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Polyimide/silica Aerogel Flexible Composite Film with High Thermal Insulation and Good Mechanical Strength

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Abstract: The large-scale application of silica aerogels is restricted due to many reasons, one of which is their poor mechanical properties. How to exert superiority of aerogels in application has always been the focus of research. In this work, the silica aerogel microspheres were added into polyimide to prepare composite films. The results show that the thermal conductivity of the composite film is declined compared with that of pure polyimide film and keeps decreasing with increasing additions, whose lowest value is 0.321 W m^{-1} K^{-1}. The mechanical strength is weakened compared with that of pure polyimide film. Therefore, the trade-off between thermal insulation performance and mechanical property is important in application of such film materials. The study enriches the application form of aerogels.

Key words: silica aerogels; polyimide; thermal insulation; mechanical strength

As a kind of nanoporous materials, aerogels, composed of three-dimensional solid structures filled with air, have attracted much attention of the chemists and materials scientists in recent decades, since they are prepared successfully by Kistler using supercritical drying in 1931[1,2]. Aerogels possess many unique properties: low density, low dielectric constant, high specific surface area, high porosity, and ultrahigh insulation value, which make applications of aerogels cover a wide range of areas including aerospace, building, optical, catalytic load and so on[3-6]. However, poor mechanical property caused by low solid content of skeleton structure is a key obstacle to large-scale application of aerogels[7]. To improve the mechanical strength to meet the practical operation without destroying the intrinsic property of aerogels, various strategies have been explored. Enhancing the skeleton strength of the aerogels with polymer coating and compositing the aerogels with different fibers and polymers are two common approaches[8-13].

As reliable high-temperature polymers, polyimides are high heat-resistant polymer with good mechanical strength, high glass transition temperature and outstanding thermal stability[14,15]. Compared with polymers as composite component such as epoxy[16], isocyanate[17], and styrene[18], polyimides can be stable at higher temperature. That the composite component can keep stable in high-temperature atmosphere is advantageous to the application of aerogel/polymer composites at higher temperature. The high-temperature performance of such composites are favorable in many aerospace applications. So the polyimides are promising candidates in thermal insulation application. The traditional preparation method of the polyimides is multi-step drying of polyamic acid followed by imidizing[19].

In this work, the silica aerogel/polyimide composite films with different mass fractions of silica aerogel microspheres in the polyimide matrix is fabricated. The size of microspheres is below 20 μm and the microspheres are prepared under ambient pressure drying condition. The thermal conductivity and mechanical tensile strength are characterized to study the thermal insulation property and mechanical property of the composite films. The micro morphology and thermal stability are also investigated.

1 Experiment

1.1 Synthesis of silica aerogel microsphere

The silica aerogel microspheres were prepared in an inverse emulsion system where sol-gel process happened. First, tetraethoxysilane (TEOS), deionized water, ethanol, and nitrate were mixed in a certain proportion and hydrolyzed. Then, the hydrolyzed sol was dispersed uniformly in an oil phase under stirring. The system gets gelation after the diluted ammonia was added drop by drop. Next, the sample was washed

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clearly in filtration process. Lastly, the sample was dried in gradient temperature. The silica aerogel microsphere was ready for subsequent use.

1.2 Preparation of silica aerogel/polyimide composite film

First, the polyamic acid (PAA) was prepared as follows: the 4,4-oxydianiline (ODA) (4.796 g) was dissolved in dehydrated 1-methyl-2-pyrolidinone (NMP) (60 ml). The pyromellitic dianhydride (PMDA) (5.195 g) was added into the solution in batches. The final solution was stirred for 10 h at room temperature. The PAA solution was prepared for use. Next, a certain amount of silica aerogel microspheres were dispersed in PAA under stirring conditions, and then the solution was evenly coated on the glass plate. The plate with film was dried in a vacuum oven to remove the excess solvent. At last, the film was cured at different temperatures in sequence. Here, in order to prevent the film from shrinking due to the thermal stress during the curing, the film on the plate must be fixed. A series of silica aerogel/polyimide composites with different weight fractions were prepared successfully. The as-prepared samples were referred to as PI/Si-*x* in this work, where the *x* denotes the mass content percentage of silica aerogel microsphere in the polyimide matrix.

