

Size and stability control during wet nanomilling using SMLS technology



Introduction

The demand for nanoparticles has been rapidly increasing with the growing nanomaterials applications - from construction and coatings to energy, cosmetic and pharmaceutical industries. The particles are mainly prepared in a milling process during which bigger particles are reduced in size to meet the requirements for the application. The characterization of manufactured nanoparticles is essential to reduce material's costs and assure quality and safety that are critical and can be highly difficult issues. Thus, the particle size and its evolution during this process are the most critical to address the issues of: end-user specification, possible agglomeration of nanoparticles, milling efficiency, optimization of the required process energy, process scaling-up...

The demands for size and stability testing during nanomilling are high. The method must provide wide size measuring range (100 nm to 100µm), wide particle concentration range, very short measuring time (reduction of process downtime), non-destructive testing, sensitivity, high cleanability and safe operation with respect to nanoparticle risk prevention.

KEY BENEFITS

FAST
NO DILUTION
SENSITIVE

This study will focus on the top-down manufacturing of nanoparticles and nanosuspensions by wet milling process. In order to optimize this process, the efficiency of the milling as well as the particles' stabilization state in the formulated slurry have been assessed.

Materials & Methods

Materials

Slurries of silica powder in demineralized water were prepared with a high shear disperser at 2 concentrations: 13 and 23 % w/w.

Equipment

The nanomilling was performed on a LabStar Zeta® (Netzsch) - a horizontal agitator bead mill at laboratory scale. The beads used were yttrium-stabilized zirconium oxide with a mean diameter of 0,4 mm. The milling chamber was filled at 90% v/v with the beads. The circulation mode (continuous pumping between a mixing vessel and the milling chamber) was chosen. The mixing vessel and the milling chamber were cooled using a double jacket system.

Method

Turbiscan® is based on SMLS technology for Static Multiple Light Scattering which consists in sending a light source (880 nm) on a sample and acquiring Backscattered (BS) and transmitted (T) signal. The signal intensity (BS) is directly linked to the concentration (φ) and the mean spherical equivalent diameter (d_{mean}), according to the Mie theory with the equation:

$$BS = f(\varphi, d_{mean}, n_p, n_f) \quad n_p, n_f: \text{refractive indexes}$$

By repeating this measurement over time at adapted frequency, the instrument enables to monitor physical stability and follow phenomena as sedimentation.

Based on this layer formation kinetics, the software enables to access directly to the hydrodynamic diameter d_h of particles using Stokes equation and knowing hydrodynamics parameters (the concentration φ , the phase densities, viscosity of continuous phase).

This technique requires no sample preparation (i.e dilution or stress) and the sample is measured at rest in its native state.

Results

Size measurement

During the milling process, a single measurement (25 seconds per sample) of withdrawn sample at specific milling time enables to compare the backscattered signal as shown on figure 1 and relates it to average particle size.

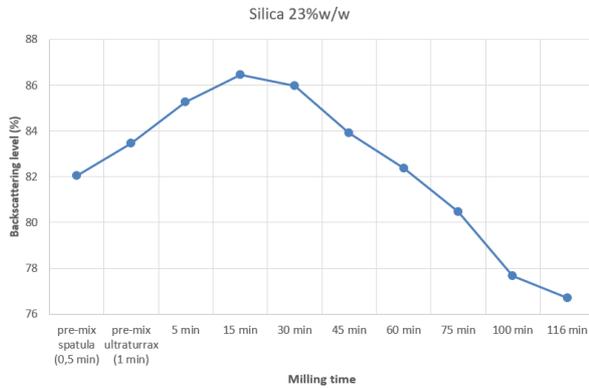


Figure 1. Backscattering level versus milling time

Figure 1 shows a bell shape curve as expected by the theory. Knowing the concentration and refractive indices it is possible to obtain the mean diameter (shown in the table 1) for both silica concentrations from the BS signal.

