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Hydrophobicity of silica thin films: The deconvolution and interpretation by Fourier-transform infrared spectroscopy

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ABSTRACT

This work investigated the synthesis of dimethoxydimethylsilane:tetraethoxysilane (DMDMS:TEOS) silica thin films as well as the effect of DMDMS:TEOS molar ratios and calcination temperature on hydrophobic properties of silica thin films and its correlation with the FTIR spectra behaviour. The silica thin films were synthesized by sol-gel method using combination of DMDMS and TEOS as silica precursors, ethanol as solvent and ammonia as catalyst, with DMDMS and TEOS molar ratio of 10:90, 25:75, 50:50, 75:25 and 90:10. The results showed that DMDMS:TEOS molar ratio had significant impact on the hydrophobic properties of silica thin films coated on a glass surface. Furthermore, the correlation between water contact angle (WCA) and DMDMS:TEOS molar ratio was found to be in a parabolic shape. Concurrently, the maximum apex of the parabola obtained was observed on the DMDMS:TEOS molar ratio of 50:50 for all calcination temperature. It was clearly observed that the silica xerogel exhibiting notable change in relative peak intensities showed FTIR peak splitting of $\nu_{\text{asymmetric}}$ Si-O-Si. To uncover what happened at the FTIR peak, the deconvolution was conducted in Gaussian approach. It was established that the changes in the Gaussian peak component were related to DMDMS:TEOS molar ratios and the calcination temperature that allowed us to tailor the DMDMS:TEOS silica polymer structure model based on the peak intensity ratios. With the increase of DMDMS:TEOS molar ratio, the ratio of (cyclic Si-O-Si)/(linear Si-O-Si) decreased, whilst the ratio of (C-H)/(linear Si-O-Si) increased. Both ratios intersected at DMDMS:TEOS molar ratio of 50:50 with contribution factor ratio of 1:16 and 1:50 for silica xerogel calcined at 300 °C and 500 °C respectively. The importance of this research is the DMDMS:TEOS molar ratio plays an important role in determining the hydrophobic properties of thin films.

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1. Introduction

Thin layers with properties governed by the design of precursors were often studied as stand-alone smart materials or functional layers used in a variety of applications [1–4]. Moreover, thin solid films, such as hydrophobic silica, have been used in many types of engineering systems and have been adapted to fulfil a wide variety of functions [5,6]. Most works improving silica thin film properties has been implemented with various surface modification (silylating) agents. Thin films (normally <1 μm in thickness) formed by dipping or spinning need fewer materials and can be processed quickly without cracking, overcoming most of the deficiency of the sol-gel process [7]. As coating method, sol-gel is widely used in thin layer formations because of the ease and convenience of its application. Sol-gel derived from organic inorganic hybrid films combines the benefits of inorganic materials (stiffness, high thermal stability) [8–10] and organic polymers (flexibility, ductility, hydrophobicity and processability) [11,12].

Usually, the silica thin films are synthesized by sol-gel method, combining metal alkoxides as precursors and various mono-, di- and tri-alkyl silylating agents [13]. Generally, the metal alkoxides, $M(\text{OR})_z$, are reactive due to the presence of highly electronegative OR groups (hard- π donors) that stabilize M in its highest oxidation state and render M very susceptible to nucleophilic attack [14]. TEOS is the most commonly used precursor in sol-gel processing [13,15]. Previously, Dimethoxydimethylsilane (DMDMS) and tetraethoxysilane (TEOS) catalyzed with acid and base have been used to protect the surface of kapton using solvothermal method to render the outer surface of silica film hydrophobic [16]. Combination between DMDMS and TEOS as an organic-inorganic intermediate layer plays a role in enhancing the adhesion of outer silica film and very good to be used as hydrophobic material. Previous work showed interesting results when the precursors silica composition was modified [17–19].

Due to the very thin layer of silica surface, with estimated thickness of <200 nm, profiling the properties of silica surface is not easy. Among the various modern surface analytical tools available, contact angle and wetting techniques remain as standard methods for benchmarking the surface quality [20]. On the other hand, infrared spectroscopy has

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proven very useful because it provides a means to determine local structure of building units which constitutes the silica network, some of the site properties, and the interaction in silica network [21]. Some authors have found that the structures of silica are proportional to FTIR reflection [22–24]. Agarwal [25] found simple IR method to determine the thermal properties of silica by measuring the IR peak position of the silica structural band. These bands are attributed to the combination and overtones of the fundamental vibrational bands [3].

In this work, our point is to examine the influence of molar ratios of dimethoxydimethylsilane: tetraethoxysilane (DMDMS:TEOS) on the hydrophobicities of the methyl-modified silica films. The effect of interface or molecule interaction forces on surface wettability is discussed. The surface structures and thermal stabilities of methyl-modified silica films were analyzed by FTIR spectroscopy. This work focused on the use of FTIR method to obtain as much information about silica carriers, particularly the characteristics of functional groups present and the changes on its surface was important. Due to the broadening effect of the instrumental response function, the spectra data recorded by spectrometer often suffer band overlapping, so that the resolution of measured spectra is degraded. Therefore, spectral restoration is necessary and important for spectral analysis and assignment. Deconvolution method is normally used for spectral restoration [26,27]. Peak-details are often smoothed when deconvolution method is applied for spectral restoration [28].

2. Experimental Section

2.1. Materials

The silica thin films were prepared using dimethyldimethoxysilane (DMDMS) (98% pure) from Aldrich and tetraethoxysilane (TEOS) (99% pure) from Merck as the silica sources along with ethanol from Merck (99% pure) as solvent. The catalyst used in the hydrolysis and condensation steps was ammonia solution (25%) from Merck. Moreover, distilled-deionized water and slide ± 2 mm thick (Sail Brand) were also used.

2.2. Preparation of Sol-gel DMDMS:TEOS Solution

DMDMS:TEOS sol with various molar ratios (10:90, 25:75, 50:50, 75:25 and 90:10) were prepared using sol-gel technique based on the reported method [29]. DMDMS:TEOS were dissolved in ammonia: ethanol solution 0.3 M (1:50 in molar ratio) using a magnetic stirrer at 300

RPM in an ice-cooled bath to avoid partial hydrolysis for 2 h. The DMDMS:TEOS solution obtained was then divided into two parts, the first part was for modification of hydrophobic coating films and the second part was for characterization in xerogels form.

2.3. Fabrication of Xerogels DMDMS:TEOS

The resulting mixtures had been stored at room temperature for a week and then dried in a temperature-controlled oven at 60 °C under normal atmospheric conditions to form a xerogel. The xerogel samples were crushed finely and calcined using a furnace (Vulcan™ 3–1300) at temperature of 300 °C and 500 °C for 2 h with a ramp rate of 2 °C min⁻¹.

2.4. Fabrication of Thin Films DMDMS:TEOS

Thin films were directly coated on 20 mm × 70 mm × 2 mm commercial glass slides via dip-coating process with dipping and withdrawal rate of 10 cm min⁻¹ and dwell time of 2 min. Each film was calcined separately at 300 °C and 500 °C in a temperature controlled furnace (Vulcan™ 3–1300), with hold time of 2 h and ramp rate of 2 °C min⁻¹. The dip-coating and calcination processes were repeated four times to get thicker hydrophobic films on the glass surface and to avoid any surface crack.

