

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Hydrophobic Silica Aerogels Strengthened with Nonwoven Fibers

Zhihua Zhang^a; Jun Shen^a; Xingyuan Ni^a; Guangming Wu^a; Bin Zhou^a; Miaoxiang Yang^b; Xiaochun Gu^b; Mingjuan Qian^b; Yuehua Wu^a

^a Pohl Institute of Solid State Physics, Tongji University, Shanghai, P. R. China ^b Shanghai Textile Research Institute, Shanghai, P. R. China

To cite this Article Zhang, Zhihua , Shen, Jun , Ni, Xingyuan , Wu, Guangming , Zhou, Bin , Yang, Miaoxiang , Gu, Xiaochun , Qian, Mingjuan and Wu, Yuehua(2006) 'Hydrophobic Silica Aerogels Strengthened with Nonwoven Fibers', Journal of Macromolecular Science, Part A, 43: 11, 1663 – 1670

To link to this Article: DOI: 10.1080/10601320600934792

URL: <http://dx.doi.org/10.1080/10601320600934792>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Hydrophobic Silica Aerogels Strengthened with Nonwoven Fibers

ZHIHUA ZHANG,¹ JUN SHEN,¹ XINGYUAN NI,¹
GUANGMING WU,¹ BIN ZHOU,¹ MIAOXIANG YANG,²
XIAOCHUN GU,² MINGJUAN QIAN,² AND YUEHUA WU¹

¹Pohl Institute of Solid State Physics, Tongji University, Shanghai, P. R. China

²Shanghai Textile Research Institute, Shanghai, P. R. China

Hydrophobic silica aerogels were prepared via a sol-gel process by surface modification at ambient pressure. Nonwoven fibers were distributed inside the silica aerogels as a composite to act as a supporting skeleton which increased the mechanical property of the silica aerogels. The morphology and pore structure of the composites were characterized by scanning electron microscopy (SEM) and N₂ adsorption analyzer. The contact angle and the adsorption capacities of the composites were also determined. The results show that silica aerogels dispersed uniformly and maintained high porosity in the aerogel-fiber composites. They have excellent hydrophobic properties and are excellent adsorptive materials.

Keywords silica aerogel, nonwoven fibers, composites, ambient pressure drying, hydrophobic, adsorption properties

Introduction

Silica aerogels are nano-porous materials with high porosity (>99%), large surface area (600 ~ 1200 cm² · g⁻¹) and low bulk density (down to 3 kg · m⁻³), and possess excellent adsorbing and catalytic properties. Thus they are potentially important to be used as gas adsorbents (1, 2) being quite efficient to adsorb hazardous gases such as CCl₄, benzene, methylene blue, etc. However, aerogels are usually obtained above the supercritical pressure and temperature of the pore liquid. Since processing at such high pressures requires the use of expensive autoclaves, their high production costs restricts their industrial application. Thus, nano-porous silica aerogels prepared under ambient pressure have recently become an interesting subject (3). However, cracking of silica aerogels is still a major obstacle in the applications due to their poor mechanical properties. Hydrophobic silica aerogels dried at ambient pressure avoid the reduction of adsorption properties of hydrophilic adsorptive material in humid atmospheres, and create the possibility of preparing useful adsorptive composites. Incorporating aerogels into any commercially available fibrous supporting materials such as fiberglass, insulation fibers, alumina tiles, dacron and cotton wool is quite effective in increasing the mechanical properties (4).

Address correspondence to Jun Shen, Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, P. R. China. E-mail: shenjj@online.sh.cn

The objective of this study was to prepare hydrophobic silica aerogel-fiber composites via a sol-gel process by prior dipping and the use of polyethoxydisiloxanes (E-40) as the silicon source. Surface modification is used to realize ambient pressure drying. The properties of the silica aerogel-fiber composites were characterized.

Experimental

Sample Preparation

The silica precursor in this paper is 'E-40', a commercially available polyethoxydisiloxane which was prepared by the catalytic reaction of ethanol and silicon. Silica sols were prepared via a sol-gel process with an E-40-water-ethanol system and catalyzed by HF. E-40, ethanol, HF and distilled water were mixed together at room temperature according to the volume proportion 1:10:0.01:0.45, and then were stirred at room temperature for 2–3 h. A silane coupling agent was added as an agglomerating agent. Silica sol was obtained several hours later.

