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# Internal structure and fragmentation kinetics of silica granules

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**Abstract.** To improve the mechanical properties of tires, silica granules can be incorporated into the elastomer as well as carbon black. Ideally, the fragmentation of the granules in the elastomer must be obtained with low mechanical stresses and lead to very small fragments distributed homogeneously in the material. On the other hand, granules must present a sufficient cohesion, in order to avoid the generation of fine particles during handling operations. Thus it appears necessary to control the mechanical strength of granules and the mechanism of their fragmentation. In this experimental study, we investigated the fragmentation of silica granules of 250 microns produced by spray drying. For this, we characterized by granulometry the evolution of the Particle Size Distribution of silica powder in water. The granules were suspended in water and submitted to ultrasounds. This treatment is used to create the fragmentation that occurs by viscous shearing in industrial rubber processing.
A core-shell structure, characteristic of granules obtained by atomization process, was observed by SEM. Furthermore, by varying the intensity of mechanical stress, the multi-scale structure of granules was evidenced as well as the existence of different regimes of fragmentation. The kinetics of fragmentation was experimentally followed on two grades of silica that showed significant differences in their behavior during the fragmentation process.

**Keywords:** Precipitated silica, ultrasound, dispersion, erosion, core-shell, kinetics.
**PACS:** 81.20.Ev

## INTRODUCTION

The use of mineral fillers in the formulation of tires is required in order to obtain a good abrasion resistance.

Carbon black is the material historically used for this purpose for reasons related to its natural affinity with the rubber. Other materials such as precipitated silica may achieve as good wear resistance as carbon black but reducing at the same time the rolling resistance of the tire and allow thus to increase the energy efficiency of vehicles equipped with such tires.

Thus, the Michelin Company has developed a green tire in 1992 by combining silica originally developed by Rhodia to a synthetic elastomer with a coupling agent.

The main disadvantage of the precipitated silica against carbon black lies in its lower ability to disperse into the rubber (Figure 1). The beneficial effects of the mineral filler on the abrasion resistance and the low rolling resistance are all the more important as the filler is distributed homogeneously in the tire. Thus its dispersion state must be optimized.

Therefore, the aim of this work was to study the dispersion of two precipitated industrial silica in liquid medium in order to identify the mechanisms of this dispersion.

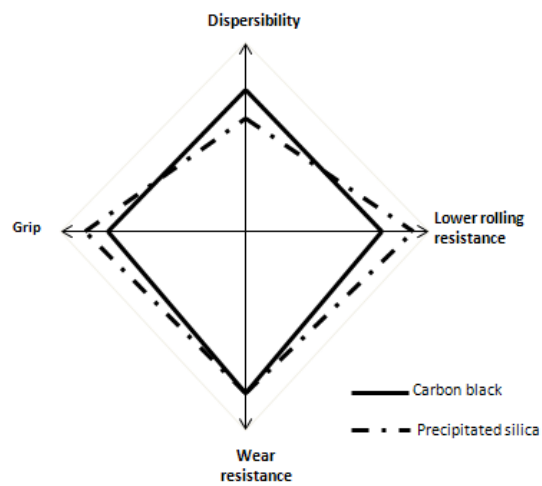


**FIGURE 1.** Advantages of precipitated silica against carbon black.

## MATERIALS AND METHODS

### Silica Powders

This study was realized with two types of industrial precipitated silica supplied by Rhodia. The products are named Z1115MP and Z1165MP. These

precipitated silica are widely used for rubber reinforcement. Observations using scanning electron microscopy (SEM FEG JEOL JSM 6500F) give information on the morphology (Figure 2). Silica granules appear as spherical micro-balls. The mean diameter of the two populations is similar (about 280 µm).

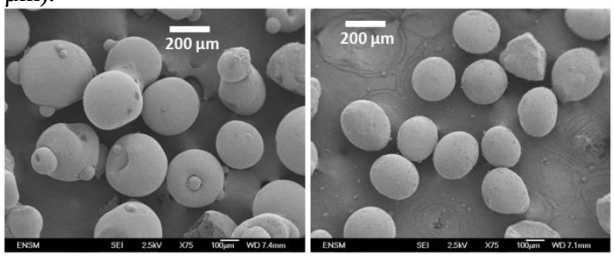


**FIGURE 2**. SEM observations of precipitated silica Z1165MP (left) and Z1115MP (right)

Physico-chemical properties of silica agglomerates are known to play a leading role during the mixing step with elastomer and other compounds. The main difference between the two precipitated silica is their specific surface area, determined with a sorptometer Micromeritics ASAP 2000, which is higher for Z1165MP (160 $m^2/g$) than for Z1115MP (110 $m^2/g$). MIP analyses (Micromeritics Autopore IV) showed that Z1115MP silica presents a bigger median pore diameter (48 nm) than the Z1165MP one (29 nm). These pores play an important role in agglomerate infiltration by the elastomer [9].

