

# Polymer–filler interactions in a tire compound reinforced with silica

Jordão Gheller Jr<sup>1</sup>, Manoela V Ellwanger<sup>1</sup>  
and Vinícius Oliveira<sup>1</sup>

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## Abstract

Elastomers, usually, are reinforced with reinforcing filler in order to improve their mechanical properties like tensile strength and abrasion resistance. The efficiency of this reinforcement is correlated with different factors like filler structure, surface area, and polymer–filler interactions. This study presents a methodology to quantify the bound rubber attached to the reinforcing filler silica using the thermogravimetric analyzer. Three typical rubber compounds used in tread tire were studied. In the samples tested, the silica content was kept constant, varying only the percentage of the coupling agents. Considering the results of the thermal analysis, physical, mechanical, and rheological tests, the thermogravimetric analysis has proved to be a very useful technique in evaluating the interaction of filler and polymer.

## Keywords

Bound rubber, filler–polymer interaction, silica reinforcement, filled rubber

## Introduction

When an elastomer and a reinforcing filler are mixed, strong interactions occur between them, in such a way that, at room temperature, a good solvent of the polymer can extract only the free rubber portion, leaving a highly swollen rubber–filler gel as the insoluble part.<sup>1</sup> Bound rubber (BdR) is, by definition, the rubber content in this gel.<sup>1–3</sup>

This structure of a thin layer of polymer attached to the filler, formed during the mixing process,<sup>4</sup> is considered one of the main factors of the degree of reinforcement and superficial activity of the fillers, as evidenced by the close correlation between the improvement of the properties and the amount of BdR.<sup>5</sup>

<sup>1</sup> Innovation Institute for Polymers Engineering SENAI, São Leopoldo, Brasil

### Corresponding author:

Jordão Gheller Jr, Innovation Institute for Polymers Engineering SENAI, Avenida Presidente Joao Goulart, 682, CEP 93030-090, São Leopoldo, Brasil.  
Email: jordao.gheller@senairs.org.br

Despite the fact that the BdR determination is a simple technique, for example, once polymer–filler interaction involves, there are different factors, such as the physical adsorption, chemisorption, and mechanical interaction, affecting the quality of results.<sup>6,7</sup> These interactions are influenced by superficial properties of the filler, morphology, and chemical structure of the polymeric molecules and its microstructure.<sup>1</sup> Furthermore, the BdR content has strong dependence on processing conditions like temperature and time. Also, the parameters used in the BdR determination, like solvent and extraction temperature, have a strong influence in the results. Because of all these different and independent factors, the BdR determination is still a subject of controversy.<sup>8</sup>

Wolff,<sup>9</sup> in his study to evaluate the correlation between the reinforcing degree and the viscosity of the compounds, concluded that higher viscosities are obtained when the effective volume of the filler ( $\phi_{\text{eff}}$ ) increases, as is presented in the equation reviewed by Einstein, Guth, Gold, and Simha.<sup>1</sup> An increment in the effective filler volume fraction results in an increase of the compound viscosity.

$$\eta_{\text{cpd}} = \eta_{\text{polymer}} (1 + 2.5 \times f \times \phi_{\text{eff}} + 14.1 \times f^2 \times \phi_{\text{eff}}^2) \quad (1)$$

Where  $\eta_{\text{cpd}}$  is the compound viscosity,  $\eta_{\text{polymer}}$  is the viscosity of the pure polymer, and  $f$  is an anisometric factor (or form factor), that is the ratio between the large and small axis of the aggregate. An increase in the effective volume of the filler results in an increase in the hydrodynamic volume by the addition of rigid particles of elastomer in the filler, with consequent increase in the viscosity of the compound.<sup>6</sup>

Leblanc<sup>1</sup> proposed that  $\phi_{\text{eff}}$  represents the sum of the filler volume + BdR ( $\phi_{\text{eff}} = \phi_{\text{filler}} + \phi_{\text{BdR}}$ ).

