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Control of porous structure in flexible silicone aerogels produced from methyltrimethoxysilane (MTMS): The effect of precursor concentration in sol-gel solutions

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Control of porous structure in flexible silicone aerogels produced from methyltrimethoxysilane (MTMS): The effect of precursor concentration in sol-gel solutions

Abstract

Controllable nanoporous structure in MTMS based silicone aerogels is required to improve their thermal conductivity. Silicone aerogels were formed in a two-step acid-base catalysed sol-gel process combined with supercritical drying. The influence of MTMS concentration, specifically the molar ratio of methanol:MTMS and water: MTMS in the sol-gel process was studied in relation to the porous structure of resultant silicone aerogels. Samples were characterised to determine the dimensions of micro, meso and macro-pore structure by means of both nitrogen gas adsorption-desorption for detection of pores less than 300 nm and by analysis of FEG-SEM images for pores greater than 300 nm. Porosity, pore volume distribution and BET surface area in the silicone aerogels were all found to be influenced by adjustment of the molar ratio of methanol:MTMS and the molar ratio of water:MTMS during sol-gel processing.

Key words: Silicone aerogel; MTMS; Sol-gel; Pore size distribution; Pore volume; Porosity

1. Introduction

Aerogels are porous structures with excellent physical properties including low density, high porosity, high surface area and low thermal conductivity, depending on the porous structure. Industrially, silica aerogel made from Tetraethoxysilane (TEOS) is one of the most popular and has the lowest reported thermal conductivity of $0.017\text{--}0.021\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [1]. However, such TEOS based aerogels tend to be rigid, brittle and hydrophilic which limits their practical applications in textiles and clothing. The hydrophobicity of TEOS based aerogel can be improved by incorporating co-precursors at the sol stage and chemically modifying the surface of resultant gels during ageing stage [2, 3]. However, modification is time consuming, costly, and tedious. Additionally, this does not resolve the issue of rigidity and brittleness.

Methyltrimethoxysilane (MTMS) based silicone aerogel and xerogel made in previous researches [4] is flexible and inherently hydrophobic, but their thermal conductivity is relatively poor, being usually greater than $0.05\text{ Wm}^{-1}\text{K}^{-1}$ [5-7], and this does not meet the requirements of highly thermal insulation materials for clothing used in extreme environmental conditions. Since the thermal conductivity of aerogels is related to their nanoporous structure, it may be possible to improve the thermal conductivity of these silicone aerogels by appropriate engineering of the material during sol-gel processing. For TEOS based aerogels extensive research [8-14] has been reported on the influence of sol-gel process parameters, such as the use of different precursors, catalysts for hydrolysis and condensation, the ratio of precursor to solvent, the ratio of precursor to water, catalyst concentration, aging

time, solvents for gel surface modification and drying methods. However, for MTMS based silicone aerogels far less is known about how porous structures respond to sol-gel processing parameters.

Sol-gel processing parameters can be grouped into two categories:

- (1) Factors affecting the concentration of MTMS in wet gels, such as the molar ratio of methanol to MTMS precursor and the molar ratio of water to MTMS precursor; the hydrolysis catalyst, oxalic acid, and the condensation catalyst, ammonia solution were added together with water, so the change of the amount of water not only alters the concentration of the MTMS in the solution but also change the amount of acid and base, and
- (2) Factors related to the condensation reaction that affect the formation of nanoparticles and agglomerations in the gelation process but that are unable to change the concentration of silicone in wet gels. This includes the concentration of condensation catalyst (ammonia solution), and the gel ageing time.

The purpose of this paper was to determine the influence of precursor concentration on the nanoporous structure of MTMS based silicone aerogels. Specifically, this involved modifying the molar ratio of methanol to the precursor MTMS, and the molar ratio of water to the precursor MTMS in a two-step acid-base catalysed sol-gel process, and then studying the pore structure on length scales from 1.7 nm to >300 nm.

2. Preparation and characterisation of MTMS based silicone aerogels

Aerogels can be formed using various sol-gel processes including the acid catalysed sol-gel process, base catalysed sol-gel process and the two-step acid-base catalysed sol-gel process. Aerogels made from the acid or base catalysed sol-gel methods are usually more rigid and have lower porosity than those from the two-step acid-base catalysed sol-gel process. However, aerogels produced by the two-step acid-base catalysed sol-gel process tend to exhibit smaller pore sizes and a narrower pore size distribution [15-17].

In the present study, the two-step acid-base catalysed sol-gel process was used to prepare MTMS based silicone aerogel. In the first step, the MTMS precursor was mixed with methanol (MeOH), at specific MeOH/MTMS molar ratios, then hydrolysed using a 0.01M aqueous solution of oxalic acid, under stirring at room temperature for 20 h to form a prepared sol. In the second step, 10M ammonia solution was gradually added into the resultant sol at a fixed feed rate of 5 ml·min⁻¹ whilst stirring to initiate the condensation reaction. The prepared sol was stored in an air-tight container at room temperature to allow gelation to occur. The elapsed time from the point of addition of the base solution to the moment of gel formation in the sol is referred to as the gelation time. After gelation, additional solvent (methanol) was added into the gel container and the silicone gel was then aged at room temperature for a fixed period of 88 h. Finally, the resultant silicone gel was dried using supercritical carbon dioxide (45°C, 200 bar) for 10 h and then depressurised at a rate of 0.5 bar·min⁻¹.

To identify the influence of the molar ratio of methanol:MTMS precursor on the structure of the aerogel, the structures of four aerogels obtained using four different molar ratios of methanol:MTMS ranging from 15:1 to 30:1 were examined. The molar ratio of water:MTMS was fixed at 6:1 because the water added in the sol formation process originated from both the addition of the acid hydrolysis solution and the base condensation solution. The molar ratio of the water from oxalic acid to water from the ammonia solution and to the MTMS was therefore fixed at 4:2:1.

Similarly, the influence of the molar ratio of water to MTMS precursor on the structure of the aerogels was studied using four different molar ratios of water to MTMS ranging from 4:1 to 10:1. The molar ratio of methanol to MTMS precursor was fixed at 15:1 and other sol-gel process parameters were constant as described above.

The porous structure of each of the sample MTMS based aerogels was characterised to determine the specific surface area, pore size distribution, pore volume, true density and porosity. The specific surface area, pore size and pore size distribution were obtained using the nitrogen gas adsorption technique (Micromeritics Tristar 3000) in which the specific surface area is determined by means of the Brunauer–Emmitt–Teller (BET) method and the pore size and pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method based on the desorption branch of the isotherm [18-20]. The true density of aerogel containing open pores was measured using an AccuPyc 1330 Pycnometer. With consideration of possible larger pores (greater than 300nm) produced in the aerogel materials, which could not be detected by both BET and true density testing methods, the porous structure of the aerogel were also characterised by image analysing the aerogel images (three specimens of each sample with magnifications of 120K) produced by FEG-SEM after the samples were platinum sputter coated.

3. Effect of MTMS concentration on nanoporous structure

Changes in both the molar ratio of methanol:MTMS and molar ratio of water:MTMS led to various concentrations of silicon in the solvent. Note that the solvent consists of a mixture of methanol and water and therefore the influence of the molar ratio of the methanol:MTMS on nanoporous structure in the aerogels was of interest. The silicone aerogels made from the wet gels using various concentrations of MTMS in solvent are summarised in Table 1. The influence of both the molar ratio of methanol to MTMS and the molar ratio of water to MTMS on the porous structure of silicone aerogels are discussed in sections 3.1 and 3.2 respectively.

Table 1 Silicone aerogels produced from wet gels at different
MTMS concentrations

Solvent MeOH:H₂O:MTMS	Solvent:MTMS ratio
15:6:1	21:1
20:6:1	26:1
25:6:1	31:1
30:6:1	36:1
15:4:1	19:1
15:8:1	23:1
15:10:1	25:1

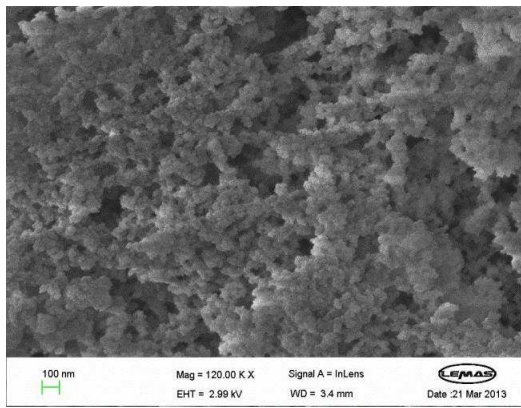
3.1 General effect of molar ratio of solvent to MTMS

The change of molar ratio of the total solvent to MTMS is effectively equivalent to a change in the concentration of silica/silicone in the sol-gel processes. Therefore, the effects of the molar ratio of the solvent (both water and methanol together) to MTMS on the porous structure of the resultant silicone aerogels are considered in this section.