1.3 Characterization

The microstructure and morphology of the composite were observed by scanning electron microscope (SEM, ZEISS SUPRA 55). The thermogravimetric and differential scanning calorimetry (TG-DSC, STA 449C) was used to study the thermal stability of the composites with different silica aerogel mass contents. The mechanical tensile strength was tested on the universal testing machine (Model-1185). The films were cut into rectangle (10 mm×10 mm) and the tensile rate of instrument was 1 mm/min. The thermal conductivity was investigated via the laser flash method on the thermal conductivity tester (Netzsch NanoFlash LFA 447). The sample was heated by a short laser pulse, and the heat diffused through the sample. The change of temperature on the both sides was monitored by the IR-detector. The density and specific heat capacity were determined separately. The density was calculated by the mass and corresponding volume, and the specific heat capacity was measured by the differential scanning calorimeter. The thermal diffusivity was obtained. The thermal conductivity λ of films was calculated by the formula [20,21]:

$$\lambda=\rho\cdot\alpha\cdot c_p \quad (1)$$

where ρ, α, and c_p represent the density, thermal diffusivity, and specific heat capacity, respectively.

2 Results and Discussion

2.1 Microstructure of the composite films

The micro morphology of polyimide/silica aerogel flexible composite film (PI/Si-*x*) measured by SEM is shown in Fig.1. The silica aerogel microspheres possess good sphericity, which is advantageous for microspheres being dispersed readily and uniformly in contrast with irregular shape of silica aerogel particles in viscous PAA solutions. The sizes are less than 20 μm and the microspheres are uniform in size. The surface of pristine polyimide film presents smooth and no cracks and wrinkles are observed. The microspheres are well-distributed in the PI/Si-*x* and they are not deformed during the mechanical dispersion process at a high stirring rate. The surface of composite films becomes apparently rough due to the addition of silica aerogel microspheres and the roughness becomes more and more obvious with the mass percentages of microspheres increasing.

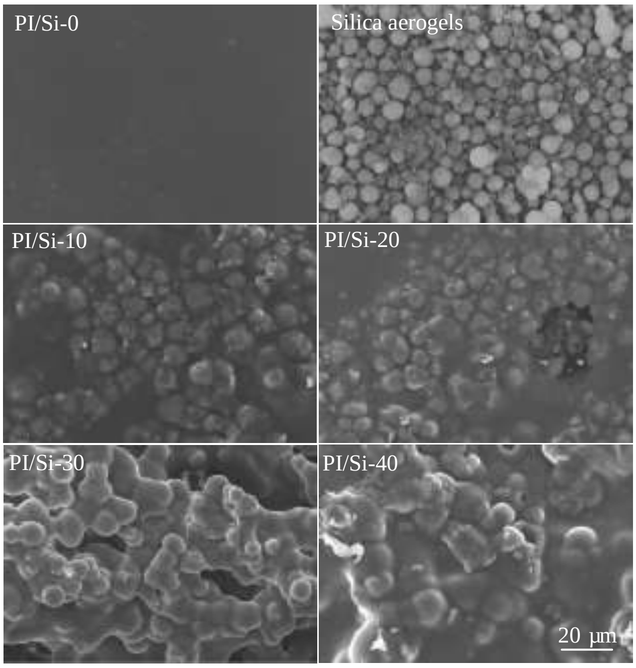

Fig.1 SEM images of polyimide with silica aerogel microspheres at different mass percentages

2.2 Thermal stability of the composite films

The thermal stability of PI/Si-*x* was analyzed by TG-DSC with heating program covering from room temperature to 600 ℃ at the rate of 10 ℃/min under oxygen atmosphere. The measuring result is exhibited in Fig.2. The decomposition temperature of pristine polyimide film is 534.8 ℃, at which the mass experiences a sharp drop from 100% to 0% between narrow temperature regions, illustrating that the heat-resisting performance of pristine polyimide film loss quickly. As shown in Fig.2, the thermal stability is enhanced with addition of silica aerogel microspheres, 28.6 ℃ at most. Additionally, the exothermic peak shifts to higher value from 534.8 ℃ to 563.4 ℃ gradually with the mass content of microspheres increasing from 0 to 30 wt%. The heat delivery is blocked or extended in the presence of microspheres when the PI/Si-*x* composite film is subjected to the high temperature; thus the thermal stability is improved compared with the pristine polyimide film. The slight decline of decomposition temperature of PI/Si-40

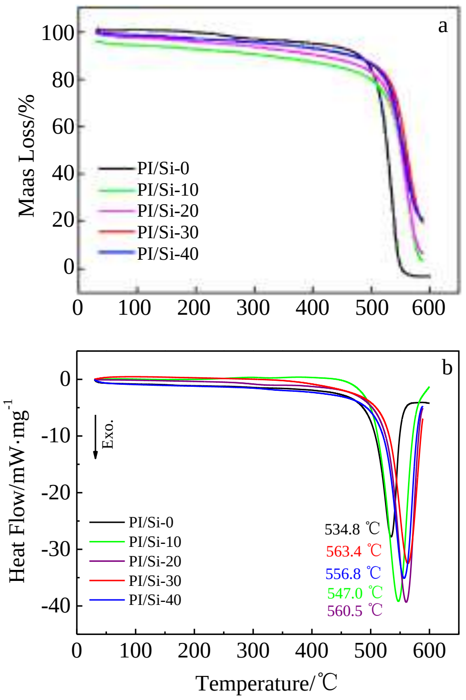

Fig.2 TG-DSC curves of polyimide with silica aerogel microspheres at different mass percentages: (a) TG and (b) DSC

