

Nanoengineering Strong Silica Aerogels

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ABSTRACT

In the quest for strong lightweight materials, silica aerogels would be very attractive, if they were not fragile. The strength of silica aerogel monoliths has been improved by a factor of over 100 through cross-linking the nanoparticle building blocks of preformed silica hydrogels with poly(hexamethylene diisocyanate). Composite monoliths are much less hygroscopic than native silica, and they do not collapse when in contact with liquids.

Silica aerogels are chemically inert, highly porous ceramic materials.^{1–3} They are the product of a sol–gel process, whose final stage involves extracting the pore-filling solvent with liquid CO₂. The latter is gasified supercritically and is vented off, leaving behind a very low density solid (0.002–0.8 g cm⁻³), with the same volume as the original hydrogel and a chemical composition identical to glass. Aerogels have been considered for thermal insulation,⁴ catalyst supports,⁵ or as hosts for a variety of functional materials for chemical, electronic, and optical applications.⁶ Practical application has been slow though, because aerogels are brittle and hygroscopic,⁷ absorbing moisture from the environment which leads to structural collapse due to the capillary forces developing in the pores.³

The poor mechanical properties of silica aerogels notwithstanding, many plastics are reinforced with glass. For example, several thermoplastics for injection molding are supplied preformulated in glass-fiber-containing pellets, and long glass-fiber-reinforced polyurethane rods are considered as a lightweight, noncorroding alternative to steel in architectural construction.⁸ Glass fiber does not improve the strength of silica aerogels,⁹ but because glass/polyurethane composites are strong enough to substitute for steel, we decided to focus on the interface between those two materials, reasoning that if a similar synergism could be engineered into the structure of monolithic silica aerogels, it would result in strong, very low density materials.

Base-catalyzed silica aerogels consist of large voids (mesopores, ~50 nm in diameter) in a “pearl-necklace” network of microporous, so-called *secondary* particles,^{10a} which are the smallest entities visible in Figure 1A (5–10 nm in diameter). Those particles are connected by “necks” formed by dissolution and reprecipitation of silica during aging.^{10b,11} Reasonably, the strength of monolithic aerogels

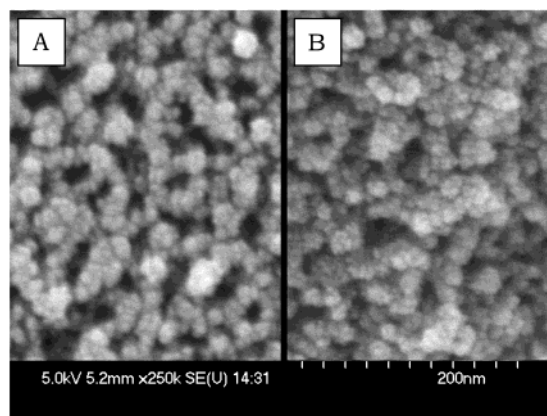


Figure 1. SEM images from randomly selected spots in the interior of fractured monoliths of a native silica aerogel with $\rho_b = 0.169$ g cm⁻³ (A) and a di-ISO cross-linked silica aerogel composite with $\rho_b = 0.380$ g cm⁻³ (B).

could be improved by making the necks wider. To accomplish this with minimum addition of new material, the contour surface of silica has to be used as a template for the deposition and growth of the interparticle cross-linker. Silica is surface-terminated with silanols (–SiOH). Polyurethane, (–CONH–R–NHCOOR’O–)_n, is formed by the reaction of a diisocyanate (OCN–R–NCO) and a diol (HO–R’–OH).^{12a} A similar reaction of an isocyanate with glass-surface silanols (–Si–OH) modifies glass fibers,¹³ chromatographic silica absorbents,¹⁴ and sol–gel derived particles.¹⁵

In a typical procedure, a diisocyanate cross-linker is introduced in the aerogel structure as follows. Hydrogels (1 cm diameter, 3–4 cm long) are prepared from tetramethoxysilane via a base-catalyzed route^{16,17} and are aged for 2 days at room temperature. Subsequently, according to a post-gelation doping protocol,^{17,18} pores are filled with a diisocyanate (di-ISO) solution by washing successively with methanol, propylene carbonate (PC), and PC/di-ISO (4 × 8

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Table 1: Properties of Silica/Di-ISO Aerogel Monoliths

