

Elastic and Superhydrophobic Monolithic Methyltrimethoxysilane-based Silica Aerogels by Two-step Sol-gel Process

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Abstract: The flexible and superhydrophobic properties of silica aerogels are extremely important material for thermal insulation and oil spill cleanup applications for their long-term use. Flexible silica aerogels were synthesized by using a two-step sol-gel process with precursors, methyltrimethoxysilane (MTMS) followed by supercritical drying. Silica aerogels were prepared at different molar ratio of methanol to MTMS (M). It was observed that the silica aerogels prepared at M=28 were monolithic but inelastic in nature, however, for M=35, the obtained aerogels were monolithic, elastic in nature with less shrinkage. The microstructural studies were carried out using scanning electron microscopy and surface area measurements. The hydrophobicity was confirmed by Fourier transform Infrared spectroscopy and water contact angle measurements. The detailed insight mechanism for flexible nature of silica aerogels and hydrophobic behavior were studied.

Keywords: Silica aerogel, flexible, hydrophobic, methyltrimethoxysilane, sol-gel process

1. Introduction

Silica aerogels are solids with open foam-type structures generally derived using sol-gel process followed by supercritical drying. Silica aerogels possess unique properties such as low density (0.04 g/cm³), high porosity (~95%), low thermal conductivity (0.04 W/mK), and high surface area.^{1,2)} As a result, these materials have been used in the variety of applications such as lightweight thermal and acoustic insulation, catalytic supports, microfilters, supercapacitors for electric cars, controlled release of drugs, inertial confinement fusion targets, and oil-spill clean-up applications.³⁾ The technological interest in the aerogels is originated from the need of high-energy physics applications for low-density materials with water repellency property.⁴⁾ A few attempts were made to use the silica aerogels as shock absorbing medium since they are indeed very fragile and brittle due to the low tensile strength.⁵⁾ Additionally, they are sensitive to the moisture. Therefore, the network structure gets deteriorated to pieces with time or upon impact of minute stress. In order to overcome these inadequacies, there is need to synthesis of superhydrophobic and highly flexible silica aerogels for actual applications of silica aerogels. Flexible nature of materials is

important as many reports suggests that the increasing mechanical strength by crosslinking with organic polymers lead to lose extreme properties of silica aerogels.⁶⁾ Hence here we focused on analysis of flexible nature of silica aerogels.

Generally, the trifunctional organosilane compounds like R₁SiX₃ (where, R=alkyl, aryl or vinyl groups, X=Cl or alkoxy groups) produces the elastic/inelastic nature in silica aerogels with good hydrophobicity since one of the ends of Si atom contains unreacted R group.^{7,8)} Due to the presence of this non-polar, unreactive group attached to the silica monomer restricts polymerization along this direction. In case of tetramethoxysilane (TMOS), four groups are hydrolysable and polymer chain will grow in all directions. Hence polymer chain in case of MTMS is little bit linear as compared with TMOS polymer chain. The methyl groups minimize inter-chain cohesions and help to form a linear chain, which result in the elastic and flexible three-dimensional matrix.⁹⁾ The produced aerogels were found to be highly compressible and elastic. Furthermore, the aerogels showed good superhydrophobic property with the water contact angle of 160°. Superhydrophobic and flexible silica aerogels will have great demand in oil absorption application, and semiconductor industries due low dielec-

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tric constant and flexibility. Rao et al.²⁾ have reported synthesis of flexible silica aerogels first time using methyltrimethoxysilane (MTMS) precursor. Although there is a lack of information regarding the detailed mechanism responsible for the flexible properties of silica aerogels. Therefore, there is need to study deep insight to understand the mechanism which is responsible for the hard/flexible nature of the aerogels. In this paper we have focused to explore the mechanism behind the flexible nature of silica aerogels and characterized material to understand the flexible nature. The flexible nature is a quite interesting phenomenon for wide applications of inorganic materials.

2. Experimental Details

2.1. Preparation of aerogels

A two stage acid-base catalyzed process was followed to prepare an alcisol and alcogel. Initially, MTMS was diluted in methanol (MeOH) solvent and was partially hydrolyzed with water under acidic conditions with oxalic acid. In the

second step, the basic water, ammonium hydroxide, was added to the sol drop by drop while stirring, after 24 h time interval. The prepared solution was poured into glass test tubes. Gelation (alcogels) were obtained after 7 h via hydrolysis and condensation reactions. The alcogels were processed into aerogels via aging in a methanol bath for 5 days and then supercritically dried in an autoclave above the critical temperature ($T_c=243\text{ }^\circ\text{C}$) and critical pressure ($P_c=7.9\text{ MPa}$) of methanol. Two aerogel samples were produced for molar ratio of MeOH/MTMS at 28 and 35 by keeping acidic water at 0.01 M, oxalic acid and basic water at 10 M, NH_4OH . The H_2O :MTMS (S) molar ratio was kept constant at 8 (S=4 acidic water (0.01 M oxalic acid) for hydrolysis and S=4 for (10 M NH_4OH) for condensation reactions. The various parameters were optimized to process the best quality aerogels in respect to higher flexibility and better hydrophobicity.

