

Influence of Aging Factors on the Properties of Aerogels with Different Degrees of Granulation

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Abstract

Aerogels are distinguished by their low density and thermal conductivity, which predisposes them for application in materials against extremely low or high temperature. Aerogel resistance to aging factors such as moisture, high temperature and thermal radiation was studied. Aerogel resistance to moisture absorption was studied by the weight method, at a relative humidity of 65% and 95%. For aerogels exposed to heat (at 260 °C) and thermal radiation (heat flux density 20 kW/m²), structural and textural characteristics (specific surface area, pore volume, pore size distribution) were determined. It was found that in an environment characterised by 95% humidity, the moisture weight absorbed was similar for all aerogels and amounted to less than 1%, corresponding to low moisture absorption capacity. The most significant changes in specific surface area were recorded for aerogels in powder form, where the value of this parameter after exposure to high temperature increased by 13% compared to the reference sample. An increase in the specific surface area can effect a reduction in thermal conductivity; thus this change is positive in character in the context of application to clothing designed against thermal factors.

Key words: aerogel, exposure to humidity, exposure to heat, aerogel surface area, aerogel porosity.

Introduction

Silica aerogels are ultralight materials with a high porosity, which, although known for over 85 years, still enjoy unwavering interest [1]. Their phenomenon stems from the unusual combination of properties, i.e. a high specific surface area (500-1200 m²/g), low density (approx. 0.003 g/cm³), high porosity (80-99.8), and an extremely low thermal conductivity usually not exceeding 0.02 W/(m · K) [2]. Additionally, they are characterised by a low refractive index, low speed of sound and low dielectric constant [3, 4]. Such a combination of properties makes aerogels widely applicable in many areas, ranging from thermal insulation, through catalytic, adsorptive and filtrating materials, window systems and acoustic insulation to kinetic energy absorbers, micro-electronics, etc. [1, 5].

The low value of the thermal conductivity coefficient of aerogel, which predisposes it to be applied as thermal insulation, among others, in clothing protecting against both low and high temperatures, is particularly important. Although aerogels can occur in various forms, in

the case of clothing they are usually applied in the form of powder or granulate. The most common solution, especially in protective clothing against extremely low temperatures, are nonwoven fabric composites consisting of silica aerogel matrix and a reinforcing material (nonwoven) [6]. These products are sometimes subjected to a process of lamination to control the undesirable aerogel dust particles. Such a technology is used, among others, by the companies Aerogel Technologies Inc. [7] and PrimaLoft [8]. The literature review carried out by Naeem et al. [9] also showed that through the incorporation of silica based aerogels into nonwoven fabrics, the thermal protective performance of firefighter protective clothing can be significantly improved. There have also been attempts to apply aerogels in woven and knitted fabrics, as well as in clothing systems. A wool-aramide fabric coated with a binder with aerogel content developed by Shaid and his team [10] for the purpose of protective clothing for firefighters can be given as an example. Also, Zrim's team [11], using the lamination method, obtained a 5-layer insulation material with a total thickness of 3 mm, where the Pyrogel®2250 aerogel composite was protected on both sides by a thin Sympatex® membrane and warp knit fabric. Its thermal resistance surpassed more than two-fold the thermal resistance of currently used commercial thermal insulation materials, such as laminated polyurethane foam and Thinsulate™ nonwoven of similar thick-

ness. Effective protection against laser radiation can be obtained by the application of granulated aerogel between glass fibre and Kevlar fabrics, as evidenced by the results of tests carried out by Venkataraman [12]. Jiang and others [13], after the application of aluminum hydroxide aerogel to polysulfonamide fibre fabric (PSA), observed not only a significant reduction in its thermal conductivity compared to the fabric without aerogels, from 0.0513 to 0.0301 W/(m · K), but also an improvement in its flame retardant properties. In view of these findings, the authors concluded that the newly developed fabric had great potential for use as a thermal insulation layer in clothing protecting against heat and flames. Traditional protective clothing against heat and flame are often made of thick, multi-layered material systems, which are more effective with increasing thickness [14], while materials with aerogels are able to provide appropriate protection when exposed to heat factors without an undue increase in the thickness and weight of clothing.

A major limitation in the application of aerogels in garments/clothing may be their sensitivity to humidity. In the case of traditional materials used in protective clothing, even a low moisture content causes a serious decline in the thermal protective behaviour [9]. The wetting of aerogel samples, both in the form of an intermediate product (granulate, powder) and finished product (mats), has a nega-

tive impact on their insulating properties, as it increases the value of the thermal conductivity coefficient [15-17]. In addition, the studies conducted to date have shown that moisture absorption by aerogel particles can damage their structure, because the concentration of water in the aerogel pores generates capillary pressure, which, in turn, causes the loss of integrity of the aerogel structure [16, 18]. Miner and his team [19] noted that in an environment where the relative humidity reached above 70%, hydrophilic silica aerogels were significantly damaged, shrunken and opacified after 20 h of exposure. This effect was attributed to the condensation of water on the surface of the sample and to capillary forces, which led the structure of the pores to collapse. Hydrophobic properties ensure the stability of the aerogel structure and, on the other hand, do not allow a weight increase, which is highly advisable in the case of their application in clothing materials. As follows from the literature data, the thermal conductivity of aerogels in the form of granules can rise after wetting up to about 10% [16], which, in turn, translates into a deterioration in the thermal insulation of materials made from them. In the case of clothing with aerogel materials applied, the excessive weight of clothing as a result of the high water absorption of aerogel particles may constitute an additional problem. Therefore, testing the resistance of aerogels to moisture absorption is essential.

One of the most commonly used methods of research in this area is the weighing method, in which a sample of aerogel is weighed before and after exposure to moisture, and water adsorption is measured from the moment of the sample weight change. Aerogels can be exposed to moisture by placing them directly on the water surface, or by leaving them for a specified period of time in an environment with a set humidity level.

