

Synthesis of silica aerogel particles and its application to thermal insulation paint

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Abstract—Silica aerogel (SA) particle was synthesized and characterized. The effects of silica content in silicic acid solution and molar ratio of trimethyl chlorosilane (TMCS)/pore water on silica aerogel physical characteristics such as surface area, pore volume, apparent density, and porosity were investigated. We observed that when the silica content increased from 4 to 7% of weight (wt%), the silica aerogel surface area increased from 628.5 m²/g to 914.4 m²/g and thereafter (>9%). When the molar ratio of TMCS/pore water increased from 0.1-0.4, the silica aerogel's surface area increased from 816.8 m²/g to 924.1 m²/g. The highest silica aerogel surface area of 924.1 m²/g and porosity of 96.4% were achieved with a silica content in silicic acid of 7.011 wt% and TMCS/pore water of 0.4. Finally, silicon aerogel particles applied to water-based paint to improve the thermal insulation was about 1.2 °C with surrounding ambient temperature of 45 °C.

Keywords: Aerogel, Silicic Acid, Sodium Silicate, Trimethyl Chlorosilane (TMCS), Surface Area

INTRODUCTION

Aerogels have been commercialized in many forms, such as powders, particles, and composites. Further, aerogel blankets have an 85% market share in the world [1]. Recently, the applications of powder and particle aerogel have expanded quickly and widely for thermal insulation paints, glass, thin films, and even blankets. Particularly, silica aerogel has a low density of 0.003 g·cm⁻³, high porosity over 90%, optical transmission of 93%, and surface area (250-800 m²g⁻¹) aerogel. Therefore, it is used for various applications such as thermal insulation, catalysts, and absorption materials. It can be used in a wide temperature range from -200 °C to over 1,000 °C and emits low-toxic gas [2].

Silica aerogel is produced using two main steps: sol-gel process and solvent drying. In the sol-gel process, silica gel is produced by condensation reaction of silica sol [3]. Common precursor for producing aerogel is silicon alkoxide, such as tetraethyl orthosilicate (TEOS) which can produce aerogel with high purity and light transmission. However, silicon alkoxide is an expensive precursor that leads to the high cost of good aerogel, which limits the market for silica aerogel. An alternative precursor for silica aerogel production is sodium silicate (water glass) due to its abundance, earth-born, environment friendly and reasonable price. However, the silica aerogel product prepared from sodium silicate is not as qualified as that of silicon alkoxide such as higher impurity, low light transmission, and low porosity due to the appearance of sodium salt. Thus, removing sodium ion in silica aerogel is necessary to produce a high quality of silica aerogel. In this direction, Sarawade et al. [4] washed the silica gel several times to remove a part of sodium

salt in gel. Actually, gels are defined as a substantially dilute cross-linked system, which exhibits no flow when in the steady-state; therefore, this is not really effective in removing sodium salt. On the other hand, ion exchange could solve the problems of sodium silicate which produces silicic acid with high purity of SiO₂. In the solvent drying process, super critical drying (SCD) method is a high cost investment technology, limited capacity of instrument, requires high energy, and materials consumption for operation [1,5]. Therefore, ambient pressure drying (APD) technique was developed, which reduces the cost of silica aerogel significantly. Actually, hydrophilic silica aerogel is not as much consumed as the hydrophobic one, because of its wide application in water based and solvent based products. To obtain hydrophobic aerogel, silica gel needs to be modified to be hydrophobic before drying by SCD method. However, this hydrophobic characteristic could act as the agent that leads to reducing the surface tension between silica gel surface and solvent; thus solvents easily vaporize out of the pores of silica gel without collapse at ambient pressure. This APD method could produce silica aerogel particle with the equivalent quality with SCD method and is much cheaper. Therefore, APD method is suitable for producing silica aerogel particle which can be applied as thermal insulation in construction such as thermal insulation coating, plaster, and concrete. Although there are many publications for synthesis silica aerogel from water glass using freeze-drying [6] or APD method [7-10], however, higher than 900 m²/g surface area of silica aerogel has not been reported. In addition, an effective explanation of two main factors, silicic acid concentration and molar ratio of trimethyl chlorosilane (TMCS)/pore water in changing volume of silica aerogel during drying process, was not deeply discussed in previous publications.

In this study, silica aerogel particles were synthesized by varying the silicic acid concentration and molar ratio of trimethyl chlorosilane (TMCS)/pore water using sol-gel process and APD method.

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The effect of silicic acid concentration and molar ratio of TMCS/pore water was carefully investigated and discussed. Silica aerogel volume and weight were measured at each step of drying to strengthen evidence for the effect of silica content in silica aerogel in its performance.

Moreover, synthesized aerogel was added into water-based acrylic paint with silica aerogel content varying from 3-7 wt%. The thermal insulation performance of paints was investigated.

