ISSN: 1410-8917
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 23 (7) (2020): 249–254

Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Synthesis and Characterization of Trimethylchlorosilane Modified Silica Xerogel

Sellen Tanheitafino [a,1], Anis Shofiyani [a,2,*], Risya Sasri [a,3], Rudiyansyah [a,4]

[a] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Tanjungpura University, Pontianak, Indonesia

* Author's email: (1) sellentan@gmail.com; (2,*) anis.shofiyani@chemistry.untan.ac.id; (3) sasrisyapin@gmail.com; (4) rudiyansyah@chemistry.untan.ac.id

https://doi.org/10.14710/jksa.23.7.249-254

Article Info

Article history:

Received: 3rd April 2020
Revised: 12th June 2020
Accepted: 27th June 2020
Online: 31st July 2020

Keywords:
synthesis; TMCS modified silica xerogel; hydrophobic

Abstract

Modification of silica xerogel with TMCS (trimethylchlorosilane) reagent has been carried out to improve the hydrophobicity of silica xerogel. Silica xerogel was synthesized based on the sol-gel method using sodium silicate as a precursor, and citric acid as a catalyst, with a mole ratio of sodium silicate and citric acid, was 0.172: 0.004. The sol-gel process was carried out through several stages, i.e., hydrolysis and condensation of sodium silicate to form sol, gelation (sol transition to gel), aging, and drying. Surface modification was performed by studying the effect of TMCS: methanol: petroleum benzine volume ratio of 0.5:1:1, 1:1:1, 1.5:1:1, 2:1:1, and 2.5:1:1 on the characteristics of silica xerogel synthesized. FTIR, SEM, and GSA characterized the synthesized results. The results of FTIR characterization on silica xerogel with volume ratios of 2:1:1 and 2.5:1:1 indicate the presence of the Si-C group absorption at a wavenumber of 848.68 cm^{-1} which shows that the formation of silyl groups on the modified silica xerogel surfaces occurs at a TMCS: methanol: petroleum benzine ratio of 2:1:1 and 2.5:1:1. SEM results indicate that the silica xerogels produced are porous. Meanwhile, the GSA analysis results show that the pore size distributions are in the mesoporous region with an average pore radius of 8-13 nm. The greater the volume of TMCS used, the higher the surface area, and the resulting xerogel's hydrophobicity. Based on the contact angle and seeped time test, the highest hydrophobicity is produced by the material synthesized at a TMCS: methanol: PB volume ratio of 2.5:1:1 with a contact angle of 116.346°.

1. Introduction

Silica gel is synthetic silica composed of colloidal silica particles that form a three-dimensional network. Some types of silica gel are hydrogels, xerogels, and aerogel. The hydrogel is a silica gel whose pores are filled with water [1]. Xerogel is a gel that is through a process of drying under normal conditions that cause capillary pressure and cause shrinkage of the tissue gel. In contrast, aerogel is a xerogel that autoclaved and dried on the conditions under supercritical without capillary pressure that causes shrinkage of tissue gel to be relatively small [2].

The method commonly used for the synthesis of silica xerogel and aerogel is the sol-gel method. The sol-gel method has advantages: it can be performed at low temperatures, and the resulting pore size distribution can be controlled. This process involves forming the sol and its transition into a gel through the gelation process. The sol-gel process includes several stages, i.e., hydrolysis and condensation of precursor molecules that form sols; gelation (sol transition to gel); aging, and drying [3]. Tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) are compounds that commonly be used as precursors in silica synthesis [1]. Another type of precursor is sodium silicate, also called water glass, which is a cheap and abundant silica source compared to alkoxy silica [4].

Synthesis of silica xerogel is relatively more facile to do than silica aerogel because it does not require a special drying process. Silica xerogel can be produced through evaporation at room pressure, in contrast to

silica aerogel, which has to go through drying under supercritical conditions [5]. The resulting silica xerogel generally has a large surface area, increasing its effectiveness for specific applications, including as an absorbent or heat absorbent material.

