SIO_2 aerogels and its application in firefighter protective clothing

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REZUMAT – ABSTRACT

Aerogeluri de SiO_2 și aplicațiile acestora la temperatură ridicată

Acest articol studiază utilitatea aerogelului pe bază de siliciu ca material de izolație în îmbrăcămintea de protecție utilizată la temperaturi ridicate, în special pentru pompieri. În trecut, aerogelurile au fost utilizate pentru izolarea clădirilor, în aplicații aeronautice și aerospațiale. Mai târziu, cercetătorii au determinat utilitatea aerogelilor ca substrat izolator în îmbrăcămintea de protecție. Mai multe investigații au evidențiat proprietățile de izolare ale aerogelului la temperatură ridicată. Există mai multe tipuri diferite de aerogel, dar în acest articol, accentul principal este pus pe aerogelul pe bază de siliciu datorită capacității excelente de izolare și a proprietăților ignifuge, împreună cu stabilitatea termică la temperaturi ridicate. Prin aplicarea unor tehnici adecvate de acoperire, aerogelul poate fi impregnat în substraturi nețesute, care pot fi utilizate ca bariere termice, cu rezultate în îmbunătățirea capacității de protecție a îmbrăcămintei multistratificate la temperaturi ridicate. Toate aceste caracteristici fac din aerogel un potențial candidat pentru a fi utilizat ca material izolator în îmbrăcămintea de protecție la temperaturi ridicate.

Cuvinte-cheie: aerogeluri, izolație termică, conductivitate termică, îmbrăcăminte de protecție

SIO_2 aerogels and its application in firefighter protective clothing

This article focuses our attention on utility of silica based aerogel as insulation materials in protective clothing especially for fire fighters at higher temperature. In past, aerogels were employed for insulation of buildings, aeronautics and aerospace applications. Later on, researchers determined the utility of aerogels as insulated substrate in protective clothing. Several investigations revealed insulation properties of aerogel at elevated temperature. There are several different types of aerogel but in this article, the main emphasis is on silica based aerogel because of its excellent insulation and outstanding flame proof properties along with thermal stability at raised temperature. By applying suitable coating techniques, aerogel can be impregnated into nonwoven substrates, which can be employed as thermal barriers resulting in enhancement of the protective capability of multilayered clothing at higher temperature. All these characteristics make aerogel a potential candidate to be used as insulation material in protective clothing at elevated temperature.

Keywords: aerogels, thermal insulation, thermal conductivity, protective clothing

INTRODUCTION

The discovery of silica based aerogels in 1930s by Samuel Stephens Kistler was based on concept of substituting the liquid phase with the gaseous phase along with little amount of shrinkage and without crumpling of gel solid network. Aerogels are smoked like substrates having resemblance of hologram and instead of appearing as solid material it looks like projection. Aerogels are synthesized by Sol-Gel process which is simple, cost effective and delivers high quality substrates [2].

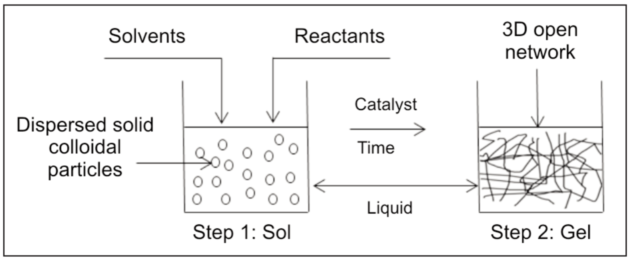

Fig. 1. Process of Sol-Gel [3]

In this method, a chemical reaction was carried out in a solution at low temperature to produce inorganic network or creation of an amorphous structure from the solution. The distinct feature of this reaction was conversion from colloidal solution to di-or multiphase gel. Silica based aerogels have 96 % of air and 4 % of silicon dioxide, making silica based aerogels as one of the lightest weight solid substrates [1]. A sol is a colloidal suspension of solid particulates in an aqueous medium in which range of dispersion phase is from (1–1000 nm) [3]. Sol can be synthesized either by condensation or dispersion of particulates. Condensation occurs when nucleation development of particulates approaches adequate size. However, dispersion includes breaking of large particulates to colloidal sizes. In case of gelatin process, a free flowing sol is transformed into a three dimensional solid structure encapsulating the solvent media. It was evident that liquid does not permit the solid structure to crumple and solid structure does not allow the liquid to move out. Figure 1 depicts the schematic diagram of Sol-Gel process [3–4].