2.5. Materials Characterization

Xerogels in powder form were characterized using a Shimadzu IRAffinity-1 Fourier-transform infrared (FTIR) spectrometer with a Pike MIRacle attenuated total reflectance accessory (ATR-FTIR) at wavelength range of 600–4000 cm⁻¹. All spectra were normalized based on reported method [30]. To quantify the analysis, a deconvolution approach of the FTIR spectra region between 1300 and 900 cm⁻¹ was performed using the Fityk computer program with nonlinear least squares fitting method, by means of Gaussian function. The same number of derived peaks was used in the entire spectral peak fitting. The half width at half maximum (HWHM) was fixed for each peak, whilst the peak position was allowed to change slightly to acquire qualified fitting. The deconvolution of FTIR spectra was previously reported in detail in literatures [15,31].

The hydrophobic properties of the silica films were examined using the $\theta/2$ method to measure water contact angle (WCA) [32]. A deionized water drop from a syringe was placed on the silica surface.

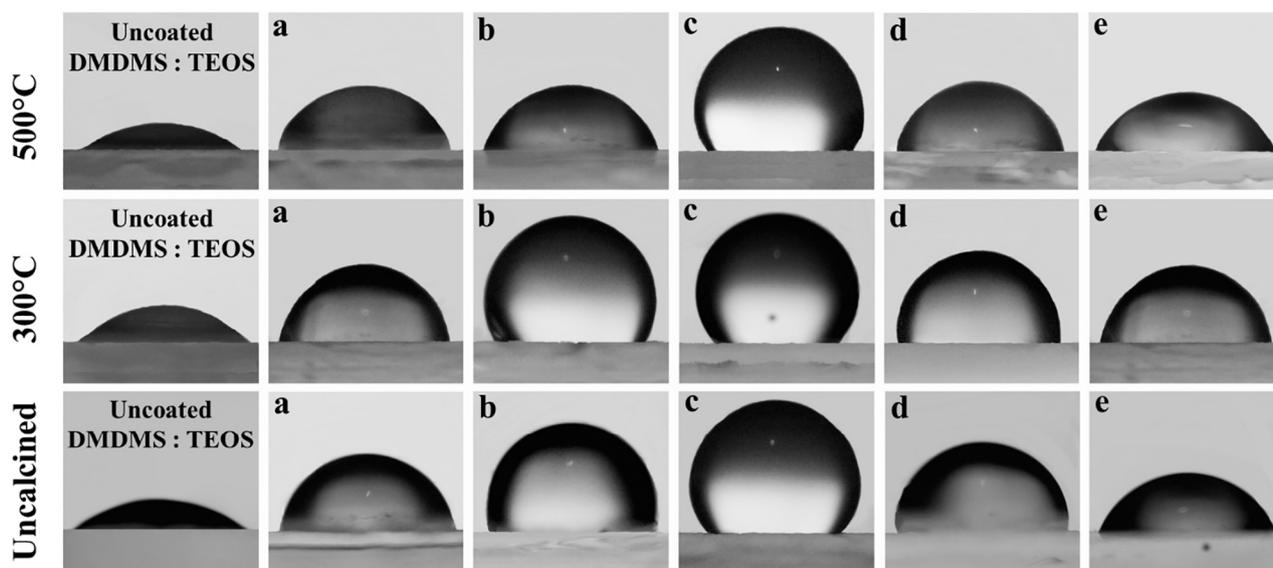


Fig. 1. Water droplets on the surface of silica thin films with various DMDMS:TEOS molar ratio of (a) 10:90; (b) 25:75; (c) 50:50; (d) 75:25; and (e) 90:10.

Table 1
Resulting contact angle of the water droplet on different silica thin film surfaces.

Molar ratio		Water contact angle (°)		
DMDMS	TEOS	Uncalcined	Calcined 300 °C	Calcined 500 °C
10	90	71 ± 1	100 ± 1	62 ± 1
25	75	105 ± 1	114 ± 1	74 ± 1
50	50	122 ± 1	128 ± 1	111 ± 1
75	25	84 ± 1	99 ± 1	91 ± 1
90	10	69 ± 1	93 ± 1	83 ± 1

Geometrically, WCA can be calculated as $\theta/2 = \tan^{-1}(h/r)$ by measuring the drop radius (r) and the height of the apex (h). The average WCA value was obtained by measuring the same sample at five different droplet positions.

3. Results and Discussion

3.1. Water Contact Angle (WCA)

Contact angle measurement is one way to investigate the interfacial interaction between solid and liquid. Wettability of the system is characterized by the “ θ ” contact angle measured between the liquid drop and the solid surface. The contact angle can also be used to measure adhesiveness. Wetting of the surface using liquid depends on the relative molecular force between molecules present in the liquid (cohesive) as well as between the liquid and the solid (adhesive). The cohesive force in the liquid prevents the liquid to contact the surface whilst the adhesive force causes the liquid to spread throughout the surface. Strong adhesion and weak cohesion produce a high degree of wetting which is characterized by low measured contact angle. Conversely, weak adhesion and strong cohesion generate hydrophobic condition with high contact angle [33].

The hydrophobicity of the silica thin films was studied by measuring the contact angle of the silica thin films with water. The WCA study was carried out for the various compositions of DMDMS:TEOS molar ratios of 10:90, 25:75, 50:50, 75:25 and 90:10 on uncalcined, calcined at 300 °C and calcined at 500 °C methyl-silica thin films, as shown in Fig. 1.

Direct observation of the images of water droplet sizes on silica thin films in Fig. 1 reveals that the composition of DMDMS and TEOS on the formation of thin films on the glass surfaces has considerable influence on the hydrophobic properties. The increase in the contact angle

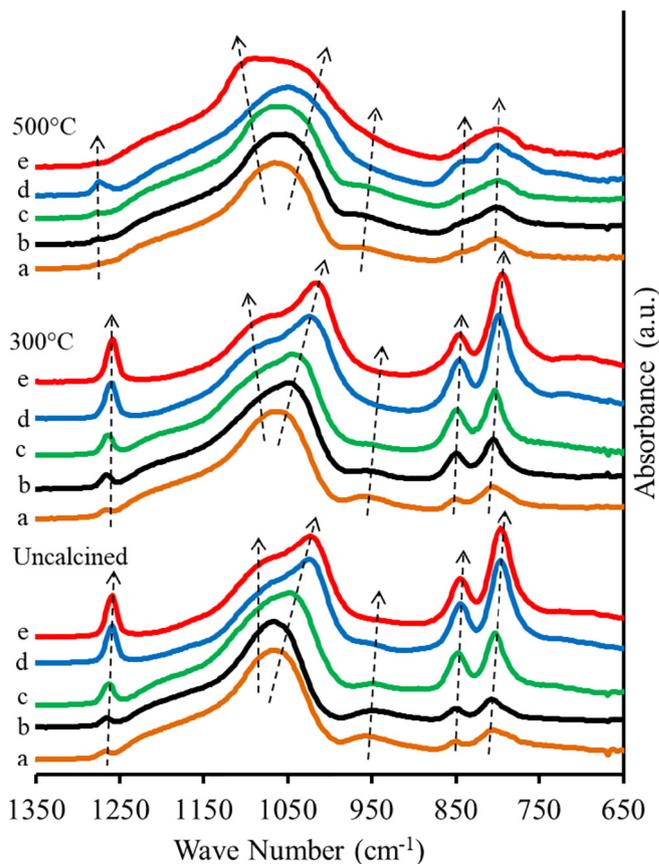


Fig. 3. The IR Spectra of silica xerogels with DMDMS:TEOS molar ratio of (a) 10:90; (b) 25:75; (c) 50:50; (d) 75:25; and (e) 90:10.

