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# IN SITU CHARACTERISATION OF DISPERSION PROCESS OF SILICA IN AN ELASTOMER MATRIX SUBMITTED TO SHEAR, IMPACT OF A FILLER TREATMENT

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## Abstract

The dispersion of a filler immersed in a polymer flow submitted to shear is the result of the counterbalance between hydrodynamic forces acting on the agglomerate and its cohesive forces. The nature of the filler, its surface treatment or its degree of infiltration by the polymer should impact its cohesivity. To better understand the influence of these parameters on dispersion, direct observations of dispersion mechanisms under shear were carried out on raw silica, silica treated with a covering agent and fully infiltrated silica agglomerates. Dispersion mechanisms and critical stresses for dispersion were determined and found to be different in those three cases.

*Key words: dispersion, infiltration, surface treatment, silica, elastomer*

## Introduction

Carbon black and silica are widely used as reinforcing fillers for rubber compounds in the tire industry. To improve the properties of the final product, it is necessary to optimize the dispersion of the filler. In the case of carbon black, two dispersion mechanisms are well known: rupture and erosion. Rupture is a sudden mechanism occurring at high hydrodynamic stresses and leading to the formation of a small number of relatively large fragments while erosion is a slow and gradual mechanism occurring at lower stresses and producing a large number of small aggregates [1], [2], [3].

Different parameters can modify the cohesivity of the agglomerate and thus change the level of stresses required for dispersion. In the case of silica, due to the poor interaction between the silica and the elastomer matrix, a coupling agent is often used to ensure the chemical junction between the filler and the matrix. The effect of such an agent is clear from the mechanical point of view: reduction of the Payne effect [4], enhancement of the dispersibility [5] and better dispersion state in the final product [6]. But its role in the dispersion process is assumed but there is no clear evidence.

Infiltration is another factor affecting the filler dispersion: it can affect both the hydrodynamic stress distribution within the agglomerate and the agglomerate cohesivity. Partial infiltration of a polymer in a reinforcing filler enhances erosion for small infiltration depth. Above a critical infiltration depth, erosion rate is reduced (see for example [7], [8]).

In this paper, we focus on the direct observation and the characterization of dispersion

mechanisms of silica agglomerates suspended in an elastomer matrix under shear. The behaviours of raw, pre-treated and pre-infiltrated by the polymer chains silica agglomerates are compared.

## Experimental

### Materials

The silica studied here is a highly dispersible precipitated silica: Zeosil 1115MP from Rhodia. Selected properties of this material are presented in Table 1.

Material	Surface area (m <sup>2</sup> /g)	Structure (ml/100g)	Surface chemistry (SiOH/nm <sup>2</sup> )
Silica Z1115MP	97	119	19,5

**Table 1:** selected properties of the silica studied

The polymer matrix used is a styrene-butadiene copolymer rubber: SBR 25E from Michelin.

The agent used to treat the silica surface is an octeosilane with the chemical formula: CH<sub>3</sub>-(CH<sub>2</sub>)<sub>7</sub>-Si-(H<sub>3</sub>C<sub>2</sub>O)<sub>3</sub>. It is a covering agent. It reacts with the silica surface via the ethoxy groups, but on the contrary to a coupling agent, there is no chemical reaction with the elastomer.

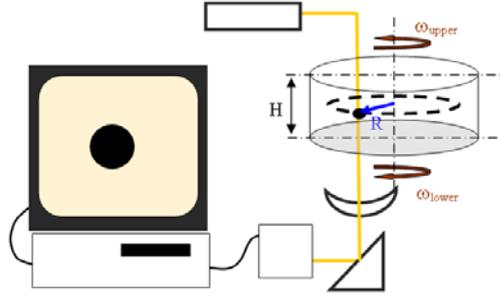
### Silica treatment

Silica was treated ex-situ in a rotational evaporator device. 80 g of silica were immersed in 320 ml of cyclohexane. 7.2 g of octeo were added to the suspension. Rotative agitation at 35 rpm and at room temperature was maintained for 30 min in order for the covering agent to react with the available surface of silica. Then, the oil bath of the device was heated at 60°C and the agitation raised to 45 rpm in order to help the evacuation of the cyclohexane. When the totality of the solvent was extracted, the oil bath temperature was raised to

90°C and maintained until all the extracted solvent was condensed. Silica samples were then rinsed and filtered with cyclohexane and tetrahydrofuran which is a polar solvent, in order to remove non grafted molecules. Samples were dried for 24 hours in a vacuum oven at a temperature of 80°C.

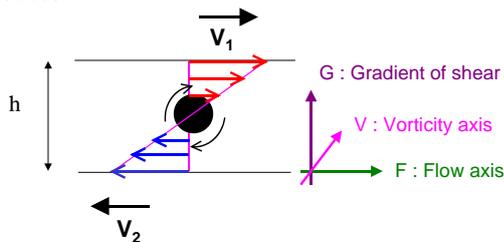
#### Dispersion experiments

Dispersion experiments were carried out using a transparent counter-rotating shear cell. This apparatus is depicted schematically in Figure 1 and the principle is represented in Figure 2. It consists of two glass plates rotating in opposite directions.