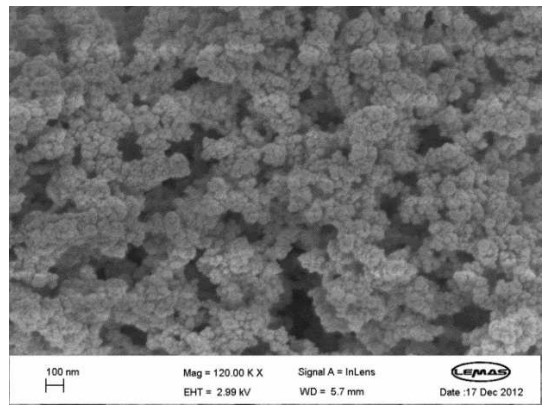
3.1.1 Effect of molar ratio of solvent to MTMS on macropores

The silicone aerogels produced were found to contain a mixture of macropores (>50nm), mesopores (2~50nm) and micropores (<2nm), which influences the specific surface area and pore volume and can be expected to affect thermal conductivity. Only pores less than 300 nm in diameter could be detected and quantified by BET nitrogen adsorption methods. However, the larger macropores of >300 nm in diameter that could not be detected and quantified using BET methods were also of interest and could not be neglected because of their likely influence on thermal conductivity. Mesopores and macropores in aerogel structures contribute differently to the bulk thermal conductivity behaviour [21-23]. In mesopores, the Knudsen effect of gas conduction dominates while in the macropores, conventional conduction can take place and larger pores can potentially act as heat bridges reducing the overall insulative properties of the bulk structure. Quantification of the larger pores was carried out by analysis of FEG-SEM images of the aerogel structure.

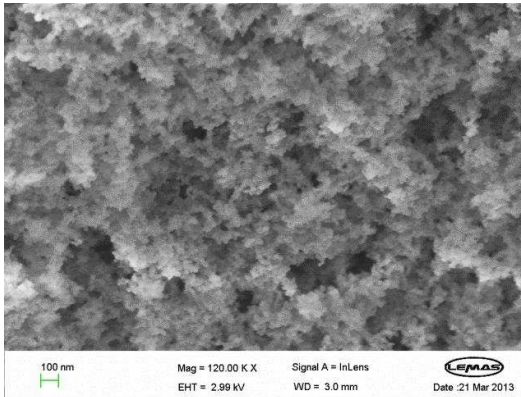
The microstructure of silicone aerogels obtained at various molar ratios of the solvent to MTMS is presented in Figure 1 and the pore size distribution of the larger pores based on image analysis of those pictures on Figure 1 are summarised in Table 2.



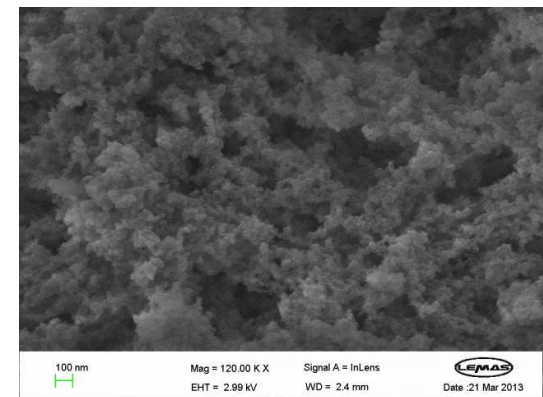
(a) 19:1



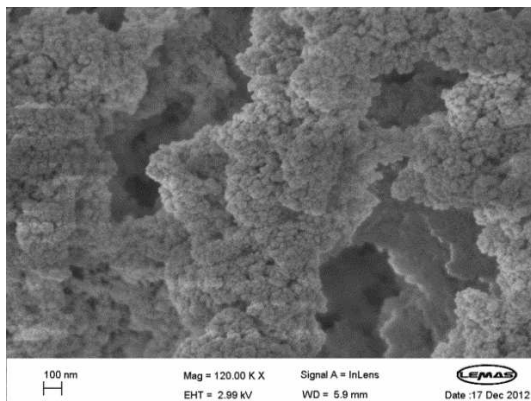
(b) 21:1



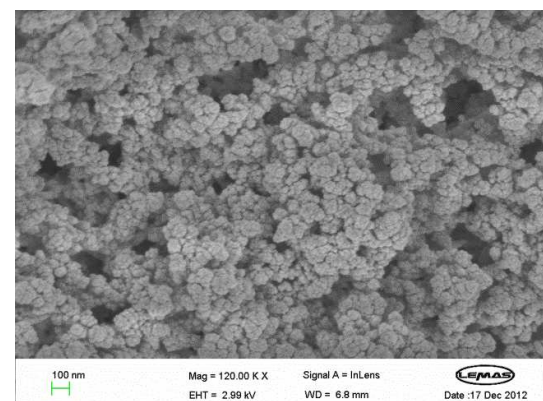
(c) 23:1



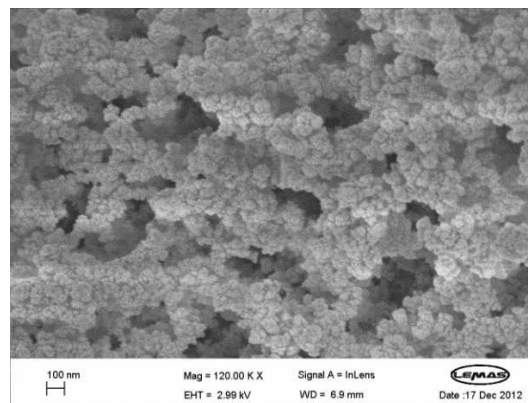
(d) 25:1



(e) 26:1



(f) 31:1



(g) 36:1

Figure 1 Large pores (> 300nm) in the silicone aerogels obtained at various molar ratios of solvent (mixture of water and methanol) to MTMS

Almost all of the pores of different sizes were found to be tortuously connected with each other, and there was no apparent relation between the pore size of the larger pores (>300nm) in the silicone aerogels and the molar ratios of solvent to MTMS in the sol-gel processes. Note that the sizes of the nanoparticle/nanoparticle agglomerations in the aerogels produced from sol-gels with different molar ratios of solvent to MTMS were nearly in the same range (Figure 1(a) ~1 (d), 1(g) and 1(f)) except at a molar ratio of 26:1 (Figure 1(e)). The aerogel obtained from the molar ratio of 26:1 contained relatively large pores between particle clusters and the particle size inside the particle agglomerations was smaller than that in the aerogels obtained using other molar ratios.

The sizes of the largest pores in this group of aerogels are shown in Table 2. It was apparent that the mean size of the largest pores was between 210~630 nm and the largest pore of around 629 nm was obtained at a molar ratio of 26:1. However, the numerical frequency of those larger pores (larger than 300 nm) was less than 1%. While the number of the larger pores was negligible in these aerogels (26:1), the proportion of larger pores in terms of the apparent pore areas in samples produced at a molar ratio of solvent to MTMS of 25:1 was markedly higher (>40%) in some cases.

Table 2 Pore size distribution of the larger pores (>300 nm) in silicone aerogels

Solvent:MTMS ratio	Proportion of pores >300nm		Maximum pores (nm)
	Number (%)	Area (%)	
19:1	0.0	0.0	278
21:1	0.07	4.4	263
23:1	0.0	0.0	218
25:1	0.7	41.3	431
26:1	0.08	25.4	629
31:1	0.0	0.0	224
36:1	0.6	31.0	415

3.1.2 Effect of the molar ratio of solvent to MTMS on smaller pores

The molar ratio of solvent to MTMS in sol-gel processes affects the formation of smaller pores (1~300 nm in diameter), as well as larger pores. The small pores were characterised in terms of bulk density, porosity, BET surface area, total pore volume, mesopore volume and mesopore volume percentage in the BET adsorption method and are presented in Figure 2.

Bulk density and porosity in these aerogels were found to be linearly related to the molar ratio of solvent to MTMS. The more dilute MTMS sol-gel solutions containing proportionately less solid MTMS in both the wet gel and resultant aerogel, led to lower bulk density and higher porosity (Figure 2 and 3).

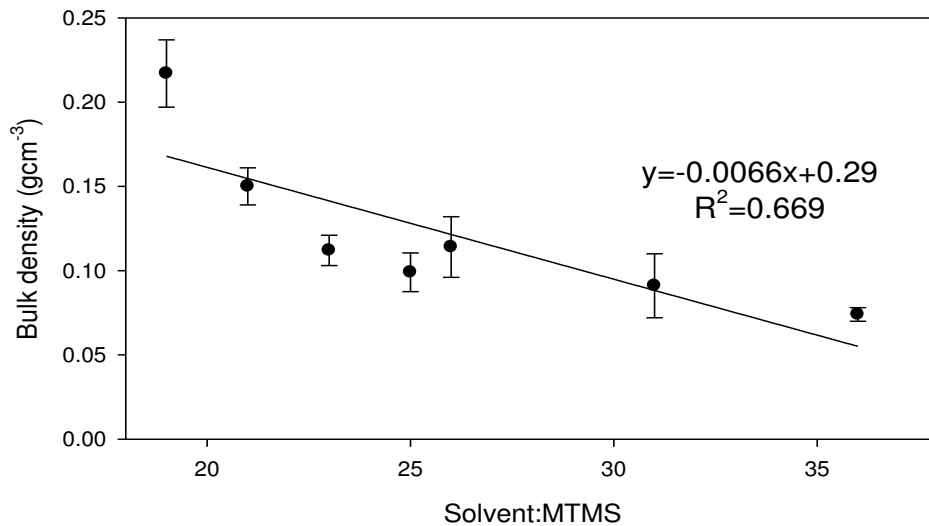


Figure 2 Relationship between the molar ratio of solvent to MTMS in sol-gel process and the bulk density of resultant silicone aerogels

