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Effects of Phenyltrimethoxysilane and *Polyvinyl Alcohol* on the Properties of Methyltrimethoxysilane-based Silica Aerogels

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Silica aerogels have attracted great attention owing to their outstanding properties such as ultralow density, high porosity, high surface area, and low thermal conductivities. Their poor mechanical properties and hydrophilicity constrain their practical applications. In this work, phenyltrimethoxysilane (PTMS) and *polyvinyl alcohol (PVA)* were added into methyltrimethoxysilane (MTMS)-based silica aerogels to enhance their mechanical properties. It was found that PTMS considerably improved the hydrophobicity of MTMS silica aerogels with an increase in water contact angles from 115° to 150°. The addition of PVA considerably increased the hardness, morphology, density, porosity, surface area, and thermal conductivity of MTMS silica aerogels. When PVA concentration was increased from 0 to 2 %, the aerogel hardness, density, and thermal conductivity were also increased from 0 to 14 %, 0.072 to 0.11 g/cm^3, and 0.035 to 0.046 W/m.K. In contrast, the aerogel became less porous and the porosity reduced from 97.2 % to 95.72 % and BET surface area decreased from 389 to 43 m^2/g.

1. Introduction

Silica aerogels are one of the lightest materials in the world (Baldino et al., 2015). They have porous structures with three-dimensional networks of mesopores (Balasundram et al., 2017). Silica aerogels, owing to their unique properties, such as high porosity (>90 %), low density, and high surface area, have attracted considerable research interest toward applications such as catalysts (Maleki, 2016) and adsorbents (Parale et al., 2018). In particular, silica aerogels are also promising for thermal insulation owing to their low thermal conductivity (<0.05 W/mK) and can be applied for doors, windows, or heat storage systems (Jelle, 2011). Since, they are commonly prepared from tetraorthosilicate (TEOS) (Hilonga et al., 2009), they have active OH groups on the surface and, thus, are hydrophilic. The hydrophilicity makes them prone to get deteriorated when exposed to moisture and water (De Marco et al., 2016). The weak mechanical and hydrophilic properties of hydroaerogels limit their practical applications (Kabeel et al., 2019). Hence, it is essential to improve their hydrophobicity as well as mechanical property. One of the most popular ways to overcome hydrophilicity is to use methyltrimethoxysilane (MTMS) as the precursor instead of TEOS for silica aerogel synthesis (Pan et al., 2017). This imparts hydrophobicity to aerogels by adding methyl groups on the surface. It is also necessary to enhance the hydrophobicity of MTMS silica aerogel. In this work, *hydrophobicity and mechanical property of MTMS aerogels* were improved by adding phenyltrimethoxysilane (PTMS) and *polyvinyl alcohol (PVA).*

2. Experimental

2.1 Chemicals

Methyltrimethoxysilane (MTMS, 95 %), phenyltrimethoxysilane (PTMS, 98 %), absolute ethanol, acetic acid (99.5 %), ammonia solution (25 %), and polyvinyl alcohol (PVA, Mw 89,000–98,000) were purchased from

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Sigma-Aldrich (Singapore). A 0.1 M acetic acid solution was prepared from 99.5 wt% acetic acid solution and de-ionized (DI) water.

2.2 Synthesis of aerogels

In a typical synthesis procedure, 7 mL of 0.1 M acetic acid, 4.5 mL of ethanol, and 2 mL of MTMS were added into a beaker and were mixed with a magnetic stirrer to form solution A. Solution B was formed from a mixture of 4 mL of ethanol and 0.33 mL of MTMS. After that, solution B was added dropwise into solution A and the mixture was stirred for 90 min. Then 1.4 mL of 25 wt% ammonia solution was slowly added into this mixture. The mixture was stirred until gelation and poured into a mold. The gel was aged for 2 d and the solvent exchange was carried out during this period by DI water. After the solvent exchange, the sample was immersed in a PVA solution for 1 h. The sample was then frozen at -30 °C for 5 h and dried in a freeze dryer (Toption TPV-50F, China).

In this work, the molar ratio of MTMS: ethanol: water was kept at 1: 9: 24. The molar ratio of PTMS: MTMS was varied from 0 to 3, 6 and 10 % while PVA concentration was changed from 0 to 1 and 2 wt%.

2.3 Characterization

X-ray diffraction (XRD) analysis was conducted on a D8 Bruker AXS (CuKα, 40 kV, 20 mA, 2θ range of 20°–50°, scan rate 0.042 °/s). The morphology of powder samples was investigated using scanning electron microscopy (SEM) with a Hitachi S4800 at 2 kV. Nitrogen adsorption/desorption was performed at -196 °C by a TriStar II 3020 (Micromeritics).

