

THE IMPACT OF PROCESS PARAMETER ON SILANE MODIFICATION OF FUMED SILICA BY USING SUPERCRITICAL CO₂

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ABSTRACT

Nano-SiO₂ particles are widely used in composite materials, biomaterials, sensors, etc. These particles possess specific characteristics and are easily agglomerated because of their dimensions and high specific surface area. The surface of nano-SiO₂ particles should be modified to achieve better dispersion and deagglomeration as well as better functionality. Coating of fumed silica with silane using a modified supercritical antisolvent (SAS) coating process was investigated in this research. An organic modification of the surface of fumed silica in a CO₂ medium was performed, where CO₂ was used as the antisolvent and a silane coupling agent γ -methacryloxypropyltrimethoxysilane (MEMO) was the modification reagent. The fumed silica was used in the form as thixotropic gel. The operating parameters that have an effect on the coating process, such as silica to silane ratio and pressure were studied as impact on the particle size, distribution and amount of coated silane. The results were compared with the modification carried out in a conventional organic solvent and it can be concluded that the process time significantly decrease by using the supercritical antisolvent coating process. It is shown that the silane to silica ratio and the operation pressure are critical for the successful coating of silica particles with minimum agglomeration. Thermogravimetric analysis showed that with pressure increase and lower silica to silane ratio the percentage of coated silane increase. The organic modification process using supercritical CO₂ as the antisolvent has the advantages of being simple, effective, and green. The results are important for obtaining nanofillers with enhanced dispersion and polymer wetting that could be used for obtaining composite materials with considerable improved mechanical properties.

INTRODUCTION

Nanoparticles have many special characteristics and are widely used in the fields of composite materials, biomaterials, sensors, etc., but they have the problem that they are easily agglomerated because of strong interactions between the particles. Good dispersion is the key in many applications. Chemical modification of the particle surface can enhance the dispersibility of nanoparticles in various continuous phases, change the surface activity, and bring about new surface physical and chemical characteristics.

Advancements in nanocomposites are highly dependent on the compatibility between the organic matrix and inorganic fillers, and the dispersion level of fillers throughout the matrix.

Alkoxysilanes have been widely used to modify the silica particle surfaces in order to improve their compatibility and dispersion properties of particles. They can change the hydrophilic properties of silica into hydrophobic or partially hydrophobic. In the literature there are some data about surface modification of nanoparticles in supercritical conditions [1-10] but there are no data about silica particle modification with γ -methacryloxypropyltrimethoxysilane.

Coating of fumed silica with silane using a modified supercritical antisolvent (SAS) coating process was investigated in this research. The supercritical CO₂ has low viscosity and the absence of surface tension in supercritical fluids allow the complete wetting of substrates with intricate geometries, including the internal surface of agglomerates [7]. An organic modification of the surface of fumed silica in a CO₂ medium was performed, where CO₂ was

used as the antisolvent and a silane coupling agent γ -methacryloxypropyltrimethoxysilane (MEMO) was the modification reagent. The fumed silica was used in the form as thixotropic gel. The operating parameters that have an effect on the coating process, such as silica to silane weight ratio and pressure were studied as impact on the particle size, distribution and amount of coated silane.

EXPERIMENTAL

1. Material

AEROSIL 380, Degussa, specific surface area $S_{\text{BET}} = 380 \pm 30 \text{ m}^2/\text{g}$ was used. Primary nanoparticles of fumed silica (7 nm) can form aggregates (300–500 nm) and agglomerates ($>1 \mu\text{m}$) under atmospheric storage condition (DLS). The initial silica was heated at $140 \text{ }^\circ\text{C}$ for 4 h to remove adsorbed compounds, then cooled to room temperature and stored in closed glass vessels. The structural characteristics of these particles were studied in previously published paper [11].

The organosilane γ -methacryloxypropyltrimethoxysilane (Dynasylan® MEMO, Hüls, Germany), with molecular formula $\text{C}_{10}\text{H}_{20}\text{O}_5\text{Si}$, was used as a coating agent for the silica surface modification.