The former method was used, among others, by Rao and Haranath [18], Wagh and Ingale [20] and Rao et al. [21]. Rao and Haranath [18] tested samples of silica aerogels placed in glass vials directly on a water surface and stored the whole system being tested for 6 months in a closed vessel with water. They noted that when the MTMS/TMOS (methyltrimethoxysilane/tetramethoxysilane) molar ratio in the aerogel was lower than 0.26, the samples absorbed water very quickly and within just 2 to 3 minutes fell to the

bottom of the beaker. After 10 min of exposure, their weight increased 8-10 times in relation to the initial weight, whereas aerogels with MTMS/TMOS molar ratios of 0.70 and 1.03 did not absorb more than 2% of moisture even after 6 months of exposure. The authors concluded that aerogels which absorb up to 2% moisture can be considered to be hydrophobic, while an aerogel weight increase greater than 2% indicates that it is hydrophilic. The same principle was also adopted by Wagh and Ingale [20] and Rao and co-workers [21], except that the tests of water adsorption by aerogels were conducted for different periods of time, i.e. for a period of 1 year (Wagh and Ingale) [20] and 3 months (Rao et al.) [21], respectively. In the research conducted by Wagh and Ingale [20], it turned out that unmodified silica aerogels obtained in the supercritical drying process in CO₂ showed a more than four-fold weight increase already within 5 minutes from placing them on the surface of the water, which indicated their high water adsorption capacity. The silica aerogels modified with MTMS (methyltrimethoxysilane), in which the surface -OH groups had been replaced by hydrophobic -CH₃ groups, when exposed to water by placing them in a beaker containing water, absorbed no more than 2% of moisture after a period of 1 year.

Bellunatio et al. [22], before exposing a hydrophobic aerogel solid to moisture, baked it in the oven at approx. 500 °C for 4 h in order to remove the water vapour previously absorbed. The aerogel was then placed on the pan of an analytical balance inside a closed chamber. Next to the aerogel solid, a beaker with water was placed to create a humid environment, and aerogel weight changes caused by water absorption were recorded for 7 consecutive days. Tillotson's research team [23], in turn, conducted moisture absorption studies on powdered silica aerogel, unmodified and modified with CF₃CH₂CH₂ (3,3,3-trifluoropropyl). Approx. 1 g of aerogel was placed in glass vials, which were then placed in a desiccator with deionised water at the bottom, where they were exposed to a humid environment for a period of 1 month. It was found that the fewer CF₃CH₂CH₂ groups the aerogel contained, the greater the ability to absorb moisture demonstrated by the aerogels tested, with the control, unmodified aerogel sample absorbing the most. A weight gain of 2.5% or less was adopted as the criterion for the hydropho-

bicity of aerogels. Gurav et al. [24], in order to assess the impact of moisture on TEOS-based silica aerogels unmodified and modified with HMDZ (hexamethyldisilazane), placed them in a humidity chamber (REMI Instrumentation Ltd.) at a relative humidity of 80% and temp. 30 °C for a period of 80 days and recorded the weight changes. At the end of the test, the lowest weight gain (below 2%) was demonstrated by the aerogel with an HMDZ/TEOS molar ratio of 0.68, which proves its hydrophobic nature. Unmodified aerogels demonstrated considerably higher weight gains throughout the test period, which was attributed to the presence of a large number of hydrophilic -OH groups on their surface.

In the case of aerogels applied in materials designed for clothing protecting against thermal factors, in addition to resistance to moisture absorption, their thermal stability and preservation of thermal insulation properties at high temperatures is of crucial importance. Studies of the properties of aerogels after exposure to thermal factors, i.e. high temperature or radiant heat, have been widely described in the literature [25-31]. The thermal properties of aerogels are highly dependent on their structural and textural features, i.e. the specific surface area, pore volume and pore size distribution. According to the commonly accepted classification for porous materials, the pores can be divided into three groups: (i) micropores with diameters smaller than 2 nm, (ii) mesopores with diameters between 2 and 50 nm, and (iii) macropores greater than 50 nm in diameter [32]. Silica aerogels have an open pore structure and are usually mesoporous (average pore diameter between 20 and 40 nm) with relatively few micro- and macropores [33-34]. They also have high values of BET surface area (600-1000 m²) relative to their mass. Because of those properties, silica aerogels are highly insulating, with a thermal conductivity lower than still air (0.01-0.02 W/mK, depending on the pressure) [35].

Shi and his team [25] subjected silica aerogels produced by them to heat treatment in an electric furnace, heating them to a temperature of 150 °C, 250 °C, 350 °C, 450 °C and 500 °C, and maintaining it for 2 h. As a result of the research, it turned out that the heat treatment had a huge impact on the hydrophobic properties and specific surface area of the aerogels. Investigations using the

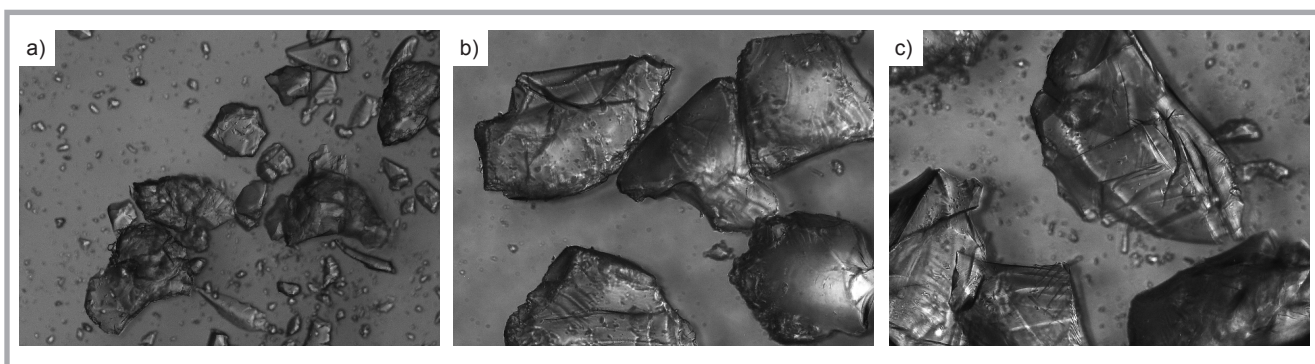


Figure 1. Optical microscope images of aerogels tested: a) CP, b) CG, c) KG

Table 1. Characteristics of aerogels selected for the study [36].

