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# Preparation and Properties of PMMA Modified Silica Aerogels from Diatomite

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**Abstract:** Diatomite was used as raw material to prepare sodium silicate with a modulus of 3.1 by alkali dissolution method and the resulted sodium silicate solution was employed as a precursor. Methyl methacrylate monomers were introduced in wet gels through solution-immersion, and upon heating at 70 °C, the mesoporous surfaces throughout the skeletal framework were coated with the polymer layer. PMMA modified silica aerogels were successfully synthesized via ambient pressure drying. The properties were investigated by FT-IR, NMR, TGA, nitrogen adsorption-desorption, FESEM and nano-indentation, *etc.* Results indicate that with the increasing of PMMA incorporated into silica aerogels, the bulk density and the BET surface area increase, the porosity decreases. Through the observation of FESEM, it is found that the interconnecting pores and the big pores add, the pore size distribution expands from 5-17 to 28-150 nm. By comparison, the PMMA modified silica aerogels achieve a 52-fold increase in hardness and a 10-fold increase in modulus.

**Key words:** silica aerogels; PMMA; diatomite; ambient pressure drying; mechanical properties

## 1 Introduction

Silica aerogels are attractive candidates for many unique thermal, optical, catalytic and chemical applications<sup>[1-6]</sup> because of their low bulk density (0.03 g/cm<sup>3</sup>), high porosity (80-99.8%), high surface area (800-1 000 m<sup>2</sup>/g), low thermal conductivity (0.02 W/(m·K)) and unique nanometer pore structure (1-100 nm)<sup>[1-4]</sup>. However, the fragility and poor mechanical properties limit the wider industrial and commercial uses of

silica aerogels. Recently, silica aerogel monoliths have limited use in specialized environments, such as in Cerenkov radiation detectors in certain nuclear reactors<sup>[7-9]</sup>, collectors of hypervelocity particles in space<sup>[10,11]</sup>, and thermal insulators in space vehicles<sup>[12,13]</sup>. Since the supercritical fluid drying technique is always needed during preparation, the mesoporous and completeness of aerogels could be obtained. Nonetheless, the complex operating process, high risk and high cost of this technique also limit large scale industrial production and application of aerogels. Besides, the traditional route for the manufacturing process of monolithic silica aerogels needs the use of silica sources, such as tetraethoxysilane (TEOS), tetramethoxysilan (TMOS) or methyltrimethoxysilane (MTMS) which are expensive and poisonous, highly restricting the commercialization of aerogels. Hence, the study on low-cost industrial production and mechanical property enhancement of aerogels monolith would be significant.

In recent years, there are some reports on employing new raw materials such as waterglass, flyash and rice husk as silica sources<sup>[9-11]</sup>. However, preparing silica aerogels from diatomite is less investigated.

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Diatomite is an amorphous silicon non-metallic mineral, formed by skeletal remains of colonies of unicellular diatom deposited in oceans or lakes. Presently, diatomite is mainly used in fields of filter aids, sewage treatment, catalyst carrier, and functional filler, etc<sup>[12-14]</sup>.

On the other hand, the most common strategy for improving the mechanical properties of silica aerogels is compositing with fibers, fiber felt, nonwovens or additives<sup>[15,16]</sup>. Nevertheless, no covalent bonding occurs between the two components of this kind of composite material, and the inherent fragility and brittle nature of silica aerogels remain unaltered<sup>[17]</sup>. Cross-linking the skeletal structure with polymer has been demonstrated recently to be effective to improve the strength of aerogels by as much as orders of magnitude while only doubling the density over those of native or non-cross-linked aerogels<sup>[18]</sup>.

In this study, diatomite was used as raw material to prepare sodium silicate with a modulus of 3.1 by alkali dissolution method and the sodium silicate solution was used as silica source to synthesize silica aerogels. Methyl methacrylate monomers were grafted onto mesoporous surfaces of aerogels to improve the fragility. The chemical, physical and mechanical properties of PMMA modified aerogels were investigated.

