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Polymer/Inorganic Superhydrophobic Surfaces

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Polymer/Inorganic Superhydrophobic Surfaces

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1 Abstract

We have designed and built electrostatically actuated microvalves compatible with integration into a PDMS based microfluidic system. The key innovation for electrostatic actuation was the incorporation of carbon nanotubes into the PDMS valve membrane, allowing for electrostatic charging of the PDMS layer and subsequent discharging, while still allowing for significant distention of the valveseat for low voltage control of the system. Nanoparticles were applied to semi-cured PDMS using a stamp transfer method, and then cured fully to make the valve seats. DC actuation in air of these valves yielded operational voltages as low as 15V, by using a supporting structure above the valve seat that allowed sufficient restoring forces to be applied while not enhancing actuation forces to raise the valve actuation potential. Both actuate to open and actuate to close valves have been demonstrated, and integrated into a microfluidic platform, and demonstrated fluidic control using electrostatic valves.

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2 Introduction

Several potential special operations WFO sponsors (Naval Special Warfare Group FOUR, Joint Special Operations Program) have expressed an interest in Sandia's R&D 100 Award winning superhydrophobic (SH) coating for applications to weapons and visual augmentation systems. (It would also have wider applications across the DoD.) However, the durability of the coating has not been developed to the point where technology development can be supported by these sponsors. This late-start LDRD investigated improvements in durability. We proposed to develop a coating capable of producing a thin superhydrophobic coating that is optically clear, but is more tribologically robust than current techniques. Other methods for superhydrophobic coatings with improved environmental resistance rely on high temperature steps and harsh chemical treatments, making the coating applicable only to surfaces that can withstand these processes, and with significant loss in transparency of the coating. In contrast, our material relies on sol-gel processing, is coated at room temperature, uses alcohols for solvents, and produces an optical quality coating that has contact angles exceeding 170º. However, our methods of achieving superhydrophobic surfaces involve a nanostructured surface with chemical treatments and these geometries make the coatings very fragile.

We studied the effect of adding polymeric based agents to the silica matrix before and after gelation. Before gelation, vinyl polymers were added to the silica sol to allow for the incorporation of the vinyl groups into the silica backbone as gelation occurs. The after gelation mixtures were made by adding polymers

with varying chain lengths to fully processed and sonicated gels. We also studied the effect sonication has on the sol as it undergoes gelation. Sonicating the sols prior to gelation should reduce the fractality of the gel ultimately creating a less porous film. This reduction in porosity may lead to on increase in the film's robustness.

3 Experimental and Results

Two main silica precursors were used in this studied tetraethylorthosilcate (TEOS) also referred to as B2 and tetramethylorthosilicate (TMOS). These bulk aerogel solutions were processed according to established procedures for the standard B2 and TMOS spring-back aerogel recipes.

3.1 B2 studies

B2 stock was made by combining starting materials in the following ratio:

- 61 ml TEOS
- 61 ml absolute ethanol
- 4.87 ml H_2O
- 0.2 ml 1 N hydrochloric acid (HCl)

This solution was stirred at 250 rpm at 60°C for 90 minutes. The fresh solution was then used to make gels with the following composition:

- 10 ml B2 stock
- 44 ml ethanol
- 1 ml 0.050 M NH_4OH (ammonium hydroxide)

The sol was then allowed to gel and age at 50°C for 1 week, and processed according to the following steps:

- 2 rinses of 25 ml ethanol for a minimum of 2 hours at 50°C
- 2 rinses of 25 ml hexane for a minimum of 2 hours at 50°C

- Surface derivitization using 25 ml of 6% (v/v) HMDS (hexamethyldisalizane) and 2-4% (v/v) APS (aminopropylsilane) in hexane for 20 hours at 50°C
- 2 rinses of 25 ml hexane for a minimum of 1 hour at 50°C
- 2 rinses of 25 ml ethanol for a minimum of 1 hour at 50°C

The gels were then drained, and mixed with ethanol in the ratio of 35 g of gel to 10 ml of ethanol. The diluted gels were sonicated for 20 minutes, and then coated onto Si substrates at 2000 rpm to determine initial values for refractive index, contact angle, and thickness.

