Carbon microfibers/silica aerogel nanocomposites based on water-glass

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ABSTRACT

In presented article the research on sol-gel synthesis of silica aerogel from cheaper precursor water glass with ambient pressure drying was shown. In addition to strengthen the silica aerogel frame the as-received and oxidized carbon microfibers from coal-tar pitch were used. The presence of carbon microfibers in silica aerogel does not influence the structural parameters, on the contrary, the carbon microfibers diminish the density and contraction during drying of silica aerogel nanocomposite. Modification of the silica aerogels in a mixture of TMCS/n-hexane in 70°C with concurrent modification of carbon microfibers results in obtaining a durable nanocomposite, up to the temperature of 600°C, characterized by high level of hydrophobicity, which is proved by tests on contact angle. Moreover, the analysis with EDS probe proved, in case of the nanocomposites with carbon microfiber, a lack of sodium, being a remnant of the silica gel synthesis from water glass, which implies a higher level of substrate reaction during the sol-gel synthesis, and results in obtaining better parameters of the silica aerogel. Copyright © 2018 VBRI Press.

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Introduction

Silica aerogels have open cell structure consisting of particles with the diameter below 10 nm which connect each other in larger-ones and create the Pearle-necklace like structures with pores diameter in the range of 2-50 nm. Those features give the silica aerogels the following parameters: density range of $0.03 - 0.35$ g/cm^3 and specific surface in the range from 500 to 1200 m^2/g. Exceptional properties of the silica aerogels enable their application in many branches of industry, for example as insulation materials (thermal and acoustic), catalysts and catalyst carriers, gas, liquid and energy absorbents, adsorbents and sensors. The greatest practical interest in silica aerogels results from their low thermal conductivity coefficient, 0.02 W/(m·K), much lower than the currently applied insulation materials, for which the lambda values equal about $0.030 - 0.040$ W/(m·K). The most commonly applied insulation materials are: mineral wool ($0.034 - 0.045$ W/(m·K)), glass wool ($0.031 - 0.043$), foam glass ($0.038 - 0.050$), expanded polystyrene foam EPS ($0.029 - 0.048$), or extruded polystyrene foam ($0.029 - 0.048$). Much lower lambda values can be found in polymer foams from phenolic resins (0.021-0.025) or polyurethanes ($0.020 - 0.029$). Among those materials silica aerogels show very good parameters and, despite high production costs, they find use in insulation materials produced by Aspen Aerogels and Cabot Corporation [1-4].

Silica aerogels are received in a three-stage process covering a synthesis, ageing and gel drying. One of the most important stages in receiving silica aerogels is the removal of the solvent from the gel structure. Drying in lower temperature and in lower pressure is accompanied by strong capillary forces that cause the contraction and cracking of the gel, as a result of which the xerogel is created. In order to eliminate them the supercritical drying is applied, which can be conducted either in a high temperature process in organic solvents (HTSCD), usually in mother alcohol, or in a low temperature process, the so-called Hunt process, in CO$_2$ (LTSCD) [5-7]. The idea of supercritical drying is the introduction of a solvent into a supercritical state, thus a state achieved in the moment of crossing the triple point of a given substance via application of proper temperature and pressure. In such conditions the solvent takes the properties of the supercritical liquid, and without any pressure on the silica frame, it can be removed from it without violating the gel structure. Due to high cost of supercritical drying, as well as the explosion danger, also the tests on silica aerogels received in the process of drying in the atmospheric pressure are conducted. In order to do that, silica gels are received via two-stage sol-gel synthesis, and next the gel surface is modified via the so-called sylilating agent consisting of replacing the silanol groups present on the silica gel surface with inert groups - O-Si(CH$_3$). Most commonly, this modification is conducted with the application of trimethylchlorosilane

TMCS, trimethylsilane TMS, tetrametylosilane MTMS or hexamethyldisiloxane HMDSO and hexamethyldisilazane HMDS. The idea of this method is to give the silica aerogel structure a hydrophobic character, so that another hydrolysis of the received aerogel (and thus complete gel contraction causing its changing into xerogel) is limited [8, 9].