## 2 Experimental

### 2.1 Materials

The diatomite adopted was reagent grade and ordered from Zhi-yuan Chem. Co. Ltd., Tianjin, China. The chemical compositions are listed in Table 1. The XRD pattern of diatomite is shown in Fig.1. Since the content of silica in diatomite material is nearly 90%, the raw material was not purified in this work. Trimethylchlorosilane (TMCS, AR,  $\geq 98.0\%$ ) was provided by Xinyaqiang Biochem. Co., China. Sodium hydroxide (NaOH, AR,  $\geq 96.0\%$ ), ethanol (EtOH, AR,  $\geq 99.7\%$ ), ammonia hydroxide (AR,  $\geq 98.0\%$ ), azobisisobutyronitrile (AIBN AR,  $\geq 98.0\%$ ) and n-Hexane (AR,  $\geq 98.0\%$ ) were obtained from Shenyang Chemical Co., China. Ion exchange resin (Amberlite, 732 Cation) was supplied by Shanghai Huizhi Co., China. Methyl methacrylate (MMA) monomer, purchased from Kemiou Chem. Co., Tianjin, China, was washed in 10% NaOH solution in a separation funnel twice, followed by three rinsings in distilled water before used to remove the inhibitor. The silane

coupling agent (KH-570), ordered from Yaohua Safety Glass. Co., Ltd, Shenyang, China, was employed to improve the chemical bonding between the silica gel phase and the PMMA. All chemicals used were domestic analytical grade reagents.

**Table 1 Chemical compositions of diatomite/wt%**

Component	SiO <sub>2</sub>	NaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	LOI
Content	89.39	2.49	2.13	1.99	0.64	1.27

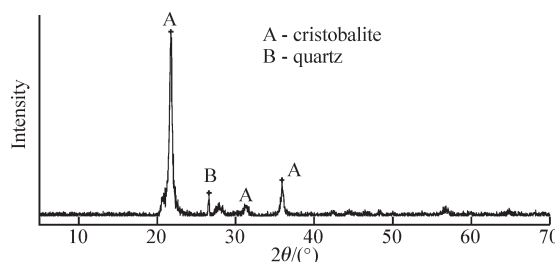


Fig.1 XRD pattern of diatomite

### 2.2 Preparation of sodium silicate from diatomite

According to our previous work, 200-mesh diatomite powder was mixed with 10 wt% sodium hydroxide solution to prepare sodium silicate at 90 °C for around 2-3 h with magnetic stirring. The chemical reaction is shown as follows:



In the chemical equation,  $m$  is the molecular ratio of SiO<sub>2</sub> and Na<sub>2</sub>O (sodium silicate modulus)<sup>[19]</sup>. The reaction product was filtered by a vacuum suction filter to obtain sodium silicate solution, and then its sodium silicate modulus was measured. The result was about  $m = 3.1$ . Finally, sodium silicate solution was diluted by distilled water with a proportion of 1:2 in order to achieve a proper gelation time during the sol-gel process.

### 2.3 Preparation of silica wet gels

The silica wet gels were prepared by sol-gel process and the sodium silicate solution prepared above was used as a precursor. The sodium silicate solution was dropped through an amberlite ion exchange resin column (5 cm in diameter, 40 cm in length). The pH of the collected silica sol was around 2.0-2.5. For gelation at room temperature, right amount of 1.0 mol/L ammonia solution was added into the silica sols to adjust pH to 5.0-5.2, and then the sols were poured immediately into polypropylene syringes (10 mm in diameter and 30 mm in height). After gelation, the shaped gel monoliths were put into 50% ethanol solution for 24 h and in pure ethanol for another 24 h to

replace the water in pores before further modification. Each of the solution should be changed in every 8 h.

#### 2.4 Preparation of blank silica aerogels

In order to achieve blank silica aerogels via ambient pressure drying with less shrinkage, the wet gel was modified by EtOH/TMCS/n-hexane solution. After solution exchanging and aging, the wet gels were immersed in EtOH/TMCS/n-Hexane solution at 50 °C for 24 h. The optimum conditions for modification were adopted as follows: the mole ratio of EtOH:TMCS=1:1 and the volume ratio of TMCS: wet gels =1:1<sup>[20]</sup>. The modified wet gels were dried at room temperature for 24 h, then dried in a vacuum drying oven at 50 °C for 24 h and then cooled to room temperature. The blank silica aerogels were obtained<sup>[21]</sup>.

