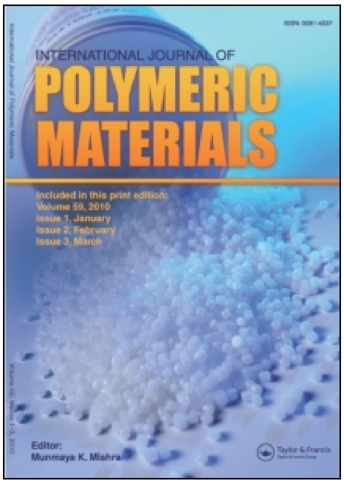

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Regeneration of Vulcanized Compounds Based on Butadiene-Styrene Copolymer

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To cite this Article Neto, José R. A. , Visconte, Leila L. Y. , Tavares, Maria I. B. , Pacheco, Elen B. A. V. and Furtado, Cristina R. G.(2007) 'Regeneration of Vulcanized Compounds Based on Butadiene-Styrene Copolymer', International Journal of Polymeric Materials, 56: 6, 565 — 578

To link to this Article: DOI: 10.1080/00914030600972774

URL: http://dx.doi.org/10.1080/00914030600972774

International Journal of Polymeric Materials, 56:565–578, 2007
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ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600972774

Regeneration of Vulcanized Compounds Based on Butadiene-Styrene Copolymer

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A chemomechanical regeneration system was used for the recycling of SBR-based (butadiene-styrene copolymer) elastomer waste. The effect of the addition of mixtures of TBBS (N-tert-butyl-2-benzothiazole sulphenamide), stearic acid, zinc oxide, and sulfur on the rheometric, mechanical, and swelling properties of SBR-based elastomers was evaluated. These mixtures were utilized as a regeneration agent for vulcanizated rubber, at room temperature. The incorporation of the regeneration agent into elastomers waste was performed in a open mill. This agent regeneration also acts as a vulcanization agent at high temperatures. The results showed that after regeneration, the waste was still capable of being revulcanized without the necessity of incorporating any other additive or another virgin elastomeric matrix. The mechanical properties showed satisfactory values for the revulcanized regenerated waste, despite the low plasticity of these materials before recuring.

Keywords: elastomers, recycling, regeneration, waste

Received 28 July 2006; in final form 14 August 2006.

The authors thank Petroflex Indústria e Comércio S/A, Bann Química, Intercuf ltda, Flexys Ltda, for supplying the raw materials, Tratamento de Resíduos Industriais de Belford Roxo (Tribel S/A) and Koleta Ambiental S/A, for the disposal of the generated wastes at IMA-UFRJ, and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support.

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INTRODUCTION

One of the biggest challenges to be faced nowadays is the destination of vulcanized elastomer-based materials [1]. The wastes of these materials are generated during the entire manufacturing process and after their post-consuption [2].

In order to be useful, elastomers must undergo a vulcanization process, which leads to the formation of crosslinks network linking the macromolecules through covalent bonds. Because of the crosslinks, the vulcanized elastomer can no longer be capable of being reprocessed unless the occurence of an intensive degradation [3].

A simple way of utilizing elastomeric waste consists in its use in the form of finely ground powder as diluent filler in new compositions with the purpose of cost reduction. However, this process leads to a low performance of the final product. This fact has motivated reseachers to reach for regeneration systems that would allow the use of elastomer waste so that the physico-mechanical properties of the new products are preserved [4].

The regeneration processes lead to a break of the chemical links, and preferably, the break of crosslinks such as monosulphidic, disulphidic, and polysulphidic ones. Regeneration can occur by mechanical, thermal, chemical, or biological process, and permits the elastomeric waste to have revulcanization capability [1,4].

Several regeneration systems have been reported in the literature [1,4–5] and the mechanical-chemical processes is one of them. In these regeneration systems, chemical compounds act in addition to shear force, produced by conventional mixers such as roll mills and extruders generally used for processing.

