



# Correlation of silane grafting density with rheological properties of silica filled rubber: Coupling of flow and temperature



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## ABSTRACT

The structure and rheological properties of butadiene rubber / silica / silane nanocomposites were investigated in this paper. The structure of the nanocomposites was characterized by NMR analysis which allowed the quantification of silane grafting rates. A time temperature equivalence parameter was defined as a unique mixing conditions parameter taking into consideration both temperature and mixing speed. A direct law between grafting rates and mixing conditions was found. Rheological properties were characterized by creep and elongation measurements, and the influence of mixing speed and temperature on these properties was determined. A competition between grafting and breaking mechanisms on elastic entities, respectively promoted by the increase of temperature and of speed, was highlighted. Therefore this paper shows correlations between temperature and speed process conditions, the mixture's structure and its rheological properties. Thanks to these results, a model of the structure of the silica-filled rubber was proposed; unusual rheological properties stem from the formation of clusters of connected aggregates by way of grafted rubber.

## 1. Introduction

Rubber/silica composites present a growing interest especially in tires industry. Indeed, since the early 1990s, silica has been added in tread blends to replace carbon black fillers in order to reduce the rolling resistance and consequently to decrease the car's fuel consumption [1,2]. However, unlike carbon black, silica has no affinity with elastomer chains and thereby the addition of a silane agent is necessary. This additive allows both a better dispersion of silica fillers and the coupling of silica with rubber chains. Then the addition of silane induces a better reinforcement of the material thanks to the reduction of filler/filler interactions and the promotion of filler/rubber interactions. The effect of silane on dispersion or reinforcement relies on the nature, properties and content of the silane [3,4] but also on the mixing conditions used for the elaboration of the filled rubber [5,6].

The influence of silane on the fillers' dispersion has been widely studied by microscopic observations and Small-Angle-X-ray-Scattering [7–9]. On the other hand, if the grafting reaction of silane on silica has also been well characterized in the literature [10–13], these studies mainly focus on simplified systems rather than on the grafting inside the entire rubber/silica/silane system where the quantification of reactions is obviously more complex.

In a previous study [14], silane/rubber reactions were characterized and grafting rates were quantified for simplified mixture without silica. Based on this first study, the quantification of rubber interactions has been extended to a complete system including

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**Table 1**  
Formulation and mixing conditions of studied mixtures.

N°	Formulation's name	BR (phr)	Silica (phr)	TESPT (phr)	Dump temperature (°C)	Mixing speed from 380 s (rpm)
1	BR_20phr_sil_R155_50 rpm	100	20	2.65	155	50
2	BR_20phr_sil_R155_90 rpm	100	20	2.65	155	90
3	BR_20phr_sil_R170_50 rpm	100	20	2.65	170	50
4	BR_20phr_sil_R170_90 rpm	100	20	2.65	170	90
5	BR_20phr_sil_R180_10 rpm	100	20	2.65	180	10
6	BR_20phr_sil_R180_50 rpm	100	20	2.65	180	50
7	BR_20phr_sil_R180_90 rpm	100	20	2.65	180	90
8	BR_sil_R155_50 rpm	100	0	2.65	155	50
9	BR_sil_R170_50 rpm	100	0	2.65	170	50
10	BR_sil_R180_50 rpm	100	0	2.65	180	50
11	BR_sil_R180_0 rpm	100	0	2.65	180	0
12	BR_sil_R180_90 rpm	100	0	2.65	180	90

silica. In a first part, this paper will therefore present, the development of a new method for the characterization and the quantification of rubber/silica interactions as a function of mixture process conditions.

Interactions between silica and rubber have a direct influence on rheological properties. These properties are mainly studied by SAOS or under larger dynamic shear by means of Payne Effect [15,16] or with tensile strength measurements [4]. In a second part of this paper, rubber/silica blends will then be characterized by creep and elongation measurements. These techniques, less developed in the literature, highlight the properties of the filled rubber in the long term or under large deformations which are more representative of the solicitations undergone during the extrusion process. Finally, rheological properties will be correlated to grafting rate, hence highlighting the influence of nanocomposite structure and process conditions on rheological behavior.

## 2. Materials and methods

### 2.1. Materials and mixtures preparation

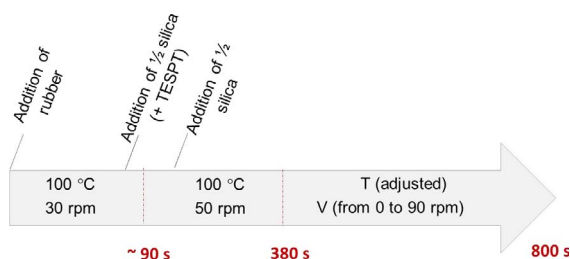
Butadiene rubber (BR) supplied by Michelin and produced by neodymium catalyst according to the patent WO 2007045417 and silica ZEOSIL 1165MP produced by Rhodia, were used for mixtures preparation. Silica is a micropellet powder with average diameters around 250–300  $\mu\text{m}$ . The butadiene rubber has a high 1,4 cis unit content (98.8 wt%) and its molecular weight ( $M_w$ ) is 500 kg/mol. Bis[3-(triethoxysilylpropyl)] tetrasulfide (TESPT) purchased from Sigma Aldrich was used as coupling agent and its quantity was chosen in order to react with all silanol functions theoretically located on the silica surface. Mixtures without silica were also prepared to characterize BR and TESPT interactions. Mixture formulation is given in Table 1.

Mixtures were elaborated in a Rheomix Haake 600 internal mixer with a of 70  $\text{cm}^3$  chamber, following the steps summarized in Fig. 1. BR was first incorporated at 100 °C and 30 rpm. Then silica with TESPT was added in two steps at 30 rpm first and then after an increase of the rotation speed to 50 rpm. At 380 s, the set point temperature of the mixer chamber was adjusted in order to obtain a specific “dump temperature” (temperature at the end of the mixing, at 800 s) between 155 and 180 °C. The mixing speed could also be adjusted at 380 s (from 0 to 90 rpm). The mixing was stop after 800 s. Dump temperatures and final mixing speeds are reported in Table 1.

The method used to calculate the grafting rate of TESPT on BR chains was developed in a previous study [14]. This method relies on  $^1\text{H}$  liquid state NMR spectroscopy of BR/TESPT unfilled mixtures. It needs the extraction of non-grafted silane. The same method was performed on BR/TESPT mixtures without silica (n°8 to 12). In order to extract these free molecules of TESPT, the mixtures were first solubilized on a chloroform solvent and then precipitated by the addition of absolute ethanol. Precipitated mixtures were finally dried under vacuum at 30 °C for 2 days.

### 2.2. Transmission electron microscopy (TEM)

The BR/silica/TESPT nanocomposites were observed with a PHILIPS CM120 transmission electron microscope at 120 kV. The



**Fig. 1.** Mixing steps for elaboration of BR/silica/TESPT composites.

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