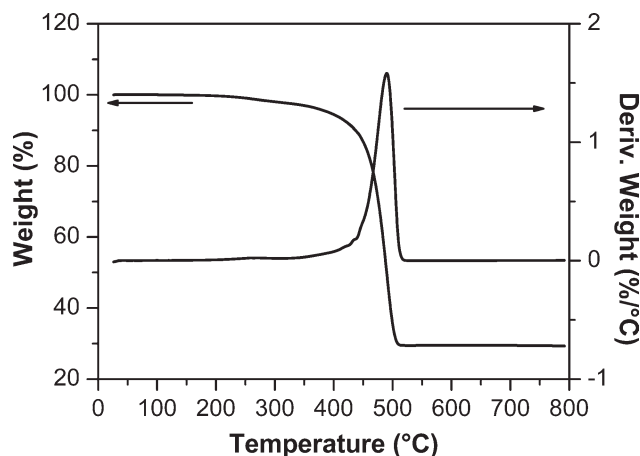| Sample name	Quantity (phr)			
	EB	Cryomilled VEB	Cryomilled TR	VS (phr)
Reference VEB*	100	—	—	—
NT50	50	50	—	3.5
NT50wvs	50	50	—	—
MW50	50	—	50	3.5
MW50wvs	50	—	50	—

Figure 2 TGA of VEB rubber.

of the solvent. The value of χ was calculated with the following relation, obtained from the tensile retraction measurements: $\chi = a \cdot \ln v_r + b$, where a and b are 0.2316 and 0.8604, respectively.[10] The values of v_r were determined by the following equation:[10,12]

$$v_r = \frac{1}{1 + \frac{d_r}{d_s}\left(\frac{1-f_{sol}}{1-f_{sol}-f_{fil}}\right)\left(\frac{W_s}{W_D}-1\right)}$$

where d_r and d_s are the densities of the rubber and solvent, respectively; f_{sol} is the weight fraction of soluble material; f_{fil} is the initial weight fraction of the filler; W_s is the weight of the swollen solvent; and W_D is the weight of the dry sample. The procedure derived from the Campbell theory[11] consisted of two steps: a first chemical treatment with a solution of 2-propanethiol and piperidine for 2 h at room temperature; this broke the polysulfidic ($S_x > 2$) bonds. This was followed by a treatment with 1-hexanethiol and piperidine for 4 h at room temperature; this broke the disulfidic (S_2) S—S bonds. Swelling in n-heptane before and after each step gave the values of the equilibrium volume fraction of rubber in the swollen state, from which crosslink density and the concentrations of monosulfidic (S_1), S_2, and S_x bridges could be obtained.

The tensile properties were measured with a stress–strain analyzer (model 5500 R) from Instron (Bucks, UK) equipped with a 10-kN load cell on specimens, as from ASTM D 412; the maximum extent of elongation recorded was 1000%. The elastic modulus, tensile strength, and elongation at break of the samples were measured at room temperature according to ISO 37 with a constant deformation rate of 200 mm/min. The dynamic mechanical tensile characterization was performed by means of a dynamic mechanical thermal analyzer (Eplexor 100 N,

GABO GmbH, Germany) equipped with a 150-N load cell. The real (E') and imaginary (E'') parts of the complex elastic modulus (E^*) were measured on specimens shaped according to ISO UNI 4661-1. Temperature sweep tests were carried out at 10 Hz under a static strain of 0.2% and a dynamic strain of 1.2%, whereas the temperature was varied from −60 to 60°C at a uniform heating rate of 5°C/min. Strain sweep tests were performed at room temperature and 10 Hz with a static strain of 40% and a dynamic strain ranging from 0.1 to 20%.

RESULTS AND DISCUSSION

TGA of VEB rubber showed that its thermal degradation under an inert atmosphere started at about 400°C, and the first derivative of weight with respect to temperature had a single main peak ending around 520°C (Fig. 2). The residual weight at 800°C corresponded to the total CB content. The solubility tests in toluene showed that VEB had a gel content of 98% and a swelling index (SI) equal to 2.5.

