Physical properties of methyltrimethoxysilane based elastic silica aerogels prepared by the two-stage sol–gel process

Nagaraja D. Hegde · A. Venkateswara Rao

Abstract The experimental results on the physical properties of methyltrimethoxysilane (MTMS) based elastic silica aerogels prepared by the two stage sol–gel process, are reported. The molar ratio of methanol (MeOH)/MTMS, (M), was varied from 14 to 42 and the molar ratios of acidic water/MTMS, (A) and basic water/MTMS, (B) were each varied from 0.8 to 7.2. The acidic water and basic water concentrations were also varied from 0–0.1 M and 6–13.36 M, respectively. The MTMS based superhydrophobic elastic aerogels could be obtained by adding only distilled water without an acid in the first step which would prevent the possible corrosion of the autoclave during the supercritical drying. With an increase in the MeOH/MTMS molar ratio, the aerogels have been found to become flexible which was characterized by the Young's modulus. The best quality elastic superhydrophobic aerogels in terms of contact angle (160°), density (37 kg/m^3), volume shrinkage (6%), porosity (98%) and thermal conductivity (0.057 Wm^{-1} K^{-1}) have been obtained for the molar ratio of MTMS:MeOH:acidic water:basic water:: 1:35:3.97:3.97, respectively. The hydrophobicity was confirmed by Fourier Transform Infrared (FTIR) spectroscopy and contact angle measurements. The microstructure of the aerogels has been studied by the transmission electron microscopy (TEM).

N. D. Hegde · A. Venkateswara Rao (✉)
Air Glass Laboratory, Department of Physics, Shivaji University,
Kolhapur 416 004 Maharashtra, India
e-mail: raouniv@yahoo.com

Introduction

Silica aerogels are unique nano materials since they are both transparent (~90% optical transparency) and highly porous (>98%) at the same time [1]. This novel combination of properties is due to the fact that the aerogels have particle and pore sizes in the nanometer (1–100 nm) range, with the particles linked together through a tenuous network. As a result, the aerogels have a large number of applications such as thermal super insulators in window systems, catalytic supports [2–4], Cerenkov radiation detectors in nuclear reactors and high-energy physics [5–7]. However, the main drawbacks with the aerogels are that they are (i) very brittle and (ii) absorb moisture from the surroundings and deteriorate with time, which limit their use in long term technological applications [8]. Hence, it is necessary to prepare the elastic (flexible) and hydrophobic aerogels, which would widen their applications.

There are some reports of hydrophobicizing the aerogel surface by the co-precursor and derivatization methods using various alkyl-alkoxy/chlorosilane compounds [9]. But the hydrophobicity of the aerogels produced by these methods is limited due to the fact that the co-precursor/precursor molar ratio cannot be increased beyond a certain limit. For example, in the case of trimethylethoxysilane (TMES)/tetraethoxysilane (TEOS) aerogels, the maximum molar ratio of TMES/TEOS can be only 0.6 and beyond which the gels do not set [10]. Since the MTMS contains three hydrolysable methoxy groups, which are the smallest among all the alkoxy groups, it can undergo hydrolysis and condensation reactions and produce the silica network. Even though the synthesis of MTMS based aerogels by a single-step sol–gel process has already been reported [11], this process limits the dilution of MTMS in methanol, resulting in dense and fragile aerogels. However, the

two-step sol–gel process has the advantage that the molar ratio of the solvent (MeOH) to the precursor (MTMS) could be increased to as much as 42, which resulted in low density and elastic aerogels, as reported in our previous paper which mainly focussed on the elastic and flexible properties of the MTMS based aerogels [12]. In this paper, we report the detailed study of the physical properties of the MTMS based silica aerogels synthesized by the two-step sol–gel process. In addition, here we report the synthesis of superhydrophobic and flexible aerogels without the use of any acid catalyst, which would prevent the autoclave corrosion during supercritical drying.

Experimental

Preparation of aerogels

The synthesis of an aerogel involves three major steps: (1) the preparation of the alcosol (2) the hydrolysis and condensation processes leading to the formation of alcogel and (3) supercritical drying of the wet gel to get the aerogel.

