MECHANICALLY STRONG LIGHTWEIGHT MATERIALS FOR AEROSPACE APPLICATIONS (X-AEROGELS)

Nicholas Leventis

Materials and Structures Division, NASA Glenn Research Center
21000 Brookpark Road, M.S. 49-1, Cleveland, OH 44135, U.S.A.
Nicholas.Leventis@NASA.gov

ABSTRACT

The X-Aerogel is a new NASA-developed strong lightweight material made by reacting the mesoporous surfaces of 3-D networks of inorganic nanoparticles with polymeric crosslinkers. Since the relative amount of the crosslinker and the backbone are comparable, X-Aerogels can be viewed either as aerogels modified by templated accumulation of polymer on the skeletal nanoparticles, or as nanoporous polymers made by templated casting of polymeric precursors on a nanostructured framework. The most striking feature of X-Aerogels is that for a nominal 3-fold increase in density (still an ultralightweight material), the mechanical strength can be up to 300 times higher than the strength of the underlying native aerogel. Thus, X-Aerogels combine a multiple of the specific compressive strength of steel, with the thermal conductivity of styrofoam. X-Aerogels have been demonstrated with several polymers such as polyurethanes/polyureas, epoxies and polyolefins, while crosslinking of ~35 different oxide aerogels yields a wide variety of dimensionally stable, porous lightweight materials with interesting structural, magnetic and optical properties. X-Aerogels are evaluated for cryogenic rocket fuel storage tanks and for Advanced EVA suits, where they will play the dual role of the thermal insulator/structural material. Along the same lines, major impact is also expected by the use of X-Aerogels in structural components/thermal protection for small satellites, spacecrafts, planetary vehicles and habitats.

1. Introduction

The main theme in materials development for space exploration is multifunction. This is because, for example, use of a structural component that simultaneously plays the role of the thermal and vibration insulator, will free weight for useful payload. Clearly, that approach will increase mission capability and reduce launch costs.

A lightweight material that has already been used as thermal insulator on planetary vehicles (Sojourner Rover, 1997; Spirit and Opportunity, 2004) is the silica aerogel.¹ That material, however, could not have played a multifunctional role in the context of the paragraph above, because aerogels are extremely fragile. Let’s see why.

Microscopically, silica aerogels consist of a so-called “pearl-necklace”-like fractal network of secondary silica nanoparticles (2-10 nm in diameter) with large void space between the chains.
Since aerogels consist of mostly empty space they are low density (0.003-0.8 g cm\(^{-3}\)), low thermal conductivity (<0.02 \(\text{W m}^{-1}\ \text{K}^{-1}\)) materials. Their fragility is traced ultimately to the interparticle connecting zones, referred to as necks. Consequently, it seemed reasonable that by rendering interparticle necks wider, the specific strength of monolithic silica aerogels could be improved without a severe weight penalty. Thus, in 2002 we invented a method by which we let the surfaces of the internal pores of a silica wet-gel play the role of a polyol reacting with a diisocyanate dissolved in the pore filling solvent.\(^2\) The scope of that process was to imitate polyurethane chemistry and furnish a conformal polymer coating over the skeletal nanoparticle framework that crosslinks and fuses adjacent nanoparticles together rendering the intreparticle necks wider. Indeed, monolithic polymer crosslinked aerogels (X-Aerogels) can be only up to 3× more dense than the same size objects based on the underlying silica framework, but up to 300× stronger in terms of the force it takes to break them in a three point bending test configuration.\(^3\) Since the porosity is maintained the thermal conductivity remains low. Overall, at their best, X-aerogels combine a specific strength similar to that of aerospace grade graphite composite with the thermal conductivity of glasswool.\(^4\)

In this article we review the design space of crosslinked aerogels, and we discuss key properties of interest to aerospace applications.