Thermal treatment

Unfortunately, conventional metallic temperature probes, such as thermocouples, even when shielded, were inappropriate for use in our MW setup because of the very high electric field densities established during irradiation, which caused local overheating or even sparking. The use of an optical fiber probe (FOT-L from FISO Technologies, Inc., Quebec, QC, Canada) did not solve the problem completely because such probes are covered with polymeric materials and are, therefore, designed to work below 280°C. Some ramp tests, followed by isothermal irradiation at 280°C, were ineffective at inducing evident structural changes in VEB. Nevertheless, such tests gave useful information about the thermal response to irradiation by the VEB sample. After that, we performed further experiments by gradually increasing the irradiation time and soon measuring the final temperature in the core of the reactor by means of a K-type thermocouple once the MW had been turned off. However, a simple glance at the material extracted from the MW oven revealed a highly inhomogeneous aspect: the rubber in the peripheral part of the reactor looked macroscopically unchanged, whereas that in the inner part of the reactor was very different and, in some tests, even partly liquefied. This indicated that some degradation processes occurred in the sample. Of course, at this stage, it was not possible to distinguish the real cause of the degradation because it might have occurred as a consequence of sulfur bridge breakage or polymer chain molecular weight reduction or, more probably, of a superposition of both such two

Sample	Oven power (%)	Residence time (s)	T_{max} (°C)	Gel content (%)	SI
E320	40	300	320	50	5.9
E340	40	300	340	25	6.5
E358	40	360	358	37	3.6
E367	40	420	367	49	4.5
E373	40	420	373	26	3.2
E380	80	300	380	8	2.5

processes. Therefore, the gel tests were performed on samples obtained after grinding and homogenization mixing and represented only an average state of the rubber. The operative conditions, average final gel content (percentage), and SI of the rubber are reported in Table III, with those experiments conducted on batches of 40 g of material. In all of the tests, the final temperature was higher than 300°C, and the average gel content was lower than 50%; this showed a significant reduction in the crosslink density. Probably because of the aforementioned lack of homogeneity, the measured gel content did not show a regular trend with the maximum treatment temperature; this revealed that the sample selection from the batch may be a quite critical operation.

On the basis of the results reported in Table III, the chosen operating conditions for the batches of 400 g were 80% of maximum power of the oven and a residence time of 5 min. At the end of MW irradiation, the temperatures were measured at the same time both in the center and at the boundaries of the reactor, and despite the thermal insulation, they were equal to 320 and 390°C, respectively.

Sulfur content and crosslink distribution

Total sulfur content analysis was carried out on samples taken from the boundaries of the irradiated batches, both just at the end of the thermal treatment [total sulfur content after thermal treatment (S_{tt}; wt %)] and after subsequent washing in toluene [total sulfur content after subsequent washing in toluene (S_{tw}; wt %)]. The latter was necessary to assess whether low-molecular-weight components, produced by devulcanization, remained entrapped in the rubber after the thermal treatment. Table IV reports the obtained sulfur contents (the value for untreated EB, as calculated from Table I, was 1.36 wt % with respect to the total weight) and the corresponding percentages of removed sulfur. The results show that the thermal treatment by MW irradiation induced a consistent reduction in the sulfur content, with the higher temperatures having been more effective in this sense.

In Table V are reported the results obtained for the crosslink distribution of VEB and E340.

Both the untreated and treated samples had a high percentage of C—S—C bonds. The starting EPDM had 4.4 wt % ethylene–norbornene; this corresponded to 0.0367 mol of unsaturations for 100 g of EPDM and 0.025 mol of unsaturations in 100 g of EB. Because the measured density of EB was equal to 986.4 kg/m³, in EB, there were 246 mol of unsaturations/m³. Moreover, the starting amount of sulfur (2 phr) was equivalent to 0.0625 mol of sulfur in 100 g of EPDM; thus, in the starting formulation, there was a ratio of sulfur atoms to double bonds of 1.7. The total amount of 56.63 mol/m³ sulfidic bonds in VEB corresponded to a maximum saturation of about 23% of the initially available double bonds, so a high content of unsaturation was still available in the cured rubber.

