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Processability of revulcanizable SBR compositions

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Summary

The problem of vulcanized rubber scraps is of high importance nowadays, and the revulcanization of these scraps is an alternative to reutilize them. This work concerns the investigation of the processability of new compositions made from revulcanizable rubber scraps, through data from the Haake torque rheometer and the Rubber Process Analyzer (RPA). By varying cure system and oil addition, powdered butadiene-styrene rubber compositions (SBR-r) scraps were used in the preparation of six formulations. A control composition of identical formulation as the scraps was supplied by the industry and analyzed in all situations. Data reveal that new products can be produced by the reutilization of these industrial scraps.

Introduction

The problem of vulcanized rubber scraps is of high importance nowadays. According to the International Rubber Study Group [1], in 2006 the world consumption of natural and synthetic rubber reached 21.5 million tons. It can be assumed that the production of residues during rubber processing is about 10% [2]. So, around 2.15 million tons of rubber scraps are produced every year. There is a need to slow down the amount of scraps by process improvement, and/or to find alternatives for the reutilization of these scraps in rubber processes.

In previous works scraps of specific size to be used as filler in crude SBR were obtained and characterized in powder form [3,4]. Another alternative to the reutilization of rubber scraps is their revulcanization with the addition of a small amount of curatives, indicating availability of crosslinking sites in the cured particles [5,6].

The purpose of this study was to characterize the processability and the viscoelastic properties of new compositions of revulcanizable rubber with the aid of the Haake torque rheometer and the Rubber Process Analyzer (RPA).

Experimental

Materials

Powdered rubber (SBR-r) was obtained from grinding of extruded SBR profile scraps, supplied by CIAFLEX Indústria de Borrachas Ltda. (Caxias do Sul, RS, Brazil), as described in a previous work [4]. Commercial additives, such as sulphur, zinc oxide, stearic acid, CTP (N-cyclohexylthiophthalimide), TBBS (N-butyl-benzothiazole-sulfenamide), DPG (diphenylguanidine) and aromatic oil were also used without purification. The formulations in parts per hundred parts of rubber (phr) are given in **Table 1**.

Table 1: Formulations for rubber compounds

Materials (phr)	1a	1b	2a	2b	3a	3b
SBR-r	100	100	100	100	100	100
S	1	1	1	1	1	1
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
CTP	1	1	1	1	1	1
TBBS	-	-	1	1	0.5	0.5
DPG	-	-	-	-	1	1
Aromatic oil	-	5	-	5	-	5

Preparation of compositions

The compounds were prepared in a laboratory roll mill at ambient temperature. SBR-r was initially processed for 5 minutes and then the other additives were added together and processed for an additional 5 minutes. For compositions containing aromatic oil, this was previously added to SBR-r then the mixing proceeded in the same way as related above.

A control composition having the same formulation as that of the scraps was supplied by CIAFLEX Indústria de Borrachas Ltda. (Caxias do Sul, RS, Brazil), and analyzed in all situations. This is a specific composition for the extrusion process.

Processability by Torque Rheometry

In this work a Haake-Rheocord-90 torque rheometer, equipped with a Rheomix 600 mixing chamber of 85cm^3 volume and a CAM type rotor was used for predicting the processability of the rubber mixtures [7]. The design of the mixing head of the equipment is similar to that of the internal mixer and hence the behavior of the rubber in actual processability can be compared. The experiments were carried out at 60 rpm during 12 min. This period of time has made possible to approach the steady sate of all the mixtures under experimental conditions, the so-called stabilized torque, and quantified in a graph of torque *versus* time provided by the equipment. This parameter can be taken as approximately equivalent to viscosity during processing. Also, according to Equation 1 [8], it is also possible to get values from the graph to calculate the specific energy (E_{spec}) spent in each mixture.

$$E_{spec} = \frac{2\pi N}{m} \int M dt \qquad \textbf{(1)}$$

Where: *N* is the speed (in rotations per minute - rpm); *M* is the torque (in N.m); *m* is the weight of the sample in the mixer (in grams - g); and *t* is the total mixing time (in minutes - min).

Integral $\int MdT$ corresponds to the totalized torque (TTQ), which is the area under the torque *versus* time curve.

Viscoelastic properties

The rheological behavior derived from viscoelastic parameters of rubber compounds can be determined with the aid of a Rubber Process Analyzer (RPA) [9-13]. An Alpha Technology RPA 2000 was used to determinate the viscoelastic properties of the proposed compositions and the control sample according to ASTM D 6204-99 [14]. Equipment stabilization conditions were temperature 100°C; frequency 0.5 Hz and strain 0.2° (2.8%) for 5 min. Strain sweep and frequency sweep tests were performed. Strain sweep was determined in advance in order to get the samples linear behavior region. The experimental conditions were: temperature 100°C, frequency 1Hz and strain angle varying from 0.5 to 30° (7% to 420% deformation). The frequency sweep test was performed at 100°C temperature, strain angle 2° (28% deformation) and the frequency varied from 0.03 to 16.7 Hz.