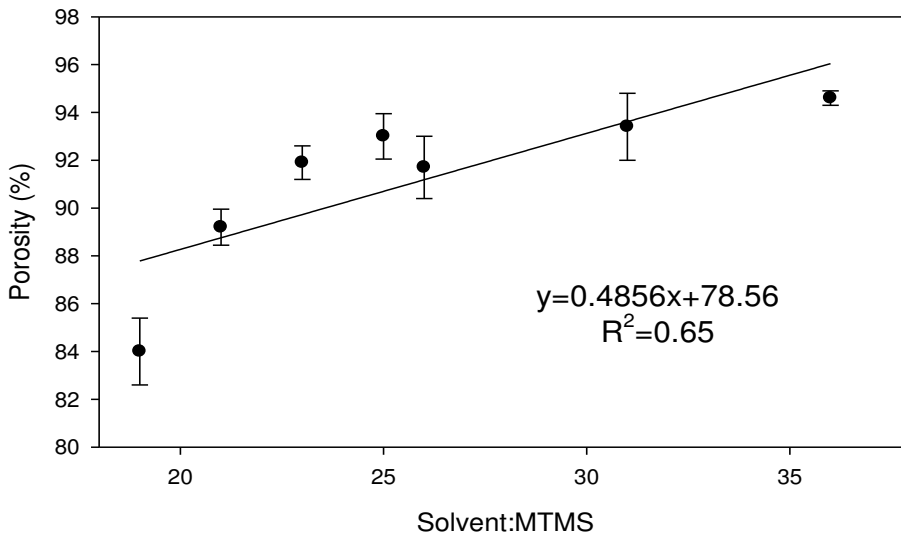


Figure 3 Relationship between the molar ratio of solvent to MTMS in sol-gel process and the porosity of resultant silicone aerogels

Figure 4 - 6 illustrate that BET surface area, total pore volume and mesopore volumes of the aerogels varied nonlinearly with increasing molar ratio of solvent to MTMS. The BET surface area, total pore volume and mesopore volume increased with an increase in the molar ratio when the molar ratio of solvent to MTMS was less than 23:1, and decreased as a result of further increases in the molar ratio. This is a function of the solvent content. When the molar ratio of solvent to MTMS was less than 23:1, increasing the amount of solvent led to more small and large pores following solvent evaporation during drying. When the molar ratio of solvent to MTMS increases beyond 23:1, it is conceivable that smaller pores could interconnect forming larger pores and a decrease in the BET surface, total pore volume and mesopore volume. This is confirmed by the relationship between the molar ratio of

solvent to MTMS and the mesopore volume percentage in the silicone aerogels (Figure 7), where the percentage mesopore volume constantly decreased with increasing solvent content.

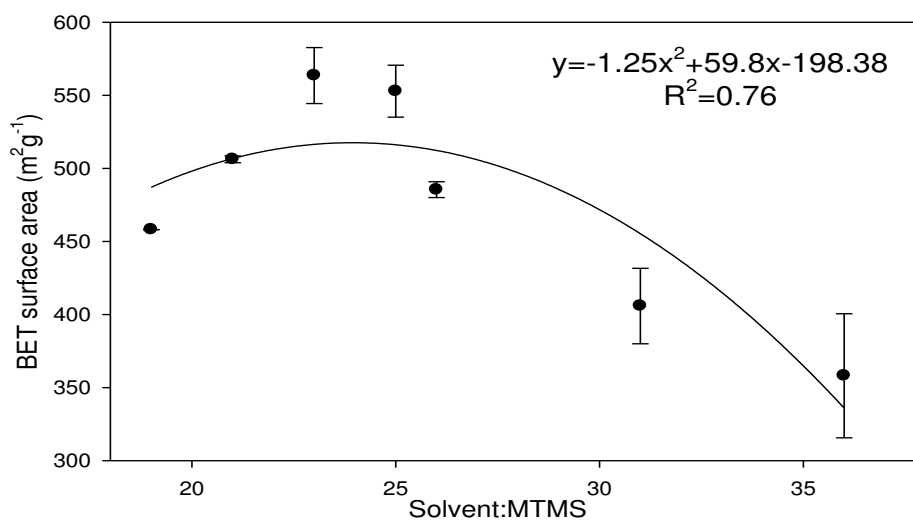


Figure 4 Relationship between the molar ratio of solvent to MTMS in the sol-gel process and BET surface areas of the resultant silicone aerogels

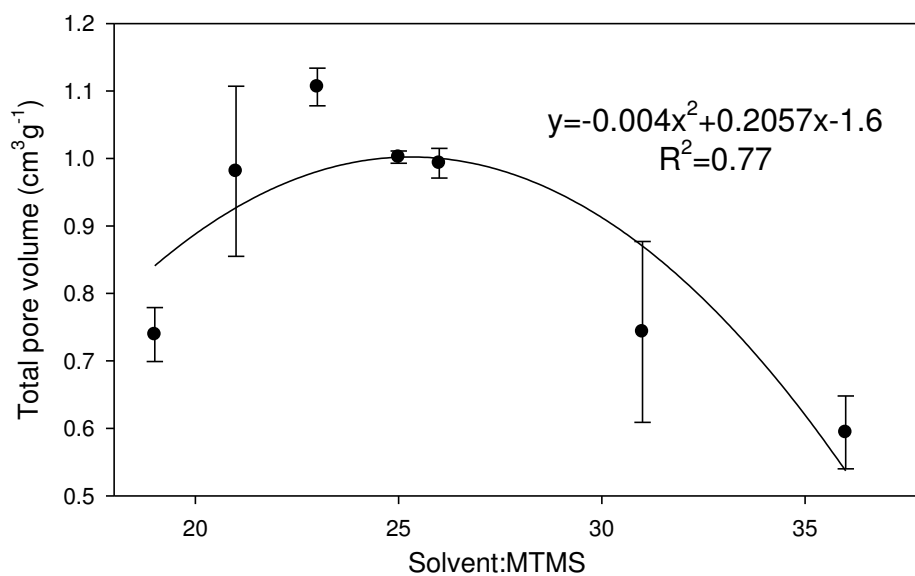


Figure 5 Relationship between the molar ratio of solvent to MTMS in the sol-gel process and total pore volume of the resultant silicone aerogels

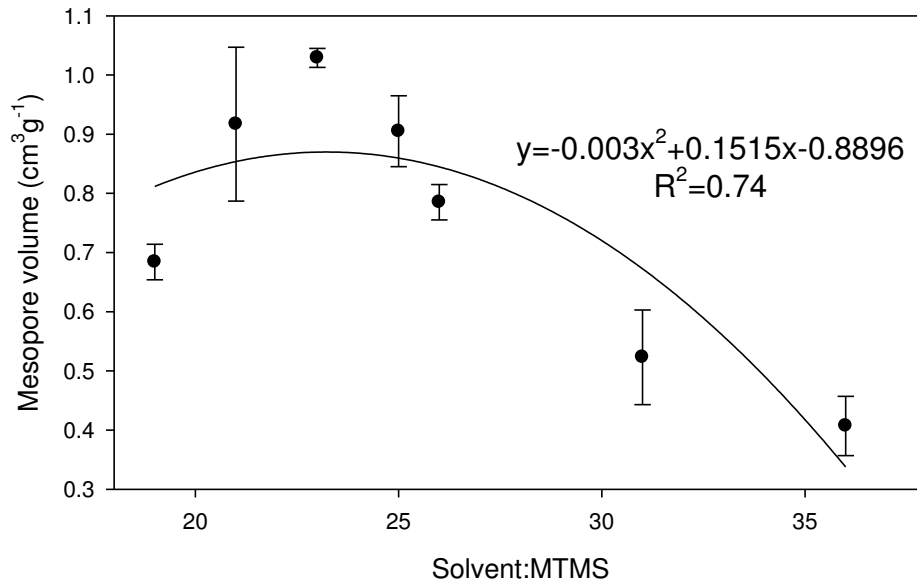


Figure 6 Relationship between the molar ratio of solvent to MTMS in the sol-gel process and mesopore volume of the resultant silicone aerogels

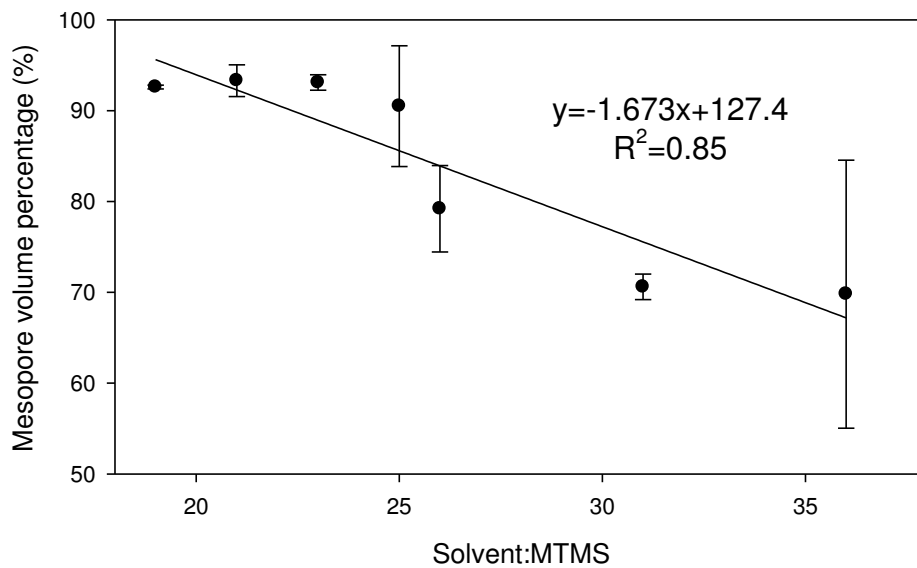


Figure 7 Relationship between the molar ratio of solvent to MTMS in sol-gel process and mesopore volume percentage of the resultant silicone aerogels

The relationships between porosity and total pore volume and mesopore volume are shown in Figure 8. When the porosity of the aerogels is smaller than 89.2% (molar ratio of solvent smaller than 21:1), the increase in porosity leads to an increase in the total pore volume and mesopore volume. When the porosity of the aerogel is greater than 89.2%, further increases in the porosity resulted in a decrease in the total pore volume and mesopore volume. It is thus noted that the relationship between porosity and pore volumes for aerogels were different.

