New methods to analyse fragmentation mechanisms of precipitated silicas

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NEW METHODS TO ANALYSE FRAGMENTATION MECHANISMS OF PRECIPITATED SILICAS

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ABSTRACT

Precipitated silica is traditionally used as reinforcing filler in rubber applications. In pneumatic manufacture, it offers several advantages compared to carbon black. Indeed, in tyres treads, precipitated silica can yield a lower rolling resistance and better wet grip at equal wear resistance than carbon black.

The development of a new method to study the fragmentation mechanism of precipitated silica is investigated. Usually, the dispersion of granules is done in high viscous media (elastomer or oils). In this paper, the study is carried out in a friendlier medium (air or water).

KEYWORDS

Structure-property, Fluidized bed, Ultrasounds, Breakage, Attrition, Silica

1. INTRODUCTION

Precipitated silica is constantly gaining importance as reinforcing filler for rubber compounds. It offers several advantages compared to carbon black. In tyres treads, precipitated silica can yield a lower rolling resistance and better wet grip at equal wear resistance than carbon black (Figure 1).

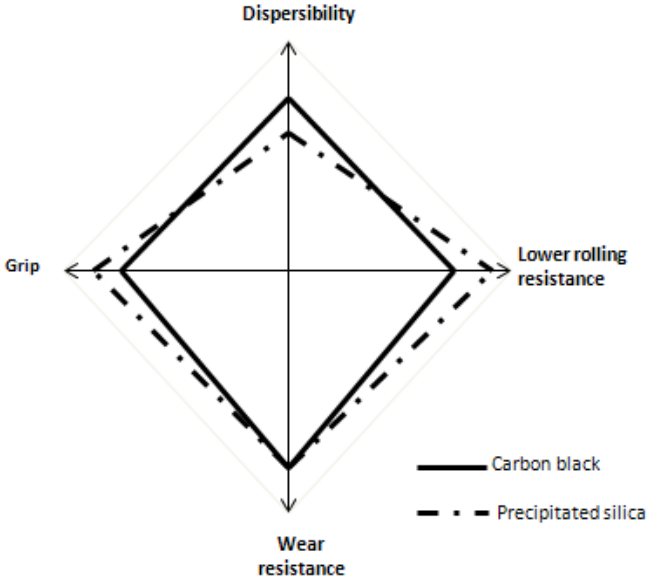

Figure 1. Advantages of precipitated silica against carbon black.

The capacity of precipitated silica in rubber is due to its high aptitude to disperse (decrease of granules size) and distribute (spatial repartition) in the elastomer during the mixing steps. Previous studies of agglomerates break-up have revealed different fragmentation mechanisms. One mechanism, denoted rupture [1,2,3], is characterized by an abrupt breakage of the agglomerate into a few large pieces. The second mechanism, named erosion [4,5,6,7,8], is characterized by the detachment of small fragments from the outer surface of the agglomerate. More recently, a third mechanism has been observed and called disintegration [7]. In this mechanism, a large number of very small fragments are created in a short period of time.

These fragmentation mechanisms are observed in viscous media (elastomers and oils) similar to the medium in which they will be dispersed (tyre rubber). In this paper, new and easier methods (in air or water) are suggested for the observation of fragmentation mechanisms and compared with previous results in viscous media. The proposed experimental protocols give the possibility to study in detail the dispersion kinetics.

2. MATERIALS AND METHOD

Products

The materials used in this study are precipitated silicas named Z1115MP and Z1165MP (supplied by Rhodia). Observations using scanning electron microscopy (SEM) 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).

