Mechanical properties of polymer-modified silica aerogels dried under ambient pressure

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1. Introduction

Silica aerogels are highly porous materials with low density and thermal conductivity. Their unique physical properties make them attractive for use in various applications [1–4]. However, silica aerogel monoliths have limited use in specialized environments, such as in Cerenkov radiation detectors in certain nuclear reactors [5–7], collectors of hypervelocity particles in space, and thermal insulators in space vehicles [6–9]. The wider industrial and commercial use of silica aerogels has been difficult to implement because of their poor mechanical properties coupled with the need for supercritical fluid (SCF) drying during manufacture.

The most common strategy for improving the mechanical properties of silica aerogels is to reinforce them using materials such as xonotlite [10,11], ceramic fibers [12–14], nonwoven fibers [15], and carbon or silica fiber felt [16,17]. However, no covalent bonding occurs between the two components of this kind of composite material; thus, the inherent fragility and brittle nature of silica aerogels remain unaltered. The reinforcement of silica aerogels using a conformal coating of polymer on the silica skeleton of silica aerogels was recently demonstrated to be effective in improving mechanical properties [7,8,18–29]. Although polymer-modified silica aerogels have good mechanical properties, SCF drying is still used in most studies except for Ref. [18]. SCF drying of silica gels features both high costs and risks, thus limiting its broader application. Moreover, few studies focus on the mechanical properties of polymer-modified silica aerogels dried under ambient pressure in Ref. [18]. In the current study, we report on the preparation and mechanical properties of polymer-modified silica aerogels dried under ambient pressure.

2. Experiment

2.1. Materials

Analytical-grade tetraethylorthosilicate (TEOS), acetone, pentane, 3-aminopropyltriethoxy-silane (APTES, 98%; Nanjing Capture Chemical Co.), toluene diisocyanate (TDI, ≥99.5%; GCP Union Chemical Co., Ltd., Zhengzhou), hydrochloric acid (HCl, 37% w/w), and double-distilled water were used as received without further purifications.

2.2. Preparation of polymer-modified silica aerogels

Fig. 1 illustrates the synthetic pathway for producing polymer-modified silica aerogels dried under ambient pressure. The preparation process can be divided into three steps.

2.2.1. Preparation of amine-modified wet gels

Amine-modified wet gels were synthesized using a two-step process involving the acid hydrolysis of TEOS, followed by base-catalyzed condensation with APTES. Amine-rich APTES eliminates the
need for additional base catalysis because the amine group of APTES serves as the gelation catalyst. Solutions A and B were mixed together to form gels in a sol–gel process. For solution A, 5.30 mL of TEOS (23.75 mmol), 2.26 mL of water (125.54 mmol, based on a 1:1 mole ratio of water to one ethyoxyl group of TEOS or APTES), and 0.01 mL of concentrated HCl (37% w/w) were dissolved in 25.03 mL of acetone (339.30 mmol) by stirring in a plastic container (100 mL) at room temperature. Solution B was prepared with 2.39 mL of APTES (10.18 mmol) and 25.02 mL of acetone (339.30 mmol). Solutions A and B were stirred for 1 h and 5 min, respectively. Both solutions were cooled in a refrigerator at −15 °C for 1 h to slow down gelation when combined. The cold solutions were mixed rapidly by adding solution B into solution A. The 60-mL output was stirred for 1 min and then poured into 12 cylindrical plastic molds, nominally 11 mm in diameter and 50 mm in height, to form the desired cylindrical monoliths for testing. The gels, which formed within 5–10 min, were aged for 24 h before being removed from their molds and subsequently placed in fresh acetone. The gels were aged at room temperature for 72 h in fresh acetone to remove excess water before further modification. The acetone-to-gel volume ratio was approximately 3:1, and the acetone was changed three times at 24-h intervals.

### 2.2.2. Modification of amine-modified wet gels with polymer

The aged gels were placed in a solution containing TDI in acetone. Sufficient diffusion of TDI into the body of the gels was allowed for 72 h at room temperature. Four percentages of mass concentrations for each TDI in acetone (0%, 2%, 10%, and 20%) were used to control the amount of polymer incorporated into the silica aerogels. Samples were removed from the TDI solution bath and then placed in a new container with fresh acetone. The modification of silica gels brought about by the reaction between TDI and amine groups was initiated at 60 °C and continued for 72 h to complete. The reaction scheme for this modification is shown in Fig. 2. Consequently, the gels were cooled to room temperature and placed in fresh acetone to remove unreacted TDI. The acetone was refreshed three times at 12-h intervals. Finally, the wet gels were immersed in a pentane bath for 36 h to exchange the solvent with pentane, and the pentane was renewed three times at 12-h intervals.