A two stage acid-base catalyzed process was followed to prepare the alcosol. Initially, methyltrimethoxysilane (MTMS) was diluted in methanol (MeOH) solvent and was partially hydrolyzed with water under acidic conditions with oxalic acid. In the second step, after 24 h time interval, the basic water (NH_4OH) was added to the sol, drop by drop while stirring. The as prepared alcosol was poured into airtight Borosil glass test tubes. By the hydrolysis and condensation reactions, the gelation took place and the alcogels were obtained. The alcogels were then aged in a methanol bath for 48 h and then supercritically dried in an autoclave at a temperature of 265 °C and a pressure of 10 MPa, to get the aerogels. The details of the drying parameters are given in our previous paper [13].

Initially, the alcosols were prepared by varying the molar ratio of MeOH/MTMS from 14 to 42 by keeping acidic water (0.001 M, Oxalic acid)/MTMS and basic water (10 M, NH_4OH)/MTMS molar ratio constant at 3.97 each. From these results, the molar ratio of MeOH/MTMS was fixed at 35 for which monolithic, less shrinkage and flexible aerogels were obtained. Then, the acid catalyst concentration was varied from 0 to 0.1 M. Monolithic aerogels were obtained even by adding only water (double distilled) in the first step without any acid catalyst. Hence, further experiments were carried out with water in the first step and the base catalyst concentration was varied from 4 to 13.36 M in the second step. Finally, the molar ratio of water/MTMS in both the stages was varied from 0.8 to 7.2 and the conditions were optimized to get the best quality aerogels in terms of low density, higher contact angle, large porosity and flexibility.

Methods of characterization

The bulk density, porosity and volume shrinkage of the aerogels were calculated as described in our previous paper [14]. The thermal conductivity was measured using the thermal conductivity meter (C-T Meter, Teleph, France). The contact angle (θ) made by a 2.4 mm diameter water droplet on the aerogel surface was measured using the contact angle meter (Tantec, USA.) and the same was confirmed by a travelling microscope using the equation [15]:

$$\theta = 2\tan^{-1}(2h/\Delta) \tag{1}$$

where h is the height of the drop and Δ is the base width as shown in Fig. 1. The microstructure of the aerogels was studied using transmission electron microscopy (TEM) and the organic modification was confirmed by the Fourier Transform Infrared (FTIR) spectroscopic studies.

The elasticity of the aerogels was studied in terms of the Young's modulus (Y) from the uniaxial compression measurements (Fig. 2) using the equation [16]:

$$\begin{aligned} Y &= \text{Stress}/\text{Strain} \\ &= \text{Slope of stress versus strain graph} \end{aligned} \tag{2}$$

Stress and strain were calculated by the following equations:

$$\text{Stress} = mg/\pi r^2 \tag{3}$$

$$\text{Strain} = \Delta L/L \tag{4}$$

where L is the original length of the aerogel sample, ΔL is the change in length of the aerogel after the application of the load, r is the radius of the aerogel sample under study, m is the mass placed on the sample and g is the acceleration due to gravity (9.8 ms^{-2}).
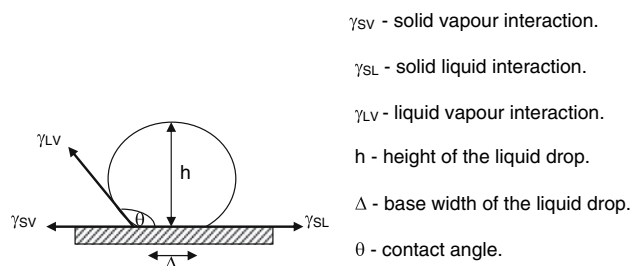

γ_{SV} - solid vapour interaction.

γ_{SL} - solid liquid interaction.

γ_{LV} - liquid vapour interaction.

h - height of the liquid drop.

Δ - base width of the liquid drop.

θ - contact angle.

