J Mater Sci (2011) 46:6371–6377
DOI 10.1007/s10853-011-5584-7

Strong, low density, hexylene- and phenylene-bridged polysilsesquioxane aerogel–polycyanoacrylate composites

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Received: 18 May 2010 / Accepted: 20 September 2010 / Published online: 11 May 2011

Abstract Nanocomposite aerogels were prepared by chemical vapor deposition and polymerization of cyanoacrylate on the surface of bridged polysilsesquioxane aerogels. Phenylene- and hexylene-bridged aerogels were prepared by sol–gel polymerizations and supercritical carbon dioxide drying. Hydrophobic organic bridging groups in the polysilsesquioxane aerogels reduced the amount of adsorbed water available for initiating polymerizations and led to higher molecular weight polycyanoacrylate than was observed with silica aerogels. Densities increased as much as 65% due to the addition of the organic polymer, but the nanocomposite aerogels remained highly porous with surface areas between 440 and 750 m^2/g. Polycyanoacrylate–phenylene-bridged aerogel composites were the strongest with flexural strengths up to 780 kPa or 16-fold stronger than the untreated phenylene-bridged aerogels and five-fold stronger than a silica aerogel of the same density. The strongest polycyanoacrylate–hexylene-bridged aerogel composites had flexural strength of 285 kPa or ninefold stronger than the untreated hexylene-bridged aerogels and twice as strong as a silica aerogel of comparable density. The greater strength of the new composites is, in part, due to the greater strength of the bridged aerogels. However, higher molecular weight polycyanoacrylate, due to less surface water on the hydrophobic bridged aerogels, also contributes to the greater nanocomposite strengths.

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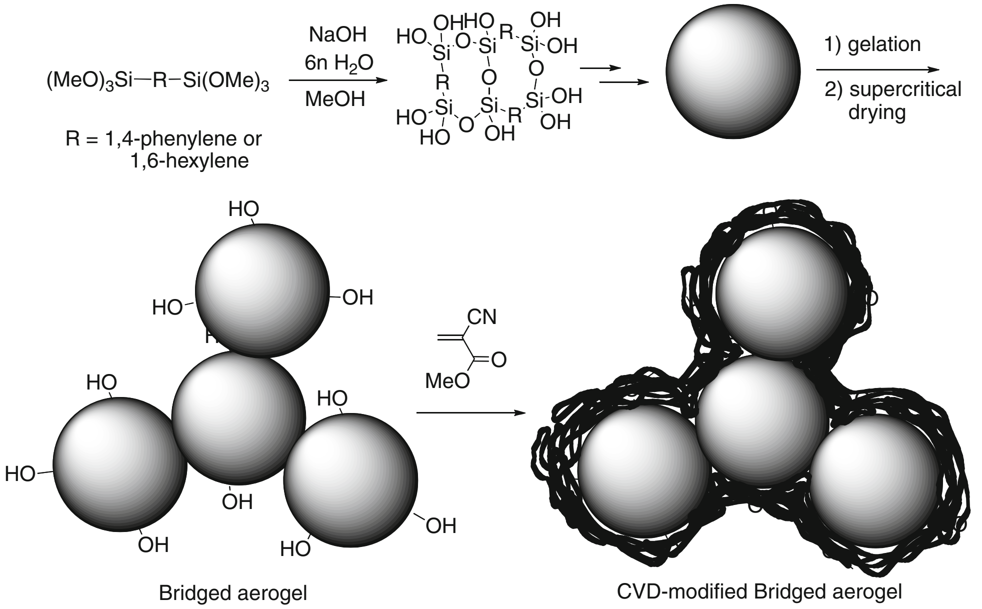
Introduction

