Evaluation of a Strain Sweep Tests Protocol as a Tool for Assessing the Homogeneity of SBR Copolymer Composition

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Abstract: Global competition in products and services demands constant improvement in production systems. Similarly, it is essential for industries to have quality control tools capable of assessing the compliance of a given product at a lower cost and with greater effectiveness. In the rubber and composite industry, where complex formulation and mixing systems can affect not only the quality of the final product but also the processing of rubber, the development of a protocol that assumes this function is important. The present study developed samples of elastomeric blends based on styrene-butadiene copolymer (SBR) with different filler concentrations (30, 60, and 90 phr of ground tire rubber as filler), which were analyzed using an oscillating cavity rheometer (MDpt-TechPro). Based on a proprietary testing protocol, the degree of homogeneity of the composites was evaluated, which was compared with scanning electron microscopy studies. The implemented protocol, which provides results within 30 minutes, proved to be promising for quality control of these blends, and it can be used by rubber processing industries, saving both time and cost, being an unprecedented study on the 'homogeneity-rheology' relationship.

Keywords: Rheology, polymer composites, quality control.

1. INTRODUCTION

To become increasingly competitive in the market, companies invest considerable part of its annual income in R&D. For new materials, this scenario is not very different, especially in polymeric composites industries [1, 2]. The polymer industry must join the high mechanical performance of the material with the needs of the consumer. As an example, there is the possibility of employing ground rubber in compositions based on butadiene-styrene co-polymer (SBR). This is an option to formulate compositions based on reclaiming process. Some applications of these kinds of articles: production of shoes, building floor impermeabilization, construction of pavements, until the development of anti-vibration systems. Thus, it is essential to the availability of tools that can be able to determine effectively and quickly how homogeneous mixtures are obtained, as well as its rheological properties. Many processing operations in the rubber industry occur at high rates of strain rheological, which results are typically in non-linear domain. This reason justifies the development of advanced research rheological tests for elastomeric compositions, such as large amplitude oscillatory strain experiments [3]. Adding solid particles into a matrix polymer changes the rheological properties of the mixture (*viscoelastic behavior*, *the viscosity* and *the elasticity*) [4]. Rheological data are usually used to estimate the behavior of polymeric mixtures under shear which will be submitted in the industry. And they can be used also to evaluate the uniformity of these mixtures. Through rotational rheology is possible to understand the dispersion, structure and interactions between the components in the mixtures [5]. The test itself consists in applying a sinusoidal strain in order to assess the resulting complex stress supported by the material. Concentrated suspensions of particles in a polymeric matrix have been studied so many times [6-9]. In viscoelastic materials, there is out-phasing of the complex stress with respect to the applied strain. Both the measure complex stress and the phase angle give access to the viscoelastic properties of the material, in terms of elastic and viscous muduli [10]. This work shows the results of the sweep strain tests for different samples of butadiene-styrene (SBR) with waste tires, made in a torsional dynamic rheometer (MDpt, TechPro – Division of Dynisco LLC), to investigate complex module responses provided by the equipment.

2. MATERIALS AND METHODS

To carry out experiments, a cylinder mixer (open system) was employed for the preparation of the elastomeric compositions and a rheometer (Moving Die Cavity Oscillatory Processability Tester MDpt – TechPro) was used for rheological research, according to sweep strain protocol. For each composition

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obtained with different values of waste tires, two samples (A and B) were loaded in oscillatory cavity. These samples were submitted at two sweep strain separated steps: the first (run 1), covered the range of 0.5 to 89.9% of strain and the second (run2), the range of 0.7 to 120%, with rest time between the runs of one minute. Once implemented this protocol, the results were exported and treated in Excel spreadsheet for evaluation. Rheological tests were conducted at a frequency of 1.0 Hz and constant temperature of 100°C.

Formulations Development

The elastomeric compositions were obtained based on the ASTM D 3182-87 standard formulation. Ground rubber, approximately 0.5 cm in length, was used as the filler.