2. Results and Discussion

2.1 Preparation of X-Aerogels

Conventional silica aerogels are prepared through the so-called sol-gel process, where a silicon alkoxide such as tetramethyloctahydrosilicate (TMOS) is hydrolyzed and condensed \textit{in situ} to form a wet gel (Fig. 1). If a wet gel is dried under ambient or lower pressure it shrinks to a small percentage (10-20%) of its original volume. That shrinkage is due to the surface tension forces exerted by the residing meniscus of the evaporating liquid through the fragile nanoparticle framework of the wet gel. Shrinkage can be avoided if the pore-filling solvent is first exchanged with liquid CO\(_2\) in an autoclave at 15 °C, and subsequently the temperature and pressure of the vessel are increased above the critical point of CO\(_2\) (31.1 °C, 1,070.4 psi). This process induces a sort of vaporization of all liquid CO\(_2\) at once, so that the skeletal framework never experiences any surface tension forces. The resulting native silica aerogels are

\[\begin{align*}
\text{H}_3\text{CO} & \quad - \quad \text{Si} \quad - \quad \text{OCH}_3 \\
\text{OCH}_3 & \quad \text{H}_3\text{CO} \\
\text{OCH}_3 & \quad \text{OH}
\end{align*}\]

\[\text{TMOS}\]

\[\begin{align*}
\text{HO} & \quad - \quad \text{Si} \quad - \quad \text{OH} \\
\text{OH} & \quad \text{HO}
\end{align*}\]

\[\text{silica sol} \quad \text{silica gel}\]

Fig. 1: The sol-gel process. (A) Acid or base catalyzed hydrolysis. (B) \textit{In situ} acid or base catalyzed condensation. (C) Formation and coagulation of nanoparticles into a silica wet gel during (B).
Fragile materials and have been used only in a few very specialized environments, for example as Cherenkov radiation detectors in certain types of nuclear reactors, and as collectors of hypervelocity particles (Stardust program) and as thermal insulators on Mars Rovers (refer to the Introduction).

For the preparation of polymer crosslinked aerogels (X-Aerogels) the above procedure has been modified by soaking wet gels in a crosslinking solution containing the monomer precursor to a polymer that can develop chemical bonding with the surface of the nanoparticles. This process results in molecular tethers between the particles, reinforcing the structure without clogging the pores. Fig. 2 summarizes and compares the native versus the X-Aerogel making processes.

![Diagram of preparation process](image)

**Fig. 2:** Preparation of native versus X-Aerogels.

In turn, Fig. 3 compares the microscopic morphology of a native and a X-Aerogel crosslinked with a polymer derived from a diisocyanate, confirming that the polymer has been coated conformally onto the surface of the skeletal nanoparticles; this is inferred by the fact that in spite of a 2x-3x increase in bulk density, the smallest features discernible in the native aerogel are still discernible in the crosslinked counterpart. This implies that about the same internal space should be accessible before and after crosslinking, and this is supported by NMR imaging of acetone filling the pores of a native and a crosslinked wet gel (Fig. 4): dark pixel density analysis shows that the concentration of acetone is practically the same in native and crosslinked samples.

The most impressive property of crosslinked aerogels, however, is their strength. But first, it should be pointed out that the amount of polymer uptake, and therefore the degree of crosslinking, can be controlled by the amount of crosslinker in the bath (refer to Fig. 2). Thus, aerogels with a variable degree of
crosslinking show a simultaneous progressive increase in stiffness, toughness and ultimate strength (Fig. 5). It is noted that a native aerogel of the same dimensions and just 3× less dense than the X-Aerogels tested in Fig. 5 does not even register in the same load force scale as it fails with about 1 N worth of force under the same conditions.

Extensive chemical analysis of X-Aerogels crosslinked with a variety of di-and tri-isocyanates has revealed that crosslinking involves urethane formation between the isocyanate and the hydroxyl groups on the surface of the silica nanoparticles. However, the bulk of interparticle tethers consists of polyurea formed by reaction of isocyanate in the solution filling the pores with amines resulting from hydrolysis of the dangling isocyanates by water remaining adsorbed on silica from the gelation step (Fig. 6).

Now, since the bulk of crosslinking is carried out by polyurea, the question is
what if we intentionally build tethers of polyurea starting from the surface of silica? After all, polyureas are in general stronger polymers than polyurethanes. That proposition requires availability of amine-terminated silica. But, if we consider modification of the silica surface, we also recognize that there are actually three variables that we may control independently in the X-Aerogel design, and these variables are reviewed in the next section.