Aerogels are a class of materials known for their exceptional low density, porosity, and high surface areas [1]. Aerogels would make remarkable thermal insulators [2], acoustical dampeners for noisy environments [3], and low-*k* dielectric materials [4], if not for their notorious fragility that makes handling and processing without breakage difficult [5]. This has spurred a variety of efforts to prepare stronger aerogels by incorporation of fibers [6, 7] or other fillers [8], Ostwald ripening [9] or addition of extra monomer before drying the gel [10]. A more recent approach has been to apply organic polymers as an adhesive to cement the colloidal particles in the aerogel together. This has been accomplished by polymerizing monomers from initiator-modified surfaces of gels before they are supercritically dried [11–15] or by chemical vapor deposition (CVD) of organic monomers onto dry aerogels [16]. CVD deposition and polymerization of methyl cyanoacrylate onto silica aerogels has resulted in improvement in aerogel strength. However, it was discovered that cyanoacrylate polymerization was initiated by surface adsorbed water and, due to the abundance of surface moisture, only low molecular weight cyanoacrylate oligomers were obtained. In order to reduce the concentration of surface initiators, relatively hydrophobic silica aerogels with aminated surfaces were prepared by copolymerizing tetramethoxysilane (TMOS) with 3-aminopropyltriethoxysilane and silating the residual silanols with trimethylsilyl groups. [17]. CVD treatment of these aminated silica aerogels with cyanoacrylate afforded covalently attached poly(methyl cyanoacrylate) that was significantly higher in molecular weight and substantial improvements in the flexural strength of the resulting composites compared with silica aerogels or CVD-modified silica aerogels of comparable density.



Scheme 1 Polymerization of hexylene- and phenylene-bridged monomers to gels and air-drying to supercritical drying to aerogels followed by CVD deposition and polymerization of methyl cyanoacrylate to afford strong, nanocomposite polycyanoacrylate-bridged polysilsesquioxane aerogels

While successful in improving mechanical properties, preparation of amine-modified, hydrophobic silica aerogels adds significant time to processing and inclusion of the amine monomer in the sol–gel polymerizations reduces the cross-link density such that the aerogels, *before CVD modification*, are weaker than silica gels without the amine groups [17]. Bridged polysilsesquioxanes, network materials composed of building blocks containing two silicons bound together through an organic bridging group and interconnected by up to three siloxane bonds per silicon (Scheme 1) [18–22], were selected to provide a more hydrophobic substrate for CVD without compromising on mechanical properties. Bridged polysilsesquioxanes readily form gels and can be supercritically dried to afford low-density aerogels [23–25]. The organic bridging groups are known to reduce adsorbed water without requiring surface modification. Since the organic groups are part of the network, the degree of cross-linking is high and a number of studies have reported mechanical properties superior to those of silica materials [26–30]. Here, we describe the preparation of cylindrical phenylene- and hexylene-bridged polysilsesquioxane aerogels, their CVD modification with methyl cyanoacrylate to afford new polymer–aerogel composites, and measurement of changes in aerogel porosity, density, and flexural strength with treatments.

Experimental

Materials

All reagents were used as received without further purification unless otherwise stated. Tetramethoxysilane (TMOS, 98%), anhydrous methanol (99.8%), anhydrous inhibitor-free tetrahydrofuran (THF, 99.9%) and 1,4-dibromobenzene (99%), and magnesium were purchased from the Aldrich Chemical Company. TMOS was distilled from molecular sieves before use in synthesis. 1,6-Bis(trimethoxysilyl)hexane (96%) was purchased from Gelest Inc.

Synthesis of 1,4-bis(trimethoxysilyl)benzene [22]