STEPS INVOLVED IN SOL GEL PROCESS

Three steps required for sol gel process are:
a. Formation of gel
b. Aging
c. Drying

Formation of gel

Mostly precursors utilized for sol-gel process are silicon alkoixdes which are available in high degree of purity. However it is very difficult to purify potassium silicate [4]. One of the most important precursors of silica based aerogel is sodium meta-silicates and it was primarily employed by Kistler for synthesizing silica aerogels [5].

$$Na_2SiO_3 + 2HCl + (x–1)H_2O \rightarrow SiO_2 \cdot xH_2O + 2NaCl \quad (1)$$

The preparatory materials for the sol-gel process must be soluble in reaction medium and sufficiently reactive to have contribution in the gel-creating process. All of these preparatory substrates are described by the existence of Si–O polar covalent bonds [6]. The covalent nature of the Si–O bond is adequate to allow distribution of ≡Si–O–Si≡ angle values creating a three dimensional structure in random manner which resembles structure of silica glass. Hydrolysis can be catalyzed via acid catalysis or base catalysis. Acids like HCl, HNO_3, H_2SO_4, HF, oxalic, formic and acetic acid are employed for acid catalysis. When pH of solution is less, the time period for gelatin formation is normally elongated [4]. According to Dieudonne et al. [7] base catalysis is a simple procedure in which there is an easy formation of network of uniform particles in the solution and the subsequent pore volume is significantly enhanced.

Aging

During aging, a neck growth due to reprecipitation of silica deliquesces from the surface of particle upon necks between particles and smaller particles dissolute and conversion into bigger ones by precipitation [8]. The purpose of this step is to mechanically reinforce the weak solid skeleton generated during sol-gel process [4].

Drying

In case of drying, the most commonly used method is Super Critical Drying method. This method is governed by evacuation of pore liquid above the critical temperature (T_c) and critical pressure (P_c). At this instant, there is no liquid-vapor boundary and consequently there is no capillary pressure. This procedure is completed in three stages [9]: In first step, wet gel along with appropriate quantity of solvent is set in an autoclave by steadily elevating the temperature. This will result in escalation of pressure. Temperature and pressure of the concerned solvent are attuned to acquire values above critical points. In second step, the fluid is gradually expelled at constant temperature causing decrease in pressure. In third step, the temperature of vessel drops to room temperature once ambient pressure is acquired. Figure 2 depicts autoclave for performing supercritical drying. Drying can also takes place via ambient pressure drying and freeze drying [10].

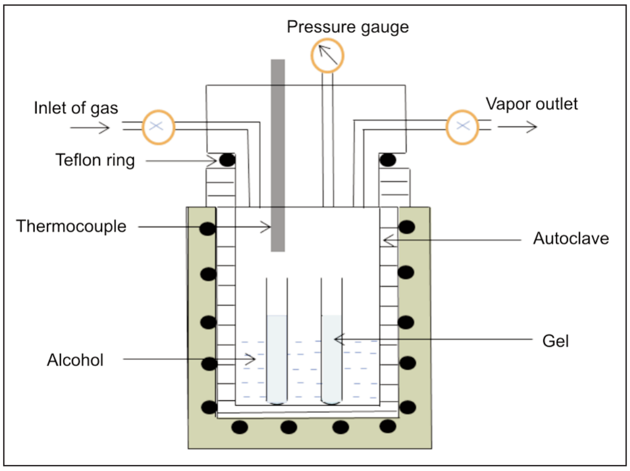

Fig. 2. Schematic representation of supercritical drying autoclave [6]

PROPERTIES AND UTILITIES OF SILICA BASED AEROGELS

Structure of pore

Silica based aerogels are mostly mesoporous having interlocked pore size with range from 5 to 100 nm. The diameter of average pore is between 20 to 40 nm. Micropores having pore size less than 2 nm becomes pertinent in aerogels produced under acidic catalysis conditions [11]. The specific surface range from 250 to 800 $m^2 g^{-1}$ and can surpass 1000 $m^2 g^{-1}$.