Results and discussion

Torque rheometry

Data obtained from the Haake torque rheometer are shown in **Table 2.** These data are stabilized torque, which can be related to the samples' viscosity, totalized torque (TTQ) that is the work during mixing, and specific energy, the energy required to perform the mixing (E_{spec}).

Table 2: Processability results obtained in the Haake torque rheometer

Sample	**Stabilized Torque (Nm)**			**Totalized Torque (Nm min)**			**Specific Energy (E_{spec}) (J g^{-1})**		
	40°C	**50°C**	**60°C**	**40°C**	**50°C**	**60°C**	**40°C**	**50°C**	**60°C**
Control	11.81	11.34	9.54	146.28	140.38	116.86	746.23	716.13	596.15
1a	12.16	11.81	9.78	153.84	143.72	115.87	784.80	733.17	591.10
1b	11.69	10.66	8.30	146.27	129.88	102.93	746.18	662.57	525.09
2a	12.86	11.94	9.66	157.48	145.53	116.40	803.37	742.41	593.80
2b	12.25	11.09	8.01	147.8	133.99	98.66	753.99	683.54	503.30
3a	13.43	11.38	9.03	157.28	136.84	112.93	802.35	698.08	576.10
3b	12.33	10.17	8.32	143.39	126.15	101.23	731.49	643.54	516.41

The small difference between data obtained from the developed compositions as compared to the control composition result from the addition of oil (compositions b) as well as from modifications in the cure systems.

By comparing the compositions with and without oil (b and a respectively) it is possible to state the small influence of this additive on the calculated parameters. The lower values of stabilized torque, TTQ and E_{spec} are consequent to the increase in free volume caused by the increased molecular mobility. The influence of temperature, from 40°C to 60°C can be explained by the same behavior: this increase makes easier the processability, resulting in lower values at 60°C.

In the temperature range used in the Haake rheometer data for the control processing parameters are close to those of the proposed formulations indicating absence of crosslinking between 40°C and 60°C, which could result from the proposed modifications.

Data, as obtained from a 40°C run, are shown in **Figure 1**.

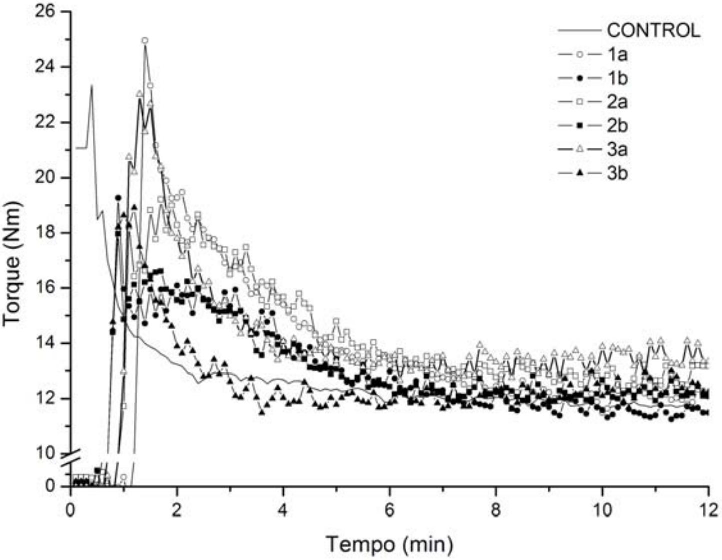

Figure 1: Behavior of compositions and control sample through mixing in a Haake torque rheometer at 40°C

Viscoelastic properties

RPA data are shown in **Figures 2-5**. Elastic torque (S') with strain variation at 100°C and 1 Hz (**Figure 2**) makes possible to distinguish linear from non-linear regimens. There is an increase in elastic torque for all compositions until strain approaches 10-15° (140 to 210%), followed by a decrease in this property. This behavior characterizes the onset of a non-linear regimen. Based on these results, deformation at 2 degrees (28%) was used in a study of the influence of frequency on rheological parameters, since under such conditions samples are submitted to a linear behavior regime.

Figure 2 data show that SBRr-containing developed formulations compared with virgin compounds (control formulation) have higher torque, as a consequence of the scraps toughness and the applied temperature (100°C). This behavior can be indicative of crosslink formation. An expected result is the higher torque value of SBRr compositions without oil addition.