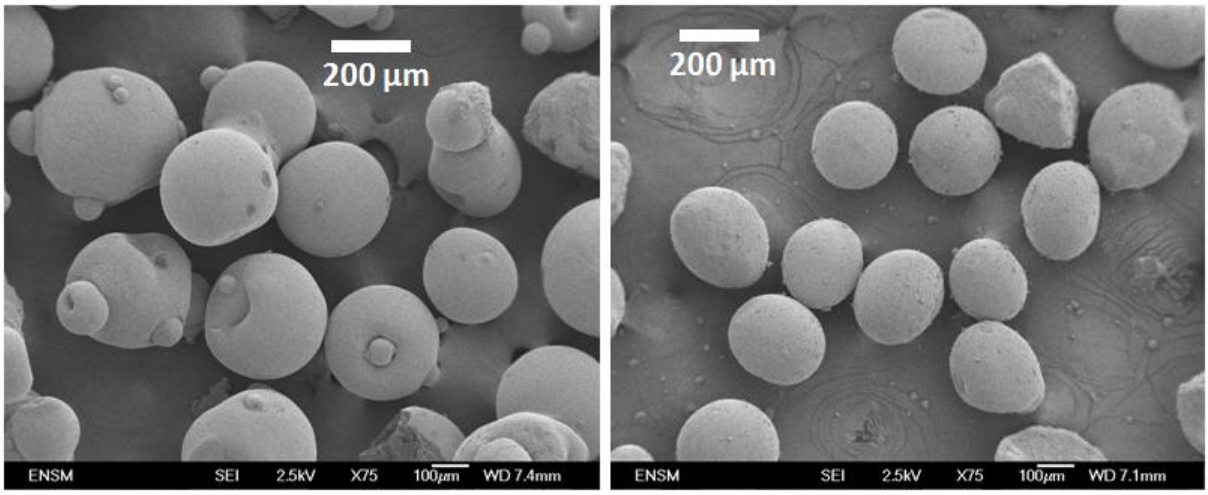

Figure 2. MEB observations of precipitated silica Z1165MP (left) and Z1115MP (right).

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 silicas is their specific surface area which is more important for Z1165MP (160 m^2/g) than for Z1115MP (110 m^2/g). Z1115MP silica presents a bigger median pore diameter than the Z1165MP one. This pore plays an important role in agglomerate infiltration by the elastomer [9]. The physical properties are presented in Table 1.

Table 1. Precipitated silica characteristics.

Typical analysis	Z1165MP	Z1115MP
BET specific surface area (m^2/g)	160	110
Median particles size (µm)	279±2	282±2
Median pore diameter (nm)	29	48
Elementary particle diameter (nm)	17	24

Devices for studying fragmentation in air

In order to evaluate the behaviour of precipitated silica granules in air, two tests have been designed: the first one is a high energy breakage test and the second one a low energy breakage test.

The first test consists in a wall impact experiment. In this test, some granules are accelerated thanks to a Venturi system and undergo high energy collisions against a wall. The Venturi system is characterized by its pressure drop. When the pressure drop increases, the granule velocity increases. The granule breaks into small fragments, which sizes are measured by laser granulometry (Malvern Mastersizer Scirocco). We can modify the pressure drop to analyze the influence of the granule velocity on the fragmentation.

The second test is led in a fluidized bed. Usually in this test, a large number of granule-granule low energy collisions are observed. The fluidization device is composed of a glass tube fed at its bottom by an air jet (flow speed: 6 cm/s). A mass of 10 grams of silica is fluidized for a time between 1 and 8 minutes. Then, the air jet is stopped and the size distribution is measured (Malvern Mastersizer HydroS).

Device for studying fragmentation in water

In water, we have been using ultrasounds (US) to solicit the granules. The experiments are performed directly in the Malvern Mastersizer HydroS which is equipped with an internal ultrasound probe (max 26 W, 20 kHz, with a liquid volume of 160 mL, 100 mg of silica).

After each US excitation, measurements of the particles' size are performed by laser granulometry.

Fragmentation description

Two complementary parameters are chosen to describe the fragmentation.

The first parameter is the weight fraction P_{50} of grains whose size remains under 50 µm. It is especially convenient to describe the generation of fine particles during the impacts.

The second parameter is the reduction index K, chosen to quantify the overall size reduction during the fragmentation.

$$K = 1 - \frac{d_{43}^{t}}{d_{43}^{0}}$$ *Eq (1)*

d_{43}^{0} and d_{43}^{t} are respectively the mean particle size (volume) at initial time and after a solicitation time t.

This parameter is mostly influenced by the biggest granules and is relatively unaware of the existence of small particles created during the solicitation.

3. RESULTS AND DISCUSSION

Fragmentation in air

High energy breakage test (impact on a wall)

The PSD curves obtained for different initial grains velocities give information on the fragmentation mechanisms (Figure 3).