**Figure 1:** Schematic representation of the counter-rotating device

Each plate is driven by an independent motor. The advantage of this geometry is that the relative velocities of the two plates can be adjusted so that the velocity of a given particle can be set to zero in the reference framework of the laboratory. This allows to observe the behaviour of a particle suspended in a matrix under shear either for a certain period of time at a given shear or while increasing the shear rate and thus the applied shear stress.



**Figure 2:** Principle of the counter-rotating shear cell

Observations during shear are performed via an optical microscope linked to a camera and a monitor and recorded with a DVD recorder. The macroscopic shear rate applied to the matrix around the particle observed is calculated as follow:

$$\dot{\gamma} = \frac{(\omega_{upper} + \omega_{lower})R}{H} \quad (1)$$

Where  $\omega_{upper}$  and  $\omega_{lower}$  are the velocities of the two plates, R is the radial position of the particle observed and H the gap between the two plates. Knowing the dependence of the viscosity versus the shear rate, the applied shear stress is given by:

$$\tau(\dot{\gamma}) = \eta(\dot{\gamma})\dot{\gamma} \quad (2)$$

Where  $\eta(\dot{\gamma})$  is the viscosity of the matrix at a given shear rate.

In the case of the SBR polymer, the Cox Merz rule was checked to be valid (superposition of dynamic and capillary rheological measurements). The applied shear stress is then obtained with:

$$\tau(\dot{\gamma}) = \eta(\dot{\gamma})\dot{\gamma} = \eta(\omega)\dot{\gamma} \quad (3)$$

Where  $\eta(\omega)$  is the viscosity of the matrix at a given oscillation frequency, during dynamic rheological measurements.

Samples were made of several agglomerates put between two discs of matrix. For raw silica and silica treated with octeosilane, experiments were started 30 min after the sample was put in the shear cell and heated at 120°C, in order to have an homogeneous matrix around the agglomerates. For the study of fully infiltrated silica, experiments were conducted after 12 hours of contact between the agglomerates and the matrix at 120°C, under static conditions. After this period of time, silica agglomerates were fully infiltrated.

The procedure for dispersion was the same for all samples: the shear rate was increased until a dispersion mechanism occurred. In order to make good comparisons between observations, agglomerates were chosen spherical.

#### Results

For raw silica agglomerates, a new dispersion mechanism was observed that we called fragmentation. It is different from the classical rupture dispersion mode observed for example on carbon black agglomerates, which leads to the formation of a small number of relatively large fragments [3]. Here, a large number of small fragments are produced. Figure 3 shows a picture of an agglomerate before and after its fragmentation.



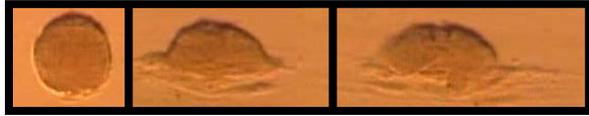
**Figure 3:** illustration of the fragmentation mechanism for a silica agglomerate with an initial radius of 37  $\mu\text{m}$  at 56s<sup>-1</sup>

Fragmentation was observed on silica for all studied agglomerates with a radius size between 10 and 100  $\mu\text{m}$ . Size of the resulting fragments was about 1 to 5  $\mu\text{m}$  large. Indeed, the dispersion is more efficient in comparison with the classical rupture mechanism.

For silica pre-treated with octeosilane, the dispersion mechanism was also fragmentation.

Pre-infiltrated silica showed a very different dispersion behaviour. At a critical stress, a slight deformation of the agglomerate followed by its

rapid gradual dislocation was observed. Figure 4 shows a sequence of dislocation of a fully infiltrated agglomerate.



**Figure 4:** Sequence of dislocation of a fully infiltrated silica with an initial radius of 35  $\mu\text{m}$

In comparison with the well known erosion mechanism, the dislocation mechanism is much faster and occurs at higher shear rates.

Criteria for dispersion were determined for the different silica agglomerates (raw, pre-treated, pre-infiltrated). The effect of the agglomerate size was investigated for each mechanism. Even if no difference in the dispersion mechanism was observed between raw silica and treated silica, critical stresses for dispersion were found to be considerably reduced by the treatment. For full infiltrated silica agglomerates, critical stresses for dispersion were directly proportional to the size of the agglomerates.

Those results will be presented in details and discussed during the presentation.

### Conclusions

Dispersion mechanisms for silica in an elastomer matrix are different from the ones observed for carbon black. Raw silica and pre-treated silica are dispersed via fragmentation while fully infiltrated silica can be dispersed by dislocation after deformation of the agglomerate. Level of stresses required for both mechanisms are different.

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