Fig. 1 The height (h), base width (Δ) and the contact angle (θ) of a water drop on a solid surface
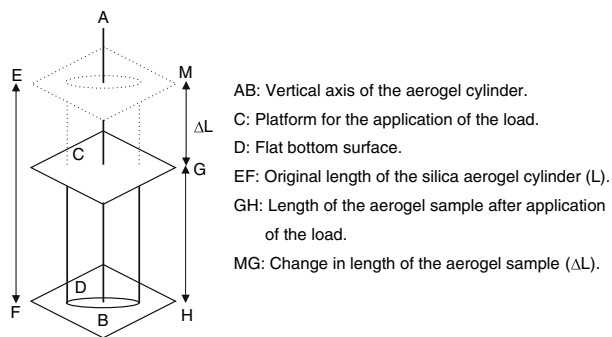
Fig. 2 Schematic diagram of the uniaxial compression test for the determination of Young's modulus of the silica aerogels

Results and discussion

Gelation time

Keeping the molar ratio of acidic water (oxalic acid, 0.001 M)/MTMS, (A) and the basic water (NH$_4$OH, 10 M)/MTMS, (B) constant at 3.97 each, the molar ratio of MeOH/MTMS, (M) was varied from 14 to 42. It was found that the gelation time increased from two and a half hours to twelve hours with an increase in M value from 14 to 39 as shown in Table 1. This is due to the fact that higher dilution of MTMS in methanol results in greater dispersion of MTMS molecules, which would take a longer time for the 3D linking of the silica particles. The increase in the gelation time is also attributed to the fact that higher dilution of MTMS in methanol reduces the acid and base catalyst concentrations in the first and the second stage of the sol–gel process, respectively. This would slow down the hydrolysis and condensation reactions, which results in an increased gelation time. At very high dilutions ($M \geq 42$), the silanol concentration reduces to such an extent that the silica network can not be formed and so the gel does not set. Further, the gelation time was found to depend largely on the basic water quantity as it reduced from 14 h to 5 h with an increase in the basic water/MTMS molar ratio from 2.4 to 7.2. This is due to the fact that once the hydrolysis is complete in the first step, the basic catalyst (NH$_4$OH) in the second step would

enhance the condensation process and the gel would set faster.

Volume shrinkage and bulk density

Table 1 shows some physical properties of the silica aerogels prepared with various MeOH/MTMS (M) molar ratios keeping the acidic (A) and basic (B) catalyst concentrations at A = 0.01 M and B = 10 M, respectively. It was found that the aerogels prepared with $M = 35$ had minimum (6%) volume shrinkage, while it was more than 11% for the other values of M. This is due to the fact that the lower dilution of MTMS in methanol results in higher catalyst concentration (acidic and basic) in the sol, which would increase the rate of hydrolysis and condensation reactions. Therefore, there is a higher nucleation rate at high concentration than at low concentration. Hence, smaller clusters are formed and get linked to each other immediately to form the gel [11]. This would result in the formation of a silica network consisting of relatively small and uniform particle and pore sizes. Since the particle and pore sizes are uniform, the drying stresses [17] and the gel shrinkage are minimal on drying. But, the dilution beyond a certain limit ($M > 35$), leads to a smaller silica content and therefore, the network becomes weak resulting in increased volume shrinkage during supercritical drying.

The bulk density of the aerogels decreased significantly from 93 kg/m^3 to 37 kg/m^3 with an increase in M from 14 to 35 as shown in Table 1. But, with the further increase in M to 39, the bulk density was found to increase to 42 kg/m^3. This is because, for higher dilution of MTMS in the solvent, the silica content is greatly reduced as seen in the Fig. 3(b) in comparison with Fig. 3(a). Therefore, the density of the aerogel sample decreased with the increase in the M value. However, at much higher dilutions ($M > 35$) the increase in the density due to volume shrinkage during drying is more than the decrease in density due to the dilution. Hence, a slight increase in the density was observed for $M = 39$. The alcosol prepared with the values of $M = 42$ or more, did not set. This is because, very high dilution of MTMS in the methanol