To a three-neck round bottom flask, magnesium (4.88 g, 0.201 mol) and a stir bar was added. The round bottom was equipped with a condenser, addition funnel, and glass stopper. The flask was then evacuated and flame dried. Once cooled to room temperature it was back-filled with argon followed by THF (100 mL) and distilled TMOS (75.0 g, 0.493 mol) were added by canula. To the addition funnel, 1,4-dibromobenzene (19.7 g, 0.0832 mol) was dissolved in THF (50 mL). The round bottom was placed into an oil bath at 70 °C and the 1,4-dibromobenzene solution was added drop-wise at a drop per second until 5% of the total volume was added. The solution began to become greenish-gray and the remaining dibromobenzene solution was added over 2 h. The reaction mixture was heated to reflux for 24 h. The salts were removed by filtration and the volatiles removed under reduced pressure. The resulting viscous oil was added to hexanes to precipitate remaining salts, which were removed by filtration, hexanes were removed under reduced pressure. The product was isolated by fractional distillation (178 °C at 300 mmHg) (short path condenser should be greater than 55 °C) to obtain 1,4-bis(trimethoxysilyl)benzene (13.3 g, 0.0418 mol, yield = 49.8%). MP 53–55 °C. (Lit. MP

52–54 °C) [22]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 4 H) δ 3.58 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.33, 132.51, 134.54; MSLRMS (EI); 318.09, 287.07, 227.04, 197.02, 167.05, 121.03, 91.02.

Preparation of phenylene-bridged aerogels

A solution containing 1,4-bis(trimethoxysilyl)benzene (0.456 g, 0.00143 mol, 0.4 M) in anhydrous methanol (1.8 mL) was mixed with a second solution containing aqueous 1N NaOH (0.155 g) in anhydrous methanol (1.8 mL) in a 4 mL poly(propylene) container at room temperature. The final volume of the solution was 3.6 mL. Gels formed within 10 min and were aged at room temperature for 48 h followed by 48 h at 50 °C at ambient pressure when syneresis was observed. After cooling to room temperature, the gels were placed in a Polaron autoclave in 100 mL methanol at 20 °C [23–25]. Liquid carbon dioxide was introduced while allowing gas to vent. Once the autoclave was filled with liquid carbon dioxide and methanol, both were allowed to mix together and permeate throughout the aerogels for 24 h. The methanol–carbon dioxide mixture was then replaced with pure liquid carbon dioxide by slowing venting while simultaneously introducing more liquid carbon dioxide over about 4–6 h. Then the system was closed and the temperature was raised to 36 °C. When the pressure reached 7.37 MPa, the outlet to the autoclave was carefully opened and carbon dioxide was vented just enough to keep the pressure between 7.37 and 9.65 MPa. The carbon dioxide was vented over 8 h to afford monolithic phenylene-bridged aerogel (0.291 ± 0.007 g, yield 115%, calculated for 100% condensation). ^{29}Si CP MAS-NMR (100 MHz) δ-63 (T^1), -71 (T^2), -79 (T^3); ^{13}C CP MAS NMR (100 MHz,) δ 238, 132, 38; IR (KBr) 3447, 3050, 2950, 1630, 1386, 1144, 1092, 1021, 912, 806, 658 cm^{-1}.

Preparation of hexylene-bridged silica aerogels

A solution containing 1,6-bis(trimethoxysilane)hexane (0.470 g, 0.00144 mol, 0.4 M) in anhydrous methanol (1.8 mL) was mixed with a second solution of the aqueous catalyst 1N NaOH (0.155 mL) in anhydrous methanol (1.8 mL) in a 4 mL poly(propylene) container at room temperature. The final volume was 3.6 mL. Gels formed within 40 min and were aged at room temperature for 48 h followed by 3 weeks at 50 °C at ambient pressure when syneresis was observed. After cooling to room temperature, the gels were dried using a standard supercritical carbon dioxide process [23–25] (vide supra) to obtain hexylene-bridged aerogels (0.281 ± 0.004 g, yield 106%). ^{29}Si CP MAS-NMR (100 MHz) δ-58 (T_1), -66 (T_2); SS ^{13}C CP MAS-NMR (100 MHz,) δ 37.4, 28.1, 17.7; IR (KBr) 3454, 2929, 2862, 1480, 1400, 1350, 1310, 1290, 1247, 1202, 1112, 1050, 924, 807 cm^{-1}.