The synthesized silica xerogel and aerogel have surfaces composed of silanol groups (OH) and siloxane groups (Si-O-Si). Hygroscopic silanol groups cause the surface of silica xerogel and aerogel to be hydrophilic [6]. The hydrophilic nature of the silanol group makes it easy to bind hydrogen strongly with water, affecting the use of xerogel and aerogel in various fields [7]. These properties can be modified by reaction with organic compounds on the surface of the silica gel to change the polarity of silica gel to non-polar. The commonly used organic compounds are TMCS (trimethylchlorosilane) or HMDS (hexamethyldisilazane) [8].

TMCS is more widely used for surface modification of silica because it is more reactive than HMDS [5]. Mahadik *et al.* [8] reported that the higher the concentration of TMCS and HMDS used, the higher the hydrophobicity of the silica aerogel produced. It is characterized by an increase in the silica aerogel's water contact angle from 123° to 155°. The same thing was stated by Bangi *et al.* [9] who reported use TMCS concentration by 20%, and 33% could produce hydrophobic silica gel with water contact angles of 133° and 146°, respectively.

In hydrophobic silica synthesis, co-solvent mixtures commonly used as solvents for TMCS agents are alcohols and saturated hydrocarbons such as *n*-heptane or *n*-hexane [6, 8, 9]. In this research, we utilized other types of organic solvents, namely petroleum benzine (PB). The use of PB is based on its non-polar nature, making it dissolve TMCS well, inert, and has a relatively low boiling point (40°-60°); thus, it is easily separated by evaporation. Also, it has relatively lower toxicity to the environment compared to *n*-hexane. Methanol was chosen as a mixture of solvents since it has ambipolar properties whose function is advantageous as an intermediate phase mediator [5].

Modification of the silica xerogel surface to be hydrophobic benefits the development of its potential utilization, among others for absorbent, specific to non-polar organic material. Based on this background, the synthesis of hydrophobic silica xerogel using sodium silicate precursors with TMCS surface modifiers is carried out. The parameters are a variation of the TMCS concentration in methanol solvent and petroleum benzine. Characterizations of synthesized material were performed through the analysis of the surface area, pore size distribution and pore volume through Gas Sorption Analysis (GSA); determination of functional groups by Fourier Transform Infrared (FT-IR) spectrophotometry; and determination of surface morphology with Scanning Electron Microscopy (SEM). The hydrophobic nature of the synthesized silica xerogel was analyzed by determining the water contact angle.

2. Methodology

2.1. Equipment and Materials

The tools used in this study included a set of glassware, hot plates, magnetic stirrers, 200 mesh size sifter, Fujitsu FS-AR210 analytical balance with an accuracy of 0.0001 g, water bath, glass plate, NOVAtouch LX4 gas sorption analyzer, JEOL JSM 6510 LA Scanning Electron Microscopy (SEM), Shimadzu Prestige-2 FT-IR spectrophotometer. Contact angle measurements were carried out using a device consisting of a high-resolution camera (Canon 1200D), magnifying glass, and a glass plate strung together with the stative, as shown in Figure 1.

Figure 1. Devices for measuring water contact angles

The materials used were monohydric citric acid ($C_6H_8O_7.H_2O$ Merck), methanol (CH_3OH Merck), sodium silicate (Na_2SiO_3 Merck), petroleum benzine (Merck), and trimethylchlorosilane (TMCS - Sigma-Aldrich). All materials used are in analytical grade.

2.2. Synthesis of Silica Xerogel using Sodium Silicate precursor

Synthesis of silica xerogel using sodium silicate precursors was carried out by the sol-gel method, according to Bangi *et al.* [9], with modification of the use of petroleum benzine solvents and variations in the TMCS: solvent ratio used. Sodium silicate with a specific gravity of 1.3057 g/mL (determined using a pycnometer) was firstly diluted to a specific gravity of 1.05 g/mL. The sol was prepared by mixing 20 mL of sodium silicate with a specific gravity of 1.05 g/mL with 2 mL of 2 M citric acid while stirring. During the gelation process, stirring was carried out rapidly at a speed of 120 rpm. The stirring process was stopped when the gel had formed completely where the stirrer no longer rotated in the formed gel. The time required was around 30 seconds. The hydrogel obtained was aging in a water bath for 3 hours at 50°C for strengthening the silica framework. Then, the hydrogels were washed with distilled water four times every 24 hours (4 x 24 hours) and then filtered. The replacement of a water solvent in the hydrogel with a methanol solvent through soaking for 24 hours, then filtered to separate the resulting alcogel.

