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Examination of the surface properties of ceramic micro and nanoparticles

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Properties

ABSTRACT

Purpose: The purpose of the article is to examine surface properties of ceramic nanoparticles applied as fillers in composite materials of polymeric warps.
Design/methodology/approach: For research there were used three types of ceramic micro and nano fillers: silver sodium hydrogen zirconium phosphate AlphaSan RC2000 (Milliken Chemical) and silica Aerosil DT4 and Aerolisl R 812 (Evonik Corporation). For the purpose of mentioned materials above there were used: scanning electron microscope SEM, Transmission Electron Microscope TEM and gas adsorption method for the purpose of qualifying specific surface area BET, Langmuria, porosity BJH and energy adsorption.
Findings: On the base of undergone research there were pointed out dependence between size, shape, porosity of particles and specific surface area BET, Langmuira and energy of adsorption.
Practical implications: Methods of measurements based on gas adsorption belong to the types of measurement methods that are very intensively developing that allows undergo measurements of various surface properties meaningful both in material engineering as well as in catalectic chemistry.
Originality/value: Specific surface area measurement by gas adsorption method execution. Examination with transmission electron microscopy technique.
Keywords: Nanoparticles; Surface area; BET; TEM; SEM

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1. Introduction

The use of micro and nano fillers is a commonly method for improvement of polymeric material properties. Fillers in composites can serve different functions from the most traditional, basic ones -when they are used as reinforcement phase - throughout improvement of specific usage properties to more complex functions like giving antimicrobial properties of materials destined for medical applications [1-4]. Particles of aluminium oxide (Al_2O_3), zirconium oxide (ZrO_2), silicon dioxide (SiO_2) or nan silver [5-8] are examples of such materials. A popular kind of filler are silica fillers. Hydrophobic Aerosil R 8 12 used in commercial scale that can be used as addition to silicone rubber in order to increase their mechanic and optical properties as well as addition to paints and cosmetics can be example here.

In the last few years they have been undertaken numerous research over abilities of composite materials having nanosilver that would be immune to fungal and bacterial infections. However it turns out that in many cases the big participation of nanosilver necessary to obtaining required antimicrobial properties leads to clear change in composite colour as a result of plasmon effect of the silver nanoparticles [9].

This phenomenon often cannot be accepted for the sake of planned material allocation, as the colour is often a decisive factor of final product appearance and essential usage property for that matter.

The described phenomenon is one of reasons for searching ceramic fillers containing biocidal silver and at the same time not causing that drastic change in colour. An example of such solution can be AlphaSan RC2000 (silver sodium hydrogen zirconium phosphate) characterized by ability to control silver ion emission to environment. The emission is activated in a moist environment as a result of reaction based on exchange ions from environment with silver ions situated on ceramic carrier. [10-11]. The material can be applied - for instance - in textiles that contribute to eliminate unpleasant smell arisen during cloths use with bacteria involvement in polymeric fibres or as addition to artificial materials produced with traditional methods [10,15]. The biocidal effectiveness of received materials against different microorganisms has been proven with research [10-11, 13-15].

2. Experimental

Within presented work with use of gas adsorption method, SEM and TEM methods there were specified structural and surficial properties of examined materials:

- silver sodium hydrogen zirconium phosphate AlphaSan San RC200030-011 Cracow, 37A Wrocławska Street (AS), Milliken Chemical,
- fumed silica Aerosil DT4, Evonik Corporation and
- fumed silica Aerosil R 812, Evonik Corporation.

Morphology of the AS was checked in scanning electron microscope (high resolution scanning electron microscope SUPRA 35, Zeiss Company), (Figs. 2-4) for other two samples (Figs. 5-6) transmission electron microscope (high resolution transmission electron microscope S/TEM TITAN 80-300, FEI Company) was used. Moreover, for all samples gas (N_2) absorption method was applied.