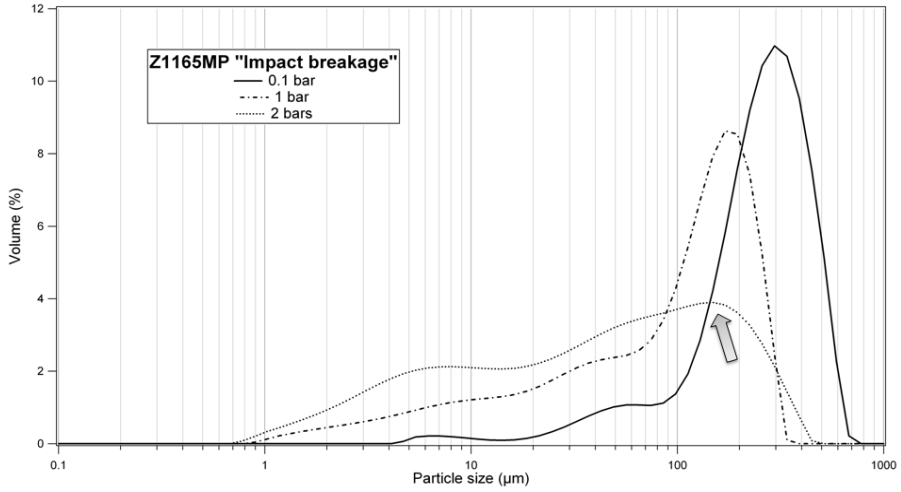

Figure 3. Impact breakage test for Z1165MP.

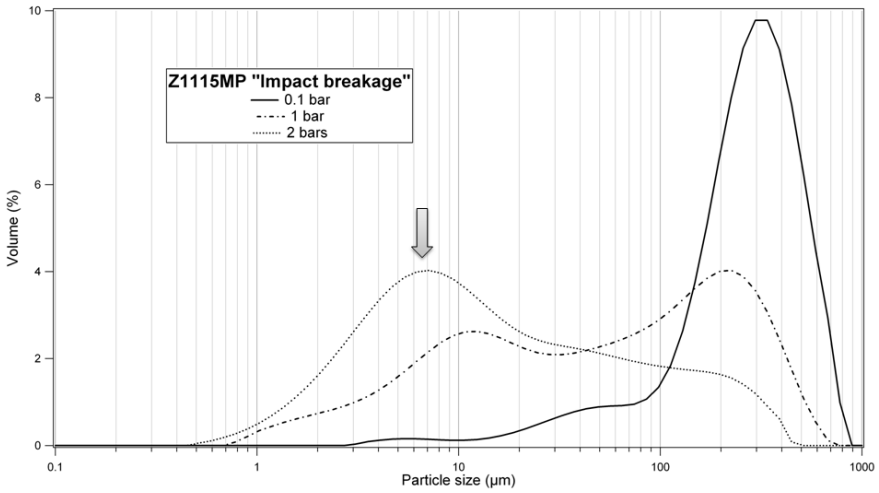

Figure 4. Impact breakage test for Z1115MP.

For a high impact velocity (ΔP=2 bars), the main population appears at 7 µm for Z1115MP while Z1165MP has its main population at 140 µm. We observed, between ΔP=0.1 bar and ΔP=1 bar, that the main peak of the initial population is shifted towards smaller sizes for Z1165MP while, for Z1115MP, only the fraction of granule of this size is reduced. According to Sahoo's [10] definition, it matches to an erosion mechanism for Z1165MP. In addition, the Z1115MP granules break quickly and with a lower impact velocity (ΔP=0.5 bar).

Low energy breakage test (fluidized bed)

In a fluidized bed, inter-granules collisions are predominant, albeit some impacts between granules and the column are present. This second type of impact is much less violent than in the impact breakage test. The PSD of the two precipitated silicas after different solicitation times are presented in Figure 5 and Figure 6.

