EFFECT OF SiO_2 NANOPARTICLES ON THE MECHANICAL/PHYSICAL PROPERTIES OF SiO_2 MICROPARTICLES MIXTURES

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Abstract

Mechanical/physical properties are the most important parameters that determine the ease with which silica powders can be handled, stored, transported and processed. Because of silica powders have wide range of its application from pharmaceutical industry, printer toners and electronic parts to application in cancer treatment. Due this fact the silica belongs to highly studied substances across different fields. This is a material with a huge potential and very unique mechanical/physical properties of SiO_2 powders which make them very attractive. In this paper, friction properties, compressibility factors and flowability of SiO_2 microparticles with nanoparticles addition have been investigated. For this purpose a several mixtures with different amount of nanosilica were prepared and characterized. Experimental work was performed by the Freeman Technology FT4 Powder Rheometer, CPS DC24000 Disk Centrifuge and laser particle size analyzer Cilas 1190 in Laboratory of Bulk Materials in Ostrava. Also a basic characterization such as SEM images, shape analysis etc. of the raw input material was made. The first results show that additions of nanoparticles influences all studied parameters. This study make a significant contribute to the valorization "dry-coated fine particles" theory, which is based on guest-host contacts.

Keywords: Silica, nanoparticles, rheological properties, flowability, compressibility

1. INTRODUCTION

The application of nanotechnology in processes related to bulk materials has registered significant growth in recent years [1]. Using a simple admixture to modify the surface of micro-particles with nano-particles is considered an effective way of improving the fluidity of the mixture (powders) without the need for solvents or fillers (binders) in the use of many types of equipment, including a conical screen mill (Comil), magnetically assisted impaction coater, etc. [2, 3, 4]. Also often talked about here is an improvement in the other properties of standard materials, both mechanical and physical, as well as e.g. thermal [5, 6]. This information could make it interesting to study whether the admixing of different concentrations of nano-silica might influence the mechanical/physical properties (flowability, angle of internal friction, wall friction, compressibility) of micro-silica powder, as shown below. The aim of this paper therefore is to characterize and compare the micro-particles of a SiO_2 sample and the nanoparticles of a SiO_2 mixture. Four mixtures were prepared with increasing proportions of the nanoparticles of SiO_2 in the sample, i.e. 0.5, 1.0, 1.5 and 2 %. The samples were tested in terms of their bulk and friction properties in a powder rotational Rheometer. An analysis of selected measured data is the content of individual sections.

2. MATERIALS AND METHODS

Micro- and nano- particles

Micro-silica is a commercially available material. This is an amorphous form of silica. It is used as filling material, as a filter, performance additive, etc. [7]. To carry out a morphological assessment, SEM photos of microsilica, nanosilica and mixtures containing 1 % nanosilica were obtained (**Fig. 1**, A-C).

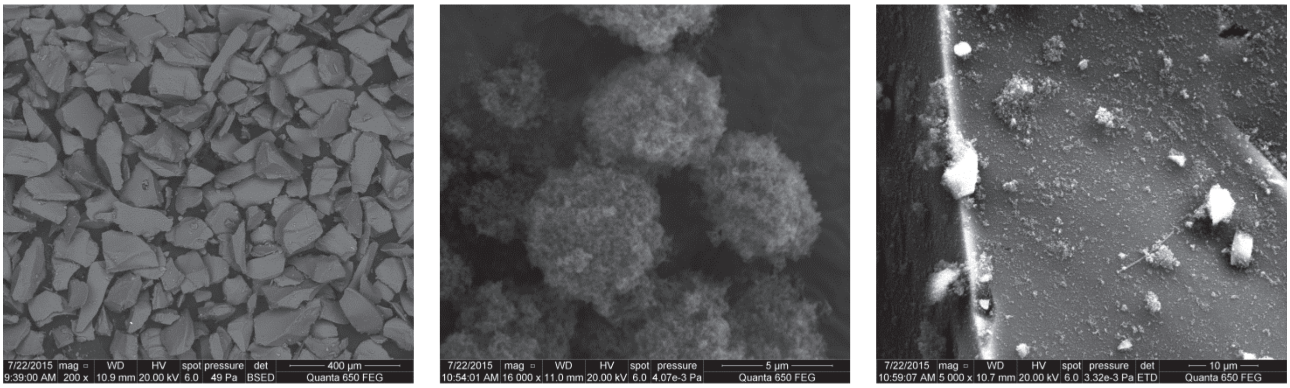


Fig. 1 SEM photos, A **-** Microsilica, B **-** Nanosilica, C **-** Surface of microparticle with nanoparticles

