Estimation of Surface Free Energy of Methyltrimethoxysilane Based Superhydrophobic Flexible Silica Aerogels Using Neumann's Equation of State

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Abstract: Assessments of the surface free energy of low-energy solids by means of easy to perform contact angle measurements would be very attractive. The surface free energy of a solid determines its surface and interfacial behavior in process like wetting and adhesion which is crucial for silica aerogels in case of organic liquid absorption and transportation of chemicals at nano-scale for biotechnological and medical applications. The "equation of state" approach of Neumann's equation which uses liquid drop contact angle with the solid surface as a single parameter for estimation of surface free energy of the solid. The surface free energy of the silica aerogels with different other liquids of known surface tension values and low volatility was measured and the estimate of the change in the surface free energy was achieved. The flexible, superhydrophobic and low density silica aerogels was prepared using a two stage sol-gel process of methyrtrimethoxysilane as a precursor. The flexible silica aerogels have been characterized by bulk density, volume shrinkage (%), porosity (%) and thermal conductivity. The quantitative analysis of hydrophobicity was done by measuring the water drop contact angles of the surface of aerogel. The micro-structural and elemental analyses studies were carried out using transmission electron microscopy (SEM) and fourier transform infrared (FTIR) spectroscopy. The thermal stability of the aerogel was checked by thermo-gravimetric and differential scanning colorimetric (TGA-DSC) analysis. Silica monolithic aerogels with ultralow density 40 Kg/m^3 and low thermal conductivity ~0.072 W/mK has been obtained by supercritical drying process.

Keywords: Surface energy, Equation of state, hydrophobicity, flexible silica aerogels, supercritical drying process

INTRODUCTION

Silica aerogels are unique nano materials since they are both transparent (~90% optical transparency) and highly porous (>98%) at the same time [1]. 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. Hence, it is necessary to prepare the elastic (flexible) and hydrophobic aerogels, which would widen their applications. Even though the synthesis of MTMS based aerogels by a single-step sol–gel process has already been reported, 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. 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 in one day. A common approach to estimate the surface free energy of the solid surface is based on an interpretation of sessile drop contact angle data. Much work has been done on the evaluation of the surface tension of the low-energy surfaces because of the relative ease of measuring contact angle values on the surfaces. Although it is impossible to measure directly the surface tension of a solid, several approaches exists that correlate the contact angle with the surface tension of the solid.

RESULTS AND DISSCUSSIONS:

1] TG-DSC Analysis of the Silica Aerogel:

Fig. 1 shows that TGA and DSC profiles of the silica aerogel. The TGA curve shows noticeable weight loss at around 463ºC accompanied with an exothermic peak in the DSC curve. The sudden weight loss in TGA curve around 463ºC is due to the decomposition of alkyl ($–CH_3$) groups. The exothermic peak in DSC curve indicates the oxidation of alkyl groups. It indicates hydrophobicity of the silica aerogel is thermal stable up to 463ºC and above this temperature the silica aerogels becomes hydrophilic in nature.

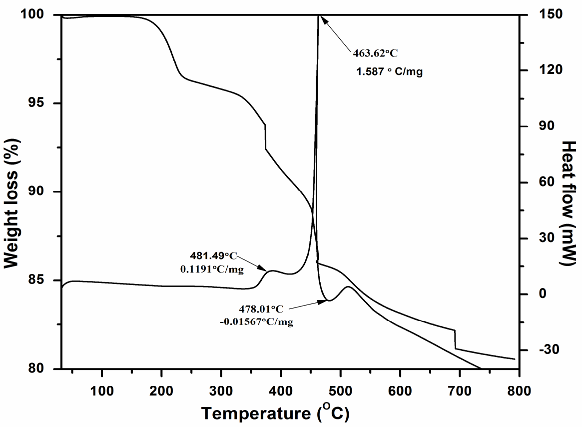


Fig. 1. TG-DT Analysis of the Flexible silica aerogels

2] Fourier Transform Infrared Spectroscopy (FTIR):

Fig.2 shows the FTIR study of the silica aerogel. The wetting behavior of superhydrophobic silica aerogel is governed by the chemical composition. Several characteristic absorption peaks were observed in the range of 450 cm^{-1} to 4000 cm^{-1} indicating the presence of methyl groups in the sample [8]. The broad absorption peak observed at 1080 cm^{-1} which is characteristic peak of the Si-O-Si bond present in both samples. The absorption bands were observed at 2950 and 1400 cm^{-1} are due to stretching and bending modes of C–H bond and the peaks observed at 765 & 1265 cm^{-1} are due to the Si–C bonds. The 1265 cm^{-1} peak indicates the presence of the Si–C bonding [9]. The absorption peaks at 1600 and 3400 cm^{-1} corresponding to the polar –OH bonds.

