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Hydrophobic and thermal insulation properties of silica aerogel/epoxy composite

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ABSTRACT

Silica aerogel/epoxy composite was prepared by dry mixing hydrophobic aerogels with epoxy powders and heat pressing method. The composite materials show a serviceability temperature up to 250 °C with low thermal conductivity (0.11–0.044 W/m k) and hydrophobic property (water contact angle of 117–140°). Transmission electron microscope photos proved that part of silica aerogels nanopores had been immersed by epoxy. Based on this phenomenon, an immersion model was build up to study the effect of immersion on the thermal insulation and hydrophobic properties. In addition a thermal conductivity prediction equation of aerogel/polymer system was obtained and confirmed by comparing the experimental data.

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1. Introduction

Silica aerogels are excellent nanoporous materials with high specific surface area (500–1200 m²/g), low density (0.003–0.1 g/cm³), low dielectric constant (1.1–2.0) and low thermal conductivity (0.013–0.04 W/m k). Therefore, they have many potential applications in thermal, acoustic, electronic and catalytic fields, especially in thermal insulation [1–4]. However, hydrophilicity and powder or the granule form of silica aerogels limits their applications. The former can be totally solved through a replacement of Si–OH groups on the surface by hydrophobic groups Si–R (R is alkyl or aryl) [5,6]. For well operability, aerogel/polymer binding system was proposed [7] and both thermoplastic polymer and wet solutions system have been proved as good binders for silica aerogels. Moreover, effects of wet, dry and dual mixing on the thermal conductivity of aerogel/PVB system were studied and dry mixing has been proved to be the best [8]. In order to improve the application temperature of composites, thermosetting polymer is used due to its higher service temperature [9]. Liquid epoxy was used as the binder to prepare aerogel/epoxy composite by wet mixing [10,11] but the thermal insulation property was not very well. The reason was thought to be the intensive immersion of epoxy into nanopores of aerogels, however, there was no further discussion.

In this work, epoxy powders were used as the binder to prepare silica aerogel/epoxy composite by hot pressing in order to decrease epoxy immersion. Thermal insulation and the hydrophobic proper-

ties of composites at various temperatures were reported. An updated microstructure model of composite was found and empirical formulas were determined to study the thermal insulation property.

2. Experimental details

2.1. Preparation

Hydrophobic silica aerogels, with surface area of 1044 m²/g, density of 0.04 g/cm³ and porosity of 95–97%, were modified by trimethylchlorosilane (TMCS). As cross-linking agent, phenol-formaldehyde resin (Mn = 700) [12] was added into epoxy (E12) and mixed at 80 °C with the ratio of 2:3. Epoxy powders with an average particle diameter of 0.08 mm were obtained after grinding at room temperature. Fig. 1 shows the flow diagram of composites' preparation. First, silica aerogels were ground into particles with diameters between 0.15 mm and 0.2 mm. Then, silica aerogel particles and powder epoxy were dry mixed in the cylindrical mixer. Finally, the composite was prepared through hot pressing at 180 °C under 1 MPa for 30 min.

2.2. Characterization

The bulk density of composite was simply measured through weight and volume. The microstructure was investigated using transmission electron microscope (TEM) as well as scanning electron microscope (SEM) techniques. A FT-IR spectrometer was used to study the co-ordinated structures of composites. Differential

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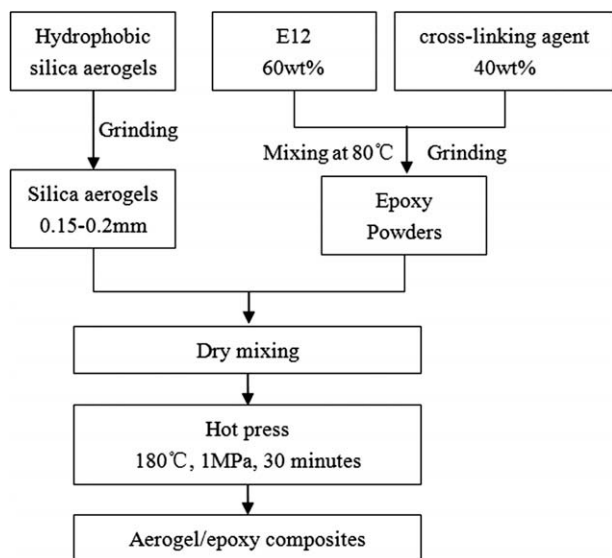


Fig. 1. Flow diagram of aerogel/epoxy composite preparation.