Fourier-transform infrared spectroscopy (FTIR) was carried out using a Nicolet 5700 (Thermo Electron Corp., USA). The thermogravimetric analysis of the samples was carried out using a Labsys Evo (Setaram) at a temperature range of 29–800 °C and a heating rate of 10 °C/min in air. Thermal conductivity measurement was done on a C-Therm TCi Thermal Conductivity Analyzer (C-Therm Technologies, Canada). The hydrophobicity of the samples was expressed as the water contact angle measured by a VCA Optima goniometer (AST Products Inc., USA). The mechanical property of the samples was determined using an Asker CL-150M Durometer Constant Load Test with a load of 1 kg.

3. Results and discussion

3.1 Effect of PTMS/MTMS ratio on the hydrophobicity and gelation time of the silica aerogels

The water contact angles of the silica aerogels were increased when the PTMS/MTMS molar ratio was increased, indicating an improvement in the hydrophobicity of the samples (Figures 1 and 2a). The water contact angle reached a value of 150° when the PTMS/MTMS ratio was 10 %, confirming the superhydrophobicity of the aerogel. The enhancement in the hydrophobicity, concomitant with increasing PTMS/MTMS molar ratio, can be explained by the increase in phenyl groups and the decrease in OH groups on the sample surface.

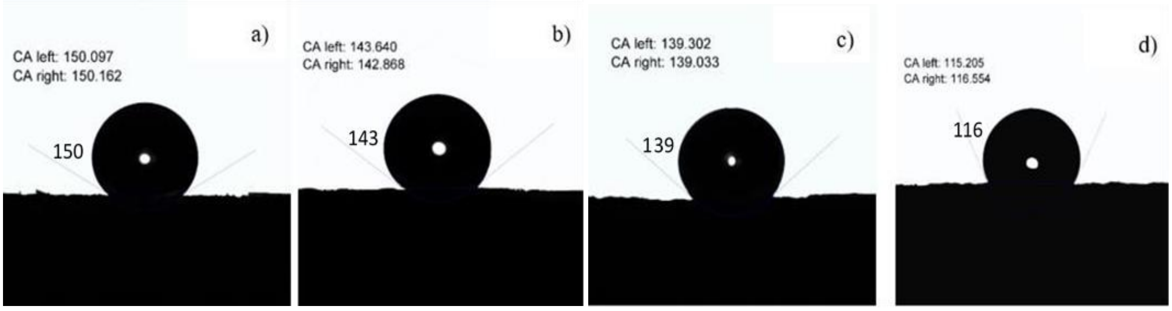

Figure 1: Water contact angles of silica aerogel samples prepared with different PTMS/MTMS molar ratios of (a) 10 %, (b) 6 %, (c) 3 %, and (d) 0 %

The rise in PTMS/MTMS molar ratio caused an increase in the gelation time, as shown in Figure 2b. It is possible that PTMS has a longer hydrolysis time than MTMS. It has been reported that the non-hydrolysable groups increase the gelation time of a sol. This made the total time of hydrolysis and condensation longer than that of MTMS.

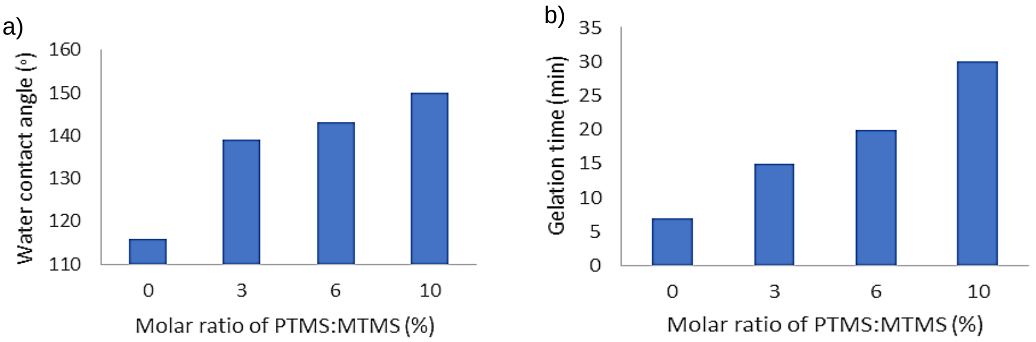

Figure 2: Effect of PTMS/MTMS molar ratio on (a) hydrophobicity of the aerogel samples and (b) gelation time