Aerogel symbol	Aerogel form	Particle size, μm	Particle density, kg/m^3	Thermal conductivity, $\text{W/m}\cdot\text{K}$	Surface chemistry
CP	powder	2-40	approx. 120-150	0.012	hydrophobic
CG	granules	100-700			
KG	granules	700-4000			

TG/DTA and FTIR methods showed that aerogels can maintain their hydrophobic properties up to a temperature of 350 °C. A further temperature increase results in the disappearance of $-\text{CH}_3$ groups due to their oxidation and, consequently, in the total loss of hydrophobicity after heat treatment at 500 °C. Along with an increase in the temperature of heat treatment within the 150-500 °C range, a gradual increase in the specific surface area of the aerogels from 610 m^2/g to 792 m^2/g was noted, which, based on SEM microphotographs, was attributed to a reduction in the particle diameter and a parallel increase in the pore size due to the heat treatment.

Similar results were obtained by Sarawade et al. [26] for aerogels modified with trimethylchlorosilane (TMCS) and exposed to high temperature, i.e. 200, 250, 300, 350, 400, and 500 °C for

1 hour. It was noted that a rise in temperature from 200 to 500 °C results in a significant increase in the aerogel specific surface area from 524 to 776 m^2/g and in a simultaneous reduction in the particle size, whereas the pore volume and pore diameter increased only for the samples subjected to heat treatment at a temperature below 500 °C. The authors observed that the increasing volume and pore diameter within the 200-400 °C temperature range results from the evaporation of residual solvent (water) and the oxidation of organic groups ($-\text{CH}_3$). This fact also influenced the reduction in aerogel density. However, at 500 °C a negative process of disintegration of micro- and mesopores occurred, which led to an increase in the density of the aerogel structure.

Huang et al. [29] assessed the changes in structural properties of silica aerogels after heat treatment at much higher temperatures (950-1200 °C) for 0.5-12 h. They found that the properties of aerogels are strongly affected by the heating time and temperature. In the case of samples heated at 950-1000 °C, their porosity throughout the test was within the range of 75-95%, while increasing the temperature to 1200 °C resulted in a reduction in aerogel porosity to approx. 30% after 0.5 h. For a sample heated at 1200 °C, it proved impossible to investigate the pore size distribution, which was probably due to the limited size of the pores, or to their disappearance.

Research on the flammability of aerogels under the influence of thermal radiation

was conducted, among others, by Li et al. [30] and Song et al. [31]. In both cases, the researchers used a cone calorimeter. Li's research team [30] exposed silica aerogels to radiant heat radiation of three different heat fluxes i.e., 15, 25 and 35 kW/m^2 . During exposure to a heat flux higher than 25 kW/m^2 , the aerogels demonstrated flammable properties and enhanced the spread of flames. The authors demonstrated the thermal decomposition of the aerogel and indicated as the cause the presence of organic groups in its structure, which were the original source of ignition, and consequent changes in the aerogel structure.

The aim of this work was to investigate the possibility of application of commercially available silica aerogels of varying grain size in materials for clothing protecting against heat. Considering the extreme conditions of use of this type of clothing, the aerogels were exposed to ageing factors such as moisture, high temperature and radiant heat. The resistance of aerogels to moisture absorption was studied using the weight method, determining the aerogel weight change before and after exposure to the environment at a relative humidity of 65% and 95%. From the point of view of the insulating properties of aerogels, we examined their structural and textural features (specific surface area, pore diameter and volume, pore size distribution) after exposure to the two main types of thermal factors, i.e. heating at 260 °C and thermal radiation of 20 kW/m^2 heat flux density. Maintaining the structural and textural features of aerogels during exposure to thermal factors is a necessary condition for increasing the insulation of protective clothing against thermal factors with aerogels, thus contributing to an improvement in its protective properties.



Figure 2. Weighing vessels with aerogel placed in a desiccator with $(\text{NH}_4)\text{NO}_3$.

Material and methods

Aerogels used in tests

Three types of silica aerogels with various degrees of granulation, i.e. one in the form of powder and two in the form of granules, were selected for the tests. Aerogels were purchased from Cabot Co., USA, the characteristics of which are shown in *Table 1*, whereas *Figure 1* shows images of the aerogels obtained using an Axiotech optical microscope (Carl Zeiss SMT Ltd., UK) with a Nikon DS-Fi1 digital camera and Nikon DS-U2 controller (Nikon Corporation, Japan).

Experimental method of exposure to humidity

A testing method for the exposure of aerogels to humidity was developed on the basis of standards for determining the hygroscopicity of textile materials, i.e. PN-80/P-04635 [37] and fire-extinguishing powders, i.e. PN-78/C-83602 [38].

Before testing, the aerogels were acclimated for 24 h in a laboratory in the following conditions: temperature $(20 \pm 1)^\circ\text{C}$ and relative humidity $(35 \pm 3)\%$.