By comparing the data of VEB and sample E340b, we observed that a partial devulcanization occurred in the latter. As expected, the S_1 bonds were more stable than the S_2 and S_x ones. The percentage of sulfidic bonds measured in E340b was only slightly lower than that of VEB; however, E340b was the sample less damaged by MW, and the measurements were done on the peripheral part of the reactor, that is, the part that underwent the lower thermal treatment.

Mechanical characterization

Dynamical mechanical tensile tests were performed on the VEB*, MW50, and NT50 samples (see Table II). To check the reproducibility of the analyses, a high number of specimens were tested. E' and the loss tangent (tan $\delta = E''/E'$) of E^* at 10 Hz are reported in Figure 3 as a function of temperature. VEB* showed a principal relaxation with a corresponding tan δ peak at temperature $T_{peak} = -20$°C, and an additional broad shoulder, maybe a secondary relaxation, visible in the E' curve around 30°C. The trends of the MW and not treated (NT) samples were quite similar, and only small differences from

TABLE IV
Total Sulfur Content Analysis on the Microwave-Treated
Rubbers as from Table III

Sample	S_{tt} (wt %)	S_{tw} (wt %)	S removed after the thermal treatment (%)	S removed after the treatment plus washing (%)
E320b	1.045	0.863	23.2	36.5
E340b	0.683	0.635	49.8	53.3
E380b	0.668	0.625	50.9	54.0

A b at the end of the sample name indicates a specimen taken from the boundaries.

the reference sample could be appreciated. Well above the glass-transition temperature, the MW samples had a flattening of the tan δ curve toward values that were always higher than both NT and VEB*; this was followed by a tendency to increase at the highest measured temperatures. This indicated that with respect to the other two samples, MW had a broader distribution of relaxation times, which could be ascribed to the presence, in the recycled part, of low-molecular-weight compounds and macromolecules with a variety of molecular weights and degrees of freedom generated during the thermal treatment and due to partial devulcanization and polymer degradation. By considering the values of T_{peak}, we determined that the glass-transition temperature was almost the same for the samples VEB* and MW50, whereas it was a little higher for NT50. Moreover, we observed that samples prepared with different percentages of NT (not reported here) showed values of T_{peak} that slightly increased with the amount of loaded NT. Because a high content of unsaturation was still available in the cured rubber, such an effect could have been due to an increase in the vulcanization degree of the cryomilled VEB, which was used as recycling component in the NT samples when it was allowed to react with the vulcanization kit of the mixed EB component. With regard to E', in the whole temperature range, the MW sample showed a modulus higher than VEB* and NT; these values, in turn, were very similar to one other. This was probably an indication that the

MW compound developed a good interfacial adhesion between the virgin and recycled material and also that the latter should have gained a quite good revulcanization capability.