normally indicates the increase in hydrophobicity [34]. On uncoated glass surface, the water droplet was widespread and had low contact angle of 49.2°. Hydrophobicity of thin films is due to the existence of methyl groups from DMDMS as co-precursor. The average WCA values based the $\theta/2$ method are tabulated in Table 1. It can be seen that the WCA values of the DMDMS:TEOS films were in the range of 69–122° and transformed to hydrophobic surfaces due to the self-assembly of

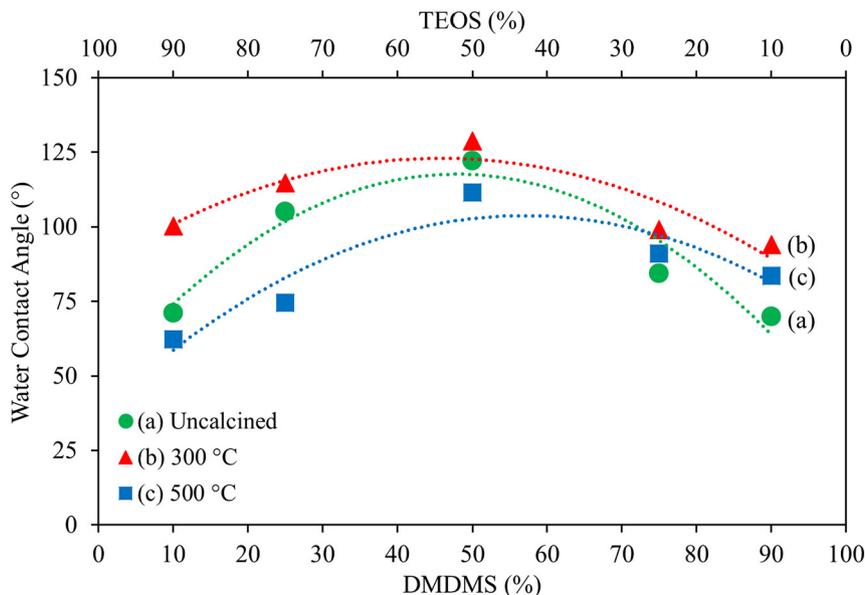


Fig. 2. Correlation between water contact angles and DMDMS:TEOS molar ratios.

DMDMS methyl groups. High composition of both on TEOS or DMDMS resulted in lower WCAs. Meanwhile, a balanced concentration of DMDMS:TEOS yielded better hydrophobicity. These results can be explained by the combined effect of the two factors: surface roughness and surface energy. We assume that DMDMS is hydrophobic whereas TEOS is hydrophilic, and changing their molar ratio affects these two factors of the coated material. Increasing the DMDMS content may reduce the surface energy. However, the surface roughness can be reduced if the DMDMS content is high enough as the extra silane fills the inter-particle gap [17–19].

Fig. 2 shows the graphs of correlation between various molar ratios and calcination temperature of silica thin films with the WCA based on Table 1. It was found that the correlation is in parabolic shape and the function is quadratic polynomial with apex on optimum WCA at DMDMS:TEOS molar ratio of 50:50. The parabolas are symmetric curves with x axis is the DMDMS:TEOS molar ratio and y axis is the WCA values. Furthermore, the obtained equations based on DMDMS contents are $y = -0.03x^2 + 2.91x + 48.13$ for uncalcined silica thin layer, $y = -0.02x^2 + 1.57x + 86.99$ for calcined 300 °C, and $y = -0.02x^2 + 2.33x + 37.45$ for calcined 500 °C. These three equations have an adequate coefficient of determination for regression (R^2) which are 0.90, 0.82 and 0.85 for uncalcined, calcined 300 °C and calcined 500 °C silica thin layers

respectively. These results indicate that there is a strong correlation between WCA value and DMDMS:TEOS molar ratio.

It is observed in Fig. 2 that the WCA are significantly affected by DMDMS:TEOS molar ratios that were calcined at different temperatures. The WCA values escalate significantly from the DMDMS:TEOS molar ratio of 10:90 to the optimum value on DMDMS:TEOS molar ratio of 50:50, then reduce at the DMDMS:TEOS molar ratio of 90:10. These results show the same tendency at different calcination temperatures. Moreover, Fig. 2 also shows that at calcination temperature of 300 °C, the entire WCA values are always higher than that of the calcination temperature of 500 °C for all variations of the DMDMS:TEOS molar ratios. In our previous papers [35], we have already reported that the methyl group which acted as hydrophobic directing agent on silica layer was eroded by the heating process above 375 °C.

3.2. Fourier Transform Infrared (FTIR)

The Fourier Transform Infrared (FTIR) investigation was carried out to confirm the existence of functional groups and the bonding types of silica xerogels as shown on Fig. 3. The observed absorption peaks between wave number of 1350 and 650 cm^{-1} are conventionally found in silica materials due to the main silicate network groups' vibrations