(556.8 ℃) contrasted with that of PI/Si-30 (563.4 ℃) is attributed to the deformation of matrix continuity because of excessive addition of microspheres in the matrix. Moreover, the differences in the finishing point of mass loss in TG curves reflect the variation of microspheres contents. After the polyimide component in composite films burns out, the mass keeps losing due to the alkyl groups being oxidized. Thus finishing point of mass loss is lower than the mass content percentage of aerogel microspheres.

2.3 Thermal conductivity and mechanical strength of the composite films

The thermal conductivity of PI/Si-*x* films was evaluated using the laser flash method. The result is depicted in Fig.3. As can be seen from Fig.3a, the density decreases significantly from 0.999 g cm^{-3} to 0.248 g cm^{-3} with the increase of microsphere contents due to the addition of a light component. The thermal diffusivity presents gradual increase with different microsphere contents, and the specific heat capacity remains little variation. The thermal conductivity in Fig.3b shows a minor decrease from 0.374 W m^{-1} K^{-1} to 0.321 W m^{-1} K^{-1} due to the contribution of silica aerogel microspheres. The microspheres introduces nano-sized pores in the polyimide matrix, but the pristine counterpart is compact. This can be also verified by the pronounced variation of density. The solid heat transfer in pure polyimide is high since the structure is compact. The presence of nano-sized pores in aerogels microsphere interrupts the continuity of solid heat transfer in polyimide matrix and makes part of solid heat transfer be replaced by the gas heat transfer; thus the thermal conductivity is lowered. Furthermore, the solid heat transfer is proportional to density, so thermal conductivity declines due to the decrease of density. The interfacial thermal resistance between the microspheres and polyimide matrix is also an important factor in lowering the thermal conductivity. However, the thermal conductivity of polyimide film with microspheres is still higher than what is expected. That parts of the pores in the microspheres are filled with the PAA solution in the preparing process, which may be the primary reason. The polyimide/silica aerogels composite films with lower thermal conductivity can be obtained if the pores in aerogels are preserved as many as possible in the matrix. A better method should be explored in the future work.

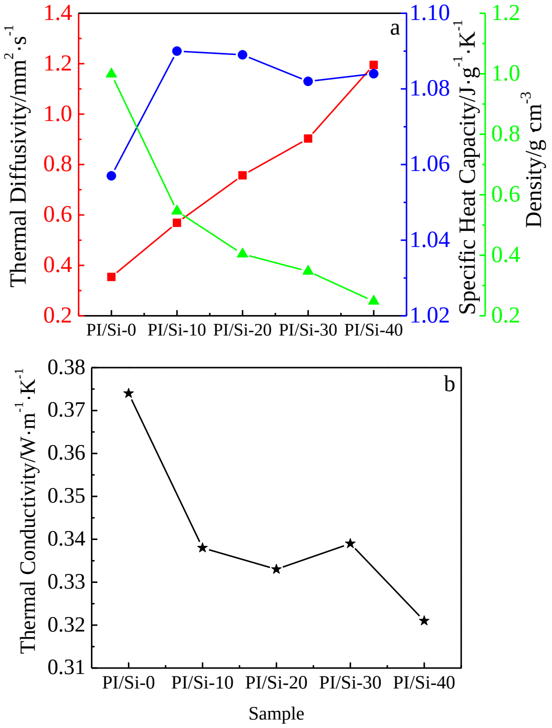

Fig.3 Thermal diffusivities, specific capacity and density (a) and thermal conductivities (b) of polyimide with silica aerogel microspheres at different mass percentages

The corresponding parameters of the tensile strength obtained are summarized in Table 1. The tensile-elastic modulus and tensile strength present evident decline with the silica aerogel microspheres addition varying from 0 to 40 wt%, which is ascribed to decrease of both the density and the crosslinking density in the presence of microspheres in polyimide matrix. Elongation decreases sharply from 32.72% to 2.05%, indicating that the flexibility of the composite film is weakened compared with that of the pristine counterpart, and

Table 1 Mechanical properties of PI/Si-*x*

Samples	PI/Si-0	PI/Si-10	PI/Si-20	PI/Si-30	PI/Si-40
E_C/MPa	1632.3	1250.8	1010.8	731.8	541.6
R_m/MPa	104.49	39.70	31.1	20.9	10.2
Elongation/%	32.72	9.37	3.53	3.07	2.05

this trend becomes more obvious with the microspheres addition increasing. This result can be attributed to failure of matrix continuity and weak interfacial interaction in this biphasic systems. It can be assumed that the stability of microspheres in matrix mainly depends on the physical forces instead of chemical forces due to no reactions between groups in the interfaces. Thus the matrix is prone to facture at the interfaces when they are subjected to the tensile force and the cracks transfer until the materials are destroyed. It should be underlined that although the mechanical strength is weakened due to the addition of silica aerogel microspheres, the PI/Si-*x* composite still deserves exploring in application of silica aerogels. After all, enriching the application form and flexibility of aerogels is an urgently to-be-solved issue and varying mechanical requirements can be met accordingly in application.

