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Geometric and mechano-sorption modification of fumed nanosilica in the gaseous dispersion media

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Methods of geometric and solvate-stymulated mechano-sorption-activated modification of fumed nanosilica in the gaseous dispersion media were developed and used to prepare functionalyzed nanofillers for polymeric systems. Non-volatile high- and low-molecular weight compounds (such as polymers, organic bioactive compounds, organic and inorganic salts) can be used as modifiers of nanofillers.

Key words: geometric modification, mechano-sorption modification, gaseous dispersion media, fumed nanosilica, Densil, Sol-Densil, nanofillers.

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Introduction

Various amorphous fumed nanosilicas synthesized using a high-temperature hydrolysis of $SiCl_4$ can have the specific surface area in the range of 50 - 500 m^2/g with the average diameter on nonporous primary nanoparticles (NPNP) from 50 to 5 nm, respectively. Surface silanols as main adsorption and reactive sites can bind a certain amount of water. NPNP form aggregates (< 1 μm) and agglomerates of aggregates (> 1 μm) (Figure 1) forming visible loose particles with the bulk density of 0.04 - 0.06 g/cm^3 [1].

Nanosilicas are widely used in various applications in industry, agriculture and medicine [1-3]. Nanosilicas, especially functionalized ones, are the best fillers of polymers, good additives to paints, effective thickeners of various dispersion media, etc. [3]. To improve the properties of nanosilicas, they can be treated using methods of chemical, adsorption, and geometric modification.

Chemical methods for nanosilica modification, such as hydrophobization or grafting functionalities with certain active groups (C=C, NH, COOR, etc.), are frequently used in industry to prepare effective fillers for various systems [4]. However, in certain cases non-chemical modification of nanosilica could be preferable [5].

At the Chuiko Institute of Surface Chemistry, laboratory and pilot technologies of geometric and adsorption modification of nanosilicas were developed for the gaseous dispersion media [6]. The aim of this study was to analyse structural features of modified nanosilica, which can be used as a filler of polymers.

I. Materials and instruments

Fumed silica A-300 with the specific surface area of 300 m^2/g and bulk density of 0.05 g/cm^3 (Kalush, Ukraine) was used as the initial material.

Two types of ball mills, such as (i) a laboratory mill with ceramic drum volume (V) ~ 1 l, and (ii) a pilot mill with V = 200 l (Ukraine), were used as simple technological equipment for nanosilica modification. The rotation speed of the mills was the same as 60 rpm.

II. Results

Gas-phase geometric modification (GM) with mechanical loading.

Promising filler "Densil" (Figure 2) was developed using mechanical activation of nanosilicas in a ball-mill. Densil is characterized by higher bulk density (300-400 g/dm^3), lower gelling ability, lower osmotic activity and lower dust formation than initial nanosilica [7].

An important property of Densil is its relatively low thickening ability. The value of the concentration of silica (wt. %) at which the gel forms (Gel point) was

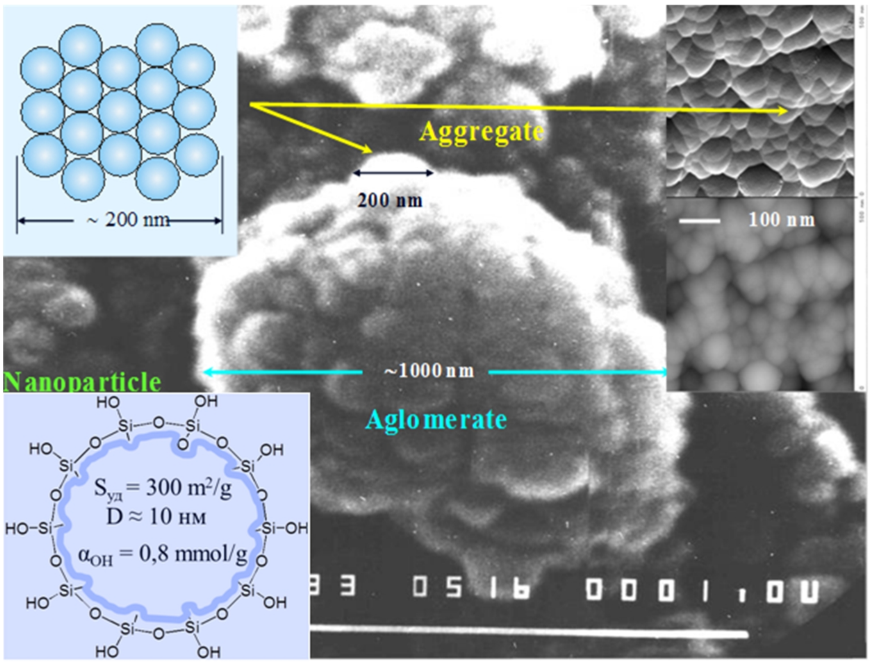


Fig. 1. Scheme and SEM and AFM images of nanosilica with primary particles forming aggregates and agglomerates.

used in express method for evaluating the thickening ability of silicas.