#### 2.5 Modification of wet gels with polymer

The aged gels prepared in Section 2.3 were placed into a mixed solution containing 20 mL silane coupling agent (KH-570) and 20 mL ethanol for 24 h and then heated in a water bath at 50 °C for 24 h to alkylate the surface of silica particles. The silane coupling agent is a compound which can bond to the silanol groups of the pores as well as the active sites on the MMA monomer<sup>[13]</sup>. Therefore, it was employed to improve the chemical bonding between the silica gel phase and the PMMA. The alkylated gels were extracted into 10%, 20%, 30%, 40% and 50% v/v MMA/Ethanol solutions. The diffusion of monomers into gels continued for 24 h. Samples were transferred from the MMA solutions to new containers in which the free radical initiator AIBN was dissolved by 70 mL n-Hexane under ultrasonic treatment. After 2 hours immersion, the polymerization reaction was initiated at 70 °C and kept for 24 h. The PMMA-modified aerogels were removed from solution, washed by n-Hexane and dried under ambient pressure at room temperature for 24 h. Then they were placed in a vacuum drying oven at 50 °C for 24 h and then cooled to room temperature. Finally, PMMA modified silica aerogels were obtained. The reaction mechanism

is shown in Fig.2.

#### 2.6 Characterization

Chemical, physical and mechanical characterization of all samples was conducted by thermogravimetric analysis (TGA), FT-IR spectroscopy, solid <sup>13</sup>C-NMR spectroscopy, field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), nitrogen adsorption porosimetry and nano-indentation. Infrared spectra were obtained in KBr pellets with a Nicolet FT-IR Spectrometer model Avatar 360. Solid <sup>13</sup>C-NMR spectra were achieved with samples ground into fine powders on a Bruker Avance 300 Spectrometer with 75.475 MHz carbon frequency using magic angle spinning (at 7 kHz) with broadband proton suppression and the CPMAS TOSS pulse sequence for spin sideband suppression. Thermogravimetric analysis (TGA) was conducted with a Mettler Toledo System under nitrogen and run at a temperature ramp rate of 10 °C/ min. For FESEM, samples were coated with Au and microscopy was conducted with an FEI Nova Nanosem 450 field emission scanning electron microscope. For nitrogen adsorption porosimetry, samples were outgassed at 200 °C for 12 h and studies were conducted with a Micromeritics ASAP 2020 Surface Area/Pore Distribution analyzer at 77 K. The modulus and hardness were measured by a nano-indentation of Hysitron Ti-950 Triboindenter on samples with a size of 4×4×4 mm. In order to keep the top and bottom of each sample smooth and parallel, grade-400 fine silicon carbide sandpaper and L-square were respectively used to sand the samples and check the surfaces. The bulk densities were calculated from the mass and the physical dimensions of the samples.

### 3 Results and discussion

#### 3.1 Density and porosity

The basic physical properties of the blank silica

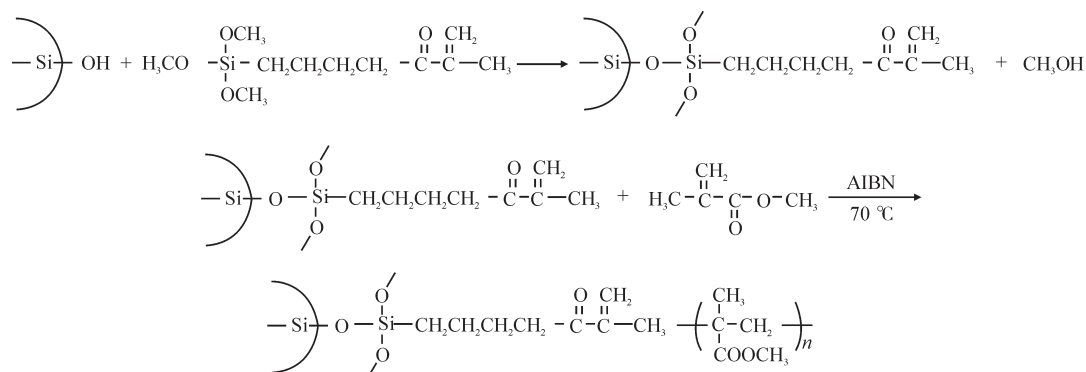


Fig.2 Reaction mechanism of PMMA cross-linked silica aerogels

**Table 2 Basic physical properties of silica aerogels**

Samples	MMA/%	Bulk density /(g/cm <sup>3</sup> )	BET surface area /(m <sup>2</sup> /g)	Porosity/%	Total mass loss by TGA/%
A-0	0	0.205	726.318	89	11
A-1	10	0.276	668.941	82	41
A-2	20	0.341	687.276	77	43
A-3	30	0.402	640.158	71	52
A-4	40	0.603	343.158	55	58
A-5	50	0.741	256.339	44	65