Modification of the alcogel surface through the substitution of the silica xerogel surface group was carried out using TMCS reagents with a volume ratio of

TMCS: methanol: petroleum benzine varied at 0.5:1:1, 1:1:1, 1.5:1:1, 2:1:1, and 2.5:1:1. The reaction was carried out for 24 hours. TMCS-modified silica gels were filtered to separate from the solvent and then allowed to stand at room temperature for 24 hours, followed by drying at a temperature of 50°C. The synthesized silica xerogels were then characterized using an FT-IR spectrophotometer, GSA, and SEM.

2.3. Determination of Hydrophobicity through Water Contact Angles Measurement

The hydrophobicity test of silica xerogel was carried out by determining the water contact angle (θ) referring to Anderson and Carroll [7] using a series of equipment, as shown in Figure 1. A certain amount of TMCS-modified silica xerogel was trimmed on a glass plate with a length of 1 cm and a width of 1 cm. A drop of distilled water was dripped on the surface of synthetic silica xerogel using a small hypodermic needle, and pictures were taken when distilled water drops on the surface of silica xerogel. Measurements were made for 3-time repetition. The contact angle measured is the angle formed from dripped distilled water on the silica xerogel surface using ImageJ software. The x-axis straight line was drawn from the meeting point between the curve of the water droplet and the surface boundary of the test material (silica xerogel on a glass plate). From this baseline, water contact angles were measured using angle measurements on imageJ.

3. Results and Discussion

3.1. Characteristics of Synthesized TMCS Modified Silica Xerogel

Surface modification of silica xerogel using TMCS reagents aims to replace the hydrophilic Si-OH group into a hydrophobic Si-O-Si(CH_3) group. In the modification process, the silanol group, which is on the surface of the silica gel, be replaced by the methyl silyl group from TMCS through the silylation reaction:

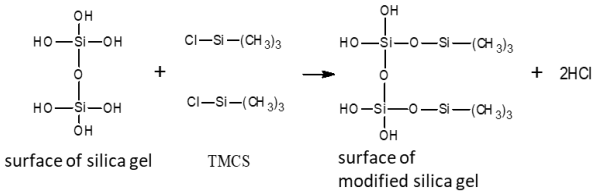

Figure 2. Silylation reaction on the surface of silica xerogel by TMCS

Changes in functional groups on the surface of silica xerogel, produced from the silylation reaction, were characterized using FTIR spectrophotometry, as shown in Figure 3.

The main functional groups in silica xerogel are characterized by wavenumbers of 3425.58 cm^{-1}, 1627.92 cm^{-1}, 1095.57 cm^{-1}, 948.98 cm^{-1}, and 470.63 cm^{-1}. The absorption peaks at 3425.58 cm^{-1} and 1627.92 cm^{-1} indicate the stretching vibration and bending of the -OH group. The absorption peak at 1095.57 cm^{-1} supported by the absorption at 470.63 cm^{-1} is the Si-O-Si vibration as the main information that explains the formation of silica network structure. The vibration of the stretching Si-OH characterizes the presence of silanol groups at the wavenumber of 960 cm^{-1}. The successful modification of TMCS on silica xerogel is characterized by vibrations at a wavenumber of 848.68 cm^{-1}, which confirms the Si-C group stretching vibration [10, 11, 12]. This absorption peak is seen mainly in Figure 3(e) and 3(f) of the silica xerogel sample synthesized with a TMCS: methanol: petroleum benzine ratio of 2:1:1 and 2.5:1:1 respectively. These results provide important information that the formation of silyl groups on the surface modification of silica xerogel begins to occur with the TMCS volumes ratio of more than two times of the solvent.

