

# Synthesis and characterisation of silica aerogel/carbon microfibers nanocomposites dried in supercritical and ambient pressure conditions

Agnieszka Ślosarczyk<sup>1</sup> · Mikołaj Barełkowski<sup>1</sup> · Szymon Niemier<sup>1</sup> · Paulina Jakubowska<sup>2</sup>

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**Abstract** Experimental results on the physical and chemical properties of silica aerogel and its composites with carbon microfibers are reported. The aerogels and silica aerogel/carbon microfibers nanocomposites were prepared via the sol–gel process of organosilicon compound followed by successive washing and drying in different conditions. Part of nanomaterials was surface modified in TMCS/n-hexane mixture in 50 °C and dried in ambient pressure. Simultaneously, the supercritical drying of aerogels and its nanocomposites in CO<sub>2</sub> atmosphere was carried out. The carbon microfibers before usage in silica aerogel composites were chemically treated in nitric acid. The physical properties of silica aerogels were studied by

measuring the bulk density, volume shrinkage, porosity, pore volume and thermal conductivity. In the case of pure aerogels dried via supercritical conditions, the structure presented much less contraction during drying and was more resistant to higher temperature. However, the properties of silica aerogels composites with carbon microfibers drying in ambient pressure were better than corresponding composites subjected to supercritical drying. It was shown that simultaneous oxidation of carbon fibres and chemical modification of silica aerogel in TMCS/n-hexane mixture contributed to the stable mesoporous structure of composite with very good physical properties, especially lower shrinkage.

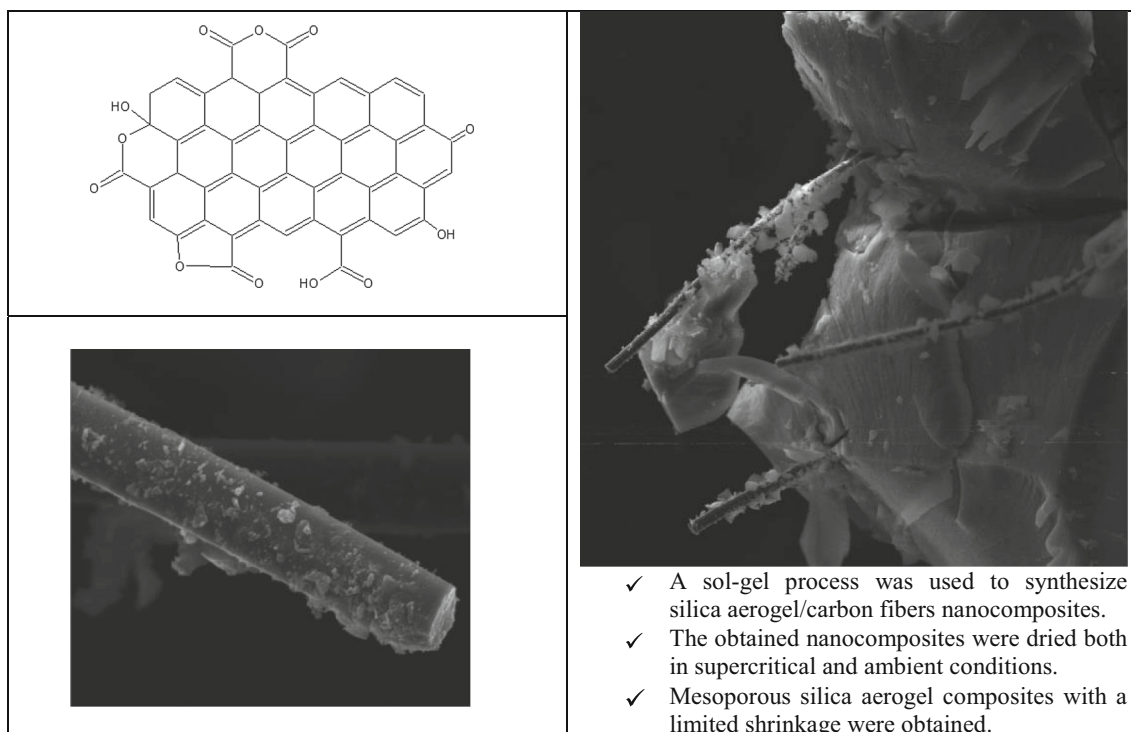
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✉ Agnieszka Ślosarczyk  
agnieszka.slosarczyk@put.poznan.pl

<sup>1</sup> Institute of Structural Engineering, Poznan University of Technology, Piotrowo 5 Str., 60-965 Poznan, Poland

<sup>2</sup> Institute of Technology and Chemical Engineering, Poznan University of Technology, Piotrowo 3 Str., 60-965 Poznan, Poland

## Graphical Abstract



- ✓ A sol-gel process was used to synthesize silica aerogel/carbon fibers nanocomposites.
- ✓ The obtained nanocomposites were dried both in supercritical and ambient conditions.
- ✓ Mesoporous silica aerogel composites with a limited shrinkage were obtained.