## Characterization of the Fragmentation of Granules in Water under Ultrasounds

In water, we have been using ultrasounds (US) to solicit the granules.

At low ultrasound power, the experiments are performed directly in the Malvern Mastersizer 2000 HydroS which is equipped with an internal ultrasound probe (max 26 W, 20 kHz, with a liquid volume of 142 mL, 100 mg of silica). After each US excitation, measurements of the particles' size are performed by Laser granulometry.

## Fragmentation Mechanisms

During several steps of the process, granules are subjected to mechanical solicitations that cause their fragmentation. Previous studies of agglomerates break-up have revealed different fragmentation mechanisms:

- The rupture mechanism [1,2,3] is characterized by an abrupt breakage of the agglomerate into a few large pieces.
- The erosion mechanism [4,5,6,7,8] is characterized by the detachment of small fragments from the outer surface of the agglomerate.
- The disintegration mechanism [10] corresponds to the creation of a large number of very small fragments in a short period of time.

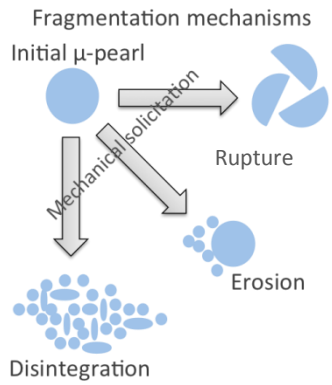


**FIGURE 3.** Fragmentation mechanisms

## RESULTS AND DISCUSSION.

The evolution of the particle size distribution of Z1115MP and Z1165MP silica with the duration of treatment is shown in Figure 4 and 5.

It is clear that the Z1115MP breaks much faster than silica Z1165MP. We also note that the initial population of the granules Z1115MP disappears in favor of a single mode population centered around about 12 µm, which suggests a mechanism of fragmentation by disintegration while Z1165MP silica gives rise to two populations, one centered on 10-12 µm, the other at about 40 microns, which rather suggests a mechanism of erosion or rupture.

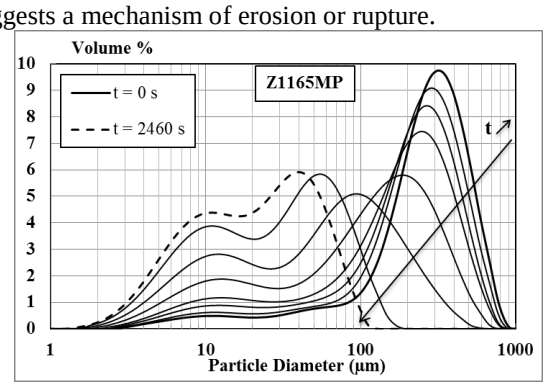


**FIGURE 4.** Evolution of PSD with time for silica Z1165MP for t=0s, t=12s, t=60s, t=120s, t=300s, t=600s, t=1200s, t=2460s

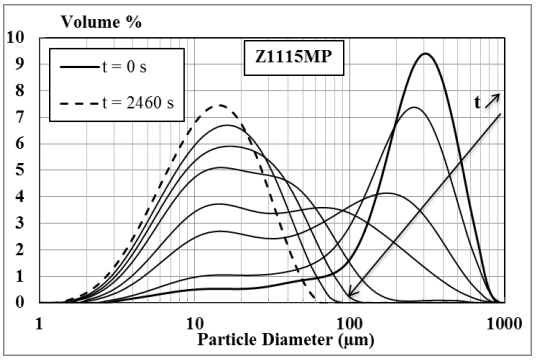


**FIGURE 5.** Evolution of PSD with time for silica Z1115MP for t=0s, t=12s, t=60s, t=120s, t=300s, t=600s, t=1200s, t=2460s

We have represented in Figure 6 for each sample studied the evolution of mean volume diameter $d_{43}$ with the duration of ultrasound treatment on a semi-logarithmic scale. $d_{43}$ is defined by : $d_{43} = \frac{\sum_i d_i^4}{\sum_i d_i^3}$

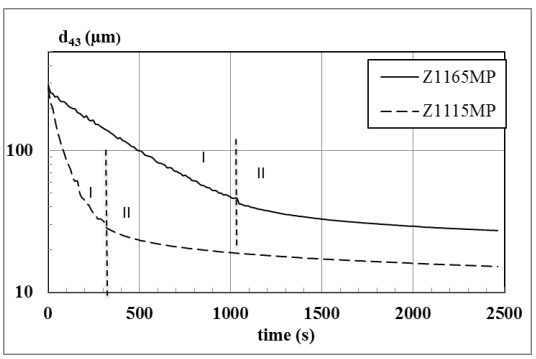


**FIGURE 6**. Evolution of $d_{43}$ with time for silica Z1165MP and Z1115MP

This representation clearly shows the presence of two regimes that can be characterized in a first approach by an exponential relation:

$$d_{43} = d_\infty + (d_0 - d_\infty)\, e^{-t/\tau} \qquad (1)$$

Values of $d_\infty$ and $\tau$ for both silica are shown in Table 1.