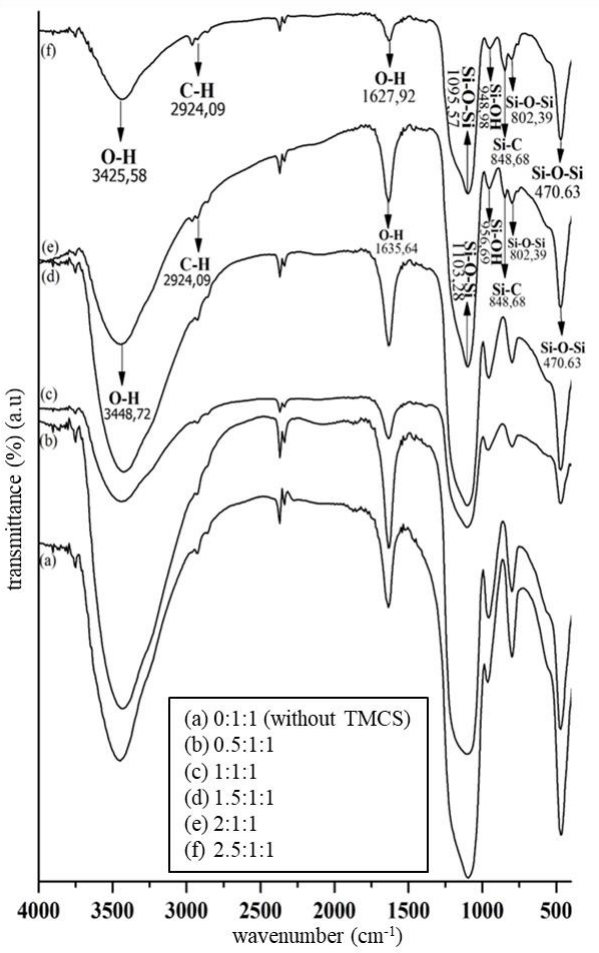

Figure 3. The FTIR spectra of TMCS-modified silica xerogels at volume ratio of TMCS: methanol: PB (a) control; (b) 0.5:1:1; (c) 1:1:1; (d) 1.5:1:1; (e) 2:1:1; (f) 2.5:1:1

The formation of three-dimensional silica networks in the silica xerogel structure makes silica xerogel a porous material. This result is confirmed by SEM to see the surface morphology of the synthesized silica xerogel, as shown in Figure 4. The surface morphology of silica xerogel with TMCS: methanol: petroleum benzine e 0:1:1 volume ratio (control) in Figure 4(a) shows the aggregates that cover the pores of silica xerogel. The silica surfaces in Figures 4(b) and 4(c) also show agglomeration. The agglomeration in Figure 4(d) is relatively smaller than the others. Figures 4(d), (e), and (f) show a steric shape with relatively homogeneous distribution and the appearance of wrinkled pores. The

SEM results are further confirmed by GSA using N_2 gas to determine the surface area and pore distribution of the synthesized silica xerogel.

The effect of the TMCS ratio on the surface area, pore size, and pore volume of synthesized silica xerogels is presented in Table 1. The surface area of the synthesized material is determined by adsorption-desorption isotherms of N_2 gas using the BET equation, while the pore volume and pore radius are determined through the BJH adsorption isotherm equation.

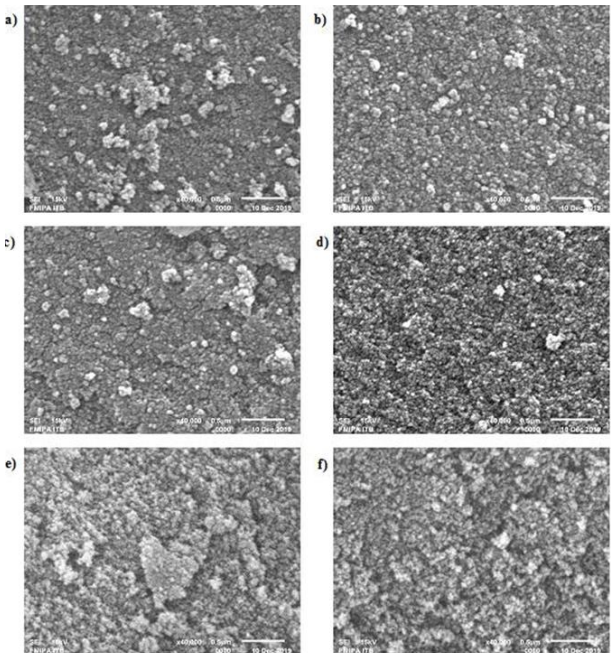

Figure 4. Photograph of the surface of the synthesized silica xerogel at a volume ratio of TMCS: methanol: petroleum benzine a) 0:1:1 (without TMCS), b) 0.5:1:1, c) 1:1:1, d) 1.5:1:1, e) 2:1:1 and f) 2.5:1:1

