

# A Novel Method to Manufacture Superhydrophobic and Insulating Polyester Nanofibers via a Meso-Porous Aerogel Powder

Z. Mazrouei-Sebdani, A. Khoddami, H. Hadadzadeh, M. Zarrebini

**Abstract**—In this research, waterglass based aerogel powder was prepared by sol–gel process and ambient pressure drying. Inspired by limited dust releasing, aerogel powder was introduced to the PET electrospinning solution in an attempt to create required bulk and surface structure for the nanofibers to improve their hydrophobic and insulation properties. The samples evaluation was carried out by measuring density, porosity, contact angle, heat transfer, FTIR, BET, and SEM. According to the results, porous silica aerogel powder was fabricated with mean pore diameter of 24 nm and contact angle of 145.9°. The results indicated the usefulness of the aerogel powder confined into nanofibers to control surface roughness for manipulating superhydrophobic nanowebs with water contact angle of 147°. It can be due to a multi-scale surface roughness which was created by nanowebs structure itself and nanofibers surface irregularity in presence of the aerogels while a layer of fluorocarbon created low surface energy. The wettability of a solid substrate is an important property that is controlled by both the chemical composition and geometry of the surface. Also, a decreasing trend in the heat transfer was observed from 22% for the nanofibers without any aerogel powder to 8% for the nanofibers with 4% aerogel powder. The development of thermal insulating materials has become increasingly more important than ever in view of the fossil energy depletion and global warming that call for more demanding energy-saving practices.

**Keywords**—Superhydrophobicity, Insulation, Sol-gel, Surface energy, Roughness.

## I. INTRODUCTION

THE wettability of solid surface is an important property of material that is controlled by the chemical composition and geometry of the surface [1], [2]. There are many applications for which a material must be water-resistant. The inadequacy of fossil fuels, which is the main resource for the industries and energy carriers, has highlighted the dependence of modern technology on cheap energy and resources. Thus, this is forcing humanity to rethink global energy strategies. In addition to a limited supply of carbon-based fuels worldwide,

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the effect a rising CO<sub>2</sub> concentration in the earth's atmosphere and its effect on the global climate, has become indubitably clear [3], [4]. Silica aerogels can have unusual properties, including high surface area, low density, low thermal conductivity, and good optical translucency [5]. This combination of properties makes hydrophobic silica aerogels attractive materials for use in applications [6]. One of the major characteristics of silica aerogels is their very low thermal conductivity, typically of the order of 0.015 Wm<sup>-1</sup>K<sup>-1</sup> at ambient temperature and relative Humidity [7]. In this research, waterglass based aerogel powder prepared via sol–gel and ambient pressure drying was introduced to the PET nanofibers in an effort to generate proper structure to improve the physical properties.

## II. EXPERIMENTAL

### A. Materials

All chemicals were of analytical grade from Merck, Germany. TMCS was prepared from Daejung, Korea.

### B. Sample Synthesize

The sodium silicate solution diluted by water (1/4 v/v) went through a long ion-exchange column filled with Amberlite IR 120 H resin. The initial pH of the silica sol was adjusted to 5 with diluted ammonia (1%) to be gelled and then, aged for 3 hours. Propan-2-ol (IPA), trimethylchlorosilane (TMCS), and n-Hexane were used for the solvent exchange and surface modification process for 1 day. The gel was air dried at room temperature for 1 day and 230°C for 1 h, and then grounded gently with a ball mill (Pm10, Retsch, Germany).

### Fabrication of the Hybrid Aerogel/Nanofibers

A mixture of PET chips in 1:1 (v/v) DCM and TFA was firstly stirred using a magnetic stirrer for 12 h and then by an ultrasonic stirrer (UP200 H lab device (200 W, 24 kHz)) for 20 min. a horizontal electro-spinning, STC-523 device, Japan was used for electrospinning process at a voltage of 13 kV.

### C. Characterization

The bulk density was measured from known volume and mass of the aerogel piece.