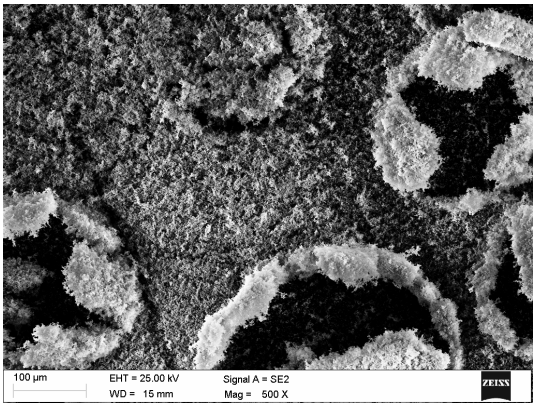
2.1. SEM investigations

AS particles were stuck to the conductive carbon film and then placed on aluminium table at the chamber of the scanning electron microscope they were not coated by conductive layer. Secondary electrons (SE) with energy 25 keV were applied for imaging (Fig. 1).

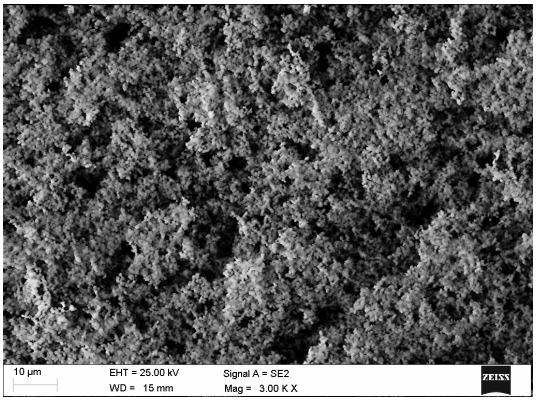
2.2. TEM investigations

The morphology and chemical composition of investigated samples were determined by electron microscopy in high resolution transmission electron microscope S/TEM TITAN 80-300 (FEI Company) with field-emission gun (FEG), bright field, dark field, and high angle annular dark field (HAADF) STEM imaging, a probe Cs corrector for atomic resolution scanning transmission imaging (STEM), energy filter and EDX. Samples for transmission electron microscopy were prepared by dispersing tested materials (white powder) in ethanol, placing in an ultrasonic bath, then putting droplets onto 3 mm copper grids coated with amorphous carbon film and drying in air at room temperature.

a)



b)



c)

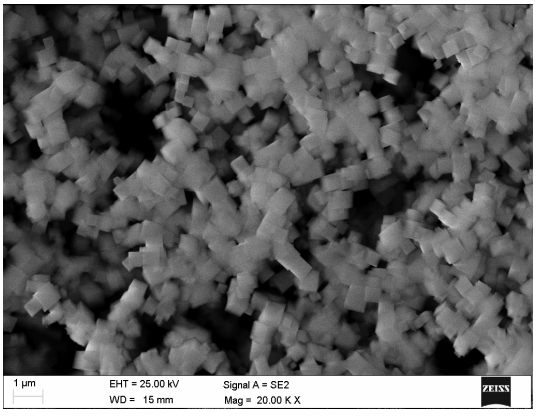


Fig. 1. SEM image of AS particles: a) mag. 500x, b) mag. 3000x, c) mag. 20,000x

2.3. Research of surface properties with gas adsorption method

For the surface research there was used specific surface area analyser Mikrometrics Geminii VII 2390 and as a gas for measurement there was used nitrogen (N_2) of purity level 5.0.

Specimens preparation for surface properties research

For the purpose of measure surface properties of given specimens at first the absorbed liquid (mainly H_20) was removed as well as gases being ingredients of atmospheric air including mainly CO_2 (Fig. 2).

To achieve that there was introduced material in amount of 0.1-0.3 g to glass test-tubes than they were placed in heating coat of 150ºC and dried in lowered pressure throughout 1.5 h.

