

Low Density Silica Gels and Solvent Permeability

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Abstract

The aerogel-like properties of the previously reported lyosils prepared by base catalyzed TMOS were further improved by using partially condensed TMOS followed by curing in TEOS. The cured and dried gels showed lower density: $<0.3 \text{ g ml}^{-1}$, higher BET surface area: $860 \text{ m}^2 \text{ g}^{-1}$ and larger pore size. The effectiveness of the curing media were tested by measuring permeability and wettability of the liquid media. The permeability values varied over time with a similar trend for methanol, ethanol and octanol which exhibited decreasing permeability attributable to re-esterification. Similar trends are grouped together for TEOS and water which exhibited increasing permeability up to $\sim 10 \text{ h}$ due to pore coarsening and decreasing values beyond $\sim 10 \text{ h}$ attributable to the chemisorption of TEOS and silanol condensation with water. The curability was consistent more with wettability than permeability of the liquids tested.

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1 Introduction

In 1991 we produced monolithic low density transparent silica gels and called them lyosil since they were produced by curing the wet gels in organic solvents.^{1,2} The silica gels were prepared by base-catalyzed hydrolysis of tetramethoxy silane (TMOS). The wet TMOS gels aged and cured in organic liquids enabled faster drying with less drying shrinkage, resulting in low density and large pore size solids.² The curing in organic liquids allowed the silica gels to be dried faster in monolithic form. Two dried gels of acid catalyzed xerogel and lyosil cured in tetraethoxy silane (TEOS) are shown in Fig. 1. A comparison of the diameter of the cylindrical gels after the drying shrinkage shows a 60% difference in the diameter, indicating the effectiveness of the lyogel curing in reducing drying shrinkage. The fully cured and dried lyosils

exhibited mean pore size of $\sim 13 \text{ nm}$ and narrow distribution with a specific gravity of 0.4 g cm^{-3} , thermal conductivity of $0.065 \text{ W (m}\cdot\text{K)}^{-1}$ and surface area of $622 \text{ m}^2 \text{ g}^{-1}$ with good visible light transparency.² Given these properties, many applications in advanced materials are envisioned.

Einarsrud *et al.*^{3–5} have produced silica xerogels aged in organic liquids. They later reported similar physical properties of their xerogels to those of our lyosils. However, they attributed the enhanced monolithicity of the gels to the strengthening effect of the gel network produced by aging.

Tillotson *et al.*^{6,7} produced silica aerogels of extremely low densities, $<0.1 \text{ g ml}^{-1}$ via partially hydrolyzed and partially condensed TMOS. It is understood that the term ‘aerogel’ is reserved for gels produced via supercritical drying,^{8,9} although the group at the University of New Mexico and Sandia National Laboratory¹⁰ used the term aerogel for silica gels not produced by supercritical drying but having similar properties. In this paper we follow the convention used by the earlier workers in aerogel research.^{6–9,11}

We combined the lyosil technique and the partially hydrolyzed TMOS technique^{6,7} to produce transparent monolithic gels with a lower density than the previous lyosils.^{1,2} The results are reported here in the first part of this paper. In the second part, we report the results of the permeability of the curing liquids for the lyosils to correlate the curability and permeability.

It is well known that drying rate of silica gels should be gradual to reduce thermal stress within the gel network.¹¹ Cracking during drying is related to the establishment of capillary forces. These forces appear when the liquid in the gel forms a meniscus upon evaporation. At the onset of drying, the surface of the liquid is flat. The curvature of the liquid front increases as the liquid of the gel evaporates. The liquid is in tension and as a consequence, the solid part of the gel is under compression. This causes the gel to shrink. The