Thermal insulation, flame proof property

Silica based aerogels have very small portion of solid silica (nearly 1–10%) due to which they have lesser solid conductivity and thus exchange lesser thermal energy [4]. At ambient pressure, temperature and relative humidity, silica based aerogels have very low thermal conductivity of the order 0.015 W/mK which is expressively lesser than thermal conductivity of air (0.025 W/mK) under same circumstances [12]. Apart from having thermal insulation property, silica aerogel has remarkable flame proof property [13]. By means of mass, Aerogel is 99.8% air making it least dense man-made substrate [14]. Aerogel can abrogate all three modes of heat transfer. Conductive heat transfer is blocked because of gaseous structure of aerogel and thermal conductivity of gas is very low. The gaseous structure of aerogel is derived from its porous construction. Convective heat transfer is averted because structure of aerogel does not allow circulation of air. Infrared radiation that plays role in transference of heat can also be absorbed by aerogel. As consequence, aerogel can function as outstanding thermal insulator [15].

Sorption and entrapment properties

Aerogels can be utilized to adsorb some chemical compounds i.e. waste water treatment for restricting radioactive waste or for filtration of gases. Silica aerogels soaked with $CaCl_2$, LiBr and $MgCl_2$ salts have also been confirmed to absorb/adsorb water for retention of heat at low temperature [16]. It was suggested hollow silica aerogel droplets for inertial entrapment of fluids, specifically blends of liquid deuterium and tritium, as the aim in fusion experimentation under very strong laser. Bacteria can also be successfully entrapped in aerogels while remaining alive.

HEAT EXCHANGE PROCESS

Heat exchange equation illustrates transfer of heat in porous substrates like aerogels [17].

$$\nabla \vec{q} + \Phi = \rho \cdot c \cdot \frac{\partial T}{\partial t} \quad (2)$$

This equation depicts law of conservation of energy by balancing heat fluxes across interfaces of infinite volume. In the above equation q is the heat flux density, ρ – the density and is the specific heat, Φ – the heat source and T – local temperature.

$$\vec{q} = -k \nabla T \quad (3)$$

k is three dimensional tensor of the thermal conductivity. This equation is the Fourier law which narrates that heat flux density is proportional to local temperature difference and describes the thermal conductivity k. The heat source Φ explains the impact of phase changes or sorption phenomenon within an aerogel associated with the discharge or intake of reaction enthalpies and increase or decrease of thermal radiation. Thermal radiation is explained by heat source term in following way:

$$\Phi = \nabla \vec{q}_r \quad (4)$$

Here q_r is radiative heat flux density. In case of isotropic aerogel and when heat exchange is dependent only on local temperature difference:

$$\Delta T = \frac{1}{\alpha} \cdot \frac{\partial T}{\partial t} \quad (5)$$

Where α is the thermal diffusivity which is equal to $k/(\rho \cdot c)$. In this situation, experimentally evaluated thermal conductivity is characteristics of the substrate. Where $\rho \cdot c$ is termed as volumetric specific heat and is suitable for the situation of nonstationary heat exchange where temperature and heat fluxes varies with time [12, 18].

APPLICATIONS OF SILICA AEROGELS AT HIGH TEMPERATURE

At present the most common utility of aerogel products are in oil and gas pipelines, building insulations along with aeronautics/aerospace and high temperature applications [19]. On commercial bases aerogel is available asNanogel^{TM}, which can be employed as superinsulating filling substrates; however CABOT is also supplying Nanogel^{TM} based components like Thermal wrap^{TM} and Compression pack^{TM} for special applications like pipe in pipe and cryogenic insulation systems. Apart from that, ASPEN company is providing blanket-based products for insulation of building on commercial scale and also developing products for utility in acute hot and cold climates (pyrogel and cryogel) [18–19]. Novel advancements of aerogel science have made it viable to create more flexible aerogels in simplified ways. All these features make aerogel favorable prospects to be utilized for enhancing thermal protection and thermal insulation in fire fighter protective clothing.

