PROCESS FOR PREPARING EPoxy-REINFORCED SILICA AEROgELS

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C08G 77/38; C08G 77/388; C08G 2101/0091

See application file for complete search history.

ABSTRACT

One-pot reaction process for preparing epoxy-reinforced monolithic silica aerogels comprising the reaction of at least one silicon compound selected from the group consisting of alkoxyxilanes, orthosilicates and combination thereof in any ratio with effective amounts of an epoxy monomer and an aminooalkoxy silane to obtain an epoxy monomer-silica sol in solution, subsequently preparing an epoxy-monomer silica gel from said silica sol solution followed by initiating polymerization of the epoxy monomer to obtain the epoxy-reinforced monolithic silica aerogel.

12 Claims, 12 Drawing Sheets
FIG. 1a

(a) APTES = 15 mol %

APTES = 45 mol %

Density, g/cm³

BTMSH, mol %

Total Si, mol/l
FIG. 1b
FIG. 2
FIG. 3

Porosity, %

Total Si, mol/l

BTMSH, mol %

- APTES = 15 mol %
- APTES = 30 mol %
- APTES = 45 mol %
FIG. 4

(a) 0.248 g/cm³, 85% porous, 322 m²/g (2)

(b) 0.278 g/cm³, 82% porous, 323 m²/g (4)

(c) 0.670 g/cm³, 53% porous, 97 m²/g (14)

(d) 0.847 g/cm³, 36% porous, 36 m²/g (16)
15 mol % APTES, no BTMSH
15 mol % APTES, 40 mol % BTMSH
45 mol % APTES, no BTMSH
45 mol % APTES, 40 mol % BTMSH

(a)

FIG. 5a
FIG. 5b

Surface area, m$^3$/g

- APTES = 15 mol %
- APTES = 30 mol %
- APTES = 45 mol %

BTMSh, mol %

Total Si, mol/l
FIG. 6a
FIG. 6b

Modulus, MPa

BTMSH, mol %

Total Si, mol/l

APTES = 45 mol %
FIG. 7a

(a)

Stain

0.00 0.05 0.10 0.15 0.20 0.25

0.00 0.05 0.10 0.15 0.20 0.25

Stress, MPa

- 0 mol % BTMSH
- 40 mol % BTMSH
FIG. 7b

- APTES = 15 mol %
- APTES = 45 mol %
**FIG. 8**

**FIG. 9**
process for preparing epoxy-reinforced silica aerogels

CROSS REFERENCE
This application is a continuation-in-part of co-pending application Ser. No. 11/582,693 filed Oct. 19, 2006, now U.S. Pat. No. 8,067,478.

ORIGIN OF INVENTION
The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefore.

FIELD OF THE INVENTION
This invention relates to a one-pot reaction process for preparing epoxy-reinforced monolithic silica aerogels and more specifically to a process for preparing epoxy-reinforced monolithic silica aerogels derived from the reaction of at least one silicon compound selected from the group consisting of alkoxysilanes, orthosilicates and a combination thereof with effective amounts of an aminoalkoxy silane and an epoxy monomer to obtain an epoxy monomer-silica sol in solution. Subsequently, forming an epoxy-monomer silica gel from said silica sol solution follow by subjecting said silica gel to conditions that promotes polymerization of the epoxy monomer followed by drying said polymerized epoxy-silica gel to obtain the epoxy-reinforced monolithic silica aerogel.

This process introduces the epoxy monomer into the silica sol solution before gelation either as an agent which reacts with the oxide gel or as a soluble epoxy precursor which does not interact with oxide gel in any way or both. Subsequent exposure of the epoxy-monomer silica gel to heat, light, catalyst or any other method of promoting polymerization of the monomer causes epoxy cross-linking without the need for any additional infiltration steps thereby significantly shortening the process steps. Another advantage is that the resulting silica aerogel monolith is more uniform, since the addition of the epoxy crosslinker is not limited by diffusion. Moreover, where complete polymerization requires a balanced stoichiometry, this requirement is more easily met by this one-pot process. The primary requirement of the one-pot reaction process is that the epoxy cross-linking agent does not interfere with gelation of the silica. This means that the epoxy monomer molecules are present in the sol, but are substantially inert until conditions are met for polymerization or they partially react with the forming gel at low enough concentration to allow gelation to take place.