### 2.2.3. Drying of polymer-modified wet gels

The polymer-modified wet gels were removed from pentane and slowly dried under ambient pressure first at room temperature and then at 60 °C. The cylindrical monoliths of polymer-modified silica aerogels were finally obtained.

#### 2.3. Characterization

##### 2.3.1. Compression tests

The mechanical properties of polymer-modified silica aerogels were assessed by uniaxial compression tests. Compression tests were carried out on a MiniMAT 2000 using a 20 N load cell at 1 mm/min. Cylindrical specimens were compressed along their axis up until they fractured. At least three replicate tests were conducted for each set of samples. Before the test, the top and bottom portions of each specimen were sanded using grade-400 fine-silicon carbide sandpaper and checked using an L-square to ensure that the surfaces were smooth and parallel. According to ASTM standards, the slenderness ratio of specimens was 2:1. Load and displacement data were directly acquired. The load–displacement curve for each test was converted to a stress–strain curve by dividing the load by the original cross-sectional area of the specimen and the displacement by the height of the specimen.

##### 2.3.2. Thermogravimetric analysis (TGA)

The amount of polymer incorporated into the silica aerogels was measured by TGA. TGA was performed using a Q500 thermal gravimetric analyzer from TA Instruments under a nitrogen gas atmosphere. The mass of each sample was approximately 2 mg. TGA tests were run at a temperature ramp rate of 10 °C/min, and the nitrogen gas flow was 100 mL/min.

##### 2.3.3. Bulk density (ρb)

Bulk density (ρb) was determined by measuring the mass and volume of a sample. The mass was measured on an analytical balance and checked using an L-square to ensure that the surfaces were smooth and parallel. According to ASTM standards, the slenderness ratio of specimens was 2:1. Load and displacement data were directly acquired. The load–displacement curve for each test was converted to a stress–strain curve by dividing the load by the original cross-sectional area of the specimen and the displacement by the height of the specimen.

##### 2.3.4. Linear shrinkage (τ, %)

The linear shrinkage (τ, %) of the silica aerogels throughout the process was taken as the difference between the diameters of the silica aerogel monoliths and that of the mold divided by the diameter of the mold. Twelve samples from each set were tested for reproducibility to obtain the average value.

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Fig. 1. Synthetic pathway for polymer-modified silica aerogels.
3. Results

3.1. Shrinkage and density

The physical properties of the polymer-modified silica aerogels and their respective preparation conditions are listed in Table 1. The amount of polymer incorporated into the silica aerogels in Table 1 was obtained through the mass loss between 300 and 400 °C from the TGA curves in Fig. 3. Blank sample 0TDI had a significantly higher mass loss below 200 °C compared with the other samples (about 10% w/w versus 4% w/w) because of the presence of organic solvents such as pentane and adsorbed water. The amount of organic material lost from 0TDI at higher temperatures (>400 °C) could be due to mainly the loss of propyl groups from APTES, which accounts for approximately 11% w/w of the total mass of the silica aerogels. Samples 2TDI, 10TDI, and 20TDI lost 53.06%, 57.32%, and 74.33% w/w of their weight.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>TDI concentration (%)</th>
<th>Linear shrinkage (%)</th>
<th>Bulk density (kg/m³)</th>
<th>Polymer content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0TDI</td>
<td>0</td>
<td>61.05</td>
<td>954</td>
<td>0</td>
</tr>
<tr>
<td>2TDI</td>
<td>2</td>
<td>46.16</td>
<td>666</td>
<td>38.72</td>
</tr>
<tr>
<td>10TDI</td>
<td>10</td>
<td>37.60</td>
<td>544</td>
<td>45.06</td>
</tr>
<tr>
<td>20TDI</td>
<td>20</td>
<td>15.73</td>
<td>392</td>
<td>65.46</td>
</tr>
</tbody>
</table>

Fig. 2. Reaction—modification scheme for amine-modified aerogel with TDI.

Fig. 3. TGA curves of polymer-modified silica aerogels under nitrogen atmosphere.
at high temperatures (>200 °C), respectively, indicating polymer counts of 38.72%, 45.06%, and 65.46% w/w in the polymer-modified silica aerogels, respectively, after correction of the data obtained from the organic matter from APTES.