There are relatively few articles covering the composites carbon fibers/silica aerogel, despite the fact that carbon fibers, in comparison to glass or ceramic fibers, are characterized by very good mechanical parameters, especially in relation to their density, dimensional stability up to 750°C, low coefficient of thermal expansion, fatigue resistance, biological compatibility and good electrical conductivity. Thanks to those properties carbon fibers are applied in many branches of industry, such as aerospace, automotive, chemical engineering, missile, nuclear field, reinforcement in composite materials, and textile [10, 11]. Therefore, in the following article the silica aerogels from water glass solution and their nanocomposites with carbon microfibers were synthesized in the double-step sol-gel process, followed by ambient pressure drying. In order to improve the adhesion between carbon fibre and silica aerogel, the fibres underwent chemical modification in the nitric acid. The structure of the received nanomaterials and the temperature resistance were tested with the following instrumental analysis methods: BET, TG FTIR, SEM with EDS and contact angle measurements.

Experimental

Materials

In the presented research, the silica aerogel was produced via sol-gel method from 10 wt.% of water glass solution supplied by SIGMA-ALDRICH, Germany. The catalyst of reaction was 1 M citric acid produced by CHEMPUR, Poland. As the silica frame reinforcement the short carbon microfibers produced by Osaka Gas Corporation were applied. Due to low production cost and very good properties these fibers are recommended for application as the reinforcement for cement/concrete mixtures, polymer composites, and high temperature materials. Short carbon fibers DONACARBO SG244A are produced from coal tar being a by-product of natural gas disintegration. The processing technology includes the mechanical separation of mesophase microbeads from crude coal tar, then the mesophases are subjected to solvent extraction, hydrogenation, and polymerization to yield isotropic and anisotropic pitches suitable for melt spinning. The short fiber is fabricated from isotropic pitch by the rotary gas jet method, and the process yields a higher quality fiber as compared to other melt spinning methods. DONACARBO are the low module carbon fibers with average diameter of 13 µm and length of 700 µm, characterized by shape factor equal L/d = 50. Those fibers show relatively low level of graphitization [12]. They also have very small specific surface of around

0.96 m2/g. To increase the adhesion between carbon microfibers and silica aerogel frame the oxidation of the carbon fiber surface in the liquid phase in nitric acid was conducted. The initial fiber sample was put in a round-bottom flask and covered with concentrated nitric acid up to 2/3 of the flask volume. The mixture of carbon fibers and nitric acid was gradually heated under the reflux condenser up to the boiling point of nitric acid, and then, keeping the temperature of 120 ^{o}C, the oxidization was conducted during 3 h. After the process was finished, the system was cooled down to room temperature, infiltrated, washed with distilled water to pH = 7 and dried in the dryer in the temperature of 105 ^{o}C. As a result of the carbon fiber modification in nitric acid the surface of the material was enriched with functional groups, which contributed to the change of the fiber character from hydrophobic into hydrophilic.
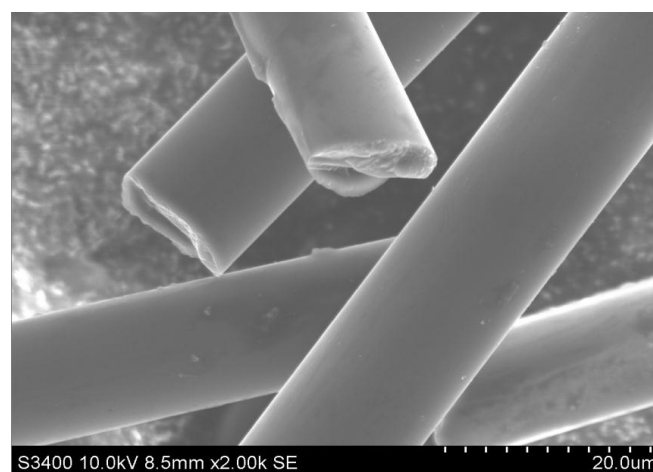
a

b

Fig. 1. SEM of carbon microfibers (a) and dispersion of unmodified (left-hand side) and modified (right-hand side) carbon microfibers in water.

The **Fig. 1b** present the fibers before and after chemical modification in water. In case of unmodified carbon microfibers it is very difficult to obtain a homogeneous fiber suspension in water, usually the fibers stay on the surface of the solution, and it is very difficult to disperse them evenly in the whole volume. Modified

fibers, on the other hand, can be easily dispersed in water, the suspension is homogeneous in the whole volume.