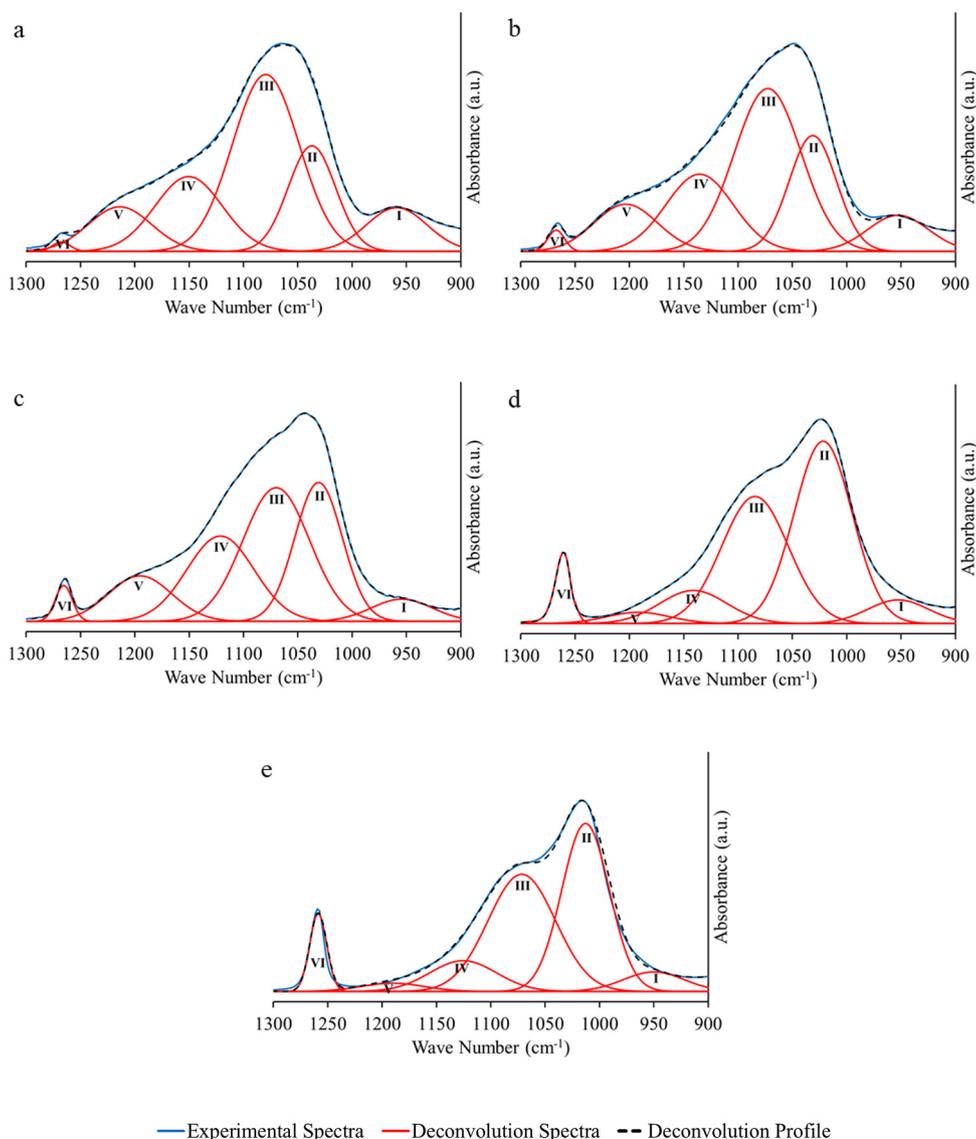


Fig. 4. Deconvolution of the FTIR spectra of silica xerogels calcined at 300 °C in the region between 1300 and 900 cm^{-1} . The DMDMS:TEOS molar ratio of (a) 10:90; (b) 25:75; (c) 50:50; (d) 75:25; and (e) 90:10.

with different bonding arrangement. The fundamental building block is the SiO_4 tetrahedral unit, where all the oxygen atoms are shared between two tetrahedral, forming a fully polymerized network [21] and methyl group acts as network modifier. An intense peak at 1260 cm^{-1} corresponds to the symmetrical vibration (ν_s) of C-H group [36], peak at $1000\text{--}1200\text{ cm}^{-1}$ is assigned to varied asymmetrical vibration (ν_{as}) of Si-O-Si group [31], peak at 860 cm^{-1} corresponds to the symmetrical vibration (ν_s) of Si-C group, and peak at 800 cm^{-1} indicates the symmetrical vibration (ν_s) of Si-O-Si group [13], wherein these groups indicate that the surface is comparatively hydrophobic. Furthermore, peak at 960 cm^{-1} relates to the symmetrical vibration (ν_s) of Si-OH group which contributes hydrophilic properties [13,37]. The IR spectra in Fig. 3 show that the intense peak of ν_s C-H group at 1260 cm^{-1} and ν_s Si-C group at 860 cm^{-1} increase significantly with the increase of DMDMS:TEOS molar ratio, which suggests that addition of DMDMS component as silylating agent influences the structure of silica thin films. The peak intensities of uncalcined silica thin films and calcined at $300\text{ }^\circ\text{C}$ are similar, however different absorption peak intensities are observed on the silica thin layer calcined at $500\text{ }^\circ\text{C}$. These results occur because the Si-C groups could preserve the thermal stability up to $375\text{ }^\circ\text{C}$, suggesting that the Si-C groups have been converted into Si-OH groups at $500\text{ }^\circ\text{C}$ [13,35]. Therefore, the peak intensities of Si-C are higher at $300\text{ }^\circ\text{C}$ whilst the peak intensities of Si-OH are higher at $500\text{ }^\circ\text{C}$.

It can be seen in Fig. 3 that by increasing the DMDMS:TEOS molar ratio, the spectral region with the wavenumbers from 1200 cm^{-1} to 1000 cm^{-1} significantly splits to certain distinct modes of ν_{as} Si-O-Si group. Changes in the hydrophobic properties are assumed and observed to be correlated with the structural changes in silica network structure [21] which are detected by a shift in the Si—O stretching infrared band located at $1000\text{--}1200\text{ cm}^{-1}$. The IR absorption spectra of the silica xerogel appear to be complicated due to their overlapping bands or nearby positions and appear to be generally more or less similar. To confirm whether the network structure is affected by DMDMS:TEOS molar ratio, a quantitative analysis was carried out by deconvolution of the FTIR absorption profile utilizing the “Fityk” program. An empirical

deconvolution method was used in more detailed study of overlapping spectra [38]. A typical deconvolution, Gaussian bands of IR spectra of silica xerogels calcined at $300\text{ }^\circ\text{C}$ is illustrated in Fig. 4. Some Gaussian peak components are used to deconvolute FTIR spectra with the same half width at half maximum (HWHM) values on the similar centre of derived peaks until the deconvolution spectra approach the experimental spectra. The peak envelope in the range of $1200\text{--}1000\text{ cm}^{-1}$ is assumed to consist of four peak components arising from the ν_{as} Si-O-Si group [15,39].

Fig. 4 shows the presence of six peak components that establish deconvolution spectra at wavelengths of $1300\text{--}900\text{ cm}^{-1}$ on DMDMS:TEOS silica films calcined at $300\text{ }^\circ\text{C}$. The peak component around 960 cm^{-1} (I) corresponds to ν_s Si-OH group. The ν_{as} Si-O-Si mode is decomposed in longitudinal optical and transverse optical components of different siloxane rings [40,41]. The shoulder at $\sim 1220\text{ cm}^{-1}$ (V) is assigned to the longitudinal optic mode (LO). The peak around 1030 cm^{-1} (II) relates to ν_{as} linear Si-O-Si group [42,43], and at around 1080 cm^{-1} (III) arises from ν_{as} cyclic Si-O-Si group (the silicon-apical oxygen units, that are O atoms shared by tetrahedral and octahedral sheets, which are perpendicular to the layers) [43–45] and also assigned to the transversal optic mode (TO) which generally appear as four-member [(SiO)₄] and six-member [(SiO)₆] ring respectively [46]. Furthermore, the other peak component at around 1150 cm^{-1} (IV) is attributed to ν_{as} Si-O within the tetrahedral sheet, which is parallel to the layer [44], and at around 1260 cm^{-1} (VI) to ν_s C-H group [36] derived from methyl group of DMDMS. The calculation of each Gaussian peak components of Si-OH, linear Si-O-Si, and cyclic Si-O-Si is calculated as the ratio of area. The cyclic Si-O-Si four-rings are stable toward hydrolysis [47], they constitute a large fraction of the oligomeric species in TEOS-derived systems [48], thus it is expected to be predominant in silica xerogels [7], as maintained on higher relative peak intensities at 1080 cm^{-1} . However, the cyclic Si-O-Si four-rings are much more tensioned ($\theta = 125^\circ$) than six-rings ($\theta = 125^\circ$) [15]. Based on Fig. 4, we propose a schematic representation of silica cluster, which indicates the ν_{as} cyclic Si-O-Si and ν_{as} linear Si-O-Si. Fig. 5 shows a schematic