To quantify the degree of hydrophobicity, the 5 μL volume of water droplet kept on the sample and water contact angle (θ) was measured using contact angle meter (rame-

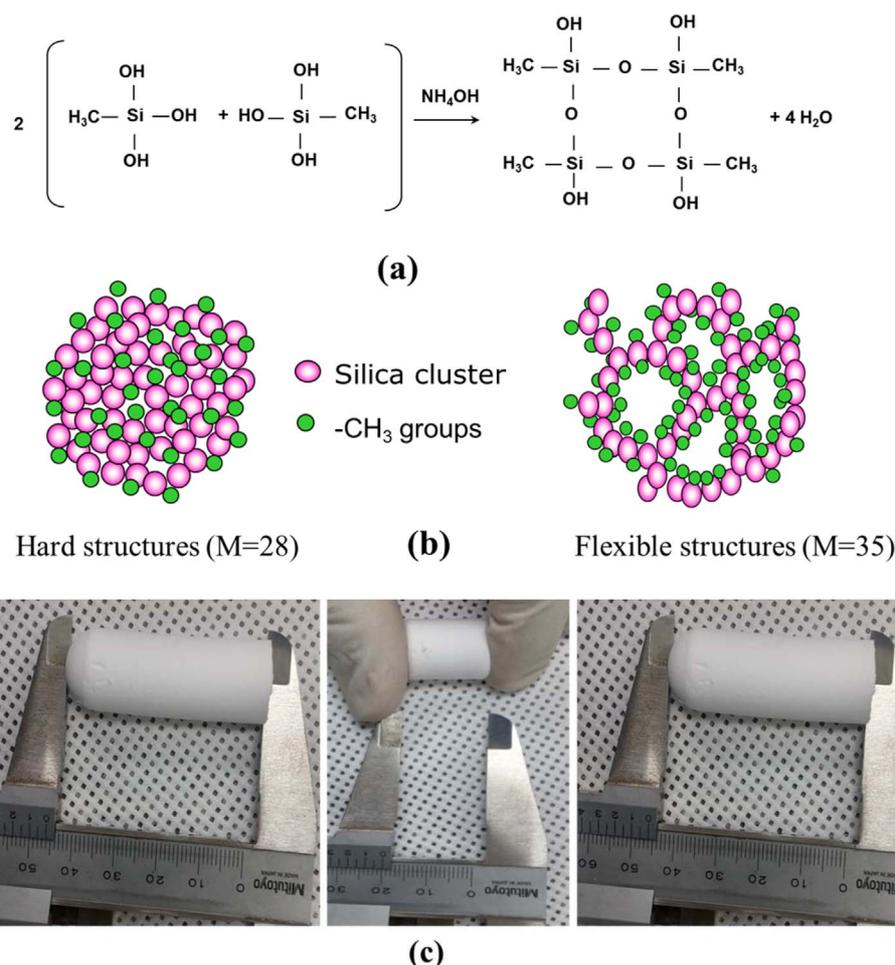


Fig. 1. (a) Condensation reaction between hydrolyzed MTMS monomers, (b) schematic representation of hard and flexible silica aerogels and (c) photographs of silica aerogel (M=35): The measured length of before/during/after 60% strain-induced loading were 45/18/44 mm, respectively.

hart). The Fourier Transform Infrared (FT-IR) spectroscopic studies of the silica aerogels were carried out using Perkin Elmer (Model no. 760) IR spectrophotometer in 400~4000 cm^{-1} range for chemical bonding structure. The Pore volume, pore diameter and specific surface area of the silica aerogels was measured using multi-point Brunauer-Emmett-Teller (BET) surface analyzer (TriStar 3000 V6.05 A). The surface morphology of silica aerogels were characterized using a scanning electron microscopy (SEM; JEOL, JSM 7001F). Thermal stability of flexible silica aerogels was evaluated by using a thermo gravimetric differential scanning calorimeter (TG-DSC, Netzsch STA 409 PC/PG, Germany).