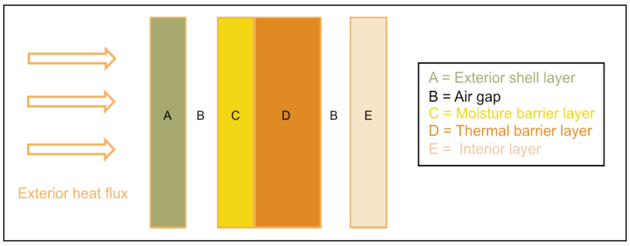

Fig. 3. Configuration of fire fighter clothing assemblies [22]

Fire fighters are subjected to several threats with respect to their working atmosphere. In addition to numerous toxic ingredients in the surrounding atmosphere, extreme radiant heat fluxes and hot flames are probable hazards in fire extinguishing activity. Thermal protective performance of fire fighter protective clothing is of huge significance to the lives of firefighters [20].

The key purpose of fire fighter clothing is to decline the rate of heat accumulation in human skin so as to give time for the firefighter to respond and avert or reduce skin burn injury [21]. Mostly fire fighter protective clothing comprised of three layers such as exterior shell, middle layer and interior layer or two layers like outer shell and inner layer with assembly of moisture barrier and a thermal barrier as shown in figure 3 [22]. The exterior layer averts body skin from hazards of heat radiation or flame and intermediate layer delivers execution of waterproof and heat insulation. Mostly the aramid fibers are utilized for insulation layer and PTFE membranes are employed as breathable waterproofing layer. Jin et al. investigated thermal protective behavior of nonwovens employed with aerogels [21]. It can be noticed that specimen coated with aerogels had greater LOI values than the untreated specimen. This might be due the fact that inorganic aerogel particles being attached on the surface of specimen might enhance the flame retardant characteristics [21]. For evaluation of effect of aerogel on thermal protective performance (TPP) of the whole fire fighter garment, aerogel treated firefighter clothing utilizing thermal liner in fighter protective garment was developed by Jin et al. [22]. Instrumented manikin system under heat flux density of 84 kW/m^2 with 8 second of exposure time was employed. For aerogel treated fire fighter clothing, total burn injury was 12.7% which was lesser than that of existing garment which was 25.1% [22]. It was also witnessed that aerogel impregnated sample when utilized next to skin can absorb moisture and discharge it ambient surrounding with great ease. Moreover there was increase in the rate of moisture absorption when aerogel impregnated layer was employed next to skin [22]. Thus it was deduced that aerogel when coated on textile substrate can enhance thermal resistance of the fabric and delivers better thermal insulation properties.

CONCLUSION

Aerogels are invented long time ago but its application in daily life started a decade ago. The application of aerogels for insulation at higher temperature is still an open field and needs to be researched deeply. In this report the application of aerogels specially for insulation properties are discussed and will be a basis for continuing research related to use for aerogels in firefighter clothing, fire protection buildings and facade insulation. With extremely low thermal conductivity and high porosity the aerogels have a great future for the application for insulation at higher temperature. Another open field of aerogels is also comfort properties and could be a great application for clothing for protection with comfort requirement. The breathe ability of aerogels can play an important role for the comfort and insulation application.

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BIBLIOGRAPHY

[1] Patel, R., Purohit, N., Suthar, A. *An overview of silica aerogels.*In: International Journal of ChemTech Research, 2009, vol. 1, no. 4, pp. 1052–1057.

[2] Chakraborty, S., Pisal, A.A., Kothari, R. *Synthesis and characterization of fiber reinforced silica aerogel blankets for thermal protection*. In: Advances in Materials Science and Engineering, 2016, pp. 1–8.

[3] Pierre, A.C., Pajonk, G.M. *Chemistry of aerogels and their applications*. In: Chem. Rev, 2002, vol. 199, pp. 4243–4266.

[4] Soleimani, D.A., Abbasi, M.H. *Review silica aerogel; synthesis, properties and characterization.* In: Journal of materials processing technology, 2008, vol. 199, pp. 10–26.

[5] Venkateswara, R.., Parvathy, R.A., Kulkarni, M.M. *Influence of gel aging and Na_2SiO_3/H_2O molar ratio on monolithicity and physical properties of water–glass-based aerogels dried at atmospheric pressure*. In: J Non-Cryst Solids, 2004, vol. 350, pp. 224–229.