Processing of the Formulations

Formulations were processed at a cylinder mixer (open system), according to ASTM 3182-89at 45°C. The standard batch mass (in grams) for the roll mixer was three times the formula mass in parts *per hundred grams* of rubber. All ingredients were measured in analytical weighing machine. The maximum opening between the rolls was 0.25 cm. Before to receiving the other products, the SBR was submitted to "chewing" process. This step consists of pre-processing of the polymer mass until it becomes processable and able to receive the ingredients of the formulation. The chewing process also raises the temperature of the rolls. The mixing process began when the temperature reached 45°C (± 1°C). The mixing cycle was concluded by passing the rolled batch through the mill six times. This allows the improvement of the dispersion. At the end of elastomeric processing, the samples were stored for 24 h before proceeding to the rheological studies.

Sweep Strain Experiments

Circumferential small pieces (3 cm diameter and 0.3 cm thickness) were obtained from the sheets. Before the feeding in rotorless rheometer, the pieces were manually compressed with two nylon sheets (3 cm x 3 cm). The cavity of the rheometer (5 cm³) was filled with a processed sample weighing 6 g. This value was chosen to ensure the cavity was fully filled [3, 9].

The rheological tests were based on strain sweep tests, at 100°C, a strain range of 0.5 to 120% and frequency of 1 Hz. Two samples (A and B) were obtained for the same elastomeric batch. They were inserted into the rheometer chamber at controlled temperature. The Figure **1** ilustrates the sample in the rheometer chamber. Each sample was submitted to increasing strain variations: the first variation between 0.5 and 89% strain (run 1) and the second between 0.7 and 120% (run 2). All samples were submitted under the same oscillation frequency (1 Hz).

The samples (A and B) from the same elastomeric batch were then subjected to the strain intervals (run 1 and run 2). Each sample was preconditioned for a period of 2 minutes at 100°C, 0.2% strain and 0 Hz before the test itself.

This protocol, as shown in Table **1**, contributed to obtaining information about the homogeneity of the

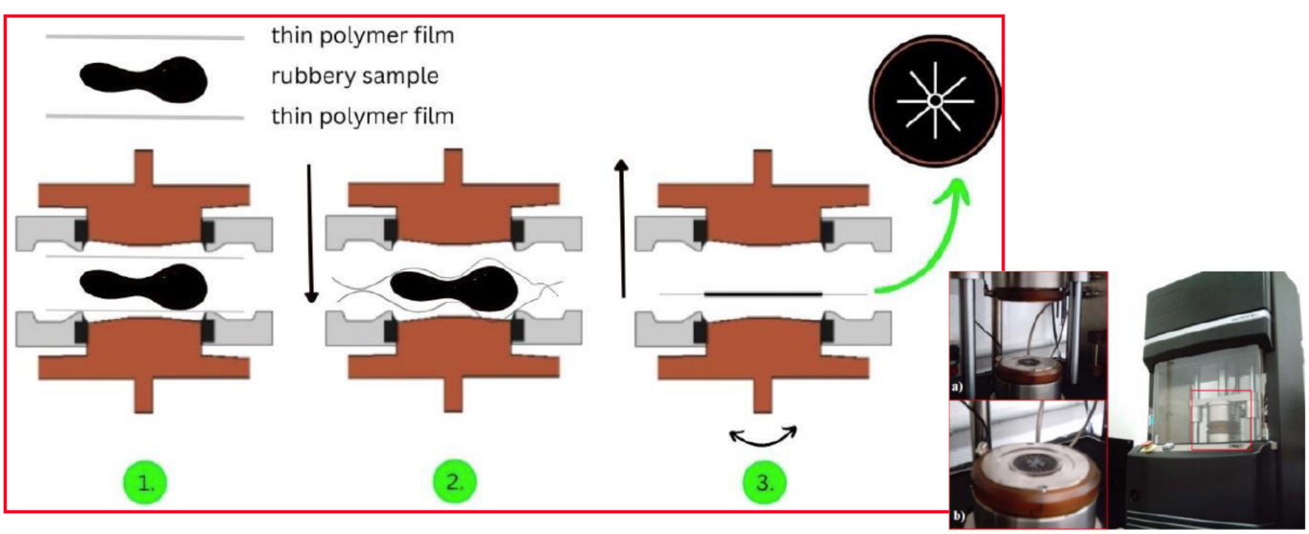

Figure 1: Samples in the rheometer test chamber: 1) sample wrapped in polyester film; 2) vertical displacement of the upper plateau; 3) sample already pressed and analyzed.