Material synthesis

Silica aerogel was produced via sol-gel process from 10 wt.% of water glass in presence of citric acid as catalyst followed by successive washing and drying in ambient pressure. In order to reduce the silica aerogel shrinkage during drying the modified carbon fibers were added in the amount of 1 vol. %. First, the carbon fibers were added to water glass solution and mix together on the electromagnetic stirrer within 5 minutes. Then, the catalyst of reaction were added and in few minutes the gel was created. In final step, the modification of gel in TMCS/n-hexane mixture in 70°C was performed. The obtained silica aerogel nanocomposites were dried in air.

Response measurements

To characterize the nanocomposites properties the following chemical analysis were carried out: BET analysis, Fourier Transform Infrared Spectroscopy FTIR, thermogravimetric measurements TG, EDS analysis and contact angle measurements. Surface area and pore volume of aerogel composites were estimated based on adsorption isotherms in low-temperature nitrogen sorption in the temperature of 77 K using the equation of BET isotherm and analyzer ASAP 2010 (Micrometrics). The average pore diameter was calculated on the basis of the $4V/Å$ equation, where V stands for total volume of the defined pores in a single point of adsorption isotherm with $p/p 0 = 0, 99$. Thermo-gravimetric analysis of aerogels was performed in nitrogen atmosphere by means of NETSCH apparatus, type TG 209 F3. During measurements the following parameters were used: flow rate of inert gas 30 ml/min, speed of sample heating 10°C/min, and temperature range 30 - 1000°C. To identify functional group on the silica aerogel – carbon fibers composites surface the infrared spectroscopy was applied. Infrared absorption spectra ATR-FTIR for tested aerogels and its composites were determined by means of FT-IR NICOLET 5700 apparatus (Thermo Electron Corporation). All measurements were performed in the wave number range from 600 to 4000 cm^{-1}. The chemical analysis of silica aerogel and its nanocomposites with carbon microfibers was carried out by means of ESD analysis with SEM observation with microscope Hitachi, model S-3400N, using the acceleration voltage of electron beam adjusted to 20 keV.

Results and discussion

Table 2 presents the basic physical and structural parameters of the received aerogels based on water glass (denoted as A) and their composites with unmodified (denoted as B) and oxidised carbon microfibers (denoted as C).

The received aerogel was characterized by density of 0.225 g/cm^3, specific surface of 449.8 g/cm^3 and average pores of size 10.8 nm. Addition of the carbon microfibers

to the silica gel did not influence the structural parameters of the received nanocomposites significantly. In case of composite B, the specific surface and the average pore diameter equaled 436.9 g/cm^3 and 11.0 nm, and for composite C respectively: 455.2 g/cm^3 and 10.2 nm. For both, pure silica aerogels and nanocomposites with unmodified and modified carbon microfibers, the adsorption/desorption isotherms N_2 were typical of the materials with mesoporous structure **(Fig. 2).**

Table 1. Structural parameters of silica aerogel (A) and its nanocomposites with unmodified (B) and modified (C) carbon microfibers.

	A	**B**	**C**
Density, g/cm³	0.225	0.148	0.139
Shrinkage, %	68	51	46
BET Surface, m²/g	449.8	425.9	455.2
Average pores diameter, nm	10.8	11.0	10.2
EDS analysis of particular chemical elements			
C, wt.%	8.34	13.29	14.26
O, wt.%	50.45	49.67	44.58
Si, wt.%	41.01	37.04	41.16
Na, wt.%	0.21	0	0

Taking into account the classification of porous materials made by de Boer in 1958 [13], from the shape of the desorption hysteresis loop it can be found that pore structures are both cylindrical capillary pores open at both ends and cylindrical pores closed at one end with a narrow neck at the other, like an "ink-bottle", which are assigned to the materials with the mesoporous structure.
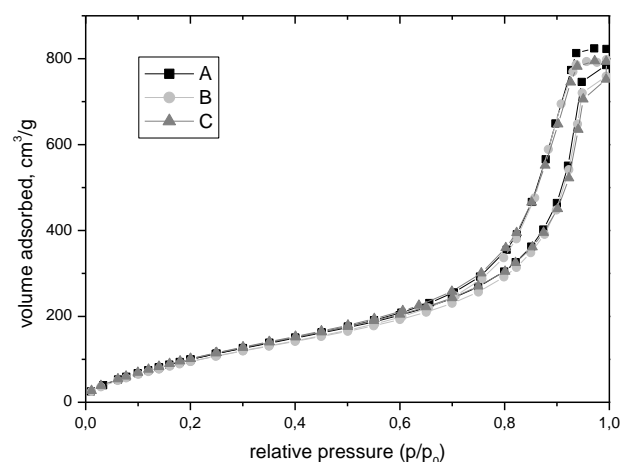