The important and unique feature of this invention is that instead of a process wherein the epoxy monomer is infiltrated into an already formed silica gel by soaking this invention introduces the epoxy monomer into the silica sol before gelation either as an agent which co-reacts with the oxide gel or as a soluble epoxy monomer which does not interact with the forming oxide gel in any way. This process eliminates multiple washing and soaking steps thereby significantly shortening the process. Essentially, the production of an epoxy cross-linked silica aerogel is produced in a one-pot synthesis. In addition, the resulting silica aerogel monolith of this invention is more uniform, since the addition of the epoxy crosslinker is not limited by diffusion. Moreover, where complete polymerization requires a balanced stoichiometry, this requirement is met more easily because diffusion is not a factor.

SUMMARY OF THE INVENTION
This invention is directed to a one-pot process of cross-linking silica aerogels with an epoxy as an effective method to increase the strength of the aerogels without adversely affecting their porosity and density. More specifically, the one-pot process of this invention introduces the epoxy monomer into the silica sol before gelation of the silica sol. Subsequent exposure of the epoxy-monomer silica gel to heat, light, catalyst or other method of promoting polymerization of the epoxy prepolymer causes epoxy cross-linking without the need for additional processing steps.

Accordingly, it is an object of this invention to provide a one-pot process for preparing epoxy-reinforced cross-linked monolithic silica aerogels.

It is another object of this invention to provide a one-pot reaction process for preparing an epoxy reinforced monolithic silica aerogel derived from epoxy monomers.

It is a further object of this invention to provide a process for preparing epoxy-reinforced monolithic silica aerogels by reacting in one-pot at least one alkoxy silane and/or orthosilicates with an epoxy monomer and an aminosilanol silane.

DESCRIPTION OF THE DRAWINGS
FIG. 1. Graphs of empirical models of data from Table 1 for (a) density and (b) shrinkage vs total silicon concentration and mol fraction BTMSH.
This invention relates to a process for preparing epoxy-reinforced cross-linked silica aerogels which comprises a one-pot reaction of at least one alkoxy silane and/or an ortho-silicate in the presence of effective amounts of an epoxy monomer and an aminoalkoxy silane in an alcohol solution, to obtain a silica sol. This silica sol in solution is then gelled and subsequently subjected to polymerization by the use of heat, UV light, catalyst or any other method that promotes polymerization causing the epoxy prepolymer to polymerize and crosslink with the nanostructured framework of the silica gel. The silica gel reaction product is supercritically dried in a closed reactor to remove all solvent and the method used to control gelation. APTES provides the amines on the silica gel surface for reaction with the epoxy monomer, whereas the hexyl links from BTMSH have been shown to improve flexibility of the underlying silica backbone, resulting in less brittle failure. Some of the preferred compounds used in the one-pot process included: Tetraethyldiamine (TMEDA), 1,1,1,3,3-pentamethyldiethoxysilane (PMDMS), 3-aminopropyltriethoxysilane (APTES) and Bisphenol-A propoxylate diglycidyl ether (BPGE).