3. Results and Discussion

3.1. Effect of MeOH/MTMS molar ratio (M) on flexible properties of aerogels

In the present paper, MTMS ($\text{H}_3\text{C-Si}(\text{OCH}_3)_3$) precursor used as a trifunctional organosilane compound to synthesize superhydrophobic and flexible aerogels. Figure 1(a) corresponds to the condensation reaction between hydrolyzed MTMS monomers. Figure 1(b) showed schematic representation of the hard and flexible structured silica aerogels prepared with $M=28$ and $M=35$, respectively. Figure 1(c) demonstrates the elastic nature of silica aerogels ($M=35$) by measuring the length of the cylindrical shaped silica aerogel with 60% strain-induced loading. The measured length of before/during/after loading were 45/18/44 mm, respectively and it could be confirmed that an excellent flexibility can be obtained for a silica aerogel by increasing solvent quantity in the sol using MTMS precursor. The flexibility was observed for higher molar ratio of MeOH:MTMS i.e. by increasing solvent quantity, linear polymerization and distance between silica clusters can be increased to get flexible properties as schematic shown in Fig. 1(b). In the case of MTMS precursor, each monomer of the MTMS has one non-hydrolysable methyl group (CH_3) and three hydrolysable methoxy groups (OCH_3). Therefore, only hydrolysable methoxy groups are responsible for the matrix formation by undergoing the following hydrolysis and condensation sol-gel reactions.²⁾

3.2. FT-IR studies of flexible aerogels

The wetting behavior of superhydrophobic surface is mainly governed by the chemical composition of the surface. Figure 2 shows the FT-IR spectrum of the flexible silica aerogel prepared at 35 molar ratio of MeOH:MTMS. Several characteristic absorption peaks were observed in

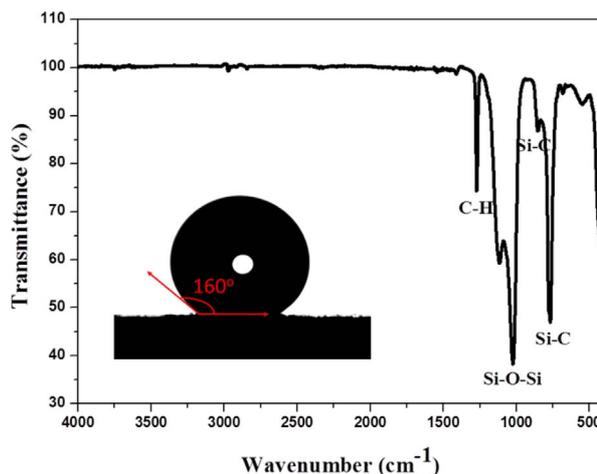


Fig. 2. FT-IR spectrum of MTMS flexible silica aerogel ($M=35$) and an image of water droplet on flexible silica aerogel as an in-set.

the range 450~4000 cm^{-1} indicating the presence of methyl groups in the sample. The broad absorption peak observed at 1080 cm^{-1} which is the characteristic peak of Si-O-Si bonds in silica aerogel sample.¹⁰⁾ The weak absorption peaks were observed at 2950 cm^{-1} and 1400 cm^{-1} were due to stretching and bending modes of C-H bonds and the strong peaks observed at 765 cm^{-1} and 1260 cm^{-1} are due to Si-C bonds.^{11,12)} The Si- CH_3 group is easily recognized by a strong, sharp peak at about 1260 cm^{-1} together with one or more strong peaks in the range of 865-750 cm^{-1} . Some $\text{CH}_3\text{Si-}$ compounds show a 1250 cm^{-1} peak split into two components with the weaker often appearing as a shoulder on the high frequency of the peak.^{13,14)} The hydrophobicity was characterized by measuring the contact angle (θ) of a water droplet placed on the aerogel surface under investigation and the result was given as an inset of Fig. 2. The contact angle (θ) measurements revealed that both aerogels samples showed superhydrophobic nature and having contact angle of $160 \pm 2^\circ$. The intensity of methyl bond indicates the number of methyl groups is high as every MTMS monomer carries one methyl group. This increased percentage of methyl (organic) groups and increased distance between silica clusters induces flexible and hydrophobic nature in silica aerogels.

3.3. Surface morphology of flexible silica aerogels

The two-dimensional surface morphology of the flexible silica aerogels measured by SEM and showed in Fig. 3. From the SEM image, it is observed that there is uniformity and homogeneity in the silica clusters. These clusters were interconnected with each other and also some empty voids were seen from SEM image. The precursor, i.e.

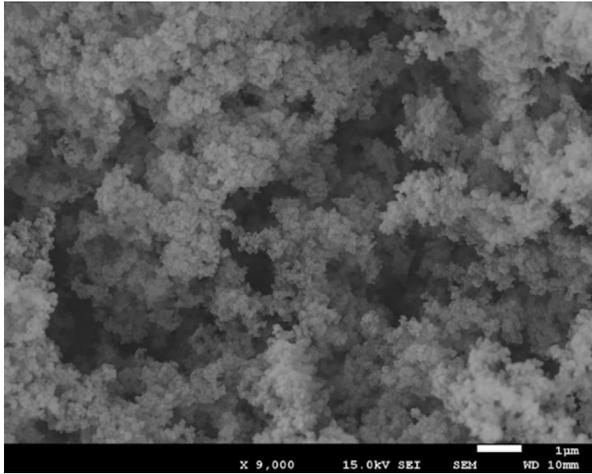


Fig. 3. SEM micrograph of flexible silica aerogel (M=35) sample.

