



Rapid fabrication of cross-linked silica aerogel by laser induced gelation



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ABSTRACT

A method for rapid fabrication of polymer cross-linked silica aerogel through laser induced photo-gelation and the effect of pre-heating, irradiation conditions, and gelation solvent on the structural and mechanical properties of the resulting aerogel material is presented here. An ethanolic solution of an alkoxy silane (tetraorthosilicate, TEOS), a monomer (hexanedioldiacrylate, HDDA), a visible-light free-radical photoinitiator (Eosin Y) and a tertiary amine (as co-initiator and pH modifier), was prepared. The solution was irradiated with a laser beam, and the energy liberated by the polymerization reactions induced gelation in a matter of seconds. The alcogel was then dried into aerogel using the ethanol-water (or acetone-water) azeotrope mixture as a drying fluid. It was observed that pre-heated solutions gelled instantly and the resulting aerogels showed density, Young's modulus and surface area values comparable to those of aerogels produced through conventional methods. The solutions without pre-heating gelled relatively slowly and yielded composites with Young's modulus values about 3 times and surface areas about 1.5 times smaller than the pre-heated samples. The replacement of ethanol with acetone as a gelation solvent accelerated gelation; however, the composites shrank about 2 times more than samples prepared using ethanol and, consequently, had higher densities and moduli and decreased surface areas. The potential exists for mold-free and rapid fabrication of bulk or thin film aerogel structures using this method to open new avenues for their application in areas such as 3D printing.

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1. Introduction

Silica aerogels are unique, porous materials consisting of 90% air and less than 10% solid silica in the form of a highly cross-linked network structure. The composition and structure of aerogels is a unique combination of high surface area, low density and extremely low thermal conductivity. Aerogels have thus been considered for applications in many fields including thermal insulation [1–3], environmental remediation [4,5], catalysis [6–8] and space exploration [9]. Aerogels, however, have not been widely commercialized due to their fragile nature and lengthy synthesis procedures. The fragility issues has been resolved to a reasonable extent by cross-linking the skeletal oxide nanoparticles with

polymers, [10] as cross-linking significantly improves mechanical strength without overly compromising porosity. A conventionally lengthy synthesis process, consisting of following steps, is the other major concern. The first step is the preparation of a wet gel which can take hours to several days' time. The wet gel, after hours of aging, has to go through a lengthy solvent exchange process. Finally, ambient pressure or supercritical drying are used to transform it to an aerogel. The drying, being a capillary forces driven phenomenon, consumes hours to a few days' time. To reduce capillary forces, which is the major cause of monolith's cracking during drying, the gelation solvent is exchanged with supercritical (SC) CO₂. However, SC CO₂ drying is considered impractical for large-scale applications as it involves multiple, time-consuming solvent exchanges. Drying issues have been partially addressed by Schwertfeger et al. [11], who diffused a hydrophobic silane through monoliths to reduce the strength of the interaction between pore walls and gelation solvent. This method, however, requires a diffusion step, which is time-consuming and limits its use to monoliths with one dimension

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smaller than 1 cm. More recently, the groups of Anderson and Carroll [12] and our own group [13] developed drying techniques that employ SC ethanol and do not require any solvent exchange steps.

Even with these improvements, a processing bottleneck is the slow synthesis of wet gels. Gelation times depend strongly on precursor concentration, temperature and pH and, in most cases, are on the order of tens of minutes to hours. After gelation, wet gels need to be cured for hours to days to strengthen the silica network. Thus a rapid method that produces robust wet gel in a very short time is needed to shorten the overall process of aerogel fabrication.

Here, we present a method that allows instantaneous fabrication of alcogel monoliths which can then be dried without any need for curing or solvent exchanges. In our method, a precursor solution of an alkoxide, a monomer and a visible-light photo-initiator is prepared and illuminated with a high intensity laser beam that starts free-radical polymerization and triggers gelation. The role of various parameters like heat of polymerization, pre-heating the solution, intensity of laser beam, gelation solvents and addition of amine in triggering the gelation has also been explored. Since an ethanol-water azeotrope (or acetone-water mixture) is used as a gelation solvent in this one-pot synthesis, wet gel is dried immediately after gelation using the technique developed by our group [13]. The rapid gelation and immediate drying allows for the fabrication of aerogel in approximately 90 min, most of which is spent to heat and cool the supercritical drier. An important aspect of this technique is that it can be extended to fabricate patterned objects and 3D structures of aerogels using masking techniques without the need for any molds.