Plastic weighing vessels (of 0.033 m height and 0.023 m diameter) designed to store aerogels during exposure to humidity were dried for 1 h in a desiccator heated to 40°C . Then they were transferred to the desiccator along with anhydrous CaCl_2 , providing a constant humidity level of ca. 20%, where they remained until they cooled down to 20°C (for approx. 10 min). The cooled weighing vessels were weighed on analytical scales with an accuracy of up to 0.0001 g.

After the period of acclimation of the aerogels, 0.5000 g of weighted aerogel samples were placed in the previously dried weighing vessels. These samples were placed in a desiccator with a saturated solution of $(\text{NH}_4)\text{NO}_3$ to obtain a relative air humidity of $(65 \pm 3)\%$ (*Figure 2*), or in a desiccator with distilled water, where the relative air humidity reached $(95 \pm 3)\%$. Two exposure times of the aerogels to moisture were adopted: 7 days and 16 days. At 24 h intervals, the vessels with aerogels were closed and weighed on analytical scales with an accuracy of up to 0.0001 g.

After 7 or 16 days of exposure, the moisture absorption capacity (W_i) of each aerogel sample was determined according to the following *Equation (1)*:

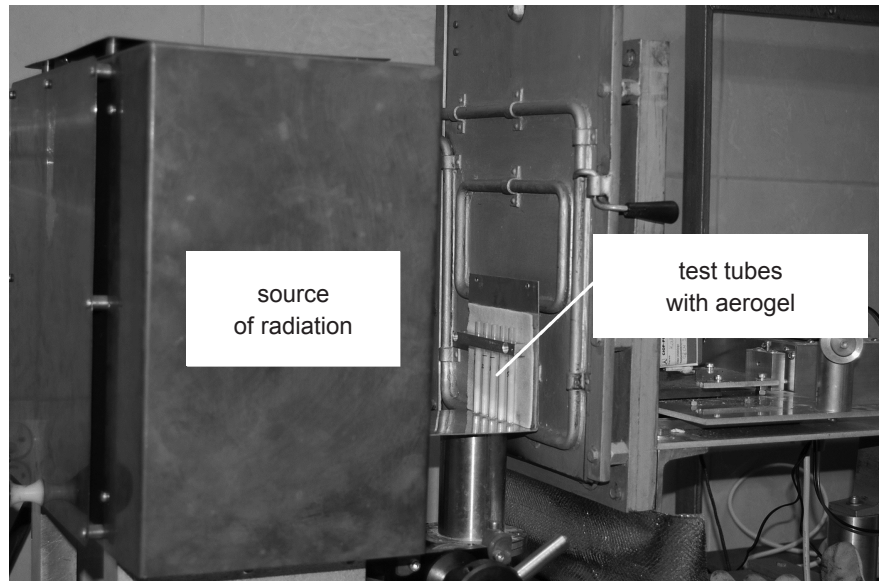


Figure 3. Test tubes filled with aerogels placed on the stand for testing resistance to radiant heat.

$$W_i = \frac{m_{nw} - m_{nas}}{m_{nas} - m_{ns}} \cdot 100\% \quad (1)$$

where:

m_{nw} – weight of the vessel with aerogel kept in a desiccator with relative air humidity of $(65 \pm 3)\%$ or $(95 \pm 3)\%$, g,

m_{nas} – weight of the vessel with aerogel before the test, g,

m_{ns} – weight of the vessel before the test, g.

As a result, the value of the arithmetic mean of moisture absorption by 3 samples of the same aerogel type calculated with two significant digits accuracy was given.

Experimental method of exposure to heat and radiation

Aerogels were also exposed to other aging factors in the form of heat and thermal radiation. Exposure of the aerogels to heat was carried out in a laboratory desiccator heated to 260°C , in accordance with the ISO 17493:2016 standard [39], concerning the testing of clothing materials. However, it was necessary to adapt this method to the study of granular materials (aerogels) by placing them in the desiccator in the weighing vessels.

In the case of the exposure of aerogels to radiant heat, we complied, in part, with the recommendations of EN ISO 6942:2002 “Protective clothing. Protection against heat and fire. Method of test: Evaluation of materials and assemblies when exposed to a source of radiant heat” [40]. The standard states that a sample of garment material should be placed on the frontal area of a calorimeter and exposed to thermal radiation, for exam-

ple, of 20 kW/m^2 . In the case of aerogels (granulate, powder), this was impossible, therefore they were placed in glass test tubes, which were mounted on a special metal rack and placed on a stand for testing resistance to radiant heat.

In the case of exposure to heat and thermal radiation, similar procedures related to the preparation of vessels for the storage of samples and to that of the aerogel samples were applicable. There were, however, differences in the method of exposure to thermal factors. To assess the impact of thermal factors on the properties of aerogels, the specific surface area and porosity were determined for the samples before and after the exposure.

Exposure to heat

Before the exposure of the aerogels to heat, glass weighing vessels (of 0.040 m height & 0.025 m diameter) designed to hold aerogels were dried to a constant weight. 0.5000 g of weighted samples of the aerogel acclimated for 24 h in the laboratory at $(20 \pm 2)^\circ\text{C}$ temperature and $(65 \pm 5)\%$ relative humidity were placed in the previously dried weighing vessels. The vessels with aerogels were placed in a desiccator heated to $(260 \pm 5)^\circ\text{C}$, where they remained for a period of 60 minutes. After the specified time of exposure to heat, the samples were transferred to a desiccator with anhydrous CaCl_2 and cooled down to $(20 \pm 2)^\circ\text{C}$ (for approx. 10 min). The samples were marked with the following symbols: C – after heat exposure, 260 – temperature of exposure in $^\circ\text{C}$, 60 – time of exposure in min.