Table 1 shows that the linear shrinkage for polymer-modified silica aerogels decreases with increasing TDI concentrations in acetone or polymer in the silica aerogels. The reduction of the bulk density of these samples is as pronounced as the increase in TDI concentration.

3.2. Mechanical properties

The typical stress–strain curves of polymer-modified silica aerogels for each set of samples with different polymer contents are shown in Fig. 4. Table 2 summarizes the mechanical properties of the individual samples measured during the compression tests, as well as the average values of at least three samples for each set of samples.

As an example, the stress–strain curve obtained from the compression of 20TDI is presented in the inset of Fig. 4. The curve can be divided into three distinct regions. Region I shows a linear trend corresponding to the elastic behavior of the material. Region II shows that the stress became nearly constant, with only a slight increase. Region III shows that although the stress was constant, a few small surface cracks began to appear on the samples, which gradually led to small fragments as the strain increased (Fig. 4, B in inset). Final failure occurs at the end of the test (Fig. 4, C in inset), together with a sharp decrease in stress. The elastic modulus of sample $E$ can be calculated from the initial slope of the stress–strain curve in Region I, as described in the inset of Fig. 4. Point “a” corresponds to the elastic limit of the silica aerogels. Point “b” is the surface cracking point of samples at the end of Region II and at the start of Region III. Similarly, the point “c” corresponds to the final failure point of the samples. The strains and stress at point “b” and “c” are defined as $\varepsilon_a$, $\sigma_a$ and $\varepsilon_c$, $\sigma_c$, respectively.

Tables 1 and 2 show that the elastic modulus and compressive strength, $\sigma_a$ and $\sigma_c$, respectively, of the polymer-modified silica aerogels gradually decrease with increasing amounts of incorporated polymer, whereas the strains of $\varepsilon_a$ and $\varepsilon_c$ increase significantly. In addition, $\sigma_b$ and $\sigma_c$ appear identical.

4. Discussion

4.1. Shrinkage and density

The shrinkage in silica aerogels consists of two parts: the shrinkage in the aging process and the shrinkage in the drying process. The shrinkage during the aging process, which is caused by the condensation of Si–OH groups on the inner surface of the silica gels, was low (~2%). This should be identical for all samples because the same preparation conditions were followed for all the wet gels before modification. Therefore, the difference in shrinkage for polymer-modified silica aerogels is due to the different shrinkage during the drying process. When silica wet gels were dried under ambient pressure, they were subjected to very large capillary forces exerted by the meniscus of the pores liquid as liquid evaporated from the wet gels [1,2]. Fig. 5A and B shows that the unmodified wet gels did not withstand the capillary forces and shrunk significantly during drying because of their filigree structure and the low mechanical properties of the silica skeleton. Hence, the linear shrinkage of blank sample 0TDI in Table 1 was large.

The shrinkage of wet gels could be reduced if they are modified with the polymer. During the modification process for wet gels, TDI monomers in acetone diffused from the solution into the interior of the body of the gels, which was driven by the concentration difference between the interior of the body of the gels and the TDI solution surrounding them. As described in Fig. 5C and D, a conformal polymer coating was formed on the silica skeleton because of the reaction of TDI monomers with amine functional groups located on the surface of silica particles. On the one hand, the polarity of the inner surface was lowered by polymer coating; thus, the capillary forces exerted by the meniscus of the pore liquid during ambient drying were reduced. On the other hand, the silica skeleton of the silica gels was reinforced by polymer coating. Therefore, polymer-modified silica gels tended to shrink less than unmodified silica gels during ambient pressure drying. In addition, the shrinkage of polymer-modified silica aerogels