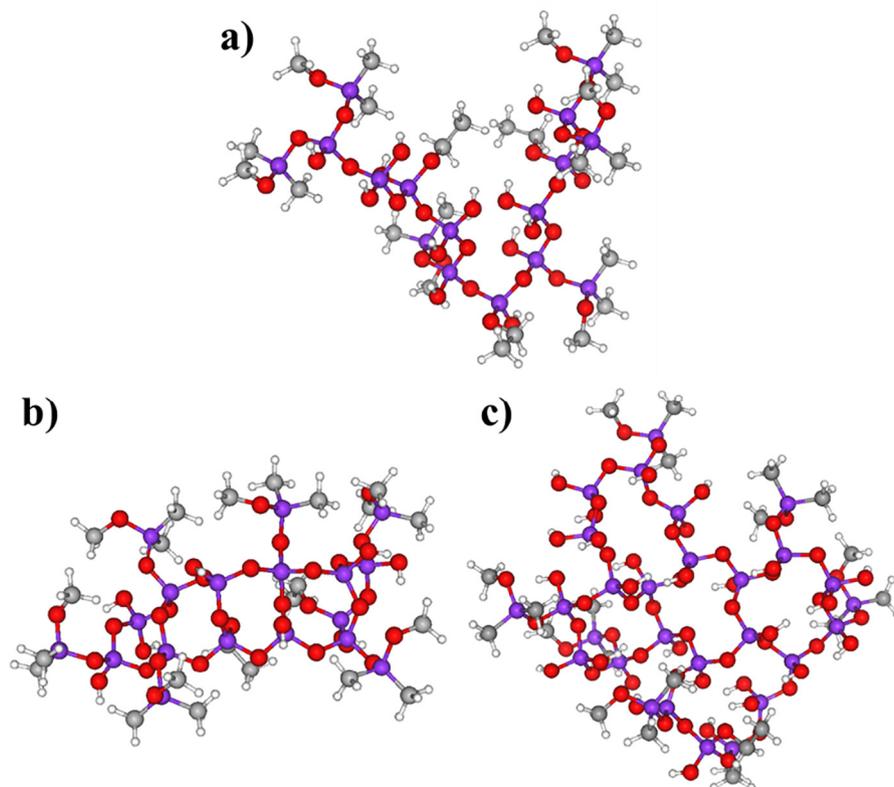


Fig. 5. Schematic representation of silica thin film structures containing 5 siloxane units on (a) linear, (b) 4-rings [(SiO)₄]; (c) 6-rings [(SiO)₆].

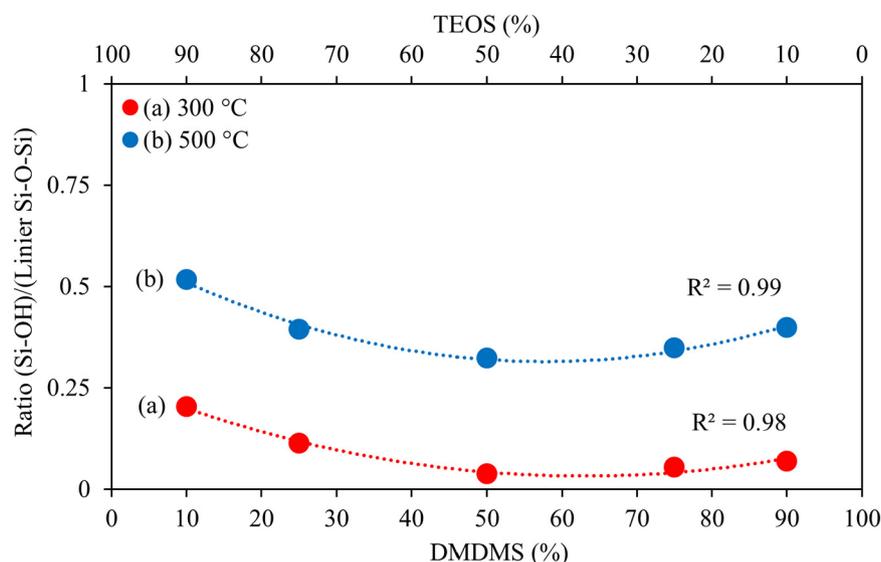


Fig. 6. The correlation between DMDMS:TEOS molar ratio and area ratio of (Si-OH)/(linear Si-O-Si).

representation of DMDMS:TEOS silica cluster obtained from a *Marvin Sketch* application.

The intense peak of ν_{as} Si-O-Si linear (II) increases, whereas the peak of ν_{as} Si-O-Si cyclic (III) decreases with decreasing amount of DMDMS:TEOS molar ratio. This trend indicates that the increasing of TEOS content make the structure of silica polymer shifts from a linear structure to a more cyclic structure which is more branched. Whilst the lower TEOS content proceeds the silica polymer structure to be linear which is less branched. Furthermore, the peak of ν_{as} Si-O (V) also decreases with decreasing of DMDMS:TEOS molar ratio. The peak of ν_s C-H (VI) rises with increasing DMDMS content that contains more methyl groups.

To explain why the highest hydrophobicity occurs in the DMDMS:TEOS ratio of 50:50, the peak areas of the silanol (Si-OH) group and the siloxane group (Si-O-Si) are compared. In general, Si-OH is the main source of hydrophilicity and obtained from the hydrolysis reaction of alkoxides on TEOS as part of sol-gel reaction before the condensation reaction leads to the formation of siloxane bridges [7,49]. Meanwhile, the Si-O-Si group is hydrophobic which arises from the condensation reaction of silica precursor in sol gel reaction. Whether the surface is hydrophilic or hydrophobic, it highly depends on the composition of the silanol and siloxane groups. If the silanol group is dominant, the silica surface will be hydrophilic. On the other hand, if the siloxane is

dominant, the silica surface will be hydrophobic. Hence, the relative absorbance of these two types of bands (Si-O-Si and Si-OH) allows assessment of the degree of crosslinking within incorporated silicon oxide phases. Fig. 6 shows the graphs of correlation between DMDMS:TEOS molar ratio and the area ratio of (Si-OH)/(linear Si-O-Si).

It can be seen that (Si-OH)/(linear Si-O-Si) ratio forms a concave parabola with the lowest value is DMDMS:TEOS ratio of 50:50 wherein this result is very much in line with the WCA value in Fig. 1. Fig. 6 shows that the sol gel reaction produces a minimum Si-OH/(Si-O-Si) ratio value at a DMDMS:TEOS ratio of 50:50. This is slightly different from the initial hypothesis which suggests that with increasing DMDMS:TEOS ratio, the Si-OH content will drop as the increasing amount of methyl groups will compete with the formation of silanol groups hence the highest hydrophobic properties will be obtained at the highest DMDMS content. However, these results indicate that the condensation reaction for the formation of Si-O-Si framework is optimum on a balanced DMDMS:TEOS composition. Conversely, if DMDMS or TEOS are dominant, it will lead to the hydrolysis reaction. The (Si-OH)/(linear Si-O-Si) ratio for silica films calcined at 300 °C is always lower than that of at 500 °C for all DMDMS:TEOS ratios. This indicates that the silica films calcined at 300 °C are more hydrophobic than silica calcined at 500 °C and this is very much in accordance with the results shown in Figs. 1 and 2. The graphs in Fig. 6a are obtained within the