Aerosil® is a commercially available product of colloidal silicon dioxide (SiO_2), which is produced by the high-temperature hydrolysis of silicon tetrachloride in an oxygen flame gas [8]. Aerosil® consists of highly dispersed, amorphous silica, the characteristics of which can be changed by the right reaction conditions. These changes do not affect the amorphous form or content of silica. What is changed, however, is the size of the particles, specific surface area, hydrophilic nature and density. Aerosil® is designated with the number 200, which indicates the specific surface area ($m^2.g^{-1}$).

Particle size distribution

The particle size analyzer CPS Disc Centrifuge DC24000 was used to measure particle sizes in the range of 0.01 micron to 40 microns. The system is most effective with particles between 0.02 and 30 microns. The analyzer measures particle size distribution using centrifugal sedimentation within an optically clear spinning disc that is filled with fluid. Sedimentation is stabilized by a density gradient within the fluid, and the accuracy of the measured sizes is ensured through the use of a size calibration standard known before each test. The concentration of particles for each size is determined by continuously measuring the turbidity of the fluid near the outer edge of the rotating disc. Also used for measuring particle size distribution was the particle laser analyzer CILAS 1190 within the range of 0.4 μm - 2500 μm [9]. Given the properties of SiO_2, the wet mode of measurement was chosen.

Bulk properties

The device used for measuring the bulk properties was the FT4 Powder Rheometer. FT4 is a universal powder tester, combining patented blade methodology for measuring flow energy with a range of shear cells, wall friction modules and other accessories for measuring bulk properties [10]. The methodologies allow flow energy to be measured in relation to many variables and all packing states, the shear properties of consolidated or unconsolidated powders, bulk properties **-** bulk density and compressibility. The above properties allow the powder samples to be comprehensively characterized for the extreme packing and environmental conditions that occur in everyday processing.

Angle of internal friction

The rotary shear module for measuring friction parameters consists of a vessel containing the sample powder and a shear head to cause normal and shear stress. The blades of the shear head sink into the mass powder and the front face of the head starts to apply normal stress to the surface of the powder bed. The shear head moves downwards until a sufficient and stable pressure is applied between the head and powder bed. Then the shear head starts to rotate slowly and thus cause shear stress within the bulk mass. The shear plane is formed just below the end of the blades. Since the powder bed prevents the rotation of the shear head, the shear stress in the measuring plane increases until slippage occurs. Then, the maximum value of transferred shear stress is recorded.

Compressibility

Compressibility is measured as the change in volume or density, respectively, depending on a normal load. The data obtained are quantified by expressing the percentage of compressibility for a normal load of 15 kPa applied by the module, which is part of the FT4 Powder Rheometer.

Wall friction angle

The wall friction angle is the angle at which bulk material begins to slide over the bed. The wall friction coefficient varies with the size of normal pressure. It strongly depends on the type and surface of the contact material. The measurement is based on the same principle as measuring the angle of internal friction. Only the shear head does not have shear blades, but a circular plate representing the contact material.

3. RESULTS AND DISCUSSION

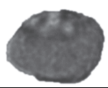
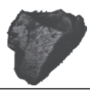
Laser diffraction particle size distribution of micro-silica was carried out using Cilas 1190 using the wet mode. The results are given in **Table 1**. The data consists of the average values from five measurements.

Table 1 Particle size distribution of microsilica

Microsilica	d_{10}, [μm]	d_{50}, [μm]	d_{90}, [μm]
Mean	56.2	117.2	191.2
Min. value	55.1	115.9	189.0
Max. value	58.2	119.0	195.1

The laser analyzer is also equipped with an instrument for particle shape analysis. The results of several parameters for samples of nanosilica and microsilica are given in **Table 2**.