3] Scanning Electron Microscopic and Contact Angle Studies:

Fig. 3. Shows the SEM

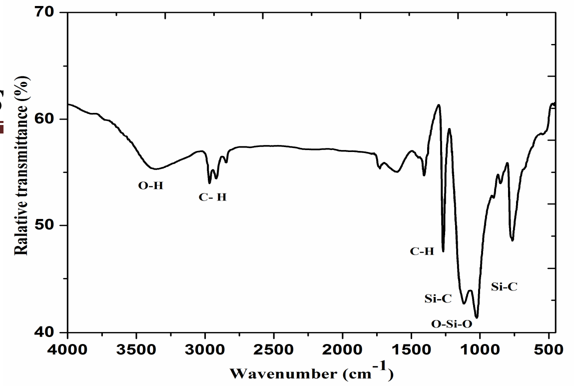
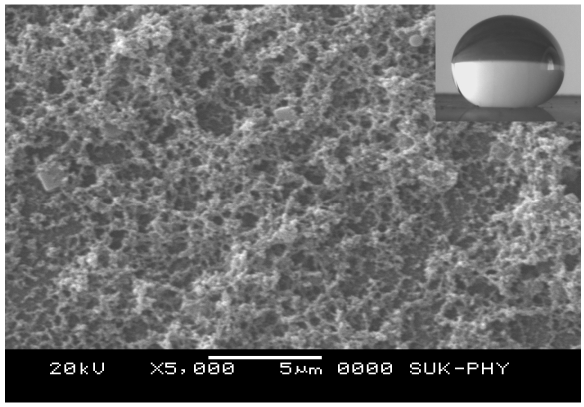


Figure.2. FTIR spectra of the Flexible silica aerogels

and water drop contact angle studies of the flexible silica aerogel.



In the SEM studies it is evident that the microstructure of the silica aerogel is composed of nanostructured microporous network of the silica particles with excellent branching. Highly nanoporous and well branched network is responsible for the flexibility. This structure of the silica aerogel showed a contact angle with water droplet as high as 163º for a droplet size of 5μL.

4] Theoretical Background of the Surface Energy of the Silica Aerogels:

The change in surface energy was quantified by using Neumann's equation of state. The hydrophobicity of the aerogels depends upon the chemical composition of the surface and surface tension of the liquid. The contact angle measurements are routinely used to monitor the changes in the chemical surface modifications carried out to quantify the hydrophobicity. The advantage of using these equations is that it requires only one liquid in the estimation of apparent surface free energy of solid but it has limitation that neither the dispersion nor the polar component can be evaluated . The calculation of solid surface tension, γ_{sv}, from the contact angle, θ, of a liquid of surface tension γ_{lv}, starts with the Young's equation

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv}\cos\theta \tag{1}$$

Where, γ_{SL} is the solid-liquid interfacial tension. Of the four quantities in Young's equation, γ_{LV} and θ are readily measurable. Thus, in order to determine γ_{SV}, further information is necessary.

4.1 Neumann's Equation of State:

It is well known that the liquid with surface tension greater than the surface of solid (γ_{LV} , γ_{SV}) make definite contact angle with solid surface and if the surface tension of liquid is less than the surface tension of solid then total wetting occurs which indicates θ = 0º [10]. Neumann et al. [11] suggested that a relationship between γ_{SV}, γ_{SL}, and γ_{LV} exists, and the Neumann's equation of state is given by [12]

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}}\,\ell^{-0.000125\,(\gamma_{lv}-\gamma_{sv})^2} \tag{2}$$

By solving and simplifying using Taylor series,

$$\gamma_{sv} = \gamma_{lv} + \frac{\sec^4(\theta/2)}{4*0.000125*\gamma_{lv}} - \sqrt{\left[\gamma_{lv} + \frac{\sec^4(\theta/2)}{4*0.000125*\gamma_{lv}}\right]^2 - (\gamma_{lv})^2 - \frac{1}{2*0.000125}} \tag{3}$$

Thus the calculated surface energy of the resulting flexible silica aerogels is as shown in the table1.

Sr. No.	MeOH/MTMS molar ratio	Water drop contact angle(θ) ±1º	Surface energy γ_{sv} (mJ/m^2)	Surface tension γ_{sl} (mN/m)
1	10	92	25.73	84.12
2	15	110	14.27	71.07
3	20	119	9.45	65.63
4	25	123	7.6	63.55
5	30	142	1.8	57.04
6	35	163	0.05	55.08

ACKNOWLEDGEMENT

The authors are grateful to the Department of Atomic Energy (DAE), Board of Research in Nuclear Sciences (BRNS), Mumbai, Government of India, for the financial support for this work through a major research project on "Aerogels" (No.2008/37/47/BRNS/2502). The authors, Mr. M. S. Kavale and D.B. Mahadik are greatly thankful to the DAE−BRNS for the Junior Research Fellowships (JRF).

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