After sonication, a small aliquot of aerogel solution was taken and heated to evaporate all the solvent then weighed to determine the mass concentration of aerogel (14 mg/ml). Polymer solutions (20 mg/ml mass concentration in methylene chloride) were added to the aerogel stock at calculated volume ratios to obtain coating solutions with the desired mass percentage of polymer in the final film. Methylene chloride was used for the polymer stock solution instead of toluene to improve polymer solubility.

Shear modulus was measured by deposition of aerogel films on 5 MHz shear-mode quartz crystal microbalance (QCM) devices (Maxtek model SC-501-1) by spin coating at 2000 rpm in ambient air followed by measurement of S11 reflection parameters using an HP 8751A network analyzer equipped with an HP 87512A transmission/reflection test set. Impedance of the test fixture and QCM cell cable were accounted for by calibration of the network analyzer before each experiment. Data was fit to a model for a finite viscoelastic film using MathCad programs written by Darren Branch (Sandia National Laboratories). First, impedance parameters were determined for the bare QCM substrate, with these

values exported to a second routine for fitting of QCM data with the film present. Data output was in the form of the storage and loss modulus, *G'* and *G''*. The shear modulus G_0 was then determined by solution of

$$G' = \frac{G_0(\omega\theta_0)^2}{1+(\omega\theta_0)^2} \text{ and } G'' = \frac{G_0(\omega\theta_0)}{1+(\omega\theta_0)^2}$$

where ω is the frequency (here 5 MHz), and θ_0 is the relaxation time. One limitation of this method is that the film density, a necessary input, is unknown. However, we find that use of an approximate density (determined by ellipsometry) yields a number suitable for examination of data trends.

3.1.1 Effect of polymer/aerogel mass ratio

Poly(methyl methacrylate) (PMMA, MW = 25,000) was added to aerogel solutions at a mass ratio (to total film mass) of 0, 15, and 26%, similar to the range examined in previous, work (D. Kissel, doctorate thesis, 2008). **Figure 1** shows that, as expected, shear modulus increases with concentration, accompanied by a significant decrease in film contact angle.

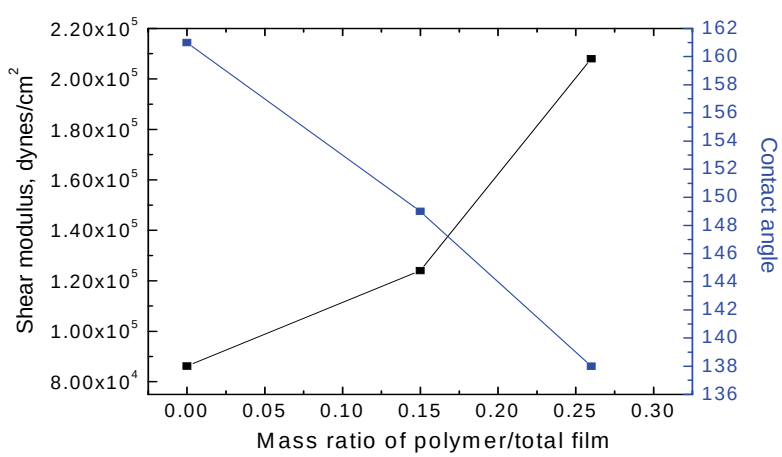

Figure 1. Effect of PMMA/total film mass ratio on shear modulus and contact angle in aerogel films.

3.1.2 Effect of polymer molecular weight

The effect of polymer molecular weight was also investigated using PMMA/aerogel films at a PMMA mass ratio of 26% (**Figure 2**). Surprisingly, an increase in PMMA MW reduced the shear modulus, while recovering some of the hydrophobicity lost by addition of polymer