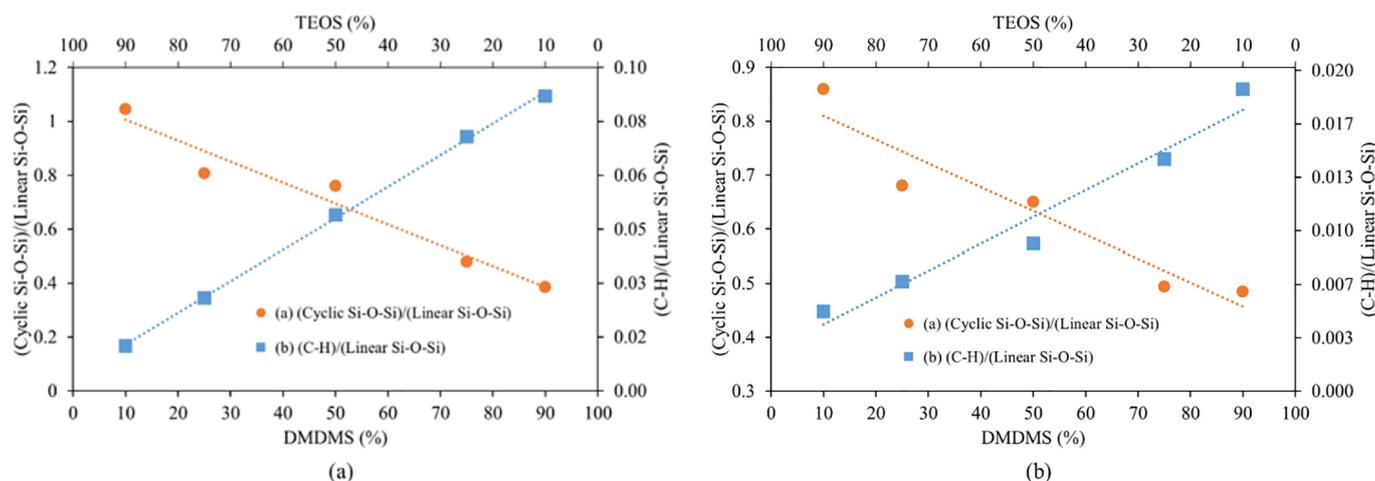


Fig. 7. The correlation between (cyclic Si-O-Si)/(linear Si-O-Si) and (C-H)/(linear Si-O-Si) area ratio with the DMDMS:TEOS molar ratio (a) calcined at 300 °C and (b) calcined at 500 °C.

Table 2

Correlation between (cyclic Si-O-Si)/(linear Si-O-Si) ratio and (C-H)/(linear Si-O-Si) ratio on the water contact angle.

300 °C					
DMDMS	TEOS	(A)	(B)	Absolute difference value ABS [(A - (16 × B))]	Water contact angle
10	90	1.045	0.013	0.832	100.3
25	75	0.808	0.028	0.366	114.8
50	50	0.760	0.052	0.076	128.8
75	25	0.479	0.075	0.728	99.2
90	10	0.386	0.088	1.015	94.0
500 °C					
DMDMS	TEOS	(A)	(B)	Absolute difference value ABS [(A - (50 × B))]	Water contact angle
10	90	0.860	0.005	0.613	62.3
25	75	0.680	0.007	0.341	74.5
50	50	0.650	0.009	0.195	111.6
75	25	0.495	0.014	0.221	91.1
90	10	0.485	0.019	0.447	83.6

calculation error of 1% at 300 °C and 2% at 500 °C which indicates both graphs have high suitability.

As far as we know, the highly hydrophobic surface is produced by the combination of the special hierarchical and the geometric parameters of the rough structures [50]. Therefore, another reason that can be used to explain why the hydrophobicity trend is parabolic is by seeing the effects of linear and cyclic Si-O-Si and also the CH₃ group. Noticeably, the (Si-O-Si) asymmetrical vibration consists of two components arising from Si-O-Si groups in linear fragment (approximately 1030 cm⁻¹) and in loop (about 1080 cm⁻¹) [44,51]. Consequently, a comparison of linear and cyclic components' absorbance magnitudes aids an understanding of the hydrophobic properties of the silica thin films [51]. It is known that the silanol (Si-OH) group is hydrophilic and the siloxane (Si-O-Si) group is more hydrophobic. We assume that the cyclic Si-O-Si group is more hydrophobic than linear Si-O-Si, so if the cyclic component is more than the linear component, it is expected that the silica thin layer will be more hydrophobic. On the other hand, the C-H group appears to be around 1260 cm⁻¹ [36] that arises from the methyl groups of DMDMS. The CH₃ group gives hydrophobic effect since all bonds on the carbon are filled and the chemical groups are non-polar, hence water molecules which are polar cannot interact with non-polar groups. To determine the contribution of the C-H

and Si-O-Si cyclic groups proportionally, the calculation of the relative comparison of the C-H and Si-O-Si cyclic groups to the Si-O-Si linear peak was carried out. The results of ratio comparison calculation of (cyclic Si-O-Si)/(linear Si-O-Si) and (CH)/(linear Si-O-Si) are presented in Fig. 7.

Fig. 7 shows that (cyclic Si-O-Si)/(linear Si-O-Si) ratio decreases with increasing DMDMS:TEOS molar ratios, whilst the (C-H)/(linear Si-O-Si) ratio increases. This suggests that the formation of cyclic Si-O-Si is more favourable when the DMDMS content is low. Meanwhile, when the DMDMS content increases, the structure of the silica chain becomes more linear. This is due to the steric factor of the -CH₃ group. The cyclic structure requires more space than a linear structure. As the CH₃ group increases due to increased DMDMS content, the silica structure organizes itself to achieve optimal structuring of the chain and favour a linear structure due to its smaller steric hindrance. On the contrary, the C-H group increases with increasing DMDMS content which is justifiable because the number of C-H groups is directly proportional to the DMDMS content. Although the molar ratios of DMDMS:TEOS 75:25 and 90:10 have higher (C-H)/(linear Si-O-Si) ratio, their resulting WCAs in Fig. 1 are smaller than those of DMDMS:TEOS ratio of 50:50. Similar results have been reported in different coating systems [17–19].

Fig. 7 presents that both ratios of (cyclic Si-O-Si)/(linear Si-O-Si) and (C-H)/(linear Si-O-Si) intersect each other at around DMDMS:TEOS molar ratio of 50:50. The ordinate scales for (cyclic Si-O-Si)/(linear Si-O-Si) ratio and (C-H)/(linear Si-O-Si) ratio are different. The comparison of ordinate scale between (cyclic Si-O-Si)/(linear Si-O-Si) ratio and the (C-H)/(linear Si-O-Si) ratio is of 1:16 for silica xerogel calcined at 300 °C and 1:50 for silica calcined at 500 °C. Values of 16 and 50 therefore refer to as contributing factors.

To determine the influence of (cyclic Si-O-Si)/(linear Si-O-Si) ratio and (C-H)/(linear Si-O-Si) ratio to hydrophobicity properties in silica films, the (C-H)/(linear Si-O-Si) ratio is multiplied by the contribution factor on each DMDMS:TEOS molar ratio to make a balanced contribution. It is found that the contribution factor to make the most fitting correlation is 1:16 at 300 °C and 1:50 at 500 °C. One of the key findings obtained from this research is the discovery of linear correlation between the absolute difference values of (cyclic Si-O-Si)/(linear Si-O-Si) ratio and (C-H)/(linear Si-O-Si) ratio with the water contact angles as shown in Table 2 and Fig. 8.