% di-ISO w/w in the bath	diameter ^b (cm)	ρ_b^b (g cm ⁻³)	BET area (m ² g ⁻¹) (Av. pore diam, nm)	hydrophilicity ^d	load at rupture ^e (kg)	diametral deflection at rupture ^f (cm)	modulus of elasticity (E) ^g (MPa)
0.0	0.999 ± 0.002	0.169 ± 0.004	997 (13.4) ^c	66 ± 16	0.12 (<i>h</i>)	<i>h</i>	<i>h</i>
4.0	0.999 ± 0.002	0.241 ± 0.003	324 (<i>i</i>)	16 ± 2	1.75 (<i>j</i>)	0.061	5.3 (<i>j</i>)
8.0	0.986 ± 0.010	0.297 ± 0.007	308 (18.1)	8 ± 2	3.95 (4.38)	0.101	12.5 (10.5)
16	0.954 ± 0.011	0.388 ± 0.006	309 (22.3)	4 ± 1	9.65 (9.73)	0.140	<i>i</i> (20.4)
25	0.936 ± 0.007	0.390 ± 0.013	245 (21.9)	4 ± 1	10.4 (9.87)	0.129	31.3 (26.1)
34	0.908 ± 0.013	0.440 ± 0.009	215 (23.2)	5 ± 2	8.70 (9.87)	0.110	<i>i</i> (40.1)
42	0.907 ± 0.006	0.447 ± 0.020	165 (16.6)	5 ± 1	14.7 (15.6)	0.199	47.5 (46.3)
51	0.897 ± 0.014	0.439 ± 0.016	178 (29.8)	4 ± 2	12.0 (11.8)	0.109	<i>i</i> (53.8)

^a Native silica. ^b Average of four samples. ^c Average of two samples with respective spreads ± 3 m² g⁻¹ and ± 1 nm. ^d Percent weight gain after three days in a water vapor saturated chamber at room temperature. Average of two samples. ^e Results from two three-point flexural bending test experiments using: (a) a homemade apparatus (1.738 cm span, see Figure 3 inset)²³ or, (in parentheses) (b) an automated Instron Instrument Model 4469 (2.286 cm span). The two series of samples for the two tests were prepared by two experimentalists at different times. Tests with the homemade apparatus were carried out with four different series of variable-density monoliths, and all loads at rupture at each density were within 5% of their average. Diametral deflection vs load, however, was recorded (see footnote f) for only a single series of samples (the one reported). The Instron test was also carried out with a single series of variable-density monoliths (the one reported). ^f Determined by analyzing close-up images obtained from a fixed distance with a Nikon CoolPix 5000 digital camera set in the macro mode and 2 \times electronic magnification. Actual deflections were calculated by multiplying deflections measured on 8.5 in. \times 11 in. prints by the experimentally determined aspect ratio (0.136). ^g Calculated (see text) either from the slopes of the linear part of the curves in Figure 3, or from the slopes given by the Instron output. ^h Beyond the capabilities of either apparatus. ⁱ Not determined.

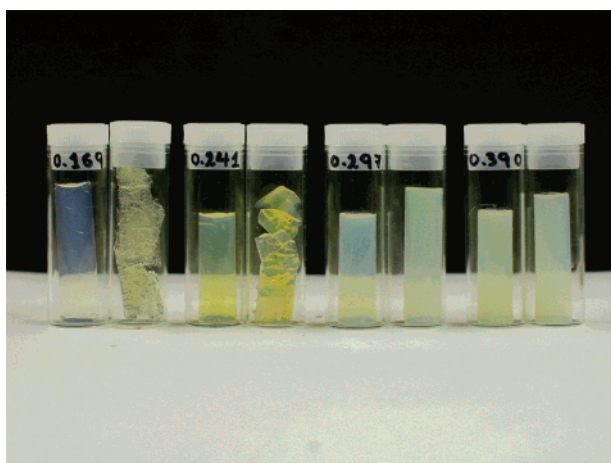


Figure 2. Photographs of four pairs of aerogel monoliths (diameter: 0.9–1.0 cm; length: 3–4 cm; densities in g cm⁻³ are reported directly on the vials). The left-most sample ($\rho_b = 0.169$ g cm⁻³) is native silica. The right vial of each pair contains a similar-density aerogel that has been submerged in liquid N₂ in a drybox.