Polypropylene nonwoven fibers were then immersed in the silica sol and stirred for several hours; silica-fiber composite gels were then formed. The composite gels were maintained at room temperature, aging for 2 days, then dipped into ethanol and aged at 70°C for one day. After the composite gels were aged, they were dipped into 10% (volume ratio) trimethylchlorosilane (TMCS) hexamethyldisiloxane solution. Two days later, these surface modified composite gels were dried at ambient pressure at 200°C, resulting in the hydrophobic silica aerogel-fiber composites.

Characterization

The morphology and pore structure of the silica aerogel-fiber composites were characterized by scanning electron microscopy (SEM, XL30FEG, Philips). Pore size distribution, specific surface area and N₂ adsorption-desorption isothermal of the samples were measured using a N₂ adsorption analyzer (ASAP2010, Micrometrics). The contact angle between the silica aerogel-fiber composites and water was tested by a sessile drop contact angle visualizer (JC2000A, Powereach). The adsorption capacities of the silica aerogels and the composites were also determined according to Chinese national standard GB-T12496.5-1999.

Results and Discussion

Morphologies

Figure 1 shows SEM photos of the fibers and the silica aerogel-fiber composites. Figure 1(a) corresponds to pure the non-woven fiber, Figures 1(b, c) show SEM photos of the silica aerogel-fiber composites at two different magnifications. The SEM photo of silica aerogel in the composites at even greater magnification is given in Figure 1(d). From the photos of the silica aerogel-fiber composites, it is obvious that the silica aerogels cover much of the surface of the fibers and maintain a spongy porous structure and high porosity in the aerogel-fiber composites. Fibers acted as a supporting skeleton that could increase the mechanical properties of the silica aerogels. The porous structure of the silica aerogels in the composites is quite similar to that of as-prepared silica aerogels (5), which is shown in Figure 2.

Pore Structures

Figure 3 shows the N_2 adsorption and desorption isothermal of silica aerogel in the composites. According to the adsorption data, the specific surface area of the silica aerogel was $700 \text{ m}^2 \cdot \text{g}^{-1}$ and the pore volume was $3.04 \text{ cm}^3 \cdot \text{g}^{-1}$ calculated by the BET method. From the shape of the desorption hysteresis loop in Figure 3, it is found that pore structures are both cylindrical capillary pores open at both ends and cylindrical pores closed at one end and with a narrow neck at the other, like an “ink-bottle”, according to hysteresis loop