The results of the study showed that the Gel point of the initial nanosilica A-300 was 10 wt.% and 5 wt% in water and vaselin oil, respectively. For Densil, these parameters had values of 50 and 26 wt. %, respectively. This means that the thickening ability of the Densil filler in both the polar (water) and nonpolar (oil) media is about 5 times lower than that of the initial fumed silica.

The Densil characteristics allow one to use it as an effective filler to prepare highly filled polymeric systems. Pilot technique for Densil production was developed on the basis of GM method. The regulatory documents were prepared: Technical conditions [8], Temporary production schedules [9] and the State sanitary-epidemiological expertise conclusion [10].

Gas-phase solvated-stimulated mechanosorption modifying nanosilica with non-volatile organic compounds.

Fig. 2. Comparison of the volumes of initial nanosilica (1) and Densil (2) at the same weight of samples of 5 g.

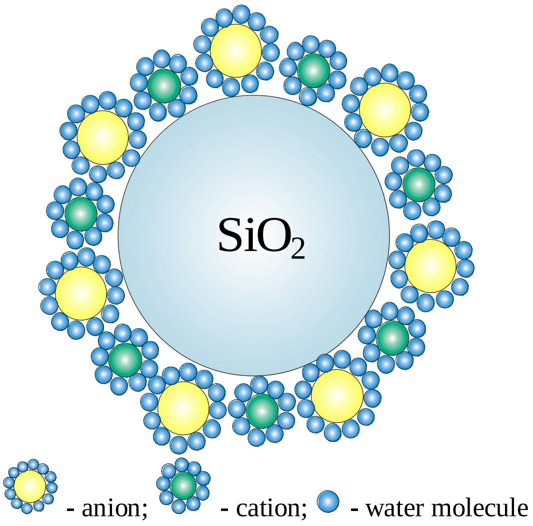


Fig. 3. Schematic image of a silica nanoparticle with a surface monolayer of an inorganic salt.

Upon mechanical treatment of a blend with initial nanosilica, non-volatile organic compounds (polymers or low-molecular weight compounds, e.g. bioactive ones) in a specific atmosphere, molecules of an organic compound are transferred from condensed state (e.g. polymer particles) toward a surface of NPNP. This causes adsorption modification of nanosilica by non-volatile compounds. Since solvation of modifier molecules and mechanical action are the main factors, this method was named as gas-phase solvated-stimulated mechanosorption modifying (GSSMSM) [11]. Note that upon the use of the GSSMSM, both sorption and geometric modification of nanosilica occur. Various compounds of different classes of organics were used as modifiers (Table 1).

Table 1

Modificators of nanosilica

Class of substances	Substance
Polymers	Polyvinylpyrrolidone, polystyrene, polyoxyethylene, vaseline oil, chitosan
Carboxylic acids and organic salts	2-(4-isobutylphenyl) propionic acid (ibuprofen), stearic acid, sodium stearate
Bis-quaternary ammonium compounds	Ethylene-1,2-bis (N-dimethylcarbodecyloxymethyl) -ammonium dichloride (ethonium), 1,10-decamethylene-bis [N-dimethyl- (carbomethoxymethyl) -ammonium] dichloride (decamethoxin)
Polyphenols	4-dimethylamino-1,4,4a, 5,5a, 6,11,12a-octahydro-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamide (tetracycline)
Saccharides and polyols	Glucose, mannitol, sorbitol, galactose, lactose, starch, glycerin