h in each bath). The di-ISO employed was poly(hexamethylene diisocyanate) (Aldrich).¹⁹ The vials containing the gels in the last bath are heated at 100 °C for 3 days, then are cooled to room temperature. The solution is decanted, and the gels are washed with PC (1 \times 8 h), PC/acetone (1:1, 1:3, v/v; 1 \times 8 h each), and acetone (4 \times 8 h) and are dried supercritically.

di-ISO modified aerogels are translucent (Figure 2), with properties (Table 1) that depend on their density, which in turn depends on the concentration of di-ISO in the PC/di-ISO bath. Relative to native silica, composite aerogels shrink by up to 10–12% and they become up to ~ 3 times more dense as the di-ISO concentration in the bath increases. Both size and density level off for bathing solutions more concentrated than $\sim 40\%$ w/w, but even the most dense monoliths fall in the density range of aerogels. Shrinking is probably associated with cross-linking. IR analysis shows that as the density increases, the urethane C=O stretch (at

~ 1690 cm⁻¹) becomes comparable to, and eventually even stronger than, the Si–O stretch at 1078 cm⁻¹. Note also that while the urethane C=O stretch is present in di-ISO,¹⁹ the dominant stretch at ~ 2272 cm⁻¹ comes from the isocyanate (N=C=O).²⁰ In all composites, however, the latter absorption is consistently extremely weak or absent. Therefore, we conclude that both ends of practically all di-ISO have reacted. A typical SEM image of one of our most dense composites (Figure 1B) shows that (a) a new material has been introduced conformally to the secondary particles, as not only the necklace-like structure but also individual particles remain clearly visible; and (b) the mesoporosity has been somewhat reduced, as several secondary particles appear fused (clustered) together, forming the larger domains that promote light scattering and haziness.⁷ These observations are all consistent with reaction and binding of di-ISO to the surface of silica. Considering the total surface area of native silica (~ 1000 m² g⁻¹, Table 1) and the density change between native silica and the most dense composite ($\rho_b = 0.447$ g cm⁻³), it is calculated that the amount of di-ISO corresponds to 4.7 monolayers. Hence, terminal NCOs must undergo not only condensation with surface-silanols but also trimerization to isocyanurate (hexahydro-1,3,5-triazine-2,4,6-trione),²¹ causing extensive cross-linking. It should be emphasized further that the estimated 4.7 monolayer coverage is actually a lower limit, because the first monolayer blocks the channels and cuts off access to the micropores of the secondary particles. This is concluded from the fact that the Brunauer–Emmett–Teller (BET) surface area decreases, and the average pore diameter jumps from ~ 13 to ~ 20 nm as the monolith density increases (Table 1).

Composite monoliths are less hygroscopic and more robust than pure silica (Table 1). Native silica aerogels submerged in liquid N₂ (in a glovebox) absorb ~ 6.5 times their weight in liquified gas (which they subsequently lose over a period of ~ 10 min). At the same time, however, those monoliths undergo extensive cracking, losing their structural integrity

completely (Figure 2). Cracking was also observed consistently with all samples of the lighter composite ($\rho_b = 0.241 \text{ g cm}^{-3}$), but the mode of fracture was different from that of native silica, yielding few large pieces with structural integrity rather than the loose foamy material obtained from the disintegration of the latter. Composites with $\rho_b > 0.3 \text{ g cm}^{-3}$ uptake < 1.7 times their weight in liquid N_2 , but no structural change was observed, even after repetitive dip-freeze/thaw cycling. The structural collapse of pure silica aerogels in contact with liquids is a known phenomenon and is due to the capillary tension at the liquid–gas interface in the pores.³ An upper bound for the volume relaxation energy, VRE (in J cm^{-3}), upon collapse is calculated from the work done per unit volume by the capillary tension via the relationship

$$\text{VRE} = \gamma_{\text{LV}} \cos(\theta) [A\rho_b/(1 - \rho)]$$

by assuming that the contact angle $\theta = 0^\circ$ and that the pore liquid is water (whose surface tension $-\gamma_{\text{LV}} = 0.072 \text{ J m}^{-2}$ is higher than that of many other liquids), A is the specific (BET) surface area of the aerogel, and the relative density $\rho \approx 0.3$.^{10c} Thus, it is calculated that upon collapse our native aerogel monoliths are stabilized by $\leq 17 \text{ J cm}^{-3}$. Meanwhile, considering the mass-gain over silica of our most dense composite (0.447 g cm^{-3}) and the heats of formation of dicarbamate and isocyanurate, it is calculated that the composite is more stable than native silica by $\sim 55 \text{ J cm}^{-3}$.²² Therefore, there should be no particular tendency for collapse upon wetting, because the energy that would be expended to destroy cross-linking is more than the energy that would be gained by the subsequent structural collapse. Even in water, denser composites have been stable for at least two months.