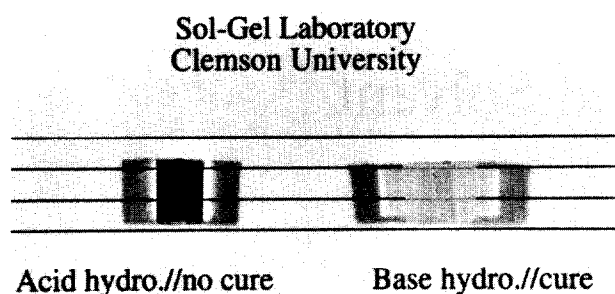


Fig. 1. Cured (3 days processing time) and uncured (7 days processing time) silica gels after drying at 150°C comparing the drying shrinkage on the diameter.

liquid flux due to the pressure gradient is shown by Darcy's Law:

$$\text{Flux (vol./area} \cdot \text{t)}, J = \frac{D}{\eta_L} \nabla P \quad (1)$$

where D is permeability, η_L is liquid viscosity and ∇P is pressure gradient.

Scherer¹² and Phalippou¹¹ reported that it is the pressure gradient (∇P), by the evaporation rate of the mother liquor that causes differential strain and cracking of the gels during drying. For this reason, fast evaporation and low permeability of the liquid present are detrimental to the gel structure since they cause a large pressure gradient. One simple method is the application of a slow drying rate. We could ease this problem by aging and curing of the wet gels in organic liquids. The results obtained from our previous works^{1,2} indicated that some liquids are more effective than others for curing silica gels. Thus we investigated the permeability of different organic liquids to understand the curing mechanism.

2 Experimental Procedure

2.1 Lyosils from partially hydrolyzed TMOS sol

Partially hydrolyzed (PH) TMOS sol was prepared by stirring and refluxing TMOS with water, methanol and nitric acid in the molar ratio of 1:1.3:2.4:10⁻⁵ for 4 h.^{6,7} The methanol produced by the hydrolysis reaction was distilled off. The viscous product, was then, diluted with acetonitrile to inhibit re-esterification. This sol was gelled by stirring with tetrahydrofuran and 50% NH₄OH.

2.2 Permeability of lyosils

An apparatus was designed to measure the flow of the curing liquids through the lyosil gel with

respect to time. With this information, the permeability (D) of the gel could be calculated at different time intervals according to eqn ((2))

$$D = \frac{L \cdot \eta \, dv/dt}{A \cdot \rho \cdot h} \quad (2)$$

where, L = gel thickness; η = viscosity of permeating liquid in poise; dv/dt = liquid flow rate; A = gel cross-sectional area = πr^2 ; g = acceleration due to gravity = 980 cm s⁻²; h = liquid height.

The apparatus used for measuring the permeability is shown in Fig. 2. Pyrex glass tubes with the inner diameter of 1 cm and approximately 10 cm in length were prepared. They were cut to the correct length using a diamond saw followed by polishing of the rough ends of the tubes.

A square piece of fine glass filter paper, approximately 2 cm, was cut to be placed at one end of the tube. The filter paper (PreSep Glass Prefilter; 0.5 μ m pore size, Micron Separations Inc., Westboro, MA) was adhered to the tube with a solvent-resistant adhesive Goop[®]. The filter pads satisfied two conditions: (a) mechanical support to thin gel disks, (b) elimination or minimization of the syneresis effect of the gel that can create a gap between the gel and the glass tube. A metal ring was placed around the filter paper and tube for extra support and to ensure a complete seal. Parafilm[®] was then placed around the filter paper to provide a seal to cast sols. Finally, the tubes were placed in a 50 ml Erlenmeyer flask. A silicone rubber stopper with a hole and a graduated capillary tube was placed into the other end of the sample