Dried up specimens were weighted again. The observed loss of mass in specimens showed effectiveness of drying process. Next dried material was placed in work panel of the device, then introducing data regarding dried specimens, specimens density, drying temperature and conditions of measurement the measurement was set in run.

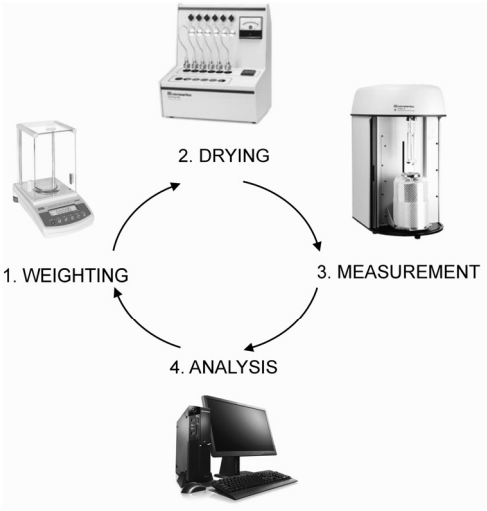


Fig. 2. The circle shows the sequence of steps taken in surface research using gas adsorption method

BET and Langmuir specific surface area research

Specific surface area is defined as the sum of surface of a given material for a unit of mass or volume. Specific surface area has essential significance in chemical industry especially in catalytic processes in which with the increase of catalyser surface increases the speed of chemical reaction. To the most frequently undergone measurements of specific surface area belong BET and Langmuir method [16-19].

Specific surface area measurement assumes:

- occurrence of the solids - so called active centers that is to say places where the adsorption process occurs - onto a given surface,
- each active center adsorbs only one particle which means that adsorbent is covered by monolayer,
- adsorbed particles do not interact with each other,
- in a unit of time the same quantity of adsorbed gas is desorbed (the dynamic balance sets up),
- the heat of adsorption is identic for each center of adsorption
- process of adsorption has dynamic balance between adsorption and reverse process to adsorption that is desorption.

Isotherm Langmuira is used to describe cases of chemisorption however it has nothing to do in case of physical adsorption because of creating multilayer phenomena. To describe that method there is used BET method [16-19].

Measurement of specific surface area via BET method assumes:

- each active center can adsorb more than one particle (multilayers emerge),
- interaction between adsorbent particles in adsorbent surface layer is neglected,
- quantity of absorbed particles depends on pressure p/po,
- heat of first adsorption layer differs from heat of adsorption of subsequent layers [16-18].

BHJ porosity research

Measurement of porosity using BJH (Barret, Joner, Halenda method) is based on the following assumptions:

- In pressure $0.4<p/po<0.98$ capilar condense phenomena happens (gas is adsorbed in pores in the form of liquid at the pressures nearing to steam resilience),
- With the increase of pressure increases the layer thickness of adsorbent on pores' walls until they becomes completely filled up,
- Obtained curves of volume pores distribution reflect adsorbent structure [16-18].

Energy of surface

Energy of surface depend on porosities of examined specimens and is highest for the first gas monolayer which is linked with forces interactions onto first adsorbent layer (solid body), which interaction with each subsequent layer decreases.

3. Results and discussion

Morphology of A samples is visible on Fig. 3, 4. Sample A consists of spherical primary particles, with a narrow size distribution, connected in aggregates. Connected particles for loose and open aggregates, which can be quantitatively characterized by fractal parameters (mass fractal dimension obtained by particle counting method D_f). An average diameter of primary Aerosil DT-4 particles can be estimated as about 5 nm. EDS analysis confirmed the presence of two elements: O and Si. No additional impurities were found. Sample R812 have similar morphology, but in that case aggregates are more compact. Also primary particles are significantly larger - an average diameter

can be estimated as about 20 nm. Beside O and Si, also Na and C were detected by EDS analysis.