Table 1: Strain Sweep Protocol

SSweep_100C_1Hz_A			SSweep_100C_1Hz_B		
Test conditions: 100°C / 1 Hz			**Test conditions:** 100°C / 1Hz		
Pre-processing of the sample: Heating: 2 minutes /0 Hz / 0.20 %			**Pre-processing of the sample:** Heating: 2 minutes /0 Hz / 0.20 %		
SS (run 1) Strain %	**Resting time**	**SS (run 2) Strain %**	**SS (run 1) Strain %**	**Resting time**	**SS (run 2) Strain %**
0.5	1 minute	0.7	0.7	1 minute	0.5
0.9		1.2	1.2		0.9
1.6		2.1	2.1		1.6
2.8		3.8	3.8		2.8
5.0		6.7	6.7		5.0
9.0		11.9	11.9		9.0
15.9		21.3	21.3		15.9
28.4		37.9	37.9		28.4
50.5		67.4	67.4		50.5
89.9		120.0	120.0		89.9

mixtures and their sensitivity when subjected to different strains.

3. RESULTS AND DISCUSSIONS

Rheological Data

The rheological data are shown in Figure **2**. The samples evaluated have virtually the same viscoelastic behavior. The curves have a linear domain region that extends well defined up to an amount of approximately 10% of strain. From this strain the polymer-filler system begins to flow essentially as non-Newtonian fluid (non-linear curve). The overlay curves obtained by strain of samples in two steps (run 1 and run 2) demonstrates that the compositions are not susceptible to strain range studied. The overlay curves generated by applying the same strain range to the samples A and B (from the same composition) indicates the homogeneity of the elastomeric mixture. However, in the composition containing 30 phr of waste tires (SBR30) with average particle sizes exceeding 1,000 µm, the displacements of the curves suggest non-homogeneity of the mixture. This can be proven by scanning electronic microscopy (Figure **3**). Another noticeable characteristic related to sweep strain tests is the appearance of data points below the curves, particularly in the linear domain. The appearance of these points in a region with up to 1% of the strain is probably associated with the sensitivity of the equipment to low deformation, since the limit established by the equipment is from 1 to 120% of the strain.

Regardless of the filler content used in the polymeric matrix, all samples exhibited the same rheological profile, displaying Newtonian behavior for strains below 10%. Although studies on chemical interactions between the fillers and the polymeric matrix were not conducted in this work, it is known that they can play a fundamental role in the flow behavior of the system [11]. Leblanc [11] pointed out that, besides chemical interactions, the concentration of particles (dispersed phase) in the polymeric matrix can affect the rheological behavior. This effect, for certain compositions, seems to be more evident when smaller particles are dispersed. This is because these smaller particles can migrate freely from regions of high to low deformation.

Scanning Electronic Microscopy (SEM)

Figure **3** shows the photomicrographs generated by the surface analysis of the samples without filler (SBR00).