3.2 Effect of PTMS/MTMS molar ratio and PVA on the specific density and porosity of silica aerogel

The effect of PTMS/MTMS molar ratio on the density and porosity of the silica aerogels is shown in Figure 3a. The porosity of aerogels was calculated using Eq(1).

$$\varepsilon = \left(1 - \frac{d_{aerogel}}{d_{silica}}\right) x\ 100\% \qquad (1)$$

where ε is porosity, $d_{aerogel}$ is the specific density of aerogel, and d_{silica} is the specific density of silica (2.56 g/cm^3)

It is clear that when PTMS/MTMS molar ratio was increased from 3 % to 6 %, the density of aerogel was increased from 0.063 to 0.072 g/cm^3. When the ratio was increased from 6 % to 10 %, the aerogel density was slightly decreased to 0.07 g/cm^3. Concomitant with these changes, the porosity of the aerogel was reduced from 97.56 % to 97.2 % and then increased to 97.26 %.

It can be concluded from Figure 3b that PVA concentration has a strong effect on the specific density and porosity of the aerogel. The density went up when PVA concentration was increased from 0 to 1 wt% and 2 wt%; this resulted in a decrease in the porosity from 97.2 % to 96.11 % and 95.72 %. This phenomenon is probably due to the fact that PVA works as a binder and blocks some pores.

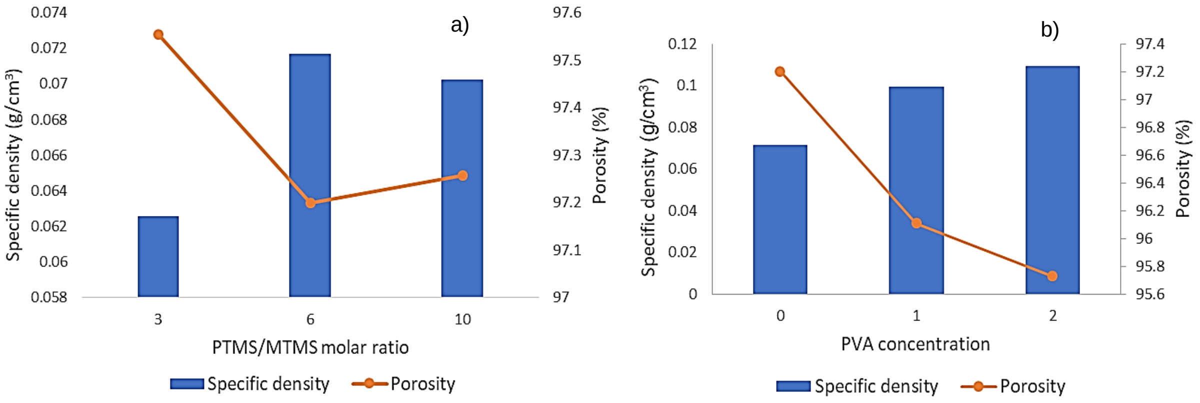

Figure 3: Effect of (a) PTMS/MTMS ratio (%) and (b) PVA concentration (wt%) on the specific density and porosity of aerogels

3.3 Structure and morphology of PTMS/MTMS silica aerogels

The 6 % PTMS/MTMS aerogel immersed in 1 wt% PVA solution was found to be the most optimum composition for the synthesis of silica aerogels and thus was selected for further investigation. Figure 4 displays the XRD patterns of the 6 % PTMS/MTMS aerogel immersed in 1 wt% PVA solution. There are no peaks in the pattern implying that the aerogel has an amorphous structure.

The SEM results showed that the PTMS/MTMS aerogel is composed of silica particles connected together to form a porous structure (Figure 5). When the sample is immersed into the PVA solution, PVA promotes bonding between silica particles, which create a stronger network. PVA also blocks some pores, making the aerogel less porous.