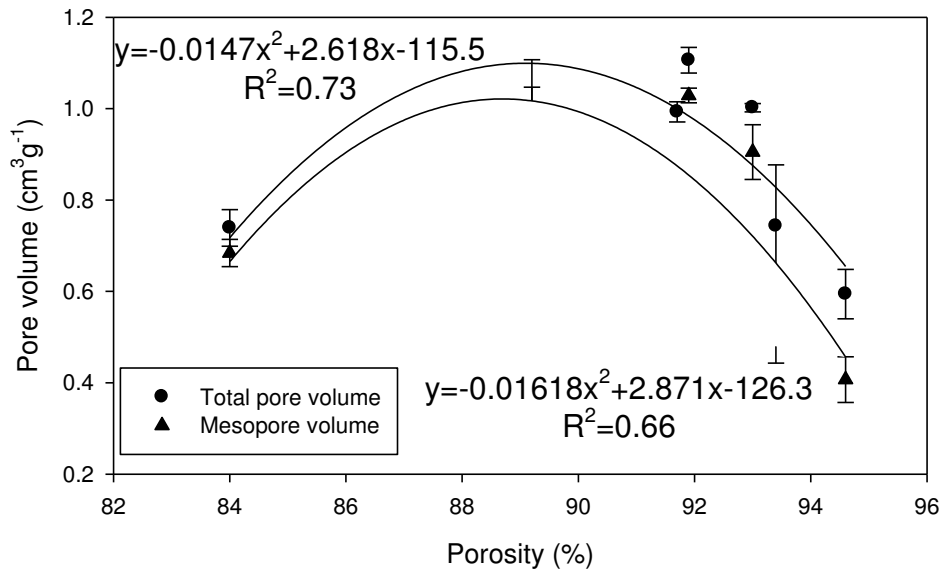


Figure 8 Relationship between porosity and pore volumes in the resultant silicone xerogels and aerogels

The influence of the effect of both the molar ratio of Methanol to MTMS and the molar ratio of water to MTMS in the sol-gel process on the porous structure of the silicone aerogels are now discussed.

3.2 Molar ratio of methanol to MTMS

An appropriate molar ratio is important in the formation of aerogel microstructure. Usually, a high precursor concentration, which means a smaller molar ratio of solvent to precursor, results in a denser gel with smaller pores [24]. Theoretically, the greater the molar ratio of methanol to MTMS is, the smaller the bulk density of the aerogel will be. This is because the amount of the precursor silica/silicone per unit volume of wet gel reduces as the solvent quantity increases. However, when the molar ratio reaches a critical threshold, either the wet gel does not set or the resultant product is a disconnected silica/silicone powder that does not form a gel or a coherent network [7, 25, 26]. For TEOS based aerogel the critical threshold is reported to be 16.6:1 [25] and for silicone aerogel from MTMS it is 42:1 [7]). Accordingly, the influence of molar ratio of solvent to precursor on the structure of resulting aerogels needs to be studied if they are to be effectively engineered in the future.

The pore size distributions of silicone aerogels obtained from four different molar ratios of methanol to MTMS are illustrated in Figure 9 and the characteristics of pore structures of both mesopores and macropores are summarised in Table 3. The mesopore distributions including the peak mesopore sizes of the two specimens for

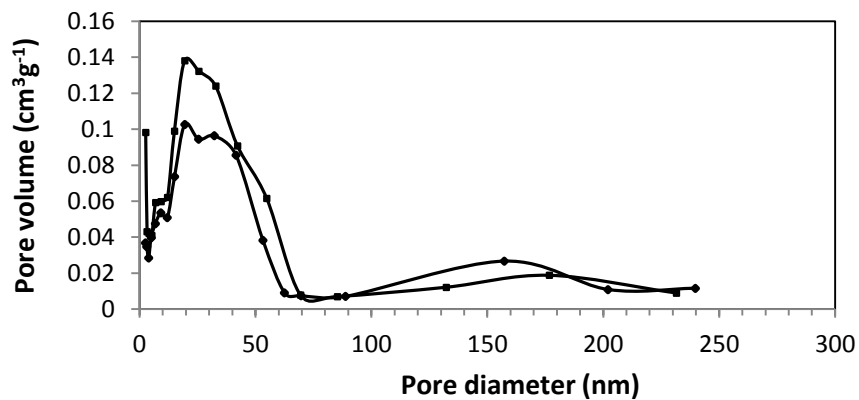
each aerogel sample in this group of silicone aerogels were quite similar and the pore distributions for each sample at various molar ratios of methanol to MTMS were bimodal (Figure 9). One peak was found to be in the mesopore size range and the other in the macropore size range.

Table 3 Characteristics of the porous structure in aerogels obtained from different molar ratios of methanol:MTMS

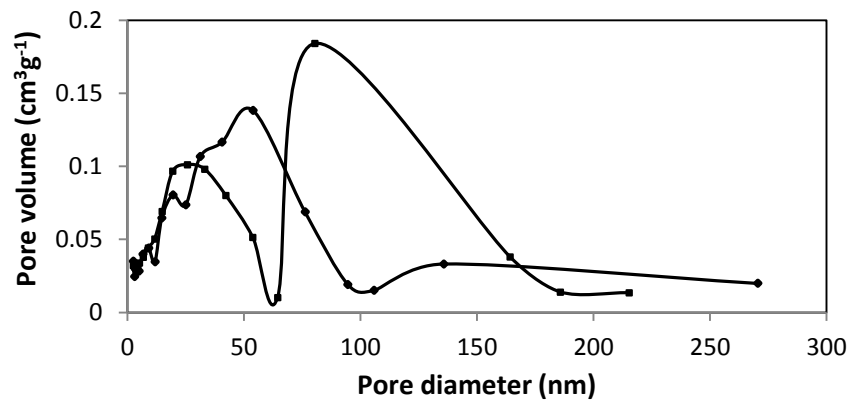
Methanol:MTMS		15:1	20:1	25:1	30:1
Bulk density (g·cm⁻³)		0.150	0.114	0.091	0.074
True density (g·cm⁻³)*		1.390	1.376	1.376	1.372
Porosity (%)		89.2	91.7	93.4	94.6
BET surface area (m²·g⁻¹)		506.2	485.4	405.8	358.1
Total pore volume (cm³·g⁻¹)		0.981	0.993	0.743	0.594
Mesopore	Pore volume (cm³·g⁻¹)	0.917	0.785	0.523	0.407
	Percentage (%)	93.3	79.2	70.6	69.8
Macropore	Pore volume (cm³·g⁻¹)	0.064	0.208	0.220	0.187
	Percentage (%)	6.7	20.8	29.4	30.2

*The true density (or skeleton density) of the aerogels was measured using an AccuPyc 1330 Pycnometer

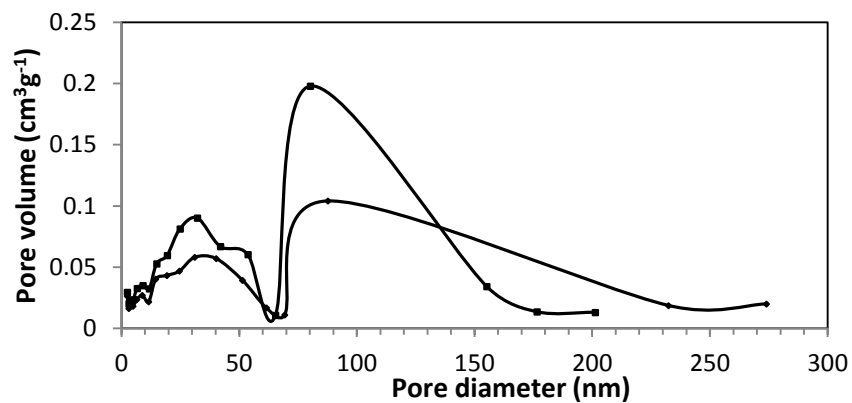
As shown in Figure 9, the peak pore size volume of macropores was much greater than that of the peak pore size in mesopores in the aerogels obtained from molar ratios of 20:1, 25:1 and 30:1. The only exception was the aerogel obtained from a molar ratio of 15:1. Note also that in Table 3 with an increase in the molar ratio of methanol to MTMS from 15:1 to 30:1, the volume percentage of macropores increased from 5.0% to 30.2% and the peak pore size of the macropores decreased from 176.7 nm to 148.2 nm. In contrast, the volume percentage of mesopores decreased from 93.3% to 69.8% with an increase in the molar ratio of methanol to MTMS from 15:1 to 30:1. The peak pore size of mesopores of the aerogels produced from different molar ratios were around 40 nm, except for the aerogel produced at a molar ratio of 30:1 which was 5.2 nm, and the pore volume was below 20%.