[6] Brinker, C., Scherer, G. *Sol-gel science*. In: The physics and chemistry of sol-gel processing, Academic Press, New-York, 1990, vol. 97, pp. 461–523.

[7] Wu, G., Wang, J., Shen, J., Yang, T., Zhang, Q., Zhou, B., Deng, Z., Bin, F., Zhou, D., Zhang, F. *Properties of sol gel derived scratch resistant nano porous silica films by mixed atmosphere treatment*. In: J. Non-Cryst Solids 2000, vol. 275, pp. 169–174.

[8] Strøm, R.A., Masmoudi, Y., Rigacci, A., Petermann, G., Gullberg, L., Chevalier, B., Einarsrud M.A. *Strengthening and aging of wet silica gels for up-scaling of aerogel preparation*. In: J Sol Gel SciTechnol, 2007, vol. 41, pp. 291–298.

[9] Reichenauer, G.J., *Proceedings of 7th international Symposium on Aerogels*. In: Non-Crystal Solids, 2004, vol. 350, pp. 189–195.

[10] Suh, D.J., Park, T.J., Sonn, J.H., Lim, J.C. *Effect of aging on the porous texture of silica aerogels prepared by NH_4OH catalyzed sol-gel process.* In: J Mater SciLett, 1999, vol. 18, pp. 1473–1475.

[11] Husing, N.,Schubert, U. *Aerogels – Airy materials: Chemistry, structure, and properties*. In: AngewChemInt Ed, 1998, vol. 37, pp. 23–45.

[12] Yoldas, B.E., Annen, M.J., Bostaph, J. *Chemical engineering of aerogel morphology formed under nonsupercritical conditions for thermal insulation*. In: Chem Mater 2000, vol. 12, pp. 2475–2484.

[13] Bheekhun, N., Talib, A.R.A., Hassan, M.R. *Aerogels in aerospace: an overview*. In: Advances in Materials Science and Engineering, 2013, pp. 1–18.

[14] Soleimani, D.A., Abbasi, M.H. *Silica aerogel; synthesis, properties and characterization.* In: Journal of Materials Processing Technology, 2008, vol. 199, pp. 10–26.

[15] Shahid, A., Wang, L., Padhye, R. *The thermal protection and comfort properties of aerogel and PCM-coated fabric for firefighter garment,* 2016, vol. 45(4), pp. 611–625.

[16] Aristov, Y.I., Restuccia, G., Tokarev, M.M., Cacciola, G. *Selective water sorbents for multiple applications, 10*. In: Energy Storage Ability. ReactKinetCatalLett, 2000, vol. 69, pp. 345–353.

[17] White, J.F. *Silica aerogel: Effect of variables on its thermal conductivity*. In: Industrial and Engineering Chemistry, 1939, vol. 31, pp. 827–831.

[18] Bankvall, C.G., *Natural convection in vertical permeable space*. In: W€arme- und Stoff€ubertragung, 1974, vol. 7, pp. 22–30.

[19] Koebel, M.M., Rigacci, A., Achard, P. *Aerogels for superinsulation: A synoptic view.* In: Aegerter, M.A, Leventis, N., Koebel, M., editors. Aerogels Handbook, Advances in Sol-Gel derived materials and technologies. New York: Springer Dordrecht Heidelberg London, 2011, pp. 625–630,

[20] Onofrei, E., Dupont, D., Petrusic, S., Soulat, D., Bedek, S., Codau, T.C. *Modeling of heat transfer through multilayer firefighter protective clothing*. In: Industrial Textila, 2014, vol. 65, pp. 277–282.

[21] Jin, L., Hong, K., Yoon, K. *Effect of aerogel on thermal protective performance of fire fighter clothing*. In: Journal of Fiber Bioengineering and Informatics, 2013, vol. 6, pp. 315–324.

[22] Jin, L., Hong, K., Nam, H.D., Yoon, K. *Effect of thermal barrier on thermal protective performance of firefighter clothing*. In: Journal of Bioengineering and Informatics, 2011, vol. 4, pp. 245–252.

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