TEOS derived gels were made using a modified two-step process involving acid hydrolysis of TEOS, followed by base catalyzed condensation with APTES and BTMSH. To illustrate, a typical procedure is outlined for a formulation with total Si concentration of 1.6 mol/L of the total sol, APTES Si fraction of 15 mol % and epoxy monomer, BPGE, in a 0.5 to 1 ratio to APTES (run 2 in Table 1). To a solution of 30.3 ml of TEOS (0.136 mol) in 16.3 ml of ethanol was added a solution of 14.4 ml of water (0.8 mols), based on a 5 to 1 ratio of TEOS and water.
of water to total Si) and 0.005 ml concentrated nitric acid in 14.4 ml ethanol with stirring. The combined solution was stirred for 1 h. In the meantime, another solution was prepared consisting of 5.6 ml APTES (0.024 mol) and epoxy monomer, BPGE, (5.48 g. 0.012 mol) in 14.4 ml ethanol. These two solutions were cooled in a dry ice-acetone bath before combining and shaking vigorously. The resulting 100 ml of solution was then poured into five cylindrical molds, nominally 20 mm in diameter, which were made by cutting the needle end of Norm-ject syringes and extending the plunger nearly all the way out. The gels, which formed in 5 to 15 min, were aged for 24 h before being extracted into clean ethanol by being pushed out of the molds with the plunger. The samples were heated to 24 h in a 70° C. oven to react the epoxy monomer with amine. After cooling and four solvent exchanges, the gels were dried by supercritical CO₂ fluid extraction followed by vacuum drying, yielding monoliths with average density of 0.365 g/cm³.

A cylindrical specimen from each run was sectioned in half with a scroll saw. The top and bottom of each specimen was sanded and checked using an L-square to make certain that these surfaces were smooth and parallel. The samples were tested between a pair of compression platens on a Model 4505 Instron load frame using the Series IX data acquisition software.

The platen surfaces were coated with a graphite lubricant to reduce the surface friction and barreling of the specimen. The specimens were tested in accordance with ASTM D695 with the exception of sample size. Although the ASTM standard calls for slenderness ratio of 11–16 to 1, typified by men. The specimens were covered with amine. Any further increase in APTES concentration results in amines inaccessible to the monomer diffusing into the gel because they are buried inside the secondary particles. Using a one-pot reaction scheme with the monomer already present in the gel as it is formed, all of the amines are accessible to monomer. As seen in the plot of the empirical model for shrinkage (standard error=1.6%, R²=0.94) shown in FIG. 1b, aerogels made using the one-pot method described herein using 15 mol % APTES tended to shrink less than monoliths made using 45 mol % APTES. However, this difference in shrinkage (10-15%) is not enough to account for the dramatic increase in density.

As expected, density also increases with increasing total silicon and mol fraction of BTMSH concentration as seen in FIG. 1a, because of greater amounts of silica and hexyl links in the resulting aerogels. Increasing the ratio of epoxy to APTES has only a small effect on density though using 0.5 equiv. of epoxy/APTES tended to result in more shrinkage of the monoliths. Thus, changes in properties which depend on density using lower equiv. of epoxy per APTES are more a result of shrinkage than an increase in polymer cross-linking. For this reason, all properties discussed and all graphs are shown with ratio of 0.7 epoxy molecules to APTES.

### TABLE 1

<table>
<thead>
<tr>
<th>Run</th>
<th>APTES (Si)</th>
<th>BTMSH (Si)</th>
<th>BPGE to APTES</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Shrinkage (%)</th>
<th>Modulus (MPa)</th>
<th>Recovered strain (%)</th>
<th>Surface area (m²/g)</th>
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Summary of Data for Epoxy Cross-Linked Aerogels from Optimization Study