Table 1 Some physical properties of the silica aerogels prepared with various MeOH/MTMS molar ratios (A = 0.01 M, B = 10 M)

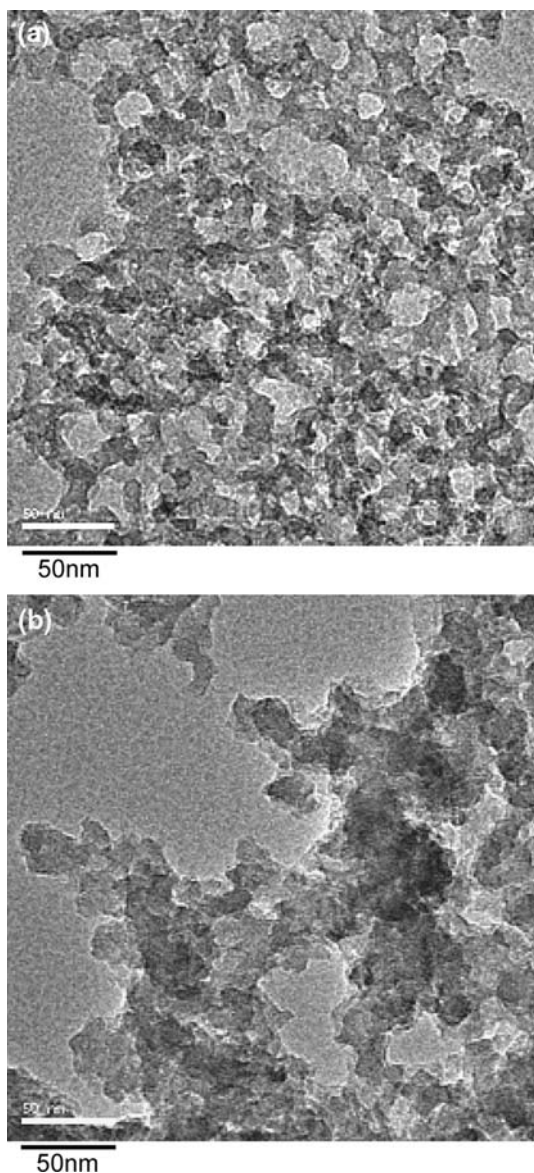| MeOH/MTMS Molar ratio	Gelation time (hrs.)	Bulk density (kgm^{-3})	Volume shrinkage (%)	Porosity (%)	Contact angle (θ)	Thermal conductivity (Wm^{-1} K^{-1})
14	2.5	93	11	95	160°	0.063
21	4.0	74	19	96	154°	0.061
28	6.5	51	19	97	152°	0.058
35	9.0	37	6	98	149°	0.057
39	12.0	42	17	98	150°	0.057

Fig. 3 Transmission electron micrographs of the aerogel samples prepared with (a) $M = 14$ and (b) $M = 35$

Fig. 4 Variation of bulk density with the acid catalyst concentration for $M = 35$

solvent results in the formation of a few silica particles which would not get connected to form the 3-dimensional network required for the gel formation. Further, the bulk density of the aerogels prepared with $M = 35$ increased from 37 to 57 kg/m³ with the decrease in the acid catalyst concentration, A, from 0.01 to 0 M as shown in Fig. 4. Even though, the density was slightly more for the aerogels prepared with $A=0$ M (only distilled water) in the first step, it resulted in better hydrophobicity and the absence of acid has an added advantage that the autoclave system does not corrode during the supercritical drying. Therefore, further experiments were performed without using any acid catalyst but only with distilled water in the first stage of the two-stage sol–gel process.
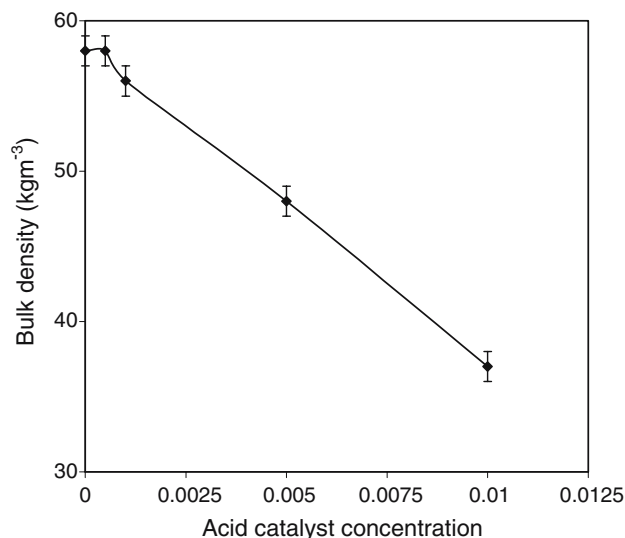
## Optical transmission and thermal conductivity