The strain sweep and stress–strain tests (Figs. 4 and 5) conducted at room temperature were very effective for helping us determine the differences between the samples. In fact, they provided information of the mechanical behavior at large deformations, which was where both the response of the filler and the characteristics of the interfacial adhesion between the matrix and filler were more involved. The strain sweep response of MW50 showed the highest values of E' and tan δ. This indicated that a vulcanization process occurred in the whole material (both matrix and recycled filler); thus, a material was produced with a modulus higher than VEB*, thanks also to the higher initial content of VS. It is useful to recall, at this point, that after cryomilling, both the MW and NT rubbers were mixed with virgin EB, either with or without further addition of VS. In the case of NT rubber, it was reasonable to assume that VS remained dispersed mainly in the virgin EB rubber and at the interface with the (untreated) recycled rubber. Instead, in the case of MW rubber, during the mixing, VS probably could have found a place in both the virgin and MW recycled rubber and at their boundaries as well. At the same time, part of the low-molecular-weight compounds generated in the treated rubber during devulcanization might have
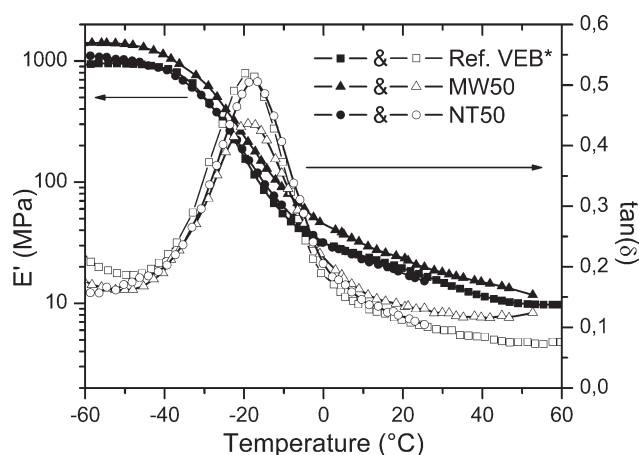

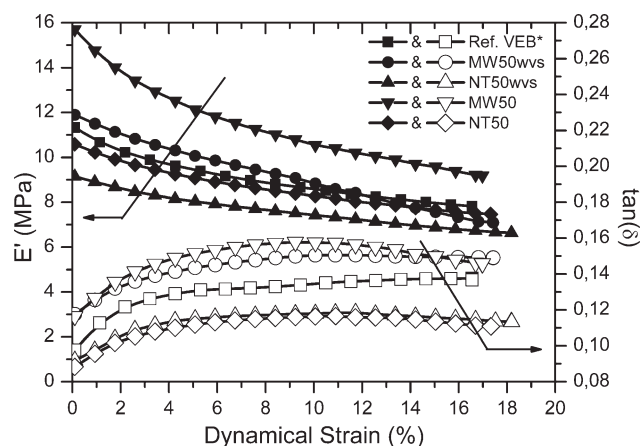**Figure 3** Temperature sweep test for VEB*, MW50, and NT50.

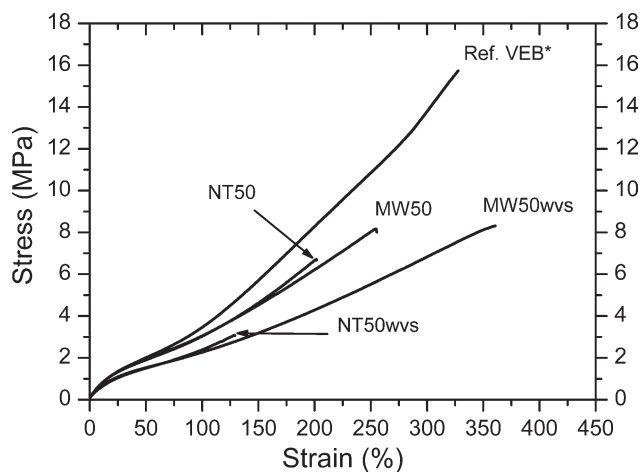**Figure 4** Strain sweep test at room temperature.

Figure 5 Stress–strain test at room temperature.

migrated in the EB matrix, where they could have acted as a plasticizer. In effect, the values of tan δ for MW50 indicated that there was a significant viscous component, which came from the aforementioned low-molecular-weight compounds. However, at high deformations, where the interchain bonds were directly involved, tan δ was found to diminish toward values closer to VEB*; this again indicated that the network connectivity was effective throughout the whole material.

MW50wvs showed a behavior qualitatively different from all of the other samples which was confirmed by the analysis of a large number of specimens and could not be considered an artifact. Its elastic modulus started at values close to those of VEB* and then, at high strains, tended to fall down faster than those of the other samples, thus crossing the curves of both VEB* and NT50. Because, in this case, there was no further addition of VS, which, therefore, came only from EB, the resulting polymeric network had a lower crosslink density through both the recycled filler and the matrix and also quite a scarce number of bridges at its interface. In fact, in comparison with MW50, MW50wvs showed poor properties at high strains, as if this time, the treated compound was acting as a nonreinforcing filler.