aerogels and PMMA modified aerogels are listed in Table 2. The bulk density of the 6 samples depends on the chemical identity and concentration of the PMMA during the incubation. The amount of PMMA incorporated in the silica aerogels was determined by the mass loss between 300 and 500 °C from the TGA curves<sup>[22]</sup>. The porosity of blank aerogels was calculated from the apparent density of A-0 ( $\rho_0$ ) and the density of pure silica ( $\rho_s=2.19$  g/cm<sup>3</sup>[23]) according to Eq.(1). And the porosity of PMMA modified aerogels was respectively calculated by Eq.(2).

$$\text{Porosity} = (1 - \rho_0 / \rho_s) \times 100\% \quad (1)$$

$$\text{Porosity} = \left( 1 - \frac{\rho_b W_p}{\rho_p} - \frac{\rho_b (1 - W_p)}{\rho_s} \right) \times 100\% \quad (2)$$

In Eq.(2),  $\rho_b$  is the bulk density of PMMA modified aerogel,  $\rho_p$  is the density of polymer ( $\rho_p=1.08$  g/cm<sup>3</sup>) obtained by measurement,  $W_p$  is the amount of PMMA incorporated in the silica aerogels shown in Table 2, and  $\rho_s$  is the density of pure silica ( $\rho_s=2.19$  g/cm<sup>3</sup>).

In our experiments, the effects of PMMA amount on bulk density, porosity and BET surface area are obvious. With the increase of MMA content in modification solution, the amount of PMMA grafted onto silica network increases.

### 3.2 FT- IR and NMR analysis

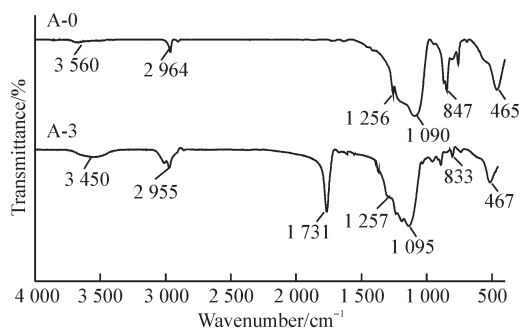
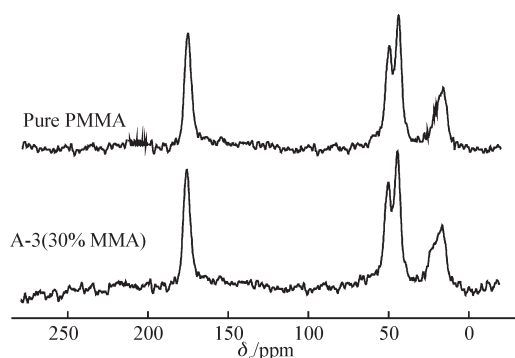


Fig.3 FT-IR spectra of aerogels

Fig.3 compares the infrared absorption spectra of blank aerogels and PMMA modified aerogels. From the IR spectra, it is revealed that A-0 and A-3 all have

strong peaks at about 1 090 and 465 cm<sup>-1</sup> which are attributed to the stretching and bending vibrations of Si-O-Si. The Si-O-Si group is the skeleton structure of silica materials, and the content is always high. In the IR spectrum of PMMA modified aerogels (A-3), as expected, the sharp absorption of C=O stretch at about 1 731 cm<sup>-1</sup> in the composites indicates the existence of PMMA. The absorption peak at 2 955 cm<sup>-1</sup> corresponds to the terminal-CH<sub>3</sub> group. The broad absorption at 3 450 cm<sup>-1</sup> is due to -OH groups on the surface of silica. More importantly, the weak peaks at 1 257 and 833 cm<sup>-1</sup> are attributed to Si-C bonding. Because of the surface modification of EtOH/TMCS/*n*-hexane solution, the -OH groups of blank silica aerogels are sharply reduced compared with PMMA modified aerogel and large amount of -CH<sub>3</sub> groups take their places. Accordingly, the absorption peak at 2 964 cm<sup>-1</sup> due to terminal -CH<sub>3</sub> group and the strong peaks at 1 256 cm<sup>-1</sup> and 847 cm<sup>-1</sup> due to Si-C can be seen obviously. What's more, the C=O stretch at 1 730 cm<sup>-1</sup> is absent which can be easily distinguished from the PMMA modified aerogel.