3 Conclusions

1) The polyimide/silica aerogel microspheres composite films are prepared. The research suggests that the influence of silica aerogel microsphere on the thermal stability, thermal conductivity and mechanical tensile strength of the resulting composite films is apparent. The trade-off between thermal insulation performance and mechanical property is important in preparation and application of such materials.

2) The 30 wt% addition of aerogel microspheres is preferable when the thermal conductivity and tensile strength are taken into consideration. The thermal conductivity does not experience an obvious decline as expected due to the pores in aerogels being filled, indicating that the composite films with lower thermal conductivity could be obtained in future work.

References

[1] Kistler S S. *Nature*[J], 1931 127: 741

[2] Soleimani A, Dorcheh M H. *Journal of Materials Processing Technology*[J], 2008, 199: 10

[3] Schmidt M, Schwertfeger F. *Journal of Non-Crystalline Solids* [J], 1998, 225: 364

[4] Hrubesh L W. *Journal of Non-Crystalline Solids*[J], 1998, 225: 335

[5] Shukla N, Fallahi A, Kosny J. *ASHRAE Transactions*[J], 2014, 120: 294

[6] Jones S M. *Journal of Sol-Gel Science and Technology*[J], 2006, 40: 351

[7] Randall J P, Meador M A, Jana S C *et al. ACS Applied Materials & Interfaces* [J], 2011, 3: 613

[8] Meador M A, Weber A S, Hindi A *et al. ACS Applied Materials & Interfaces*[J], 2009, 1: 894

[9] Özbakır Y, Ulker Z, Erkey C. *The Journal of Supercritical Fluids*[J], 2015, 15: 108

[10] Maleki H, Durães L, Portugal A. *Microporous and Mesoporous Materials*[J], 2014, 197: 116

[11] Bai F, Wu J T, Gong G M *et al. Journal of Materials Chemistry A*[J], 2015, 3: 13198

[12] Gupta N, Ricci W. *Journal of Materials Processing Technology*[J], 2008, 198: 178

[13] Kim H M, Noh Y J, Jaesang Y *et al. Composites: Part A*[J], 2015, 75: 39

[14] Guo H Q, Meador M A, McCorkle L *et al. ACS Applied Materials & Interfaces*[J], 2011, 3: 546

[15] Meador M A, Malow E J, Silva R *et al. Applied Materials & Interfaces*[J], 2012, 4: 536

[16] Meador M A, Scherzer C M, Vivod S L *et al. Applied Materials & Interfaces*[J], 2010, 2: 2162

[17] Meador M A, Capadona L A, McCorkle L *et al. Chemistry of Materials* [J], 2007, 19: 2247

[18] Nguyen B N, Meador M A, Tousley M E *et al. Applied Materials & Interfaces*[J], 2009, 1: 621

[19] You N H, Suzuki Y, Yorifuji D *et al. Macromolecules*[J], 2008, 41 :6361

[20] Sheindlin M, Halton D, Musella M *et al. Review of Scientific Instruments*[J], 1998, 69: 1426

[21] Guo K, Hu Z J, Song H H *et al. RSC Advances*[J], 2015, 5: 5197

高隔热性能和机械性能的聚酰亚胺/二氧化硅气凝胶复合膜

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摘　要：二氧化硅气凝胶的大规模应用受限于许多原因，机械性能差是其中之一。如何在应用中发挥气凝胶的优势一直是研究关注的重点。本研究将二氧化硅气凝胶微球添加到聚酰亚胺中成功制备了聚酰亚胺/二氧化硅气凝胶复合膜。实验结果显示：与纯聚酰亚胺膜相比，复合膜的热导率降低，并且随着添加量的增加而继续下降，最小值为 0.321 $W\ m^{-1}\ K^{-1}$。与纯聚酰亚胺膜相比，复合膜的机械性能有所下降。因此，在膜材料应用中兼顾机械性能和隔热性能是很重要的。本研究丰富了气凝胶的应用形式。

关键词：二氧化硅气凝胶；聚酰亚胺；隔热性能；机械强度

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