

ISOCYANATE CROSS-LINKED SILICA: STRUCTURALLY STRONG AEROGELS¹

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Introduction

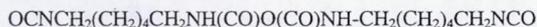
Silica aerogels are chemically inert, highly porous ceramics.² They are produced via a sol-gel process, whose final stage involves extracting the pore-filling solvent with liquid CO₂. The latter is gasified supercritically and is vented off, leaving behind a very low density solid (0.002 - 0.8 g cm⁻³), with the same volume as the original hydrogel and a chemical composition identical to glass. Aerogels have been considered for thermal insulation,³ catalyst supports,⁴ or as hosts for a variety of functional materials for chemical, electronic, and optical applications.⁵ Practical application has been slow though, because aerogels are brittle and hygroscopic,⁶ absorbing moisture from the environment which leads to structural collapse due to the capillary forces developing in the pores.^{2,3}

The poor mechanical properties of silica aerogels notwithstanding, many plastics are reinforced with glass. For example, several thermoplastics for injection molding are supplied pre-formulated in glass-fiber-containing pellets, and long glass-fiber-reinforced polyurethane rods are considered as a lightweight, non-corroding alternative to steel in architectural construction.⁷ Glass fiber does not improve the strength of silica aerogels,⁸ 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, which are the smallest entities visible in Figure 1A (5-10 nm in diameter). Those particles are connected by "necks" formed by dissolution and re-precipitation of silica during aging. Reasonably, the strength of monolithic aerogels 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). A similar reaction of an isocyanate with glass-surface silanols (-Si-OH) modifies glass fibers,⁹ chromatographic silica absorbents,¹⁰ and sol-gel derived particles.¹¹

Experimental

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 route¹² and are aged for 2 days room temperature. Subsequently, according to a postgelation doping protocol,¹³ pores are filled with a diisocyanate (di-ISO) solution by washing successively with methanol, propylene carbonate (PC), and PC/di-ISO (4 × 8 h in each bath). The di-ISO employed (Aldrich) was based on hexamethylene diisocyanate:



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 × 8 h), PC/acetone (1:1, 1:3, v/v; 1 × 8 h each), and acetone (4 × 8 h) and are dried supercritically.

Results and Discussion

di-ISO modified aerogels are translucent, with properties 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 from zero to 51% w/w. Both size and density level off for bathing solutions more concentrated than ~40% w/w, but

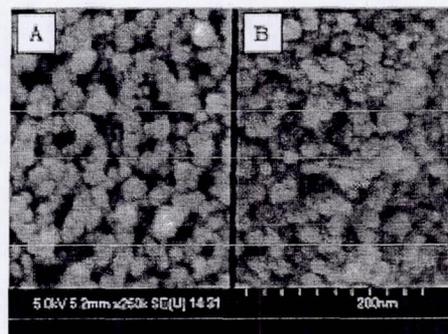


Figure 1. SEM images from random spots in the interior of fractured monoliths of a native silica aerogel with density = 0.169 g cm⁻³ (A) and a di-ISO cross-linked silica aerogel composite with density = 0.380 g cm⁻³ (B).

even the most dense monoliths fall in the density range of aerogels. Shrinking is probably associated with cross-linking. IR analysis (Figure 2) shows that as

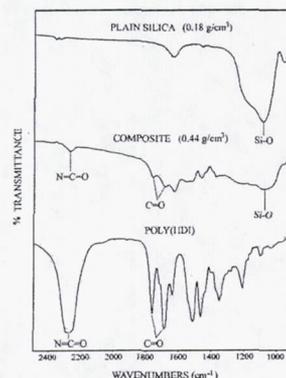


Figure 2. Comparative IR analysis of plain silica, di-ISO and cross-linked silica composite with density 0.447 g cm⁻³.

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, the dominant stretch at ~2272 cm⁻¹ comes from the isocyanate (N=C=O). In all composites, however, the latter absorption is consistently extremely weak or absent. Therefore, 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.⁶ 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) and the density change between native silica and the most dense composite (density = 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),¹⁴ causing extensive cross-linking (see Figure 3). 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 (from ~1000 m² g⁻¹ to ~200 m² g⁻¹), and the average pore diameter jumps from ~13 to ~20 nm as the monolith density increases.

Composite monoliths are much less hygroscopic and more robust than pure silica.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 under-

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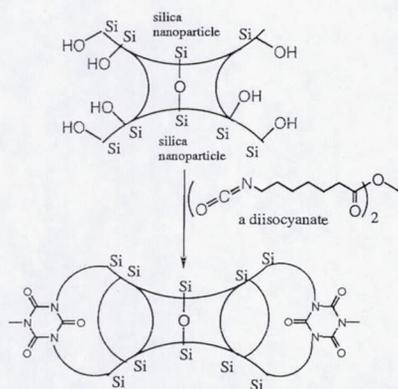


Figure 3. Mechanism of cross-linking silica nanoparticles with diisocyanate.

go extensive cracking, losing their structural integrity completely.¹ Cracking was also observed consistently with all samples of the lighter composite density = 0.241 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 density $> 0.3 \text{ g cm}^{-3}$ uptake < 1.7 times their weight in liquid N_2 , but no structural change was observed, even after repetitive dip freeze/thaw cycling. These results are significant because they imply that: (a) cross-linked aerogels can be used for storage of liquefied gases; and, (b) cross-linked aerogels can be dried without supercritical fluid extraction.

However, the most dramatic improvement yet is in the strength of the new material, as tested with a three-point flexural bending method.¹ 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 4

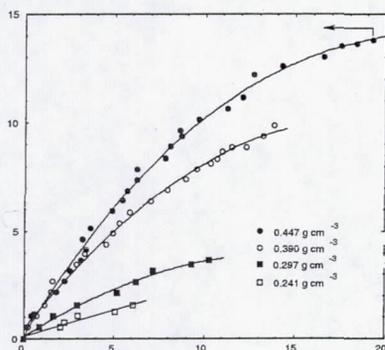


Figure 4. Load-strain curves for four cross-linked silica aerogel monoliths of variable density.

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. 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

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

where L is the span (1.738 cm) and r the radius of the aerogel.¹⁵ Measuring the deformation of native silica was not possible; however, accepting that for a native silica aerogel with density = 0.2 g cm^{-3} and the value of E is $\leq 1.0 \text{ MPa}$,⁶ 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.¹⁶ Eventually, even the stiffer composites bend, accommodating up to 20% diametral deflections before rupture (see Figure 5). The more work (i.e., the area underneath the load/deformation curve of Figure 4) 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.

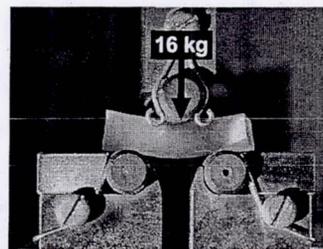


Figure 5. Bending under 16 kg load of the monolith with density 0.447 g cm^{-3} using an automated Instron Instrument Model 4469 (2.268 cm span).

In summary, molecular-level synergism between the silica nanoparticles of pre-formed monoliths 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.¹⁷ 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.

According to more recent studies, if propylene carbonate is replaced with acetone, it leads not only to shorter processing times, but also to much stronger gels that can tolerate loads in excess of 40 kg in the arrangement of Figure 5. We attribute that behavior to the lower viscosity of acetone, that allows faster diffusion of the di-ISO solution within the pores before di-ISO has time to react with the surface of silica. Further studies are underway to vary the chemical identity of the diisocyanate,¹⁸ as well as the composition and density of silica.

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