Silica aerogel preparation

A solution containing tetramethoxysilane (0.548 g, 0.535 mL, 0.01 mol) in anhydrous methanol (1.8 mL) was mixed with a solution containing 1N ammonium hydroxide (0.259 mL) diluted to 1.8 mL with anhydrous methanol. Gels formed within half an hour of mixing the two solutions and were aged at room temperature for 48 h followed with 48 h at 50 °C at ambient pressure when syneresis was observed. After cooling to room temperature, the gels were dried using a standard supercritical carbon dioxide process [23–25] (vide supra) to afford transparent silica aerogels (0.234 ± 0.006 g, yield 108%). ^{29}Si CP MAS-NMR (100 MHz) δ-103 (Q_3), -113 (Q_4); IR (KBr) 3450, 2957, 2900, 2848, 1215, 1160, 1099, 1005, 924, 806, 664 cm^{-1}.

Instrumentation

Mechanical property measurements were determined using a three-point flexural compression test with an Instron 5540 series single column testing system with a 10 N load cell set with a 0.04 inch min^{-1} crosshead speed according to ASTM D790 and ASTM C1684. For each data point, four samples were prepared. Dry aerogel samples with KBr were ground using a mortar and pestle and pressed into a pellet, and infrared spectra were obtained with a Perkin Elmer FT-IR spectrometer. Surface area and pore sizes were determined by nitrogen adsorption porosimetry of one representative sample. Samples were degassed at 30 °C for 24 h under vacuum and analyzed with an Autosorb-1 porosimeter (Quantachrome Instruments) at 77 K. ^{29}Si NMR spectra were obtained on a Bruker 400 spectrometer, using cross-polarization and magic-angle spinning at 10 and 70 kHz ^{n}H decoupling. Solid ^{29}Si spectra were externally referenced to the silicon peak of the [tetrakis(trimethylsilyl)silane] (TTMSS) at −9.7 and −135 ppm [31]. Solid State ^{13}C NMR spectra were obtained on a Bruker 400 using cross-polarization and magic-angle spinning at 10 and 70 kHz ^{1}H decoupling. The samples were externally referenced to the carbon chemical shift of adamantine [31].

Results and discussion

Sol–gel polymerizations of the bridged monomers proceeded as described in earlier reports with gels forming within an hour. By aging the gels at 50 °C until syneresis occurred, it was possible to transfer the cylinders from their polymerization container into the autoclave for supercritical drying without damage. Phenylene-bridged polysilsesquioxane aerogels were transparent with a strong blue tint from Rayleigh scattering and were rigid and relatively inflexible. The hexylene-bridged aerogels were opaque, white, and flexible. Solid state ^{29}Si NMR and infrared spectroscopy on ground samples were consistent with phenylene- and hexylene-bridged polysilsesquioxanes [18–22].

Before CVD treatments were performed, the relative hydrophilicity of phenylene- and hexylene-bridged polysilsesquioxane aerogels after supercritical drying was examined. Water content remaining was determined by thermal gravimetric analysis (TGA) (Fig. 1). Loss in weight between room temperature and 225 °C corresponds to the adsorbed water on the aerogel [32, 33]. TGA analysis revealed that our silica aerogels possessed 5–10 wt% water. In contrast, the phenylene-bridged polysilsesquioxane aerogels contained, on average, less than 1% water by weight and the hexylene-bridged aerogels lost only ~0.2% mass up to 225 °C. Mass losses at higher temperatures (hexylene bridged: 350 °C, phenylene bridged: 470 °C) were due to decomposition of the organic bridging group [18–22].

Hydrophobicity of the bridged silsesquioxane aerogels was quantified by measuring the contact angles from 1 µL water droplets onto the surface of bridged polysilsesquioxane aerogels (Fig. 2). The contact angles for phenylene- and hexylene-bridged aerogels are 92° and 115°, respectively. The higher contact angle observed for hexylene-bridged aerogels is most likely due to a slightly higher degree of condensation [34]. In comparison, contact angles for these silica aerogels could not be determined due to the rapid adsorption into the aerogel pores. However, literature values for water contact angles on silica aerogels range between 20 and 30° [35]. Higher contact angles observed for bridged polysilsesquioxane aerogels confirms less water (initiator) remained in bridged polysilsesquioxane aerogels after supercritical drying.