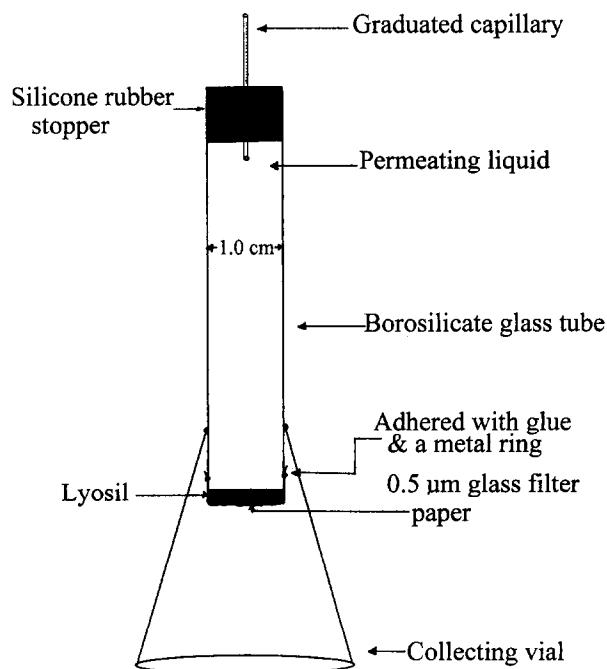


Fig. 2. Flow rate apparatus for lyosil.

glass tube. This served as an accurate way to record the small changes of liquid volume with respect to time. After the tubes had been prepared, the sol was prepared by mixing 5 ml TMOS, 6 ml methanol, 3 ml distilled water and 2 drops of 50% ammonium hydroxide following the previous lysil procedure.¹

After ~5 min of stirring for the hydrolysis at room temperature, the sol was cast into at least five flow tubes with a Wheaton Micropipet[®] to a thickness of 3 mm. This thickness was believed to be small enough, as compared with the diameter, to ignore the elastic effect of the gel during the liquid flow. Immediately after the sol had gelled, 3 ml methanol was introduced onto the gel to wash off the aqueous phase by allowing it to flow for 3 h. For washing, the Parafilm seal was quickly removed and the tube was placed back into the Erlenmeyer flask. The sample tube was then filled to the correct height, when the stopper–capillary tube assembly was added. Once the assembly was firmly in place, the capillary tube was filled with the liquid using a pipette and the liquid level was marked. The flow of the curing liquids through the gel was carried out in an oven at a constant temperature of 45°C.

Five apparati of the tube and Erlenmeyer flask for a given liquid were then placed, along with a control apparatus containing the liquid with no gel but sealed bottom, in an oven at a constant temperature of 45°C. The changes in liquid level were measured at determined time intervals and recorded. Any changes in the liquid level in the control apparatus was used to adjust the sample liquid level readings in each experiment. It was found that the liquid level changes in the control were negligible. After the experiment was performed, the thickness of the gel was measured and recorded. From these data, the permeability values (at least five) of the gel for a given liquid were calculated using eqn (2) at different time intervals. The mean values were used to plot the graphs, D versus time.

Wetting angles of the curing media on dried lysils may be related to the curability. A better wetting liquid may increase the permeability and hence

make a positive contribution to the curability and to the slow drying rate problem. They were determined by the method used by Kondo *et al.*¹³ and shown by eqn (3) below:

$$\frac{l^2}{t} = \frac{r \cdot \gamma \cos \theta}{2\eta} \quad (3)$$

where, l = osmotic liq. height; t = time; r = pore radius; γ = surface tension of liquid; θ = wetting angle; η = liq. Viscosity.

3 Results and Discussion

3.1 Lysils from partially condensed TMOS

BET surface area, pore size and bulk density measurements were conducted on the gel samples using Micromeritics instruments (Norcross, GA, USA). The results are given in Table 1. They show that the gels prepared from PH TMOS yielded a very high surface area of 954 and 1119 m² g⁻¹ with bulk density of ~0.6 g⁻¹ ml and mean pore size of 5 nm. The adsorption isotherm revealed a typical curve for porous solids of Brunauer classification Type IV of capillary condensation. The hysteresis of the isotherms from the adsorption and desorption indicate that the pores have a narrow 'ink bottle' shape. Figure 3 shows a moderately broad pore size distribution ranging from ~2 nm—10 nm with a mean diameter of ~5 nm and the maximum pore volume at ~6 nm. When this gel in Fig. 3 was cured in 1-heptanol, the surface area was reduced to 750 m² g⁻¹. One of the effects of curing is to reduce the surface area. When the gel was cured in TEOS, the bulk density and surface area were reduced to half and to ~860 m² g⁻¹, respectively, as given in Table 1. The mean pore diameter increased more than twice to ~13 nm with much larger pore volume and the maximum at pore diameter ~22 nm as shown in Fig. 3. When compared with the previous lysils^{1,2} made by fully hydrolyzed and fully condensed TMOS, the values are somewhat different, signifying that the partially hydrolyzed and partially condensed gels yielded higher