Fig. 2. Adsorption hysteresis loops for pure silica aerogels (A) and their nanocomposite with unmodified (B) and modified (C) carbon microfibers.

On the other hand, the presence of the carbon microfibers in the structure of the silica gel resulted in substantial lowering the nanocomposite density and limiting the silica gel contraction during drying. Densities of B and C nanocomposites equaled respectively

0.148 g/cm^3 and 0.139 g/cm^3, whereas the contraction of the materials during drying equaled respectively for the pure aerogel 68%, and for the nanocomposites with unmodified and modified carbon microfiber 51% (sample B) and 46% (sample C). The lower shrinkage during drying for the C nanocomposite is a result of a chemical reaction between oxygen functional groups present on the surface of the modified carbon microfibers with the hydroxide groups present on the surface of the silica aerogel.

The above is proved by lowered intensity of the band in FTIR spectrum, by wavenumber length from 1050 to 1100 cm^{-1} attributed to the Si-O-Si bond of a siliceous structure **(Fig. 3)** [14, 15]. On the other hand the increase of this band for silica aerogel without and with unmodified carbon fibers was observed. Pure silica aerogel is characterized by higher number of free hydroxyl and hydrocarbon groups on the surface, and therefore on the FTIR spectrum the increase of intensity of band at wavenumber range from 1050 to 1100 cm^{-1} occurs. This effect is strengthen by the addition of unmodified carbon microfibers which disorganize the silica aerogel structure and introduce the additional free spaces with functional groups containing oxygen.
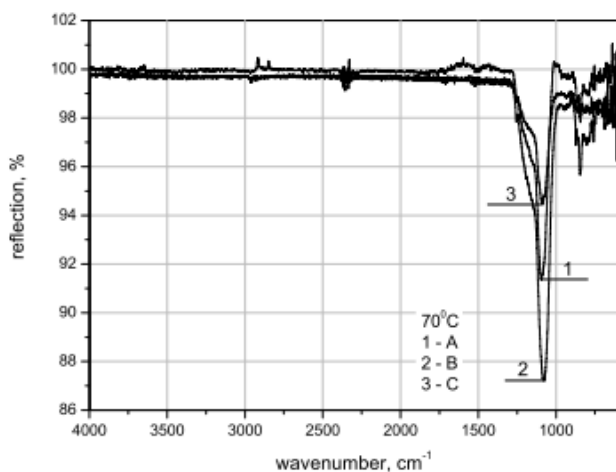

Fig. 3. FTIR analysis for pure silica aerogel (A) and their nanocomposites with unmodified (B) and modified (C) carbon microfibers.

The results of FTIR analysis are coherent with the thermogravimetric measurements presented on **Fig. 4**. The analysis proved that the aerogels chemically modified in the mixture of TMCS/n-hexane and air-dried had high thermal resistance. In this case, a 1% weight loss was observed in the temperature range of 300-400°C, and only 6% loss in 700°C. Silica aerogel/carbon fibres composites had slightly better temperature resistance in the whole research range. In the case of aerogels with unmodified carbon microfibers a 2% weight loss was observed in the temperature of 400°C, whereas in higher temperatures those materials achieved 7% weight loss in 700°C. The obtained results were much better than those obtained in our previous research for silica aerogel from TEOS, both
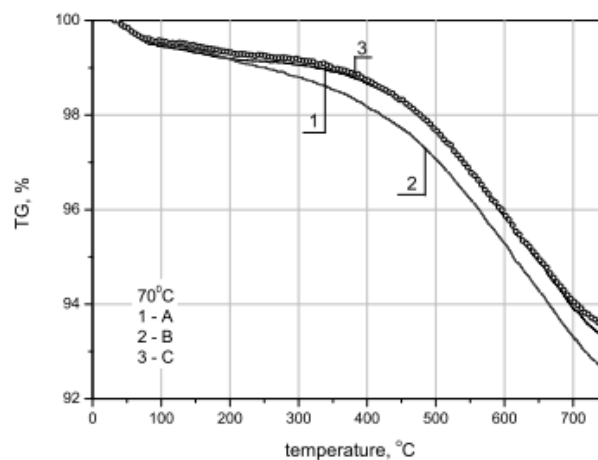