Further, from Fig. 3(a) and (b), it is evident that the MTMS based aerogels have very large pore and particle sizes. According to Raleigh, the scattered intensity of light (I) is given by the relation [18]:

$$I = \frac{8\pi^4 r^6}{d^2 \lambda^4} \frac{n^2 - 1}{n^2 + 2} \left(1 + \cos^2 \theta \right) \qquad (5)$$

where θ is the scattering angle, d is the distance from the particle to the detector, n is the refractive index, r is particle or the pore size and λ is the wavelength of light. Therefore, as r is very large in the case of MTMS based aerogels, most of the incident light is scattered. As a result, these aerogels show very little transparency (<5%) in the visible range.

The thermal conductivity of the as produced aerogel sample was very low and found to vary with M. It was observed that the thermal conductivity (K) decreased from 0.063 to 0.057 Wm⁻¹ K⁻¹ with an increase in M from 14 to 39. Also, with the decrease in K, the heat capacity per unit volume of the aerogel samples decreased from 250 to 160 kJm⁻³ K⁻¹. In an aerogel, the thermal transport is through the solid silica network. Since the aerogels are highly porous (>95%) and contain a very small fraction (<5%) of solid silica, the thermal conductivity (K) is very low. Further, as M increases, the silica content in the aerogels decreases further and therefore, the thermal conductivity decreases. Since the bulk density of the aerogel also depends on the silica content, it was observed that the thermal conductivity increases almost linearly with an increase in the density of the aerogels as seen from Table 1.

Fig. 5 FTIR spectra of the aerogel sample prepared with $M = 35$
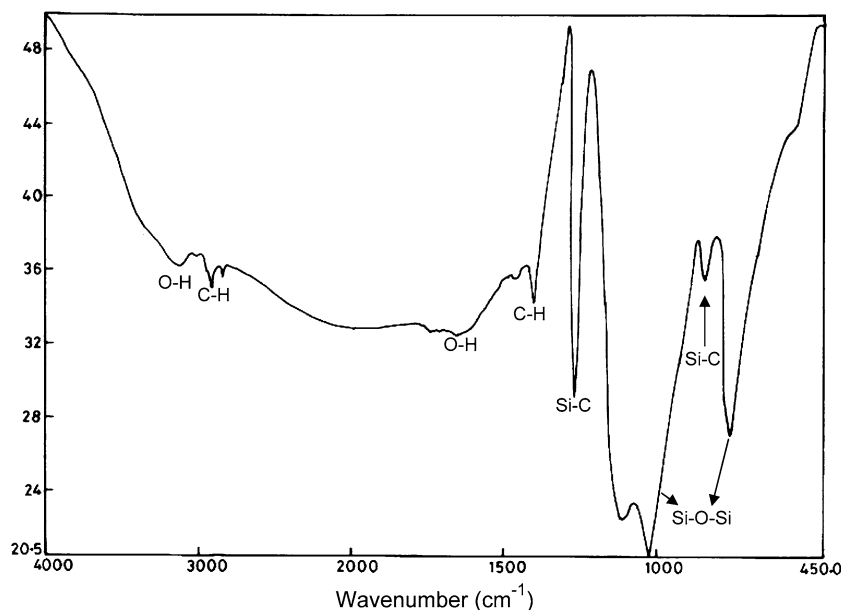
Hydrophobicity and contact angle