Fig.4 Solid-state <sup>13</sup>C CPMAS NMR spectra of pure PMMA and PMMA modified silica aerogels

The <sup>13</sup>C CPMAS NMR spectra of pure PMMA and PMMA modified aerogel are depicted in Fig.4. The NMR evidence clearly indicates that the two samples have the same peaks at the same site. The -C=O carbon at 175 ppm and the -O-CH<sub>3</sub> carbon at 49 ppm are clearly visible which directly respect the major structure of PMMA. The two peaks at 51 ppm and 20

ppm respectively assign to carbons of ruleless  $-CH_2-$  and  $-CH_3$ . There is no evidence of the  $C=C$  seen from FT-IR spectra and  $^{13}C$  CPMAS NMR spectra, so we could say that the polymerization is sufficient.

### 3.3 TGA analysis

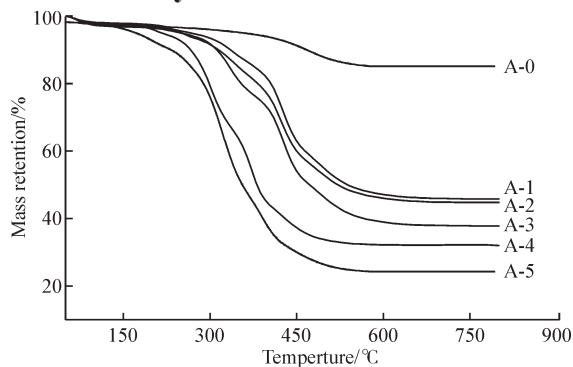


Fig. 5 TGA curves of silica aerogels

Comparative thermogravimetric analysis in Fig. 5 shows that blank silica aerogels (A-0) experience a high mass loss at 450 °C, which is due to the oxidation reaction of  $-CH_3$  groups on the surface of blank silica aerogels. When the temperature reaches 800 °C the mass no longer changes. The total mass loss of blank silica aerogels is about 11%. There is a little mass loss of PMMA modified aerogels (A-3) at 100 °C, which is attributed to the evaporation of the absorbed water and remaining solvent in material. An obvious mass loss at 190°C is due to the oxidation of Si-OH. The amount of polymer incorporated into the silica aerogels in Table 2 was obtained from the mass loss between 300 and 500 °C in the TGA curves.

### 3.4 XRD analysis

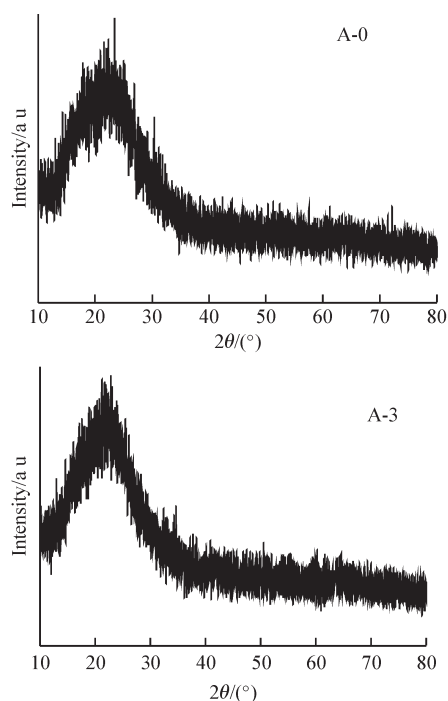


Fig. 6 XRD spectra of pure  $SiO_2$  aerogels and PMMA cross-linked silica aerogels

From the XRD patterns of blank silica aerogels and PMMA cross-linked silica aerogels, we could find nothing different between the two samples. Sample A-0 and sample A-3 all have an obvious signal peak at 20-25°. It is illustrated that the blank silica aerogels and PMMA modified silica aerogels are amorphous.