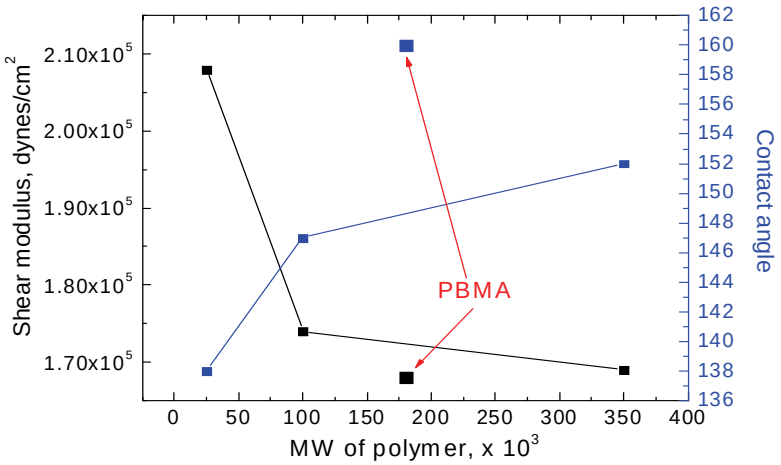

Figure 2. Effect of PMMA molecular weight on shear modulus and contact angle for composite polymer/aerogel films, at a constant mass ratio of 26% PMMA/ to the total film mass. Also shown are points for a PBMA film (MW of PBMA = 180,000) with the same polymer mass ratio.

3.1.3 Optical properties of polymer-modified SH films

The effect of polymer addition on the optical transparency of the above SH films was also investigated. Polymer/aerogel films were deposited by spin coating at 2000 rpm onto glass substrates, and the transmission spectra taken with the coated side of the substrate facing the light source of the spectrometer. The percent transmission at 500 nm was taken as a measure of optical clarity:

Table I. % Transmission at 500nm of aerogel/PMMA films

Polymer added to 1.0ml SH solution	**% Transmission at 500nm**
None	92.0%
2.5 mg PMMA, MW = 25,000	87.8%
5 mg PMMA, MW = 25,000	85.8%
5 mg PMMA, MW = 100,000	88.5%
5 mg PMMA, MW = 350,000	2.1%
5 mg poly(n-butyl methacrylate)	85.5%

From this data, it is clear that addition of PMMA with a molecular weight of 25,000 leads to only a minor reduction in optical clarity of SH films. Increasing the molecular weight of PMMA to 100,000 also has little effect on optical properties. However, PMMA with a MW of 350,000 shows significant cloudiness, yielding a %T of only ca. 2%. Use of poly(n-butyl methacrylate) as the polymer additive reduces the transmission by approximately the same amount as PMMA.

3.1.4 Use of polymers other than PMMA

Poly(styrene) (PS, MW range = 125,000 to 250,000) and poly(n-butyl methacrylate) (PBMA, MW = 180,000) were also tested for suitability as stiffening agents inside aerogel films at a mass ratio of 26%. PS, although easily soluble in methylene chloride, precipitated from solution upon addition of the PS stock to the ethanol-based aerogel sol. QCM analysis of the resulting film yielded unreasonable values for *G'* and *G''*. PMBA, however, resulted in films with similar mechanical properties as would be expected from use of PMMA with the same molecular weight (**Figure 2**) but greatly improved contact angle,

presumably due to the increased hydrophobicity of the polymer from the larger side chain.

Use of methyl ethyl ketone (MEK) in the polymer stock instead of methylene chloride was also tested. MEK was selected for a comparison as it is a good solvent for polymers, while having a volatility similar to that of ethanol (BP = 79.6°C for MEK, 78.4°C for ethanol, 40°C for methylene chloride). Compared to PMMA/aerogel films using methylene chloride-based polymer stock solutions at the same polymer mass ratio (26%), use of MEK yielded a film with increased contact angle (145° vs. 138°), but greatly reduced shear modulus (56,600 dynes/cm^2 instead of 208,000 dynes/cm^2).

3.1.5 Poly(n-hexyl methacrylate)

From the above contact angle and QCM study of polymer addition to aerogel-based SH films, it is apparent that the ideal polymer additive is of low molecular weight, and possesses a hydrophobic side chain. Based upon these characteristics, we hypothesized that poly(n-hexyl methacrylate) (PHMA) would be a good candidate for improving the mechanical properties of SH films, while maintaining superhydrophobicity as the ratio of polymer to total film mass increased. To test this hypothesis, we synthesized PHBA by addition of a thermal initiator, azobisisobutyronitrile (AIBN), to n-hexyl methacrylate at mass ratios of 0.3, 1, and 3%, presumably producing polymers with differing average molecular weights. Addition of the resulting polymer to aerogel solutions (mass ratio = 25%) yielded contact angles of between 145° and 150°. The optical properties of these films were very poor, however (%T from 15 to 2%), presumably due to phase separation of the polymer. This phase separation

made a fit of QCM data difficult, preventing a quantitative assessment of mechanical properties in aerogel/PHMA films.