The M value was found to affect the hydrophobicity of the aerogel samples which was quantified in terms of the contact angle (θ) of a 2.4 mm water droplet on the aerogel surface as shown in Table 1. It was observed that θ reduced from 160° to 149° with an increase in M from 14 to 35. Further, to determine the effect of acid catalyst (oxalic acid) concentration (A) on the hydrophobicity of the aerogels, the alcogels were prepared by varying the A value from 0.0 to 0.01 M keeping the MeOH/MTMS molar ratio constant at 35. It was observed that for $A = 0$, the contact angle was maximum (158°) and decreased to 152° for $A = 0.01$ M. The effect of the base catalyst (NH$_4$OH, Fluka) concentration (B) was studied by keeping the molar ratio of MTMS: MeOH: distilled water: basic water at 1:35:3.97:3.97, respectively. The value of B was varied from 6 to 13.36 M (maximum available). It was observed that for B values less than or equal to 8 M, the alcosol did not set. For B values from 10 to 13.36 M, the bulk density of the aerogels decreased from 57 to 52 kgm^{-3}. The contact angle of the aerogel samples also decreased from 158° to 147°.

The sphericity of a water drop on a solid surface is characterized by the contact angle (θ). Increasing the hydrophobicity of the solid surface, increases the contact angle and the sphericity of the water drop. Under equilibrium conditions, the relation between the solid-vapour (γ_{sv}), solid-liquid (γ_{sl}) and liquid-vapour (γ_{lv}) interactions at the intersection of the three phases, is given by the Young's equation [19]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \qquad (6)$$

For a hydrophobic surface, $\theta > 90°$ and therefore, from the above equation it follows that solid-liquid (γ_{sl}) interaction is greater than solid-vapour (γ_{sv}) interaction. Table 1 shows that the contact angle (θ) decreases with the increase in MeOH/MTMS molar ratio. This is because each monomer of MTMS contains one non-hydrolysable $\equiv$Si–CH$_3$ group. Hence, after the completion of condensation reactions, the surface of the aerogel clusters would mostly be covered by these $\equiv$Si–CH$_3$ groups. The hydrophobicity of the aerogels depends on the number of such $\equiv$Si–CH$_3$ groups on the surface. As the MeOH/MTMS molar ratio increases, the concentration of MTMS decreases and so the $\equiv$Si–CH$_3$ groups on the surface would decrease. Therefore, the contact angle was found to decrease with the increase in MeOH/MTMS molar ratio.

The organic modification and the hydrophobicity of the aerogels were confirmed from the Fourier Transform Infrared (FTIR) studies. Figure 5 shows the FTIR spectra of an aerogel sample prepared with $M = 35$. The strong peaks are observed at 3,000 cm^{-1} and 1,400 cm^{-1} corresponding to the stretching and bending of C–H bonds [20]. The peaks at 1,270 cm^{-1} and 845 cm^{-1} are due to Si–C bonds [21, 22]. The peaks at around 1,100, 770 and 470 cm^{-1} are due to the asymmetric, symmetric and the bending modes of SiO$_2$, respectively [20]. The figure shows very small peaks around 3,200 cm^{-1} and 1,650 cm^{-1} corresponding to O–H bonds clearly indicating the surface chemical modification of the aerogel sample.