The regeneration agents constitute, in some cases, of a mixture of accelerators, activators and curing agents, which are able to plasticize the vulcanized elastomeric mass at temperatures below 80°C and revulcanize them at temperatures higher than 140°C [6]. However, regenerated waste normally presents serious problems related to scorch time [7]. Thus, the utilization of accelerators that provide major security (a longer scorch time) during the reprocessing of regenerated elastomeric waste, is fundamental to reduce the effects of undesirable low scorch time.

The compounds classified as sulphenamides belong to one of the groups of accelerators known to be able to retard the scorch time. Nowadays, these compounds are considered the most important class of accelerators as they present important characteristics such as high curing speed, safety in the processing, and high solubility in rubber [8]. Particularly, among the sulphenamides, the N-tert-butyl-2-benzothiazole sulfenamide

(TBBS) presents good performance in relation to the safety in the processing of rubber. In addition, when used in content, equal to another accelerator of its group, TBBS provides the highest maximum torque values of the elastomeric compounds [9].

Nuclear Magnetic Resonance (NMR) is one the most powerful among the various methods for characterization of elastomeric systems [10]. The analysis of NMR comprises several techniques and the spin-network relaxation measurement has been found as a potential tool for the evaluation of domains, homogeneity, and phases dispersion [11].

The objective of the present research is the evaluation of the effect of TBBS as a regeneration agent, along with stearic acid, zinc oxide, and sulfur for SBR-based vulcanized waste. Molecular mobility, as well as rheometric, mechanical, and swelling properties of vulcanized, regenerated, and revulcanized compositions were investigated. In this work, the NMR technique was utilized through spin-network relaxation measurement as a potential tool to evaluate the regeneration system for SBR-based vulcanized compounds.

EXPERIMENTAL

A SBR-based standard composition was prepared in a Berstoff mixer, 10 × 22 cm, with cylinders speed ratio of 1:1.25, as shown in Table 1. The elastomers were supplied by Petrofex Industria e Comércio S/A; MBT (2-mercaptobenzothiazole) and TMTD (tetramethylthiuram disulphide) were supplied by Bann Química Ltda; sulfur was supplied by Intercuf Ltda; stearic acid and zinc oxide were supplied by Flexys Ltda.

TABLE 1 Formulation of Standard Composition

Constituents	Content (phr)
SBR 1502	50.0
SSBR B30	50.0
Silica	15.0
Calcium carbonate	30.0
Banox S (antioxidant)	1.5
Stearic acid	3.0
Zinc oxide	3.0
MBT[1]	1.2
TMTD[2]	0.6
Sulfur	3.0

[1] MBT: 2-Mercaptobenzothiazole.

[2] TMTD: Tetramethyl thiuram disulfide.

TABLE 2 Composition of Regeneration Agent

Constituents	Content (g)
TBBS	16.0
Stearic acid	2.0
Zinc oxide	2.0
Sulphur	30.0

The standard composition was vulcanized in a Carver Press model C at 160°C and pressure of 0.5 MPa. The vulcanized sheets which were milled in the Berstoff cylinder mixer. These milled vulcanized sheets were used as raw material in this study; they are named vulcanized waste. The milled waste was regenerated by a chemomechanical system, in which 5 phr of the regeneration agent (Table 2) were used in conjunction with the mechanical shear of the mixer at an approximate temperature of 40°C for 10 min. The regenerated waste was revulcanized by compression molding in a Carver Press model C at 160°C and pressure of 0.5 MPa, leading to the revulcanized regenerated waste.

The molecular mobilities of the raw, vulcanized, regenerated, and revulcanized samples were determined by solid state T_1H NMR in a low field Maran Ultra 23 MHz at 27°C, using a inversion-recovery pulse sequence, with a range of τ varying from 10 to 1000000 us.

The cure parameters of the virgin and regenerated samples were determined on a TI 100 oscillating disk curemeter at 160°C (ASTM 2084-81).

The tensile properties were determined on an Instron 1101 universal machine, according to ASTM D412-83. For the accelerated aging tests, the samples were conditioned in an air-circulating oven at 70°C for 168 h. The determination of tear strength followed ASTM D 624-86. The hardness tests were performed according to ASTM D 2240-86, whereas the abrasion resistance was determined in an abrasionmeter (DIN 53516).