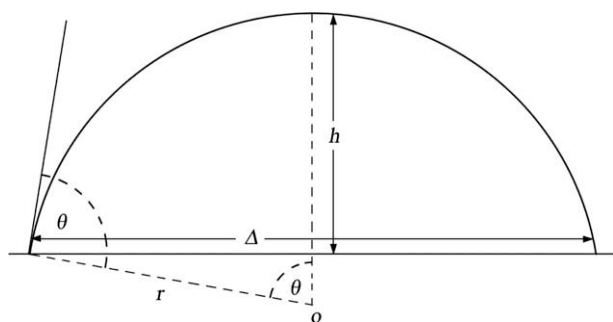


Fig. 2. Schematic diagram of the contact angle calculation.

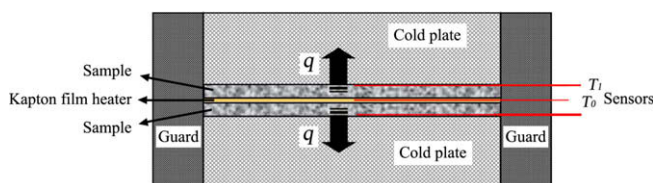


Fig. 3. Measurement equipment of thermal conductivity.

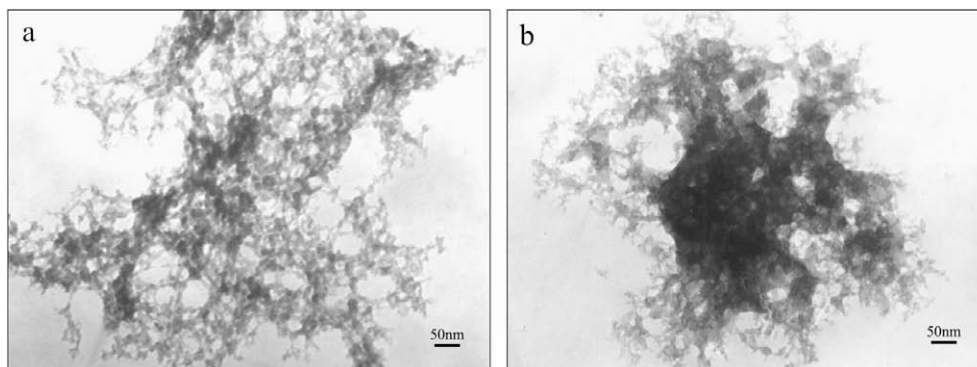


Fig. 4. TEM micrographs of (a) silica aerogels and (b) silica aerogel/epoxy composite.

Thermal Analysis (DTA) was done at a heating rate of 10 °C/min. Fig. 2 shows a photograph of water droplet on the composite surface, which was used to calculate the contact angle (θ) from the following formula [13]:

$$\tan(\theta/2) = 2h/\Delta \quad (1)$$

where h is the height of the water droplet and Δ is the width of droplet.

The thermal conductivity measurement equipment of composites by guarded hot plate method [14] was described in Fig. 3. The size of samples was 100 × 100 mm. The thermal environment temperature was defined as the average of two sides' temperatures of sample at thermal stable state. Thus, the thermal conductivity of the composites at various temperatures was calculated as follows:

$$\lambda = \frac{qd}{S(T_0 - T_1)} \quad \text{and} \quad T = (T_0 + T_1)/2 \quad (2)$$

where λ , q , d , S represent the thermal conductivity, thermal flow, thickness and surface area of the composite, respectively. T , T_0 and T_1 represent the thermal environment temperature, hot surface temperature and cold surface temperature, respectively.

3. Results

3.1. Microstructure of composites

Fig. 4(a) shows that silica aerogels have 3D net structure and the diameters of nanopores are around 50 nm. After the mix, part of the nanopores of the silica aerogels have been immersed by epoxy shown as the dark sections in Fig. 4(b) although the composite retains the 3D net structure. This phenomenon is different with silica aerogels/polymer composite prepared by wet mixing in previous researches [8,9], in which the nanopores are totally immersed by polymer. Compared with wet mixing, the hot press method depresses the immersion of polymer into pores.

3.2. Molecular properties of composites

Fig. 5 shows the FT-IR spectra of the composites with various volume fractions of hydrophobic silica aerogels. Peaks at 754 cm^{-1} , 845 cm^{-1} and 863 cm^{-1} all represent $\equiv\text{Si}-\text{CH}_3$ of tetramethylsilane (TMS) in hydrophobic silica aerogels. Hydrophobic silica aerogels also have hydrophilic functional groups like $-\text{OH}$ (3440 cm^{-1}), $\text{H}-\text{OH}$ (1645 cm^{-1}) and $\equiv\text{Si}-\text{OH}$ (940 cm^{-1}). The FT-IR spectrum of epoxy has distinctive peaks from phenyl group at 1460 cm^{-1} , 1506 cm^{-1} , 1636 cm^{-1} and absorption band of $\text{C}-\text{O}-\text{C}$ at 1100 cm^{-1} . Weak peaks of $\text{Si}-\text{CH}_3$ groups are shown in the composite's FT-IR spectra due to the infrared absorption of epoxy at spectrum below 1000 cm^{-1} . The peak of 940 cm^{-1} representing $\text{Si}-\text{OH}$