The porosity of the resulted aerogel was calculated using (1).

$$P = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100 \quad (1)$$

where,  $P$ ,  $\rho_b$ , and  $\rho_s$ , represent the porosity (%), bulk density ( $\text{g}/\text{cm}^3$ ), and skeletal density of amorphous silica ( $\text{g}/\text{cm}^3$ ), respectively.

FTIR spectra of the samples were recorded by MB-Series 100, Hartman & Braun, Canada.

Belsorp mini II apparatus built by BelJapan, Japan (ISO 9277) was used for BET. SEM of the samples was obtained using EM3200, KYKY in order to study the sample surface topology and porosity. The location of a droplet on the surface of the hydrophobic treated samples allows evaluating the contact angles. The angles between the liquid/solid and liquid/vapor interfaces were measured using the Digimizer software. The dynamic heat transfer [8] of the fabric samples was investigated using previously methods.

### III. RESULT AND DISCUSSION

#### A. Aerogel Characterization

The  $\text{SiO}_2$  aerogel was synthesized in the presence of waterglass as an available and non-toxic precursor with drying at atmospheric pressure. The aerogel characteristics and nanostructures were shown in Table I and Fig. 1 (A), respectively. As can be seen from Table I, it is clear that the porous aerogel powder was successfully synthesized with a surface area of  $815 \text{ m}^2/\text{g}$  and porosity of 88.6%, obtained by BET and BJH analyses. Thus, the resulted dried gel in this work can be named aerogel because aerogels are composed of 10 nm or below nanoparticles and have nano-pores with diameters of less than 50 nm [4].

TABLE I  
AEROGEL CHARACTERISTICS

Density ( $\text{g}/\text{cm}^3$ )	Total pore volume ( $\text{m}^3/\text{g}$ )	Mean pore diameter (nm)	Surface area ( $\text{m}^2/\text{g}$ )	Porosity (%)	Water contact angle ( $^\circ$ )
0.2	3.5	24	815	88.6	145.9

Although Table I shows that the aerogel granules exhibit water contact angle usually associated with that of high hydrophobic gels modified by the TMCS hydrophobic agent, beyond inclination of  $180^\circ$ , the detachment of the water droplet from the aerogel surface did not occur. This could be attributed to the existence of the nano-pores and subsequent high water absorbency of the aerogel surface that is resemblance of gecko toes. As for gecko toes, the millions of setae can trap air inside the nano-scale structures forming strong adhesion and contact angle [9].

Hydrophobic properties of the aerogel can be explained by FTIR analysis, Fig. 2. According to Fig. 2, the peak at around  $1650 \text{ cm}^{-1}$  is due to the adsorbed water and the broad absorption band at  $3445 \text{ cm}^{-1}$  corresponds to Si-OH band [10]. The FTIR spectrum of the hydrophobic silica aerogel shows negligible Si-OH ( $3445 \text{ cm}^{-1}$ ) and adsorbed  $\text{H}_2\text{O}$  ( $1650 \text{ cm}^{-1}$ ) peaks along with C-H ( $3000 \text{ cm}^{-1}$ ) peak.

A significant peak at  $2961 \text{ cm}^{-1}$  arising from the C-H bonding proved the silylation of the OH groups to the O-Si( $\text{CH}_3$ )<sub>3</sub> with TMCS. So it could be concluded that TMCS successfully reacted by the gel hydrophilic groups.