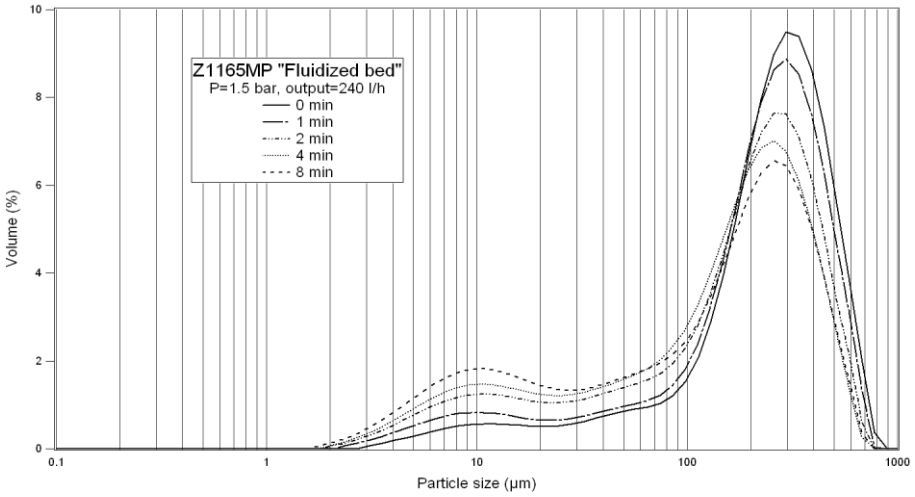

Figure 5. Fluidized bed test for Z1165MP.

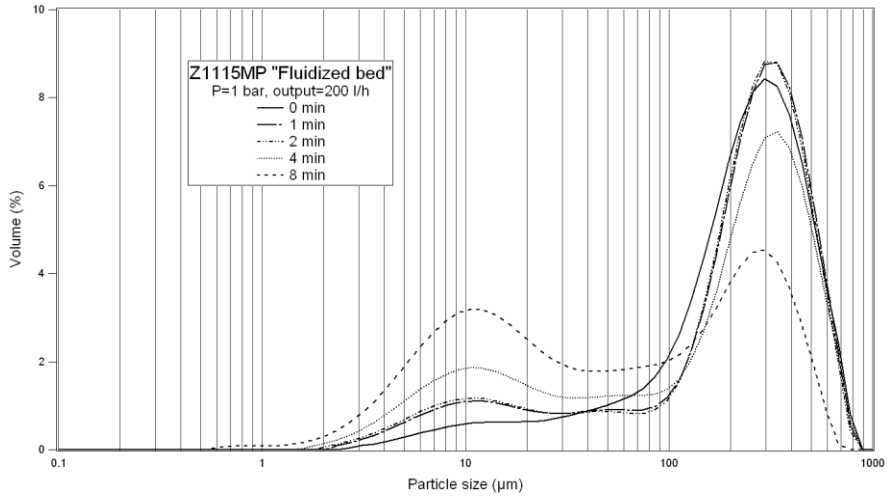

Figure 6. Fluidized bed test for Z1115MP.

After solicitation in fluidized bed, we can observe the same kind of results as with the previous high energy test, that is to say an important population appears at 10 µm for Z1115MP. The initial population disappears more quickly for Z1115MP than for Z1165MP.

Now, we shall use the two parameters, the reduction index K and P_{50} previously introduced, to study the fragmentation.

In a fluidized bed (Figure 7), we do not observe a major variation of K and P50 for a solicitation time between 1 and 4 minutes. For a much longer time (8 min), Z1115MP generates many small fragments with an important reduction of size. An energy gap seems to appear between 4 and 8 min. Indeed, for the three first points (at 1, 2, and 4 min) there is no large variation of the two parameters. But between 4 and 8 min, increases of K (for the two silicas) and P_{50} (for Z1115MP) are observed.

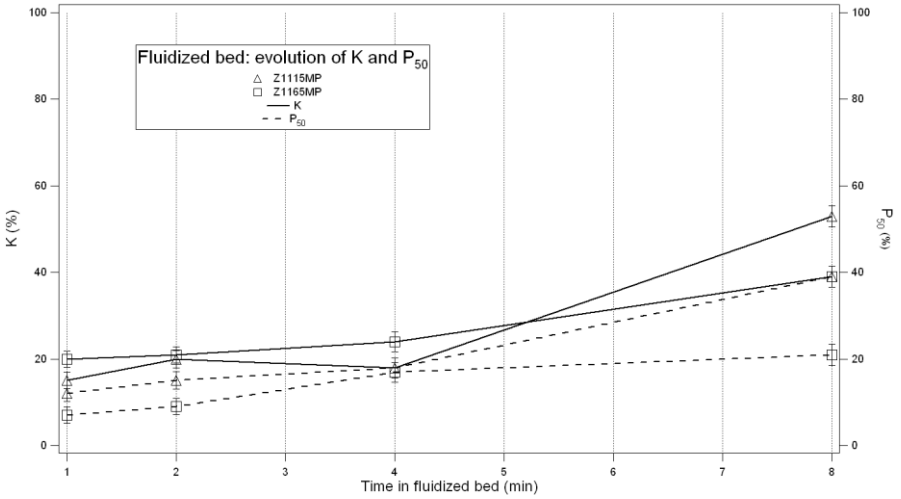

Figure 7. Fluidized bed results about reduction index K and P_{50}.