Preparation conditions and resulting properties of monoliths made in the study are shown in Table 1. Variables used in the study include the total concentration of silicon used to prepare the gels, mol fraction of the total silicon derived from APTES and BTMSH (noting that BTMSH contributes two silicon atoms for every molecule, and the rest of the silicon is derived from TEOS), and the amount of epoxy (BPGE) in the sol given as a mole ratio to APTES. It is assumed that one epoxy molecule will react with two APTES amines. Hence, a BPGE to APTES ratio of 0.5 is stoichiometric, whereas a ratio 0.6-0.7 represents an excess of epoxy. By including the epoxy monomers in the initial sol, the synthesis is not only shortened but, because of the fact that cross-linking is not dependent of diffusion, polymer reinforcement is more efficient and more uniform. This is evidenced by the bulk densities of the monoliths made in the study, which ranged from 0.2 to up to 0.885 g/cm³. Shown in FIG. 1a is a graph of the empirical model for density (standard error=0.019 g/cm³, R²=0.994) derived from the measured monoliths. As seen in this graph, densities are much higher for aerogels made with higher concentrations of APTES. For aerogels made using 15 mol % APTES, densities are comparable to those previously made using a multistep synthesis, while the monoliths derived from 45 mol % APTES are 2-3 times more dense than previously reported. In fact, in earlier studies of aerogels made using APTES as an amine cross-linking site, increasing APTES was seen to increase density much less than expected. Preferred or to level off after a certain concentration, presumably because of surface saturation effects. That is after a certain concentration of APTES, the surface of the secondary particles is completely covered with amine. Any further increase in APTES concentration results in amines inaccessible to the monomer diffusing into the gel because they are buried inside the secondary particles. Using a one-pot reaction scheme with the monomer already present in the gel as it is formed, all of the amines are accessible to monomer. As seen in the plot of the empirical model for shrinkage (standard error=1.6%, R²=0.94) shown in FIG. 1b, aerogels made using the one-pot method described herein using 15 mol % APTES tended to shrink less than monoliths made using 45 mol % APTES. However, this difference in shrinkage (10-15%) is not enough to account for the dramatic increase in density.
Solid CCP-MAS NMR spectra of aerogels from the study are shown in FIG. 2a–d. In all spectra, peaks in the aromatic region and the peak at 70 ppm are due to epoxy links. Peaks at 9–20 ppm are due to the propyl groups from APTES (and the hexyl links from BTMSH if present). The peak at approximately 30 ppm arises from the methyls on the isopropylidene group of the epoxy (and the middle methylenes from BTMSH, if present). Peaks at 40 and 50–60 ppm are due to the carbons next to nitrogen from the propyl group of APTES and the reacted epoxy links, respectively. As shown in FIGS. 2a–d, the peaks due to epoxy and the 40 ppm peak due to methylene group of the epoxy (and the middle methylenes from APTES again grow larger, but remain about the same size relative to each other.

A response surface plot of porosity (standard error = 1.6%, R² = 0.99), calculated from the bulk density and skeletal density measured by helium pycnometry, graphed vs total silicon concentration and BTMSH fraction is shown in FIG. 3. Note that porosity decreases slightly because of increasing total silicon and BTMSH mol fraction, and dramatically decreases because of an increase in APTES concentration. Because porosity is a feature of aerogels important to their application, maintaining high levels of porosity is critical. Only monoliths made using APTES concentration of 15 mol % have porosities in excess of 80%. Except at the lowest total Si concentration studied (1 mol/L), higher concentrations of APTES in a one-pot reaction scheme result in porosities too low for use in typical aerogel applications.

Scanning electron micrographs of representative monoliths made using 1.6 mol/L total silicon concentration are shown in FIG. 4. Monoliths shown in FIGS. 4a (no BTMSH) and 4b (40 mol % BTMSH) made using 15 mol % APTES are similar in appearance to those previously reported using a multistep diffusion process. Note that the particle sizes are quite uniform in appearance in both micrographs, whereas the pores appear larger in FIG. 4b, as previously observed for hexyl-linked monoliths. The monoliths are somewhat similar in density and porosity to those previously prepared using the multistep process. In contrast, monoliths shown in FIGS. 4c (no BTMSH) and 4d (40 mol % BTMSH) made with 45 mol % APTES are twice as dense and 20–30% less porous than the same formulations made using a multistep process, again because of the near-complete reaction between APTES amines and epoxy obtained when diffusion is not a factor.

