

Characterization of Ground SBR Scraps from Shoe Industry

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Expanded poly(butadiene-co-styrene) (SBR), a residue of the shoe industry of Rio Grande do Sul, is a crosslinked material. For further utilization in recycling and reclaiming processes this residue was ground under ambient conditions. The obtained powder (SBR-r) was physically, thermally and chemically characterized and the results were analyzed as for its suitability for reuse methods. This characterization provides a better understanding of the SBR residue components, which may lead to economic and environmental advantages. The SBR-r (35-48 mesh) is composed by 22.2% of SBR and 77.8% of filler. The elastomeric fraction has 71.4% of crosslinked material. The results demonstrate that SBR can be recycled for use in microcellular composites.

Keywords: *SBR residue, grinding, characterization*

1. Introduction

The recycling of residues in the form of materials for different applications has provided an alternative solution for several problems related to environmental issues, both in terms of the reduction in the volume of residues generated and their discharge hazards, and the decrease in the use of increasingly scarce natural resources.

In this context lies the shoe industry in which, with the development of petrochemistry and with the appearance of synthetic materials, alternative raw materials began to be used¹, reflected in an increase in the generation of wastes which are difficult to degrade in the production process and post consumption. According to data from Fundação Estadual de Proteção Ambiental (State Foundation for Environmental Protection), FEPAM, the shoe industry is responsible for 23% of the solid waste generated in the state of Rio Grande do Sul (RS)². Studies carried out in 2001 by Serrano et al.³ showed that the shoe sector in the region of Vale do Rio dos Sinos, RS/ Brazil, generated a quantity of polymeric residues over 180 t.mth⁻¹, poly (butadiene-co-styrene) (SBR) being in the greatest quantity (25.1%).

Of the types of polymeric materials, rubbers or elastomers have their own unique characteristics. They have elasticity, which is the capacity to allow great deformation under low tension and, on removing the tension, return almost immediately to the initial condition, without significant loss of shape and dimensions, in a reversible process⁴. According to statistics from the International Rubber Study Group, the world consumption of natural and synthetic rubber in 2005 was 20.7 million tonnes⁵. With technological progress in the recycling area, rubber residues are seen as a valuable raw material for other applications, such as: strengthening/filling materials; incorporation into asphalt; flooring for leisure and recreation areas; among others.

The nature of rubber residues generates great environmental problems, since its natural degradation occurs over long time periods due to the presence of cross-linking in its structure and of stabilizers and other additives. The solution to minimize this problem is the recycling and recovery in new materials⁶⁻⁸.

Landfills were the first means of disposal of rubber residues. This alternative is expensive since it involves a high cost of transport of material to the site and the maintenance of the landfill under adequate

conditions. It must also be considered that during the decomposition of rubber, many of the additives decompose quickly and migrate to the surface of the landfill, causing serious environmental problems⁹.

According to Adhikari et al.⁹ in general, low quantities of residues can be added to virgin rubber without significant changes in its properties occurring. In some cases the filler can act as a support material improving the properties, depending on the type of residue and the process used⁹⁻¹².

The residues used in this study are expanded SBR chips, generated during the operation of cutting insoles, which are not used in the production process. The chips are sent to the Central de Resíduos do Sindicato das Indústrias Calçadistas de Três Coroas, (Waste Center of the Shoe Industry Union of Três Coroas), RS, in duly identified packs.

The objective of this study is the obtention and characterization of SBR-r powder, aiming at a later application in a mixture with virgin SBR, in order to obtain cellular composites.

2. Experimental

2.1. Sample grinding

The SBR was ground in a Seibt AS/30/500 agglutinator (25 kg; time = 5 minutes; rotation = 285 rpm) at room temperature and homogenized by wheel blasting 25 kg of SBR were ground and stored.

2.2. Sample characterization

The powder obtained in the previously described process, SBR-r, was characterized by physical, thermal and chemical methods¹³.

2.3. Physical characterization

The particle size determination was carried out according to the norm ASTM D 5644-96, using a Produtest sieve and a set of sieves normalized by the Brazilian Association of Technical Norms (Associação Brasileira de Normas Técnicas - ABNT) by means of EB-22.

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The scanning electron microscopy (SEM) was carried out with a Philips XL 30 scanning electron microscope. The sample was metallized in a P-S2 DIODE Sputtering System metallizer. The qualitative analysis of the fillers was carried out in an energy-dispersive spectrometer (EDS) coupling at SEM.

2.4. Thermal characterization

The thermal degradation was carried out by thermogravimetric analysis (TGA) in a Shimadzu TGA-50, with a nitrogen flow of 50 mL/min, from ambient temperature up to 800 °C, with a heating rate of 10 °C/min. The differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-50, under a nitrogen flow, from -100 °C up to 250 °C, with heating rate of 10 °C/min.

2.5. Chemical characterization

The determination of gel content was carried out in triplicate, by extraction in Soxhlet with toluene, using 1 g of sample, for 24 hours according to the norm ASTM D 3616-95. The residue was then removed and dried at 60 °C, under vacuum, for approximately 6 hours.