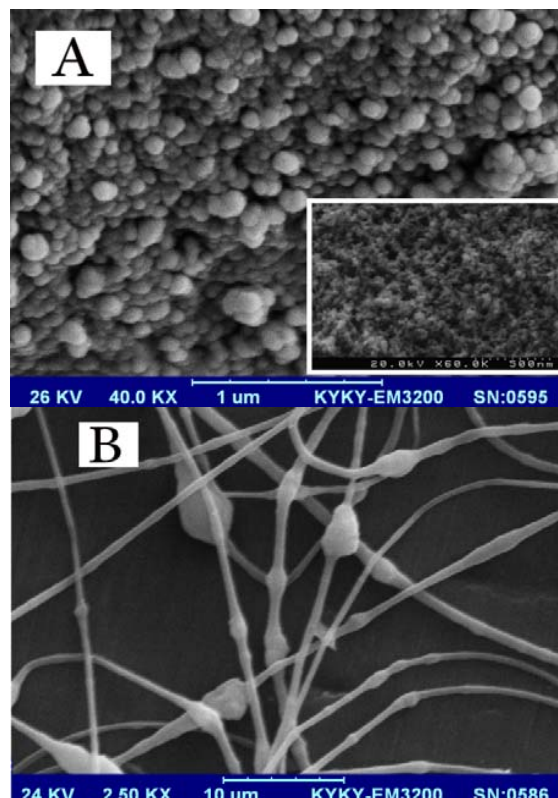


Fig. 1 SEM micrographs: (A) pure nanofibers, (B) 4% aerogel/nanofibers

Since the aerogel attained from this method was in the form of granules, the powder was generated by moderate ball milling to prevent disturbing of the porous structure and the effect of the porous inorganic aerogel on the bulk and surface properties of the organic PET nanofibers was investigated due to importance of hybrid organic/inorganic compounds nowadays.

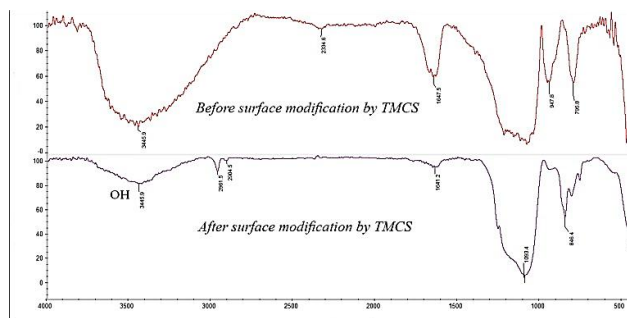


Fig. 2 FTIR analysis of the synthesized aerogel

#### B. Hybrid Aerogel/Nanofibers and Their Properties

According to the microscopic analysis, beads-like PET nanofibers with the diameter of 391.31 to 176.17 nm were successfully formed in the presence of the aerogel powder.

In this work, the micro-size beads were formed in the nanofibers due to the presence of aerogel particles. The beads

did not cause discontinuity and breakage up to concentration of 4%, as shown in Fig. 1 (B). Therefore, it can be deduced that the PET polymeric material coats the aerogel particles with more diameter than the nanofibers. This can be regarded as a novel phenomenon in which not only porous regions are created in the nanofibers, but also beads formation provides a unique surface topography and new structural features in the hybrid aerogel/nanofibers which demands further research.

The fiber diameter can be calculated from the SEM micrographs using the Digimizer software, Fig. 1. There was an indirect relation between the nanofibers diameter and aerogel amount in the nanofibers. Thus, the diameter was reduced from 400 nm for the pure nanofibers to 176 nm for the 4% aerogel/nanofibers. To explain this effect, it is necessary to consider the physical aspects of the electrospinning. Thus, during ejection of the drop from the syringe tip, the aerogel particles ejection can lag behind the polymeric materials and due to strong electrical field on the drop, a tension is created between the aerogel particles and the polymer which leads to thinning of the fibers without excessive breakage.

Following provides an explanation to the effect of the addition of the porous aerogel powder to the PET nanofibers in terms of surface structures, hydrophobicity and heat transfer.

Beads can act as a secondary topological feature on the electrospun fibers surface which is able to create a proper surface roughness to enhance the hydrophobicity and superhydrophobic fibers [11]. Therefore, attempts have been made to create beads on the surface of the nanofibers by manipulation of electro-spinning parameters [11].