2. Preparation of silica thixotropic gel

Silica powder (10 mass %) was dispersed in absolute ethanol on magnetic stirrer for 15 min. After that the solution was treated with ultrasound for 30 min on temperature between $20 \text{ }^\circ\text{C}$ i $30 \text{ }^\circ\text{C}$ to formed sol solution. The additional evaporation and sedimentation leads to forming of thixotropic gel.

3. Supercritical process

The experimental set-up, schematically shown in **Fig. 1**, consists of a CO_2 cylinder, refrigerator supply, high pressure pump and a high-pressure vessel (Autoclave Engineers Supercritical Extraction Screening System) having a capacity of 300 ml. The high-pressure vessel has a temperature and pressure control. A metering pump (tip) was used to deliver liquefied CO_2 from a CO_2 cylinder to the high-pressure vessel. However, before entering the pump head the liquefied CO_2 was cooled down to around $0 \text{ }^\circ\text{C}$ by using a cryostat.

The prepared sample of silica and silane was placed in the extractor vessel and desired temperature and pressure was achieved during continuous stirring. Process was remained under the same conditions for two hours. After that, the extractor was depressurized by 5 bar per minute and extracted with 250 g fresh CO_2 to remove the rest of ethanol and silane.

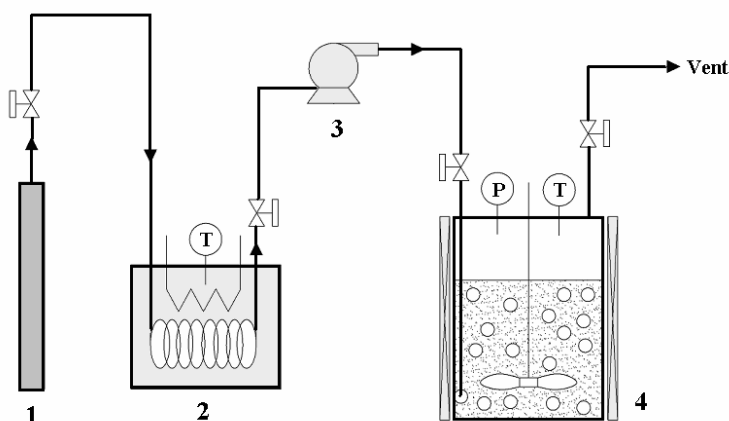


Figure 1. Schematic diagram of nanoparticle coating process: (1) CO_2 cylinder; (2) cryostat (3) high pressure pump (4) extractor

4. Characterization

Distribution of particle sizes was obtained using by system for detection of light scattering (Brookhaven Instruments Light Scattering System) equipped with BI-200SM goniometer, BI-9000 AT correlator, temperature controller and argon-ion laser (Coherent

INOVA 70C argon-ion laser). Measurements of Dynamic Light Scattering (DLS) were performed using by laser excitation at 514.5 nm and detection angle of 90°. Distributions of the particle sizes were calculated by software ``Brookhaven Instruments Particle sizing software``. The dispersion solutions of the nanopowders in ethanol were prepared for measurement of light scattering.

The thermal gravimetric analyzer (SDT Q600, TA Instruments, USA) was used to measure surface absorption of silica before and after surface treatment. The silica powders were heated from room temperature to $T_1 = 120\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$, held at this temperature for 10 min and then heated at $20\text{ }^\circ\text{C}/\text{min}$ to $T_2 = 800\text{ }^\circ\text{C}$ and held at this temperature for 10 min under a nitrogen atmosphere. The percentage of coated silane onto silica surface was calculated only in the temperature interval between 120 and $800\text{ }^\circ\text{C}$. In that interval only the chemisorbed silane was detected and the physisorbed silane was dried on the temperature below $120\text{ }^\circ\text{C}$.

FTIR spectra were obtained in transmission mode between 400 and 4000 cm^{-1} using a resolution of 8 cm^{-1} and using spectrophotometer ``BOMEM``, (Hartmann&Broun, MB-series, Baptiste, Canada) for detection the availability of the silane groups on the surface of the nano-SiO₂ particles.