3. Results and Discussion

3.1. Physical characterization

In the granulometric analysis, Table 1, it was verified that the ground residue had an average particle size between 35 and 48 mesh (0.425 and 0.30 mm). According to the literature, the particle size of the rubber powder to be added to virgin rubber must be less than 0.60 mm to achieve a better incorporation¹⁴. Thus, the grinding was effective, producing a powder adequate for incorporation into virgin material.

The micrographs of SBR-r are shown in Figure 1. The micrographs indicate the heterogeneous granulometry of the residue, Figure 1a and 1b, as observed in the granulometric analysis. The presence of fillers in the powder was also verified (Figure 1c), corroborating the TGA analysis. The qualitative analysis of the fillers, indicated the presence of calcium (CaCO_3), silica (SiO_2) and magnesium (talc) $\text{Mg}_3\text{H}_2\text{Si}_4\text{O}_{12}$, which are common in this type of material.

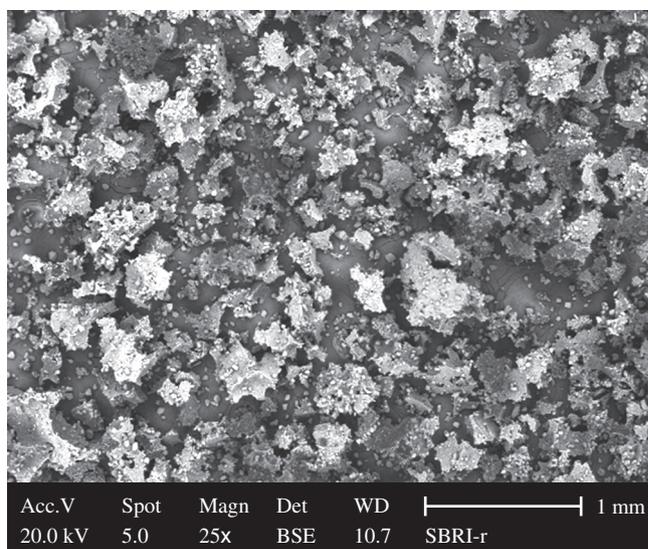
3.2. Thermal characterization

The TGA allowed the identification of sample mass loss as a function of temperature in a controlled atmosphere. The mass loss below 300 °C refers to the presence of volatile agents such as plasticizers and antioxidants. The mass loss between 300 and 600 °C corresponds to the polymeric content. The mass loss between 600 and 950 °C relates to inorganic additives, pigments or metal oxides¹⁴.

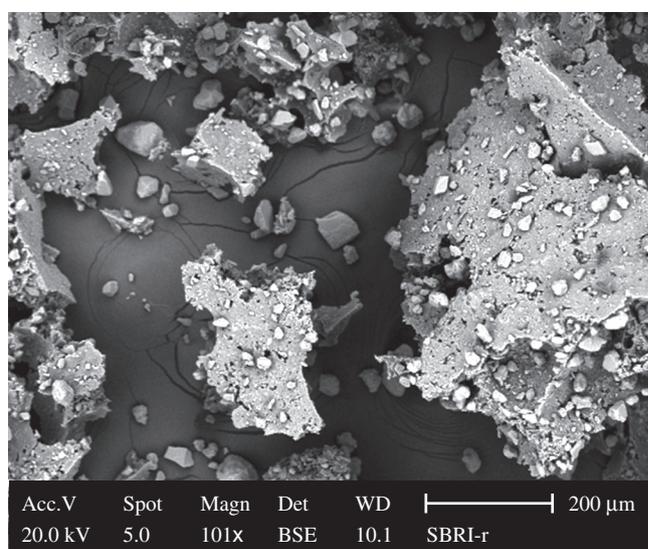
In the TGA of the SBR-r, two mass loss stages were observed (Figure 2). The first loss was of approximately 22.2% in the range of 390 to 445 °C, corresponding to the elastomer. The second loss of

Table 1. Particle size of SBR-r powder.

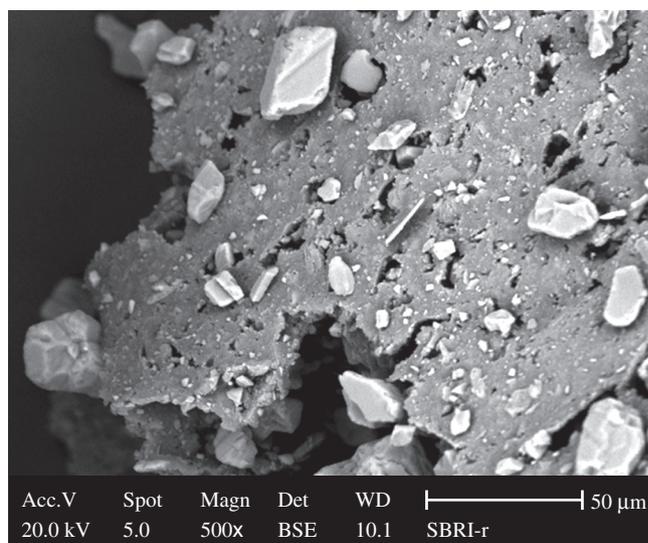
Sieve size		Retained (%)
(mesh)	(mm)	
24	0.71	6.10 ± 0.30
28	0.60	11.4 ± 0.66
35	0.43	34.7 ± 0.40
48	0.30	20.4 ± 0.61
65	0.21	14.2 ± 0.44
100	0.15	6.70 ± 0.46
<100	<0.15	3.30 ± 1.29



(a)



(b)



(c)

Figure 1. Micrographs of the SBR residue a) magnification of 25x; b) magnification of 100x and c) magnification of 500x.