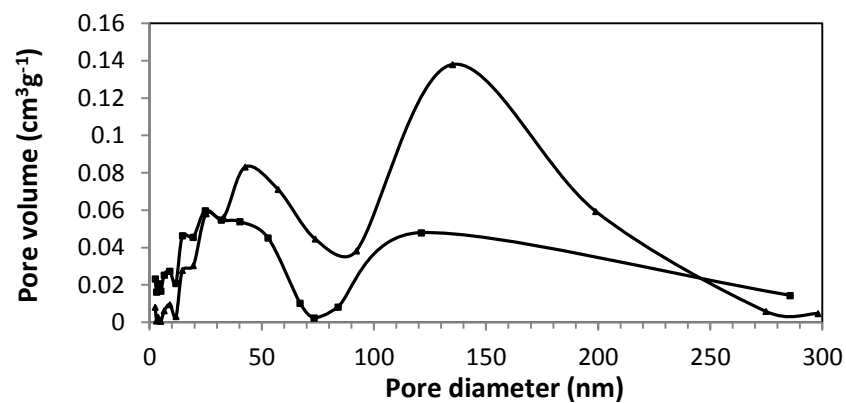
(a) 15:1



(b) 20:1



(c) 25:1



(d) 30:1

Note: the two lines in each graph are pore size distributions from two different samples of each aerogel
 Figure 9 Pore size distribution of the silicone aerogels made at various molar ratios of methanol to MTMS

It was also found that the molar ratio of methanol to MTMS influenced other structural parameters. When the molar ratio of methanol to MTMS increased from 15:1 to 30:1, the porosity of the resultant aerogels increased from 89.2% to 94.6% (Table 3 and Figure 10), and the BET surface areas decreased markedly from 506.2 $\text{m}^2\cdot\text{g}^{-1}$ to 358.1 $\text{m}^2\cdot\text{g}^{-1}$ (Figure 11).

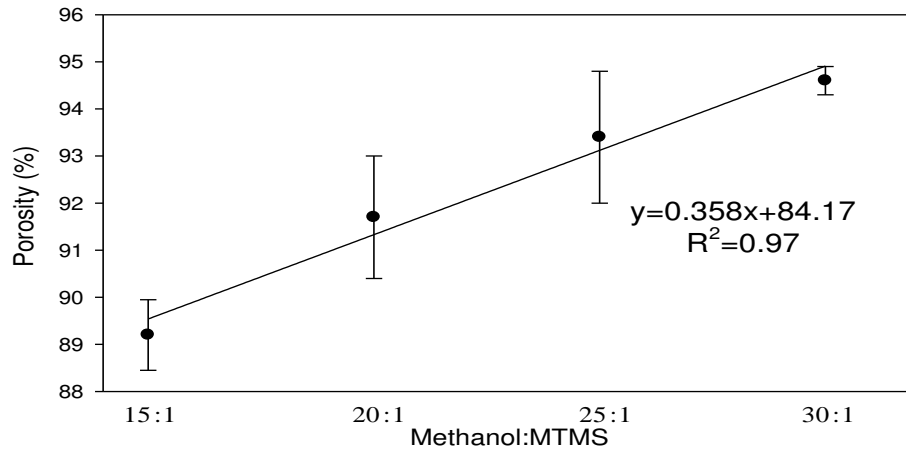


Figure 10 Porosity of the silicone aerogels made from various molar ratios of methanol to MTMS

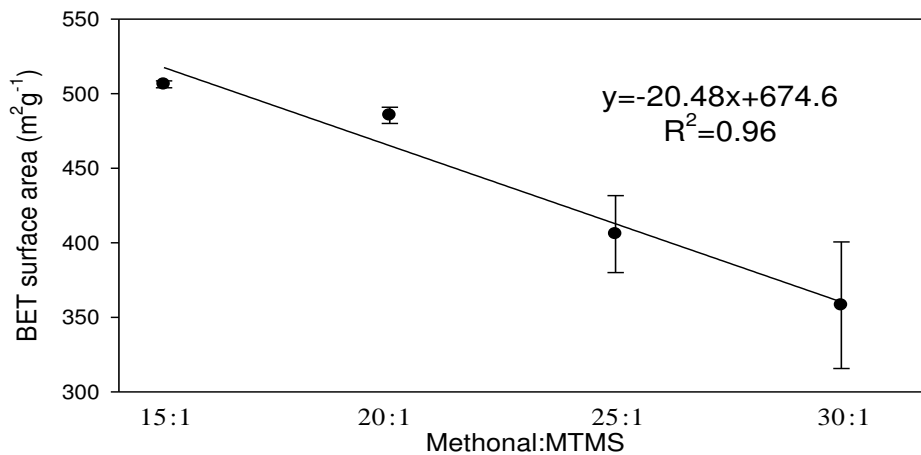


Figure 11 BET surface area of the silicone aerogels made from various molar ratios of methanol to MTMS

As indicated in Figure and 13, when increasing the molar ratio of methanol to MTMS from 15:1 to 30:1, both the total pore volumes, the mesopore volumes and the percentage of the mesopore volumes decreased, while the percentage macropore volume increased (see Figure 13). Therefore, it is apparent that the greater the molar ratio of methanol to MTMS, the more macropores and fewer mesopores are formed. This is because the lower precursor (MTMS) concentration is likely to increase the space between reacting precursor particles/clusters leading to the separation of those

particles/clusters and the formation of much larger clusters with less cross-linkage [27]. If the concentration of the precursor is high (for example, a molar ratio of 15:1), then aerogels with a denser porous structure and smaller porosity are obtained. In contrast if the concentration of the precursor is low (for example, a molar ratio of 30:1), the resultant aerogels are more porous and have larger pores. Silicone powder particles rather than an integrated porous silicone aerogel foams are produced if the concentration of the precursor is too low. In this research, this happened when the molar ratio of methanol:MTMS is greater than 30:1.

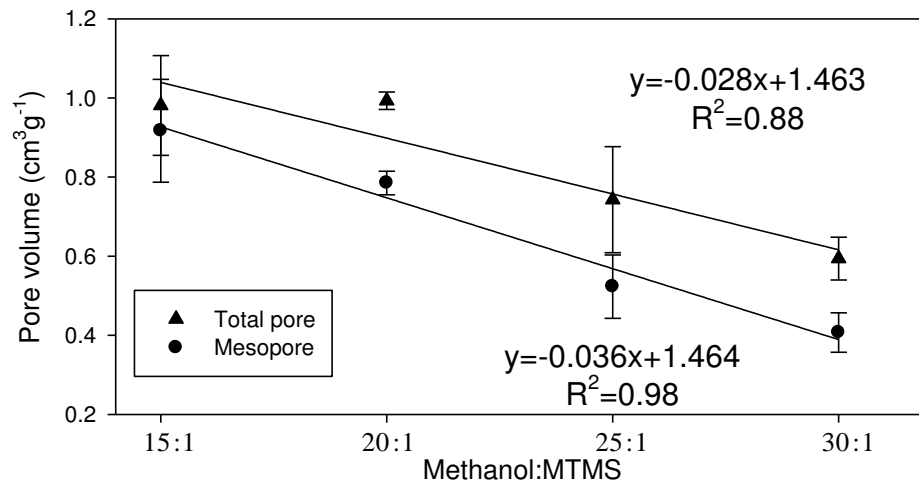


Figure 12 Pore volume distributions of the silicone aerogels made from various molar ratios of methanol to MTMS

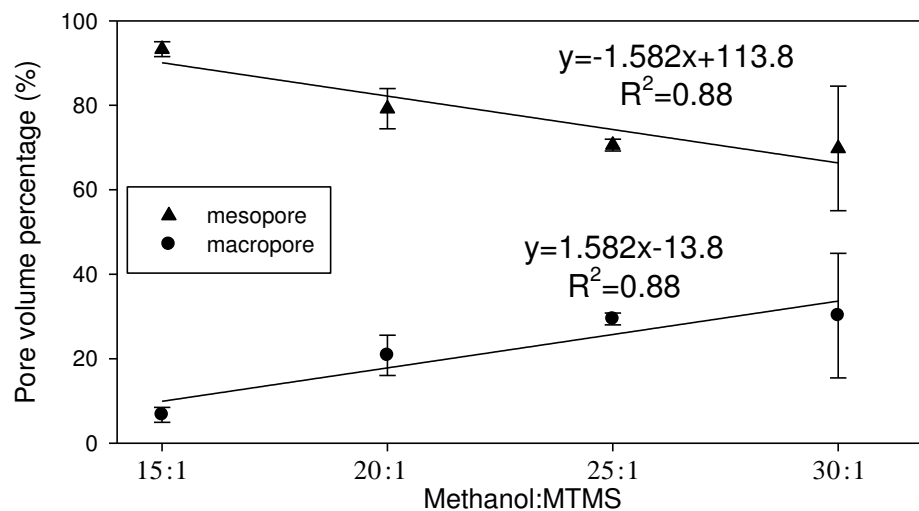


Figure 13 Mesopore and macropore volume percentages of the silicone aerogels made from various molar ratios of methanol to MTMS

Also, with an increase of the molar ratio from 15:1 to 30:1, the bulk density of the silicone aerogels decreases (Figure 14) and the true density of the aerogel decreases

from $1.390 \text{ g}\cdot\text{cm}^{-3}$ to $1.372 \text{ g}\cdot\text{cm}^{-3}$ (Figure 15), which could be indicative of the formation of a greater number of closed pores when the molar ratio increases.