RESULTS AND DISCUSSIONS

1. Silica nanoparticles modified with silane in conventional procedure

Fumed silica was modified in conventional procedure described in previously published paper [11]. The nanoparticles obtained on such way show the very narrow particle size distribution with average particle diameter about 361.7 nm.

2. Influence of the pressure of supercritical process

The experimental data and the results for fumed silica coated with silane in SCCO₂ realized by changing the pressure using above explained procedure, is shown in **Table 1**.

Table 1. The experimental data for silica nanoparticles coated with silane in SCCO₂

Sample	T, °C	P, bar	Weight of SiO ₂ , g	Volume of silane, ml	Percent of coated silane, %	Particle dimension, nm	Distribution
Pure silica (a)	-	-	-	-	-	1068.3	bimodal
(b)	40	160	5.0	9.0	63.3	423.3	bimodal
(c)	40	200	5.0	9.0	70	373.2	mono

The FT-IR spectroscopy of γ -MPS-functionalized SiO₂ (**Fig. 2a**) showed the absorption bands at 2953 , 1718 , and 1633 cm^{-1} result from the stretching vibration of CH₃, C=O, and C=C groups of γ -MPS, respectively. The changes of FT-IR spectra between modified and unmodified particles confirmed that γ -MPS was successfully attached to the surface of the nanoparticles.

By increase of pressure the obtained nanoparticles are smaller and amount of coated silane is higher (**Figs. 2b** and **3**). That was the consequences of CO₂ density increase with pressure at the same temperature. At higher CO₂ density the diffusion coefficient is higher and mass transfer through material is faster as results like smaller particles (the powder is deagglomerat) with narrow distribution and more attached silane on the surface of the particles. These results show that CO₂, in supercritical state has a high solvating power like organic solvent and on the other side it possesses physical properties (low viscosity and surface tension, rapid osmosis in micro-porous materials as well as high diffusion coefficient) similar to gasses enabling very well and uniform wetting of the nano-SiO₂ particle surface.

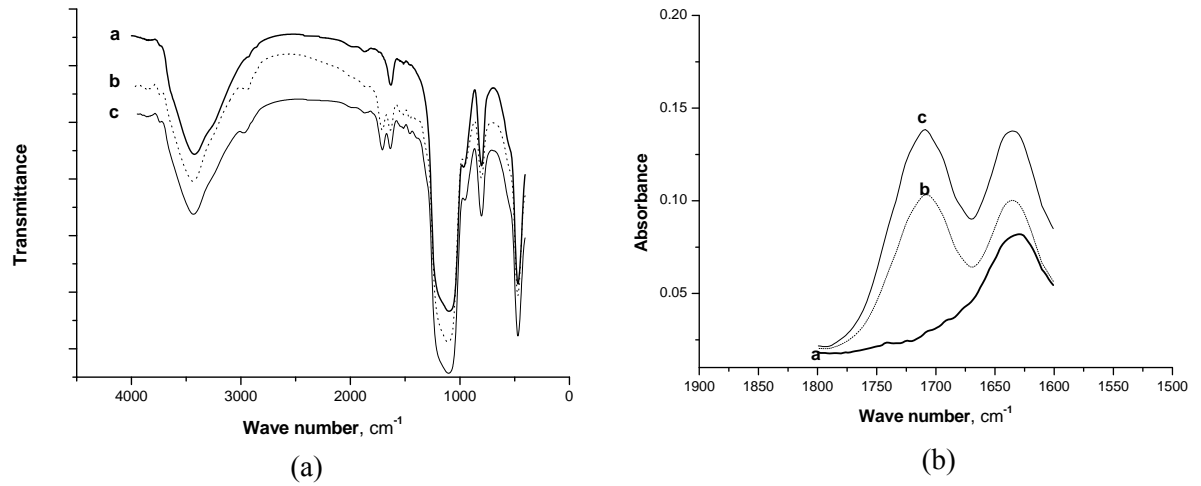


Figure 2. FT-IR spectra of silica nanoparticles: (a) pure (1068.3 nm), (b) coated with silane at 40 °C and 160 bar (423.3 nm) and (c) coated with silane 40 °C and 200 bar (373.2 nm)

