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COMPRESSIVE BEHAVIOR OF CROSSLINKED MESOPOROUS SILICA AEROGELS AT HIGH STRAIN RATES

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Introduction

Aerogels are low-density mesoporous materials with exceptionally low dielectric constants, low thermal conductivities (up to 40 times better thermal insulators than the best fiberglass) and high acoustic impedance.¹ Their practical applications, however, have been slow due to their hydrophilicity and brittleness. The fragility problem was resolved by nanocasting a ~2-4 nm thick polymer layer on the skeletal silica nanoparticles that strengthens the weak inter-nanoparticle necks.²⁻¹⁰ The thin polymer coats conformally the skeletal framework without clogging the mesopores and reinforces the structure by chemically crosslinking the nanoparticles. With a density increase by only three times, crosslinking aerogels have the flexural strength increased by 300 times.² The method has been applied for crosslinking aerogels consisting of oxides of more than 30 different elements from the periodic table.²⁻¹⁰ The mechanical properties of crosslinked silica aerogels with different polymers^{6, 8-10} were improved to a similar level since the polymer bond energy was similar among polymers.¹¹ Therefore, to improve the mechanical properties further, we turn to the network morphology.^{1,4,11,12} For this study we turned to certain micelle-templated aerogels¹³ known to have a worm-like microstructure with a macro/mesoporous skeletal framework. For comparison, macroporous monolithic silica aerogels consisting of both random and ordered mesoporous walls have been synthesized via an acid-catalyzed sol-gel process from tetramethoxysilane (TMOS) using a tri-block copolymer (Pluronic P123) as a structure-directing agent and 1,3,5-trimethylbenzene (TMB) as a micelle-swelling reagent. Although those monoliths are more robust than base-catalyzed silica aerogels of similar density, the mechanical properties can be improved dramatically by letting di-isocyanate react with the silanols on the mesoporous surfaces.

The compressive behavior of both crosslinked templated silica aerogels with/without ordered mesostructure and non-templated silica aerogels was characterized under high strain rates using a long split Hopkinson pressure bar (SHPB). Their mechanical properties at different strain rates are compared with those of engineering plastics polymethyl methacrylate (PMMA) and polycarbonate (PC). The effect of water absorption and of low temperatures on the compressive behavior was also investigated.

Experimental

Material Preparation. Following the approach described by Nakanishi and Leventis,^{12,13} macroporous monolithic silica aerogels have been synthesized via an acid-catalyzed sol-gel process using a constant amount of tetramethoxysilane (TMOS). The detailed preparation of templated aerogels is described in reference 12. Unreacted templating agent (Pluronic P123) was removed using Soxhlet extraction. Finally, wet gels were crosslinked with Desmodour N3200 diisocyanate, and unreacted diisocyanate was removed with four acetone washings. Aerogels in monolithic form were obtained by extracting the pore filling solvent with liquid CO₂, which eventually was taken out supercritically. For comparison purposes, crosslinked non-templated aerogels, X-MP0, were also prepared. Those samples were prepared in the same way as the rest of the X-MP samples except that Pluronic P123 was replaced by an equal volume of methanol. Finally, in order to compare the mechanical properties of those gels with those of standard acid-catalyzed silica aerogels, non-templated acid-catalyzed wet gels (denoted as -AC) were also prepared according to the procedures described by Merzbacher et al.,¹⁴ and wet-gels were dried with SCF CO₂ after crosslinking in a solution of Desmodur N3200 in acetonitrile (9.86% g/mL), resulting in dry X-AC. For comparison with engineering polymers, a clear extruded PMMA round bar and a translucent molded PC round bar were obtained from McMaster and they were characterized under the same conditions.

Compression Characterization. Compressive tests at high strain rates were conducted on a long split Hopkinson pressure bar (SHPB). The SHPB