The vulcanization and revulcanization reactions of the raw virgin and non-revulcanized regenerated waste, respectively, were monitored by differential scanning calorimetry performed on a DSC-7 Perkin Elmer calorimeter under nitrogen atmosphere and heating rate of 5°C/min.

For the determination of crosslink density, samples of 0.5 g were placed in 50 ml of heptane for 24 h at 23°C. After this period, the samples were taken from the solvent, roughly dried with a filter paper, and immediately weighed in an analytical balance. The samples were then dried in an air circulating oven, at 70°C, until they reach constant weight.

The interaction parameter (χ) was determined following the procedures established by Hayes [12], with heptane and hexane as solvents. The value of χ_{heptane} determined at of 23°C in a concentration of 0.01 g/ml of elastomer in solvent was 0.554.

The crosslink density was determined in heptane using the Flory-Rehner Equation [12]:

$$-[\ln(1 - v_r) + v_r + \chi v_r^2] = \upsilon V_s \left(\frac{v_r^{1/3} - 2v_r}{f} \right) \tag{1}$$

where v_r is the volume fraction of rubber in the swollen network, υ is the number of moles of the sulfur crosslink per unit volume of the rubber, V_s is the molar volume of the solvent. The functionality of crosslinks (f) was assumed as four [12].

The v_r was then calculated by Eq. (2) [13]:

$$v_r = \frac{[(d - \Phi\, w)\, \rho_r^{-1}]}{[(d - \Phi\, w)\, \rho_r^{-1} + A_s\, \rho_s^{-1}]} \tag{2}$$

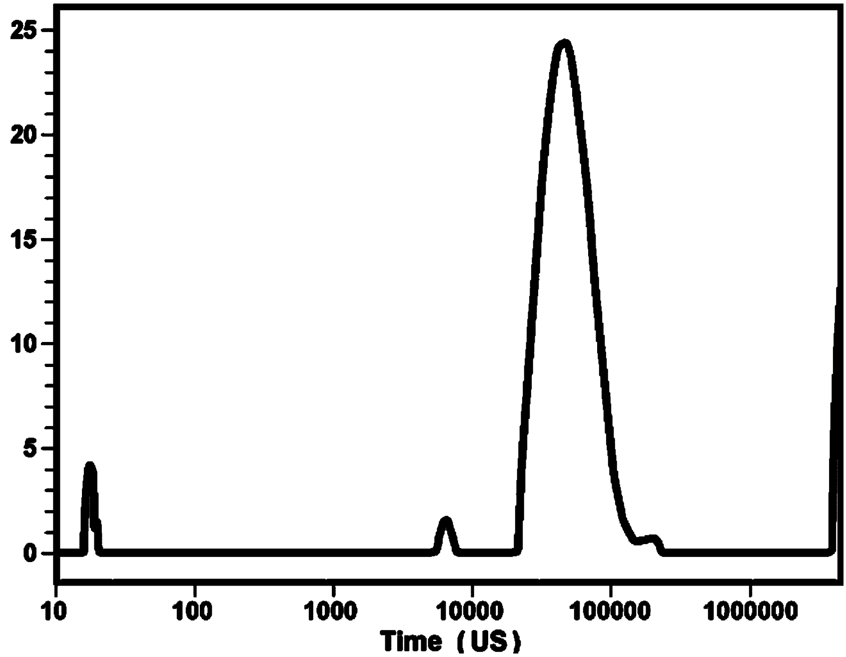

FIGURE 1 Raw standard composition specimen domains profile of times of relaxation.

where d is the deswelled test specimen, Φ is the volume fraction of the filler (fraction of the insoluble components), w is the sample initial weight, ρ_r and ρ_s are, respectively, the polymer and solvent densities and A_s is the weight of the absorbed solvent.