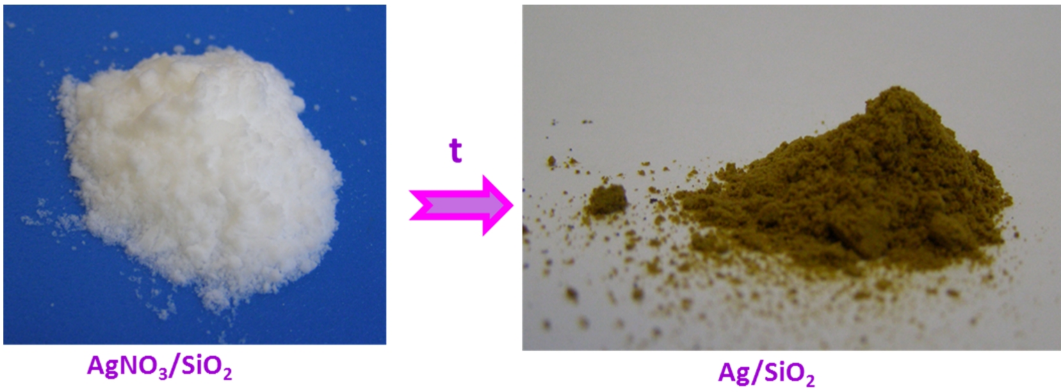
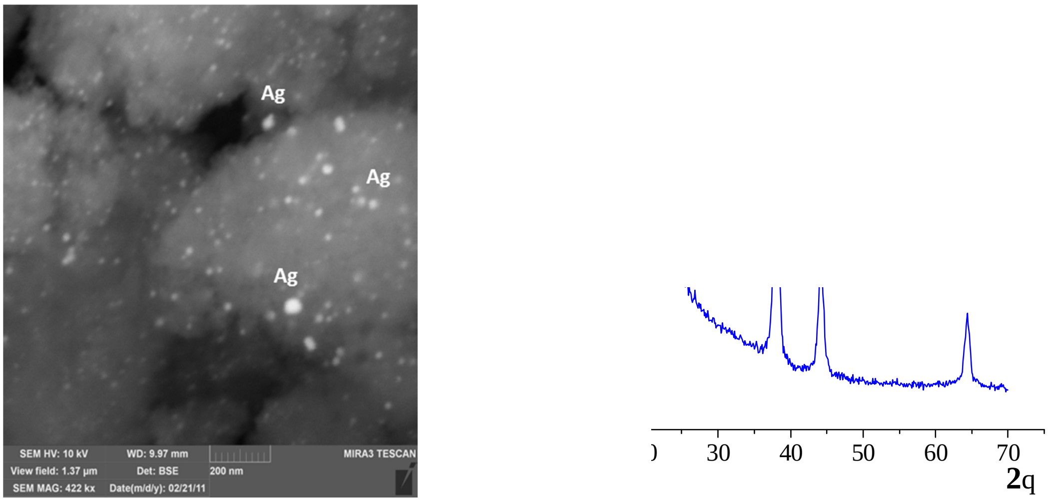


Fig. 4. Thermal transformation of the nanofiller Sol-Densil.



a **b**

Fig. 5. SEM image (a) and X-ray spectra (b) of high-disperse silica with nanosilver.

Gas-phase solvated-stimulated mechanosorption modification of nanosilica with inorganic salts.

Upon deposition of inorganic salts onto a solid surface using a sublimation method under vacuum, clusters or particles of salts but not separated ions are formed. Sometimes this can be a disadvantage.

It was shown that the GSSMSM can be used to form submonolayer or monolayer coverage of a surface of silica NPNP that is composed from highly hydrated ions. This modification can be represented as follows (Figure 3).

Nanosilicas modified by various inorganic salts using the GSSMSM were named as "Sol-Densil". By heating of such samples containing different salts at atmospheric pressure, it is possible to carry out thermal transformations on the surface of nanosilica (Figure 4).

The results of the study of samples by SEM and XRD methods testify to these transformations of the salt into silver nanoparticles (Figure 5).

It was shown that if different salts (e.g. $AgNO_3$ and NaCl) are deposited onto a surface of nanosilica that they can react in situ upon tight contacts between them to form new compounds (e.g. AgCl and $NaNO_3$).

A pilot technology was developed to produce "Sol-Densil", and the regulatory documents were obtained: Technical conditions [12], Temporary production schedules [13], and the State sanitary-epidemiological expertise conclusion [14].

Thus, the GSSMSM technique allows us to transform inorganic salts into a nanoscale state, which is more active than monolithic one, and these nanofillers can be used for various polymeric systems.

Conclusion

Gas-phase geometric and solvated-simulated mechano-sorption modification methods applied to nanosilicas were developed to produce effective functionalized nanofillers for various polymeric systems. Non-volatile high- and low-molecular weight organic (polymers, bioactive compounds, organic salts) and inoranic salts can be used for modification of nanosilicas as the most effective nanofillers of various polymers.

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Геометричне та механо-сорбційне модифікування високодисперсного кремнезему в умовах газового дисперсійного середовища

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Були описані геометричне та сольвато-стимульоване механосорбційне модифікування високодисперсного кремнезему в умовах газового дисперсійного середовища. Такі способи модифікування дозволяють одержувати функціоналізовані наповнювачі полімерних систем на основі нанорозмірного кремнезему. Для модифікування можна використовувати нелеткі високо- та низькомолекулярні органічні сполуки – полімери, біологічно активні сполуки, органічні солі, а також неорганічні солі.

Ключові слова: геометричне модифікування, механосорбційне модифікування, газове дисперсійне середовище, високодисперсний кремнезем, Денсил, Сол-Денсил, нанонаповнювач.