CHEMISTRY OF MATERIALS

VOLUME 20, NUMBER 9 MAY 13, 2008

Communications

Formation of Polycyanoacrylate−Silica Nanocomposites by Chemical Vapor Deposition of Cyanoacrylates on Aerogels

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Received November 28, 2007
Revised Manuscript Received March 13, 2008

Silica aerogels are low density, porous materials whose unusual physical properties make them attractive for applications ranging from radiation detectors to ultraefficient insulation.[1] However, the fragility of aerogels, coupled with the time and cost of their preparation, has limited their use outside of laboratories. Generally formed by supercritically drying gels prepared by sol−gel polymerizations, aerogels are weakly interconnected aggregates of colloidal particles.

Efforts to strengthen aerogels have focused on reinforcing the necks between the particles in the aggregate structure. This can be done in the wet gel before drying by reacting additional tetraalkoxysilane monomer with the gel,[2] redistributing the silica in the gel from the particles to the necks via Ostwald ripening or by solution polymerizations from a modified gel surface.[3–5] Solution/predrying approaches are time-consuming due to the slow diffusion rates of reagents in the wet gel structure. Alternatively, silica aerogels can be coated *in a matter of hours* through chemical vapor deposition of an inorganic monomer, such as $SiCl_4$, onto the dried gel surface,[6] despite slower gas diffusion in aerogels at ambient pressures (compared to diffusion in air).[7] In this paper, we describe the first CVD reinforcement of aerogels using cyanoacrylates to create a silica−polycyanoacrylate nanocomposite (Scheme 1). Anionic polymerization of cyanoacrylates esters is readily initiated by Michael addition of water or other nucleophiles[8] and is the basis for "superglue" adhesives. In addition to demonstrating the feasibility of cyanoacrylate CVD, our goals were to determine if monolithic structures would be homogenously coated, whether adsorbed water molecules or silanols were initiating the polymerization reactions, and if the reinforcement led to improvements to the aerogels' strength.

Cylindrical silica aerogels (10 cm^3) were prepared by standard base-catalyzed sol−gel techniques[9] followed by supercritical carbon dioxide drying.[10] After drying, the monolithic aerogels (0.077 g/mL) were then exposed to a stream of dry nitrogen gas (0.1 L/min) carrying methyl cyanoacrylate. Cyanoacrylate esters are ideal candidates for

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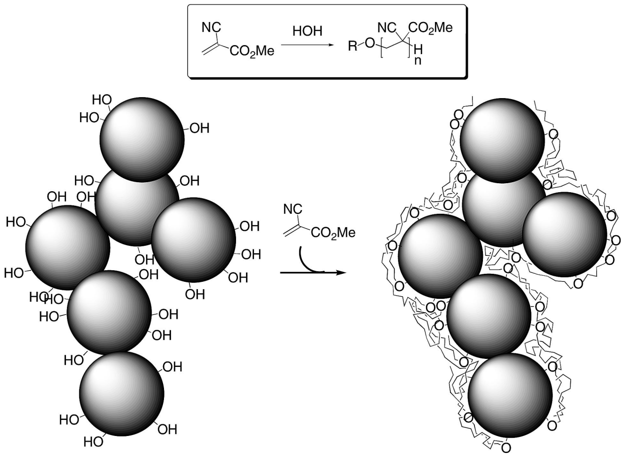
10.1021/cm703381e CCC: $40.75

Scheme 1. Chemical Vapor Deposition and Polymerization of Methyl Cyanoacrylate on the Surface of Silica Aerogels To Generate a Polycyanoacrylate−Silica Nanocomposite Aerogel (right)[a]



[a] Hydroxyls (OH) on surface of gel represent adsorbed water.

CVD modification of aerogels due to their relatively high vapor pressure (0.2 mmHg at STP) and propensity to polymerize upon adsorption onto a surface with adsorbed water or bearing nucleophilic substituents. These characteristics have led to the use of chemical vapor deposition of cyanoacrylates to rapidly "develop" fingerprints in forensic investigations,[11] as well in plasma coating of silica nanoparticles.[12] With a simple glass apparatus [see Supporting Information] we were able to deposit cyanoacrylate on a 650 mg aerogel at approximately 7 mg/h at ambient pressure and temperature. Depositions at higher temperatures were faster, but the treated aerogel monoliths suffered from numerous cracks and heterogeneous coatings. The observed linear deposition rate at room temperature of methyl cyanoacrylate provided excellent control over the thickness of the resulting polycyanoacrylate coating as determined by scanning electron microscopy. No residual monomer was detected in the coatings using solid state ^{13}C cross polarization magic angle spinning NMR of the nanocomposite aerogels or solution NMR of acetone extracts of the aerogels. We did discover that Soxhlet extraction with acetone quantitatively removed all of deposited organics from modified aerogels. This indicates that the cyanoacrylates were not covalently attached to the surface, suggesting that adsorbed water, rather than surface silanols, were the initiating species for the polymerization reactions. Furthermore, analyses of the acetone extracts revealed that only oligomeric cyanoacrylates were formed, as would be expected with adsorbed water providing a large number of initiators for the polymerization reaction.

Deposition of cyanoacrylate caused the aerogels to change from transparent (though blue tinted from scattering) to opaque white (Figure 1). Inspection with scanning electron microscopy (SEM) revealed the observed increase in scattering is likely due to coarsening of silica nanoparticles comprising the aerogels (Figure 2).