In a second step, results of impact breakage (Figure 8) are analyzed with the two descriptors. For Z1115MP a larger reduction of size and a more important formation of fine fragments than for Z1165MP are observed. The reduction index is always 20% bigger for Z1115MP for a pressure drop greater than 1 bar.

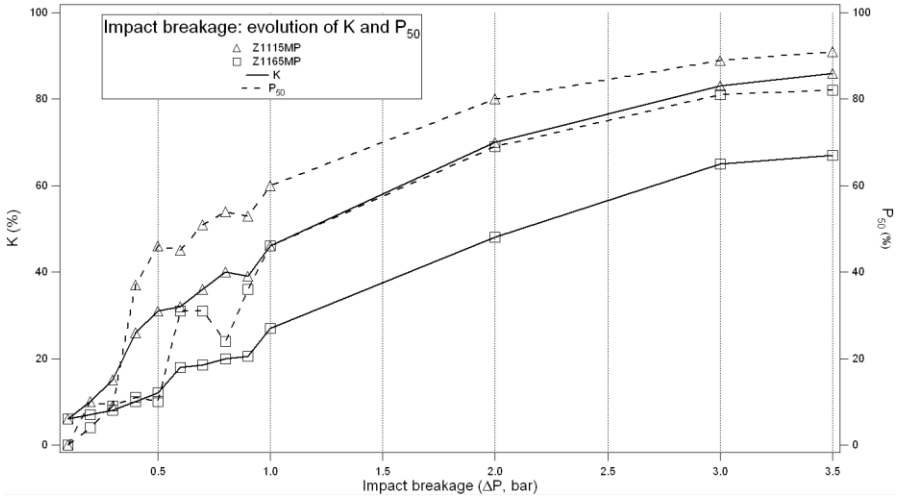

Figure 8. Impact breakage results about the reduction index K and P_{50}.

Whatever the test and the associated collision energy, we observe that the Z1115MP silica creates more fine particles than the Z1165MP one, and that a fraction of the main peak of initial population is always present for Z1165MP. That suggests an erosion or rupture in small fragment

mechanism. For Z1165MP, the fine generation is less intense but a reduction of size is observed with a shift of the main peak of initial population. That is consistent with a rupture mechanism.

Put all together, these results suggest that:

- The Z1115MP is more brittle than Z1165MP for high energy collisions.

- Fracture is favoured vs. Erosion when the impact energy increases.

- The energy of solicitation plays a role in the fragmentation mechanisms.

- Collision energy in fluidized bed is approximately equal to collision energy in impact test with a pressure drop of 0.5 to 1 bar.

Fragmentation in water

An observation of the fragmentation in water is done with an ultrasound probe (0.26 W) to disperse the agglomerates.

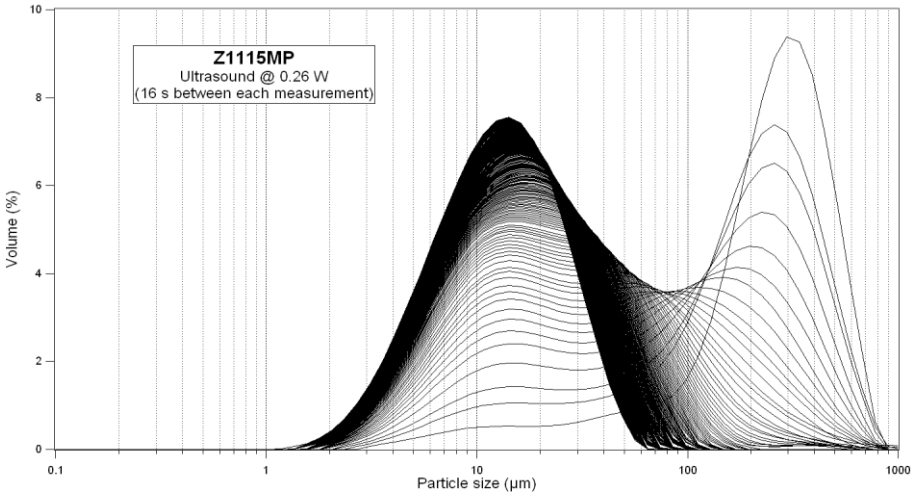

Figure 9. PSD evolution of Z1115MP during ultrasonic excitation (16 s of ultrasound between each curves).