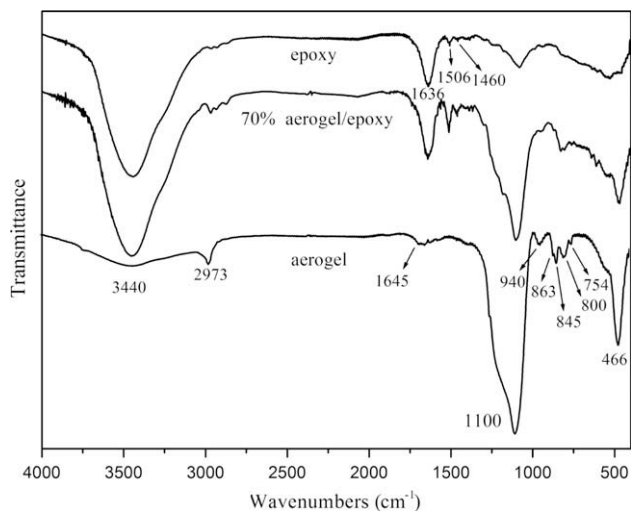


Fig. 5. FT-IR spectra of epoxy, hydrophobic silica aerogels and composites.

almost is obvious in the hydrophobic silica aerogels while not in the composite. It is indicated that Si–OH reacted with C–OH bond through ring opening of epoxy and Si–O–C bond was generated.

3.3. Hydrophobic properties of composites

The contact angles (θ) of the composites with various silica aerogel volume fractions were shown in Fig. 6 and Table 1. The con-

Table 1
Contact angle of a water droplet with the composite surface.

Aerogel vol.%	Contact angle (°)		
	Untreated	250 °C/30 min	300 °C/30 min
0	45	45	43
40	117	121	Water absorption
50	120	124	Water absorption
60	126	128	Water absorption
70	132	136	Water absorption
80	140	143	147

tact angle increases with the silica aerogels volume fraction and reaches 120° when the volume fraction of silica aerogels reaches up to 50%. In contrast, the contact angle of epoxy surface is only 45°. The high contact angle is due to the hydrophobic groups in silica aerogels [15] on the surface.

The contact angles of the composites treated at different temperatures were also listed in Table 1. The composites have excellent hydrophobic property at the temperature below 250 °C. Therefore the composites have applications at higher temperature than traditional thermal insulation polymers such as polyurethane foam. However, the hydrophobicity of composites is destroyed once the temperature is up to 300 °C. Seen from DTA curves in Fig. 7, there is an endothermic valley between 250 °C and 300 °C. It is demonstrated that epoxy carbonizes and macro pores appear on the surface, which results in absorption of water in the composite. But the composites containing 80% aerogels still are waterproof and have a high contact angle. It may be because that at high aero-