Table 1. Bulk density, surface area and pore size of silica gels prepared by partially hydrolyzed TMOS sol and dried at 150°C

Sample description	Bulk density, ^a g ml ⁻¹	BET surface area, m ² g ⁻¹	Mean pore diameter, ^b nm
PH TMOS/THF no curing	0.62	954	4.9
PH TMOS/THF heptanol cured		750	
PH TMOS, direct gelation no cure		1119	
PH TMOS/THF TEOS cured	0.28	857 ^b	13.2
		866 ^c	
Prev. lysil ^d	0.3–0.4	622	13.1

^a Measured by Micromeritics GeoPyc 1360.

^b By Micromeritics ASAP 2405N.

^c By Micromeritics Gemini 2360.

^d For fully condensed gels, Ref. 2.

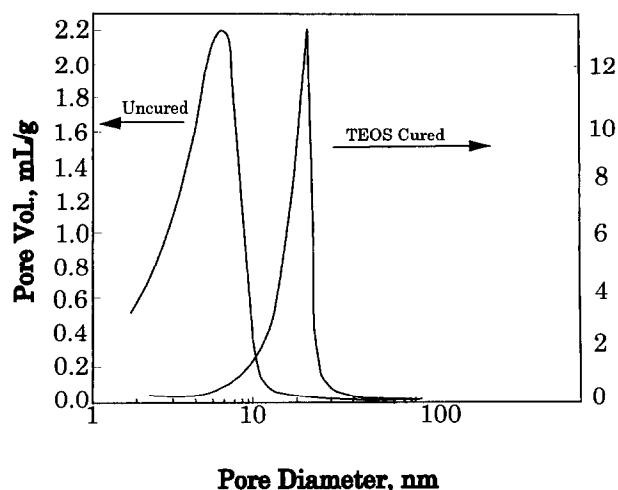


Fig. 3. Pore size distribution of lyosils from partially condensed TMOS without curing and after curing.

surface area and lower density gels $<0.3 \text{ g ml}^{-1}$ with minimal increases in pore size and pore volume. The adsorption isotherm (Fig. not given) showed that the pore shape became more cylindrical and more uniform, suggested by less hysteresis than the uncured gel in Fig. 3. This is also supported by the narrower pore size distribution by curing shown in Fig. 3. This demonstrates the effectiveness of curing on lowering density, enlarging the pore size (i.e., reduced drying shrinkage) but narrowing pore size distribution with a minimal reduction in surface area. It is concluded that larger surface area, larger pore size and the lower density lyosils can be obtained by utilizing partially hydrolyzed and partially condensed TMOS sols.

3.2 Permeability of lyosils

Figure 4 shows the permeability, D , as a function of the gel thickness. The straight line followed eqn (2) as predicted by the equation. It may be noted that the increase in D linearly as the gel thickness increases, up to 1.6 cm, can be an indication of the insignificance of the elastic effect of the gel as the permeating liquid is introduced to the gel.

