Mechanically reinforced silica aerogel nanocomposites *via* surface initiated atom transfer radical polymerizations†

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Here we report the preparation of mechanically robust silica aerogel polymer nanocomposites using surface-initiated atom transfer radical polymerization. This approach was used to grow poly(methyl methacrylate) (PMMA) with low polydispersities and establish the first structure–property relationship between the grafted PMMA molecular weight and bulk physical properties of the hybrid aerogel.

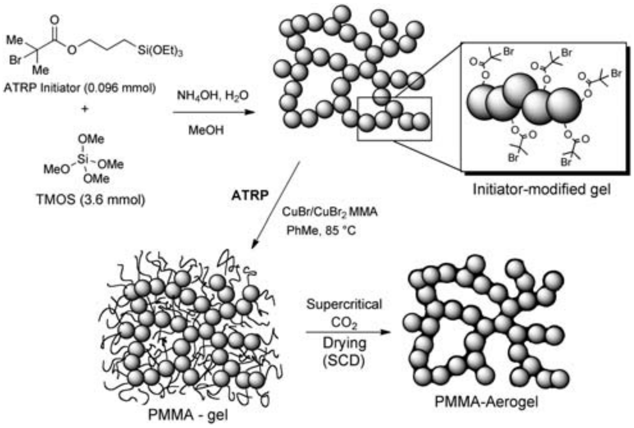
The addition of organic polymers to the aggregate structure of silica aerogels has proven to be an effective strategy to enhance the mechanical properties of these otherwise fragile materials.[1] Silica aerogels are typically formed *via* sol–gel processes when the solvent is removed (generally by supercritical drying (SCD)[2]) without dimensional shrinkage due to drying stresses. The resultant material is a transparent solid that is predominantly porous with air percolating through a diaphanous network of aggregated nanoparticles.[3] The combination of low density, large pore volume, and high surface area has made aerogels attractive for thermal[4] and acoustic insulators,[5] catalyst supports[6] and low-*k* dielectric materials.[7] However, their intrinsically low density and fragility greatly complicate handling or processing without catastrophic fracture of the material.[8] Hence, improving the mechanical properties of aerogels is an important fundamental challenge towards achieving the full potential of these materials for various applications.

Ideally, the reinforcement of silica aerogels should be achieved with minimal changes to the overall density and porosity of the material as possible. Recent efforts to prepare robust aerogels have applied a reinforcing agent to the "necks" between particles in the aggregate structure.[1] Employing this general strategy, gels have been mechanically enhanced, before supercritical drying, by a number of different approaches, such as the redistribution of existing silica in the aggregate (Ostwald ripening), the introduction of additional tetralkoxysilane monomer to the aggregate, or the growth of cross-linked (epoxy, urethane, urea and styrene) polymer networks from the surface of the gel.[9] Recently, we reported a more rapid method for reinforcing dried aerogels using vapor deposition of cyanoacrylates.[10] In all of these cases, while the strength of the aerogels was improved, undesirable increases in the solid state density and reduction of the effective surface areas of the material were also observed. Based on our observations from reinforcing aerogels with polycyanoacrylates, we hypothesized that optimal mechanical reinforcement of aerogels could be achieved by the attachment of higher molecular weight organic macromolecules with low grafting densities onto SiO_2 surfaces without significantly increasing the density of the material.

Herein, we report the preparation of mechanically enhanced hybrid aerogels using *surface initiated atom transfer radical polymerization* (SI-ATRP)[11] to grow well-defined poly(methyl methacrylate) (PMMA) onto the surface of SiO_2 aerogels (Scheme 1). We observe for the first time a tunable structure–property correlation between the molar mass of grafted PMMA and the toughening of the hybrid aerogel.

To ensure covalent attachment of polymers to the silica aerogel, copolymerization of tetramethoxysilane with an α-haloester functional triethoxysilane[12] was conducted and afforded a modified aerogel with an approximate surface coverage of 0.05 initiators per nm^2. The lower reactivity of the triethoxysilyl group compared to tetramethoxysilane during the ammonia-catalyzed sol–gel polymerization ensured that the majority of initiating groups would be segregated to the aerogel surface.[13]

SI-ATRP of MMA was conducted in solution using a copper(I)-bromide, copper(II)bromide, and 4,4′-dinonyl-2,2-bipyridine (dNbpy) catalyst system in the presence of a monolithic gel. Care was taken to completely exchange the solvent in the gels with the ATRP monomer and catalyst at room temperature before heating to start the polymerizations. A target degree of polymerization of $[M]_o/[I]_o = 200$ was chosen. Polymerization times were varied from 6–40 h, thus allowing for control over the grafted polymers molecular weight (Table 1). The difference in morphology between a polymer free aerogel and an aerogel composite after SI-ATRP is pronounced and appears to be thickened (Fig. 1).