2. Experimental

2.1. Chemicals

Reagent-grade tetraethyl orthosilicate (TEOS), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), trimethoxysilylpropyl methacrylate (MTMS), methyldiethanolethylamine (Amine), Eosin Y were purchased from Acros Organics. Hexanedioldiacrylate (HDDA) was purchased from Sigma–Aldrich. All reagents were used as received. The ethanol–water azeotrope mixture (containing 4.4% water and 95.6% pure ethanol by volume) was used as gelation solvent and as supercritical fluid in the drying process for the samples prepared in ethanol, whereas the acetone–water mixture (with the same water content) was used for the samples prepared in acetone. Unless stated otherwise, all references to ethanol or acetone in this manuscript refer to their respective water-mixtures.

2.2. Illumination conditions

A 2 Watt, continuous wave, diode-pumped solid-state laser emitting light at a wavelength of 532 nm was employed in this study. In all experiments, except where power level is mentioned, samples were exposed to the laser source operating at full power. The exposure times ranged from a few seconds to a few minutes as specified in the following sections. Experiments were also conducted at 75% and 50% of the maximum power of the laser source to find effect of power on gelation. The experiments performed below 50% of full power are not reported due to their limited practical significance. To illustrate this, illumination of the sample at different power levels is shown in Fig. S1. Laser power below 50% was not sufficient to illuminate the sample appropriately. Consequently, the gelation proceeded very slowly and non-uniformly. Illumination with a full intensity beam induced gelation instantly throughout the monolith. No vertical or rotational movement of the sample was required. Although samples gelled

rapidly, they were rotated and moved vertically to ensure uniform gelation at 75% and 50% of maximum power levels.

2.3. Preparation of precursor solutions

Two solutions were prepared and kept in separate polypropylene containers before mixing. Solution A (SA) was prepared by mixing 0.88 ml (4.0 mmol) of TEOS, 0.04 ml (0.2 mmol) of MTMS and 1.85 ml of the ethanol-water azeotrope mixture, into which $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ had been dissolved (concentration: 1.4 mmol/l). Solution B (SB) was prepared by mixing 0.15 ml (0.87 μmol) of Eosin Y, 0.05 ml (0.434 mmol) of amine, 1.12 ml (5.0 mmol) of HDDA and 0.5 ml of the ethanol-water azeotrope. Eosin Y, which absorbs in the green region of the visible spectrum, was used as the photo-initiator and the tertiary amine acted as co-initiator, and pH modifier. Upon light absorption, charge is transferred between Eosin Y and the amine, resulting in a reduced radical dye and a radical capable of initiating polymerization [14,15]. Typical exposure time ranged from 30 s to 120 s, and the dose in terms of photon bombarded was 1.6×10^{20} to 6.4×10^{20} photons, when the beam intensity at sample location was 0.16 W/mm². Processing conditions were varied as described below and illustrated in Fig. 1. Sample preparation conditions are indicated using the following abbreviations. Pe (pre) indicates samples irradiated prior to gelation; Pt (post) indicates samples irradiated post-gelation; Hy indicates that samples were pre-heated before irradiation; Hn indicates that samples were not heated before gelation; and Ac indicates samples prepared in acetone as the gelation solvent and as supercritical fluid.

2.3.1. Sample preparation without pre-heating and pre-gelation exposure (PeHn)

SA was kept at room temperature for 60 min to ensure hydrolysis of the alkoxide. SB (also kept at room temperature) was mixed with SA. The solution was then transferred into a mold and immediately exposed to a laser beam. Gelation started immediately in the exposed region and spread throughout the sample within about 2 min. Note: all molds used in our experiments were plastic syringes with an inner diameter of 12.5 mm and with liquid column height of 30 mm.

2.3.2. Sample preparation by pre-heating and pre-gelation exposure (PeHy)

SA and SB were separately heated and kept at 50 °C for 5 min, and then mixed. The solution was transferred into a mold and irradiated immediately. Gelation started without any noticeable delay in the illuminated region and spread through the sample in less than a minute.

2.3.3. Sample preparation by room temperature post-gelation exposure (PtHn)

SA was kept at room temperature for 60 min and then mixed with SB, which had also been kept at room temperature. The mixed solutions was then transferred into the mold where gelation occurred within about 60 min. The gelled sample was irradiated with laser beam for 4 min to initiate photopolymerization.

2.3.4. Sample preparation by pre-heating and post-gelation exposure (PtHy)

SA and SB were separately heated, kept at 50 °C for 5 min and then mixed. The solution was then transferred into the mold where it gelled within 2 min. The gelled sample was then exposed to laser beam for 4 min to initiate photopolymerization.

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