Table 1. Surface area, pore volume and average pore radius of the synthesized silica xerogels at various TMCS concentrations

Silica xerogel at TMCS: MeOH: PB ratio	Surface Area (m^2/g)	Total Pore Volume (cc/g)	Average Pore Radius (nm)
0:1:1 (control)	267.705	0.867	6.478
0.5:1:1	376.398	1.236	5.013
1:1:1	450.221	0.965	5.131
1.5:1:1	504.005	1.088	4.834
2:1:1	393.984	1.622	8.241
2.5:1:1	329.833	2.179	13.213

The N_2 gas adsorption isotherm in TMCS-modified silica xerogel in Figure 5 shows the type IV type isotherms, which are characterized by the presence of loop hysteresis associated with capillary condensation that occurs in mesoporous material [13]. This result indicates the occurrence of multilayer adsorption on xerogel solids [14]. Based on the IUPAC classification, the loop hysteresis is shown in the adsorption-desorption isotherms graph in Figure 5 (a), 5 (b), 5 (c) and 5 (d) is H1 type, while the desorption adsorption isotherm in Figure 5 (e) and 5 (f) is H3 type [13]. Based on the shape of the silica xerogel adsorption-desorption isotherm, the synthesized xerogels silica is indicated as mesoporous materials with porous materials with pore diameters between 2-50 nm [15].

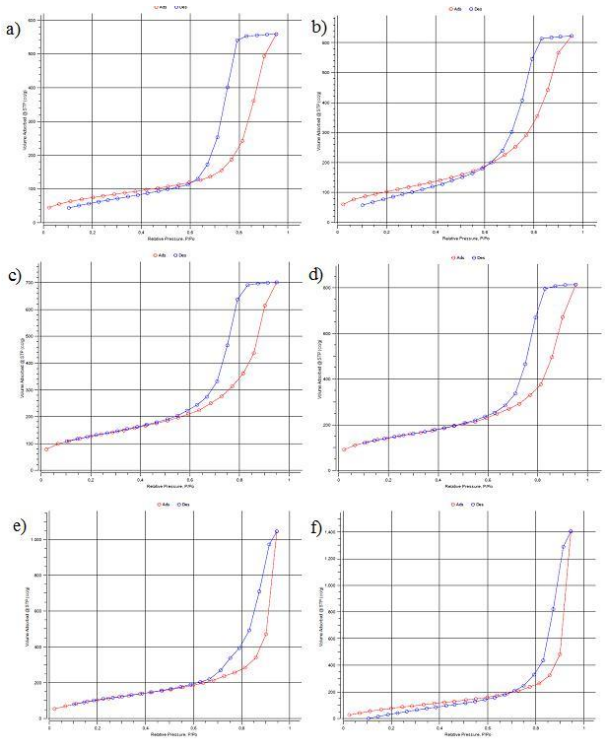

Figure 5. Adsorption-desorption isotherms of silica xerogel at TMCS: methanol: petroleum benzine volume ratio of a) 0:1:1 (control), b) 0.5:1:1, c) 1:1:1, d) 1.5:1:1, e) 2:1:1 and f) 2.5:1:1