The cure systems used can also be distinguished. Among the compositions, the higher torque was found for composition 1a having a retarder additive (CTP) for the sulfur vulcanization system, while the lower torque was for composition 3b containing the higher accelerator amount. As the experiments were made at 100°C in a pressurized mold the addition of a vulcanized system suggests that the original scraps still contain enough residual accelerators to promote additional vulcanization while in the 3b formulation it seams to be in excess.

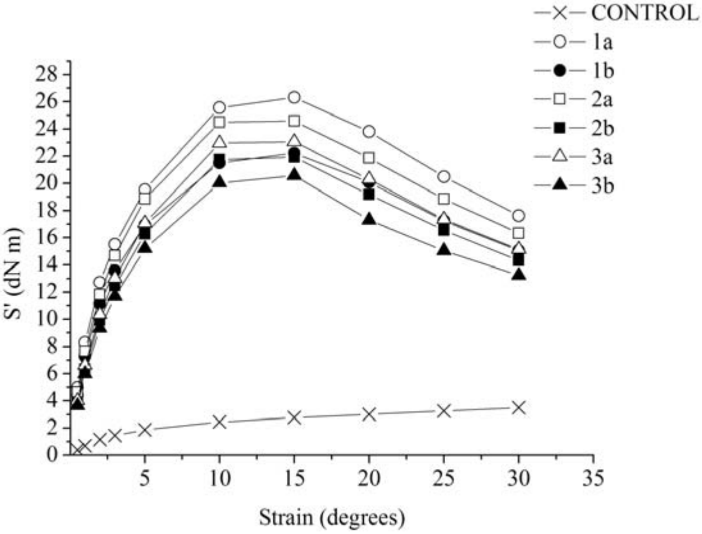

Figure 2: Elastic torque *versus* strain for compositions and for the control sample at 1Hz and 100°C

So, the torque values obtained by RPA are different from the Haake rheometer not only by the performance of each equipment but mainly by the applied temperature.

Data of storage modulus *versus* log strain are presented in **Figure 3**. There is a decrease in this parameter as a function of strain, indicating a breakdown of filler agglomerates during deformation. This behavior can be evaluated by the Payne effect and in this work this was calculated by the ratio between the modulus at 7% and 70% deformation [15]. These values are reported in **Table 3**.

Since the compositions have the same amount of filler, it is possible to observe that values reported in **Table 3** are similar, but lower than those of the control sample, showing more breakdown of fillers in the control composition that impart better mechanical properties [15].

Table 3: Ratio between storage modulus at 7% and 70% strain

Sample	Control	1a	1b	2a	2b	3a	3b
G' 7%/G' 70%	0.47	0.39	0.38	0.40	0.42	0.42	0.42

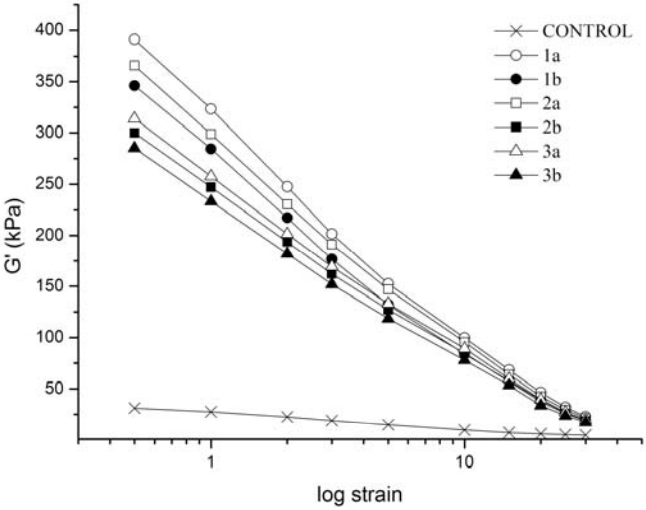

Figure 3: Storage modulus (G') *versus* log strain for compositions and the control sample

In **Figure 4**, viscous modulus, G", is plotted as a function of frequency at 100°C and 2° strain (28%).

An expected result is the increase in G' with the frequency [13], as shown by the behavior of the control formulation. As for the developed compositions, all values of G" are similar but higher than those of the control. These values are not influenced by the frequency variation and the compositions without oil addition (compositions a) have higher G".

These losses are related to the high energy input required for the motion of the molecular chains of the polymer. Such behavior can be explained, as stated before, on the basis of crosslinking formation at the test temperature.