Mean pore diameter and surface area measurements were derived from nitrogen sorption data for all the samples using the Brunauer-Emmett-Teller (BET) method. Surface areas are listed in Table 1 and under micrographs shown in FIG. 4. The pore size measured by nitrogen sorption is known to be underestimated for aerogels because of contraction of the structure. Nevertheless, observed trends are consistent with that seen by SEM. Graphs of pore volume vs pore diameter in FIG. 5a illustrate a comparison of the same monoliths shown in the micrographs in FIG. 4 which were made using 1.6 mol/L total silicon concentration. Note that the narrowest pore size distribution and smallest pores are obtained for monoliths made using 15 mol % APTES and no BTMSH. Increasing APTES and BTMSH broadens the pore distributions and also causes a shift to larger pore sizes as seen previously with monoliths made using a multistep process. Similar results are seen with lower total silicon concentrations. BET surface areas are also much reduced by increasing APTES concentration as seen in FIG. 5b. FIG. 5b shows empirical models for surface area (standard error = 0.01 R² = 0.99) vs total silicon concentration and BTMSH fraction. As can be seen in the plot, only 15 mol % APTES derived monoliths have surface areas higher than 300 m²/g. Decreasing total silicon concentration and increasing BTMSH fraction also causes a small though significant decrease in surface area. In addition, as shown before with density and porosity, surface areas obtained for monoliths in this study prepared using 15 mol % APTES are comparable to the same formulations obtained from the multistep diffusion process whereas for those prepared with 45 mol % APTES the surface areas are reduced by a factor of 2.

The monoliths were also characterized using compression testing. Young’s modulus taken from the initial slope of the stress-strain curves was modeled using multiple linear regression analysis. Graphs of the empirical model for modulus (standard error = 0.2, R² = 0.98) vs total silicon concentration and BTMSH fraction are shown in FIG. 6 for aerogels made using (a) 15 mol % APTES and (b) 45 mol % APTES. Increasing total silicon concentration and BTMSH fraction both significantly increase modulus as expected due to small increases in density. It is interesting to note that modulus of monoliths prepared using the multistep diffusion method in the previous study did not increase with increasing BTMSH mol fraction. This was due to the fact that in the previous study, use of BTMSH was seen to reduce shrinkage, especially for lower APTES formulations, resulting in lower densities. Using a one-pot reaction scheme, shrinkage is more dependent on the amount of APTES and the ratio of epoxy to APTES used. In the graphs shown in FIG. 6, APTES mol fraction and epoxy to APTES mol fraction and epoxy to

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>continued</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Total Si (mol/L)</th>
<th>APTES Si (mol %)</th>
<th>BTMSH Si (mol %)</th>
<th>BPGE to APTES</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Shrinkage (%)</th>
<th>Modulus (MPa)</th>
<th>Recovered strain (%)</th>
<th>Surface area (m²/g)</th>
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</table>

Note: a = not measured.
APTES ratios are held constant, making shrinkage a nonfactor in these plots. As seen in FIG. 6b, monoliths made from 45 mol % APTES are an order of magnitude stronger because of the dramatic increase in density. However, as previously discussed, except for monoliths made using the lowest total Si concentration, these monoliths have extremely low porosity and surface area, reducing their utility as insulators or other applications usually considered for aerogels.

Elastic recovery after compression was also assessed by compressing samples to 25% strain, followed by allowing them to relax. Typical stress strain curves for repeat compression tests are shown in FIG. 7a for monoliths from Table 1 made using 1.6 mol/L total silicon and 15% APTES. The solid black curves are the first and second compression for run 3 (no BTMHS) and the dashed red curves are for run 12 (40 mol % BTMHS). Interestingly, most of the samples made from the one-pot reaction scheme recover better than those made with the multistep diffusion process previously reported. In the examples shown, the sample containing no hexyl links recovered all but 2.2% of the 25% compared to 5% for the multistep sample reported previously. Clearly, epoxy is contributing more to elastic recovery when included in the initial sol in the one pot reaction scheme. This may be due to the presence of epoxy inside of the secondary particles, whereas these smallest pores may not be accessible to epoxy in the diffusion controlled process. The sample with hexyl links recovered all but 1.3% of the 25%, which was similar to the multistep sample previously reported (all but 1% unrecovered strain).