30.1% at 726 °C, corresponds to the loss of CO₂ due to the thermal decomposition of CaCO₃. The residual mass at 800 °C was 47.7%. Thus, the residue has 22.2% of SBR and 77.8% of filler.

In Figure 3, DSC thermograms of SBR-r is shown. The DSC thermogram of SBR-r showed the presence of a T_g (glass transition temperature) of the material at -43.93 °C. The T_g value of SBR-r is very close to the T_g for virgin SBR (-48 °C)⁴. There is no exothermic peak in the region of 200 °C, showing that the amount of residual accelerators and/or sulfur is not sufficient to cause sample vulcanization. The absence of this exothermic peak can also be explained by the natural heating of the samples that occurs during the grinding process. It is possible that during grinding there was further sample vulcanization, since industrial and not post-consumption scraps were utilized.

3.3. Chemical characterization

The gel fraction of the SBR-r was calculated based on Equations 1 and 2¹⁵.

$$\% \text{ extraction of polymeric material} = \frac{\% M_{\text{extracted}}}{100 - \% M_{\text{residual}}} \times 100 \quad (1)$$

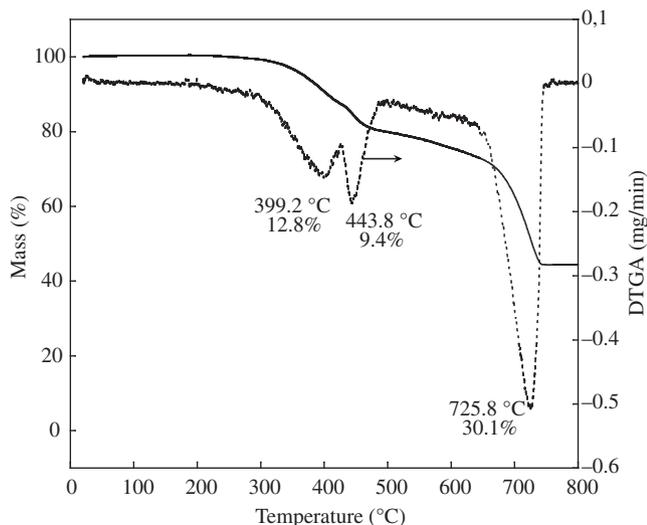


Figure 2. TGA thermogram of SBR-r (N₂ flow of 50 mL/min with a heating rate of 10 °C/min)

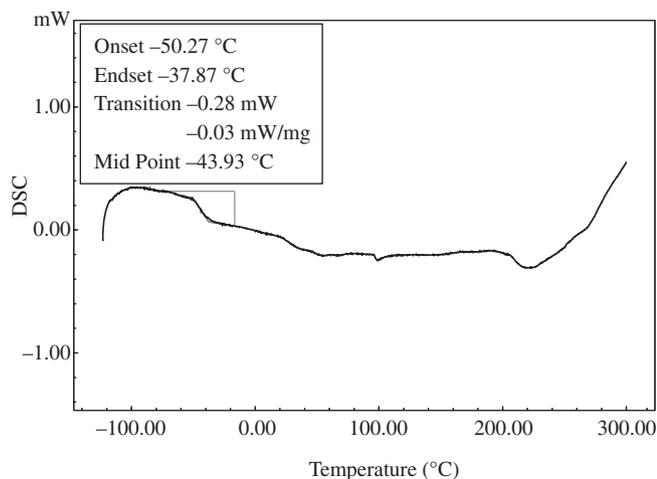


Figure 3. DSC thermogram of SBR-r (N₂ flow of 50 mL/min with a heating rate of 10 °C/min).

$$\text{Gel content} = [100 - (\% \text{ extraction of polymeric material})] \quad (2)$$

where, M_{extracted} is the percentage mass extracted in the gel determination test;

M_{residual} is the residual percentage mass obtained in the TGA analysis.

Thus, the SBR-r had 71.4% of reticulated material and 28.6% of soluble material (relating to the 22.2% of rubber present in SBR-r, determined by TGA).

4. Conclusions

From the results obtained it was possible to verify that the grinding of SBR residue was effective, producing a powder adequate for use in virgin SBR mixtures, with the aim of later application in the obtention of SBR foams.

Through the thermogravimetric analysis it was possible to observe that the residue is composed by 22.2% of SBR and 77.8% of fillers.

On evaluating the SEM micrographs, a heterogeneous granulometry of the residue was verified, with the presence of fillers in the rubber powder.

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