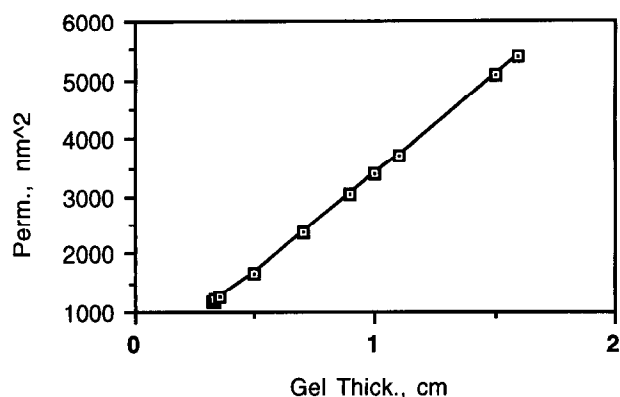
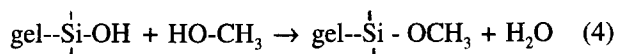


Fig. 4. Permeability, D , as a function of gel layer thickness.

Figure 5 shows the permeability of methanol and ethanol over time. The permeability of methanol dropped sharply over the first 9 h. Methanol has the smallest molecular size in alcohols and would be expected to flow the fastest. The methoxy re-esterification of the silanol groups on the gel that are in contact with methanol may be written as follows:



When this happens, the pore channel for the methanol flow is somewhat narrowed. The kinetics of methoxy re-esterification is shown to be in the order of tens h. After 10 h of the gel in methanol, the permeability continued to decrease more gradually. The permeability of ethanol shown in Fig. 5 revealed essentially the same trend as for methanol as expected. The permeability values are a little less than those of methanol, which can be understood by the slightly larger molecular size. There is a slightly more gradual decrease in permeability in the first 9 h period with ethanol. This can be explained by the larger molecules of ethanol taking a longer time to pass through the gel and slower ethoxy re-esterification for a more stable ethoxy-silicon bond formation. There was a period from 9 h to 12 h where the permeability changed little. Then after 12 h, the permeability began to decrease again.

The permeability of 1-octanol for lyosil gel can be seen in Fig. 6. Octanol exhibited anomalously high initial permeability as compared with the other liquids tested. The reason for this high permeability of octanol is not clear. It is suspected that the liquid is too reactive toward TMOS gels, based on the visual observation of the gels afterward, thus breaking down the structural network of the gel. Octanol exhibited a decrease in permeability over the first 9 h period of time. Within this time period the re-esterification reaction between

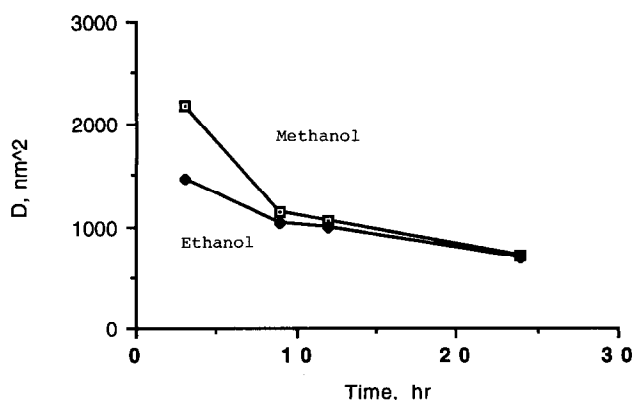


Fig. 5. Permeability, D , of methanol and ethanol at different time intervals.

Table 2. Permeability of curing liquids for lysil

Liquid	Permeability, nm ²		
	3 h	9 h	24 h
Methanol	2170 ± 213	1150 ± 125	710 ± 98
Ethanol	1470 ± 157	1040 ± 88	700 ± 82
1-Octanol	15800 ± 2633	8610 ± 1450	7690 ± 980
TEOS	650 ± 154	830 ± 137	550 ± 102
Water	1060 ± 98	1230 ± 88	1009 ± 84