| 13% | d_{mean} (nm) | 23% | d_{mean} (nm) |
|-----------------------------|-----------------|-----------------------------|-----------------|
| pre-mix spatula (0,5 min) | 1860 | pre-mix spatula (0,5 min) | 1840 |
| pre-mix ultraturrax (1 min) | 1210 | pre-mix ultraturrax (1 min) | 1690 |
| 5 min | 1150 | 5 min | 1520 |
| 10 min | 1080 | 15 min | 1420 |
| 15 min | 330 | 30 min | 240 |
| 20 min | 310 | 45 min | 230 |
| 25 min | 310 | 60 min | 220 |
| 32 min | 290 | 75 min | 210 |
| 45 min | 250 | 100 min | 200 |
| 60 min | 230 | 116 min | 190 |

Table 1. Mean diameter d_{mean} versus milling time for both silica concentrations

BS signal is very sensitive to small diameter evolution as it still evolves for long milling time whereas diameter values seem to reach a plateau.

CONCLUSION

Turbiscan® allows the mean diameter of suspensions to be measured in only 25 seconds. Longer analysis permits to follow stability of sample and reach hydrodynamic diameter from sedimentation kinetics layer. The advantage is to determine the sample characteristics without sample preparation or dilution and provide information relative to actual dispersion state during the milling process.

Stability measurement

Figure 2 gives the mean diameter on left axis and on right axis the TSI (Turbiscan Stability Index) which sums all the variations in the sample and quantifies sample overall stability at given time.

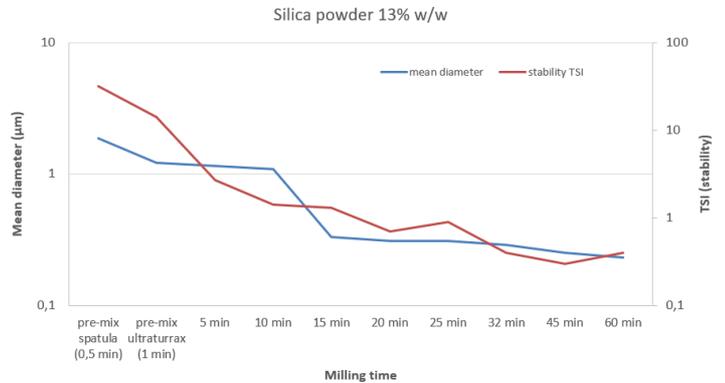


Figure 2. Mean diameter d_{mean} and TSI stability versus milling time for silica 13%w/w

At the beginning of the milling process the stability varies most. With milling time, aiming to reduce particle size to reach hundreds of nanometers, the dispersions are more and more stable showing the efficiency of milling.

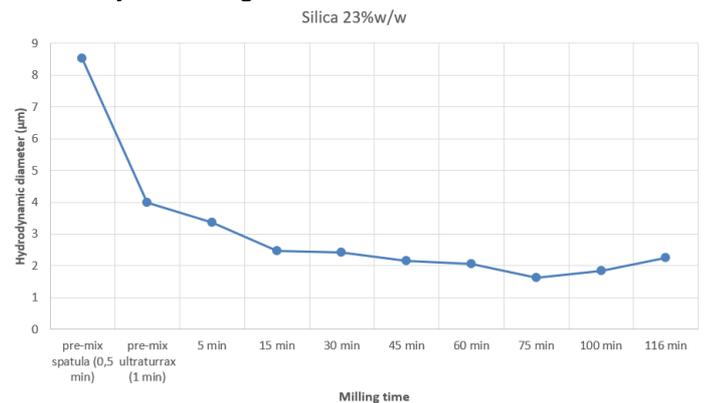


Figure 4. Hydrodynamic diameter d_h versus milling time for silica 23%w/w

Hydrodynamic diameter is higher than mean diameter as it is sensitive to the presence of bigger particles that are settling first. This diameter decreases with milling time. At long times, it starts to increase again showing a re-agglomeration process.