In NT50, the elastic modulus was similar to that of VEB*, whereas tan δ was lower (and, therefore, also $E''_{NT50} < E''_{VEB*}$); this was a behavior that could be reasonably expected in a rubber loaded with another rubber of similar properties but where the filler was not efficiently bonded with the matrix. NT50wvs had a trend similar to NT50, but in this case, the lower content of VS led to a lower crosslink density in the matrix and, thus, to a decay in the E' value, with tan δ almost identical to that of NT50.

We analyzed the behavior at the highest deformations by considering the stress–strain tensile char-

acteristics of Figure 5. In this case, VEB* responded with the highest stresses (at comparable deformations), followed by the two samples added with both recycled rubber and VS, whereas the lowest stress values were found in the samples without further content of VS. In both cases (MW50 cf. NT50 and MW50wvs cf. NT50wvs), the behavior of samples with recycled filler was very similar, at least until a strain level where each curve of NT samples became slightly higher than the corresponding MW and then suffered breakdown. Notably, the MW samples always showed a higher deformation at break than the corresponding NT samples. In other terms, at the lowest deformations, the matrix of the MW and NT samples behaved in a similar way, with a small observed difference because of the presence of the low-molecular-weight plasticizing molecules present in MW, whereas the higher elongation at break of the MW samples was ascribed to a better matrix–filler interfacial adhesion. In the MW50 samples, the filler ended up revulcanized to an extent that contributed in to the buildup of the specimen resistance at very high elongations, whereas in the MW50wvs, the filler acted both as a plasticizer and as a nonreinforcing material included in the matrix; this allowed a final elongation comparable with that of VEB*. On the contrary, the lower performance exhibited by the NT50wvs samples was due to both a smaller crosslinks concentration and worse interfacial adhesion.

CONCLUSIONS

Thermal treatments carried out by MWs were shown to be capable of inducing partial degradation and devulcanization of EPDM rubber loaded with CB. MWs can be applied easily and have many advantages, such as a very high heating rate, which allows a reduction in the total time to a few minutes of lightening without any need for additional mechanical or chemical treatments. On the other hand, at least on a laboratory scale, the main problems in the use of a MW oven are related to the difficulties of (1) having a homogeneous temperature profile in the reactor and (2) the design of an affordable temperature record and control system.

Effective devulcanization phenomena seemed to start only at temperatures above 300°C, and the measurements of sulfur content and of the crosslinks distribution in the untreated and treated rubber showed that they were significantly affected by the treatment, with the S_x bonds those that were less stable. The presence of residual unsaturations and a highly reduced gel content made the treated rubber capable of revulcanization. Therefore, the material recovered from the oven was cryomilled and then mixed with virgin rubber to obtain samples with a partial content of recycled rubber. Samples

containing a 50/50 w/w virgin/recycled were subjected to revulcanization and characterized from the mechanical point of view. As a reference material, a rubber containing a corresponding quantity of cryomilled untreated rubber was used.

When subjected to very small amplitude oscillation, the virgin, recycled, and reference materials behaved quite similarly, with the behavior of the MW samples probably characterized by higher chain mobility and wider stress relaxation spectra compared with the other two materials. Other mechanical tests involving large deformations, either sinusoidal or not, were performed and showed significant differences between the various kinds of samples. When the collected data were compared, it seemed that given the appropriate operating conditions and chemical agents, a partial revulcanization of the MW-treated material took place, and at the same time, the formation of chemical bonds led to a high interfacial adhesion between the virgin matrix and the recycled material.

In conclusion, this preliminary investigation gave indications that thermal treatment induced by MWs can be a promising method for the recycling of vulcanized rubbers. Further investigations are needed to optimize the starting formulation for the EPDM rubber and the quantity of material that can be recycled.

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