Fig. 8 shows that WCA value decreases with increasing absolute difference value of (cyclic Si-O-Si)/(linear Si-O-Si) ratio and (C-H)/(linear Si-O-Si) ratio. It is proposed there is a trade-off between (cyclic Si-O-Si) and (C-H) that makes DMDMS:TEOS molar ratio of 50:50 silica

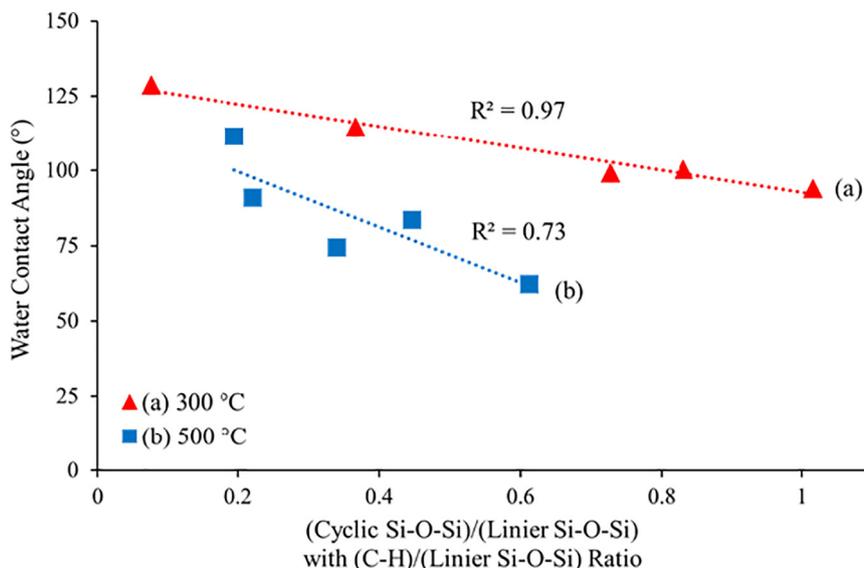


Fig. 8. Correlation graph between (cyclic Si-O-Si)/(linear Si-O-Si) ratio and (C-H)/(linear Si-O-Si) ratio on the water contact angle.

film to be the highest hydrophobic film. Fig. 8 also demonstrates that to attain appropriate correlation between absolute difference value and WCA, the contribution factor values are influenced by thermal treatment. The contribution factor of silica calcined at 500 °C is threefold higher than that of calcined at 300 °C. This is because at 500 °C the C-H groups are already oxidized [13], therefore the amount of C-H groups is very small.

4. Conclusion

This work shows that molar ratio of DMDMS:TEOS has a considerable influence on hydrophobic properties of thin film deposited on glass surface. The importance of this research is the DMDMS:TEOS molar ratio plays an important role in determining the hydrophobic properties of thin films. To obtain the highest hydrophobic properties, it is necessary to optimize the molar ratio. The silica xerogels exhibiting notable change in relative peak intensities showed splitting ν_{as} Si-O-Si in their infrared reflection. It is considered that changes in Gaussian peak components are related to the different molar ratio of DMDMS:TEOS and heat treatments which allow us to tailor the polymer structure of DMDMS:TEOS silica thin films based on its peak intensities ratios. One of the key finding obtained from this research is the discovery of linear correlation between the absolute difference values of (cyclic Si-O-Si)/(linear Si-O-Si) ratio also (C-H)/(linear Si-O-Si) ratio and the water contact angle.