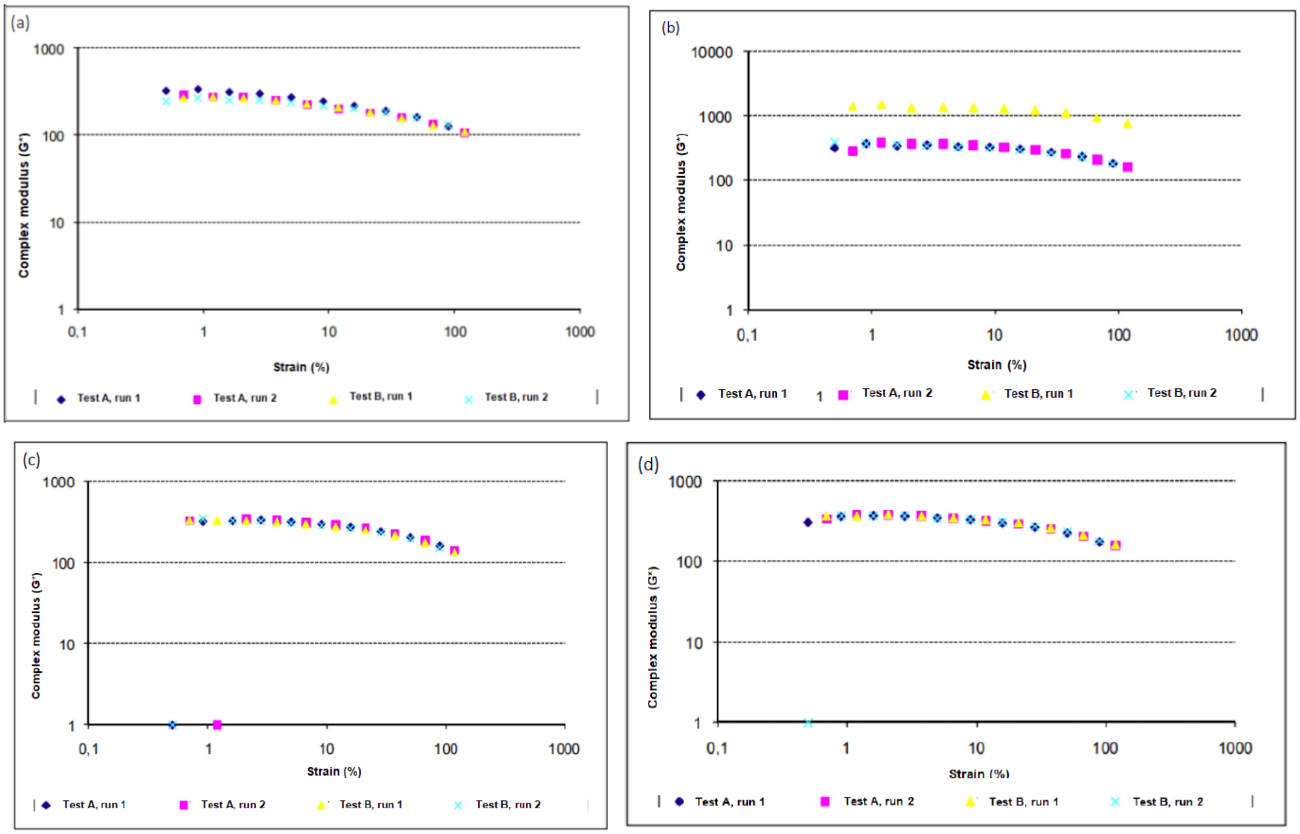

Figure 2: Rheological data obtained for sweep strain protocol at 1 Hz and 100°C, for samples without filler (SBR00) (**a**) and samples filled with 30 (**b**), 60 (**c**) and 90 phr (**d**) of ground rubber.

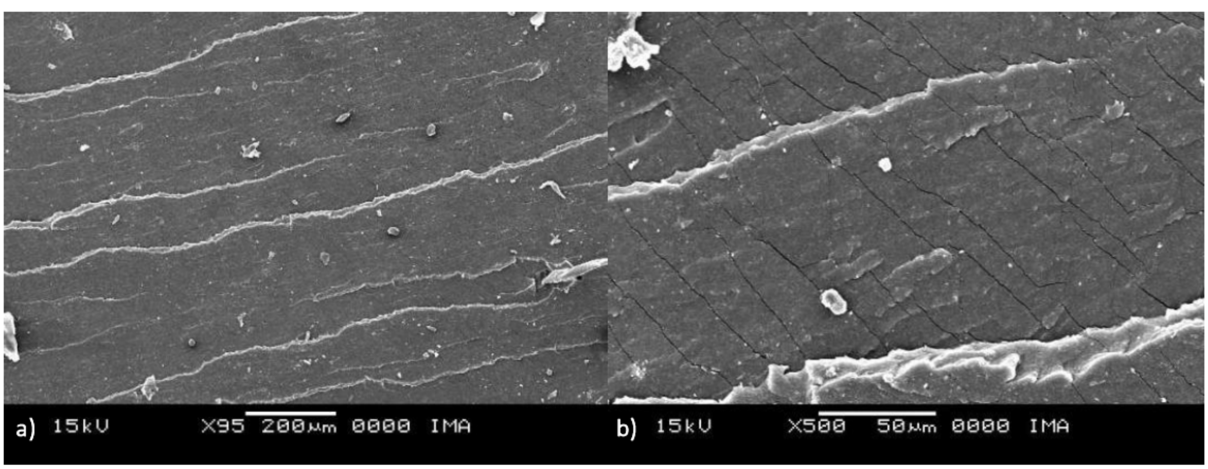

Figure 3: SEM photomicrography of sample prepared without ground rubber, with an increase of 95 times (**a**) and 500 times (**b**).