3.1.6 Addition of bis(triethoxysilyl)ethane (BTESE) to SH aerogel formulations

Another series of experiments in strengthening our aerogel films were based upon the addition of a hexafunctional silane (BTESE) to the standard aerogel recipe; it was believed that the extra bonds formed relative to tetrafunctional silanes such as TEOS would strengthen the aerogel network. 1, 2, 5, or 10 mmol BTESE was added to the standard aerogel recipe described above and allowed to gel. With 1 mmol BTESE added, the aerogel films were not superhydrophobic (CA less than 100°). Films made from solutions including 2 or 5 mmol BTESE did not form a gel with sufficient integrity for processing into a SH material. However, after rinsing of the film in DI water, films made from solutions where 10 mmol of BTESE was added were SH, with contact angles above 160°. However, casual investigation of the film toughness did not show any apparent increase in mechanical properties relative to films made without BTESE.

3.1.7 Cross-linkable SH films incorporating [3-(trimethoxysilyl)propyl methacrylate] (3-(TMS)PM)

Finally, a strategy of adding polymerizable cross-linking groups to the aerogel network was attempted, but again with little success in increasing film toughness or maintaining surface superhydrophobicity. After gelation, a standard recipe gel was split into 4 equal (ca. 12 ml) portions. 1 to 20 mmol of 3-(TMS)PM was added to each portion, and allowed to react with the silica surface before further gel processing with HMDS. As deposited, the aerogel films made from

these solutions had contact angles of between 135° to 140°. Addition of 1% AIBN, a thermal polymerization initiator, to the aerogel solutions did not significantly affect the contact angle of deposited films (again, this angle ranged between 135 and 140°); heating of the films containing AIBN to 150° C did not result in any changes in contact angle or, as determined by QCM measurements, shear modulus, suggesting that no polymerization had occurred within the film.

3.2 TMOS studies

Bulk TMOS sols were made combining starting materials in the following ratio.

- 4.45 ml TMOS
- 4.14 ml Methanol
- 40.77 ml diH_2O
- 0.12 ml 1.0N HCL

The sol was then allowed to gel and age at 50°C for 1 week, and processed according to the following steps:

- 2 rinses of 50 ml hexane for a minimum of 2 hours at 50°C
- Surface derivitization using 25 ml of trichlorosilane (TMCS) for 8 hours at 50°C
- 2 rinses of 50 ml hexane for a minimum of 1 hour at 50°C
- 2 rinses of 50 ml ethanol for a minimum of 1 hour at 50°C

The gels were then drained, and mixed with ethanol in the ratio of 35 g of gel to 35 ml of ethanol. The diluted gels were sonicated for 20 minutes, and then coated onto Si substrates at 2000 rpm to determine initial values for refractive index, contact angle, and thickness.

3.2.1 Sonication pre-gelation

The effect of sonication pre-gelation was investigated using TMOS sols made according to the above route. Immediately after mixing, the sols were subjected to sonication via a horn or bath and then three times a day afterwards until gelation occured 3 days later. After gelation the gels were processed as above. Spin coated films @ 2000 rpm possesed CA angles greater than 160° with refractive indexes between 1.08 and 1.10. The horn sonicated gels demonstrated better resilience to a simple wipe test than did the bath sonicated, and both appeared to perform better than the standard TMOS recipe.

3.2.2 VTMS TMOS gels

Standard techniques used for strengthening superhydrophobic aerogel coatings involve preparing a superhydrophobic aerogel coating solution and reinforcing the structure with a polymer either during the coating process or after deposition of the aerogel. This procedure allows for the placement of polymerizable moieties in the aerogel matrix during the initial synthesis. The raw gels were then derivatized using TMCS and sonicated in the same manner as the initial formulation. Gels were made according to the recipes in Table II. Samples numbers 1, 2, and 3 gelled within 6 days at 50°C while Sample 4 never gelled.