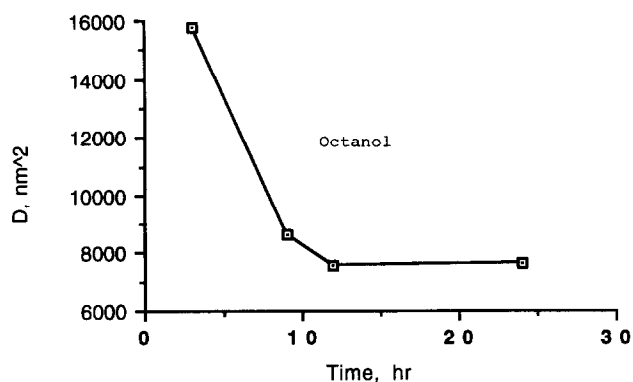


Fig. 6. Permeability, *D*, of 1-octanol at different time intervals.

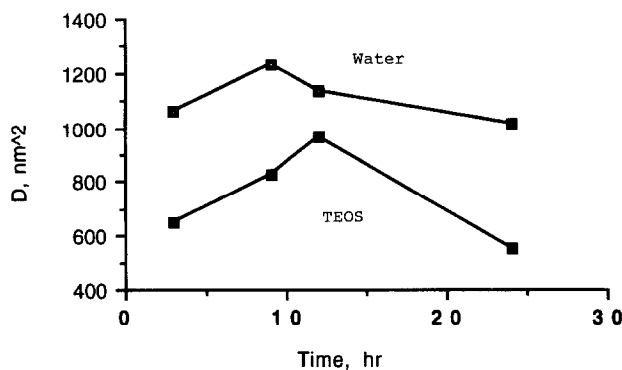
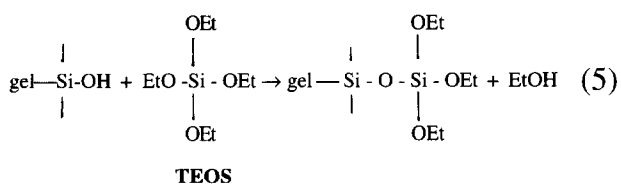


Fig. 7. Permeability, *D*, of TEOS and water at different time intervals.

silanol and the gel and octanol groups of the liquid took place. Under the hydrolysis conditions used, one can expect a substantial number of unhydrolyzed methoxy groups on the gel surface. In this case octoxy groups will replace the methoxy groups slowly in addition to the silanol/octoxy reaction. These reactions will lead to a reduction in the liquid flow rate. Indeed the reduction in flow rate continued from 9 h to 24 h. The re-esterification reaction is shown to be rather fast, i.e. as fast as methanol and ethanol.

In Fig. 7 the permeability of TEOS and water is shown over time. The permeability of TEOS increased at a constant rate up to about 12 h due to the pore coarsening prelude to TEOS chemisorption. The chemisorption of TEOS by hydrolysis with the silanols on the gel surface, as shown in eqn (5), must be very slow, i.e. took 12 h to complete:



When this happened, the effective pore size narrowed and the liquid flow was hampered leading to lower permeability. The large triethoxy silane groups adsorbed on the gel lowered the permeability, and at the same time prevented the pore collapse leading to the most effective curing medium.¹

The permeability trend of water shown in Fig. 7 is similar to that of TEOS. This must be because the interaction mechanisms of the permeating

liquid and the gel are similar to each other. In the first 9 h period, there is an increase in the permeability of water. Water would hydrolyze the residual methoxy groups in the gel to silanols, then the pore channel is broadened. After 9 h, condensation of the silanol Si-OH is taking place, hence the liquid flow is impeded and the permeability decreased. Then the permeability of the gel decreased continuously for the rest of the measurements. The impediment by the silanol condensation in water is shown to be faster than the hydrolysis of TEOS by Si-OH in TEOS curve.

Table 2 lists the average permeability values of lysil gel in each of the fluids at different time intervals. The permeability values rank as follows: octanol > methanol > ethanol > water > TEOS after 3 h. After 9 h the ranking of the permeability values are: octanol > water > methanol > ethanol > TEOS. The permeability ranking remained the same after 24 h.