These results confirm that fragmentation is much faster for Z1115MP in the first instants and also that final size obtained is smaller for this precipitated silica powder.

To study the influence of the initial size of the granules on their fragmentation behavior, we separated the two silica powders into different size fractions by a soft sieving to avoid fragmentation of granules during this operation. Five classes were obtained: $\phi$<75µm, 75µm<$\phi$<125µm, 125µm< $\phi$<200µm, 200µm< $\phi$<250µm, $\phi$>250µm

The kinetics curves for each class exhibited similar exponential behavior.

The evolution of the first regime characteristic time $\tau$ with the initial size of the granules is given (Figure 7).

**TABLE 1.** Values of $d_\infty$ and $\tau$ for both silica powders

| | **Z1115MP** | **Z1165MP** |
|---|---|---|
| *First Regime* | | |
| Characteristic time $\tau$ /s | 53 | 192 |
| Initial diameter $d_0$ /µm | 273 | 274 |
| Limit diameter $d_\infty$/µm | 52 | 117 |
| *Second Regime* | | |
| Characteristic time $\tau$ /s | 1696 | 884 |
| Initial diameter $d_0$ /µm | 23 | 69 |
| Limit diameter $d_\infty$/µm | 12 | 24 |

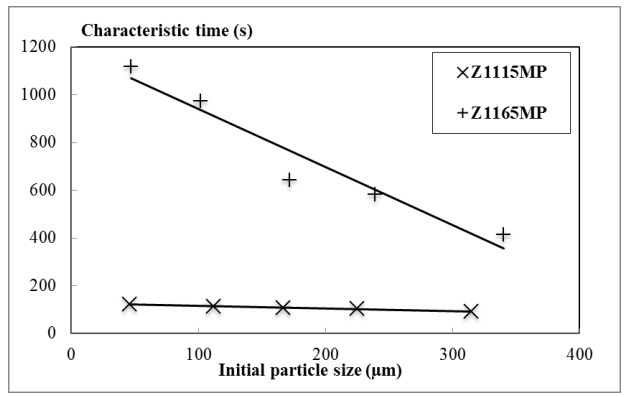


**FIGURE 7.** Evolution of the first regime characteristic time $\tau$ with initial particle size

It is clear that $\tau$ does not depend on the initial size of the granules for Z1115MP, but decreases as the size of the initial granules Z1165MP silica increases.

The results can be explained from the microstructure of the granules studied. Indeed it appears on the micrograph of a fragment of silica granule Z1165MP that they present a core-shell like structure with a denser surface (Figure 8), structure that the Z1115MP granules do not possess. This leads in particular to a micro hardness of the Z1165MP granules (3.3 $Nm^{-2}$) significantly higher than that of Z1115MP (1.3 $Nm^{-2}$).

We can thus easily understand that Z1115MP granules break much faster than the Z1165MP ones and we can also explain that the fragmentation of Z1165MP granules is as faster as the initial granules are large since the (granule surface area / granule volume) ratio decreases when the diameter of the granule increases, decreasing thereby the reinforcing effect of the surface shell with respect to the mass of solid concerned.

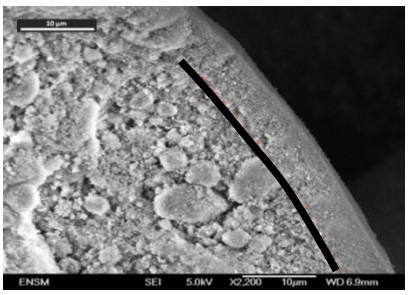


**FIGURE 8.** SEM picture of a Z1165MP fragment showing a core-shell structure (areas separated by the bold line).

## CONCLUSIONS

Silica agglomerates can be dispersed by two main mechanisms: disintegration and erosion. Many studies have clearly shown the efficiency of these mechanisms of dispersion in viscous media. In this paper, we have presented a new method to analyze the dispersion of precipitated silica in water. We have observed the same dispersion mechanism as in elastomer. This new method gives also access to the kinetics of dispersion. A size evolution equation introduced a new parameter, the characteristic time of dispersion. This parameter has been shown to be related to morphological information of the product in the case of a core-shell structure for Z1165MP micropearl.

## ACKNOWLEDGMENTS

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