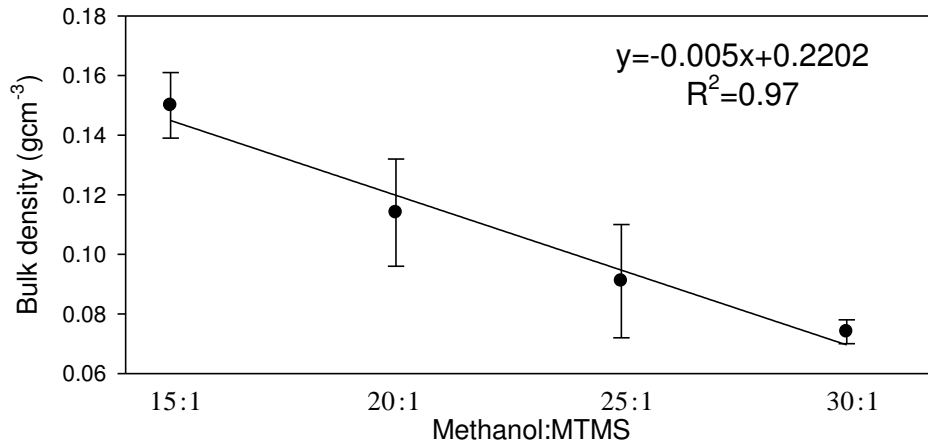


Figure 14 Bulk densities of the silicone aerogels made from various molar ratios of methanol to MTMS

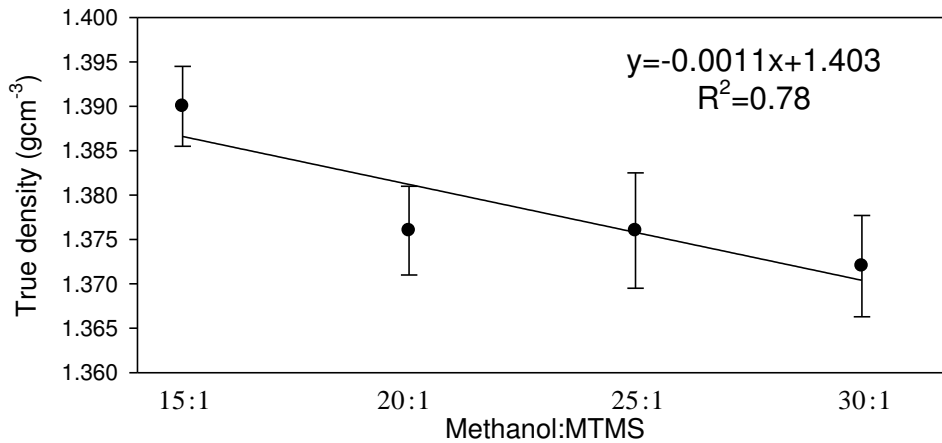


Figure 15 True densities of the silicone aerogels made from various molar ratios of methanol to MTMS

Based on the molar ratio of solvent (methanol and water) to precursor (MTMS), the porosity of the resultant aerogels was calculated. This calculation is based on the assumptions that (1) the solution weight is constant during the entire sol-gel process; (2) the chemical components of the resultant silicone is considered as $\text{SiO}_{1.5}\text{CH}_3$; (3) the mass of methanol evolved during condensation of the gelation process is neglected.

Then the total weight of solution (W_{total}) is the sum of the molecular weights of MTMS, methanol and water. Given the molar ratio between methanol, water and MTMS, is 15:6:1 and 1 mol of MTMS is used, the total weight of solution, W_{total} , is,

$$W_{\text{total}} = 136.22 + 32.04 \times 15 + 18 \times 6 = 724.82g$$

where, the molecular weight ($\text{g}\cdot\text{mol}^{-1}$) of MTMS, methanol and water are 136.22, 32.04 and 18.00 respectively, and their bulk densities ($\text{g}\cdot\text{cm}^{-3}$) are 0.96, 0.79 and 1.00 respectively.

The total volume (V_{total}) of the solution is the sum of the values of the molecular weight of MTMS, methanol and water divided by their bulk density ($\text{g}\cdot\text{cm}^{-3}$) respectively:

$$V_{\text{total}} = \frac{136.22}{0.96} + 15 \times \frac{32.04}{0.79} + 6 \times \frac{18.00}{1.00} = 858.99 \text{ cm}^3.$$

Thus, the bulk density of the aerogel was estimated using weight divided by volume. Because the molecular weight of the silicone ($\text{SiO}_{1.5}\text{CH}_3$) is $67 \text{ g}\cdot\text{mol}^{-1}$, the weight of the resultant solid in the solution is 67g, and the percentage of solid weight in the solution (and the wet gel and resultant aerogel) is around 9%, shrinkage of the wet gel during drying was neglected.

The estimated weight fractions of the aerogel solids produced from different molar ratios of methanol to MTMS are given in Table 4. it was reported that when the molar ratio of methanol to MTMS is greater than 42:1 [25], a nanoporous network would not be expected to form, but rather, silica/silicone nanoparticles [7]. Therefore, a maximum molar ratio of methanol to MTMS slightly greater 42:1 (i.e., 45:1) has been used in Table 4.

Table 4 Calculation of solid percentage and bulk density of resultant silicone aerogel

Ratio of Methanol :MTMS	15:1	20:1	25:1	30:1	35:1	40:1	45:1
Weight percentage of solid (%)	9	7.6	6.4	5.6	4.9	4.4	4.0
Estimated bulk density of silicone aerogel ($\text{g}\cdot\text{cm}^{-3}$)	0.083	0.066	0.055	0.047	0.041	0.037	0.033
Measured bulk density ($\text{g}\cdot\text{cm}^{-3}$)	0.150	0.114	0.910	0.740	N/A		
Estimated porosity (%)	94.0	95.2	96.0	96.6			
Measured porosity (%)	89.2	91.7	93.4	94.6			

As shown in Table 4, the measured porosities of the aerogels obtained using different molar ratios of methanol to MTMS from 15:1 to 30:1 were smaller than the calculated porosities in Table 3. There are two reasons for this, firstly the methanol used in the formation of the aerogel is evaporated in the sol-gel process leading to a decrease in the total volume of the solution in comparison with that of original solution used to predict the porosity. Secondly the wet gel shrinks during the drying process. The observed trend in the aerogel porosity as the molar ratios of methanol to MTMS increase, are similar for both the measured porosity and the predicted porosity as shown in Figure 16.

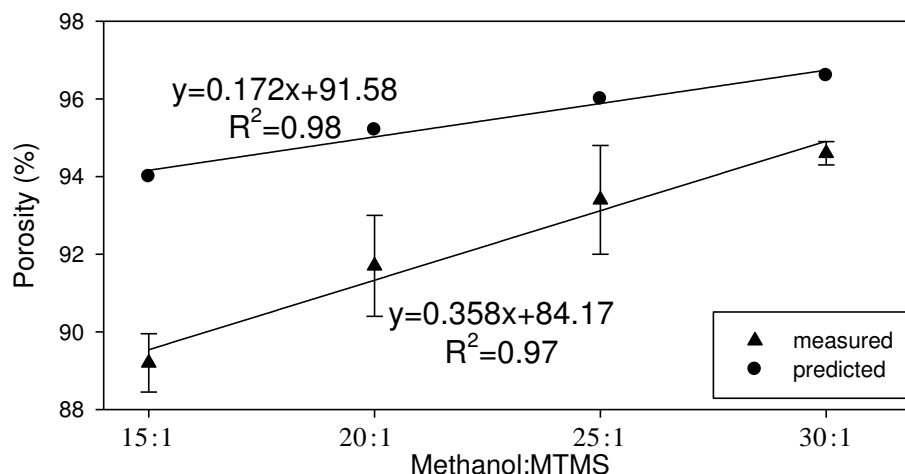
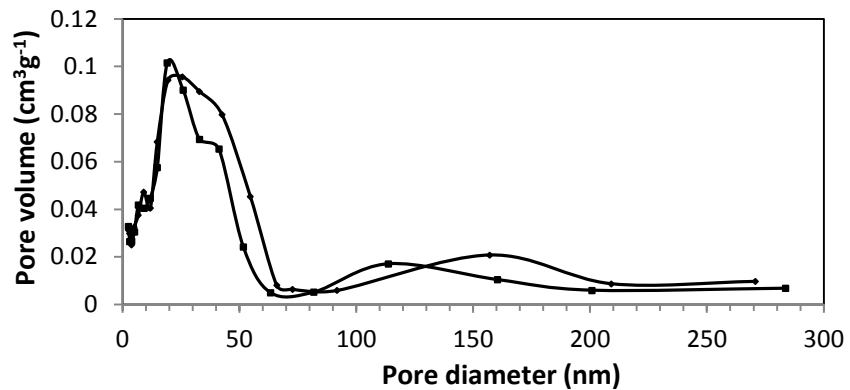