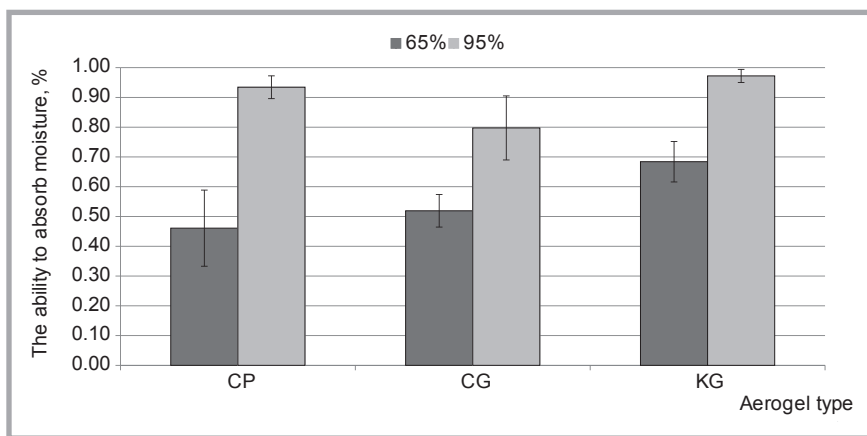


Figure 4. Moisture absorption capacity of the test aerogel types exposed to a humid environment for 7 days.

Exposure to radiation

To store the aerogels during exposure to thermal radiation, test tubes of 0.08 m height and 0.005 m inner diameter were used. Before testing, these tubes were dried to a constant weight in the same way as for the weighing vessels used to test the heat resistance of the aerogels. The aerogels were subjected to 24-hour acclimation under the conditions described in *Exposure to heat* chapter. The dried test tubes were filled with the aerogel to a height of 50 mm, corresponding to the height (width) of the garment material sample used during the test of resistance to radiant heat according to EN ISO 6942:2002 [40]. Then the tubes with the aerogel were placed in a special metal rack on a stand for testing resistance to thermal radiation (**Figure 3**). Prior to testing, the radiation source was calibrated so as to obtain a heat flux density of (20 ± 0.2) kW/m², and then the samples were exposed to radiant heat for 95 s. The exposure time applied represents the maximum time for the highest protection level – 4 according to EN ISO 11612:2015-11 [41], concerning the requirements for clothing protecting against thermal factors. After completion of the test, the samples were transferred to a desiccator along with anhydrous CaCl₂, where they were kept until they cooled down to (20 ± 2) °C. The samples were marked with the following symbols: Pr – after radiation exposure, 20 – heat flux density in kW/m², 90 – time of exposure in s.

Surface area, pore volume and pore size analysis

The adsorption/desorption isotherms of N₂ at 77K were measured using an Autosorb iQ analyser (Quantachrome, USA).

Prior to the adsorption/desorption measurements, each sample was riffled, and then 1g of aerogel was placed in the bulb cell. Then two-stage outgassing of the samples was performed (1st stage: 50 °C, 90 min, 2nd stage: 200 °C, 240 min) according to the recommendations of the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce [42]. Adsorption/desorption measurements were carried out at 34 measuring points (relative pressure P/P₀ from 10⁻⁸ to 0.995) and desorption measurements at 16 measuring points (P/P₀ from 0.995 to 0.35).

Analysis of the test results was carried out using ASiQwin V.3.01 software (Quantachrome Instruments, USA). The specific surface area was calculated using the multipoint BET method for 6 points at P/P₀ ranging from 0.05 to 0.30. The volume and size distribution of mesopores was determined using the BJH method and a desorption curve for P/P₀ > 0.35.

Statistical analysis

Statistical analyses were conducted using an R statistical software package. The results concerning moisture absorption capacity and the weight of the moisture absorbed by aerogels were analysed using two-factor analysis of variance (with the level of moisture and type of aerogel as the factors) and the Tukey post-hoc test. A test probability at the level of $p < 0.05$ was adopted as significant, and $p < 0.01$ – as highly significant. The purpose of the statistical analysis was to determine whether there are significant differences in the properties of aerogels for the different aerogel samples tested: Granulate K, Granulate C, Powder C for exposure to moisture at 65% and 95% humidity levels.

Results and discussion

The influence of moisture exposure on aerogels

The results of the research on the resistance of 3 types of aerogels with various degrees of granulation to the effect of an environment characterised by a relative humidity of 65% and 95% for 7 days demonstrated that, regardless of the aerogel type, the samples absorbed much more moisture under conditions of greater humidity (95%). A highly significant ($p = 0.0078$) difference in moisture absorption by the KG granulate at 65% and 95% humidity was observed. The findings for the CG granulate ($p = 0.0101$) and CP powder ($p = 0.0002$) were similar.

In an environment characterised by 95% relative humidity, the weight of absorbed moisture was similar for all 3 types of aerogels tested and amounted to 0.0020 g for the CG granulate, 0.0023 g for powder C and 0.0025 g for granulate KG. These values corresponded to a moisture absorption capacity of less than 1%, with the lowest value obtained for the CG granulate: 0.79%, and the highest for the CG granulate: 0.97% (**Figure 4**). Such low values indicate, therefore, that the aerogels tested are not prone to absorbing moisture.

In the case of the exposure of aerogels to a lower, i.e. 65% humidity environment, it was noted that the ability to absorb moisture increased with an increase in the aerogel granulation degree. The greatest ability to absorb moisture of 0.68% was reported for aerogel in the form of granulate with the largest particle size (KG), while the lowest – 0.46% – characterised the aerogel in powder form (CP). It should be noted, however, that the differences between the CG granulate and CP powder were not statistically significant.