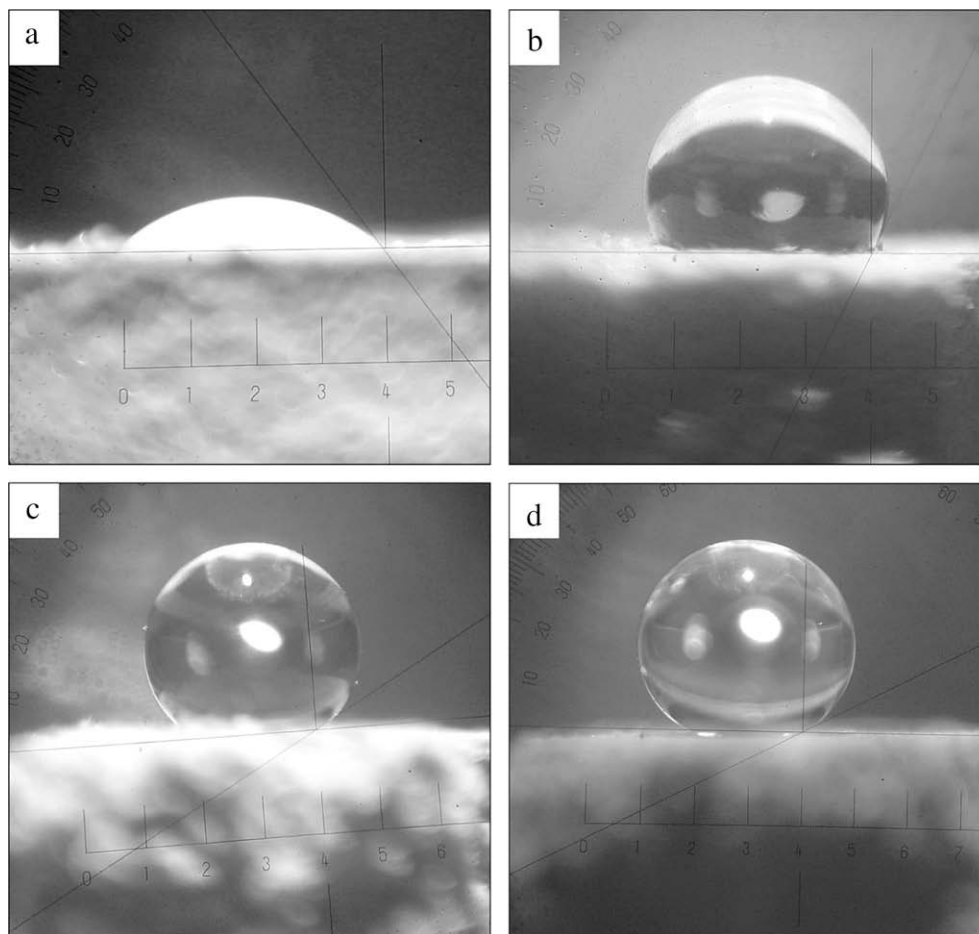


Fig. 6. Photographs showing a water droplet on the surface of (a) epoxy, (b) 40%, (c) 80% silica aerogel–epoxy composite and (d) 80% silica aerogel–epoxy composite treated at 300 °C.

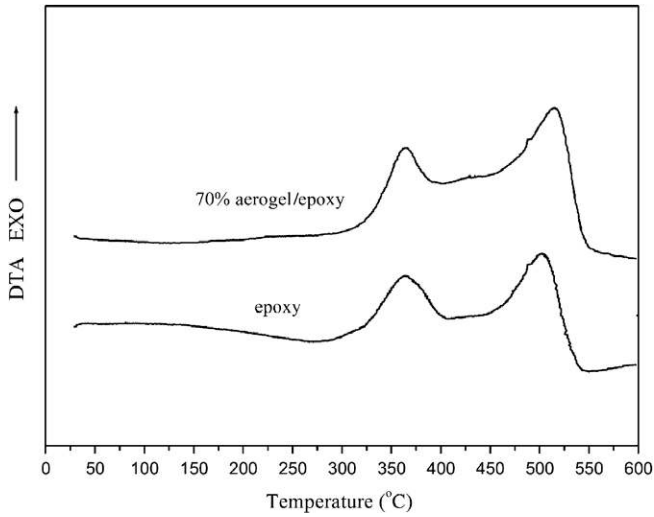


Fig. 7. DTA curves of epoxy and composite with 70 vol.% silica aerogel.

gel volume fraction the epoxy almost immerses into the nanopores. So carbonization of the epoxy only exposes the nanopores

in the interface and improves the area fraction of silica aerogel on the surface.

3.4. Thermal insulation of composite

Fig. 8(a) shows that the thermal conductivities of composites decrease as the volume fraction of aerogels rises. When the volume fraction is lower than 70%, it decreases faster. Fig. 8(b) shows the thermal conductivity of composites with different fractions at different temperatures. A linear relation ($\lambda = A + BT$) is found fitted very well and composites have much better thermal insulation performance compared with epoxy. Silica aerogel/liquid epoxy composites were also prepared. Their thermal insulation performance is shown in Fig. 8(c) and SEM photograph (Fig. 8(d)) shows the nanopores are almost immersed by epoxy. It is found that the thermal conductivity of the aerogel/epoxy powder composite is extremely lower than aerogel/liquid epoxy composite due to much weaker immersion of polymer into pores in aerogels.

4. Discussion

Based on the SEM photos, an immersion microstructure model was found to describe the evolution during preparation shown in