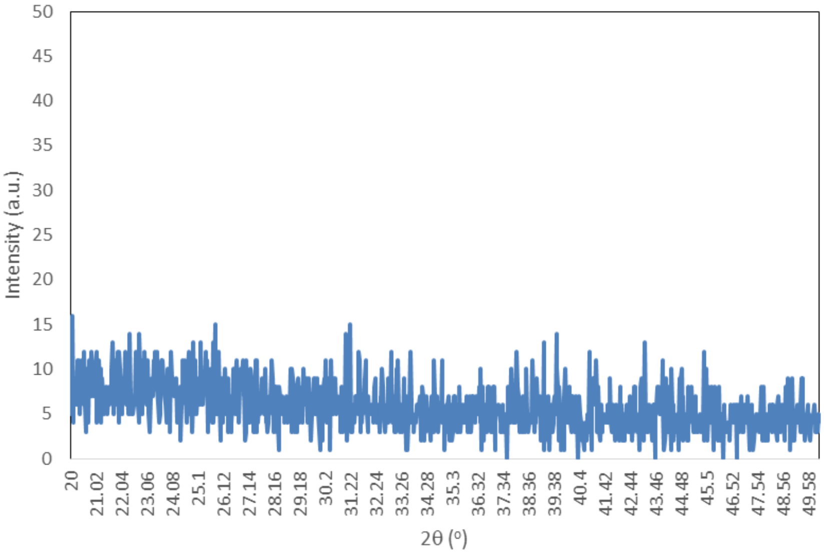

Figure 4: XRD patterns of the 6 % PTMS/MTMS aerogel immersed in 1 wt% PVA solution

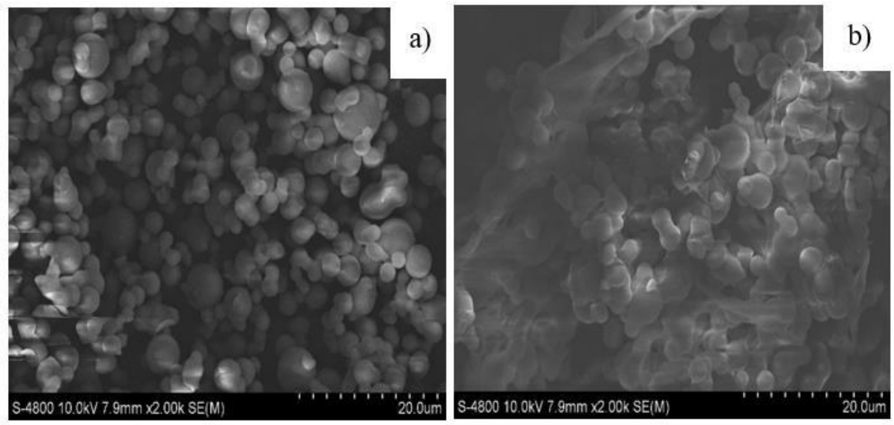

Figure 5: SEM images of the 6 % PTMS/MTMS aerogel (a) without PVA; (b) and after immersion in 1 wt% PVA solution

BET surface areas of the 6 % PTMS/MTMS aerogel without PVA is 389 m^2/g, which is considerably larger than that of the 6 % PTMS/MTMS aerogel immersed in 1 wt% PVA solution (Table 1). As shown in Figure 5, this can be explained by the fact that PVA blocks some pores, resulting in a smaller BET surface area.

Table 1: BET surface of PTMS/MTMS aerogel samples

Sample	BET surface area (m^2/g)
6 % PTMS/MTMS aerogel without PVA	389
6 % PTMS/MTMS aerogel immersed in 1 wt% PVA solution	43

The FTIR spectrum of 6 % PTMS/MTMS aerogel immersed in 1 wt% PVA solution is shown in Figure 6. Two peaks at 3,438 cm^{-1} and 1,630 cm^{-1} caused by –OH groups were observed. Two small peaks at 2,974 cm^{-1} and 1,382 cm^{-1} could be attributed to vibration of C–H groups. The peak at 1,430 cm^{-1} corresponds to Si-phenyl and confirms the existence of phenyl groups. Peaks at 1,024 cm^{-1} and 776 cm^{-1} belong to the vibration of Si-O-Si.

