



## INFLUENCE OF PHENYLTRIMETHOXYSILANE ON PHYSICOCHEMICAL PROPERTIES OF TEOS BASED MONOLITHIC SILICA AEROGELS PREPARED BY SUPERCRITICAL DRYING PROCESS

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### ABSTRACT

The objective of the present research work is to synthesize transparent, hydrophobic, monolithic silica aerogels with ultralow density by using supercritical drying process. The effect of phenyltrimethoxysilane as a hydrophobic reagent on the physicochemical properties of the silica aerogels has been studied. The total processing time for the synthesis of monolithic silica aerogels minimized to 29 h which was ~2 days. We have succeeded to get ultralow density of the silica aerogels as low as 24 Kg<sup>m</sup><sup>-3</sup> with 165° water droplet contact angle. The ultralow density affects the thermal conductivity of the silica aerogels.

**KEY WORDS:** hydrophobicity, silica aerogels, Sol-gel process, thermal conductivity, ultra-low density,

### INTRODUCTION

S.S. Kistler in 1931 made efforts for the opening the new field of the low density solid materials i.e. silica aerogels by supercritical extraction of the solvent from the gel (Kistler, 1931). These porous materials have sole combination of physical properties such as ultralow density, low-thermal conductivity, index of refraction nearly equal to air, and high optical transmission (A Parvathy Rao *et al.*, 2008). Hence, these fascinating features of aerogels have various scientific and technological applications in super-thermal insulators in thermos flasks, in solar thermal devices, in the inertial confinement fusion (ICF) target materials, storage media for rocket liquid propellants (Pajonk, 1991) and radio luminescent devices (Reed *et al.*, 1990; Pierre, 2002) etc, with bulk density as low as 3 Kg<sup>m</sup><sup>-3</sup> (Hrubesh, 1990), which is only three times greater than the density of the air at sea level due to their high porosity (> 98%) and extremely large specific surface area (>10<sup>6</sup> m<sup>2</sup>Kg<sup>-1</sup>) (Mulder and Van Lierop, 1986). The key issue in the production of the monolithic aerogels is maintaining the integrity of the network in the supercritical drying, leaving back only light weight solid, porous network of silica filled with air (Tang and Wang, 2005). In the present study, there are only a few reports available in the literature on the effect of phenyltrimethoxysilane on the physicochemical properties of the TEOS based monolithic silica aerogels. The preparation of PTMS/TEOS based optically transparent superhydrophobic aerogels of ultra low density and low thermal conductivity plays a vital in technological and scientific applications. The synthesized silica aerogels has been analyzed by various techniques viz., FTIR, TEM. Optical transmission, hydrophobicity and thermal conductivity. These hydrophobic silica aerogels does not degrade with the attack of atmospheric vapor for long term exposure to humid surrounding.

### MATERIALS AND METHODS

The synthesis of silica aerogels was done by using tetraethoxysilane (TEOS, Reagent grade, 98% Sigma-Aldrich chemicals) phenyltrimethoxysilane (PTMS, Fluka, Purum grade), Formamide (99% GC, Spectrochem Pvt. Ltd. Mumbai, India), HCl (Thomas Baker, Mumbai, India), NH<sub>4</sub>OH (s. d. Fine chem. Ltd. Mumbai, India). Silica aerogels were prepared by two step sol-gel process using tetraethoxysilane (TEOS) as the precursor and phenyltrimethoxysilane (PTMS) as the co-precursor diluted in methanol (MeOH) solvent. Initially, the mixing of precursor and solvent was carried out at room temperature with stirring for one hour and kept for 1 h under refluxing conditions in order to have complete hydrolysis. The optimal composition for the preparation of monolithic, transparent aerogels was obtained at the molar ratio of TEOS: MeOH: H<sub>2</sub>O: at 1:55:12:1.55 with an acid catalyst HCl at (0.001 M) and NH<sub>4</sub>OH (5 M), the molar ratio of PTMS/TEOS (P), varied from 0.05 to 1.2.

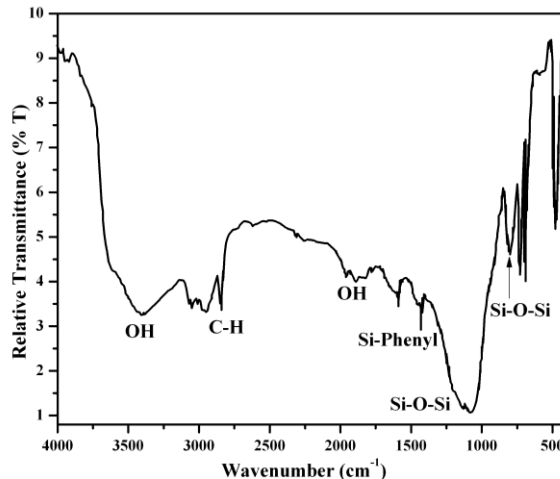
These gels were aged at 50 °C for 12 h, and the glass test tubes containing aerogels were placed directly in an autoclave of 600 ml volume capacity of autoclave for the supercritical extraction of the solvent. The temperature was ramped to 270 °C at a rate of 25 °C h<sup>-1</sup>, while holding the pressure generated by the solvent vapor at approximately 14 MPa<sup>-1</sup>. The vessel depressurized at a rate of 2.8 MPa<sup>-1</sup> and allowed to cool slowly with total processing time for getting monolithic silica aerogels was 29 h.