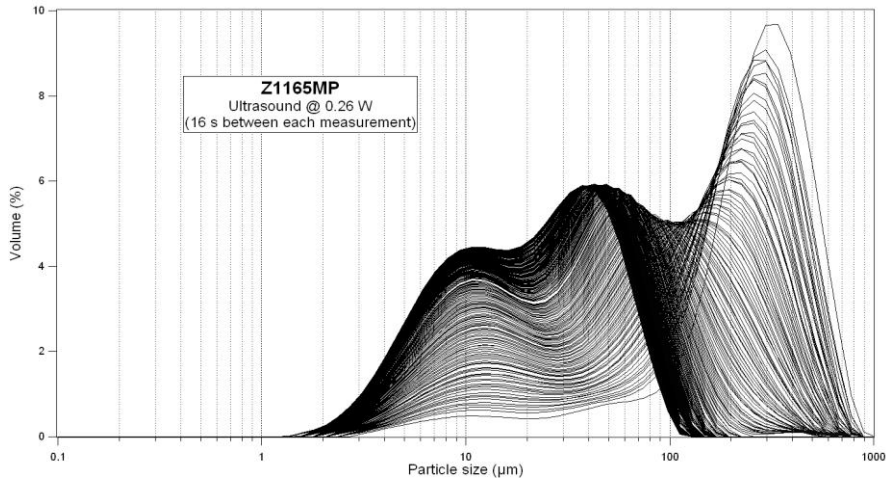

Figure 10. PSD evolution of Z1165MP during ultrasonic excitation (16 s of ultrasound between each curves).

The silica Z1165MP seems to break slowly in comparison with Z1115MP. During the solicitation by ultrasounds, two modes of population appear for the Z1165MP (maximum at 10 and 60 µm) whereas the Z1115MP presents only one population mode (at 10 µm). This observation leads us to postulate the existence of two different fragmentation mechanisms linked to the solicitation route.

When analyzing with the descriptors introduced before (K and P_{50}: Figure 11) more information about the mechanisms can be derived.

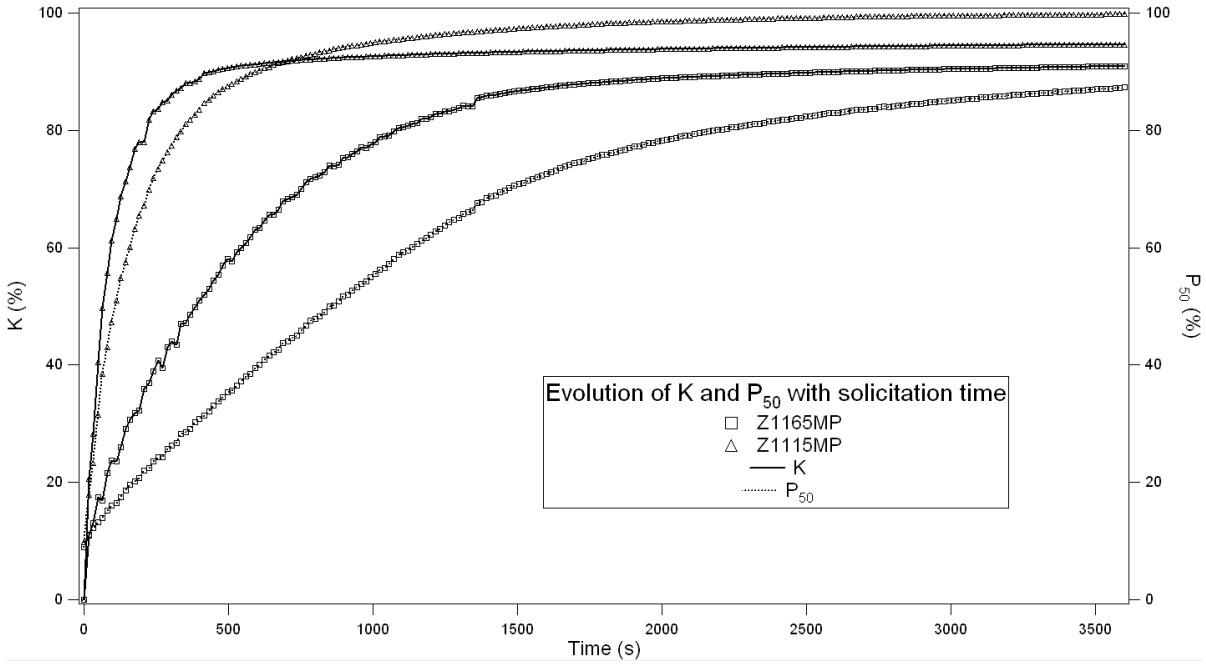

Figure 11. Time evolution of the average size reduction (K) and the fines generation (P_{50}).