Table II. Volume Fractions of Components for TMOS / VTMS gels

Sample no.	TMOS	VTMS	MeOH	DI H2O	1.0N HCl
1 (10%)	0.088984	0.010175	0.083176	0.815265	0.002399
2 (20%)	0.079075	0.020344	0.083152	0.815031	0.002399
3 (30%)	0.069170	0.030508	0.083128	0.814796	0.002398
4 (50%)	0.049379	0.050817	0.083080	0.814328	0.002397

Once sonicated, methyl methacrylate (MMA) was added to VTMS sols in volume percents ranging from 0-20%. Figure 3 shows the film's contact angle, refractive index, and thickness as it relates to the volume percent of MMA. The 30% VTMS sols were found to exhibit the highest contact angle (>160° for all samples), the lowest refractive index (1.08) and to follow the trend of a reduction in the film's thickness as concentration of MMA increases. Figure 4 shows the percent transmission (%T) of the coated films. All the films show higher %T than the uncoated substrate. This is due to the difference in refractive indexes (RI) between the blank (air/substrate) and the sample (air/film/substrate) demonstrated by the following equation:

$$R = \frac{\left(n^1 - n\right)^2}{\left(n^1 + n\right)^2} \qquad \%T = 100 - 100R$$

where R is the amount of non-transmitted light , n^1 and n are the RI of materials #1 and #2. Air has an RI of 1.00 and the RI for a microscope slide is 1.51. Solving the above equation and %T = 95.9%. Using 1.08 as the RI of our 30% VTMS film and subtracting the RI's for film/substrate and air/film interfaces, one obtains a %T = 97.1%.

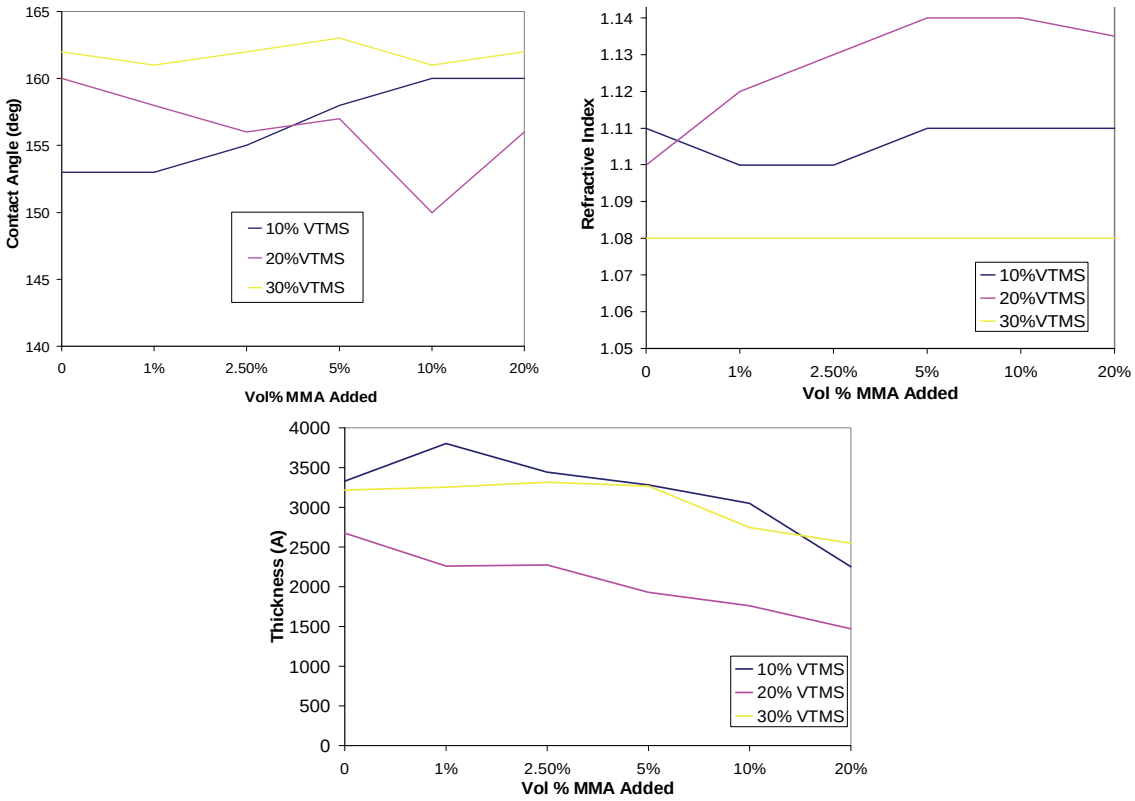

Figure 3. CA(top left), RI(top right), and film thickness (bottom) all with respect to the vol% of MMA added.