Wolff<sup>10</sup> studied intensively the adsorption energies and the interactions between carbon black and silica with polar and nonpolar polymer structures. The main conclusion from their studies was that a better reinforcement can be obtained with silica and polar polymers like acrylonitrile butadiene rubber. For nonpolar elastomers, like the styrene butadiene rubber (SBR) and/or polybutadiene (BR), largely used in tire compositions, coupling agents between polymer and filler are necessary.

The role of the coupling agents is to raise the interaction between the filler particles and rubber chains, resulting in deep modifications in the properties of the final rubber products, like better filler reinforcement, lower softening effect in higher strain, lower filler–filler interactions as well as better dispersions of the filler particles in the polymer matrix.<sup>1</sup> These singular properties are the basis to the green tire technology, started at the 90s, consisting in the use of silica as reinforcing filler, improving the rolling resistance and fuel economy.<sup>11,12</sup>

The use of coupling agents resulted in a series of changes in the processing conditions and production costs. Moreover, one of the main difficulties in this process is to evaluate the efficiency of the polymer–filler interactions formed by the coupling agents,<sup>13–27</sup> considering that for an efficient polymer–filler interaction, it is necessary to process the compounds at different temperatures and varying the ingredients of addition sequence.

In this study, the efficiency of the addition of different quantities of bifunctional silane bis(triethoxysilylpropyl)tetrasulfane (TESPT) in the polymer–filler interactions in rubber formulations used in tire tread compounds with low rolling resistance, besides the quantification of the BdR content in these compounds has been analyzed.

The evaluation of this efficiency will be done based on the results of physical, mechanical, rheological, dynamic mechanical tests, and the BdR content determined by thermogravimetric analysis (TGA).

## Experimental

### *Equipment and procedures*

The rubber compounds were prepared in a HAAKE™ PolyLab™ Torque Rheometer from Thermo Scientific (U.S.) with two wings rotors and, in another step, in an open mill from Copé (Brazil).

The sample tests were vulcanized in a compression press, at 170°C at a time of 2 min more than the optimum cure time determined by the rheometric curve.

Mooney viscosity was determined in an MV 2000 viscosimeter from Alpha Technologies (U.S.), according to the American Society for Testing and Materials (ASTM) D1646. TGAs were done in a TGA Q500 from TA Instruments (New Castle, Delaware, USA). Tensile tests were done in EMIC DL 5000 equipment (Brazil), according to ASTM D412 Die C. Evaluation of the dynamic modulus (Payne effect) was done in a rubber process analyzer under the following conditions: 5 Hz, 70°C, and varying the strain from 0.3% to 100%. Compounds were evaluated after vulcanization (7.5 min at 170°C in the equipment cavity).

The heat building up (HBU) tests and the mechanical dynamic properties were done in an MTS 831.50 machine (Material Testing Systems, Eden Prairie, Minnesota, USA) under the following conditions: 50°C, compression force –245 N, strain amplitude  $\pm 20\%$ , and 30 Hz of frequency.

### *Materials and formulations*

Elastomers used were the copolymer SBR 1502 and BR45 from Lanxess (Germany), the natural rubber used was Granulado Escuro Brasileiro (GEB01) from Mafer (Brazil). Reinforcing filler used was precipitated silica Zeosil 185 Plus from Rhodia (France). Coupling agent used was TESPT from Wenda (China). Curing system used was sulfur based, with zinc oxide and stearic acid as activators.

The quantity of each ingredient was defined in parts per hundred of rubber (phr) as shown in Table 1.

### *Processing and sample preparation*

According to Leblanc,<sup>1</sup> the polymer–filler interaction occurs in the first stages of the mixture, resulting in a direct correlation with the rheological properties of the compounds. The silanization process was divided in two steps as follows<sup>1,9</sup>:

Silanization: First, one ethoxy group from silane reacts quickly with an isolated silanol (around 85% on silica surface) or a silanediol from silica (15%); then, there is hydrolysis of the remaining ethoxy groups, which produce a reticulation of silane molecules through siloxane bonding.