**Keywords** Silica aerogel · Carbon microfibers · Sol-gel synthesis · Chemical modification · Supercritical and ambient pressure drying · Nanocomposites

## 1 Introduction

Aerogels are characterised by very good compressive strength, but poor fracture toughness, which results from poor flexural and tensile strength. One of the ways for improving this disadvantage is an application of dispersed reinforcement, such as short fibres or directional reinforcement in the form of the mats [1, 2]. In the literature, little attention is paid to the application of short carbon fibres as silica aerogel reinforcement. Carbon fibres, in comparison with the other fibres, such as polypropylene or glass, are characterised by very good mechanical parameters, especially with regard to their density, very high chemical strength, stable structure up to 750 °C and very good electrical conductivity [3, 4]. In the following article, the silica aerogels and their nanocomposites with carbon microfibers were synthesised in the double-step sol-gel process, followed by ambient pressure drying as well as drying in supercritical conditions. 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 and SEM.

## 2 Experimental

Precursor for the aerogel synthesis was alkoxide compound, tetraethylorthosilicate (TEOS), in water solution of ethanol. 0.5 % water solution of hydrochloric acid was used as the catalyst of the sol-gel reaction. Chemical

**Table 1** Physical and mechanical parameters of carbon microfibres

Properties	Pitch-based carbon fibres
Diameter ( $\mu\text{m}$ )	13
Length ( $\mu\text{m}$ )	700
Carbon content (wt%)	Min. 99
Density ( $\text{g}/\text{cm}^3$ )	1.64
Bulk density ( $\text{g}/\text{dm}^3$ )	290
Resistivity ( $\Omega \text{ cm}$ )	$0.3 \times 10^{-2}$
Moisture content (wt%)	0
Tensile strength (MPa)	750
Modulus of elasticity (GPa)	40
Elongation (mm)	1.9
pH	7
Temperature resistance ( $^{\circ}\text{C}$ )	750

modification of the surface of aerogels and their composites with carbon microfibers was conducted in the solution of TMCS (chlorotrimethylsilane)/n-hexane with the volumetric ratio of 1:5 in the temperature of 50 °C for 48 h. The supercritical drying in CO<sub>2</sub> was conducted in the research stand built in Institute of Structural Engineering at Poznan University of Technology, according to the procedure described in the article [5].

Carbon microfibers from carbon pitch of 700 μm length and 13 μm diameter in the amount of 15 wt% of silica aerogel mass were used as reinforcement. Parameters of the carbon microfibers are presented in Table 1. The carbon fibres applied are characterised by very small specific surface area and low degree of surface oxidation; they are practically hydrophobic. Oxidation of the carbon fibre surface was conducted in the liquid phase in nitric acid. Initial fibre sample was placed in the round-bottom flask and poured with concentrated nitric acid. The oxidation process was conducted in the boiling temperature of nitric acid under the reflux condenser for 5 h. Next, the fibres were washed with water to pH 7 and dried to constant weight in the temperature of 105 °C [6].

For the synthesis of silica gel, two solutions were prepared: solution A consisting of TEOS compound, alcohol and water, and solution B consisting of reaction catalyst (acidic), alcohol and water. Mixing of the two solutions initiated a hydrolysis reaction, as a result of which sol was created, which was further formed into gel in the process of condensation. Before initiating the gelation, the fibres were mixed in solution A in the magnetic stirrer, then the solution B was added, and within a few minutes, the gelation occurred. After the gelation, the samples were taken for 24 h to the water solution of alcohol and then for 7 days to pure ethanol. After this time, the samples of the gels and composites gel/modified fibres were put into a mixture of TMCS/n-hexane in the volumetric ratio of 1:5 for 48 h in the temperature of 50 °C, in order to modify their surface. After the modification, the gels were put for 24 h to a solution of n-hexane and then air-dried until the structure of aerogel was achieved. The silica aerogel was marked as A, and the nanocomposites silica aerogel/modified carbon microfibers relatively as A + CFmod. In the case of supercritical drying, the samples of aerogel and nanocomposite with modified carbon fibres were dried in

CO<sub>2</sub>, in the temperature and pressure ensuring the supercritical fluid conditions. The silica aerogel received as the result of the supercritical drying was marked as B, and the nanocomposites silica aerogel/modified carbon microfibers, respectively, as B + CFmod.