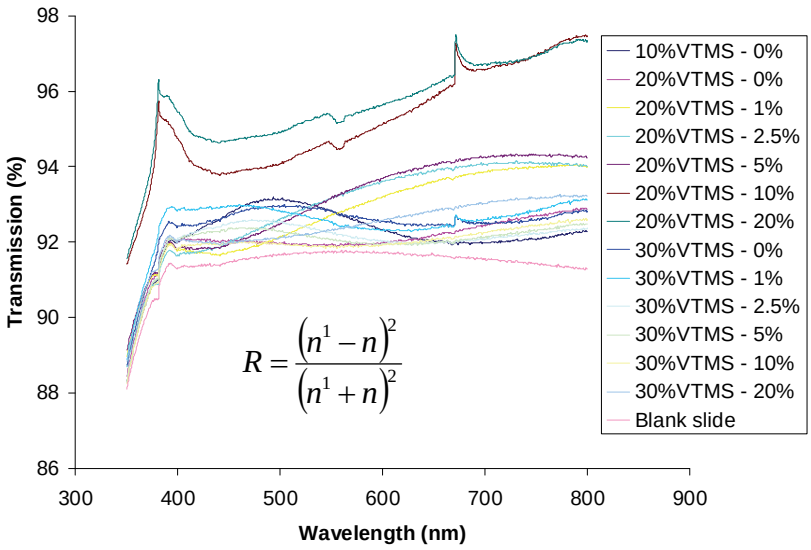

Figure 4. Percent transmission (%T) of spin-coated VTMS / MMA films. The equation shows why the %T of the film is greater than that of the uncoated slide.

3.2.3 TMOS / Iso-Butyl Methacrylate sols

TMOS gels were processed and sonicated following the initial recipe above. Volume percents ranging from 13-30% of iso-butyl methacrylate / MMA copolymers were added to 4ml of fully prepared TMOS sol. A 13% film spin coated at 2000 rpm possessed a contact angle of 161°. After rubbing with a Kimwipe the contact angle was 125°. Although the CA decreased, the continued presence of aerogel film is indicated by a CA above that of a uncoated wafer which has a CA < 90°. Table III shows the change in contact angle after rubbing for each of the varying vol% films. The films show increased durability with higher vol% of copolymer, but the CA values are reduced to a point where the films are no longer considered superhydrophobic (CA>150°). To determine the adhesion of the film to the substrate, a scotch tape test was conducted. This test is done by pressing a piece of scotch tape onto the coated aerogel film and then simply pulling the tape away. The samples showed minimal signs of damage after tape lift-off indicating that the aerogel film was more resilient to uniaxial stress than shear stress.

Table III. Contact angle change for a TMOS iso-butyl methacrylate after rubbing with a Kimwipe.

Volume of Copolymer added	Vol% Polymer	Initial CA (deg)	CA after rubbing (deg)
0.6ml	13.0%	162	125
0.8ml	16.7%	160	130
1.0ml	20.0%	159	125
1.2ml	23.0%	162	130
1.4ml	26.0%	154	132
1.6ml	28.6%	146	137
1.8ml	31.0%	147	138

4 Conclusions

A broad array of operations was investigated to improve the properties of superhydrophobic aerogel coatings. Strategies were applied to both TEOS and TMOS derived aerogels. Both types of aerogel were found to respond similarly to attempts at improving the material properties despite processing differences. As well as building on previous work, involving the addition of polymers to fully-processed coating solutions, a variety of new polymers were investigated for post-processing addition. QCM measurements made on these coatings found that the effect of increasing polymer content was twofold. Shear modulus increased and contact angle decreased with increasing PMMA concentrations. Examining different molecular weights of polymer showed that lower molecular weight polymers provide the best combination of durability enhancement and optical clarity. Better understanding post-processing polymer addition could be improved by visualizing the material using SEM or other microscopy techniques. Polymers other than methacrylates which posses a better combination of hydrophobicity and optical clarity could also be investigated. Pre-gelation strategies were also employed to modify the material. Techniques include both horn and bath sonication, and the successful incorporation of vinyl polymer groups into the silica aerogel backbone. Horn sonication was found to moderately improve the durability of the material. Incorporation of vinyl groups was used as a means for adding functionality to the silica backbone. The functionality could be utilized for improving durability by means of chemically

grafting polymer to the silica backbone. Functionality could also be exploited for other novel effects and is an area of interest for further research.

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