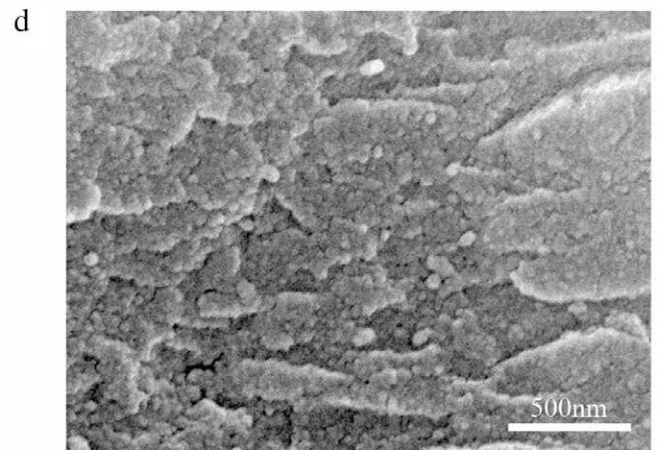
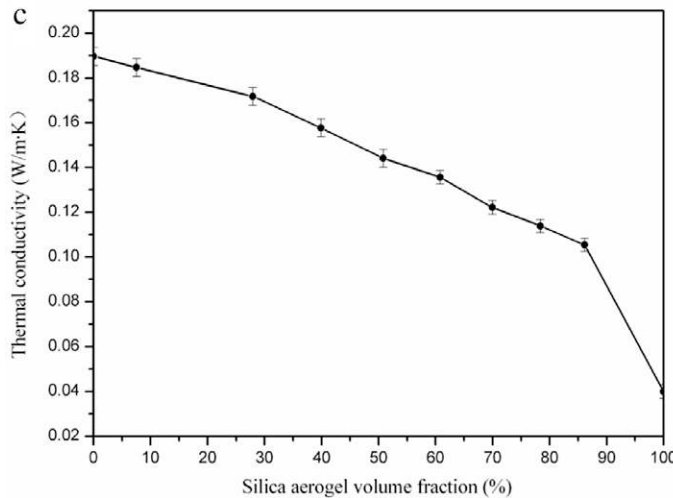
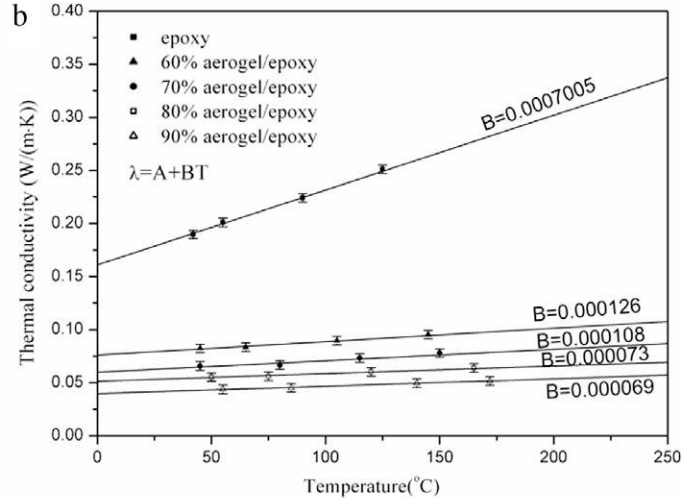
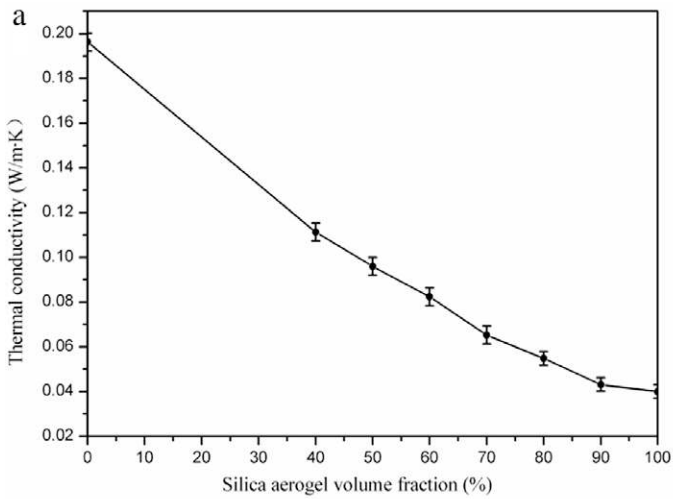


Fig. 8. (a) Thermal conductivity of composite at 50 °C with different fractions, (b) thermal conductivity of composites at various temperatures, (c) SEM micrograph of silica aerogel/liquid epoxy composites and (d) thermal conductivity of aerogel/liquid epoxy composite.