For the determination of ATR–FTIR spectrums of the tested samples (silica aerogels and its composites with carbon microfibres), the FTIR NICOLET 5700 machine from Thermo Electron Corporation with ATR attachment (crystal: ZnSe) was used. ATR–FTIR measurement was taken in the wave number range from 600 to 4000 cm<sup>-1</sup> (scan number 64), and the spectrums received equalled: % reflection = f (wave number).

The structural properties of the received silica aerogels and nanocomposites silica aerogel/carbon microfibers were tested with the use of BET method, on the basis of nitrogen adsorption isotherm (77.35 K). The ASAP2010 porosimeter from Micrometrix was applied. On the basis of the received adsorption isotherms, the following parameters were defined: the specific surface area and the volume of the micropores of the unmodified and modified carbon fibres, specific surface area and average diameter of the pores for pure aerogels and silica aerogel/carbon microfiber composites. The average pore diameter was calculated on the basis of the 4 V/Å equation, where V stands for total volume of the defined pores in a single point of adsorption isotherm with  $p/p_0 = 0.99$ .

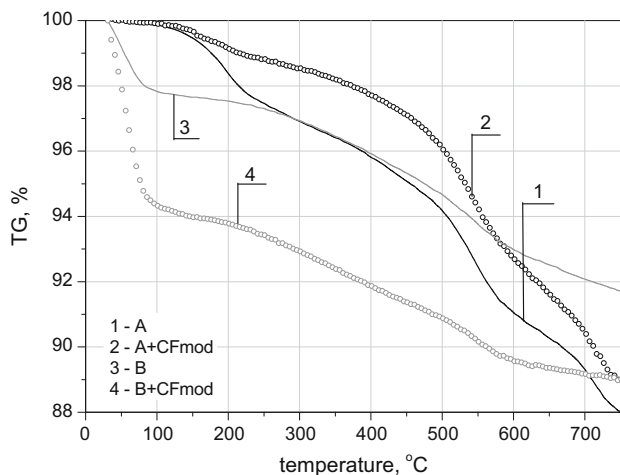
TGA of the tested materials was conducted in nitrogen, with the use of NETSCH machine, model TG 209 F3. The following measurement parameters were applied: strength of inert gas flow 30 ml/min, rate of sample heating 10 °C/min, analysis temperature range from 30 to 1000 °C.

### 3 Results and discussion

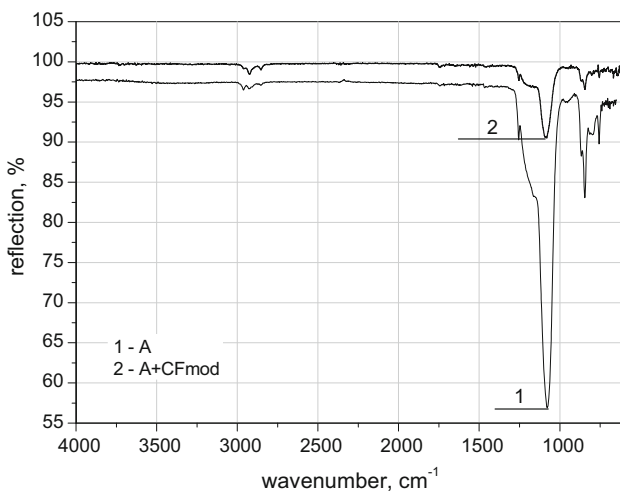
Table 2 presents the basic physical and structural parameters of the received aerogels and their composites with carbon fibres. Research proved that as a result of drying under supercritical conditions, the same initial formula gives aerogels and their composites with carbon microfiber characterised by lower density and much lower contraction during drying, in comparison with aerogels dried in atmosphere. For pure aerogels dried in supercritical