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References

- [1] C. Sanchez, C. Boissière, D. Grosso, C. Laberty, L. Nicole, Design, synthesis, and properties of inorganic and hybrid thin films having periodically organized nanoporosity, *Chem. Mater.* 20 (2008) 682–737.
- [2] T. Al-Harbi, F. Al-Hazmi, W.E. Mahmoud, Synthesis and characterization of nanoporous silica film via non-surfactant template sol-gel technique, *Superlattice. Microst.* 52 (2012) 643–647.
- [3] T. Sirinakom, K. Imwiset, S. Bureekaew, M. Ogawa, Inorganic modification of layered silicates toward functional inorganic-inorganic hybrids, *Appl. Clay Sci.* 153 (2018) 187–197.
- [4] H. Fabre, D. Mercier, A. Galtayries, D. Portet, N. Delorme, J.-F. Bardeau, Impact of hydrophilic and hydrophobic functionalization of flat TiO₂/Ti surfaces on proteins adsorption, *Appl. Surf. Sci.* 432 (2018) 15–21.
- [5] L.B. Freund, S. Suresh, *Thin Film Materials: Stress, Defect Formation and Surface Evolution*, Cambridge University Press, 2004.
- [6] M.A. Hood, N. Encinas, D. Vollmer, R. Graf, K. Landfester, R. Muñoz-Espí, Controlling hydrophobicity of silica nanocapsules prepared from organosilanes, *Colloids Surf. A Physicochem. Eng. Asp.* 532 (2017) 172–177.
- [7] C.J. Brinker, G.W. Scherer, *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*, Academic press, 2013.
- [8] A.A. Al-Ghamdi, W.E. Mahmoud, S.J. Yaghtmour, F.M. Al-Marzouki, Structure and optical properties of nanocrystalline NiO thin film synthesized by sol-gel spin-coating method, *J. Alloys Compd.* 486 (2009) 9–13.
- [9] F.A. Al-Agel, W. Mahmoud, Synthesis and characterization of highly stoichiometric AgInSe₂ thin films via a sol-gel spin-coating technique, *J. Appl. Crystallogr.* 45 (2012) 921–925.
- [10] H.A. Al-Khanbashi, W. Shirbeeny, A.A. Al-Ghamdi, L.M. Bronstein, W.E. Mahmoud, Spectroscopic ellipsometry of Zn_{1-x}Cu_xO thin films based on a modified sol-gel dip-coating technique, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 118 (2014) 800–805.
- [11] T. Yabuta, E.P. Bescher, J.D. Mackenzie, K. Tsuru, S. Hayakawa, A. Osaka, Synthesis of PDMS-based porous materials for biomedical applications, *J. Sol-Gel Sci. Technol.* 26 (2003) 1219–1222.
- [12] H.A. Al-Khanbashi, W. Shirbeeny, A.A. Al-Ghamdi, L.M. Bronstein, W.E. Mahmoud, Development of highly conductive and transparent copper doped zinc oxide thin films via 2-methoxyethanol modified sol-gel dip-coating technique, *Ceram. Int.* 40 (2014) 1927–1932.
- [13] A.P. Rao, A.V. Rao, G. Pajonk, Hydrophobic and physical properties of the ambient pressure dried silica aerogels with sodium silicate precursor using various surface modification agents, *Appl. Surf. Sci.* 253 (2007) 6032–6040.
- [14] D. Uhlmann, B.Z.G. Wnek, in: C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), *Better Ceramics Through Chemistry*, 1984 North Holland, New York 1984.
- [15] A. Fidalgo, L.M. Ilharco, Chemical tailoring of porous silica xerogels: local structure by vibrational spectroscopy, *Chem. Eur. J.* 10 (2004) 392–398.
- [16] Y. Xie, Y. Gao, X. Qin, H. Liu, J. Yin, Preparation and properties of atomic oxygen protective films deposited on Kapton by solvothermal and sol-gel methods, *Surf. Coat. Technol.* 206 (2012) 4384–4388.
- [17] C. Zeng, H. Wang, H. Zhou, T. Lin, Self-cleaning, superhydrophobic cotton fabrics with excellent washing durability, solvent resistance and chemical stability prepared from an SU-8 derived surface coating, *RSC Adv.* 5 (2015) 61044–61050.
- [18] H. Wang, H. Zhou, S. Liu, H. Shao, S. Fu, G.C. Rutledge, T. Lin, Durable, self-healing, superhydrophobic fabrics from fluorine-free, waterborne, polydopamine/alkyl silane coatings, *RSC Adv.* 7 (2017) 33986–33993.
- [19] A. Hussain, J. Calabria-Holley, D. Schorr, Y. Jiang, M. Lawrence, P. Blanchet, Hydrophobicity of hemp shiv treated with sol-gel coatings, *Appl. Surf. Sci.* 434 (2018) 850–860.
- [20] V. Madhurima, D.D. Purkayastha, N.V.S. Rao, Wettability, FTIR and dielectric studies of 1,4-dioxane and water system, *J. Colloid Interface Sci.* 357 (2011) 229–233.
- [21] E.M.A. Khalil, F.H. ElBatal, Y.M. Hamdy, H.M. Zidan, M.S. Aziz, A.M. Abdelghany, Infrared absorption spectra of transition metals-doped soda lime silica glasses, *Phys. B Condens. Matter* 405 (2010) 1294–1300.
- [22] P.J. Lezzi, M. Tomozawa, R.W. Hepburn, Confirmation of thin surface residual compressive stress in silica glass fiber by FTIR reflection spectroscopy, *J. Non-Cryst. Solids* 390 (2014) 13–18.
- [23] C.Y. Li, M. Tomozawa, Fictive temperature and fictive pressure measurement of silica glasses using FTIR method: for thick samples and samples containing Si-H, *J. Non-Cryst. Solids* 358 (2012) 3365–3371.
- [24] J. Yang, J. Chen, J. Song, Studies of the surface wettability and hydrothermal stability of methyl-modified silica films by FT-IR and Raman spectra, *Vib. Spectrosc.* 50 (2009) 178–184.
- [25] A. Agarwal, K.M. Davis, M. Tomozawa, A simple IR spectroscopic method for determining fictive temperature of silica glasses, *J. Non-Cryst. Solids* 185 (1995) 191–198.
- [26] P.A. Jansson, in: Peter A. Jansson (Ed.), *Deconvolution. With Applications in Spectroscopy*, 1984, Academic Press, New York, 1984.
- [27] Z. Mou-Yan, R. Unbehauen, A deconvolution method for spectroscopy, *Meas. Sci. Technol.* 6 (1995) 482.
- [28] H. Zhu, L. Deng, Spectral restoration using semi-blind deconvolution method with detail-preserving regularization, *Infrared Phys. Technol.* 69 (2015) 206–210.
- [29] A. Xing, Y. Gao, J. Yin, G. Ren, H. Liu, M. Ma, Preparation and atomic oxygen erosion resistance of silica film formed on silicon rubber by sol-gel method, *Appl. Surf. Sci.* 256 (2010) 6133–6138.
- [30] A. Darmawan, L. Karlina, Y. Astuti, Sriatun, J. Motuzas, D.K. Wang, J.C.D. da Costa, Structural evolution of nickel oxide silica sol-gel for the preparation of interlayer-free membranes, *J. Non-Cryst. Solids* 447 (2016) 9–15.
- [31] M.A. Karakassides, D. Gournis, D. Petridis, An infrared reflectance study of Si-O vibrations in thermally treated alkali-saturated montmorillonites, *Clay Miner.* 34 (1999) 429–429.
- [32] H.J. Lee, J. Owens, Superhydrophobic Superoleophobic Woven Fabrics, INTECH Open Access Publisher, 2011.
- [33] D.D. Purkayastha, V. Madhurima, Interactions in water-THF binary mixture by contact angle, FTIR and dielectric studies, *J. Mol. Liq.* 187 (2013) 54–57.
- [34] R. Pang, K. Zhang, Fabrication of hydrophobic fluorinated silica-polyamide thin film nanocomposite reverse osmosis membranes with dramatically improved salt rejection, *J. Colloid Interface Sci.* 510 (2018) 127–132.
- [35] A. Darmawan, R. Utari, R.E. Saputra, Suhartana, Y. Astuti, Synthesis and Characterization of Hydrophobic Silica Thin Layer Derived From Methyltrimethoxysilane (MTMS), IOP Conference Series: Materials Science and Engineering, 299, 2018 012041.
- [36] H. Homma, T. Kuroyagi, K. Izumi, C. Mirley, J. Ronzello, S. Boggs, Diffusion of low molecular weight siloxane from bulk to surface, *IEEE Trans. Dielectr. Electr. Insul.* 6 (1999) 370–375.
- [37] D.Y. Nadargi, R.R. Kalesh, A.V. Rao, Rapid reduction in gelation time and impregnation of hydrophobic property in the tetraethoxysilane (TEOS) based silica aerogels using NH₄F catalyzed single step sol-gel process, *J. Alloys Compd.* 480 (2009) 689–695.
- [38] K. Ghanbari, M. Ehsani, A. Jannesari Ladani, M. Mohseni, M. Ghaffari, Thermoanalytical study of siloxane-polyurethane thermosets: kinetic deconvolution of overlapping heterogeneous curing reactions, *Prog. Org. Coat.* 112 (2017) 234–243.
- [39] L. Lerot, P.F. Low, Effect of swelling on the infrared absorption spectrum of montmorillonite, *Clay Clay Miner.* 24 (1976) 191–199.
- [40] H.C. Lam, Y.W. Lam, Physical and conduction measurements of spin-on oxide, *Thin Solid Films* 41 (1977) 43–56.
- [41] L.B. Capeletti, I.M. Baibich, I.S. Butler, J.H.Z. dos Santos, Infrared and Raman spectroscopic characterization of some organic substituted hybrid silicas, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 133 (2014) 619–625.
- [42] S.K. Young, *Organic-Inorganic Composite Materials: Molecular Tailoring of Structure-Property Relationships*, 1999.
- [43] B.D. Ratner, D.G. Castner, *Surface Modification of Polymeric Biomaterials*, Springer Science & Business Media, 2013.
- [44] V.T. Farmer, J. Russell, The infra-red spectra of layer silicates, *Spectrochim. Acta* 20 (1964) 1149–1173.
- [45] A.K.H. Achyuta, A.J. White, H.G. Pryce Lewis, S.K. Murthy, Incorporation of linear spacer molecules in vapor deposited silicone polymer thin films, *Macromolecules* 42 (2009) 1970–1978.

- [46] A. Fidalgo, R. Ciriminna, L. Lopes, V. Pandarus, F. Béland, L.M. Ilharco, M. Pagliaro, The sol-gel entrapment of noble metals in hybrid silicas: a molecular insight, *Chem. Cent. J.* 7 (2013) 161.
- [47] L.C. Klein, *Sol-gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*, William Andrew Publishing, 1988.
- [48] M. Cima, R. Chiu, W. Rhine, $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ Powder Preparation by Sol-gel Emulsion Techniques, *MRS Online Proceedings Library Archive*, 99, 1987.
- [49] A.J. Vega, G.W. Scherer, Study of structural evolution of silica gel using ^1H and ^{29}Si NMR, *J. Non-Cryst. Solids* 111 (1989) 153–166.
- [50] G. Yang, J. Song, X. Hui, Fabrication of highly hydrophobic two-component thermosetting polyurethane surfaces with silica nanoparticles, *Appl. Surf. Sci.* 439 (2018) 772–779.
- [51] C.-S. Wu, Characterizing polycaprolactone/ SiO_2 - TiO_2 nanocomposites synthesized via in situ sol-gel polymerization, *Designed Monomers and Polymers* 10 (2007) 311–326.