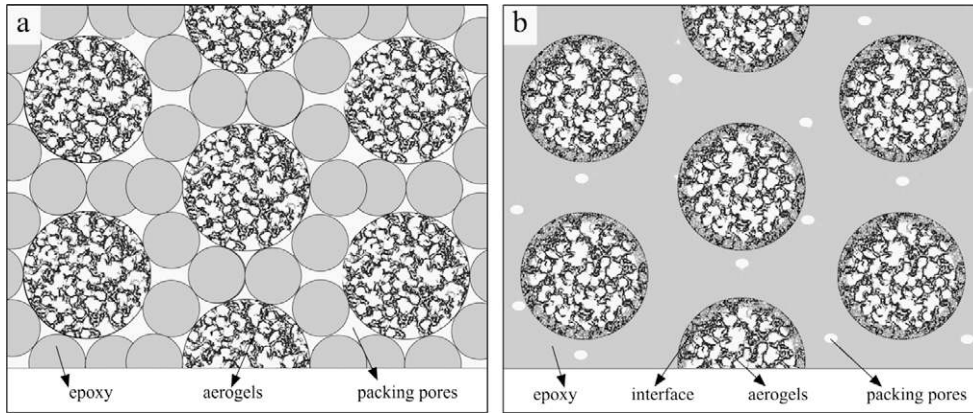


Fig. 9. Schematic diagram of pores (a) before and (b) after hot pressing procedure.

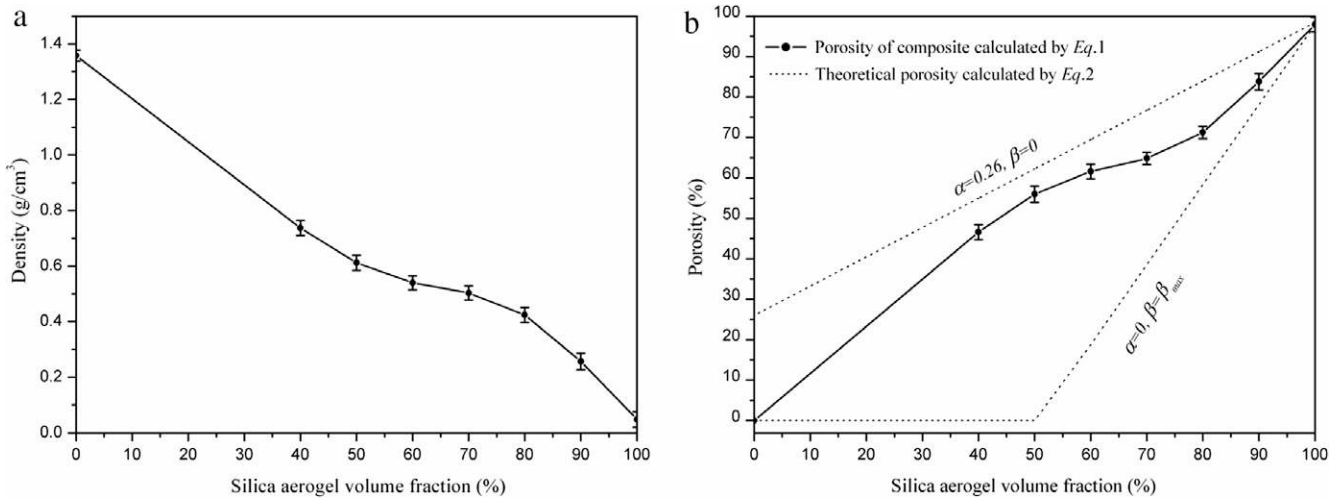


Fig. 10. (a) Density and (b) porosity of silica aerogel/epoxy composite.

Fig. 9. Once silica aerogels and epoxy are mixed, epoxy particles surround the silica aerogels particles because the size of silica aerogels particles is 2–3 times larger than that of epoxy particles. Therefore, there are two kinds of pores existing: nanopores in silica aerogels and macro pores from packing process. During the hot pressing procedure, epoxy softened and slowly immersed into the pores, thus interfaces between silica aerogels and epoxy appeared. Therefore, after the curing of epoxy, it can be considered that composite includes four parts: epoxy, interface, silica aerogels and packing pores shown in Fig. 10(b). A similar but more simplified model was proposed before, in which the interface was omitted [8].

To understand the thermal insulation performance of composites, the porosity should be obtained. The porosity can be indirectly obtained based on the densities and weight fractions of each component and the composite [16]:

$$p = 1 - \rho \left(\frac{m_{epoxy}}{\rho_{epoxy}} + \frac{m_{aerogel}}{\rho_{aerogel}} \right) \quad (3)$$

Based on the immersion model, the theoretical porosity is shown as Eq. (4). Here α is the fraction of packing pores and β is the immersion fraction which describes the immersion of epoxy into nanopores in silica aerogels.

$$p = \alpha + (1 - \alpha)(1 - \beta)v_{aerogel}P_{aerogel} \quad (4)$$

Before curing, the factors are $\alpha = 0.26$ and $\beta = 0$ for hexagonal close packing. After curing the pores are immersed and there are two ultimate situations. When $\alpha = 0$ and $\beta = 0$, the packing pores are all immersed but nanopores in silica aerogels are out of immersion. The other is $\alpha = 0$ and $\beta = \beta_{max}$ for all the pores immersed and β_{max} can be obtained:

$$\beta_{max} = \begin{cases} 1 & P_{aerogel}v_{aerogel} < v_{epoxy} \\ \frac{v_{epoxy}}{P_{aerogel}v_{aerogel}} & P_{aerogel}v_{aerogel} \geq v_{epoxy} \end{cases} \quad (5)$$

where p , ρ , m , v are porosity, density of composites, weight fraction and volume fraction, respectively. For two-component system, there is $v_{epoxy} + v_{aerogel} = 1$.