### 3.5 Pore structure and pore size distribution

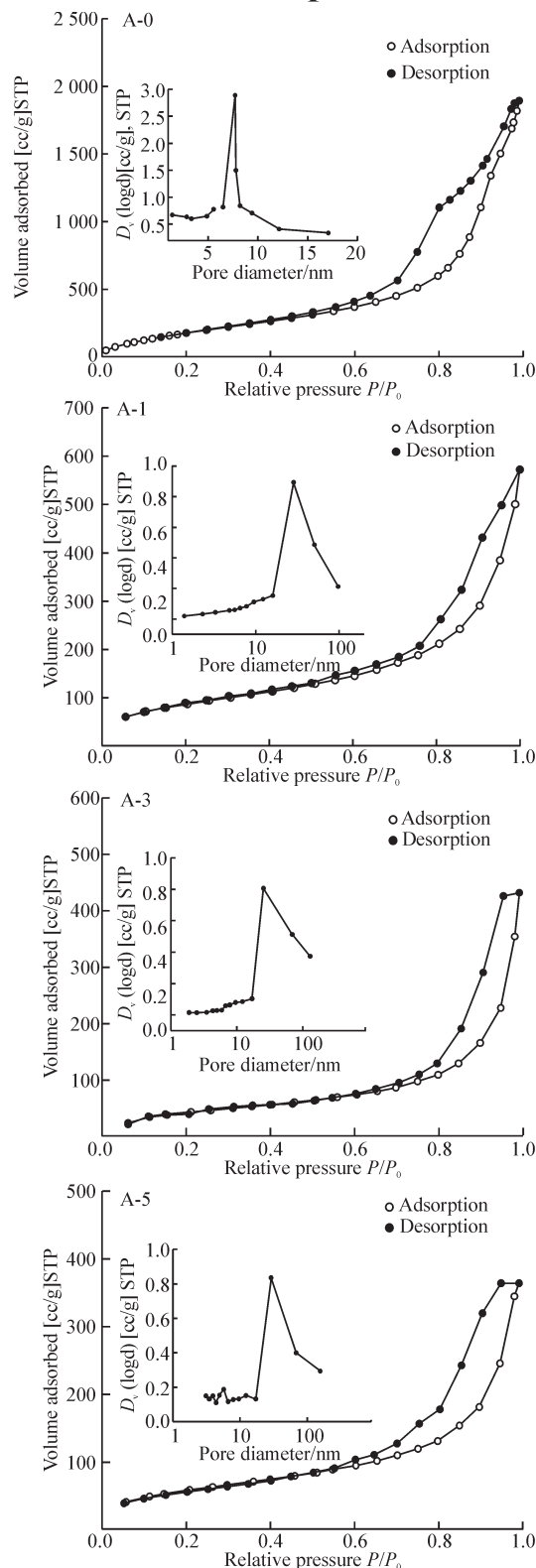


Fig. 7  $N_2$  adsorption-desorption isotherms and pore size distribution curves



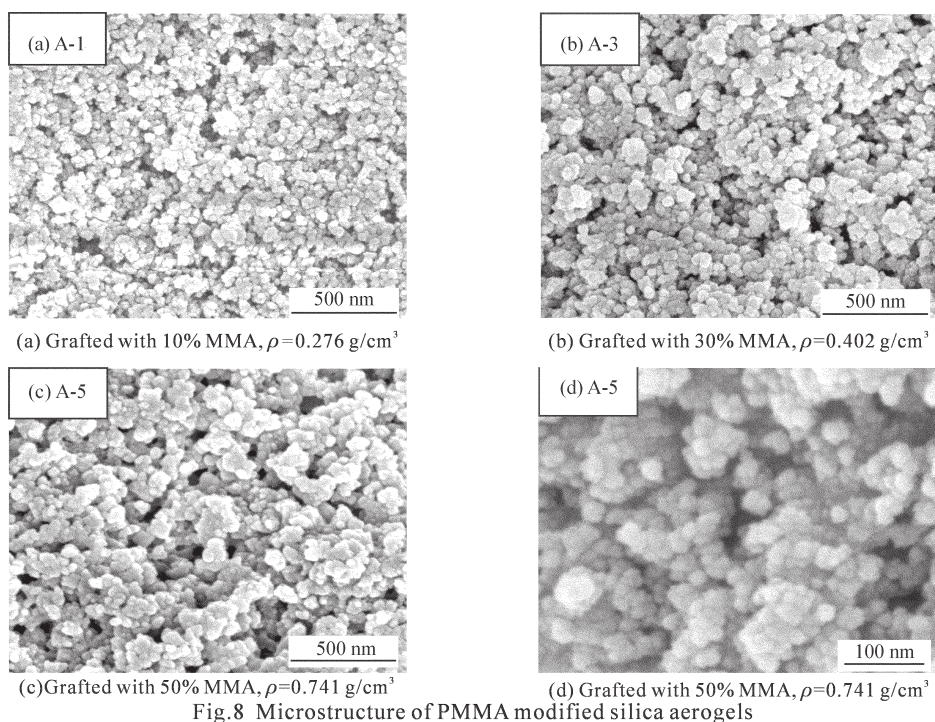


Fig.8 Microstructure of PMMA modified silica aerogels

As demonstrated in Fig.7,  $N_2$  sorption porosimetry yields typical IV isotherms for both blank aerogel and PMMA modified aerogels, characteristic of mesoporous materials. The pore size distribution of samples determined by the BJH method shows a shift toward larger pore diameters, from 5-17 nm of A-0 to 28-150 nm of A-5. Moreover, it can also be seen that the BET surface area listed in Table 2 indicates a reduction with increasing PMMA concentration. When the MMA content in ethanol solution reaches 50%, the BET surface area declines by 65% compared with that of blank aerogels. Because of the PMMA layer coating on the surface of the silica particles, silica skeleton is strengthened; the capacity of defending the capillary forces is improved and the shrinkage of monolith is reduced. As a result, the pore diameter increases and pore size distribution widens when the content of MMA increases from 0% to 50%.

### 3.6 Microstructure analysis

To determine the effect of PMMA on the microstructure of PMMA modified aerogels, FESEM was used to image micrograph of fracture surfaces of the samples. As can be seen from Fig.8, the skeleton network structure of PMMA modified aerogels is obvious and the silica nanoparticles show the typical aggregated structure. Comparing the three pictures of A-1, A-3 and A-5, it can be easily found that the content of PMMA in aerogels influences the size of pores and primary particles. The diameter of silica nanoparticles ranges from 6-12 to 32-36 nm when