2.2 The X-Aerogel Design Space

The X-Aerogel properties may be controlled by one of the following three parameters: the nanoparticle surface chemistry, the chemical identity of the polymer or the network morphology (Fig. 7). In that regard, although deve-

development of X-Aerogels was based on the remarkable increase in strength induced by polymer crosslinking (refer to Fig. 5), nevertheless, with the role of the polymer being to render interparticle necks wider, we do not expect any further significant increase in strength by changing the chemical identity of the polymer. Thus, the driving force behind use of different polymers has been the need for enhanced hydrophobicity, optical clarity, thermal stability and chemical inertness. On the contrary, using different metal oxide aerogels instead of silica aims not only to take advantage of properties innate to those oxides (e.g., pholuminescence, paramagnetism), but also to further increase strength, reasoning that different network morphologies would dissipate loads differently. In this context, and as it may also have become apparent by the last paragraph, modification of the nanoparticle surface chemistry is not the goal, but just the means for attaching different crosslinkers. In the following sections we review advancements along the three degrees of freedom delineated in Fig. 7.

2.2.1 X-Aerogels through nanoparticle surface modification

As outlined above, in the presence of isocyanate, an amine rich surface of silica would become the focal point for accumulation of polyurea. However, as shown in Fig. 8, the same amine groups

Fig. 7: The design space of X-Aerogels.

Fig. 8: Crosslinking possibilities for amine surface-modified silica.
can become the point of departure for crosslinking with a variety of polymers, as for example polystyrene, or –by imitating epoxy glue chemistry– a polymer derived from an epoxide. Microscopically, all amine-modified, polymer-crosslinked X-aerogels look similar, but their thermal stability and their hydrophilicity are significantly different. Polyurea crosslinked aerogels loose all the organic matter at ~320 °C, while polystyrene crosslinked samples do not loose the polymer before 450 °C (Fig. 9). Thermal conductivity measured by a laser flash method is also low: non-evacuated polyurea crosslinked samples with density around 0.5 g cm⁻³ have a thermal conductivity of ~0.04 W m⁻¹ K⁻¹, while polystyrene crosslinked samples of the same density have a thermal conductivity of ~0.03 W m⁻¹ K⁻¹. These values are in the range of glass wool and styrofoam. Furthermore, although all these X-Aerogels are much less hygroscopic than plain silica, nevertheless their behavior in contact with water is vastly different: polyurea crosslinked aerogels uptake water in the mesopores and eventually sink, while polystyrene crosslinked samples are hydrophobic and float on water indefinitely.

But again the most significant property of all these X-Aerogels is their mechanical strength. For example, Fig. 10 shows the stress strain curve under compression of a polyurea crosslinked sample (0.48 g cm⁻³). The sample undergoes tensile failure at ~80% strain under an extreme pressure (~30,000 psi). Overall, it is emphasized that X-Aerogels present a very unusual combination of materials properties as we practically deal with a material having a specific compressive strength higher that that of steel and the thermal conductivity of glasswool.
2.2.2 X-Aerogels through changes in the network chemical identity

Fig. 11 highlights all chemical elements of which we have been able to prepare crosslinked oxide aerogels using the same isocyanate chemistry of Fig. 6. Several of these aerogels rely on photoluminescent, catalytic electrically conducting or paramagnetic oxides and may comprise platforms for a variety of novel optical, chemical electronic and magnetic applications in energy conversion, separations, sensors, actuators and catalysis.

![Fig. 11: Elements of which aerogels have been prepared and crosslinked with isocyanates in analogy to the chemistry outlined in Fig. 6](image)

3. Summary and Outlook

A first application of silica-based X-Aerogels explored at NASA is as dual-function materials that will play the role of a thermal insulator/structural component in all-composite cryogenic tanks. Although in this brief X-Aerogel technology review we have focused on mechanically stronger, higher density materials, nevertheless, low-density silica X-Aerogels have been also synthesized and characterized. These materials are flexible and they are investigated as thermal insulators in Advanced Space Suits.

Other applications include fuel cell membranes, platforms for optical sensors, chromatographic separations, while optically clear X-Aerogels are evaluated as fillers in thermally insulating windows and skylights.

Acknowledgements

The project is supported by the IR&D fund of the NASA Glenn Research Center, NASA Code T (Exploration), the UAV program and the AEVA Suit program. The name “X-Aerogel” was contributed by Dr. Paul Curto of NASA Headquarters.

References