Scheme 1 Formation of initiator-modified gel, ATRP growth of PMMA on surface and supercritical drying to afford a silica–PMMA composite aerogel.

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Table 1 Properties of silica, PMMA–silica aerogel composites and polymer characterization

Aerogel polymerization time/h	PMMA M_w/g mol^{-1}	PDI	Aerogel density/g cm^{-3b}	Flexural strength/kPa	Surface area/m^2 g^{-1}	Mean pore dia./nm	Pore volume/cm^3 g^{-1}
0[a]	—	—	0.092 ± 0.001	3.4 ± 0.1	1483	11.4	9.76
6	20 390	1.55	0.116 ± 0.017	15.4 ± 0.49	403	23.6	5.83
20	43 013	1.22	0.162 ± 0.032	30.2 ± 0.52	301	32.8	3.47
30	63 284	1.68	0.236 ± 0.038	48.5 ± 1.3	221	27.0	0.96
40	75 246	1.82	0.330 ± 0.072	63.5 ± 1.7	185	26.4	0.81

[a] Silica aerogel prepared without PMMA. [b] Density values are an average from four gels.

Determination of tethered PMMA molar mass was achieved by dissolution of SiO_2 gels with hydrofluoric acid (HF) and size exclusion chromatography (SEC) of recovered polymers. Controlled SI-ATRP was achieved, as evidenced by SEC of cleaved PMMA indicated that polymers in the range of $M_n = 13$ to 43 kg mol^{-1} were grown with polydispersities in the range of $M_w/M_n = 1.2$ to 1.8.

After SCD, aerogel composites were slightly blue tinted due to residual copper catalyst that was as high as 1% of the original copper concentration in aerogels that were treated for 40 hours.

The initiator efficiencies ranged from 21–33%. While these molecular weight distributions were more broad than those observed for typical homogeneous MMA ATRP in solution, these higher polydispersities are typical for SI-ATRP systems observed from SiO_2, concave surfaces and polysilsequioxane colloidal initiators.[11a,14] Additionally, it is anticipated that the complex environment of aerogel surfaces contained sterically inaccessible initiation sites that also affected the overall control of the SI-ATRP.

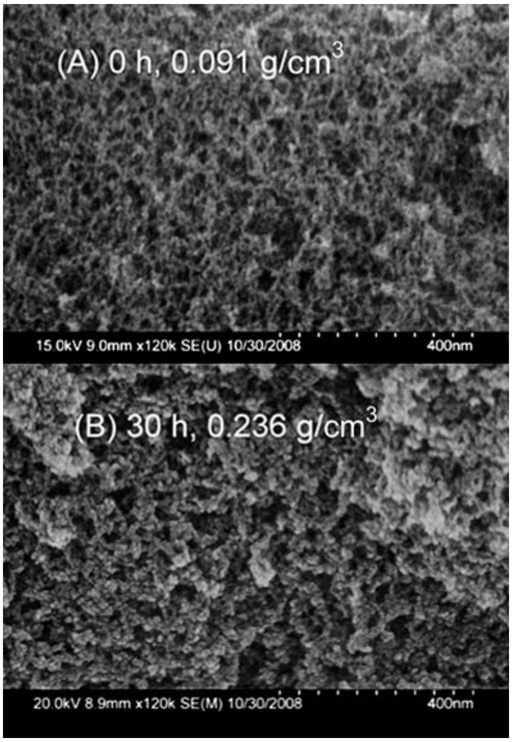

Fig. 1 (A) SEM image of silica aerogel with pendent α-haloester functional silane and (B) silica aerogel–PMMA composite after 30 h polymerization time.

Thermogravimetric analysis of poly(methyl methacrylate) grafted silica aerogels (PMMA-*g*-SiO_2) also confirmed that the organic content of hybrid nanocomposites scaled with increasing molar mass of SI-ATRP grown PMMA (Fig. 2).

By comparing the analyses of samples taken near the center of the monolithic aerogels to those from the surface, we were able to show that with excess monomer present early in the ATRP treatment the concentration of PMMA is relatively uniform with the difference in weight-percent organic between the center and exterior of the aerogels differing only by a couple of percent. After twenty hours of ATRP, the difference in organic content between the interior and exterior of the aerogels has increased to 10%. We believe that this is due to monomer depletion within the gel as the polymerization proceeds. As polymer forms, diffusion of more monomer into the gel is restricted leading to larger polymer concentrations and higher molecular weights on the exterior of the gel compared to the interior of the gel and increasing PMMA polydispersity in the aerogel. Similar, surface heterogeneities were observed in the CVD polymerization of cyanoacrylates on silica aerogels modified with amine groups[15] and may be analogous to monomer diffusion/polymerization approaches to gradient refractive index materials.