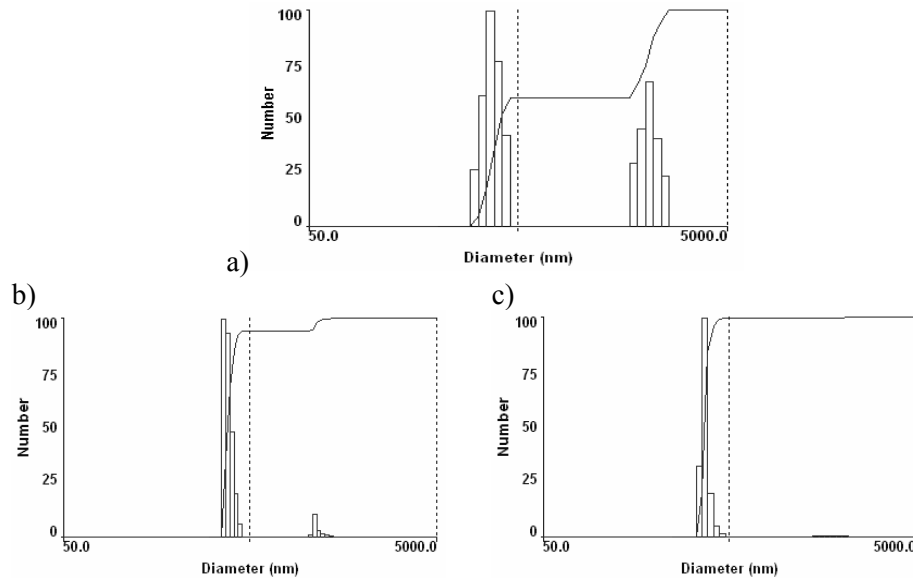


Figure 3. DLS of silica nanoparticles: (a) pure fumed silica (1068 nm), (b) coated with silane at 40 °C and 160 bar (423.3 nm) and (c) coated with silane 40 °C and 200 bar (373.2 nm)

3. Influence of the silica to silane ratio

The results of influence of silica to silane ratio at two different pressures applied during SCCO₂ fumed silica coating are given in **Table 2**.

Table 3. The experimental data for fumed silica coated with silane in SCCO₂ with different silica to silane ratio

Sample	T, °C	P, bar	Ratio silica to silane	Percent of coated silane, %	Particle dimension, nm	Distribution
Pure silica	-	-	-	-	1068.3	bimodal
1	40	160	1.0 : 2.0	56.6	557.2	mono
2	40	160	1.0 : 1.5	63.3	423.3	bimodal
3	40	200	1.0 : 1.0	80.0	387.4	bimodal
4	40	200	1.0 : 1.5	70.0	373.2	mono

The particles treated by SCCO₂ with higher silica to silane ratio at the both experimental conditions (160 and 200 bar) (Table 2) show very narrow distribution of particle sizes (557.2 and 373.2 nm, respectively). The lower silica to silane ratio at the same conditions indicates that a bimodal distribution could be obtained. At the 200 bar and molar silica to silane ratio 1.0 : 1.0 the agglomerates of about 280 nm as well as small amounts of agglomerates higher average size of 1115 nm were appeared (Fig. 4b)

The lower silica to silane ratio (1:1) gives the higher amount of coated silane on the surface of the silica particles as can be concluded from the FT-IR analyzes (Fig. 5b).