The results show that the use of TMCS succeeds in increasing the surface area and pore volume of silica xerogel material. The GSA measurement results are shown in Table 1 display that surface modification with TMCS has succeeded in increasing the surface area of the material by a range of 23%-89%. Similar results were reported by Pisal and Rao [4] and Sarawade *et al.* [16], who synthesized TMCS-modified silica xerogel using TEOS precursors, where an increase in the surface area of xerogel material was reported as a result of surface modification Table 1 also shows that increasing concentrations of TMCs to a ratio of 1.5:1:1 tends to increase the surface area silica xerogel, however the subsequent increase in the concentration (2:1:1 and 2.5: 1; 1), the surface area tends to down with the inverse pore volume. This is thought to be caused by the spring back effect, i.e., reversible shrinkage that occurs during the drying process due to the modification of the -OH group by the trimethylsilyl group Si-$(CH_3)_3$ from TMCS on the silica xerogel surface [9, 16]. In TMCS-modified silica xerogel with volume ratios of 2:1:1 and 2.5:1:1, modification of the -OH group by -CH_3 from TMCS on the silica xerogel surface occurs more thoroughly, therefore, it produces a stable hydrolytic Si-$(CH_3)_3$ which causes repulsion between the -Si$(CH_3)_3$ group, so that framework shrinkage occurs at drying process [9]. The largest average pore size of silica xerogels was obtained in a variation of 2.5:1:1, which is 13.213 nm. The overall

pore diameter value is in the range of mesoporous material.

3.2. Hydrophobicity of the Synthesized TMCS-Modified Silica Xerogel

The contact angle and the water seeped time are parameters that can be used as a reference for determining the hydrophobicity of a material. Material is stated hydrophilic if it has a contact angle ≤ 90°, and vice versa is hydrophobic if it has a contact angle ≥ 90° [17]. The hydrophobic nature of TMCS-modified silica xerogel in this study was determined by calculating the water contact angle images processed using ImageJ. The results are shown in Figure 6. The effect of TMCS concentration on contact angle value and fluid seeped time on the synthesized silica xerogel are summarized in Table 2.

Table 2. Contact angle and seeped time of TMCS-modified silica xerogel

Silica xerogel at TMCS: MeOH: PB ratio	Contact Angle (°)	Seeped time
0:1:1 (control)	26.423 ± 0.42	4 seconds
0.5:1:1	28.787 ± 0.26	25 seconds
1:1:1	32.811 ± 0.25	30 seconds
1.5:1:1	36.787 ± 0.23	15 seconds
2:1:1	111.066 ± 0.18	3 hours 18 min
2.5:1:1	116.346 ± 0.20	3 hours 49 min

Contact angle measurements show that the greater the concentration of TMCS, the higher the resulting contact angle with a longer seeped time. The resulting contact angle is influenced by the adhesion and cohesion forces. The contact angle value < 90° is caused by the greater adhesion force between the xerogel solid (substrate) and the liquid than the cohesion force so that it can spread on the surface. The contact angle >90° is caused by low surface energy due to the presence of hydrophobic -CH_3 groups on the xerogel surface and the cohesion force in the adhesive is greater than the adhesion force between the liquid and the xerogel solid (substrate) to form liquid droplets on the surface [18].

Silica xerogels were synthesized at TMCS: methanol: PB = 0:1:1 ratio (control); 0.5:1:1; 1:1:1 and 1.5:1:1 show the water contact angles below 90°. This result indicates that the xerogel material synthesized under these conditions is still hydrophilic. At a TMCS: methanol: PB ratio of less than 1.5:1:1, the available TMCS concentrations are thought to be insufficient to make most of the silanol groups replaced into hydrophobic Si-$(CH_3)_3$ groups. The lack of TMCS makes Si-OH groups more dominant on the silica xerogel surface, so the resulting xerogel material is hydrophilic. When in contact with a water droplet, the silanol group easily forms hydrogen bonds with water. Then, the water is directly absorbed and spread on the surface of hydrophilic silica due to the cohesion force, which is large enough, making the contact angle produced is relatively small. At TMCS concentrations above 40% (ratio >1.5:1:1), the silylation reaction takes place completely. Hence, most of the silanol groups on the silica surface are replaced by hydrophobic trimethylsilyl, which is characterized by a large contact angle.

TMCS-modified silica xerogels in the ratio of TMCS: methanol: PB of 2:1:1 and 2.5:1:1 give contact angles greater than 90°, which respectively amounted to 111.066° and 116.346°. These results indicate that the silica xerogel produced is hydrophobic. This significant increase in the contact angle values indicates that the silanol group on the surface of the silica xerogel has been replaced by trimethylsilyl, which makes the xerogel surface properties non-polar and results in an increase in its hydrophobic properties.