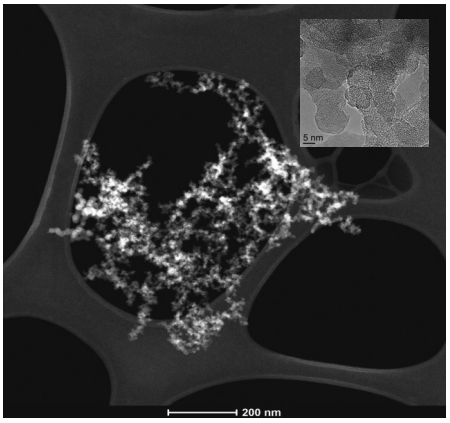


Fig. 3. HAADF STEM image of typical Aerosil DT4 aggregate

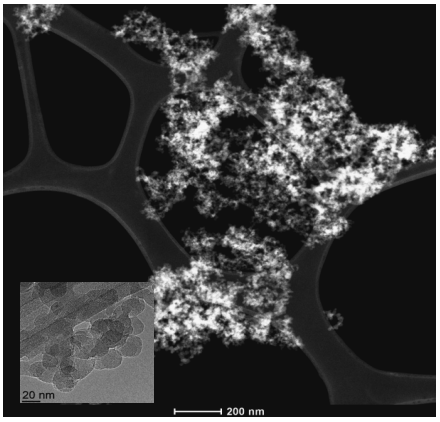


Fig. 4. HAADF STEM image of typical R812 aggregate

The test results of the particle gas adsorption method (Figs. 5-7).

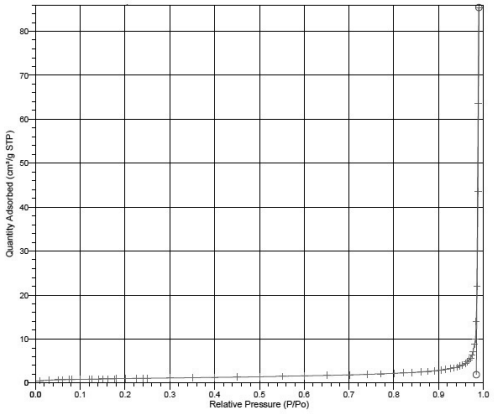


Fig. 5. Isotherm linear plot for AS

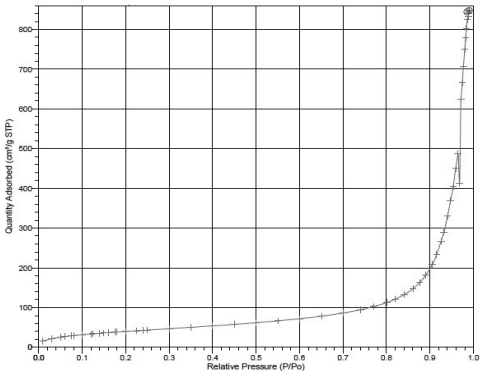


Fig. 6. Isotherm linear plot for Aerosil dt-4

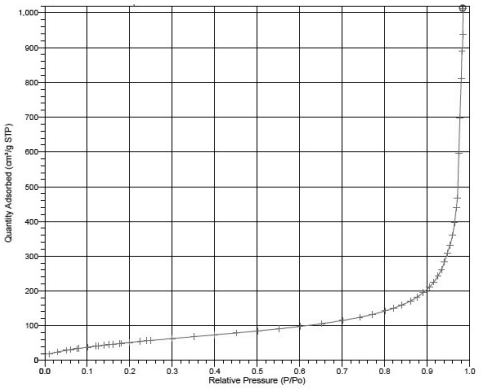


Fig. 7. Isotherm linear plot for Aerosil R812

Defining BET, Langmuira and single pointed specific area surface was calculated with isotherm of adsorption/desorption read from the MIkrometric Gemini VII 2390t device. Isotherms of adsorption and desorption made on specimens showed significant difference between BET specific area surface and Langmuira of examined specimens. Significantly bigger surface was shown for Aerosil Dt-4 and Aerosil R812 specimens in comparison to particles AS (Figs. 8-15).