The analysis of the aerogel moisture absorption capacity test carried out over an extended period of time (16 days) showed that the weight of the moisture absorbed by the aerogels in granular form – KG and CG as well as in CP powder form increased slightly. Under conditions of 65% relative humidity, an increase in aerogel weight from 0.0012 g to 0.0021 g for the KG granulate, from 0.0010 to 0.0019 g for the C granulate and from 0.0012 to 0.0015 g for C powder were noted (**Figure 5**). This is reflected in 0.58 to 0.83% of the moisture absorption capacity. Similar weight growth was recorded for the granulates.

A similar trend was observed for aerogel samples exposed to an environment of 95% relative humidity. For both types of granulate and for the powder, the mass of moisture absorbed after 16 days increased slightly, from 0.0026 to 0.0035 g for the K granulate, from 0.0022 to 0.0025 g for the C granulate, and from 0.0027 to 0.0032 g for C powder (**Figure 6**). In the case of C the granulate, the mass had undergone the smallest change, which corresponded to over 1% of the moisture absorption capacity, with the least – 1.01% – being in the case of the C granulate.

The results obtained in the tests of aerogel resistance to humidity are in accordance with the criterion of the hydrophobicity of aerogels adopted by Wagh [20], Rao [21] and Bellunatio [22], because the weight gain of the aerogels tested, as a result of the exposure to moisture, was much lower than 2%, and thus they can be classified in the group of hydrophobic aerogels. This is a very important finding, as the resistance of aerogels to moisture absorption is important from the point of view of the insulating properties of materials for protective clothing.

In the case of the aerogels examined by us, which had undergone exposure to an environment with a relative humidity of 95%, the weight gain did not exceed 1.5%, even after 16 days of exposure. A similarly low weight gain (no more than 2%) was obtained by Wagh and In-gale [20].

Miner and his team [19], at a relative humidity of 62%, noted an aerogel weight gain of 9.98%, while those tested by us at similar moisture level, i.e. 65%, showed a much higher resistance to moisture absorption after 24 hours of exposure, as evidenced by the almost ten-fold lower weight gain – approx. 1%. In the case of the aerogels tested by us, no changes in the appearance and size of the aerogel particles were also noted, even after exposure of the samples to an environment with 95% humidity.

The process of adsorbed moisture mass changes during the test is similar to the results of the research carried out by Bellunatio [22] and presented in the literature. In the initial phase of research, Bellunatio's team observed a steep increase in aerogel mass, showing that in the beginning the aerogel can absorb large amounts of water vapour, whereas later

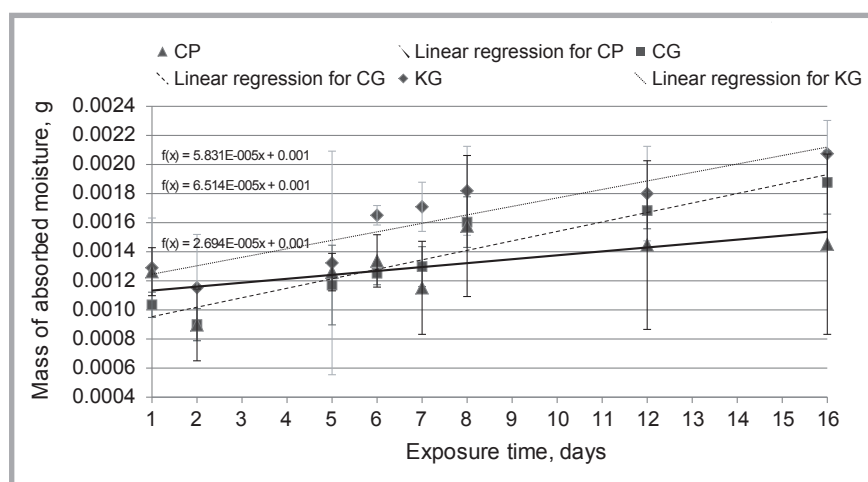


Figure 5. Weight of moisture absorbed by the aerogel types tested during exposure to a humid environment (relative humidity 65%).

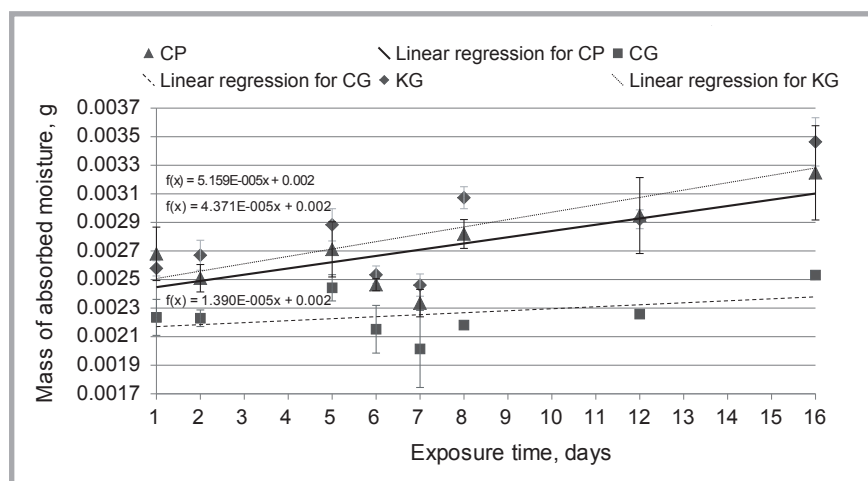


Figure 6. Weight of moisture absorbed by the aerogel types tested during exposure to a humid environment (relative humidity 95%).

the water absorption rate markedly decreased. A similar trend was noted during the tests carried out by us, as in the initial period of testing (up to day 5), there was a slight increase in aerogel mass, which then decreased on days 6 and 7, with a slight increase observed again starting from day 8 (**Figure 6**).