A very quick size reduction is observed for Z1115MP since more than 50% of granules have a size under 50 µm after 110 seconds of solicitation. Again, this is compatible with erosion mechanism. The Z1165MP is slower to break, the fraction of granules with size under 50 µm increases linearly during the first minutes of solicitation. 850 seconds are needed to have 50 % of the granules under 50 µm. The initial population of Z1165MP disappears slowly while a population of fine particles (10 µm) is created. This analysis for Z1165MP confirms the rupture mechanism.

Size evolution equation

From the PSD, the evolution of particle size (d_{43}) as a function of the solicitation time t is studied (Figure 12). A fit of the curve by an exponential law (Eq. 2) with a characteristic time τ is performed and gives a fairly good agreement.

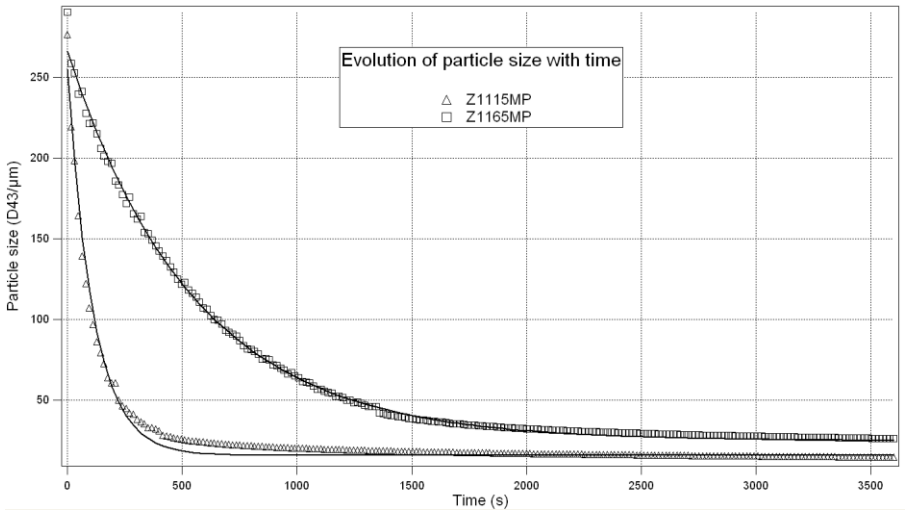

Figure 12. Evolution of particle diameter with solicitation time t.

$$d_{43}(t) = d_{\infty} + (d_0 - d_{\infty}).e^{-\frac{t}{\tau}} \qquad Eq\ (2)$$

$d_{43}(t)$ is the particle size diameter (averaged in volume), d_0 and d_∞ the sizes at the beginning and after an infinite time of solicitation, τ the characteristic time of granule fragmentation.

For a given set of experimental conditions, this equation brings us quantification of the limit size (thermodynamics data) and characteristic time of granule fragmentation (kinetics data) (Table 2).

Table 2. Characteristic time for Z1165MP and Z1115MP.

	Z1165MP	Z1115MP
Characteristic time τ (s)	510	100
Limit size d_∞ @ 0.26 W (µm)	22	12

Thanks to this characteristic time, we find again that Z1165MP breaks-up slowly in comparison with Z1115MP. The asymptotic fragment size is also different for these silicas. Z1165MP seems harder to fragment with a limit fragment size of 22 µm and only 12 µm for Z1115MP. These two results show that the Z1165MP silica presents a better strength resistance to breakage.

4. CONCLUSION

Silica agglomerates can be dispersed by rupture and erosion. Many studies have observed these mechanisms of dispersion in viscous media. In this paper, we have presented new methods (in air and in water) to analyse the dispersion of precipitated silica. We have observed the same dispersion mechanism as in elastomer. These new methods give also access to the kinetics of dispersion. Finally a size evolution equation introduced a new parameter, the characteristic time of dispersion.

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