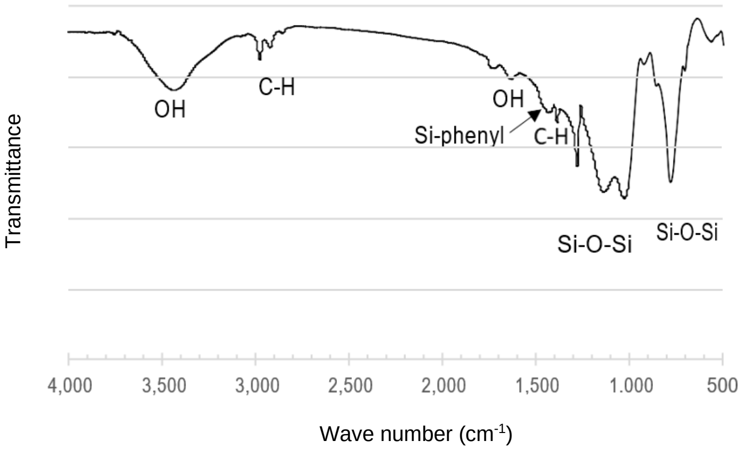

Figure 6: FTIR results of 6 % PTMS/MTMS aerogel immersed in 1 wt% PVA solution

3.4 Thermal properties of PTMS/MTMS silica aerogels

TGA-DSC investigation was performed to evaluate the thermal stability of the aerogel samples. Figure 7 presents TGA-DSC results for the 6 % PTMS/MTMS aerogels immersed in 0 and 1 wt% PVA solutions. It can be observed that the sample without PVA shows an exothermal peak at 500 °C due to the oxidation of methyl and phenyl groups and the destruction of aerogel structure, causing a weight drop of 14 %. In the figure, two exothermic peaks at 320 °C and 500 °C for the aerogel with PVA can be seen. The first peak is probably due to the oxidation of PVA, which causes a small weight loss of 7 %. The large and strong peak represents the oxidation of methyl and phenyl groups and the deterioration of the aerogel structure, resulting in a weight loss of 19 %. The remaining weight is due to silica with 74 % of the original weight. No weight loss or endothermic peaks were observed at 100–150 °C for the two aerogels indicating the hydrophobic nature of the samples.

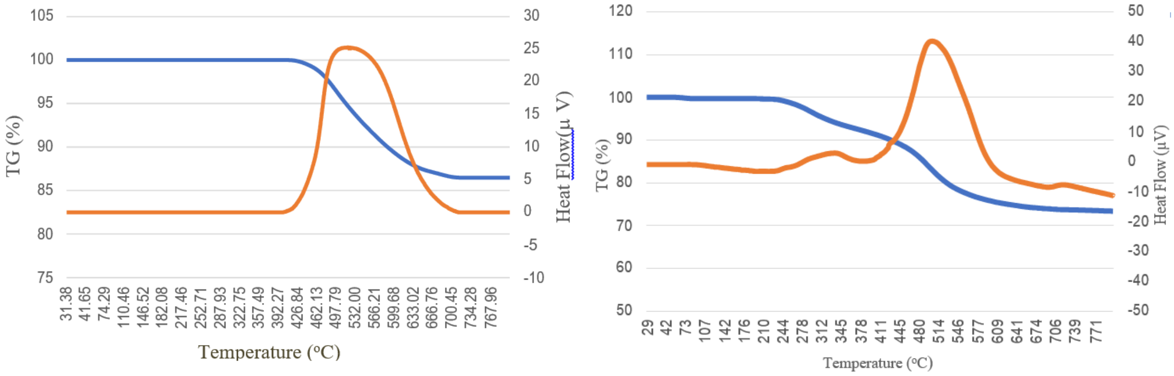

Figure 7: TGA result of 6 % PTMS/MTMS aerogel immersed in (left) 0 and (right) 1 wt% PVA solution

The effect of PVA concentration on the thermal conductivity of the PTMS/MTMS aerogel is shown in Table 2. The thermal conductivity rises from 0.035 to 0.046 W/m.K when the PVA concentration increases from 0 to 2 wt%.

Table 2: Thermal conductivity of 6 % PTMS/MTMS aerogels immersed in PVA solutions of different concentrations

PVA concentration (wt%)	Thermal conductivity (W/m.K)
0	0.035
1	0.045
2	0.046

It can be explained by the fact that PVA blocked some pores, which reduced the porosity of the aerogel (Figure 3b) and increased thermal conductivity. The thermal conductivities of the 6 % PTMS/MTMS aerogels are comparable to those of common insulation materials, such as mineral wool (0.037–0.055 W/m.K), expanded polystyrene (0.030–0.040 W/m.K), and cellulose (0.040–0.050 W/m.K), making them promising in thermal insulation applications (Jelle, 2011).

3.5 The hardness of aerogel samples

The effects of PVA concentration on the hardness of 6 % PTMS/MTMS aerogel samples is shown in Table 3. It is obvious that the hardness of the aerogel increases with the rise in PVA concentration. It can be explained as a higher PVA concentration promotes binding in the aerogel to improve the bonding between silica particles, which make the structure more rigid and stable.

Table 3: Effect of PVA concentration on the hardness of 6 % PTMS/MTMS aerogels immersed in PVA solutions of different concentrations

PVA concentration (wt%)	Hardness (%)
0	0
1	11
2	14

4. Conclusions

The incorporation of PTMS as a co-precursor with MTMS to form hydrophobic silica aerogels was successful. The as-prepared aerogels showed significantly improved hydrophobicity compared to MTMS silica aerogels. The treatment of PTMS/MTMS silica hydrogel with PVA solutions enhanced the mechanical property of the final aerogel product but reduced its porosity. The PTMS/MTMS aerogel showed low thermal conductivity, which is favorable in thermal insulation applications.

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