Our studies showed that the aerogel with the largest particle size, i.e. KG has the greatest moisture absorption capacity out of the 3 types of aerogels tested both in an environment with a relative humidity of 65% and in that with 95%. This trend continued throughout the period of the research. However, in the case of aerogels CG and CP, it cannot be determined unequivocally which one is more likely to absorb moisture, because the results are not conclusive. Similar studies aiming to assess the impact of aerogel particle size on the moisture content adsorbed were also conducted by Ihara and his team

[16]. The research was carried out using the desiccator method but for a much shorter period of time, which was only 72 hours. It was found that the granulate with smaller particle sizes (0.7-1.2 mm) at temp. 20 °C showed a higher moisture content than that with 1.2-4.0 mm particle sizes at the same relative humidity, while small granules had a lower moisture content at 50 °C. According to the authors, these inconsistencies resulted from the fact that the same sample was not consistently used at different temperatures during the measurements. It was therefore concluded that the differences in particle size do not affect the moisture content adsorbed. The big granules of silica aerogel used by Ihara [16] correspond to the particle size of the KG aerogel tested by us. However, taking into account the content of moisture adsorbed during exposure to the environment with similar relative humidity i.e. approx. 95-97% and a temperature of 20 °C, it can be

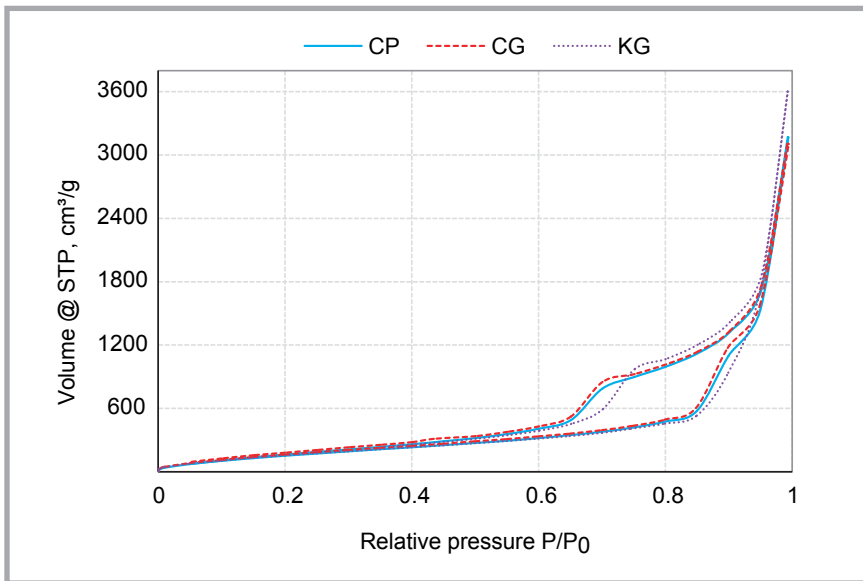


Figure 7. Adsorption/desorption isotherms of untreated aerogel samples.

Table 2. Textural properties of aerogel samples.

Sample type	BET surface area, m ² /g	BJH		
		Surface area, m ² /g	Pore volume, cm ³ /g	Pore diameter, nm
CP	687.5	1198.9	5.13	6.56
CP C 260; 60	776.9	1247.6	5.14	6.55
CP Pr 20; 95	728.2	1184.4	4.92	6.56
CG	740.7	1265.9	5.04	6.56
CG C 260; 60	740.3	1290.5	5.15	6.57
CG Pr 20; 95	705.8	1225.1	5.55	6.57
KG	697.4	1190.8	5.81	7.83
KG C 260; 60	687.3	1208.1	6.03	7.82
KG Pr 20; 95	688.4	1174.2	5.31	7.83

concluded that the KG granulate is much more resistant to a humid environment, as evidenced by the weight gain of only approx. 1%, while the aerogel tested by Ihara [16] showed a weight gain level of approx. 3%.

The influence of heat exposure on surface area, pore volume and pore size analysis of aerogels

The nitrogen adsorption/desorption isotherms of untreated aerogel samples are shown in Figure 7. Similar results were obtained for the samples subjected to thermal and radiation treatments. According to the recommendation of the International Union of Pure and Applied Chemistry (IUPAC) for physisorption analysis, all isotherms belong to the IV(a) type, which is characteristic of mesoporous materials [43]. However, instead of the plateau at high P/P_0 observed for purely mesoporous materials, a steep increase in the volume adsorbed can be noticed (as for type II isotherm), which can be associated with the presence of macropores. The hysteresis loop, which can be generally attributed to either the metastability of the multilayer adsorbed, network effects, or pore blocking [44], is located within the multilayer range of physisorption (for P/P_0 approx. from 0.4 to 0.95), indicating capillary condensation. This type of hysteresis loop (H1) is characteristic for a narrow range of uniform mesopores, which is consistent with