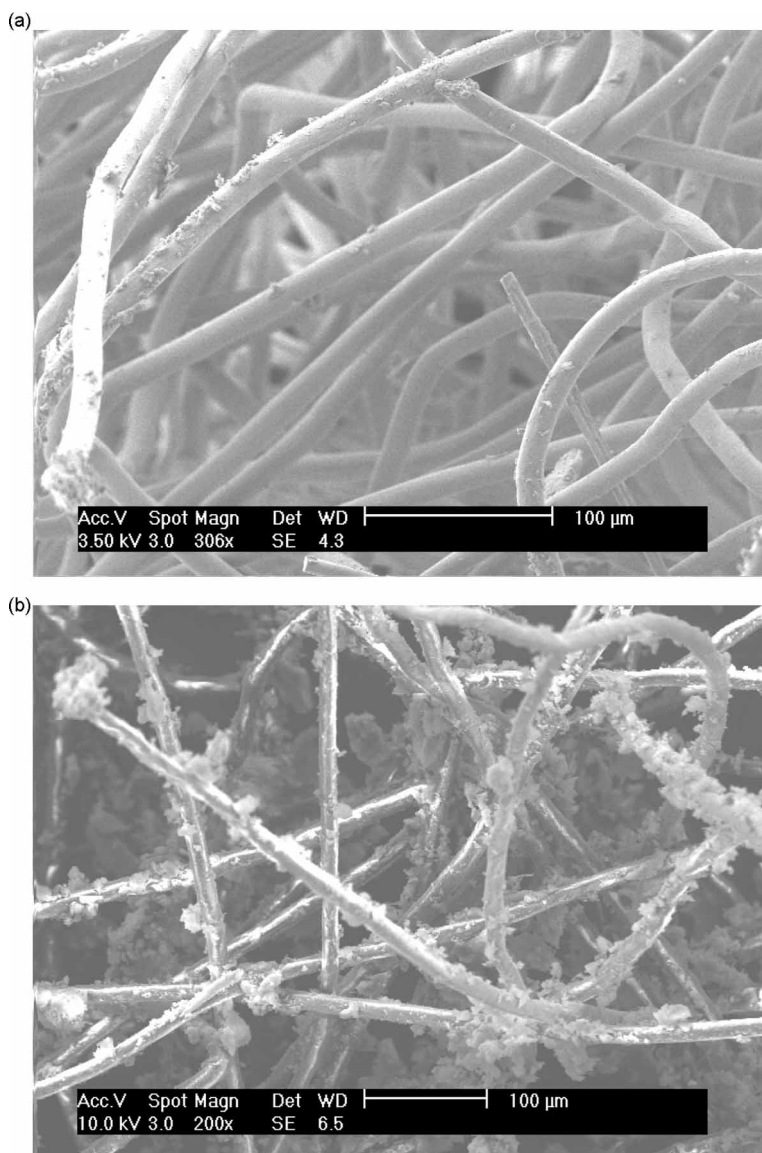


Figure 1. SEM photos of the aerogel-fiber composites with different magnifications: (a) Nonwoven fiber ($\times 300$); (b) silica aerogel-fiber composites ($\times 200$); (c) silica aerogel-fiber composites ($\times 1000$); (d) silica aerogel in the composites ($\times 25000$).