The number-average molecular weight of the chain segments between crosslinks in the network (Mc) was determined by Eq. (3) [14]:

$$\mathrm{Mc} = \frac{-\rho_r V_s v_r^{1/3}}{\ln(1 - v_r) + v_r + \chi v_r^2} \tag{3}$$

The swelling index, which measures the resistance of the elastomeric compound to swelling, was determined by Eq. (4) [13]:

$$\text{Swelling index } (\%) = \left(\frac{\mathrm{As}}{\mathrm{W}}\right) \times 100 \tag{4}$$

RESULTS AND DISCUSSION

Figures 1–4 show the profile of the relaxation time (T_1H) domains for the following samples: raw standard composition, vulcanized standard

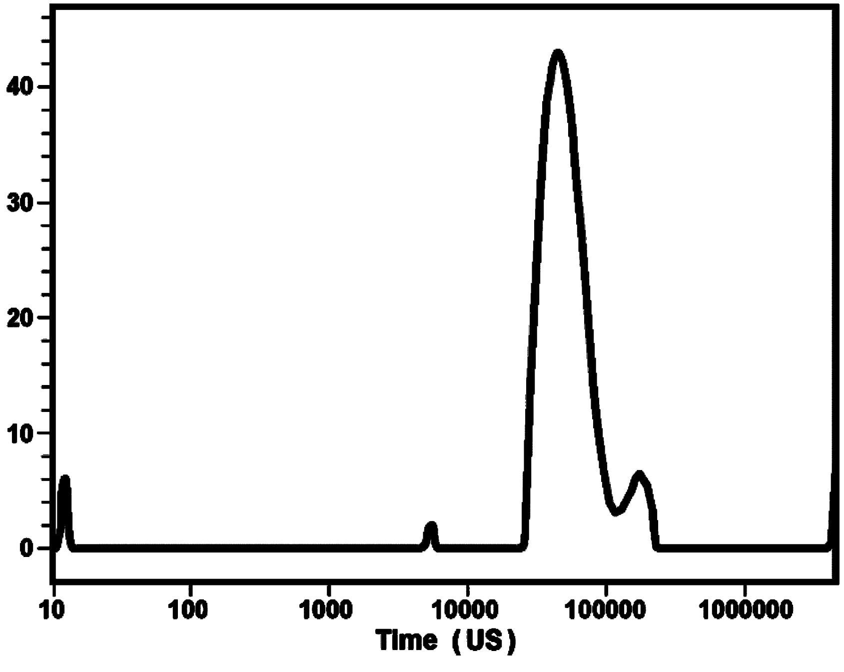

FIGURE 2 Vulcanized standard composition specimen domains profile of times of relaxation.

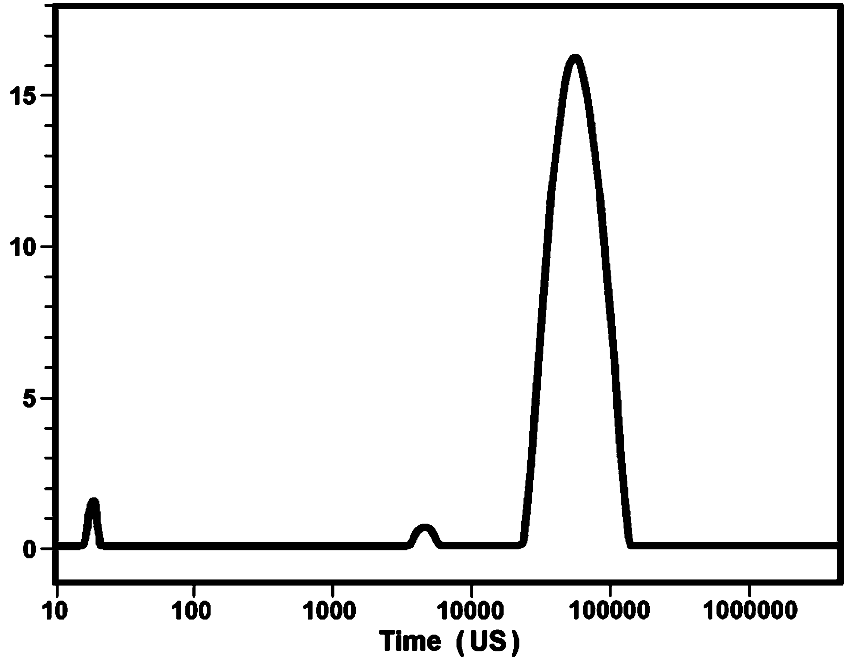

FIGURE 3 Non-revulcanized regenerated waste specimen domains profile of times of relaxation.