Figure 16 Comparison between predicted and measured porosities of the silicone aerogels obtained from the different molar ratios of methanol to MTMS

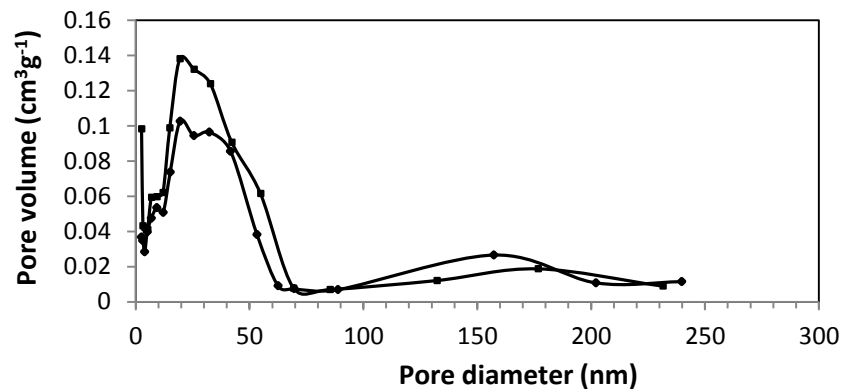
3.3 Molar ratio of water to MTMS

Water was added in the sol-gel process together with both hydrolysis catalyst (e.g., oxalic acid in this research) and the condensation catalyst (e.g., ammonia solution in this research), it attends hydrolysis of MTMS and is also a by-product of condensation reaction, the change of molar ratio of water to MTMS in sol-gel process would thus alter both the MTMS concentration in the wet gel and the amount of acid and base added into the sol-gel process. Therefore, the amount of water determines the rates of both precursor (MTMS) hydrolysis and the condensation reaction. It has been reported [28] that the particle sizes of TEOS silica aerogels change nonlinearly with an increase of the molar ratio of water:TEOS from 1.7:1 to 100:1 (or the concentration of water from 17M to 0.5M). Other studies [29] found that particle size decreased when the molar ratio between water and TEOS increased from 1.3:1 to 55.6:1. However, little is known about the effects of water content on pore sizes in aerogels in both TEOS based silica aerogels and MTMS based silicone aerogels. Therefore the influence of water content in the sol-gel process on pore size and pore size distribution in MTMS silicone aerogels was investigated. In the present research, the molar ratio of water from acid to water from base and to MTMS were 4:2:1, and therefore the effect of increasing the molar ratio of water to MTMS on the porous structure of resulting silicone aerogels is effectively equivalent to the proportional decrease of the hydrolysis/condensation catalysts in the sol-gel process.

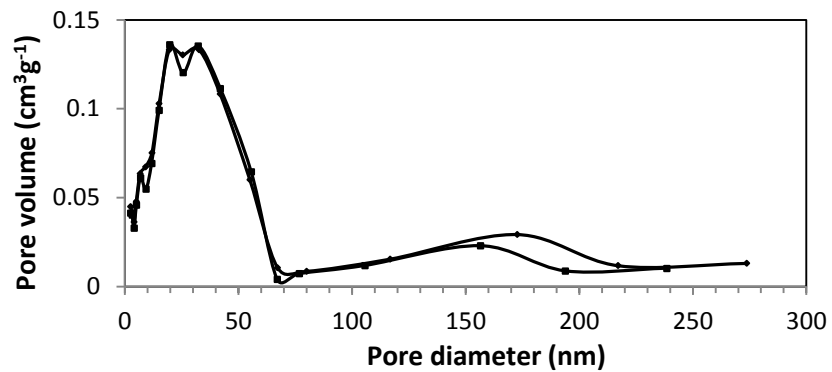
The pore size distribution of smaller pores of <300 nm in the silicone aerogels produced at various molar ratios of water to MTMS were found to be consistently bimodal (Figure 17). The characteristics of the porous structure produced are summarised in Table 5. Similar to the aerogels formed at various molar ratios of methanol to MTMS as described in section 3.2, the reproducibility of the silicone aerogels at various molar ratios of water to MTMS was also good, especially with respect to mesopore size distributions.



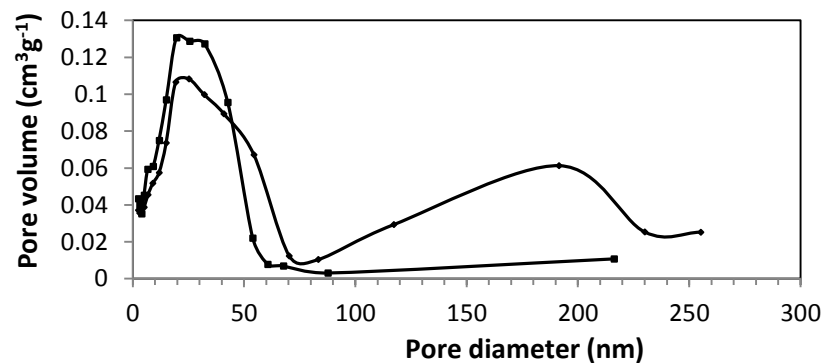
(a) 4:1



(b) 6:1



(c) 8:1



(d) 10:1

Note: the two lines in each graph are pore size distributions from two different samples of each aerogel

Figure 17 Pore size distributions of the silicone aerogels from various molar ratios of water:MTMS

In both Table 5 and Figure 17 there are apparent differences in the macropore volumes but little difference in the mesopores. In these aerogels, mesopores were volumetrically dominant (84-93%) regardless of the molar ratios of water:MTMS. The pore volume of peak sizes in mesopore range was much greater than that of the peak sizes in the macropores, regardless of the molar ratio of water:MTMS.

Table 5 Characteristics of the porous structure of resultant aerogels obtained using various molar ratios of water:MTMS (molar ratio of methanol to MTMS was 15:1)

Molar ratio of water: MTMS		4:1	6:1	8:1	10:1
Bulk density (g·cm⁻³)		0.217	0.150	0.112	0.099
True density (g·cm⁻³)		1.357	1.390	1.380	1.405
Porosity (%)		84.0	89.2	91.9	93.0
BET surface area (m²·g⁻¹)		458.1	506.2	563.5	552.8
Total pore volume (cm³·g⁻¹)		0.739	0.981	1.106	1.002
Mesopore	Pore volume (cm³·g⁻¹)	0.684	0.917	1.029	0.905
	Percentage (%)	92.6	93.3	93.1	90.5
Macropore (>50 nm and <300 nm)	Pore volume (cm³·g⁻¹)	0.055	0.064	0.077	0.097
	Percentage (%)	7.4	6.7	6.9	9.5

The influence of the molar ratios of water:MTMS on the BET surface area, pore volume and pore volume percentage of the resultant aerogels are shown in Figure 18 ~ 20. The BET surface area increased as a result of increasing the molar ratios from 4:1 to 10:1 (Figure 18), and both the pore volume and pore volume proportions changed nonlinearly over a small range of molar ratios of water:MTMS. Aerogels produced in molar ratios of water:MTMS ranging from 6:1-8:1 produced the greatest total pore volume (0.981~1.106 cm³·g⁻¹) and the largest mesopore volume (0.917-1.029 cm³·g⁻¹) (see Figure 19). Additionally, the aerogels produced from the same molar ratios of 6:1-8:1 produced the greatest mesopore volume proportions (93.1-93.3%) (Figure 20), which is greater than in aerogels produced from the other range of molar ratios of water to MTMS (90.5%-92.6%). This indicates that smaller pores are created by increasing the molar ratio of water to MTMS when the molar ratio is less than 8:1.