All samples exhibited 3M water repellency of 1 which can just repel water. Thus, the differences between contact angles are due to the changes in the surface topology [11]. In addition, the samples with aerogel content showed higher values of contact angles, compared to pure polyester. As shown in Table II, the water contact angle value increased from 103.4° for the pure nanofibers to 123.8° and 126.1° for 0.5 and 4% aerogel/nanofibers, respectively. Sessile water droplets on the nanofiber surfaces were shown in Fig. 3. It can be stated that the addition of aerogel led to an enhancement of the fiber surface porosity with strong adhesion similar to rose petals or gecko toes on which water droplets, due to air trapped inside the nano-scale structures, are firmly pinned to the surface but at the same time keep a large water contact angle [9].

This is important in cases like micro-liquid droplet transportation, protective coatings, biochemical separation, and so on [12].



Fig. 3 Sessile water droplets on the nanofiber surface

These phenomena as shown in Fig. 1 (B) can be attributed firstly to congenial multi-scale surface roughness of the samples and also to the formation of the aerogel based beads. The importance of topological roughness hierarchy in relation to superhydrophobic properties and self-cleaning has also been reported in previous works [13].

It can be stated that the inherent topology of nanoweb is a key factor rendering the samples as hydrophobic as compared with contact angle values of 55.6° for the smooth polyester film achieved by ambient drying of PET solution on the bottom of a vessel. The SEM micrographs confirm proper surface irregularity occurs at concentration of 4%. This led to an enhancement in the hydrophobicity of the aerogel/nanofibers, which is compatible to findings of the previous works [13].

Global CO<sub>2</sub> emission concern together with scarcity of conventional energy resources and space saving restrictions have emphasized the necessity of research on insulation in general and thermal insulators in particular [4]. Fibrous materials such as the hybrid PET samples of this work are textile structures that provide various insulations. The heat transfer of the nanofibers without and with 0.5 and 4% aerogel content were indicated in Table II. As shown, the calculated 21% heat transfer for pure nanofibers is significantly more than that of 16% and 8% calculated for hybrid 0.5 and 4% aerogel/nanofibers, respectively. Therefore, the results indicated the existence of an indirect relation between the heat transfer coefficient and the aerogel content. The reduction in the heat transfer of the samples can be attributed to embedding of the porous aerogel inside the nanofibers [14]. Lower heat transfer of 0.5% aerogel/nanofibers in comparison with pure nanofibers was strongly points to existence of the porous particles in these nanofibers since their physical properties more or less were similar. Lower than air thermal conductivity in order of 0.015 Wm<sup>-1</sup>K<sup>-1</sup> at ambient temperature, pressure, and relative humidity is the pronounced character of silica aerogels [4]. The low heat transfer of the sample with 4.0% aerogel, beside aerogel content, is also due to the high fineness of the fibers which has led to formation of smaller voids formed between the nanofibers resulted in less heat transfer via the gaseous phase (Fig. 1 (A)) [4].

#### IV. CONCLUSION

In this paper potential of novel aerogel/nanofibers with a view to various applications was exploited. The developed

TABLE II  
DIAMETER, WATER CONTACT ANGLE AND HEAT TRANSFER OF THE  
ELECTROSPUN PET NANOFIBERS WITH AND WITHOUT AEROGEL CONTENT

Sample	Diameter (nm)	Water contact angle (°)	Heat transfer (%)
Pure nanofibers	400 (83)	103.4 (0.2)	20.9 (0.1)
0.5% A/NFs	391(100)	123.8 (0.9)	16.4 (0.9)
4% A/NFs	177 (43)	126.1 (0.8)	8.3 (0.1)

hybrid aerogel/nanofibers while potentially possessing low dust releasing feature, have the other beneficiary aspects such as enhanced hydrophobicity and insulation properties. According to the results, silica aerogel powder was fabricated with mean pore diameter of 24 nm, surface area of 815 m<sup>2</sup>/g, and water contact angle of 146.6°. A successful synthesis of the beads-like aerogel/nanofibers using aerogel content up to 4% concentration was achieved. Aerogel content of 4% in the electrospinning solution showed hybrid aerogel/nanofibers with fewer diameters in comparison with the pure nanofibers with no aerogel content. The aerogel/nanofibers due to changes in their surface topology showed higher hydrophobicity in respect to the pure nanofibers. For the 4% aerogel/nanofibers, the water contact angle was found to be 126.3°, compared to 103.4° for the pure nanofibers. Also, a decreasing trend in the heat transfer percentage, from 21 to 8%, in proportion to the aerogel content in the samples was observed. Therefore, the low weight aerogel embedded nanofiber materials with absorbing and hydrophobic characteristics can be one of the most important materials for insulation and absorption applications.