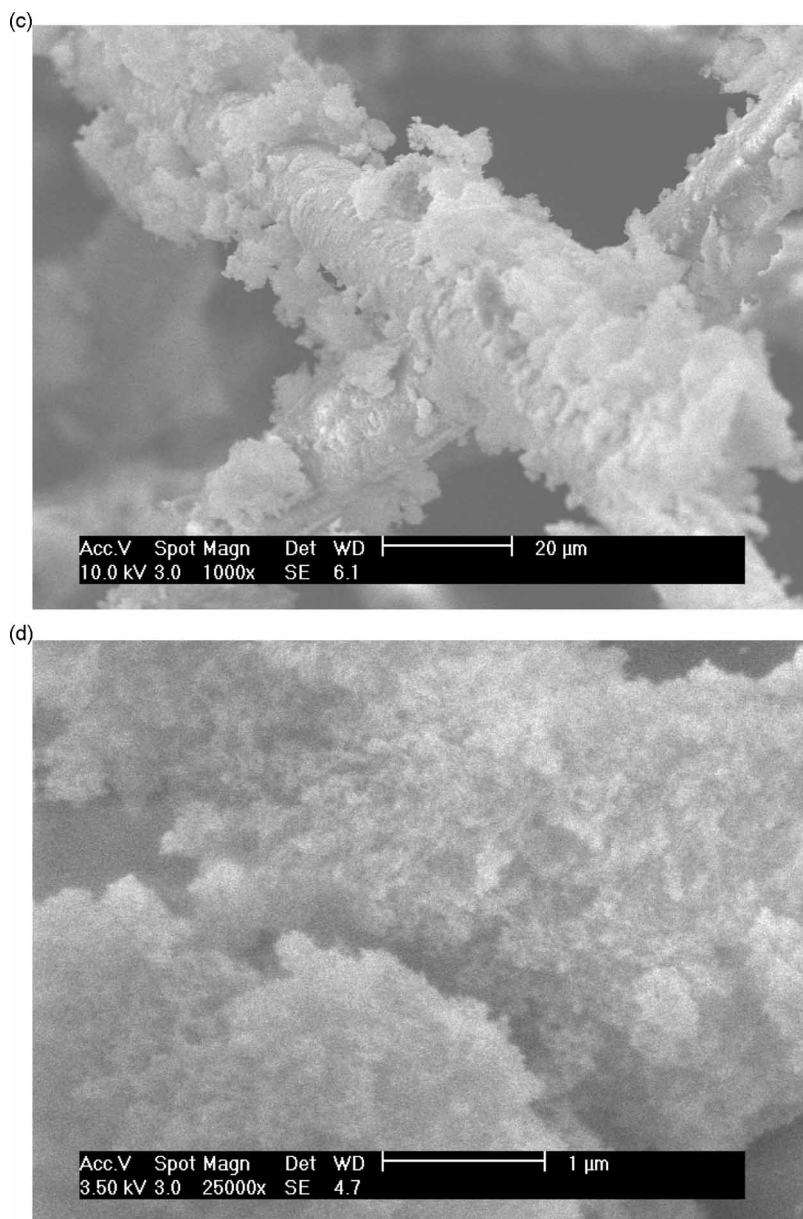


Figure 1. Continued.

classification of porous materials by de Boer in 1958 (6). Because of the cylindrical capillary pores open at both ends, dispersion of adsorption and desorption branches occurs in the medium relative pressure region, and the two branches are very sharp. For the “ink-bottle” pores, the adsorption branch varies slowly, but the desorption branch has a rapid change in the medium relative pressure region (7). Figure 4(a) shows the pore size distribution of the silica aerogel in the composites; it is mainly between 10 nm and 40 nm, and the average pore diameter is 19 nm, which is similar to that of the as-prepared silica aerogels (Figure 4(b)).

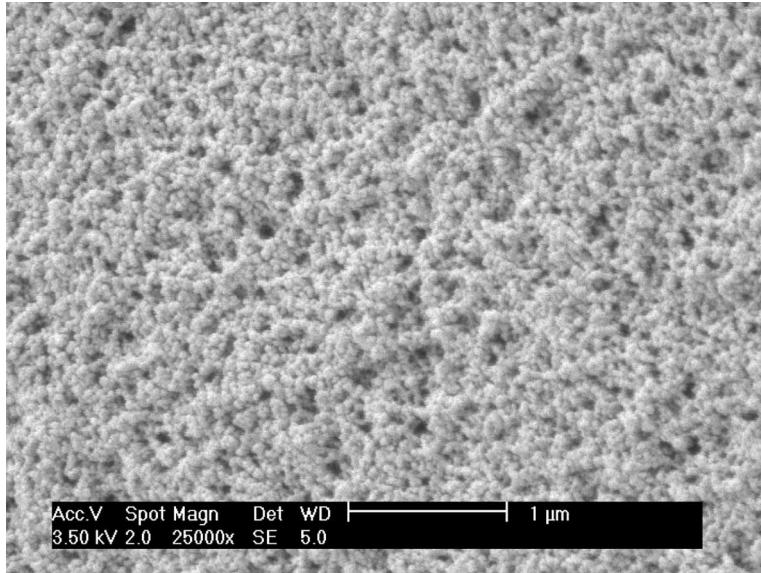


Figure 2. SEM photo of silica aerogel dried at ambient pressure.

Surface Property

The contact angle of the aerogel-fiber composites with water was 135° (Figure 5), which indicated aerogel-fiber composites have excellent hydrophobic properties. The excellent hydrophobic properties are due to the existence of $\text{Si}-(\text{CH}_3)_3$ on the surface, The $-\text{CH}_3$