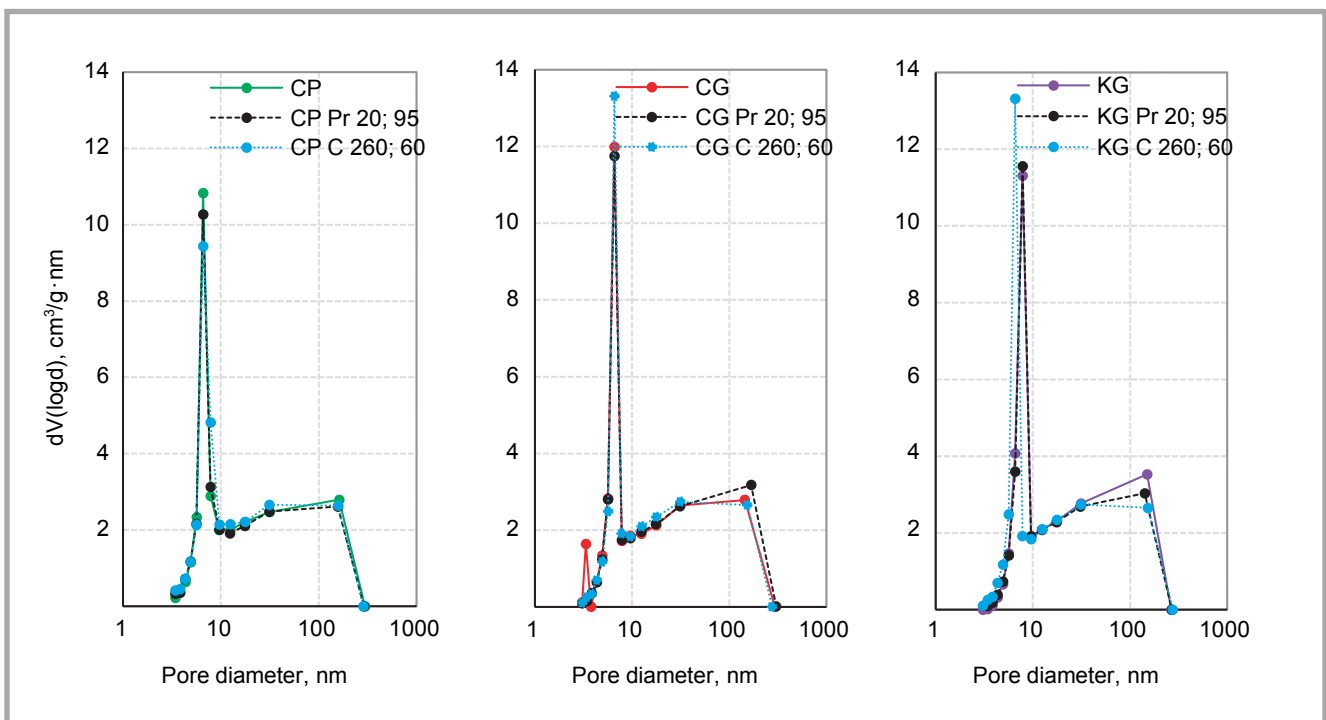


Figure 8. Pore size distribution of aerogel samples based on BJH method.

the BJH pore size distribution of aerogels shown in **Figure 8**.

Textural features of aerogels before and after treatment, calculated using the BET and BJH methods, are presented in **Table 2**. For CP aerogel with the smallest grain sizes, an increase in the BET specific surface area was observed after high temperature and radiation treatment, while in case of the CG and KG samples, no such relation was established. In all cases, the BJH surface area and pore volume were slightly higher for samples treated at high temperatures compared to the untreated ones. No significant influence of the radiation treatment on those parameters was observed. The average pore diameters of samples CP and CG were comparable to and lower than for the KG samples. BJH pore size distributions in aerogels before and after treatment (**Figure 8**) indicate that the size of most of the pores ranged from 6 to 10 nm (small mesopores). Micropores were not observed in either of the samples, and only a small number of macropores was observed at the same time, which is consistent with the shape of the adsorption/desorption isotherm.

Overall, the results indicate that neither the heat treatment nor radiation treatment, within the specified temperature and time range, affect the surface area, pore volume or pore size of the samples tested, which is in agreement with the results previously described by Sarawade et al. [26] who reported a small change in the BET surface area of sodium silicate-based hydrophilic silica aerogels when heated in air for 1 h at 200 °C and 250 °C and larger differences in textural parameters for temperatures above 300 °C [26]. Different findings were reported by Cui et al. [27], who studied the microstructure of hydrophobic silica aerogels modified with methyltriethoxysilane within the temperature range from 200 °C to 500 °C by means of physisorption analysis (BET) and scanning electron microscopy. The surface area of the aerogels ranged from 850.2 m²/g for an untreated sample to 545.5 m²/g for a sample treated at 300 °C. The pore size increased after heat treatment at 200 °C and 500 °C (from 14.71 to over 18 nm) and was stable for the remaining temperatures (from 16.25 to 16.58 nm after treatment at 300-450 °C). At the same time, a mixed effect of heat treatment on the pore volume was observed for treatments at 200-400 °C, which increased at temperatures above 450 °C [27].

■ Conclusions

The results of tests of aerogel resistance to humidity, both in granulate and powder forms, carried out under conditions varying in terms of relative humidity: 65% and 95%, demonstrated that, regardless of the aerogel type, they absorbed much more moisture in conditions of greater humidity (95%). There was a significant difference in moisture absorption between 65% and 95% humidity. In an environment characterised by 95% humidity, the moisture weight absorbed was similar for all aerogels, which was approx. 0.0023 g on average. This value corresponded to the absorption capacity at a level lower than 1%, which is a low value, evidencing that the new aerogels were not susceptible to moisture absorption, which is a very important conclusion, as the resistance of aerogels to moisture absorption is essential from the point of view of the characteristics of materials intended for use in protective clothing. On the one hand, hydrophobic properties ensure the stability of the aerogel structure and low thermal conductivity, while preventing weight increase, which is beneficial in the case of application in clothing materials.

Similarly, in the case of the test of resistance to high temperatures and radiation, no adverse changes in the structural and textural characteristics of the aerogels were observed. The greatest changes in specific surface area were recorded for aerogels in powder form (a 13% increase in BET surface area after exposure to high temperature compared to untreated samples). Due to the fact that a specific surface area increase can result in a reduction in thermal conductivity, this change is of a positive nature in the context of application in clothing to protect against heat. In other cases, the textural properties of the aerogels were stable, and some of the changes exceeded 5% as compared to the untreated samples. This allows to presume that these materials can be used successfully in the construction of garments protecting against thermal factors to improve their protective properties by increasing thermal insulation.

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