Table 2 Shape analysis of nano- and micro- silica

Material	Nanosilica	Microsilica
Shape		
Sphericity	0.7	0.5
Heywood circularity factor	1.0	1.2
Elongation	0.16	0.25
Convexity shape factor	0.9	0.7

The Heywood Circularity Factor (HCF) is the ratio between the perimeter of the particle and the perimeter of a circle with the same area. The closer the shape of the particle is to the ideal circle, the closer HCF equals 1. Nanosilica consists of extremely small spherical particles (see **Table 2**), unlike microsilica, where angular particles can be seen. The parameter of elongation is useful for acicular or needle-like particles. Microsilica particles have a higher elongation parameter. The convexity shape factor is the ratio between the convex polygon perimeter and the perimeter and suggests the possibility of wedging particles. A value close to 1 approximates a spherical shape [11].

The resulting values of the particle size distribution of the nanosilica of Aerosil® are shown in **Fig. 2**.

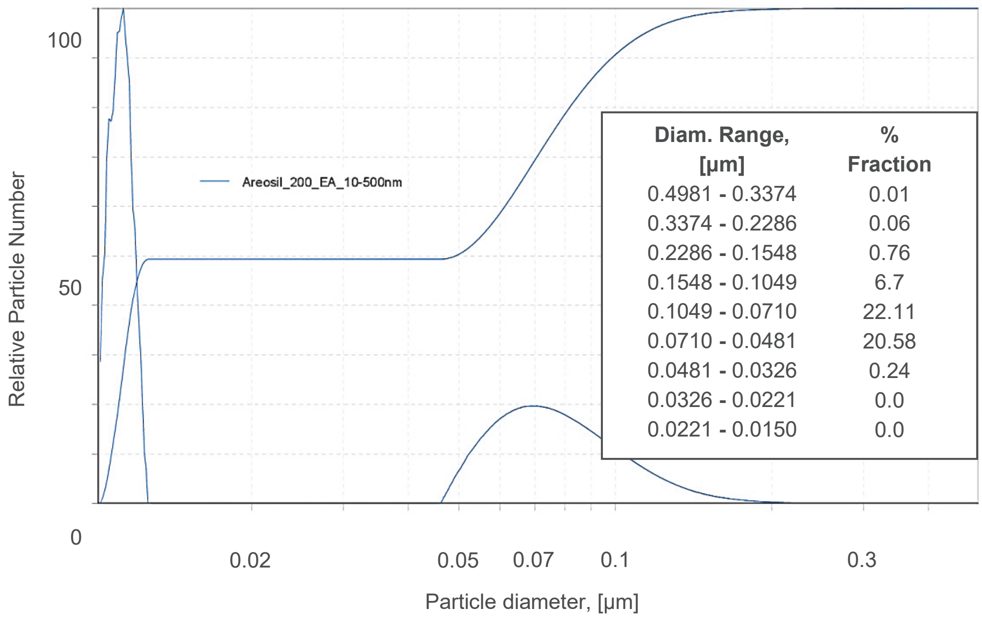


Fig. 2 Particle size distribution of silica nanoparticles

Aerosil® 200 contains a substantially larger fraction of nanoparticles in the range of 10 - 15 nm (greater representation in the number of particles observed in the sample) and furthermore a fraction with larger particles of around 70 nm, which logically corresponds to a volumetric greater representation (lower representation in the number of particles observed in the sample).

The data obtained from measuring the angle of internal friction, compressibility and wall friction for all of the prepared mixtures is shown in **Fig. 3**. The results of several parameters such as cohesion, bulk density, compressibility at different pressures for all samples of nanosilica and microsilica are given in **Table 3**. According to the flow function (ff > 10) all mixtures are in the mode of free-flowing materials, expect for a mixture with 0.5 % nanoparticles, which falls under easy-flowing mode [12]. The chart shows that with an increasing amount of nanosilica, the angle of internal friction, compression factor and the wall friction angle slightly increase. This trend demonstrates also values in **Table 3**.