Figure **4** shows the photomicrographs of the samples containing 30 and 90 phr of elastomeric waste of tires with average sizes exceeding 1,000 µm. The mixtures with 90 phr of ground rubber presented more homogeneous surface (no particle projection) than the surface of the sample containing 30 phr of elastomeric filler. The photomicrograph of a sample containing 30 phr of filler indicates (as shown in the red region pointed out in Figure **4a**) tire shred particles poorly adhered to the polymeric matrix. With an increase of 95 times, it is possible to observe a partial adhesion of polymer particle (90 phr) to the matrix, with phases more strongly bonded to each other.

4. CONCLUSIONS

It can be concluded that:

1. Rheological experiments, especially the sweep strain test protocol looks like to be an important

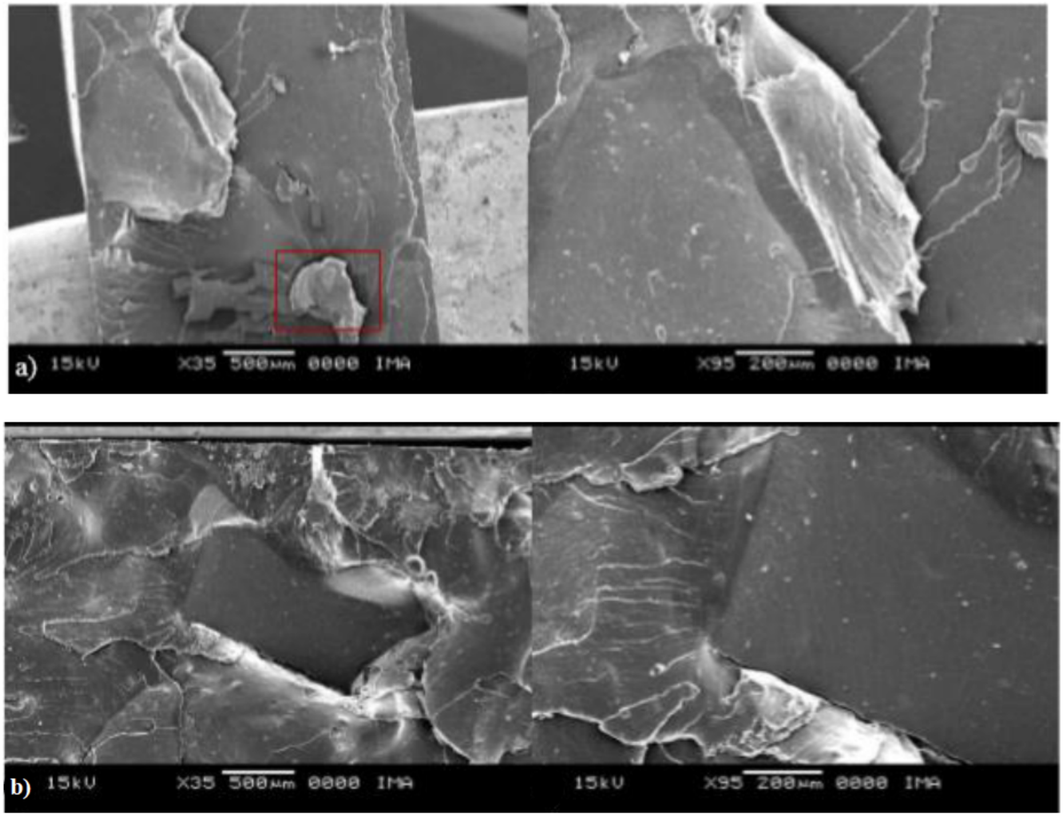

Figure 4: SEM photomicrography of sample with (**a**) 30 phr of ground rubber, and (**b**) 90 phr.

and promising tool for discussion of the homogeneity of polymer-filler system;

2. The elastomeric fillers were reasonably well anchored to continuous phase (polymer matrix). In contrast, the photomicrograph analysis of the sample containing 30 phr of filler with average particle sizes exceeding 1,000 µm showed a less homogeneous surface compared to the other compositions.

3. The analysis time for each composition (approximately 30 minutes), along with the convergence of interpretations between SEM and rheological data regarding the uniformity of elastomeric compositions, suggests that the sweep strain tests protocol is a useful tool to implement in quality control processes in industries.

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DECLARATION OF NON-USE OF ARTIFICIAL INTELLIGENCE

The author declares that no Artificial Intelligence was used for the text writing.

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