composition, non-revulcanized regenerated waste, and revulcanized regenerated waste, respectively. It is possible to observe the existence of three domains: one domain of high flexibility, a semi-stiff domain, and a stiff domain. It can also be observed that the stiff domain controls spin-network relaxation in all samples. The intensities of the peaks, which are found to be related to the domains, show that the samples are heterogeneous, although presenting good dispersion of phases.

Table 3 shows the measurements of spin-network relaxation time for the hydrogen for the raw standard composition, vulcanized standard composition, non-revulcanized regenerated waste and revulcanized regenerated waste. T_1 data presented in Table 3 show that the raw standard composition flexible domain suffer some stiffness after the cure process. At this stage, the value of T_1 in the flexible domain rises from 0.1 (raw standard composition) to 23.9 (vulcanized standard composition). In the following stage, the regeneration of the material occurs and the value of T_1 in the flexible domain falls to 6.4 (non-revulcanized regenerated waste). There was, therefore, an increase in the molecular mobility of non-revulcanized regenerated waste in

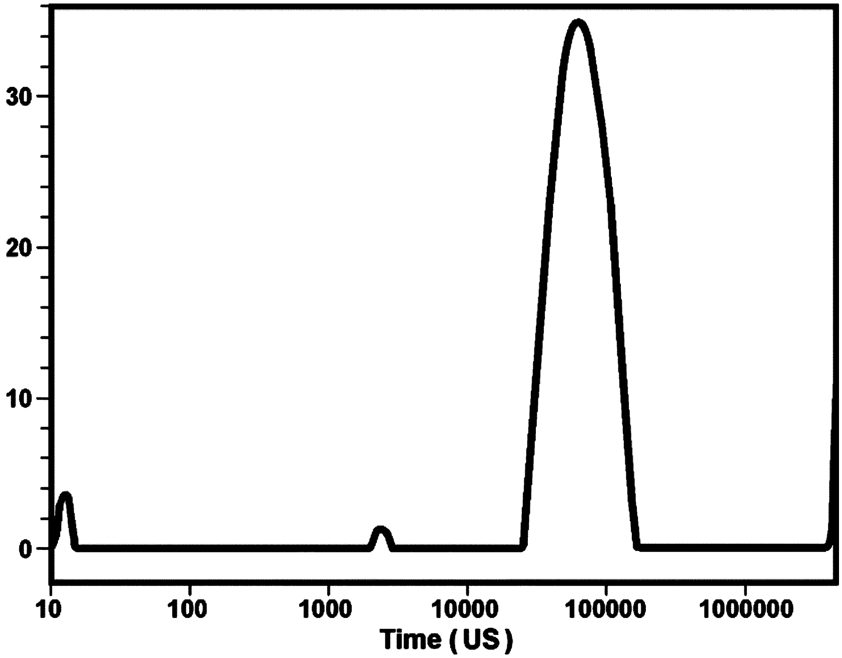

FIGURE 4 Revulcanized regenerated waste specimen domains profile of times of relaxation.

relation to vulcanized standard composition, which is an evidence that regeneration does occur in the vulcanized elastomer. However, T_1 for the non-revulcanized regenerated composition is much higher than T_1 for raw standard composition in the flexible domain, suggesting that molecular mobility is considerably bigger in the raw standard

TABLE 3 Times of Relaxation for All Specimens

Samples	High flexibility domain [T_1 (ms)]	Semi-stiff domain [T_1 (ms)]	Stiff domain [T_1 (ms)]
Raw standard composition	0.1	42.4	114.8
Vulcanized standard composition	23.9	55.3	170.6
Non-revulcanized regenerated waste samples	6.4	55.0	154.8
Revulcanized regenerated waste	25.9	60.9	102.4