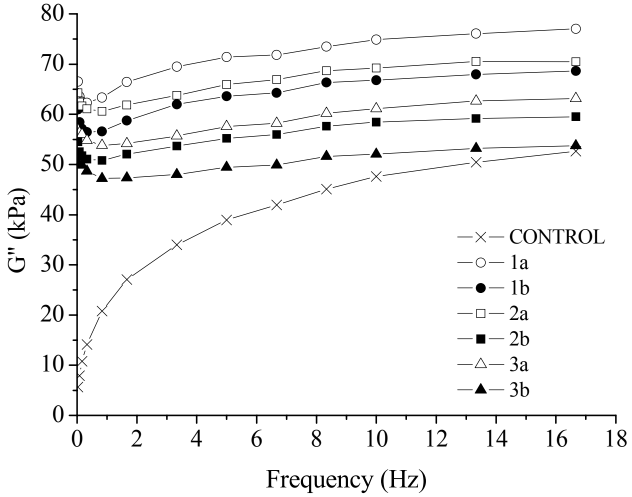

Figure 4: Viscous modulus (G") *versus* frequency for compositions and the control sample

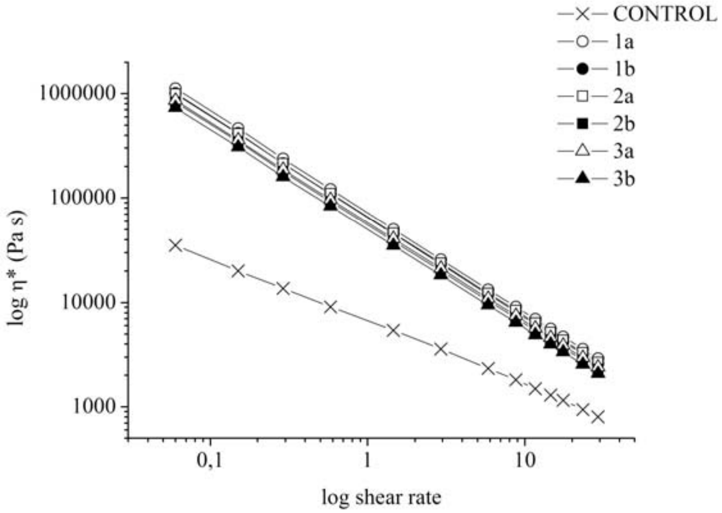

Figure 5: Dynamic viscosity *versus* shear rate of the compositions and of the control sample

In **Figure 5** values of dynamic viscosity versus shear rate, obtained from frequency sweep measurements are presented. The shear rate range is equivalent to that used for a compression molding process [16]. All compositions show a typical pseudoplastic behavior, with a decrease in viscosity with increasing applied shear rate.

It is also possible to verify that the slope of the curves is more accentuated for compositions than for the control sample, meaning lower stability of the compositions during processing.

A detail of this plot is shown in **Figure 6,** where it is possible to observe some differences among the compositions. In a general way, compositions with a better

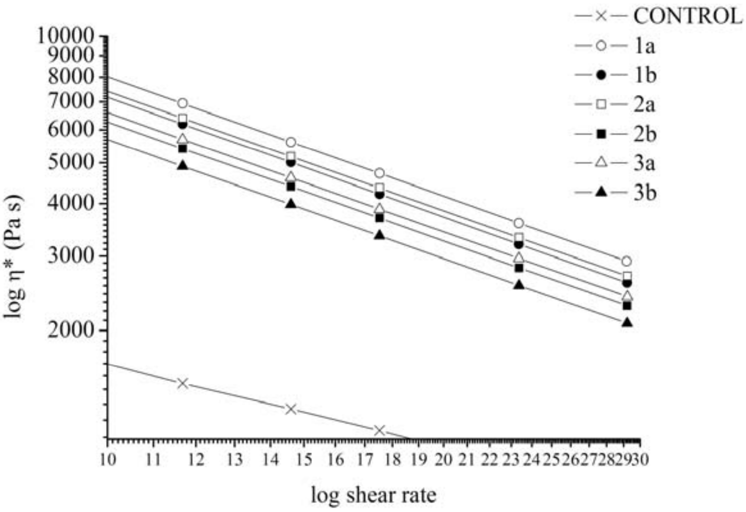

Figure 6: Detail of dynamic viscosity *versus* shear rate of the compositions and of the control sample

amount of cure system (composition 1) and without oil (compositions a) are more viscous. These data demonstrate the great utility of dynamic testing as a quality control test sensitive to small compound variation.

Conclusions

The Rubber Processing Analyzer (RPA) and Haake Torque Rheometer were good tools to quantify the different behaviors exhibited by the developed compositions.

It was possible to determinate the processability and to distinguish linear from non-linear regimens from strain sweep. As calculated by the Haake torque rheometer and RPA, the addition of oil facilitates the processability by decreasing viscosity but the processability is lower for the compositions than for the control sample in the range of 40 to 60°C.

The Rubber Process Analyzer data also reveal that: all compositions show a pseudo-plastic behavior, and that the compositions without accelerators addition presented the highest torque value, thus suggesting that the original scraps still contain enough residual accelerators to promote additional vulcanization.

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