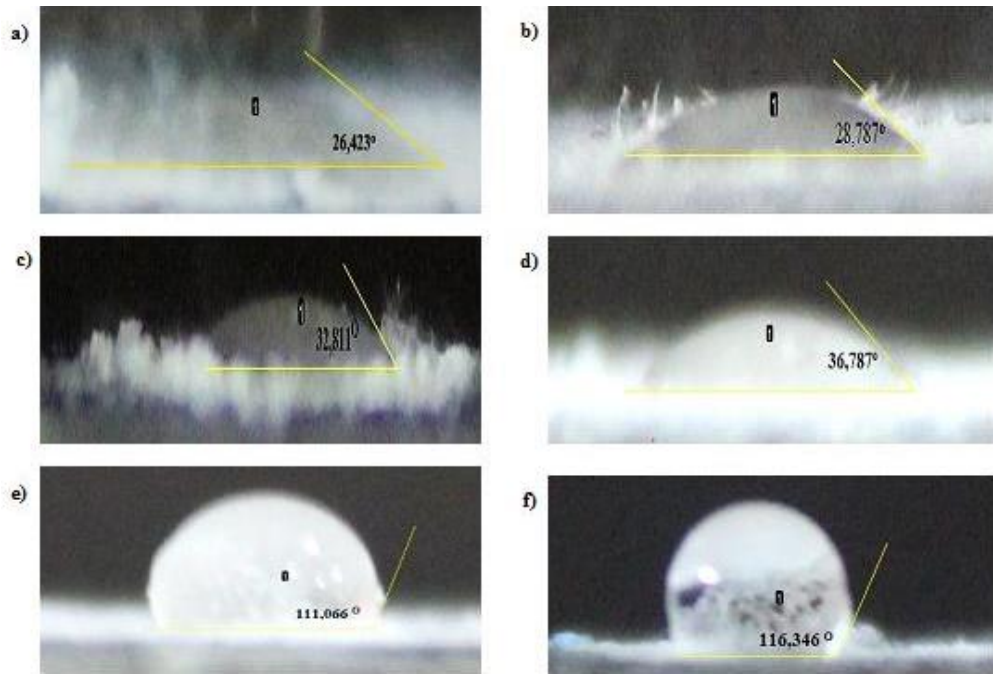

Figure 6. Water contact angles of synthesized silica xerogel at TMCS: methanol: petroleum benzine volume ratio of a) 0:1:1, b) 0.5:1:1, c) 1:1:1, d) 1.5:1:1, e) 2:1:1 and f) 2.5:1:1

The resulting contact angle value is directly proportional to the seeped time, where the TMCS-modified silica xerogel at a ratio of 2.5:1:1 has the longest seeped time compared to the others. These results are in line with FTIR spectra data (Figure 3), especially on silica xerogel synthesized at the TMCS ratio 2:1:1 and 2.5:1:1, which clearly shows the presence of vibrations of Si-C groups as an indication of the success of surface modification of silica xerogel.

4. Conclusions

Hydrophobic silica xerogel was successfully synthesized using a TMCS surface modifying agent with petroleum benzine-methanol solvent. The change in the silica nature to be hydrophobic is marked by the success of the replacement of the trimethylsilyl group replacing silanol on the xerogel surface. SEM and GSA results show that TMCS modified silica xerogel morphology is a porous material with a pore radius of 8-13 nm, classified as mesoporous. The hydrophobic nature of TMCS-modified silica xerogel increases along with the increase in the number of TMCS used. The highest hydrophobic nature is produced by the material synthesized with a volume ratio of TMCS: methanol: PB = 2.5:1:1 with a contact angle of 116.334°.

Acknowledgment

Authors thank the DP2M Dikti, who helped fund this research through the 2019 Postgraduate Grants scheme.