Note, however, that modulus is slightly higher for the hexyl linked samples made using the one-pot reaction, again because of the slight increase in density. Streamlining the process of making epoxy reinforced aerogels by eliminating the diffusion step produces aerogels of similar density and pore structure to those previously reported with a one-pot reaction scheme. However, by comparing aerogels fabricated from higher APTES concentrations made using both methods, we also present evidence for the first time that monoliths made using 15 mol % APTES as amine cross-linking site. Aerogels made using a one-pot reaction scheme and high concentrations of APTES are extremely high in density with low percent porosities and extremely low surface areas compared to multistep aerogels. This is due to the complete reaction of epoxy with all amines present when diffusion into the gel is not a factor. In fact, using the one-pot method, only monoliths made using 15 mol % APTES can truly be considered aerogels and suitable for use as insulation or other applications requiring high surface areas, high porosity, and small pore sizes.

Slight improvements to mechanical properties over aerogels made using a multistep diffusion process are also evidenced. In particular, hexyl-linked aerogels made using 1.6 mol/L and 15 mol % APTES are similar in elastic recovery, density, and surface area to those previously reported using a multistep process, whereas the modulus is increased by a factor of 2. Most importantly, the method of making the aerogels is greatly simplified by eliminating two wash steps before cross-linking and the epoxy diffusion step. This reduces the amount of solvent needed to make the aerogels by at least half with no compromise in properties. While this invention has been described with preferred embodiments, it should be understood that various modifications and variations will be apparent to one skilled in the art and that such modifications and variations come within the scope of the appended claims.

The invention claimed is:

1. A one-pot process for preparing a polymer-reinforced monolithic silica aerogel which comprises:
   - providing a one-pot process for preparing a polymer-reinforced monolithic silica aerogel capable of reacting at least one silicon compound selected from the group consisting of an orthosilicate, an alkoxysilane and a combination thereof with effective amounts of multifunctional cross-linking agent and an aminoalkoxy silane in an alcohol solution, wherein the multifunctional cross-linking agent does not react with alcohol but is soluble in alcohol,
   - wherein the molar ratio of cross-linking agent to the aminoalkoxy silane is stoichiometric to obtain a silica sol in solution also containing the cross-linking agent;
   - subsequently forming a silica gel which contains said cross-linking agent in the solution phase of the gel;
   - subjecting said gel to conditions that promote reaction of said cross-linking agent to silica gel;
   - drying said polymer reinforced silica gel to obtain the polymer-reinforced monolithic silica aerogel.

2. The process of claim 1 wherein the silicon compound is an orthosilicate.

3. The process of claim 1 wherein the silicon compound is an alkoxysilane.

4. The process of claim 1 wherein the silicon compound is a combination of the orthosilicate and an alkoxysilane.

5. The process of claim 2 wherein the orthosilicate is tetraalkyl orthosilicate.

6. The process of claim 1 wherein the aminoalkoxy silane is 3-aminopropyl-triethoxysilane.

7. The process of claim 1 wherein the sol solution contains alcohol.

8. The process of claim 1 wherein promoting the reaction of the cross-linking agent to silica gel is initiated by conditions selected from the group consisting of heat, U.V. light, catalyst, and combinations thereof.

9. The process of claim 1 wherein the temperatures of the one-pot reaction range from about 70° to about 200° C. 

10. The process of claim 1 wherein the one-pot reaction consist essentially of an orthosilicate and an alkoxysilane in the presence of the cross-linking agent to obtain the silica sol reaction product in solution which is subsequently gelled, polymerized and supercritically dried.

11. The polymer-reinforced monolithic silica aerogel obtained by the process of claim 1.

12. The polymer-reinforced monolithic silica aerogel obtained by the process of claim 4.