The effects of grafting PMMA to strengthen the aerogels are shown in Fig. 3. Triplicate (or more) aerogels were analyzed at each represented point using a three-point flexural bend analysis according to ASTM C1684. Flexural strengths of pure silica aerogels as a function of density are provided as a baseline (triangles in Fig. 3). The diamonds represent the strengths of the aerogels with grafted PMMA. The first point ($\rho = 0.092$ g cm^{-3}) is that of the initiator modified aerogels with no PMMA. These aerogels were slightly weaker (340 ± 10 kPa) than a pure silica aerogel. The minor

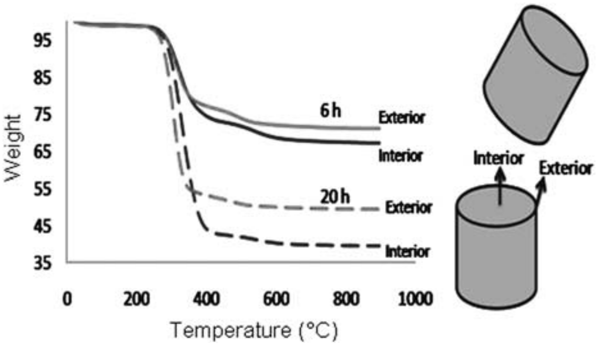

Fig. 2 TGA analyses of samples from the interior and exterior of silica aerogels ATRP modified with PMMA for 6 (bold) and 20 hours (dashed).

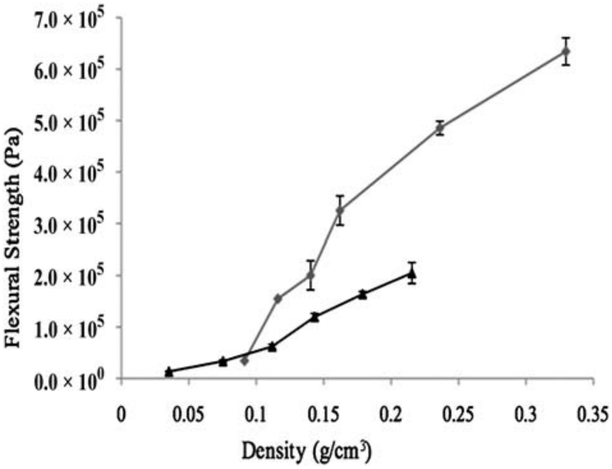

Fig. 3 Flexural strength as a function of density for PMMA–silica aerogel composites. The triangle line is for polymer free silica aerogels, and diamond line is for PMMA–silica aerogel composites.

reduction in strength is observed in other silica aerogels prepared with trialkoxysilane co-monomers.[16] The strength of the PMMA–silica aerogel composites increases with the density of the composite aerogel and the molecular weight of the PMMA. PMMA–silica aerogel composite prepared from a polymerization time of 6 h with a grafted molecular weight of ~20 kg mol^{-1} increased the flexural strength to 154 ± 4.9 kPa. This is approximately 5× stronger than the initiator-modified aerogels with only a 25% increase in the density ($\rho = 0.116$ g cm^{-3}). The strongest PMMA–silica aerogel composite had a density of 0.327 g cm^{-3}, a molecular weight (M_w) of 63 kg mol^{-1} and a flexural strength of 635 ± 1.7 kPa. This is 18× stronger than the initiator-modified silica aerogel. From these results, the strengths observed are higher than what can be attributed due to mass addition, thus the molecular weight of the grafted polymer plays an important role in the composites mechanical properties.

In addition to increasing density, most approaches to strengthen aerogels using the addition of mass lead to reduction in surface area. Nitrogen sorption surface area analyses of the composite aerogels reveal that the smaller pores fill first. As the polymerization time is extended a pore volume reduction is noticed accompanied by a shift in the composites average pore size and an attenuation of the composites surface area. The surface area of a polymer-free, initiator-modified silica aerogel was 1483 m^2 g^{-1} with an average pore size of 114 Å, a PMMA composite with a density of 0.236 g cm^{-3} had a surface area of 221 m^2 g^{-1} and an average pore size of 270 Å. The average pore size shift to larger sizes and the lower surface areas are due to the filling of the micropores (<2 nm) with the silica aerogel. This also results in the surface area reduction observed as micropores have a higher contribution to the surface area.

In conclusion, we have demonstrated the controlled growth of a grafted polymer with polydispersities between 1.2 and 1.8 from the surface of a silica gel. Once the composites were SCD, we established the first relationship of a silica aerogel composites bulk mechanical properties to those of a polymers molecular weight used to reinforce the composite. It was found that as the molecular weight increases, so does the composite mechanical properties while retaining many of the aerogel like physical properties.

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