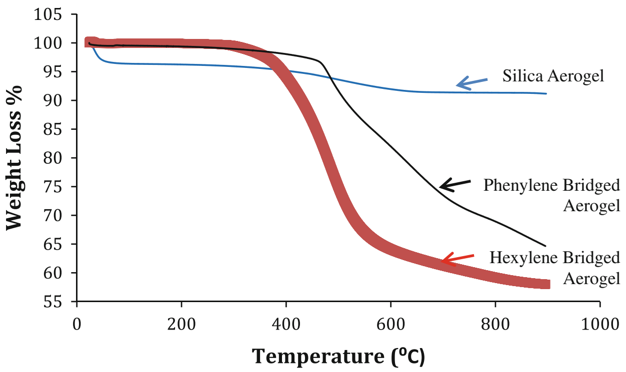


Fig. 1 TGA of bridged polysilsesquioxanes aerogels showed that hexylene- and phenylene-bridged silsesquioxane aerogels have lower water content than found with silica aerogels

CVD and polymerization of methyl cyanoacrylate was achieved using the same experimental parameters as previously described by Boday [11–15, 17]. In short, methyl cyanoacrylate was carried by dry nitrogen gas (0.1 L/min) through the vapor deposition system into the reaction chamber where either hexylene- or phenylene-bridged polysilsesquioxane aerogels were suspended. This arrangement allows for a constant (3 mg/h) deposition of the methyl cyanoacrylate on the aerogels' surfaces where adsorbed water initiates polymerization. This rate of deposition is slower than observed for silica aerogels (5 mg/h) and is consistent with a lower concentration of adsorbed water on the surface of bridged polysilsesquioxane aerogels than found with silica aerogels.

Because of the constant CVD rate, the amount of polycyanoacrylate deposited on the aerogels and the density of the resulting aerogel–polycyanoacrylate nanocomposites could be controlled by varying the deposition time. Polymerization of 0.4 M 1,4-bis(trimethoxysilyl)benzene or 1,6-bis(trimethoxysilyl)hexane, aging and supercritical drying led to the formation of aerogels with densities around 0.095 g/cm^3 [23–25]. CVD treatments were used to deposit up to 0.065 g/cm^3 polycyanoacrylate, increasing the density of the aerogels by a maximum two-thirds. At a deposition rate of 3 mg/h, it took 60 h to coat the aerogels with sufficient polycyanoacrylate to reach 0.162 g/cm^3.

Mechanical properties for the phenylene- and hexylene-bridged polysilsesquioxane and CVD-modified aerogels were determined by a three-point flexural bend beam analysis method [16, 17, 36–38]. Flexural strengths of the bridged aerogel composites are plotted against their density in Fig. 3. The plot of silica aerogel strength versus density provides a baseline for the contribution to flexural strength arising from additional material being added to the colloidal network.[1] The flexural strengths for the silica aerogels are in agreement with literature values providing validation for characterization of cylindrical aerogels with a 5:1 length: diameter ratio. Analysis of bridged aerogel poly(methyl cyanoacrylate) composites revealed that the flexural strength increases significantly as the density increases. The most dense phenylene-bridged CVD-modified aerogel (0.162 g/cm^3) had a flexural strength of 779.0 ± 53.0 kPa. This is 16 times stronger than the un-modified phenylene-bridged aerogel precursor (0.097 g/cm^3) and over *5 times stronger* than polymer-free silica aerogels of the same density. The phenylene-bridged composite is even *3 times stronger* than the CVD-modified aminated silica aerogel of the same density [17]. In contrast, the hexylene-bridged