#### ACKNOWLEDGMENT

Financial support of the Isfahan University of Technology (IUT) is gratefully appreciated.

#### REFERENCES

- [1] M. Yu, G. Gu, W.D. Meng, and F.L. Qing, "superhydrophobic cotton fabric coating based on a complex layer of silica nanoparticles and perfluorooctylated quaternary ammonium silane coupling agent" vol. 253, pp.3669-3673, 2007.
- [2] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, and D. Zhu, "A superhydrophobic and superoleophilic coating mesh film for the separation of oil and water", *Angewandte Chemie International Edition*, vol. 43, pp. 2012-2014, 2004.
- [3] P.M. Cox, R.A. Betts, C.D. Jones, S.A. Spall, I. Totterdell, "Acceleration of global warming due to carbon cycle feedbacks in a coupled climate model", *Nature*, vol. 408, pp. 184-187, 2000.
- [4] M.A. Aegerter, N. Leventis, M.M. Koebel, *Aerogels handbook*, Springer, New York, 2012.
- [5] A.P. Rao, A.V. Rao, G. Pajonk, P.M. Shewale, "Effect of solvent exchanging process on the preparation of the hydrophobic silica aerogels by ambient pressure drying method using sodium silicate precursor", *J Mater Sci*, vol. 42(20), pp. 8418-8425, 2007.
- [6] A.C. Pierre, G.M. Pajonk, "Chemistry of aerogels and their applications", *Chem Rev*, vol. 102, pp. 4243-4265, 2002.
- [7] B.E. Yoldas, M.J. Annen, J. Bostaph, "Chemical engineering of aerogel morphology formed under nonsupercritical conditions for thermal insulation" *Chem Mater*, vol. 12, pp. 2475-2484, 2000.
- [8] G. Song, P. Chitrphiromsri, D. Ding, "Numerical simulations of heat and moisture transport in thermal protective clothing under flash fire conditions", *JOSE*, vol. 14(1), pp. 89-106, 2008.
- [9] Y. K. Lai, Z. Chen, Ch. J. Lin, "Recent progress on the superhydrophobic surfaces with special adhesion: from natural to biomimetic to functional", *JNAN*, vol. 1, pp. 18-34, 2011.
- [10] A.V. Rao, R. Kalesh, G. Pajonk, "Hydrophobicity and physical properties of TEOS based silica aerogels using phenyltriethoxysilane as a synthesis component", *J Mater Sci*, vol. 38(21), pp. 4407-4413, 2003.
- [11] J. Fang, H. Wang, X. Wang and T. Lin, Superhydrophobic nanofiber membranes: effects of particulate coating on hydrophobicity and surface properties, *J. Text. I.*, vol. 103(9), pp. 937-944, 2012.
- [12] Q. Yu, Z. Zeng, W. Zhao, M. Li, X. Wu, Q. Xue, "Fabrication of adhesive superhydrophobic Ni-Cu-P alloy coatings with high mechanical strength by one step electrodeposition", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 427, pp. 1-6, 2013.
- [13] Z. Mazrouei-Sebdani, A. Khoddami, "Alkaline hydrolysis: A facile method to manufacture superhydrophobic polyester fabric by fluorocarbon coating", *J Prog Org Coat.*, vol. 72, pp. 638-646, 2011.
- [14] M. Venkataraman, R. Mishra, J. Wiener, J. Milityk, T.M. Kotresh and M. Vaclavik, "Novel techniques to analyse thermal performance of aerogel-treated blankets under extreme temperatures", *J. Text. I.*, 2014, DOI: 10.1080/00405000.2014.939808.