the content of MMA increase from 10% to 50%. Because of the polymer coating, the pore size increases inside the aerogels and the number of interconnecting pores and big pores also increases. Clearly, the polymer conformally coats the surface of the skeletal nanoparticles, leaving the mesoporous voids open.

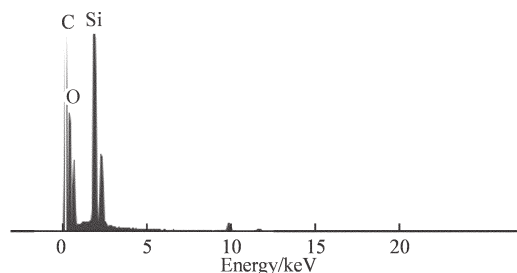


Fig.9 Elements spectrum of PMMA modified aerogels

Table 3 EDS results of PMMA modified aerogels in Fig.8

Samples	Properties	Si	O	C	Total
A-1	Weight percent	24.46	28.64	46.90	100.00
	Atomic percent	15.42	26.80	57.78	100.00
A-3	Weight percent	20.97	29.75	49.28	100.00
	Atomic percent	9.88	28.69	61.43	100.00
A-5	Weight percent	9.55	35.78	54.67	100.00

Fig.9 shows the elements spectrum of PMMA modified aerogels. The EDS results shown in Table 3 were obtained by scanning the PMMA modified aerogel samples (A-1, A-3, A-5) on surfaces in Fig.8. All data suggest that aerogels consist of three elements, carbon, oxygen and silica.

It is obvious that the amount of carbon atoms, oxygen atoms and silica atoms has a relationship with

the PMMA content. With the PMMA content going up, the carbon and oxygen increase, the silica reduces. The reason may be that the rising of PMMA content in aerogels leads to the increase of silica particles diameter. As a result, the number of silica particles reduces in the scanning area of same size and the PMMA layer coated on silica particles grows thick. Therefore, the strength of silica skeleton could be improved.