The density of the composite was tested and the porosity was obtained by Eq. (3), shown in Fig. 10. The porosities are all between two ultimate situations, i.e. $\alpha = 0.26$, $\beta = 0$ and $\alpha = 0$, $\beta = \beta_{max}$ because of the partial disappearance of pores during epoxy melting. However, there is no linear relationship between those and the volume fraction of silica aerogel. When $v_{aerogel} \leq 50\%$, it is deduced that β is very big and decreases with the increase of $v_{aerogel}$. Moreover, the packing pore fraction α increases due to the increase of particles. With the continuous increase of $v_{aerogel}$, α keeps increasing and the second term will be reduced accordingly. Thus the increase of porosity will be weakened. When $v_{aerogel}$ is greater than

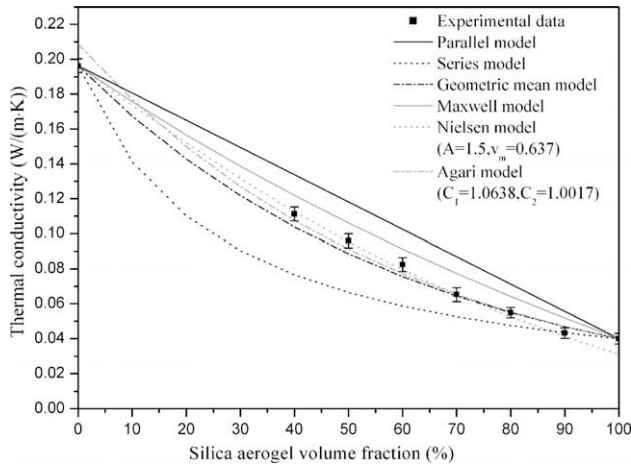


Fig. 11. Curves of thermal conductivity predictive models.

80%, α keeps stable and β goes on decreasing. Then the porosity increases rapidly.

The thermal insulation performance of composites is influenced by three factors, i.e. gas conduction, solid conduction and radiation heat transfer. At low application temperature, the radiation heat transfer accounts for a very small part. Gas conduction heat transfer can be decreased by the nanopores and the 3D net structure decreases solid conduction heat [17]. Therefore, silica aerogel has lowest thermal conductivity and keep steady as temperature rises. Furthermore, the thermal insulation performance is also improved through the increase of heat transfer path due to the addition of aerogel particles. Meanwhile, the polymer immersion has much influence on the thermal conductivity. According to the immersion model (Fig. 9), intensive epoxy immersion means high interface volume and low volume of silica aerogels.

The thermal conductivity of two-component system has been studied theoretically and empirically. For example, parallel and series models give the top and bottom bounds of the effective thermal conductivity as follows:

$$\lambda_c = v\lambda_f + (1-v)\lambda_m \quad (6)$$

$$\frac{1}{\lambda_c} = \frac{v}{\lambda_f} + \frac{(1-v)}{\lambda_m} \quad (7)$$

where λ_c , λ_f and λ_m are thermal conductivity of composites, filler and epoxy and v is the volume fraction of filler, respectively.

Geometric mean model is given the effective thermal conductivity by:

$$\lg \lambda_c = v \lg \lambda_f + (1-v) \lg \lambda_m \quad (8)$$

Maxwell model [18] obtained the conductivity of randomly distributed and non-interacting homogeneous spheres based on the Laplace equation

$$\lambda_c = \lambda_m \frac{\lambda_f + 2\lambda_m + 2v(\lambda_f - \lambda_m)}{\lambda_f + 2\lambda_m - v(\lambda_f - \lambda_m)} \quad (9)$$

Nielsen model [19] is a semi-theoretical model including the effect of shape of the particles and the orientation or type of packing for two-component system.

$$\lambda_c = \lambda_m \frac{1 + A\beta v}{1 - \beta\psi v}, \quad \text{here } \beta = \frac{\lambda_f/\lambda_m - 1}{\lambda_f/\lambda_m + A}, \quad \psi = 1 + \frac{1 - \lambda_m}{v_m^2} v \quad (10)$$

In this model, constant A depends upon the shape and orientation of the dispersed particles. v_m is the maximum packing fraction of the dispersed particles. For randomly packed spherical particles $A = 1.5$ and $v_m = 0.637$.