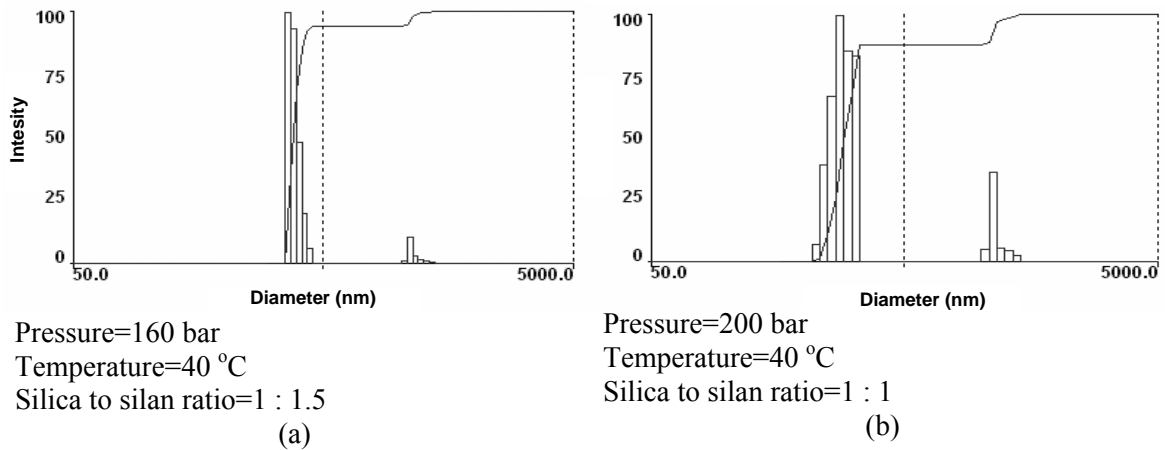


Figure 4. DLS of silica nanoparticles coated with silane at different conditions

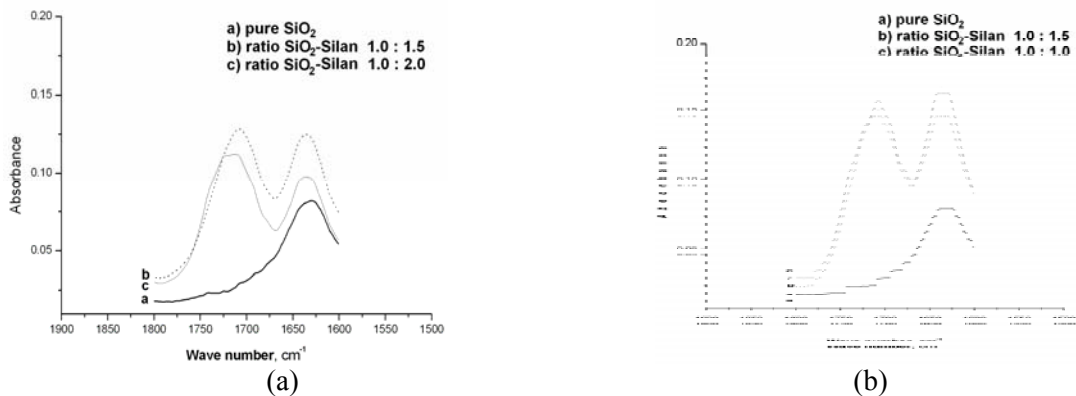


Figure 5. FT-IR spectra of silica nanoparticles: influence of silica to silane ratio at (a) 40 °C and 160 bar i (b) 40 °C and 200 bar

CONCLUSION

The operating parameters that have an effect on the coating process performed using SCCO₂ (silica to silane molar ratio and pressure) were studied. They have impact on the particle size, distribution and amount of coated silane. The results were compared with coating process based on usages of conventional organic solvent. It was found that almost the same dispersion and deagglomeration could be realized with the both used method (supercritical CO₂ and conventional) but the process time was significantly reduced (2 hours in comparison to about 8 hours in conventional method). It is shown also that the silane to silica ratio and pressure are critical for the successful coating of silica particles producing particles with minimum agglomeration. Thermogravimetric analysis showed that particles treated in supercritical CO₂ were more thermal stable than particles treated by conventional method. Process modified of SiO₂ particles coating by supercritical CO₂ as antisolvent has the advantages being simple, effective, and environmentally benign process. The results are important for obtaining useful nanofillers with enhanced dispersion and polymer wetting that could be used for obtaining composite materials with considerable improved mechanical properties.

AKNOWELEDGEMENTS

The financial support of the Eureka project: E!3524-Poly-Comp is gratefully acknowledged.

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