Fig. 4. Thermogravimetric analysis for pure silica aerogel (A) and their nanocomposite with unmodified (B) and modified (C) carbon microfibers.

dried in ambient and supercritical conditions. In that case the aerogel / carbon fibre composites had much lower temperature resistance in the whole research range, achieving the highest weight loss of 11% and 9 % in 700°C for ambient and supercritical dried nanocomposites, respectively [16]. The presence of carbon microfibers in silica aerogel structure had another positive effect. Namely, the SEM analysis with EDS probe presented in **Table 1** proved, in case of the nanocomposites with carbon microfiber, a lack of sodium, being a remnant of the silica gel synthesis from water glass, which implies a higher level of substrate reaction during the sol-gel synthesis, and results in obtaining better parameters of the silica aerogel.

The hydrophobicity of the silica aerogel depends on the chemical composition of the solid surface. In one-step synthesis via introducing to the silica gel co-precursor we received the silica aerogel with surface with the reduced amounts of silanol groups. To calculate approximately the surface free energy on the silica aerogel the contact angle measurements has been applied. When the contact angle is below 90° we get the hydrophilic silica aerogel, on the contrary above 90° - hydrophobic. **Fig. 5** presents the contact angle measurement of hydrophobic silica aerogel synthesized in one-step process from TMOS and TMCS precursors (143°).
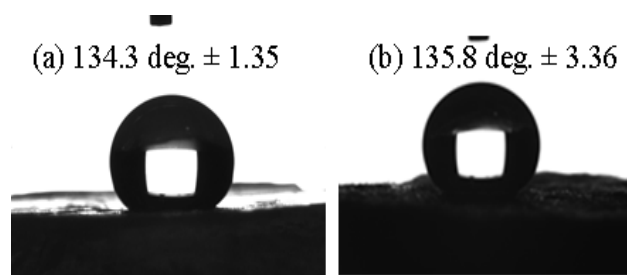

(a) 134.3 deg. ± 1.35   (b) 135.8 deg. ± 3.36

Fig. 5. Contact angle analysis of silica aerogel surface without (a) and with (b) modified carbon microfibers.

Conclusion

In order to sum up the above presented research, the following conclusions can be made:

- As a result of the research a silica aerogel was obtained from a much cheaper silicon precursor – water glass with satisfying structural parameters, with the use of ambient pressure drying.

- Application of the short carbon microfibers, from such a cheap precursor as the pitch, resulted in obtaining much lighter nanocomposites, with a reduced contraction during drying. Moreover, the presence of the fibres resulted in total removal of the sodium from the structure of the silica aerogel, which is usually difficult to rinse out in the direct process of the synthesis from water glass and results in disintegration and deteriorated parameters of the final product.

- Application of an additional modification of the carbon fibres in the nitric acid helped to improve the surface of the fibres with the functional groups (carboxyl and hydroxyl), as well as to obtain a good dispersion of the fibres in the silica precursor, which resulted in an even distribution of the fibres in the gel and the silica aerogel. Additionally, a chemical reaction occurred between the hydroxyl groups present on the surface of the silica gel and the oxygen groups present on the surface of microfibers, giving a solid bond, which was confirmed by the FTIR analysis. In the effect, the density was also reduced, as well as the contraction of the nanocomposite during drying, in comparison with pure aerogel and the aerogel with unmodified carbon microfibers.

- Moreover, it was proved, that concurrent modification of the fibre surface and the silica gel structure in a mixture of TMCS/n-hexane in 70ºC gave a nanocomposite of much better temperature stability, up to 700ºC and a high level of hydrophobicity, which was confirmed in tests of the contact angle. Relatively light carbon microfibers with high temperature stability, up to 750ºC, influenced positively both, the structural parameters, as well as the durability of the received nanomaterial.

Supporting information

Supporting informations are available from VBRI Press.

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