The variations of the permeability for each liquid and the different values at different time periods signify the different interactions between the TMOS gel surface and the permeating liquids. The re-esterification effect of octanol on the permeability is shown to be the greatest followed by the ethanol and methanol. This is in the order of the size of the alkyl groups of the alcohol and also corresponds to the stability of the corresponding alkoxide, i.e. the stability order of octoxy silane > ethoxy silane > methoxy silane.

Although Scherer¹² had never reported and discussed the permeability changes as a function of time, we compared the values. Using the *D* values

Table 3. Wetting angles of dried lysil after curing in TEOS and being stored in air for 1 year (number of samples = 5)

Liquid	Wettability, degree
Methanol	81 ± 3
1-Octanol	72 ± 4
TEOS	73 ± 4
Water	83 ± 2

after 9 h, the D value of $\sim 1000 \text{ nm}^2$ for methanol, ethanol, water and TEOS is ~ 80 times larger than Scherer's value of $\sim 15 \text{ nm}^2$. His D values were for the mother liquor on a base-catalyzed gel of $\sim 5 \text{ nm}$ mean pore diameter and the D values extrapolated to zero gel layer thickness. The large difference in the permeability D value may be originated from the ~ 4 times larger pore radius of $\sim 6.5 \text{ nm}$ versus $\sim 2.5 \text{ nm}$, the flow temperature of 45°C versus 25°C and the much larger gel layer thickness in our experiment. Our gel layer thickness was at least $10\times$ larger than that of Scherer's.¹² Since the flow rate dv/dt is directly proportional to the square of pore size,¹⁴ the difference between the d^2 of Scherer's 25 and our 400 yields a factor of $8\times$. Substituting these differences into the D equation in eqn (2), i.e. $10\times$ for larger gel thickness and $8\times$ pore size, should produce a D value at least $\sim 70\times$ larger than Scherer's D value. This just happened to be the case.

Wettabilities of the dried lysils, after being cured in TEOS and stored in a sealed plastic bag for 1 year, are given in Table 3 in terms of wetting angle. They indicate that the gel surface is partially hydrophobic and partially hydrophilic. Water and methanol wet the gel the least, and TEOS and 1-octanol the most, as one would expect for partial hydrophobicity.

The previous research works on the curability of as-synthesized silica gels in various liquids revealed¹ that the order of effectiveness of the liquids is TEOS > 1-octanol > low molecular weight alcohols > water. This is not consistent with the order of the permeability D values given in Table 2. The D value of water is shown to be approximately $1.5\times$ of TEOS. On the other hand, the wettabilities of 1-octanol and TEOS (given in Table 3) are consistent with the curability. This means that wetting angle values of curing media may be a better indication of the curability and be used for effective curing of gels. Nevertheless, the experimental difference between the determination of permeability and wettability is that the former used wet gels and the latter dried gels due to the experimental conditions. It is then clear that the permeability is not a good indicator to predict the effectiveness of a curing medium and the curing mechanism is not based on the permeability in eqn (1).

4 Conclusions

- (1) partial hydrolysis and partial condensation of TMOS yields higher surface area and lower density gels upon curing than fully condensed TMOS gels;
- (2) there is no correlation between the permeability and curing/drying rate of lysils for monolithicity;
- (3) there may be correlation between wettability and the effectiveness of curing/drying of lysils;
- (4) there is a direct relationship between the molecular size of the liquids and the gel's permeability except 1-octanol;
- (5) 1-octanol exhibits an anomalously large permeability when compared with the other liquids;
- (6) ethanol and methanol exhibit the same general trends of permeability in lysil gel indicating similar interaction mechanism;
- (7) TEOS and water exhibit a similar behavior indicating that the interaction mechanism with the gel is similar;
- (8) variation of permeability for the different liquids comes from the different degree and kinetics of interaction between the gel and the liquids;
- (9) permeability is not a good indicator to predict the effectiveness of a curing medium, and the curing mechanism is not based on the permeability in eqn (1).

Acknowledgements

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