### Table 2
Mechanical properties of polymer-modified silica aerogels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E$ (MPa)</th>
<th>Average $E$ (MPa)</th>
<th>$\varepsilon_a$ (%)</th>
<th>Average $\varepsilon_a$ (%)</th>
<th>$\varepsilon_c$ (%)</th>
<th>Average $\varepsilon_c$ (%)</th>
<th>$\sigma_a$ (MPa)</th>
<th>Average $\sigma_a$ (MPa)</th>
<th>$\sigma_c$ (MPa)</th>
<th>Average $\sigma_c$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0TDI</td>
<td>50.27</td>
<td>52.71</td>
<td>5.79</td>
<td>5.48</td>
<td>5.79</td>
<td>6.36</td>
<td>1.24</td>
<td>1.20</td>
<td>1.24</td>
<td>1.20</td>
</tr>
<tr>
<td>51.67</td>
<td>56.20</td>
<td>40.89</td>
<td>4.82</td>
<td>4.98</td>
<td>7.36</td>
<td>7.85</td>
<td>0.61</td>
<td>0.67</td>
<td>0.61</td>
<td>0.67</td>
</tr>
<tr>
<td>37.10</td>
<td>30.82</td>
<td>25.84</td>
<td>4.72</td>
<td>4.68</td>
<td>7.35</td>
<td>6.85</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>21.66</td>
<td>15.95</td>
<td>19.53</td>
<td>3.57</td>
<td>3.25</td>
<td>12.35</td>
<td>15.00</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>16.10</td>
<td>15.37</td>
<td>14.57</td>
<td>2.26</td>
<td>2.36</td>
<td>45.93</td>
<td>45.93</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>12.15</td>
<td>26.33</td>
<td>56.33</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>
decreased more when more polymers were incorporated into the silica aerogels.

The variation of the density of polymer-modified silica aerogels depends on the shrinkage and the amount of incorporated polymers. In our experiments, the effect of polymer amount on density increase was offset by the reduction of the shrinkage, thus monotonically decreasing the density.

For normal silica aerogels, the correlation between the bulk density ($\rho_b$) of cylindrical silica aerogels and the linear shrinkage ($\tau$,%) during preparation follows the equation

$$\rho_b = \frac{4m}{\pi \phi^2 l} \left(1 - \tau \right)^3; \quad (1)$$

where $m$, $\phi$ and $l$ are the mass of silica skeleton, the diameter, and the length of a wet silica gel, respectively.

Eq. (1) shows a linear relationship between log[$\rho_b$] and log[1 − $\tau$], and the slope of the line is −3. Although Eq. (1) is only valid for normal silica aerogels, we plotted log[$\rho_b$] versus log[1 − $\tau$] for polymer-modified silica aerogels, as shown in Fig. 6A to determine the relationship between bulk density and linear shrinkage for polymer-modified aerogels. A linear relationship with a slope of −1.16 was clearly observed, obviously larger than the theoretical slope value of −3 in Eq. (1). The increased slope of the polymer-modified aerogels is believed to be contributed to the polymers incorporated into the silica aerogels. The polymers in the silica aerogels effectively reduced shrinkage during drying and contributed to the increase in bulk density. In general, the bulk density continued to decrease with increasing polymer content in the silica aerogels.

4.2. Mechanical properties

4.2.1. Elastic modulus

The decrease in elastic modulus with increasing amounts of incorporated polymer is caused by the decrease in density or shrinkage of the silica aerogels brought about by polymer modification.

Similar to the calculation of density as a function of shrinkage in Eq. (1), the elastic modulus of normal silica aerogels as a function of shrinkage can also be calculated. If we define the elastic modulus of the silica skeleton of a silica aerogel as $E_s$ and the porosity as $\alpha$, then the apparent elastic modulus of the silica aerogel $E_a$ is

$$E_a = E_s (1 - \alpha); \quad (2)$$

The porosity $\alpha$ of normal silica aerogels depends on the shrinkage during preparation, as described by Eq. (3):

$$(1 - \alpha) = (1 - \tau)^{-2}(1 - \alpha_0). \quad (3)$$

where $1 - \alpha_0$ is the fraction of the silica skeleton at the radial section of the silica gel.
One can easily deduce that the $E_a$ and the linear shrinkage comply with Eq. (4), specifically, $\log[E_a]$ is proportional to $\log[1 - \tau]$ with a slope of $-2$:

$$E_a = E_s(1 - \alpha_0)(1 - \tau)^{-2}. \quad (4)$$

For a normal silica aerogel, the apparent modulus is related to only the shrinkage because the elastic modulus of silica skeleton $E_s$ is believed to be constant regardless of the shrinkage. For polymer-modified silica aerogels, $E_s$ may change because of the polymer coating on the silica skeleton. For polymer-modified silica aerogels, the log[$E_a$] as a function of log[$1 - \tau$], plotted as shown in Fig. 6B, appears to be a perfect linear curve, although the slope is $-1.72$, which is close but not equal to the theoretical value of $-2$ in Eq. (4). If we assume that the function of the polymer incorporated into the silica aerogels is to reduce only the shrinkage during preparation, then the slope should be around $-2$ when we plot log[$E_a$] as a function of log[$1 - \tau$]. The increased slope suggests that the function of the polymer in aerogels was not only to reduce the shrinkage during preparation but also provide stiffening effects on the silica skeleton in silica aerogels.