Mechanical properties

The tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) based aerogels are brittle and even by slight

deformation lose their monolithicity. But, the MTMS based aerogels, especially with higher MeOH/MTMS molar ratios ($M > 35$), were found to be highly flexible and elastic. The samples could easily be compressed with very little stress (<50 g) without any damage to their structure. After the removal of the weights, the samples regained their initial size fully indicating the elastic nature. Figures 6(a) and (b) show the microstructure of TEOS based and MTMS based aerogels. From these figures, it is clear that the TEOS based aerogels have a compact structure with smaller pore and particle sizes, while the MTMS based aerogels have very large pores and open ended network in between. This is due to the fact that in TEOS based aerogels, Si is bound by four polar groups (OH) which are
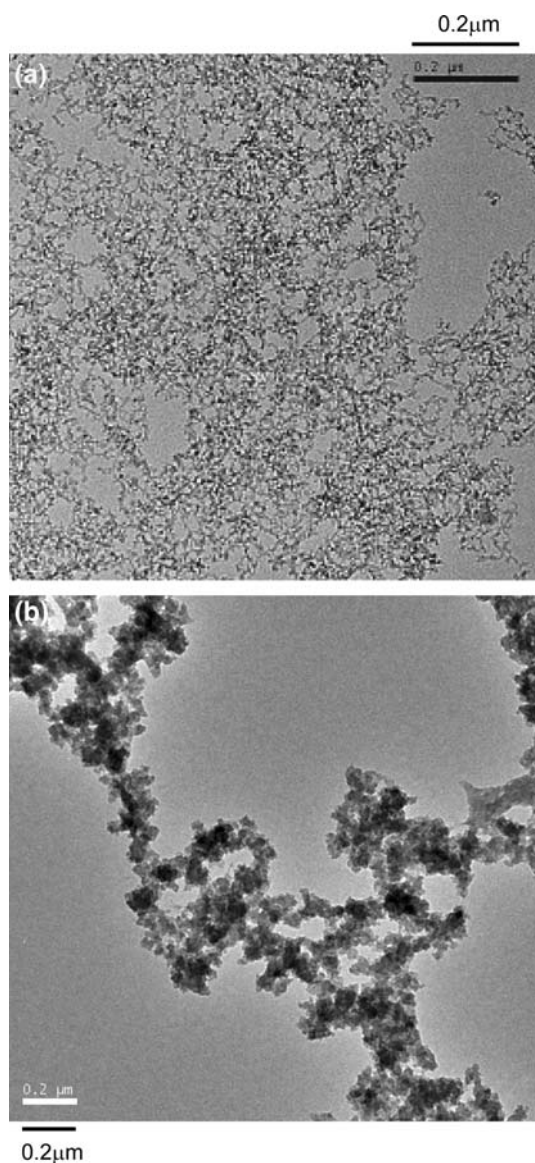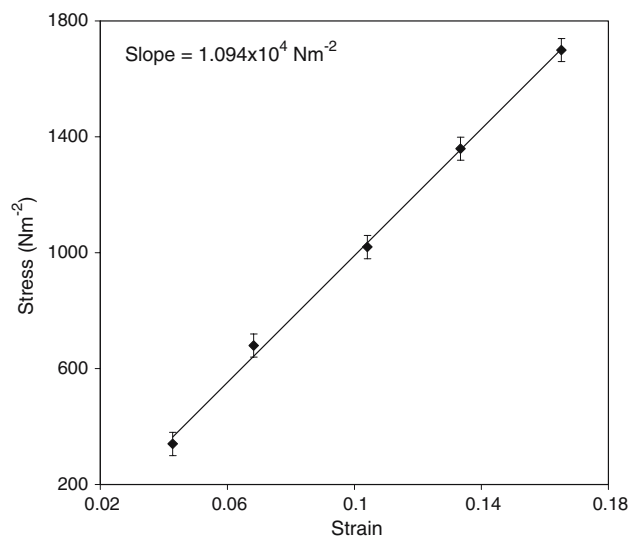

Fig. 7 Stress versus strain graph of an aerogel sample prepared with $M = 35$

hydrolyzable and therefore, the network grows in all the four directions. But, in the MTMS based aerogels, Si is bound by three hydrolyzable and one non-hydrolyzable (CH_3) group. Therefore, the network remains open-ended on one side and gets connected on the remaining three sides. As a result, large pores are seen in the microstructure of the MTMS based aerogels. The presence of such large pores and the CH_3 groups in the network, are possibly responsible for the elastic behaviour of the MTMS based aerogels.