### RESULTS AND DISCUSSION

#### Fourier Transform Infrared spectroscopy

The organic modification and the hydrophobicity of the aerogels were confirmed from the Fourier Transform Infrared (FTIR) spectroscopic studies. Fig 1 shows FTIR spectrum of an aerogel sample. The broad absorption peak around 3423 cm<sup>-1</sup> arises from the -OH bonding of physically adsorbed water molecules and the peak at 1600 cm<sup>-1</sup> arises from

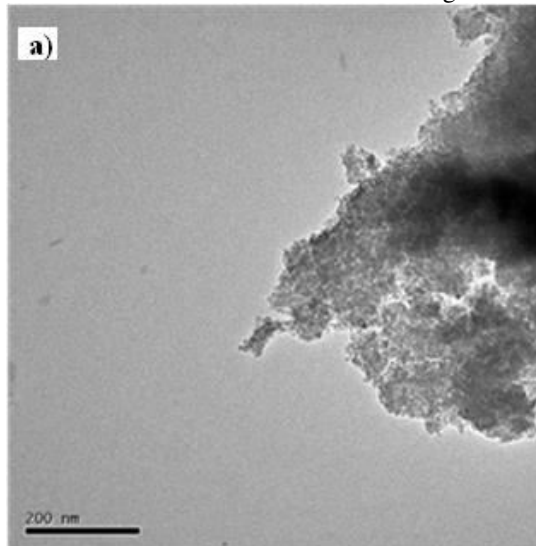
the bending modes of  $\text{-OH}$  bond. Strong peak observed at  $2845$  and  $1412\text{ cm}^{-1}$  indicating the presence of stretching and bending of  $\text{C-H}$  groups in the sample. The peak arises at  $1425\text{ cm}^{-1}$  is corresponding to  $\text{Si-Phenyl}$  group (Jeong *et al.*, 2000). The characteristic absorption peaks at  $1100$  and  $750\text{ cm}^{-1}$  is corresponding to the asymmetric, symmetric and the bending modes of  $\text{≡Si-O-Si≡}$  confirms that the polymerization of the  $\text{≡Si-OH}$  species resulting in a three dimensional  $\text{≡Si-O-Si≡}$  aerogel network (Sharad *et al.*, 2007). The reduction in relative intensity of  $\text{Si-OH}$  peaks and increase in the intensity of  $\text{Si-Phenyl}$  in the PTMS modified aerogels confirms the surface modification with the replacement of the  $\text{Si-OH}$  by non-hydrolysable  $\text{Si-Phenyl}$  groups. The intensity of the peak at  $3423\text{ cm}^{-1}$  due to free water adsorption is also reduced in the surface modified aerogels. This is due to the increased moisture conflict of the PTMS modified hydrophobic aerogels.



**Figure 1: FTIR analysis of the hydrophobic silica aerogel**

#### TRANSMISSION ELECTRON MICROSCOPIC ANALYSIS (TEM)

The TEM analysis of the silica aerogels prepared using two stage sol-gel process of TEOS shows the  $25\text{ nm}$  particle size of the silica aerogels. The high optical transmission of the silica aerogels can be well understood with the TEM analysis. This analysis revealed the nano-structured nature of the silica aerogels.



**Figure 2: TEM analysis**

#### THRMAL CONDUCTIVITY AND SPECIFIC HEAT

The thermal conductivity of the aerogel sample was measured using C-T meter (Teleph Company, France, accuracy  $10^{-3}\text{ W}^{-1}\text{m}^{-1}\text{K}^{-1}$ ) of ring probe type which measures the thermal conductivity (K) by sandwiching the ring probe in between the granular pieces made from the monolithic aerogels. The rise in the temperature of the sample ( $\Delta T$ ) due to the supplied heating power ( $0.09\text{ W}$ ) is given below.

$$\Delta T = \left( \frac{RI^2}{L} \right) * \left( \frac{1}{4\pi k} \right) * [\ln(t) + C^{te}] \quad (1)$$

The bulk density of the aerogels was calculated by dividing their masses (measured by microbalance,  $10^{-5}$  g precision) with their volumes. The thermal conductivity of the aerogels was very low and found to vary with P. It was observed that the thermal conductivity of the PTMS/TEOS based hydrophobic aerogels was found to increase from  $0.058$  to  $0.129 \text{ Wm}^{-1}\text{K}^{-1}$  with an increase in the PTMS/TEOS molar ratio from 0 to 1.15. Also, with the increase in  $k$ , the heat capacity per unit volume of the aerogel samples increased from  $166$  to  $209 \text{ kJm}^{-3}\text{K}^{-1}$  with an increase in P from 0 to 1.15. In an aerogel, the thermal transport is through the solid silica network. Since the solid network is hardly 10 % of the bulk aerogel while the remaining 90 % is porous, containing air hence thermal conductivity found to be very low. The high porosity in turn produces the aerogels with low density ( $24 \text{ Kg m}^{-3}$ ) and low thermal conductivity ( $0.091 \text{ W/m K}$ ). Therefore, higher the porosity lesser is the thermally conducting solid content in the network and hence the thermal conductivity of aerogels is low (A. Venkateswara Rao, 2001). Therefore, the thermal conductivity depends on the density of the aerogel sample and hence it was found to decrease with an increase in the PTMS/TEOS molar ratio because in general organic compounds have low thermal conductivity.