However, the most dramatic improvement yet is in the strength of the new material (Table 1), as tested with a three-point flexural bending method. It takes more than 100 times higher load to break a monolith with density 0.447 g cm^{-3} ($\sim 15 \text{ kg}$) than to break a native silica aerogel monolith ($\sim 120 \text{ g}$). Figure 3 shows the load–strain curves of four representative composite monoliths on the way to their respective rupture points. The least dense sample is linearly elastic, while the more dense samples behave as nonlinear elastic.²⁴ The modulus of elasticity, E , (a measure of stiffness) is calculated from the slope (S) of the linear part of the load–deformation curves using

$$E = SL^3/12\pi r^4$$

where L is the span and r the radius of the aerogel.²⁵ Measuring the deformation of native silica was not possible; however, accepting that for a native silica aerogel with $\rho_b = 0.2 \text{ g cm}^{-3}$ and the value of E is $\leq 1.0 \text{ MPa}$,⁷ the trend in the modulus of the cross-linked monoliths is the same as the trend in the rupture load. Namely, more dense monoliths are not only stronger but also more difficult to bend (stiffer). This is consistent with wider interparticle necks as the amount of accumulated di-ISO increases.²⁶ Eventually, even

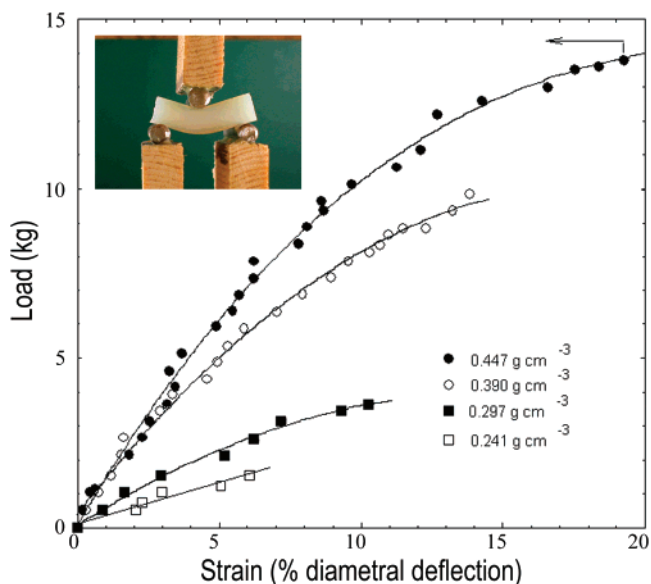


Figure 3. Load–strain curves for the four composites of Figure 2. The arrow correlates the particular data point with the image in the inset (bending under 14.4 kg load of the monolith with $\rho_b = 0.447 \text{ g cm}^{-3}$; span = 1.738 cm).

the stiffer composites bend, accommodating up to 20% diametral deflections before rupture (see Figure 3 inset). The more work (i.e., the area underneath the load/deformation curve) required by denser composites to break indicates that stiffer composites are also tougher. This behavior is attributed to the flexible organic nature of the wider necks.

In summary, molecular-level synergism between silica nanoparticles and molecular cross-linkers inverts the relative host–guest roles in glass–polymer composites, leading to new strong low-density materials. Attempts to load gels with variable amounts of polyurethane precursors such as di-ISO and diol end-capped polybutylene adipate followed by heat treatment, washing, and supercritical drying led to opaque materials, somewhat stronger than silica but still quite brittle and much inferior to the materials described above. Direct mixing of a diisocyanate and an alcohol-free sol has been attempted recently by Yim et al.²⁷ Reportedly, that procedure leads to week-long gelation times and requires an at least equally long aging period. In our attempt to add various amounts of di-ISO in a base-catalyzed sol in PC, we also noticed a week-long gelation time. The resulting aerogels were translucent but no less brittle than native silica.

Further studies are underway to (a) reduce the processing time by replacing PC with less viscous solvents and oven heating with microwave heating; (b) vary the chemical identity of the diisocyanate,²⁸ as well as the composition and density of silica; and (c) cross-link the few residual NCO groups by introducing appropriate diols.

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