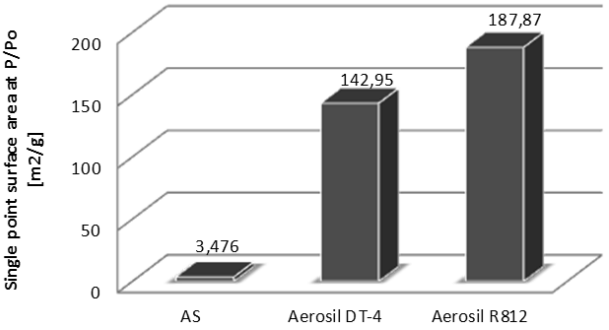


Fig. 8. Single point surface area at P/Po [m^2/g]

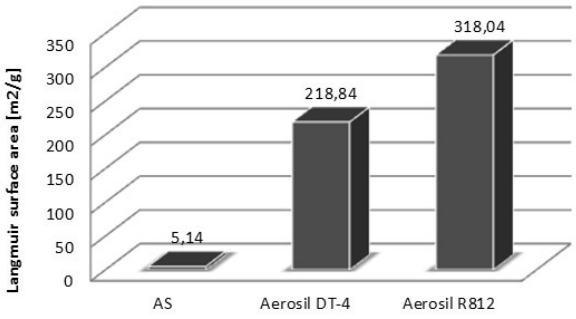


Fig. 9. Langmuir surface area [m^2/g]

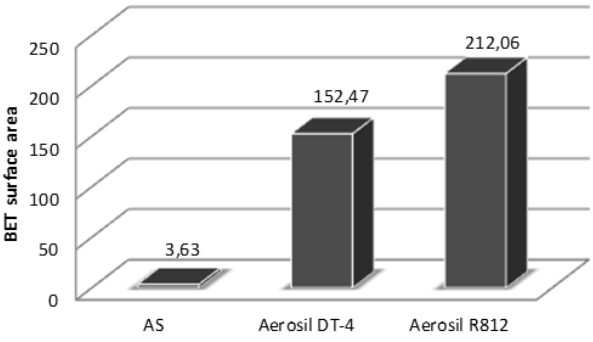


Fig. 10. BET surface area [m^2/g]