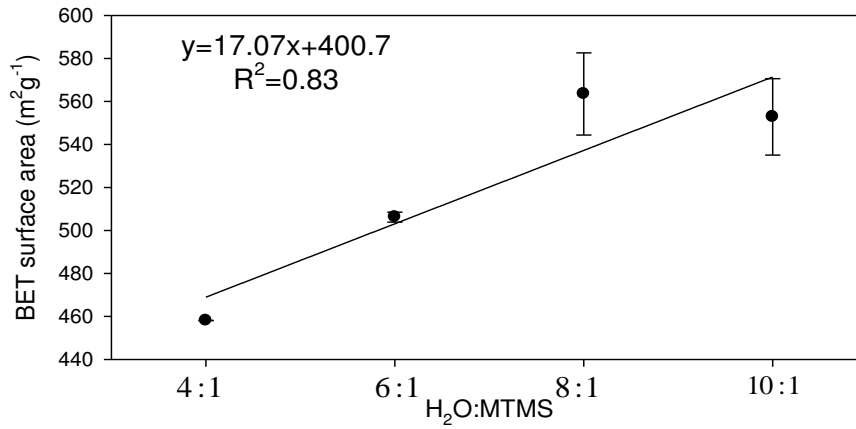


Figure 18 BET surface area of silicone aerogels made at various molar ratios of water:MTMS

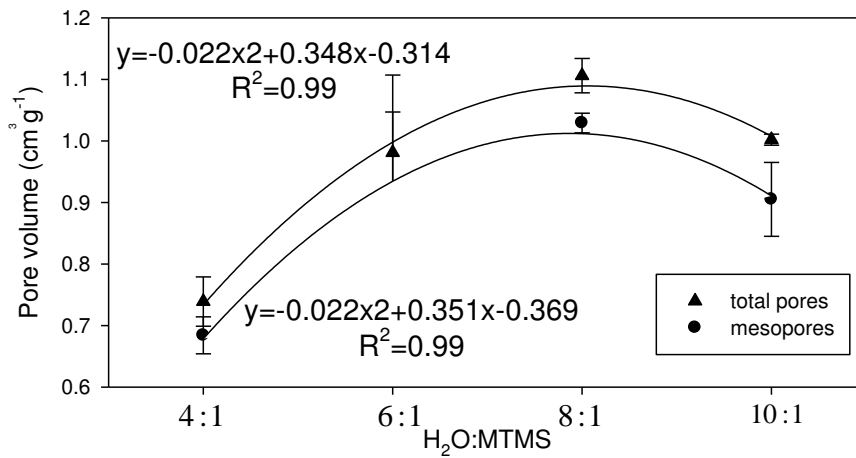


Figure 19 Pore volumes of the silicone aerogels made at various molar ratios of water to MTMS

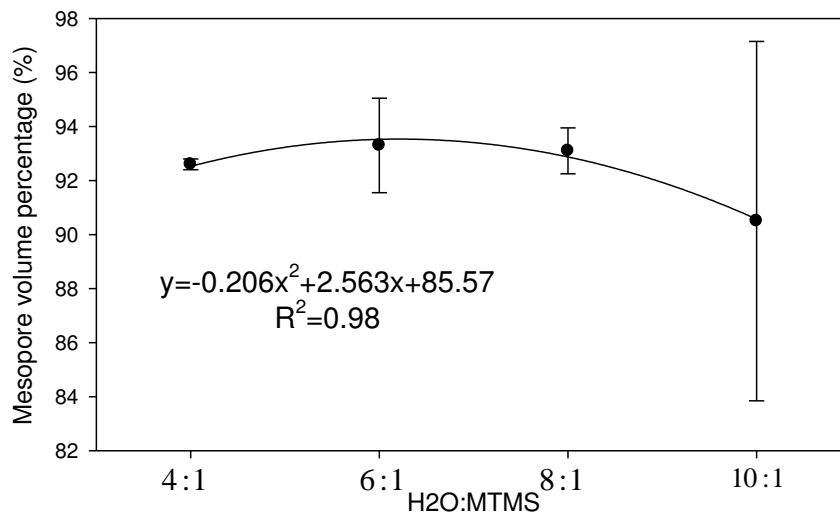


Figure 20 Mesopore volume percentage of the silicone aerogels at various molar ratios of water to MTMS

The increase of the molar ratio of water to MTMS, from 4:1 to 8:1, leads to an increase in the concentration of hydrolysis catalyst which speeds up the hydrolysis reaction. As a result, the concentration of hydrolysed monomers increases. With a high concentration of hydrolysed monomers, the dominant process of particle growth mainly occurs as a result of nucleation of hydrolysed monomers and the formation of more particles of smaller size rather than the growth of monomers on the surface of an already existing larger particle [28]. It is also known that silicone aerogels made from high concentrations of oxalic acid can have smaller particles and pore sizes [4]. With further increases in the molar ratio of water:MTMS, the increased concentration of condensation catalyst leads to quick condensation of the sol particles in the sol and the particles in the sols have no chance to connect with other particles. Instead they form clusters first and as a result, larger particles and pore sizes are formed.

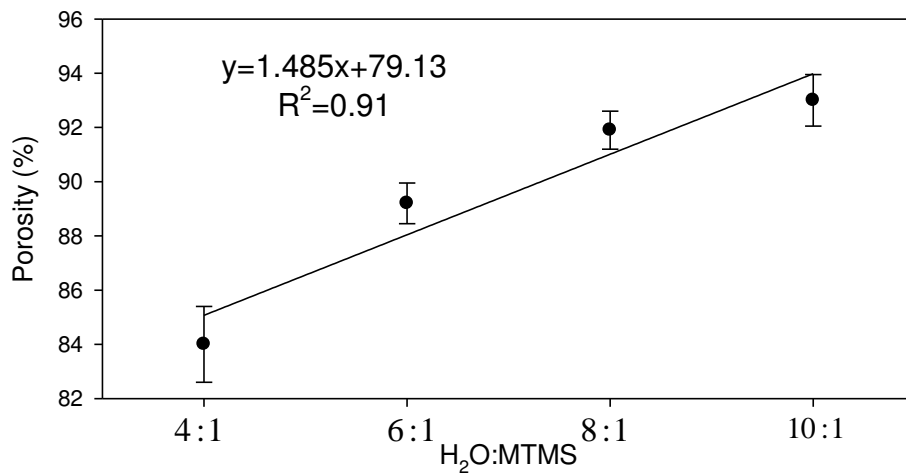


Figure 21 Porosities of the silicone aerogels produced at different molar ratios of water:MTMS

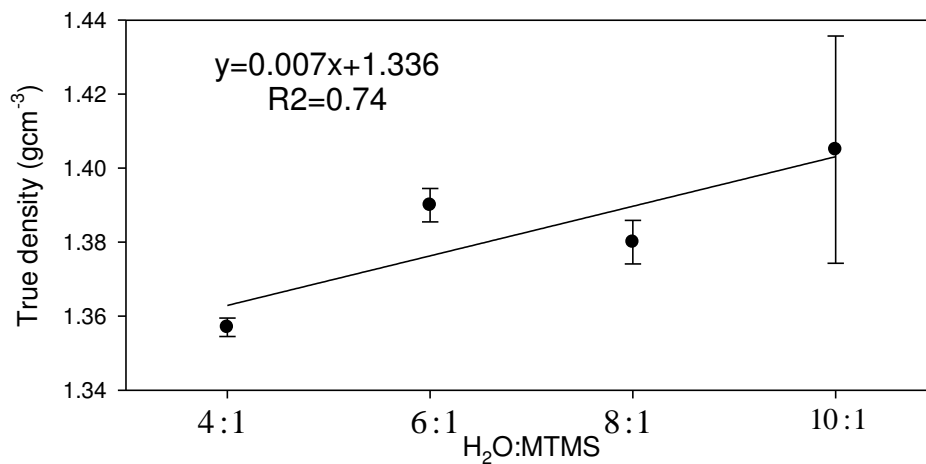


Figure 22 True densities of the silicone aerogels made at different molar ratios of water:MTMS

It is indicated in Figures 21 and 22 that both porosity and true density of the aerogels are greatly influenced by the molar ratio of water:MTMS. The porosity and the true density increase with

increasing molar ratio of water to MTMS from 4:1 to 10:1. Such a clear relationship between true density/porosity and the molar ratio of water to MTMS is quite similar to the relationship between true density/porosity and the molar ratio of methanol to MTMS observed in section 3.2.

4. Conclusions

In the formation of silicone aerogels made from MTMS in a two-step acid-base catalysed sol-gel process, the influence of MTMS concentration, i.e., the molar ratio of methanol:MTMS and the molar ratio of water:MTMS in the sol-gel process on the porous structure of resultant silicone aerogels was studied. In respect of silicone aerogels produced from wet gels using various concentrations of MTMS, it was found that,

- (1) The majority pores in the resultant silicone aerogels are mesopores, such that larger macropores greater than 300 nm in diameter numerically represent less than 1% of the total. The maximum pore size in the silicone aerogels was found to less than 630 nm.
- (2) With an increase in the molar ratio of methanol:MTMS from 15:1 to 30:1, the BET surface area, total pore volume, mesopore volume, mesopore volume proportion, bulk density and the true density of the resultant aerogels decrease, while the porosity increases from 89.2% to 94.6%.
- (3) With an increase in the molar ratio of water to MTMS from 4:1 to 10:1, the true density, BET surface area and porosity of the silicone aerogels increased. The highest total pore volume, mesopore volume, and mesopore volume proportion were obtained when the molar ratios of water to MTMS were increased to a level of 6:1 to 8:1.
- (4) The molar ratio of solvent (the mixture of methanol and water) to MTMS on the bulk density and porosity of the resultant aerogels are linearly related. The greater the molar ratio, the smaller is the bulk density and the greater is the porosity.
- (5) The effect of the molar ratio of solvent to MTMS on the BET surface area, total pore volume and mesopore volume is non-linear. The BET surface area, total pore volume and mesopore volume increase with increasing molar ratio when the molar ratio of solvent to MTMS is less than 23:1 but decreases with further increases of the molar ratio.
- (6) The porosity of MTMS based silicone aerogels is not linearly related to the total pore volume and mesopore volume. The total pore volume and mesopore volume increase with increasing porosity when the porosity less than 89.2%. However, the total pore volume and mesopore volume decrease as the porosity increases beyond 89.2%.

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