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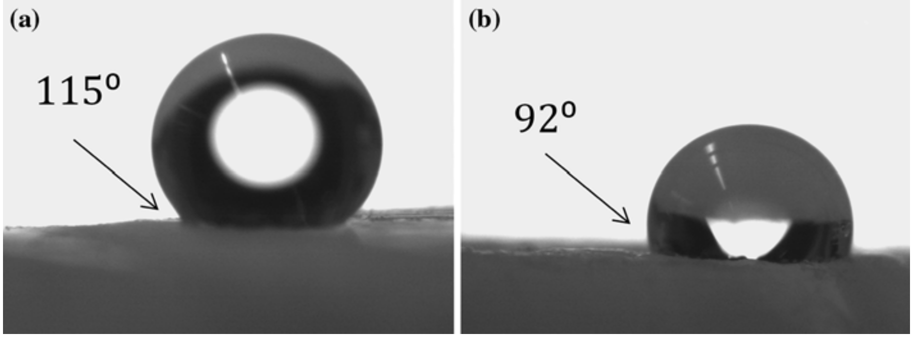
[1] Only two data points are shown for the mechanical properties of various density silica aerogels [17] with in the density range in Fig. 2. The plot extends to silica aerogels with densities as high as 0.215 g/cc, but to adequately show the mechanical properties of the bridged composites, the density range was reduced.

Fig. 2 Contact angle for a 1 μL water droplet on a hexylene-bridged polysilsesquioxane was found to be 115° (**a**). Phenylene-bridged polysilsesquioxane aerogels were found to have contact angles of 92° (**b**). These are significantly higher than silica aerogels



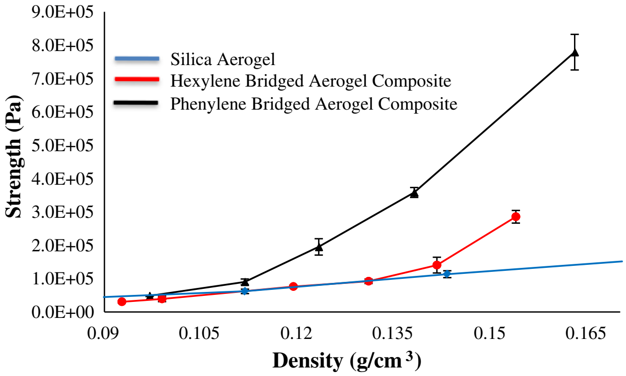


Fig. 3 Flexural strengths of the phenylene-bridged aerogels (*triangles*) are significantly stronger than hexylene-bridged (*circles*) aerogels, or polymer-free silica aerogels (*diamonds*) [22]. Mean values from 3 to 6 duplicate experiments are plotted along with their standard deviation

aerogel–polycyanoacrylate composites' flexural strengths were found to increase linearly with density and were nearly the same as the various polymer-free aerogels until densities above 0.135 g/cm^3 were reached. Unmodified hexylene-bridged aerogels were mechanically weaker than the same density silica aerogels. Flexural strengths of the hexylene-bridged aerogel at densities greater than 0.135 g/cm^3 increase more than what can be attributed to mass addition. The most dense hexylene-bridged aerogel composite (0.154 g/cm^3) had a flexural strength of 285.0 ± 18.0 kPa or *ninefold* stronger than the untreated hexylene-bridged aerogels and *2 times* as strong as an untreated silica aerogel of the same density. This is similar to flexural strengths of silica aerogel–poly(methyl cyanoacrylate) composites with similar densities [16].

As determined previously, methyl cyanoacrylate polymerization initiated by adsorbed water on the aerogels surface could be quantitatively removed by soxhlet extraction with acetone. Methyl cyanoacrylate polymerization within hexylene- and phenylene-bridged aerogels, we discovered that the poly(methyl cyanoacrylate) could be completely extracted. This demonstrates that the polymer was not covalently attached to surface and was initiated by adsorbed water. The molecular weight of extracted poly(methyl cyanoacrylate) was determined using matrix-assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectroscopy with an acidic matrix ensuring that depolymerization did not occur [39]. The molecular weight of poly(methyl cyanoacrylate) extracted from the bridged polysilsesquioxane aerogel composites increased with the CVD time, but in general was approximately 30% higher (DP = 13–45) than that extracted from silica aerogel composites (DP = 10–30) [16]. This is consistent with the reduction in the surface water due to the hydrophobic organic bridging groups. However, the poly(methyl cyanoacrylate) molecular weights were *lower* than that extracted from the CVD-modified, amine-modified aerogels (DP = 50–120) [17]. Based on this observation, coupling the higher molecular weight methyl cyanoacrylate than observed in CVD reinforcement of silica aerogels and a stronger phenylene-bridged aerogel scaffold, aerogels composites with greater strength resulted.