**Table 1.** Compositions of the four samples produced.

Ingredients	Reference	5% Silane	7% Silane	10% Silane
	Quantities (phr)			
SBR 1502	60.0	60.0	60.0	60.0
NR	10.0	10.0	10.0	10.0
BR45	30.0	30.0	30.0	30.0
Zinc oxide	3.00	3.00	3.00	3.00
Stearic acid	2.00	2.00	2.00	2.00
Antioxidant	1.00	1.00	1.00	1.00
Precipitated silica	40.0	40.0	40.0	40.0
Silane TESPT	–	2.00	2.80	4.00
Accelerator CBS	2.50	2.50	2.50	2.50
Curing agent sulfur	1.40	1.40	1.40	1.40
<b>Total</b>	<b>149.9</b>	<b>151.9</b>	<b>152.7</b>	<b>153.9</b>

SBR: styrene butadiene rubber; phr: parts per hundred of rubber; BR: polybutadiene; TESPT: bis(triethoxysilylpropyl)tetrasulfane; NR: natural rubber; CBS: *N*-cyclohexyl-2-benzothiazole-sulfenamide.

**Vulcanization:** The tetrasulfane group (with TESPT silanated silica) is broken and forms covalent bonds with the polymer during the rubber cross-linking.

The compounds were processed in three steps as follows:

1. Step 1: Mixture of the elastomer, filler, TESPT, and antioxidant in a closed chamber at 110–120°C with a rotor speed of 60 r min<sup>-1</sup> for 10 min;
2. Step 2: Silanization of the system in a closed chamber at 150–155°C with a rotor speed of 60 r min<sup>-1</sup> for 3 min;
3. Step 3: Addition of the vulcanization agents in the open mill at 60–80°C for 10 min.

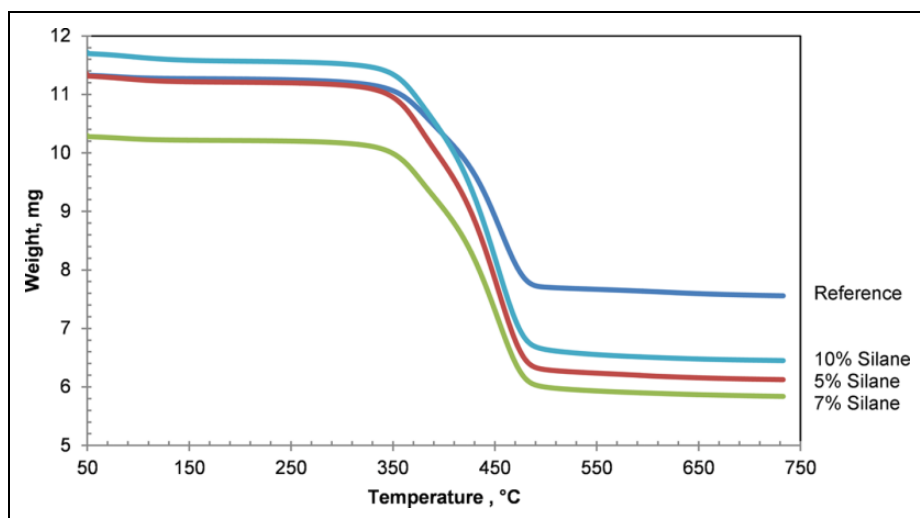
### **BdR determination**

BdR content is measured by extracting unbound polymer chains and organic additives from the filled rubber compound with a good solvent at room temperature, while tightly BdR content is measured by extracting the unbound materials and loosely bound polymers.<sup>12,28–30</sup>

A fraction of each sample was removed from the step II of processing, without the curing system, in order to avoid the elastomer vulcanization during hot extraction.

About 1.5 g of each sample were extracted with 75 mL of toluene in a Soxhlet extraction system for a period of 60 h, and the insoluble material was dried in an oven at 100°C for 6 h.<sup>1</sup>

Approximately 10–12 mg of this material was analyzed using a thermogravimetric analyzer, heating the sample from room temperature to 750°C, with a heating rate of 10°C min<sup>-1</sup>, using nitrogen (N<sub>2</sub>) as inert atmosphere during the analysis, which was performed in duplicate.