### 3.7 Mechanical properties

**Table 4 Mechanical properties of silica aerogels**

Samples	Yong's modulus/MPa	Hardness/MPa
A-0	5.3	0.7
A-1	32.6	5.0
A-2	44.1	11.1
A-3	52.7	24.4
A-4	61.6	37.2
A-5	60.4	36.7

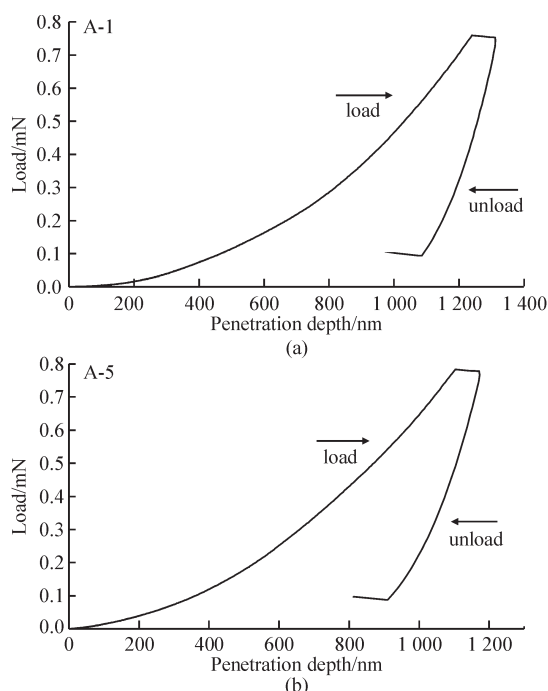


Fig. 10 Hysteresis curve penetration depth vs load for the samples: (a) A-1 and (b) A-5

The monolithic PMMA modified silica aerogels are white with a random shape. We could find the shrinkage cracks, which makes it difficult to test the mechanical properties through compressing test. In this study, the nano-indentation test instrument was used to characterize the Young's modulus and hardness. The indenter was pressed into materials for 1  $\mu\text{m}$ , and then the load-displacement curve (p-h curve) was obtained. The Young's modulus and hardness of all samples are calculated according to the p-h curves<sup>[24]</sup>. The load-displacement hysteresis curves of A-1 and A-5 are shown in Fig. 10. We tested 9 different points

of each sample and calculated the average values. The results are listed in Table 4. It is clear that introducing of PMMA in aerogels significantly improves the Young's modulus and hardness of the samples. A 52-fold increase in hardness and a 10-fold increase in Young's modulus of PMMA modified aerogels are achieved compared with blank aerogels. The monomers polymerize in the pores of gels and on the surface of silica skeleton nanoparticles, form PMMA layer coats and enhance the weak neck region between secondary particles. Thus, silica skeleton is strengthened to defend the capillary force under ambient pressure drying. The PMMA modified silica aerogels perform good mechanical properties at the macro level.

## 4 Conclusions

a) In this study diatomite was employed as raw material to prepare sodium silicate solution. And then wet gels were synthesized by sol-gel process using sodium silicate solution as the precursor. PMMA was incorporated into silica skeleton to enhance the strength. Finally, the PMMA modified silica aerogels were successfully prepared via ambient pressure drying.

b) With the increasing of PMMA incorporated in aerogels, the bulk density and the BET surface area increases, the porosity drops. When the MMA content in ethanol solution comes to 50%, the bulk density of aerogels goes up to 0.741  $\text{g}/\text{cm}^3$ , but is still less than that of water.

c) Under the observation of FESEM, the mesoporous structure and the typical nanoparticles skeleton network of PMMA modified silica aerogels are clear. The size of skeleton nanoparticles increases, the largest particle diameter (A-5) could reach 36 nm. Besides,  $\text{N}_2$  adsorption-desorption isotherms and pore size distribution all illustrate that the diameter of pores increases from 5-17 to 28-150 nm, big pores and interconnecting pores increase with the rising of PMMA content.

(d) Polymer monomers polymerize in the pores of wet gels and on the surface of silica skeleton nanoparticles, form polymer coats and enhance the weak neck region between secondary particles. As a result, the silica skeleton is strengthened. A 52-fold increase in hardness and a 10-fold increase in Young's modulus of PMMA modified silica aerogels are achieved compared with blank aerogels.

(e) Although grafting with PMMA could improve

the fragility of silica aerogels efficiently, the properties such as low bulk density, low porosity and high surface area are all affected to some extent. Therefore, how to enhance the mechanical properties and keep the excellent characteristics of aerogels at the same time still needs more experiments and further studying.

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