**Table 2** Structural parameters of silica aerogel and its composites depending on drying method

Parameter	Drying in ambient pressure		Drying in supercritical conditions	
	A	A + CFmod	B	B + CFmod
Marked in text	A	A + CFmod	B	B + CFmod
Density (g/cm <sup>3</sup> )	0.20	0.13	0.125	0.10
Surface area by BET (m <sup>2</sup> /g)	863.9	775.1	801.5	820.9
Average pore diameter (nm)	12.2	15.8	10.7	10.9
Volume shrinkage (%)	27.7	8.8	9.1	5.9

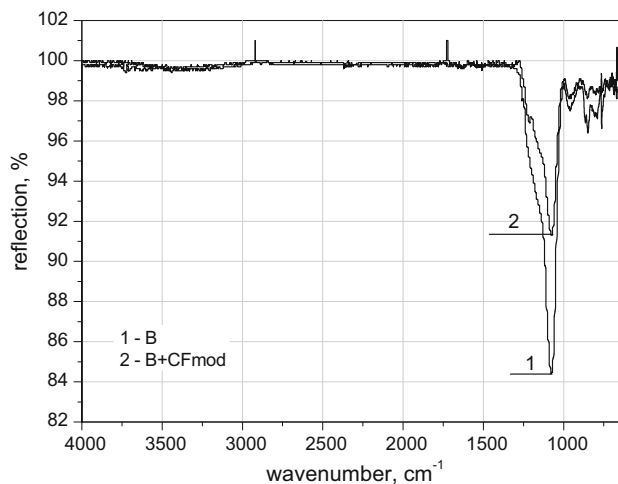


**Fig. 1** TGA for pure silica aerogels and its composites with carbon fibres in relation to drying in different conditions

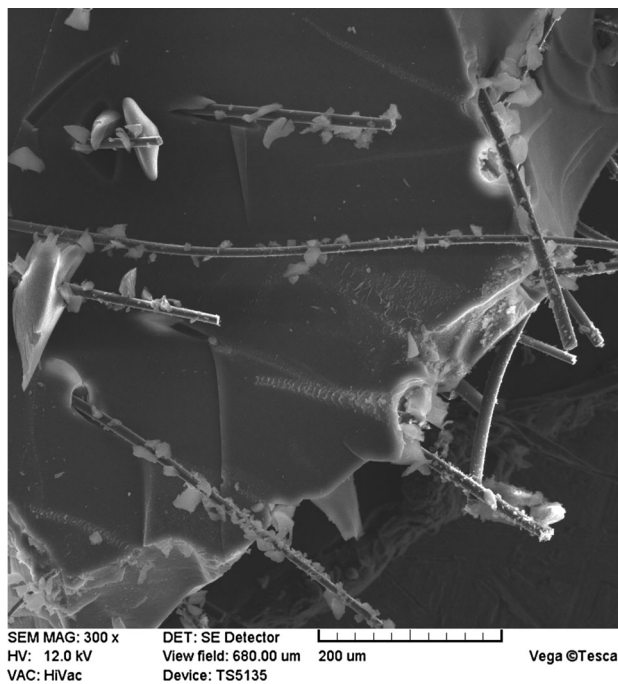


**Fig. 2** FTIR analysis of pure silica aerogel and its composite with carbon fibres drying in ambient pressure

conditions, the values oscillated in the range of  $0.125 \text{ g/cm}^3$ , whereas for the aerogels dried in atmosphere those values equalled  $0.2 \text{ g/cm}^3$ . Differences in density, although not so high, were also noticed for the aerogel/carbon microfiber composites, dried relatively under supercritical conditions— $0.1 \text{ g/cm}^3$ —and air-dried— $0.13 \text{ g/cm}^3$ . The research also proved that the presence of carbon fibres in the aerogel structure, regardless of the way of drying, diminishes the contraction of the samples during drying resulting in three times lower contraction (in the case of drying in atmosphere) and 1.5 times lower for samples dried under supercritical conditions. Moreover, on the basis of the analysis of nitrogen adsorption isotherm with BET method, specific surface areas of the aerogels and their composites were defined, which oscillated between  $775$  and  $863 \text{ m}^2/\text{g}$ . It was noticed that the fibres influence the



**Fig. 3** FTIR analysis of pure silica aerogel and its composite with carbon fibres drying in supercritical conditions



**Fig. 4** SEM image of silica aerogel/carbon microfibers nanocomposites

difference in values of the specific surface area of the aerogel composites, depending on the way of drying. In the case of drying under supercritical conditions, the growth of the specific surface area was gained for the composite aerogel/carbon fibres, whereas for drying in the atmosphere, the specific surface area decreased. The way of drying had also a significant influence on the average diameter of the pores of the aerogels and their composites. Higher values of the average pore diameter ( $12.2 \text{ nm}$ —pure aerogel,  $15.8 \text{ nm}$ —composite aerogel/carbon fibres)

were gained for materials dried in atmosphere. Nevertheless, based on the IUPAC classification [7], it can be concluded that the synthesised silica aerogels and silica aerogel/carbon fibres nanocomposites maintain a porous structure and belong to mesopores materials.