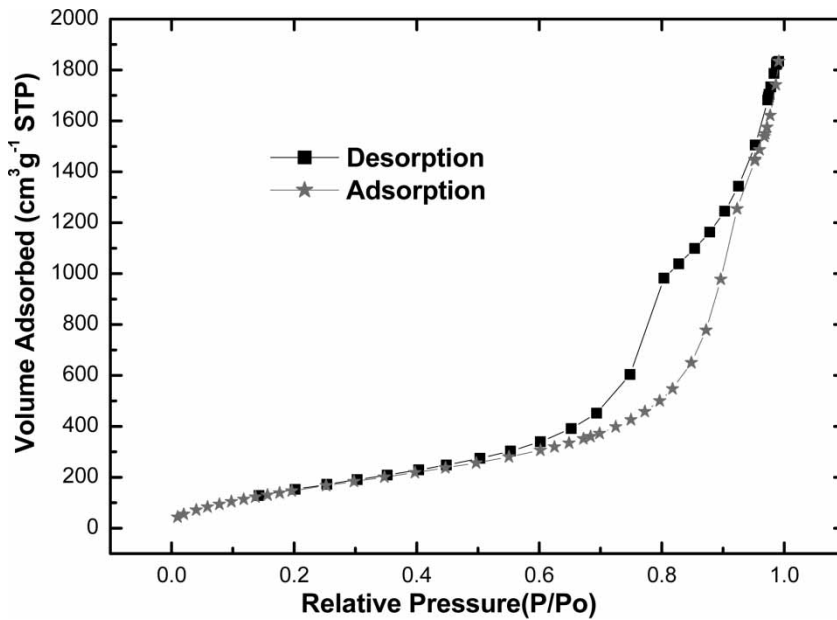


Figure 3. Adsorption and desorption isothermal curve of SiO_2 aerogel in the composite.

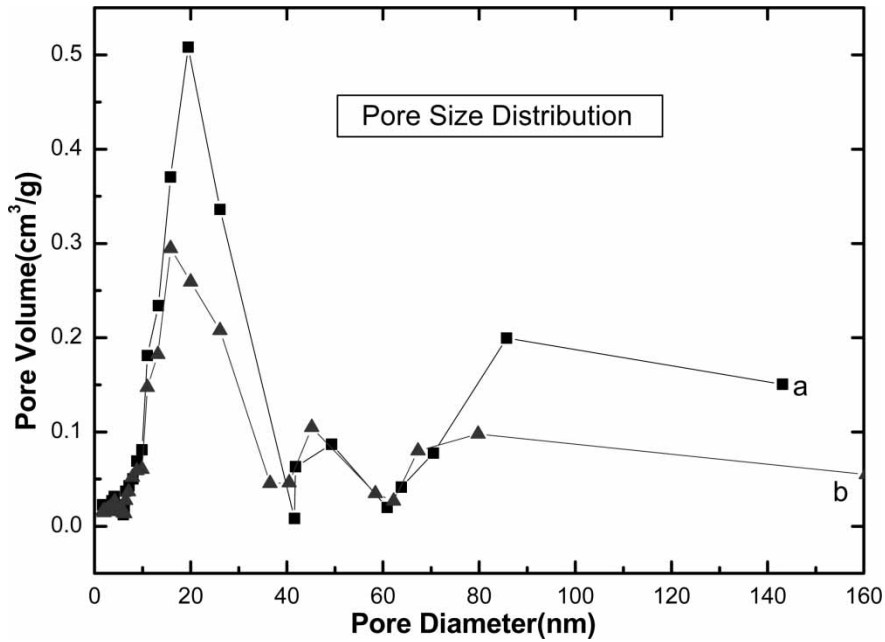
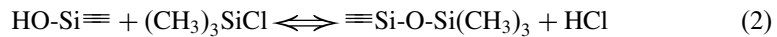
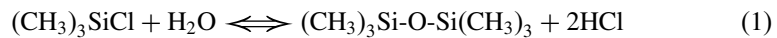


Figure 4. Pore size distribution of silica aerogel in the composite.

groups replaced the -OH groups on the surface of aerogels by surface modification. Silylation was the main reaction in the trimethylchlorosilane (TMCS) hexamethyldisiloxane solution modification process. In principle two different reactions can occur:



TMCS reacts with the pore water to yield hexamethyldisiloxane and HCl in a spontaneous, exothermic reaction 1. Hexamethyldisiloxane can again react with HCl to form TMCS and water. It is a reversible reaction. In the two possible reactions TMCS reacts with the hydroxyl groups on the surface of the silica gel. To avoid the first reaction, the water content is controlled in the preparation process, and hexamethyldisiloxane is the solvent, so the equilibrium of the first reaction is clearly on the TMCS side. It is favorable for the second reaction of TMCS with the hydroxyl groups on the surface of the silica gel to obtain $-\text{Si}(\text{CH}_3)_3$. It is also useful to dry the silica aerogels at ambient pressure to increase the modification due to the TMCS. The resulting silica aerogel-fiber composites have excellent hydrophobicity.