References

[1] E. F. Vansant, P. Van Der Voort, K. C. Vrancken, *Characterization and Chemical Modification of the Silica Surface*, Elsevier Science, 1995

[2] C. Jeffrey Brinker, George W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Elsevier Science, 2013

[3] Ulrich Schubert, Nicola Hüsing, *Synthesis of Inorganic Materials*, 4th ed., Wiley-VCH, 2019

[4] Abhijit A. Pisal, A. Venkateswara Rao, Comparative studies on the physical properties of TEOS, TMOS and Na2SiO3 based silica aerogels by ambient pressure drying method, *Journal of Porous Materials*, 23, 6, (2016), 1547-1556 https://doi.org/10.1007/s10934-016-0215-y

[5] A. Venkateswara Rao, G. M. Pajonk, Uzma K. H. Bangi, A. Parvathy Rao, Matthias M. Koebel, Sodium Silicate Based Aerogels via Ambient Pressure Drying, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.) *Aerogels Handbook*, Springer New York, New York, NY, 2011 https://doi.org/10.1007/978-1-4419-7589-8_5

[6] Petar Ivanov, Bogdan Bogdanov, Yancho Hristov, Synthesis of hydrophilic and hydrophobic xerogel, *Journal of Chemical Technology and Metallurgy*, 52, 3, (2017), 457-462

[7] Ann M. Anderson, Mary K. Carroll, Hydrophobic Silica Aerogels: Review of Synthesis, Properties and Applications, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.) *Aerogels Handbook*, Springer New York, New York, NY, 2011 https://doi.org/10.1007/978-1-4419-7589-8_3

[8] D. B. Mahadik, A. Venkateswara Rao, A. Parvathy Rao, P. B. Wagh, S. V. Ingale, Satish C. Gupta, Effect of concentration of trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDZ) silylating agents on surface free energy of silica aerogels, *Journal of Colloid and Interface Science*, 356, 1, (2011), 298-302 https://doi.org/10.1016/j.jcis.2010.12.088

[9] Uzma K. H. Bangi, A. Venkateswara Rao, A. Parvathy Rao, A new route for preparation of sodium-silicate-based hydrophobic silica aerogels via ambient-pressure drying, *Science and Technology of Advanced Materials*, 9, 3, (2008), 035006 https://doi.org/10.1088/1468-6996/9/3/035006

[10] Poonam M. Shewale, A. Venkateswara Rao, A. Parvathy Rao, Effect of different trimethyl silylating agents on the hydrophobic and physical properties of silica aerogels, *Applied Surface Science*, 254, 21, (2008), 6902-6907 https://doi.org/10.1016/j.apsusc.2008.04.109

[11] Donald L. Pavia, Gary M. Lampman, George S. Kriz, James A. Vyvyan, *Introduction to Spectroscopy*, 4th ed., Cengage Learning, 2008

[12] Bogdan Bogdanov, Petar Ivanov, Yancho Hristov, R. Raykova, Synthesis of Hydrophilic and Hydrophobic Xerogel, *Science & Technologies*, 3, 4, (2013), 16-20

[13] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984), *Pure and Applied Chemistry*, 57, 4, (1985), 603-619 https://doi.org/10.1351/pac198557040603

[14] Lindy Heath, Lifan Zhu, Wim Thielemans, Chitin Nanowhisker Aerogels, *ChemSusChem*, 6, 3, (2013), 537-544 https://doi.org/10.1002/cssc.201200717

[15] Vijay K. Tomer, Sunita Devi, Ritu Malik, Surender Duhan, Mesoporous Materials and Their Nanocomposites, in: V. P.M., M.J.M. Morlanes (Eds.) *Nanomaterials and Nanocomposites*, Wiley-VCH Verlag GmbH & Co., 2016 https://doi.org/10.1002/9783527683772.ch7

[16] Pradip B. Sarawade, Jong-Kil Kim, Askwar Hilonga, Dang Viet Quang, Hee Taik Kim, Synthesis of hydrophilic and hydrophobic xerogels with superior properties using sodium silicate, *Microporous and Mesoporous Materials*, 139, 1, (2011), 138-147 https://doi.org/10.1016/j.micromeso.2010.10.030

[17] Guo Li, Jiang Yue, Chenhao Guo, Yongsheng Ji, Influences of modified nanoparticles on hydrophobicity of concrete with organic film coating, *Construction and Building Materials*, 169, (2018), 1-7 https://doi.org/10.1016/j.conbuildmat.2018.02.191

[18] J. Anthony von Fraunhofer, Adhesion and Cohesion, *International Journal of Dentistry*, 2012, (2012), 951324 https://doi.org/10.1155/2012/951324