**Figure 1.** TG curves of samples tested under an inert  $N_2$  atmosphere. TG: thermogravimetric;  $N_2$ : nitrogen.

The content of BdR was calculated in accordance with the equation described below<sup>7</sup>:

$$\%BdR = \frac{\text{phr filler} \times \Delta_{\text{extracted}}}{\text{residue}}, \quad (2)$$

where  $\Delta_{\text{extracted}}$  represents the weight variation of the extracted material when heated in an inert atmosphere between 250°C and 700°C and the residue is the weight of the residues (remaining material) at 700°C in the thermogravimetric analyzer.

## Results and discussion

The TG curves obtained from the extracted material are presented in Figure 1. It is possible to observe that, as the content of silane was increased, a higher weight loss in the extraction productions was produced, indicating the presence of a higher amount of polymer connected to the filler (BdR).

Based on weight loss obtained and using equation (2), the contents of BdR calculated are shown in Table 2. The BdR contents calculated are close to the values reported in the literature.<sup>1</sup> As noted, the silane concentration above 5% is not efficient in increasing the BdR.

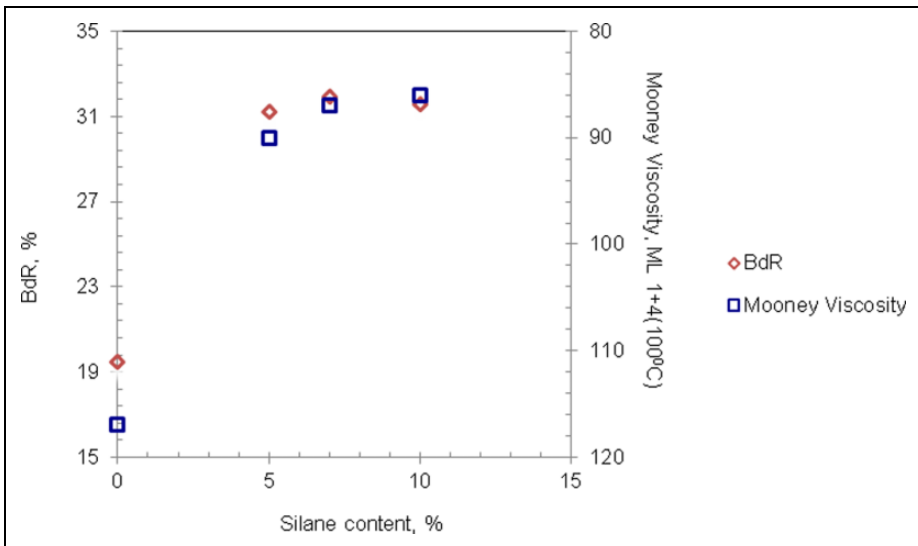
In the comparative evaluation among the results of Mooney viscosity and BdR of the four compounds analyzed (Figure 2), it is observed that, with the increase of BdR content, the Mooney viscosity decreases. This behavior is due to the decrease of filler–filler interactions, responsible for the greatest increase on the viscosity of the compounds, with consequent increase in filler–polymer interactions.<sup>10</sup>

Analyzing the results of tensile  $\times$  elongation (Figure 3), it is noted that samples with 5% and 7% of silane showed an increase in the values of modulus 300% and tensile strength

**Table 2.** BdR content calculated according to the content of silane added to the compound.

% of silane TESTP	% BdR calculated
0	19.5
5	31.2
7	31.9
10	31.5

BdR: bound rubber; TESPT: bis(triethoxysilylpropyl)tetrasulfane.