The elasticity is expressed in terms of the Young's modulus (Y) of the aerogel samples measured by the uni-axial compression test. The Young's modulus was measured for a sample of length 5.5×10^{-2} m prepared with the MeOH/MTMS molar ratio equal to 35. Figure 7 represents the graph of stress versus strain. The slope of the graph gives the Young's modulus of the aerogel sample which was found to be 1.094×10^4 Nm^{-2}.

Conclusions

The two-step sol–gel processing of MTMS precursor diluted in methanol results in elastic, flexible and super-hydrophobic aerogels. Monolithic and flexible aerogels can be obtained even without any acid catalyst (only water) in the first step of the two-step sol–gel process which avoids the corrosion of the autoclave systems during the super-critical drying. Very high contact angle (~160°) is observed for a 2.4 mm water droplet on the aerogel prepared with MeOH/MTMS molar ratio 14. The bulk density of the MTMS based aerogel decreases with an increase in the MeOH/MTMS molar ratio. The aerogel samples prepared

Fig. 6 Transmission electron micrographs showing the microstructure of the (a) TEOS and (b) MTMS based aerogel samples

with $M = 35$ or more are highly elastic and flexible with the Young's modulus as low as $1.094 \times 10^4 \, Nm^{-2}$.

References

1. Venkateswara Rao A, Wagh PB, Pajonk GM, Haranath D (1998) J Mater Sci Technol 14:236
2. Hrubesh LW (1998) J Non-Cryst Solids 225:335
3. Fricke J, Tillotson T (1997) Thin Solid Films 297:212
4. Herman G, Iden R, Mielka M, Feich F, Ziegler B (1995) J Non-Cryst Solids 186:380
5. Carlson PJ, Johansson KE, Norrloy JK, Pingot O, Tavernier S, Van den Bogert F, Van Luncker L (1979) Nucl Instru Meth 160:407
6. Buzykaev AR, Danilyuk AF, Ganzbur Sf, Gorodtskaya TA, Kolachev GM, Kravchenko EA, Mikerov VI, Minakov GD, Onuchin AP, Shamov AG, Tayursky VA (1998) J Non-Cryst Solids 225:381
7. Venkateswara Rao A, Pajonk GM, Bhagat SD, Barboux P (2004) J Non-Cryst Solids 350:216
8. Venkateswara Rao A, Kulkarni Manish M, Amalnerkar DP, Seth T (2003) Appl Surf Sci 206:262
9. Venkateswara Rao A, Kalesh RR (2004) J Sol-Gel Sci Tech 30:141
10. Venkateswara Rao A, Kalesh RR, Amalnerkar DP, Seth T (2003) J Porous Mater 10:23
11. Venkateswara Rao A, Kulkarni MM, Amalnerkar DP, Seth T (2003) J Non-Cryst Solids 330:187
12. Venkateswara Rao A, Bhagat SD, Hirashima H (2006) J Colloid Interf Sci 300:279
13. Venkateswara Rao A, Haranath D, Pajonk GM, Wagh PB (1998) Mater Sci Technol 14:1194
14. Parvathy Rao A, Pajonk GM, Rao AV (2005) J Mater Sci 40:3481
15. Bikerman JJ (1958) Surface chemistry: theory and applications, 2nd edn. Academic Press, New York, p 343
16. Beiser Arthur (1962) The mainstream of physics. Addison Wesley Publishing Company Inc., second printing, p 124
17. Scheidegger AE (1974) The physics of flow through porous media, 3rd edn. University of Toronto, Toronto
18. Venkateswara Rao A, Kulkarni MM (2002) Mater Res Bull 37:1667
19. Adamson AW (1982) Physical chemistry of surfaces. John Wiley, New York, p 338
20. Jeong Ae-Y, Goo S-M, Kim D-P (2000) J Sol-Gel Sci Technol 19:483
21. Hering N, Schriber K, Riedel R, Lichtenberger O, Woltersodorf J (2001) Appl Organometal Chem 15:879
22. Laczka M, Cholwa-Kowalska K, Kogut M (2001) JNon-Cryst Solids 287:10