Agari and Uno [20] proposed an empirical model based on the parallel and series model of composites:

$$\lg \lambda_c = v C_2 \lg \lambda_f + (1-v) \lg C_1 \lambda_m \quad (11)$$

where C_1 , C_2 are experimentally determined constants of order unity. Based on the experimental data, the values of the co-efficients are $C_1 = 1.0638$ and $C_2 = 1.0017$ here.

Thermal conductivity models are usually set for predicting the effective thermal conductivity of polymer filled by high thermal conducting particles and it has well prediction values at low particles volume fractions [21,22]. For silica aerogels particles with low thermal conductivity and high particles volume fractions, the experimental data under six models are plotted in Fig. 11. The traditional models like parallel model and series model are not fitted well and Maxwell model is far away from the experiment due to no considering of the interface. However, Geometric mean, Nielsen and Agari models match the experimental data very well in the whole range. Thus, the thermal conductivities of composites with interface which the nanopores were immersed by matrix can be predicted by these three models.

5. Conclusions

Hydrophobic silica aerogels/epoxy powder composites were prepared by hot pressing. Results show the composites have low density ($0.72\text{--}0.25 \text{ g/cm}^3$), well hydrophobic property with water contact angle of $117\text{--}140^\circ$, low thermal conductivity ($0.11\text{--}0.044 \text{ W/m K}$) in a wide temperature range. Contact angles measurements of the composites show the composites can be applied at an atmosphere of up to 250°C . An immersion model was established in which the interfaces and packing pores were also considered. The existing of interface has been proved to decrease the thermal insulation property of composites. Geometric mean, Nielsen and Agari models are well co-incident with the experimental results about the thermal conductivity of composites at high aerogel volume fractions.

References

- [1] L.W. Hurbesh, J. Non-Cryst. Solids 225 (1998) 336.
- [2] R. Tomasi, D. Sireude, R. Marchand, Y. Scudeller, P. Guillemet, Mater. Sci. Eng. B 137 (2007) 225.
- [3] J.E. Fesmire, J.P. Sass, Cryogenics 48 (2008) 223.
- [4] C. Moreno-Castilla, F.J. Maldonado-Hódar, Carbon 43 (2005) 461.
- [5] A.V. Rao, M.M. Kulkarni, D.P. Amalnerkar, T. Seth, J. Non-Cryst. Solids 330 (2003) 187.
- [6] A.P. Rao, G.M. Pajonk, A.V. Rao, J. Mater. Sci. 40 (2005) 3481.
- [7] M. Schmit, F. Schwertfeger, J. Non-Cryst. Solids 225 (1998) 365.
- [8] G.S. Kim, S.H. Hyun, J. Mater. Sci. 38 (2003) 1962.
- [9] P.L. Teh, M. Mariatti, A.N.R. Wagiman, K.S. Beh, Polym. Compos. 29 (2008) 35.
- [10] J.P. Zhao, D.T. Ge, S.L. Zhang, X.L. Wei, Mater. Sci. Forum 546–549 (2007) 1583.
- [11] N. Gupta, W. Ricci, J. Mater. Process. Technol. 198 (2008) 179.
- [12] C.P. Reghunadhan Nair, Prog. Polym. Sci. 29 (2004) 437.
- [13] A.V. Rao, M.M. Kulkarni, Mater. Res. Bull. 37 (2002) 1669.
- [14] W.M. Moses, F.W. Witthaus, H.A. Hogan, W.R. Laster, Exp. Therm. Fluid. Sci. 11 (1995) 35.
- [15] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, Adv. Mater. 14 (2002) 1858.
- [16] E. Cilley, D. Roylance, N. Schneider, Composite Material: Testing and Design (Third Conference), ASTM STP, vol. 546, 1975, p. 241.
- [17] M. Rein, W. Körner, J. Manara, S. Korder, M. Arduini-Schster, H.-P. Eber, J. Fricke, Sol. Energy 79 (2005) 134.
- [18] W.S. Lee, J. Yu, Diam. Relat. Mater. 14 (2005) 1652.
- [19] T. Lewis, L. Nielsen, J. Appl. Polym. Sci. 14 (1970) 1449.
- [20] Y. Agari, T. Uno, J. App. Poly. Comp. Sci. 32 (1986) 5705.
- [21] Q.H. Mu, S.Y. Feng, G.Z. Diao, Polym. Compos. 28 (2007) 127.
- [22] H. He, R.L. Fu, Y.C. Han, Y. Shen, J. Mater. Sci. 42 (2007) 6751.