### OPTICAL TRANSMITTANCE PROPERTIES

The optical transmittance (%) of monolithic aerogels analyzed using UV-VIS Spectrophotometer (Shimadzu, UV 1800, Japan). The effect of P on the optical transmission of the retrieved silica aerogels are shown by the graph in figure 3. The superiority of the retrieved silica aerogels as supported by the nature of the graph of the optical transmission is as shown in fig.4.

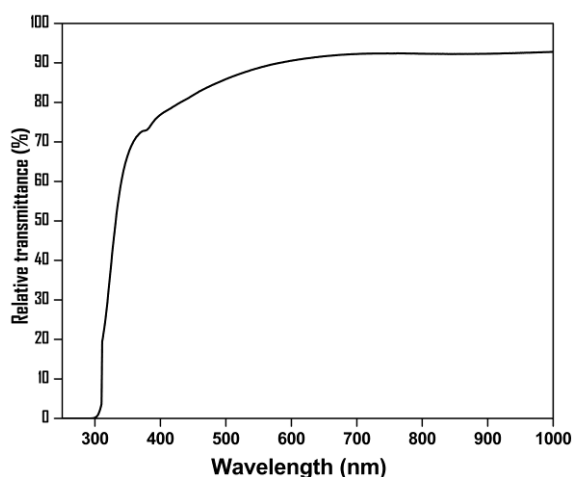


Figure 3: Optical transmittance



Figure 4: Photograph of monolithic Silica aerogels

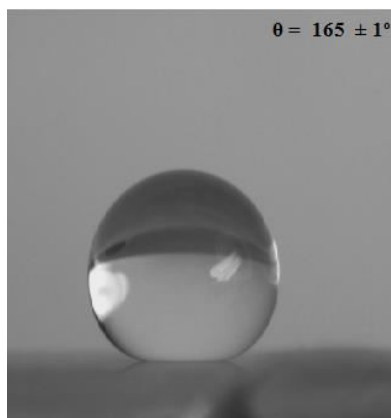
Further, increase in P value from 0.057 to 1.23, the percentage of optical transmission reduced from 91% to almost zero. This is may be due to the fact that as the PTMS increases, more and more  $\text{Si}-(\text{OCH}_3)_3$  groups are attached to the already formed silica clusters from the TEOS precursor which resulted in decrease in the cross-linkage between the clusters leading to smaller pore and larger particles of non-uniform sizes can be supported from the TEM analysis. Further, the size of the silica particles of the silica aerogels as shown in the TEM analysis and hence this supports the  $> 80\%$  optical transmission in the visible region. The particle sizes of the silica aerogels prepared using both aforesaid molar ratios are responsible for the scattering of the blue light. Hence, the silica aerogels showed bluish nature supporting the Rayleigh scattering equation (Da Silva, 1992).

$$I \propto \frac{a^6}{\lambda^4} \quad (3)$$

Where, 'a' is the pore or particle size and ' $\lambda$ ' is the wavelength of the incident light. Therefore, the opacity increases as P increases.

## HYDROPHOBICITY AND CONTACT ANGLE

The hydrophobic behavior of aerogel was quantified by keeping 5  $\mu\text{L}$  value of the water droplet on the surface of the aerogel by using contact angle meter. The small value of mass of water droplet helps to ignore gravitational effects while measurement of the water contact angle with the aerogel surface. The contact angle photographs supporting this table are shown in the fig. 5. The contact angle of the water droplet of 5  $\mu\text{L}$  size recorded with the hydrophobic aerogel surfaces was  $165 \pm 1^\circ$ . Thus the high contact angle of water droplet prevents the aerogels from the degradation due to the atmospheric vapor and which is crucial for the long term applications in both academia as well as for industrial purpose.



**Figure 5: Water drop contact angle image on aerogel surface**

## CONCLUSION

The effect of phenyltrimethoxysilane (PTMS) as a co-precursor with TEOS precursor resulted hydrophobic silica aerogels. The presence of Si-Phenyl groups made the silica aerogels hydrophobic and those were an integral part of the network structure which was confirmed from the FTIR analysis. The TEM analysis revealed nano-structured particle size of the silica aerogels which supports the high optical transmission. The monolithic, hydrophobic, ultra low dense, low thermal conducting silica aerogels was prepared by using the two stage sol-gel process of the tetraethoxysilane. Thus, these aerogels may be used for the various scientific and technological applications viz, for low dense material for Cerenkov radiation detection, high energy particle physics, and in the thermal insulation applications.

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