setup has been documented in detail.¹⁵ The SHPB consists of striker, incident and transmission bars, as well as a multi-channel strain acquisition system. A cylindrical specimen was sandwiched between incident and transmission bars. A compound pulse shaper, consisting of a copper disk stacked on another larger copper disk, was used to generate a desired smooth incident wave. The pulse shaper assists to reach dynamic stress equilibrium state and keep the strain rate constant in a specimen, necessary in a valid SHPB experiment.^{16,17} The working principle of SHPB has been well documented in literature.¹⁶⁻¹⁹ Under a valid SHPB experiment, the acquired strain data on bars was further deduced into the history of stress, strain rate and strain in a specimen.¹⁵ For comparing the mechanical properties of templated aerogels, disk PMMA and PC samples with similar dimensions and shapes as our aerogel samples were also tested under compression on SHPB. The experiments were conducted at room temperature (23 ± 1°C) under relative humidity 35 ± 3%. For these tests, aerogel cylindrical samples with 9.40 mm diameter and 2.54 mm thickness, and engineering plastics PMMA and PC disk with 9.50 mm diameter and 3.75 mm thickness were used in measuring the stress-strain relations at strain rates within the 1000~2000 s⁻¹ range. SHPB experiments on wet samples at room temperature and on dry samples at low temperatures were also conducted. To prepare water saturated samples, samples were immersed in water until their weight did not increase further. To conduct experiments at low temperatures, samples were placed inside ice or dry ice. Under each condition five or more specimens were tested to confirm repeatability of experimental data, and the average results are reported.

Results and Discussion

Following the Nakanishi/Leventis notation, crosslinked templated aerogel samples are designated as X-MP4, X-MP4-T310-1, X-MP4-T310-2, X-MP4-T310-3, and X-MP4-T045, and crosslinked non-templated aerogel samples as X-MP0 and X-AC. The physical and chemical properties of these native aerogels, templated silica aerogels and the non-templated aerogel type X-AC have been reported elsewhere.¹² SEMs of templated aerogel show macroporosity, with pore sizes in the order of microns. Crosslinked samples with no templating agent, X-MP0, appear compact at the micron-size regime, showing no macroporosity. Crosslinked non-templated samples prepared with a standard acid-catalyzed recipe, X-AC, show that polymer has coated conformally the mesoporous surfaces in analogy to polymer crosslinked base-catalyzed silica aerogels we have reported before.^{2,11,15}

A preliminary study of the compressive behavior under quasi-static conditions of templated silica aerogels can be found in reference 12. Under compression at high strain rates using the SHPB, the typical oscilloscope recordings for the incident, transmitted and reflected signals are similar to those of crosslinked base-catalyzed silica aerogels, or X-SiOx.¹⁵ With the use of pulse shaping, the specimen deformed nearly uniformly under a constant strain rate. Specific energy absorption data were obtained always under the same striker impact momentum.

Figure 1 shows the compressive stress-strain curves for templated and non-templated aerogels under unconfined conditions at high strain rate 1000~2000 s⁻¹. At these high strain rates, all samples show a linearly elastic behavior under smaller strains (~3%), yield at ~3.5% compressive strain and exhibit plastic hardening during compaction until ~45% strain. After that, samples were condensed further and failed at ultimate strain of 50~80%, indicating very high ductility at high strain rates. Unloading was conducted only after reaching the maximum stress. Unloading curves became steeper at higher compressive strain levels (e.g., between 53% and 85%), resulting in plastic deformation at ~50% compressive strain or higher.

At strain rates above 1000 s⁻¹, samples did not break into fragments, remaining as single pieces despite cracks and chips formed at the lateral surfaces during unloading. One change observed from quasi-static to dynamic compression is that the elastic region is extended up to 100 MPa, which is more than twice of the yield stress (~40 MPa) at the quasi-static state (strain rate 0.01 s⁻¹). Thus, the mechanical properties of the crosslinked templated and non-templated aerogels depend highly on strain rates. The specific energy absorptions are determined to be 89.99 J/g, 108.36 J/g, 45.81 J/g, 108.06 J/g and 116.97 J/g for templated silica X-MP4-T310-1, X-MP4-T310-2, X-MP4-T310-3, X-MP4-T045 and X-MP4, respectively, and 110.56 J/g and 110.98 J/g for the crosslinked non-templated aerogels X-MP0 and X-AC, respectively. The specific Young's modulus, specific yield strength and specific ultimate strength of templated aerogels are 1-2 times higher than the corresponding values of non-templated aerogels, X-AC and X-MP0.

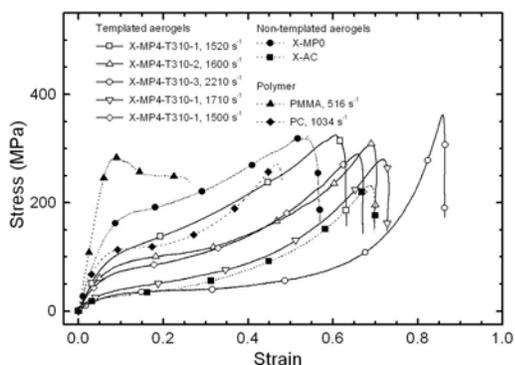


Figure 1. Compressive stress-strain curves of different templated aerogels at high strain rates within the 1000–2000 s⁻¹ range.