Adsorption Properties

Table 1 shows the adsorption capacities of the as-prepared silica aerogels, composites, activated carbon fiber (ACF), and granules of activated carbon (GAC) measured according to Chinese national standard GB-T12496.5-1999. The adsorbates were reagent grade benzene, methylbenzene, carbon tetrachloride, and acetaldehyde, respectively. It is found that the as-prepared silica aerogel and aerogel-fiber composites better adsorption capacities compared with ACF and GAC. The adsorption capacities of the as-prepared



Figure 5. Photographs showing a water droplet on the surface of silica aerogel-fiber composites dried at ambient pressure (the contact angle = 135°).

silica aerogel in this table are higher than that of the composites. This is because the adsorption capacities are measured according to the samples' weight (per gram). With fibers inside, the composites have less pure silica aerogel compared to the as-prepared silica aerogel with the same weight. However, the as-prepared silica aerogels are quite easy to be damaged because of the poor mechanical strength, while the aerogel-fiber composites are more applicable because their mechanic strength has been improved a lot. These adsorptive materials can be applied extensively in such fields as air purification, sewage disposal, chemical industry sublimation, medicine filtering, sea water desalting, etc.

Conclusions

Silica aerogel-fiber composites were prepared successfully via a sol-gel process and surface modification. The composites have a typical nano-porous microstructure with

Table 1
Adsorption properties of silica aerogel and composites, ACF
and GAC ($\text{mg} \cdot \text{g}^{-1}$)

Medium	Silica aerogel	Aerogel-fibre composites	ACF	GAC
Benzene	1300	900	450	350
Methylbenzene	850	600	470	300
Carbon tetrachloride	4600	2800	1500	800
Acetaldehyde	1100	800	520	130

hydrophobic properties. Aerogel dispersed uniformly and maintain high porosity in the composites because of the existence of Si-(CH₃)₃ on the surface. Aerogel-fiber composites have better adsorption capacities compared with activated carbon fiber (ACF), and granules of activated carbon (GAC), and have much better mechanical properties than that of pure silica aerogel. They are excellent adsorptive materials with wide applications.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (contract No. 20133040), Chinese National Foundation of High Technology (2002AA842052), Shanghai Committee of Science and Technology (055211010, 0352nm056, 0452nm088), Shanghai Key Subject Programme, Shanghai Phosphor program (05QMH1413), and Trans-Century Training Programme Foundation for the Talents by the State Education Commission.

References

1. Hrubesh, L.W. (1998) *J. Non-Cryst Solids*, 225: 335–342.
2. Schmidt, M. and Schwertfeger, F. (1998) *J. Non-Cryst Solids*, 225: 364–368.
3. Zhang, Z., Ni, X., Chen, S., Shen, J., Wu, G., and Zhou, B. (2004) The Proceedings of Fifth Annual Conference for Young Scientists of China Association for Science and Technology, Shanghai, China, November 2–5, 1: 176–180.
4. Adebajo, M.O., Frost, R.L., Kloprogge, J.T., Adebajo, M.O., Frost, R.L., Kloprogge, J.T., Carmody, O., and Kokot, S. (2003) *Journal of Porous Materials*, 10: 159–170.
5. Zhang, Z., Ni, X., Shen, J., Wu, G., and Zhou, B. (2005) *Materials Review*, 19: 115–117 (in Chinese).
6. Gregg, S.J. and Sing, K.S.W. (1982) *Adsorption, Surface Area and Porosity*; Academic Press Inc.: London, 2–39.
7. Yan, J. and Zhang, J. (1979) *Adsorption and Condensation (Surface and Pore in Solid)*; Science Press: Benjing, 111–120.