As with other CVD-modified aerogels, increases in density were accompanied with decreases in surface area (Table 1). Phenylene-bridged composite (0.162 g/cm^3) had a surface area of 750 m^2/g. This is a ~10% decrease in surface area from the polymer-free phenylene-bridged aerogel (807 m^2/g). A shift in the average pore diameter is observed from the deposition and polymerization of methyl cyanoacrylate. The observed shift in the average pore diameter is expected from filling smaller pores within the phenylene-bridged polysilsesquioxane aerogels. Polymer-free hexylene-bridged aerogels have a surface area of nearly 800 m^2/g. With methyl cyanoacrylate CVD, the surface area for the most dense (0.153 g/cm^3) hexylene-bridged aerogel composite decreased 47% to 423 m^2/g. Similarly, the average pore diameter shifted higher as result of the addition of poly(methyl cyanoacrylate) to the hexylene-bridged aerogel. In both, the reduction in surface area is significantly less than that observed with CVD treatment of silica aerogels [16, 17].

Table 1 Surface area, average pore size, and flexural strength results for the phenylene- and hexylene-bridged aerogels and composites

Sample	Density (g/cm^3)	Flexural strength (kPa)	Surface area (m^2/g)	Pore size (Å)
Polymer-free phenylene	0.097	48 ± 2	1080	165
Phenylene–cyanoacrylate	0.112	91 ± 9	808	169
Phenylene–cyanoacrylate	0.123	195 ± 24	790	185
Phenylene–cyanoacrylate	0.138	359 ± 14	760	181
Phenylene–cyanoacrylate	0.163	779 ± 53	748	210
Polymer-free hexylene	0.093	31 ± 3	778	160
Hexylene–cyanoacrylate	0.099	39 ± 8	595	239
Hexylene–cyanoacrylate	0.119	77 ± 4	569	232
Hexylene–cyanoacrylate	0.131	92 ± 6	504	230
Hexylene–cyanoacrylate	0.142	113 ± 24	443	212
Hexylene–cyanoacrylate	0.154	285 ± 18	423	225
Polymer-free silica aerogel	0.092	36 ± 3	1330	132

Each composition was prepared and tested in at least triplicate

Conclusions

The CVD of methyl cyanoacrylate onto hexylene-and phenylene-bridged aerogels provides a method to prepare strong, low-density, and polycyanoacrylate–silica aerogel composites. It was determined that the hexylene- and phenylene-bridged aerogels contain >75% less water than silica aerogels, which reduces the initiator concentration and allows for higher molecular weight polymer to be coated on the aerogel particles. Coupling the higher molecular weight and, in the case of the phenylene-bridged aerogel, a stronger, bridged aerogel scaffold, composites with very low densities and exceptional improvements in the bulk mechanical properties were realized. The strongest composite was the 0.162 g/cm^3 polycyanoacrylate–phenylene-bridged aerogel, 5 times stronger than the polymer-free silica aerogel of the same density, while retaining many of the aerogel's physical properties.

Acknowledgements We thank the Energy Materials Corp. for supporting this study. We also thank the University of Arizona, Marcus Perry and Mike Read from the Chemistry Instrumentation and Electronics Facility, University Spectroscopy and Imaging Facility, Mass Spectroscopy Facility, and Brian Cherry from the Department of Chemistry at Arizona State University for solids NMR work.

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