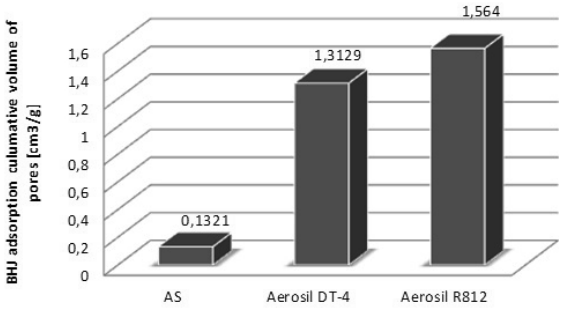


Fig. 11. BHJ adsorption cumulative volume of pores

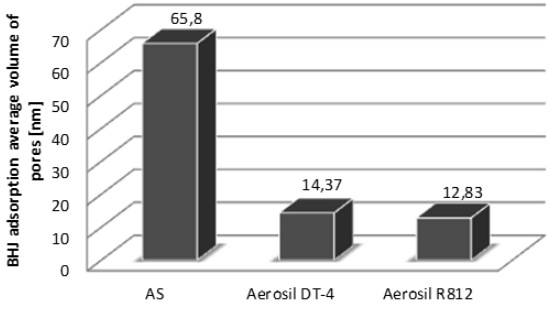


Fig. 12. BHJ adsorption average volume of pores

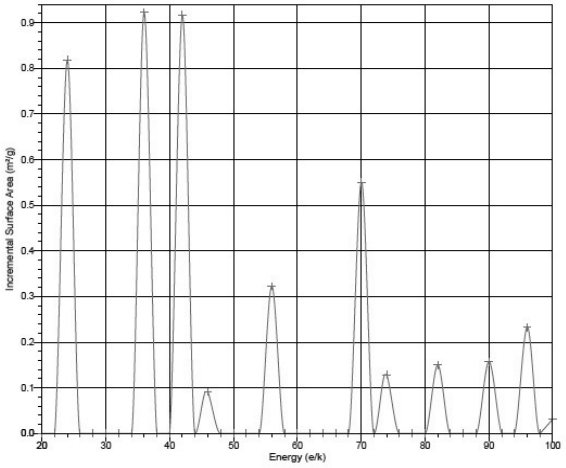


Fig. 13. Incremental Surface Area vs. Energy for AS

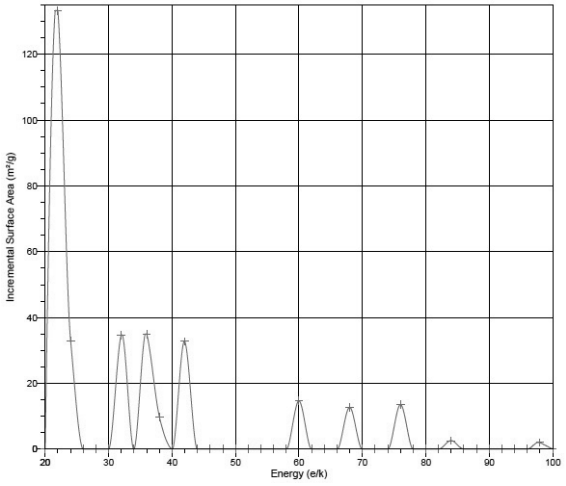


Fig. 14. Incremental Surface Area vs. Energy for Aerosil DT-4

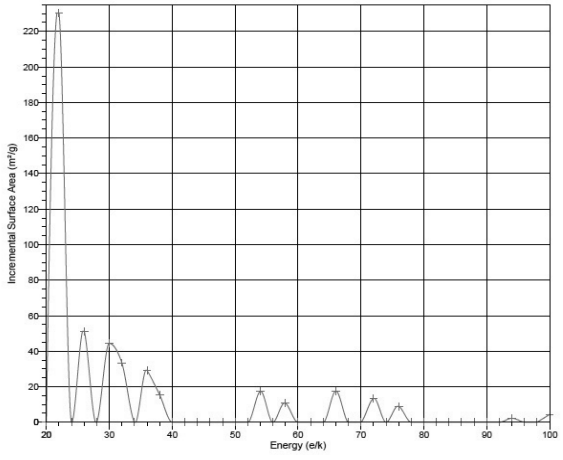


Fig 15. Incremental Surface Area vs. Energy for Aerosil R812

Obtained differences results from:

- Size of examined particles. AS particles measured from 0.4 to 0.7 μm, while Aerosil DR-4 particles measured circa 5 nm whereas Aerosil R812 measured about 20 nm,
- Size and surface of elementary particles. AS particles have shape of cubes while Aerofil Dt-4 and R812 particles have irregular shape,
- Porosity of examined powders on the base of research showed that porosity of examined specimens is differential, the highest porosity is observed in Aerosil R812 and Aerosil DT-4 cermics where dominant pores were of size below 50 nm whereas for AS ceramics dominant pores were of size above 50 nm,
- It was shown that AS ceramics belongs to the micro porous materials (of size above 50 nm), whilst Aerosil Dt-4 and Aerosil R812 ceramics belong to mezzo porous materials (of size of pores 2-50 nm),
- With the increase of specimen porosity increases BET specific surface area as well as adsorption energy of absorbent that was highest for Aerosol R812 and lowest for AS ceramics.

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