Figure 1. Photograph of uncoated aerogel (left) and of polycyanoacrylate coated aerogel (right). Monolith is homogeneously opaque. Aerogels are 0.9 cm thick and 3.5 cm in diameter.

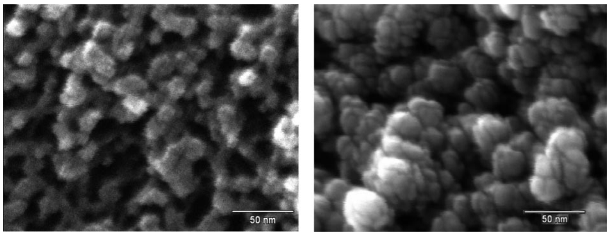


Figure 2. SEM images of uncoated aerogel (left), with particle diameters of ∼10 nm and of polycyanoacrylate coated aerogel (right) with particle diameters ∼35 nm.

Particles making up the untreated aerogels were approximately 10 nm in diameter. After coating the silica aerogels for 72 h, their mass had increased by 51% and their constituent particles had grown to near 35 nm in diameter. In order to determine the homogeneity of the polycyanoacrylate coatings at different depths in the aerogel, samples were excised from the surface, midway to the center (0.2 cm from surface) and the center (0.4 cm from surface) of a monolith. SEM analysis of these samples revealed that the polycyanoacrylate coating was nearly uniform through the monolithic structure. Gas sorption porosimetry[13] revealed that CVD treatment attenuated the surface area from near 1550 m^2/g for the unmodified aerogels to 190 m^2/g, mostly through filling of the micropores.

In order to establish the effects of the polymeric coatings on the mechanical properties, the silica aerogel monoliths were analyzed using a three-point compression analysis. Unmodified silica aerogels were found to have rupture strengths (0.539 N) (Figure 3) consistent with aerogels of this density ($\rho \sim 0.077$ g/cm^3).[5] With increasingly thick polycyanoacrylate coatings on the silica aerogels, the rupture strength increased (32×) to 17.6 N while the density only increased (3×) to 0.235 g/cm^3. While an improvement over untreated aerogels was observed, it is likely that the low molecular weights of the polycyanoacrylate making up the coating limited improvement in mechanical strength relative to the unmodified aerogel. Efforts to test this hypothesis by reducing the number of initiating sites on the aerogel surfaces and increase the molecular weight of the polycyanoacrylates are underway.

Another unexpected characteristic of the treated aerogels was an increase in the surface hydrophobicity. While un-

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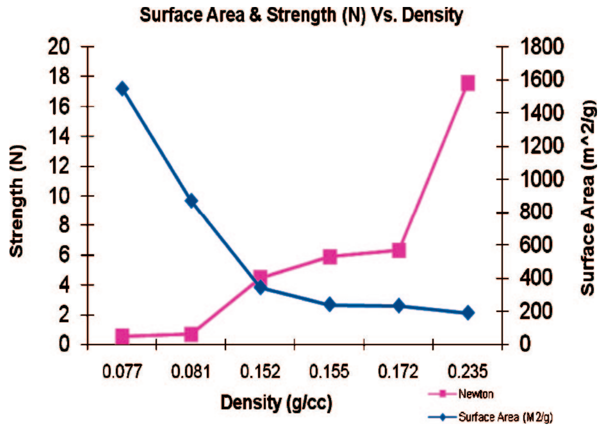

Figure 3. Resulting strengths and surface areas made to silica aerogels. Unmodified aerogel has density of 0.077 g/cm^3.

Figure 4. Hydrophobic polycyanoacrylate−silica nanocomposite aerogels float in water while unmodified silica aerogels adsorb water wet, burst into fragments and sink to the bottom of the container.

treated aerogels will immediately adsorb liquid water and break into many pieces, the CVD modified aerogels would float intact on water for months without wetting or cracking (Figure 4). By CVD modifying glass slides (as a model system) with polycyanoacrylates, we measured contact angles for water (129°) consistent with ultrahydrophobic surfaces.[14]

In summary, we were able to demonstrate that CVD and polymerization of methyl cyanoacrylate on silica aerogels are possible under STP conditions. Furthermore, we were able to show that CVD occurs evenly throughout monolithic aerogels. The resulting nanocomposites were stronger (30-fold) than untreated aerogels and inherently hydrophobic making them more likely to withstand degradation and weathering. These experiments also revealed the coatings were oligocyanoacrylates that were not chemically attached to the surface, suggesting that adsorbed water initiates the polymerization of the cyanoacrylates on the aerogel surface. By reducing the population of initiating species on the aerogel surfaces, it should be possible to prepare tough and strong nanocomposites based on high molecular weight polycyanoacrylates with significantly smaller increases in density and surface area.

Acknowledgment. We thank the University of Arizona, the Triffet Graduate fellowship foundation, and the Department of Energy (for work at Los Alamos National Laboratory LA-UR-07-6675) for supporting this work.

Supporting Information Available: Sol−gel preparations, CVD apparatus, NMR spectrum of solid state CVD coated aerogel, and data table of results from coatings (PDF). This material is available free of charge via the Internet at http: //pubs.acs.org.

CM703381E

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