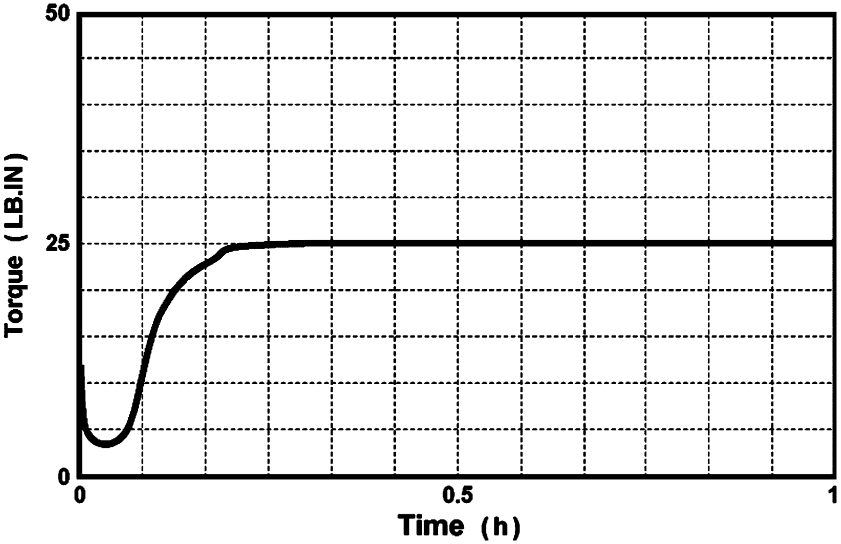

FIGURE 5 Oscillating disk curemeter curve for raw standard composition samples.

composition. In summary, it is observed that revulcanized regenerated sample presented the highest value of T_1 in the flexible domain, which means that this material possesses the most restricted molecular mobility.

Figures 5 and 6 show the cure curves of raw standard composition and non-revulcanized regenerated samples, respectively. The cure parameters are presented in Table 4. The cure index (CI) was calculated from Eq. (5) [15]:

$$CI = \frac{100}{t90 - ts2} \qquad (5)$$

where t90 stands for the optimum cure time and ts2 is the scorch time.

The higher value of maximum torque presented by the regenerated sample, vulcanized *in situ* while running the test (revulcanized regenerated waste), suggests that the crosslink density for the revulcanized regenerated sample is superior to that for the vulcanized standard compound. The minimum torque is also higher in the regenerated sample, which is an evidence that part of the crosslinks originally formed remained unbroken during the regeneration process. The scorch time and optimum cure time for the regenerated sample underwent a significant decrease and the cure rate was found to be 7.3 times faster.

Table 5 shows the results of mechanical properties for vulcanized standard composition, non-revulcanized regenerated waste and

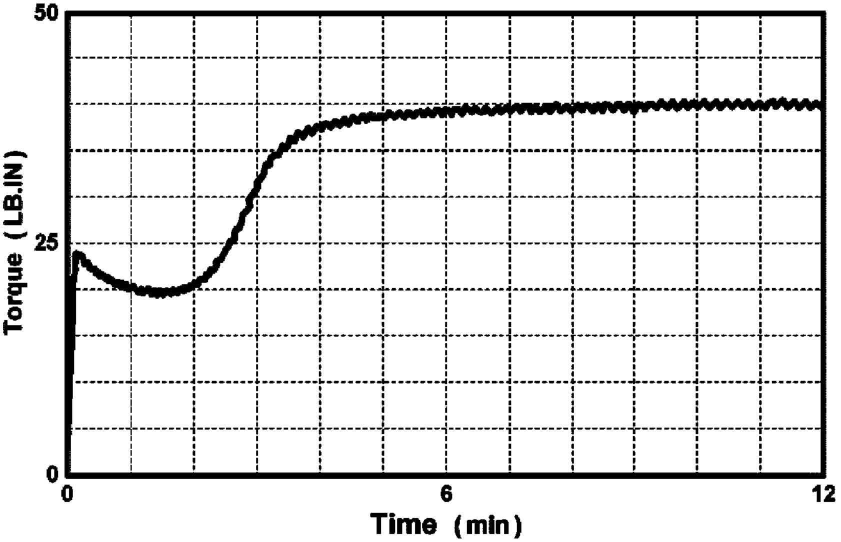

FIGURE 6 Oscillating disk curemeter curve for non-revulcanized regenerated waste samples.