MTMS, used in this study, contains one hydrolytically stable methyl group, which is responsible for the hydrophobicity in the silica aerogels and also restrict polymerization along one direction.¹⁵⁾

3.4. Surface area measurement of flexible silica aerogels

The specific surface area of flexible silica aerogels was measured using a multi-point BET analyzer. Figure 4 shows the adsorption and desorption isotherms were obtained for flexible silica aerogels (M=35). The curves indicate the adsorption and desorption branches of the isotherm in the range of capillary condensation. According to the IUPAC classification scheme, the isotherm shows the characteristic type II shape with H3 hysteresis loop.¹⁶⁾ The presence of the hysteresis loop, aroused by the capillary condensation in the mesopore (2~50 nm), suggests that the resulting aerogels are mesoporous material.¹⁷⁾ The flexible silica aerogels showed 398.1 m²/g BET surface area, pore vol-

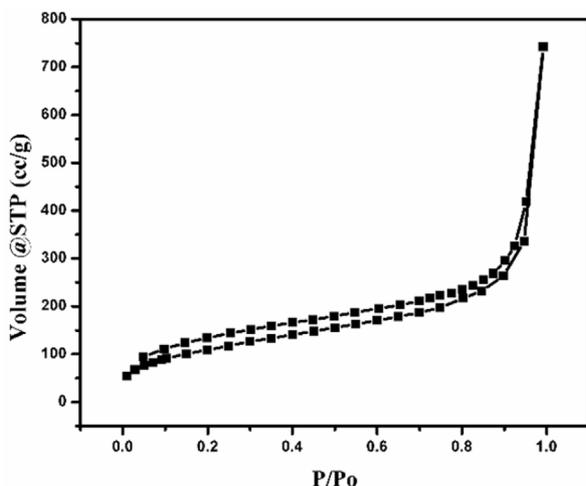


Fig. 4. Adsorption and desorption profiles for flexible silica aerogel (M=35) sample.

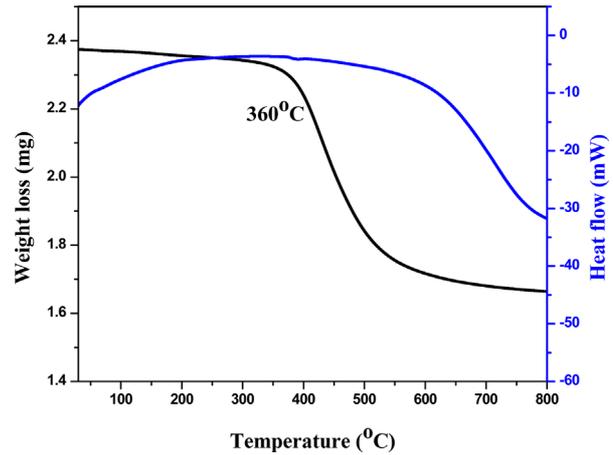


Fig. 5. TG-DSC of flexible silica aerogel (M=35) sample.

ume (1.15 cc/g) and pore diameter (11.5 nm) and mesoporous material. The mechanical strength of brittle ceramics is related to both the total pore volume and the pore size distribution whereas a decrease in the pore volume of aerogels is favorable to the strength development of aerogels.

3.5. Thermal analysis of flexible silica aerogels

Figure 5 shows TG-DSC profiles of the flexible silica aerogels sample (M=35). The TG curve shows noticeable weight loss at around 360 °C accompanied with an exothermic peak in the DSC curve. The sudden weight loss in TG curve around 396 °C is due to the thermal decomposition of alkyl (-CH₃) groups. The exothermic peak in DSC curve indicates the burning of methyl groups.¹⁸⁾ It indicates that flexible silica is thermally stable up to 360 °C in the air atmosphere and above this temperature the silica coating becomes hydrophilic in nature.

4. Conclusions

Highly flexible and superhydrophobic silica aerogels could be obtained using MTMS precursor by two-step acid-base sol-gel process for the molar ratio of MeOH:MTMS at 35. Very high dilution of the MTMS precursor in the methanol solvent and the presence of non-polar methyl groups in the silica polymer chains resulted in the flexible silica aerogels with elastic nature. The FT-IR spectrum clearly showed the presence of Si-CH₃ bonds, which make the aerogel surface non-polar and hence superhydrophobic. TG-DSC analysis indicates that flexible silica aerogels are thermally stable up to 360 °C in the air atmosphere, and above this temperature, the silica coating became hydrophilic in nature. Thus, the elastic superhydrophobic aerogels could be used as efficient shock absorbing materials.

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