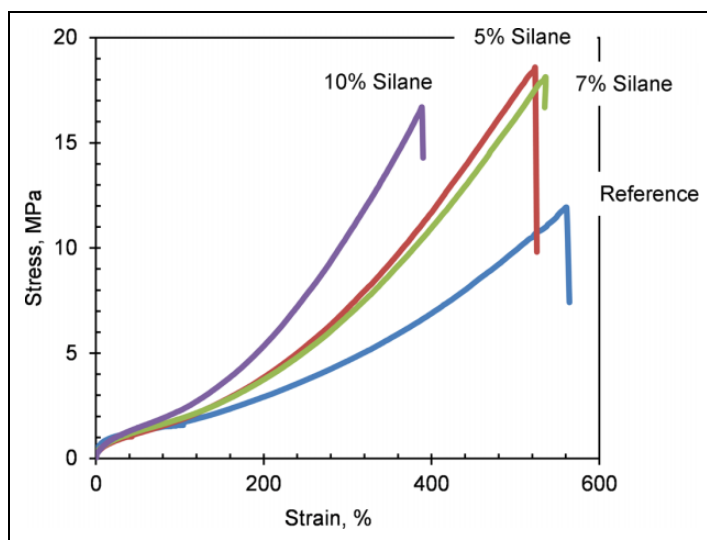
**Figure 2.** Results from BdR content and Mooney viscosity as a function of the silane added in the compounds. BdR: bound rubber.

when compared with the compound without silane (reference sample) characterizing a better polymer–filler interaction and an improvement in the degree of reinforcement of the filler.

A decrease in the tension and elongation at break occurred in the compound with 10% of silane, possibly due to an increment in the degree of cure of this compound resulted by the sulfur that is present in the silane composition, that was added in excess.

By the variation of elastic modulus ( $G'$ ), as a function of dynamic strain (Payne effect), it is possible to evaluate the decrease in filler–filler interactions in compounds containing different amounts of silane (Figure 4). The influence of the addition of silane on the dependence reduction of the elastic modulus ( $G'$ ) and deformation is evident. At higher deformations (100%), contents of TESPT 5, 7, and 10% presented proportionally a reduced dependency on the elastic modulus and the imposed deformation.

Evaluating the HBU in the four compounds analyzed (Figure 5 and Table 3), it is observed that contents of 5 and 7% silane resulted in similar properties; however,



**Figure 3.** Stress  $\times$  strain curves for the tire compounds with different silane contents.

contents of 10% silane resulted in a compound with lower HBU and lower value of  $\tan \delta$  (Table 3).

As shown in Table 3, as the coupling agent (TESPT) was added, the values of elastic modulus increased and the viscous modulus decreased. This behavior can be easily correlated with the interactions formed. As the filler–filler interactions increase (reference sample), it is possible to observe an increment in the viscous modulus or loss modulus ( $K''$ ). In contrast, as the filler–polymer interactions increase (sample with 10% silane), it is possible to observe an increment in the elastic modulus or storage modulus and decrease in the loss modulus. This behavior leads to a decrease in  $\tan \delta$  value, resulting in compounds with lower HBU as discussed by Wang.<sup>9</sup>

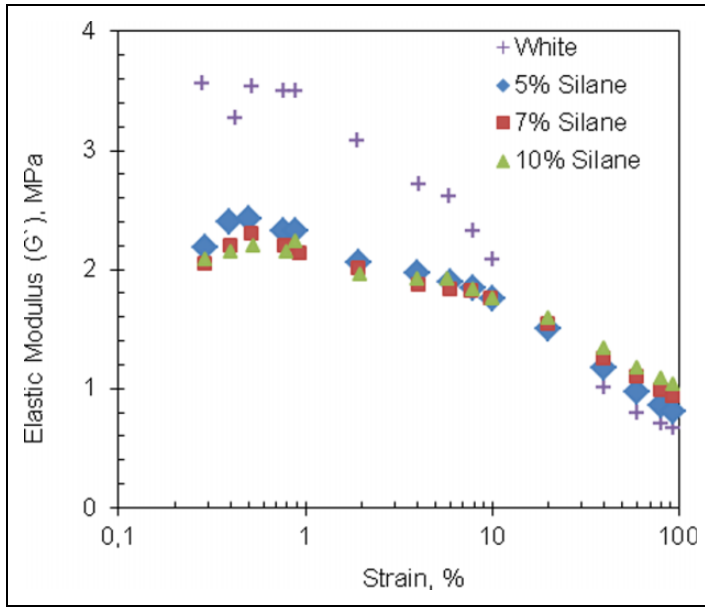
## Conclusions

Evaluating the results obtained in the Mooney viscosity test, as a function of the reduction on filler–filler interaction, a decrease in the viscosity in the compounds with silane TESPT was observed.