revulcanized regenerated samples. It can be observed that the tensile strength of revulcanized regenerated waste and vulcanized standard samples were approximately the same. However, the elongation at break for revulcanized regenerated waste decreased from 350% to 150% when compared to the vulcanized standard composition. It can also be observed that a drastic decrease has also occurred in the tear strength while abrasion loss increased for revulcanized regenerated waste in comparison to vulcanized standard composition. The aged samples showed a small decrease in both tensile strenght and elongation at break, for the two samples.

TABLE 4 Cure Characteristics of Raw Standard Composition and Non-Revulcanized Regenerated Waste Samples

Parameters	Raw standard composition	Non-revulcanized regenerated waste samples
Torque maximum (lb.in)	26.9	42.6
Torque minimum (lb.in)	3.3	19.5
ts2 (min)	5.4	2.4
t90 (min)	13.0	4.4
Cure index (s^{-1})	0.219	0.833

TABLE 5 Results of Mechanical Properties of Specimens

Properties \ Samples	Vulcanized standard composition	Revulcanized regenerated waste	Non-revulcanized regenerated waste samples
Tensile strength (MPa)	7.0	7.6	—
Elongation at break (%)	350.0	150.0	—
Tensile strength of aged samples (MPa)	6.0	6.1	—
Elongation at break of aged samples (%)	250.0	100.0	—
Tear strength (kN/m)	32.0	16.0	—
Volume loss (mm^3)	260.0	460.0	—
Hardness (Shore A)	67.0	71.0	26.0

In general, there was some loss in mechanical properties of revulcanized regenerated waste in relation to vulcanized standard composition, suggesting that the combined action of mechanical shear for grinding and the incoporation of the regeneration agent resulted in a degradation process of the regenerated waste. Another factor that may have influenced this degradation can be related to the submission of the regenerated waste to a new cycle of pressing and heating, necessary to revulcanize the material. The significant decrease in hardness of non-revulcanized regenerated waste brings to evidence the degradation of vulcanized standard compositions. These results correspond to NMR ones.

The differential scanning calorimetry analysis on the raw standard composition and non-revulcanized regenerated waste samples revealed the existence of two exothermic peaks, shown in Figure 7(A) and 7(B), respectively, which reflect the global sum of the reactions of cure in each sample. The variation of enthalpy of vulcanization was of -53.36 J/g for the sample raw standard composition and -68.77 J/g for the non-revulcanized regenerated waste, which led to the formation of a major quantity of crosslinks in revulcanized regenerated waste. The first exothermic peak came out around 179°C in raw standard composition sample. This peak appears at lower temperature, around 154°C for non-revulcanized regenerated waste. A secondary transition can also be in non-revulcanized regenerated waste, possibly due to a rearrangement of sulfur crystalline structures [16]. The second peak, due to cure of the two samples, was observed at about 200°C.

In the regenerated samples, revulcanization probably occurs faster and at lower temperatures, due to the existence of accelerator residues still remaining from the first cycle of cure.