Figure 1 presents the thermogravimetric curves registered for the silica aerogels and their composites with carbon microfiber dried in the atmospheric pressure and under supercritical conditions, respectively. The analysis proved that the aerogels chemically modified in the mixture of TMCS/n-hexane and air-dried had much better thermal resistance. In this case, a 2 % weight loss was observed in the temperature of 200 °C and only 10 % loss in 700 °C. Silica aerogel/carbon fibres composites had slightly better temperature resistance in the whole research range. In the case of aerogels dried under supercritical conditions, a 2 % weight loss was observed in the temperature of 100 °C, whereas in higher temperatures, those materials were characterised with higher temperature stability achieving only 8 % weight loss in 700 °C. By contrast, the aerogel/carbon fibre composites had much lower temperature resistance in the whole research range, achieving the highest weight loss of 11 % in 700 °C. FTIR analysis for the aerogels and their composites, depending on the way of drying, is presented in graphs in Figs. 2 and 3. For pure aerogels, regardless of the drying conditions, by the wave number around  $1100\text{ cm}^{-1}$ , a high intensity peak is observed that comes from the bond Si–O–Si [8, 9]. In the case of composites silica aerogel/carbon microfibers, in both, supercritical drying and air-drying, the intensity of this band is significantly decreased. For the materials modified in TMCS/n-hexane and air-dried, the intensity of this band is definitely the smallest. Intensity decrease in the peak coming from the Si–O aerogel frame suggests that this bond is blocked in the structure of the silica aerogel/carbon microfibers. Oxygen functional groups present on the surface of the carbon microfibers, during the gelation of the organosilane compound, react with the hydrogen groups present on the surface of the gel, creating a fixed chemical bond [10]. This results in a significant decrease in the contraction during drying. Moreover, the research proved that the additionally conducted modification of the aerogels in the mixture of TMCS/n-hexane reinforced the structure of the pure aerogel, and especially contributes to gaining a very stable structure of the silica aerogel/carbon microfibers composite, and in this case, it is much more effective than drying under supercritical conditions.

In Fig. 4, the SEM image of silica aerogel/carbon microfiber nanocomposite was present. On the carbon fibres surface, there are visible silica aerogel particles which occurrence indicates the very good adhesion between carbon fibres and aerogel frame. Moreover, it can

point out that the growth of silica gel starts on the oxidised surface of carbon microfibers.

## 4 Conclusions

As the precursor of silica aerogel in the presented work, the TEOS in the ethanol solution was applied, and as the catalyst of the gelation reaction—the hydrochloric acid. Thus, the received silica aerogels and their composites with carbon microfibers were dried under supercritical conditions and in the atmospheric pressure after the initial modification of the aerogel structure in the TMCS/n-hexane mixture. The silica aerogels generated in this way were characterised by density in the range of  $0.125\text{--}0.2\text{ g/cm}^3$  and specific surface areas of  $801.5\text{--}863.9\text{ m}^2/\text{g}$ , relatively for those dried under supercritical conditions and those that were air-dried. In the case of pure aerogels dried under supercritical conditions, the structure presented much less contraction during drying and was more resistant to higher temperature. Moreover, the conducted research proved the advisability of the applied chemical modification of the carbon fibres. The oxygen functional groups present on the surface of the carbon microfibers, during the gelation of the organosilicon compound, reacted with the hydroxyl groups present on the gel surface, creating solid chemical bonds. This resulted in lowering the contraction during drying, both for the composites dried under supercritical conditions and in the atmospheric pressure. Moreover, the research proved that additional modification of the aerogels in the mixture of TMCS/n-hexane contributes to receiving a very stable structure of the silica aerogel/carbon microfiber composite and in this case is much more effective than drying under supercritical conditions, which was confirmed by the conducted FTIR and TG tests.

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