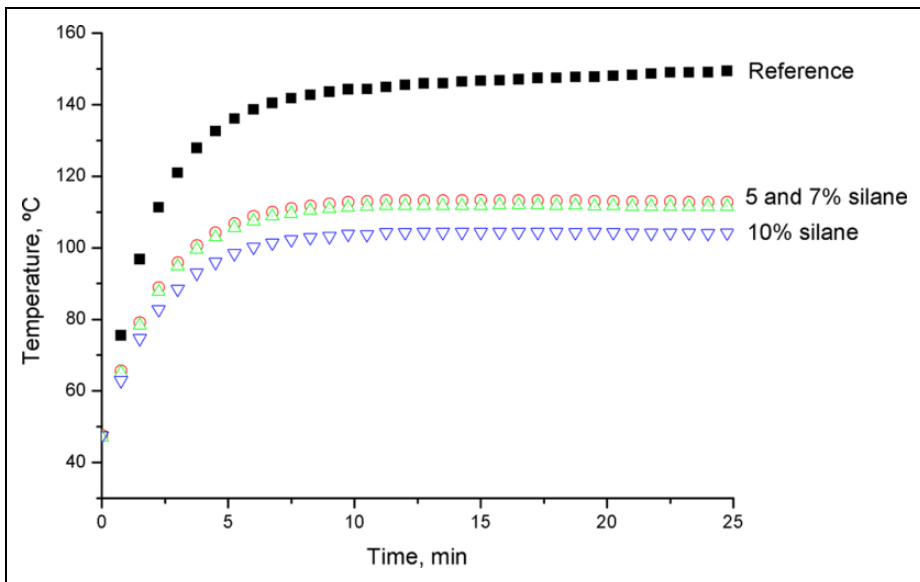
On the results of BdR, obtained by the TG curves, there was a good correlation of this technique and the rheological results of Mooney viscosity, where the amount of 5% silane TESPT calculated using the quantity of silica as reference has been proved adequate in obtaining polymer–filler interactions

From the evaluation of the curves tension  $\times$  elongation, it is noted that the levels of TESPT higher than 7% raised stiffness (tensile strength at 300% of elongation) and lowered the tensile properties and elongation at break of the compounds.

In the HBU analysis, similar results for the samples with 5% and 7% of silane was observed, although, 10% silane resulted in a lower  $\tan \delta$  and HBU value.



**Figure 4.** Evaluation of the variation of elastic modulus  $G'$  in function of strain in compounds with different silane contents.



**Figure 5.** Temperature  $\times$  time under dynamic compression – HBU (frequency 30 Hz, amplitude of deformation  $\pm 20\%$ , average load  $-245$  N, and initial temperature  $50^\circ\text{C}$ ). HBU: heat building up.



**Table 3.** Temperature variation in the HBU test,  $\tan \delta$ , elastic, and viscous modulus.

Sample	$\Delta T$ ( $^{\circ}\text{C}$ )	$\tan \delta$	$K'$ ( $\text{N mm}^{-1}$ )	$K''$ ( $\text{N mm}^{-1}$ )
Reference	102.2	0.150	81.5	12.2
5% Silane	65.2	0.099	84.1	8.3
7% Silane	64.6	0.089	85.9	7.7
10% Silane	56.6	0.081	87.7	7.1

HBU: heat building up.

Correlating the BdR and HBU results was possible to observe that silane levels above 5% didn't result in a higher amount of BdR; however, analyzing the results of HBU and  $\tan \delta$ , a greater influence of silane content above 5% was observed, especially in the compound containing 10% silane. This behavior can be explained by a possible increase in the efficiency of the cure, which influences the storage and loss modulus. We considered that the cure agent (sulfur) is present in the structure of silane and may not have been fully utilized forming the polymer–filler interactions.

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