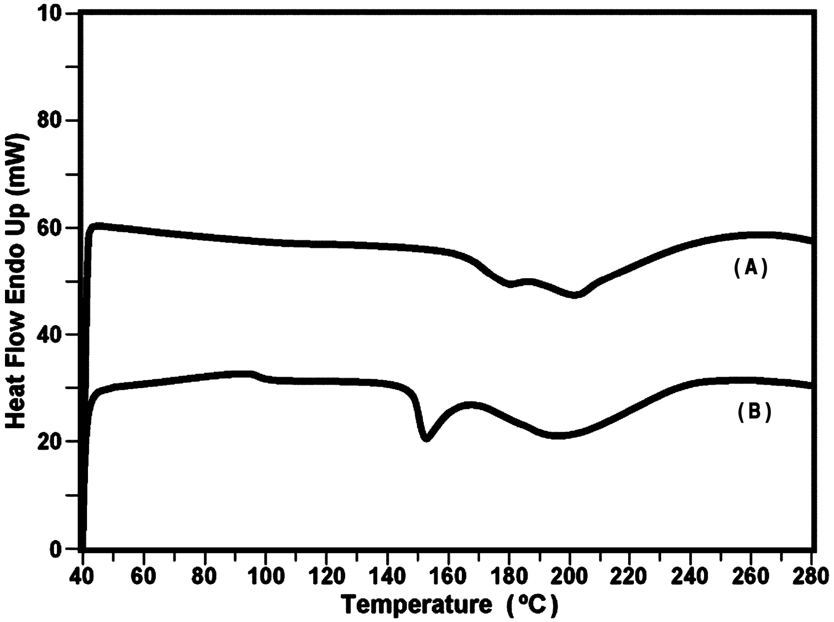

FIGURE 7 Differential scanning calorimeter curves for raw standard composition (A) and non-revulcanized regenerated waste (B) samples.

The swelling parameters for vulcanized standard compositions, non-revulcanized regenerated waste, and regenerated revulcanized samples are shown in Table 6. According to these results, it is observed that non-vulcanized regenerated samples presented a higher swelling index, which results from a reduction in the crosslink density of the vulcanized standard composition. These results corroborate the results of minimum torque and stiffness, giving evidence of crosslinks break and the increased solvent absorption. The revulcanized regenerated samples presented the lowest swelling index among all tested samples, that is, it absorbed the least quantity of solvent. The crosslinks density for revulcanized regenerated samples increased 515% relative to vulcanized standard composition samples. The excessive number of crosslinks formed in samples submitted to revulcanization may have also contributed to a decrease in the tear strength and elongation at break observed in these compositions.

The Mc values increased considerably in non-revulcanized regenerated samples. This means that the number of repeating unit of elastomer between crosslinks also increased considerably in such a way that the number of double bonds between crosslinks available for a new attack by the cure system at higher temperatures was larger in

TABLE 6 Swelling Parameters of Specimens

Parameters	Vulcanized standard composition	Non-revulcanized regenerated waste samples	Revulcanized regenerated waste
Swelling index (%)	76.0	108.0	38.0
v_r	0.3249	0.2715	0.4863
Mc (g/mol)	17,157.0	31,909.0	3,744.0
$\upsilon \times 10^4$ (mol/cm^3)	1.1557	0.5327	5.9588

non-revulcanized regenerated samples. This fact may have helped the recuring of the material.

The effect of reduction in crosslink density on the increase in plasticity of non-revulcanized regenerated composition was discreet, as observed in comparison with the minimum torques of raw standard composition. This fact can be attributed to the remaining crosslinks from the first vulcanization process.

CONCLUSION

A vulcanized elastomeric compound can be regenerated in a two-roll mixing mill, in the presence of a regeneration system such as a mixture of TBBS, stearic acid, zinc oxide, and sulfur. The waste milled in the two-roll mixer was converted into a regenerated sheet after the incorporation of the regeneration agent at low temperature and were revulcanized with no need of additional additives or virgin elastomeric matrix. The NMR analysis showed that the samples increased in stiffness in the following order: raw standard composition < non-revulcanized regenerated waste < vulcanized standard composition < revulcanized regenerated waste. The rheometric properties showed a low plasticity of the regenerated waste, as suggested by the high values of minimum torque, as well as by the swelling values, from which a reduction of about 50% of the crosslinks after the regeneration process has been observed. These results were a strong evidence that the remaining crosslinks endow the regenerated waste with a reduced plasticity although not enough to prevent the material from being reprocessed without the addition of raw elastomers. The mechanical properties were considered satisfactory.

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