4.2.2. Compressive strength

The decrease in the compressive strength of polymer-modified silica aerogels is caused by the decrease in shrinkage and density. Analogous to the calculation of elastic modulus as a function of shrinkage for normal silica aerogels, the compressive strength as a function of shrinkage can also be calculated. If the compressive strength of the silica skeleton of a normal silica aerogel is $\sigma_s$, the apparent compressive strength $\sigma_a$ of the normal silica aerogel is

$$\sigma_a = \sigma_s(1 - \alpha_0)(1 - \tau)^{-2}. \quad (5)$$

According to Eqs. (3) and (5), the relationship between $\sigma_s$ and $\tau$ is

According to Eqs. (3) and (5), the relationship between $\sigma_s$ and $\tau$ is

$$\sigma_a = \sigma_s(1 - \alpha_0)(1 - \tau)^{-2}. \quad (6)$$

Therefore, the plot of log[$\sigma_a$] versus log[$1 - \tau$] should be a straight line with a slope of $-2$. For polymer-modified silica aerogels, the log[$\sigma_a$] as a function of log[$1 - \tau$], plotted as shown in Fig. 6B, appears to be a perfect linear curve with a slope of $-2$, which is exactly equal to the theoretical value in Eq. (6). This demonstrates that the apparent compressive strength of polymer-modified silica aerogels is mainly influenced by shrinkage. The incorporated polymer in the modified silica aerogels does not contribute to the strength.

4.2.3. Strains

In previous studies [7,28–30], the fragility of normal silica aerogels subjected to SCF drying can be traced through interparticle necks. Because the silica skeleton is an aggregate of spherical particles, its mechanical properties are limited by the narrow necks of silica that interconnect the neighboring secondary silica particles. Fig. 7A–C shows that during the compression test, the bending of the silica skeleton at the axial section took place, and deformation increased gradually with increasing strain. The failure process sequentially includes skeleton deformation, bond-breaking between secondary particles, crack propagation, and final failure. Blank samples of OTDI unmodified with polymer showed inherent stress and strain in the skeleton framework before the compression test because the deformation of silica skeleton took place during the preparation. Hence, they were brittle and fragmented at low strain on compression, which resulted in small breaking strains. One should be noted that the failure breaking of the silica aerogels is mainly due to the disconnection of secondary particles. Therefore, the strength and the deformation ability of neck region is the dominant factor in the mechanical behavior of silica aerogels.
Once silica wet gels are modified with polymer, their shrinkage during drying can be reduced as previously discussed. Therefore, the inherent stress and strain were smaller in the silica framework. More importantly, as shown in Fig. 7D–F, the polymer coating on the silica skeleton reinforced the neck region between neighboring secondary particles, and the macropores did not link into macroscopic cracks. In summary, the polymer-modified silica aerogels were less brittle and more ductile than the blank sample OTDI. Thus, they can be deformed at high strains.

5. Conclusions

(1) Polymer-modified silica aerogels with significantly improved mechanical properties can be successfully prepared through ambient pressure drying. In this approach, the process of SCF drying can be eliminated.

(2) The successful preparation of polymer-modified silica aerogels depends on the control of shrinkage during drying. When incorporating polymers into the structure of silica aerogels, the shrinkage decreases with increasing amounts of incorporated polymers.

(3) With increasing amounts of incorporated polymers, the apparent elastic modulus and compressive strength of polymer-modified silica aerogels decrease because of the decreasing shrinkage and density. In contrast, the strains at the surface crack point and the final failure point significantly increase during compression.

(4) The elastic modulus of the silica aerogel skeleton increases because of the incorporated polymers. The polymers have no effects on the compressive strength of silica skeleton.

(5) The variations in the apparent elastic modulus and compressive strength of polymer-modified silica aerogels are closely related to the shrinkage during preparation, and this relationship can be quantitatively expressed. \( \log[E_a] \) and \( \log[\varepsilon_a] \) are linearly proportional to \( \log[1 - \tau] \) with slopes of \(-1.72\) and \(-2\), respectively.

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