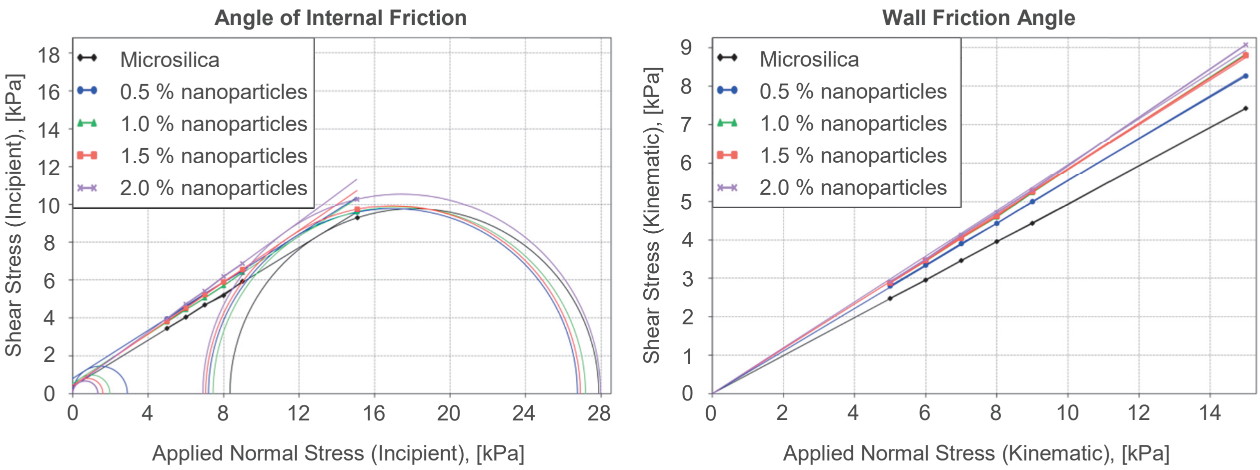


Fig. 3 Angle of internal friction and wall friction angle for different concentrations of nanosilica

Table 3 Flowability, compressibility and friction tests results for different mixtures

Material	Microsilica	0.5 % nanosilica	1.0 % nanosilica	1.5 % nanosilica	2.0 % nanosilica
Cohesion, [kPa]	0.374	0.796	0.535	0.422	0.337
Unconfined Yield Strength, [kPa]	1.34	2.90	1.97	1.60	1.32
Major Principle Stress, [kPa]	27.9	26.8	27.2	26.9	28.0
Flow Function ff, [-]	20.9	9.23	13.8	16.8	21.1
Angle of internal friction, [°]	31.5	32.4	33.0	34.4	36.1
Bulk Density, [g/cm³]	1.91	1.71	1.69	0.973	0.955
Compressibility at 10 kPa [%]	3.22	5.63	6.02	7.46	12.2
Compressibility at 15 kPa [%]	3.62	6.15	6.75	8.43	13.4
Wall Friction Angle, [°]	26.3	28.7	30.9	30.7	31.7

The reason may be a high degree of aggregation of nanoparticles. Acting between the nanoparticles of silica are London-van der Waals forces, which occur as a result of their temporary and fluctuating dipole nature due to the deformation of electron density [13]. These interactions are inversely proportional to the sixth power of the particle radius.

It is for this reason that this force becomes important for nanoparticles, whose natural tendency is aggregation. This is why it is very difficult to isolate primary Aerosil nanoparticles in a dry system. This will probably lead to only a partial (slight) separation of the primary nanoparticles that adhere to the surface of the microsilica and, on the contrary, to an increase in the overall roughness of the surface thanks to the discontinuity of the cover of the entire surface area. This will increase the angle of internal friction and wall friction. A partial separation of the primary particles of Aerosil® will probably occur due to the negative triboelectric charge on its surface. Siloxane ($Si\text{-}CH_3$) and silanol (Si-OH) groups are created during the production of fumed silica - Aerosil® [14]. These groups tend to generate the aforementioned negative triboelectric charge. This negative charge on the surface can cause the mutual repulsion of particles of nanosilica. Interactions with micro SiO_2 can therefore also exist. For a more efficient separation of primary nanoparticles (effective guest-host contacts) in dry systems, it is probably necessary to use external energy (strong mechanical vibrations, noise), which would help overcome their inter-particle interactions.

4. CONCLUSION

The results presented in this article show a change in the mechanical and physical properties of the microparticles of powdered silica due to the incorporation of the nanoparticles of silica Aerosil® 200. In all samples containing 0.5 - 2 % silica nanoparticles, a slight increase in the angle of internal friction, wall friction and the compression factor was observed. This fact highlights the very difficult isolation of primary nanoparticles and their natural tendency to agglomerate into larger clumps in the dry mode due to London-van der Waals forces. The probable unnoticed adhesion of a minority portion of nanoparticles to the surface of microsilica can cause surface imperfections (low number of quest-host contacts) and this increases the above mechanical and physical properties.

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