Figure 1 also shows stress-strain curves of PMMA and PC at high strain rates. The slight effect of strain rate on the stress-strain relationship is neglected here as in SHPB it is difficult to generate an absolutely constant strain rate even under the same loading condition due to the dynamic nature of the experiment. PMMA failed in the ductile mode (stress softening) whereas developing surface cracks lead to axial splitting of the specimen; its specific energy absorption was 51.93 J/g at strain rate 516 s⁻¹. PC failed in ductile mode associated with stress hardening, while its specific energy absorption was 56.38 J/g at strain rate 1034 s⁻¹. Both materials expanded in the lateral direction significantly, whereas the crosslinked aerogels show little lateral expansion. It is noted that X-MP4-T310-1 failed in nearly ductile mode and its specific energy absorption was found to be ~90 J/g at strain rate 1520 s⁻¹. This specific energy absorption of templated aerogels is 70% higher than that of PMMA, and 60% higher than that of PC, indicating that templated aerogels can absorb higher specific energy without incurring much lateral expansion.

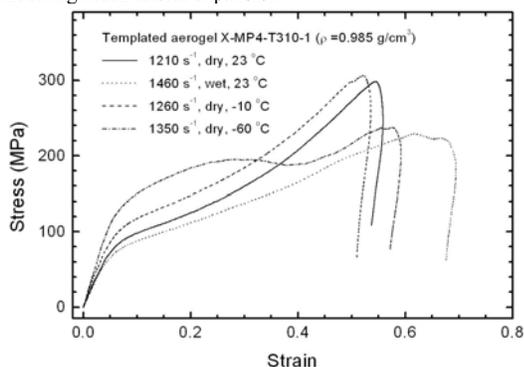


Figure 2. Compressive stress-strain curves of templated aerogels X-MP4-T310-1 at high strain rates for investigation of the effects of water absorption and low temperatures.

Figure 2 shows the effect of water absorption and low temperature on the compressive behavior of templated aerogel X-MP4-T310-1. After the sample was immersed in water for 196 hours, pores were completely filled with water and the density was increased 15%. Despite that stress-strain curves are lower than those obtained under dry conditions, water-soaked templated aerogels are still mechanically strong materials albeit somewhat weaker than their dry counterpart. For dry samples, low temperature causes the material to become stiffer and shifts the stress-strain curve obtained at -10 °C above of the one obtained at room temperature, thus achieving higher energy absorption. However, when the temperature is decreased to -60 °C, the stress-strain curve shows stress softening at the 30% strain level and weakening at even higher strain levels while the overall load-bearing capability remains high. There seems to exist a critical transition temperature beyond which templated aerogel become weaker. Overall, it can be concluded that templated aerogel possess rather exceptional mechanical properties even at the worse possible environments such as under water and at low temperatures. These results indicate the potential use of crosslinked templated aerogels as a material for energy absorption in dynamic loading conditions such as in armor. Although the crosslinked templated silica aerogels tested are found to be already stronger

and tougher than other types of crosslinked aerogels investigated thus far,^{11,12} further work is needed to optimize the morphology of the nanostructure to improve and optimize the mechanical properties of this class of materials.²⁰

Conclusions

Crosslinked, templated macr/mesoporous silica aerogels (X-MP4, X-MP4-T045 and X-MP4-T310-1 to -3) and non-templated acid-catalyzed mesoporous silica aerogels (X-MP0 and X-AC) made by encapsulating the native 3D skeletal framework with polymers derived from di-isocyanate, have been investigated under dynamic compression. The stress-strain relationships of these aerogels were determined at high (1000–2000 s⁻¹) strain rates. Templated aerogels show much improved yield strength and excellent ductility, deforming only at compressive strain of 50% or more. The water absorption can weaken the mechanical properties of templated aerogel to some degree. Nevertheless, at high strain rates templated aerogels retain good toughness at temperature even down to -60 °C. The specific energy absorption of templated aerogels was 60–70% higher than that of engineering polymers PMMA and PC under high strain rates, indicating their potential use in energy absorption applications like for example in armor.

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