EXPERIMENT SECTION

1. Material

Sodium silicate from Bien Hoa Chemical Factory (VICACO) with molar ratio $\text{SiO}_2 : \text{Na}_2\text{O} = 2.74$; proton exchange resin C100H from Purolite (England), silylating agent trimethyl chlorosilane (TMCS) from Richest Group Ltd (China), acrylic resin PRIMALTM AC-261 from Dow Chemical Company (USA), TiO_2 Ti-PureTM R-104 from Dupont (Chemours, USA), CaCO_3 Omyacarb® 10 from Omya (Switzerland), film-forming agent and surfactants from Evonik (Germany). And ammonia solution, hydrochloric acid, sodium hydroxide, n-hexane, and isopropanol (IPA) from Xilong Scientific Co., Ltd (China) were purchased.

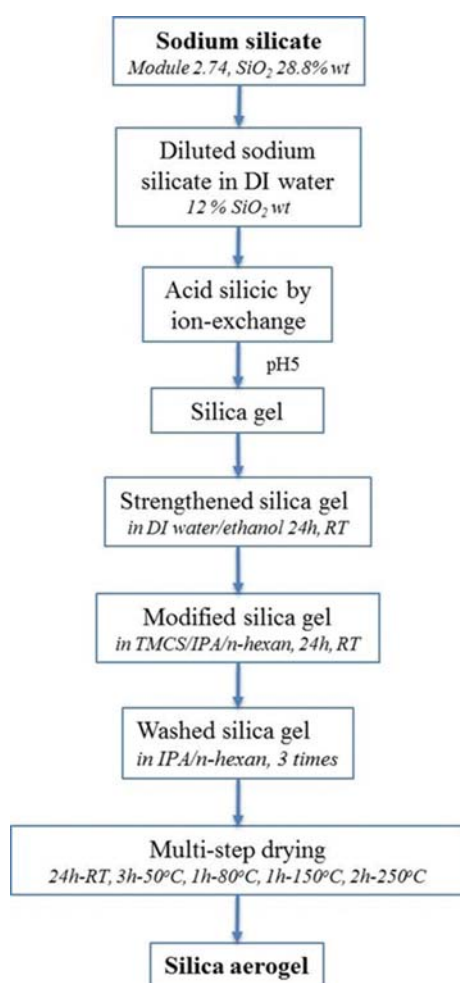
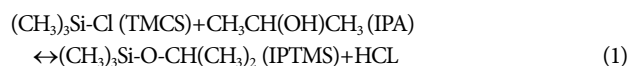


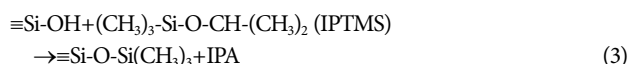
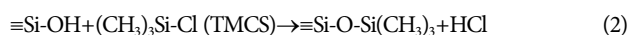
Fig. 1. Flowchart of silica aerogel preparation.

2. Silica Aerogel Preparation

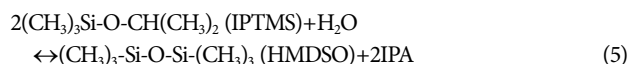
The flowchart of silica aerogel preparation is shown in Fig. 1. The silica aerogel preparation was mainly separated into two proper steps: sol-gel (step-1) and drying process (step-2). In the sol-gel process, sodium silicate 28.8% SiO_2 by weight (wt%), molar ratio 2.74 was dissolved in de-ionized (DI) water for the preparation of sodium silicate solution 12 wt% SiO_2 . Sodium silicate solution then passed through a proton ion exchange resin column to obtain the silicic acid pH in the range of 2.5-3.5 about 9 wt% SiO_2 contained, which is also called silica sol. Silicic acid was dissolved in DI water to get a range of silicic acid solution containing 4%, 5%, 6%, 7%, 8% and 9 wt% silica (Samples were labeled as AE x with x as silica content in acid silicic varying from 4 to 9 wt%). Then, ammonium solution 10 wt% was slowly dropped into those solutions with stirring to reach the pH 5, then each solution was quickly poured into separate 30 mL plastic cylindrical vessels to be molded. After 1 h, silica gels (wet gel) were aged in DI water for 6 h and ethanol for 18 h to strengthen their 3D cross linking in their structure and replace a part of water within the silica gel pores by ethanol. In ambient pressure drying, silica gel needs to be modified for less surface tension. The wet gels after aging 24 h were much stronger due to increasing the Si-O-Si linking and leading to leak out water for shrinkage of gels. Wet gels then were cut down to a small piece in 8-10 mm dimension in order for easy surface modification with TMCS. Those pieces of each wet gel sample were dipped into a mixture solution of TMCS, IPA, and n-hexane. In the mixture, TMCS reacts with IPA to form isopropoxytrimethylsilane (IPTMS) as a silylating and HCl (Formula 1).



When the gel was dipped in to the mixture, surface silanol group of silica gel modification occurred following Formulas 2 and 3



However, the TMCS and IPTMS could react with water in pore gel following Formulas 4, 5



In the case of using TMCS as silylating agent without the presence of IPA, TMCS could react with H_2O to form HMDSO and HCl violently (Formula 4) which causes crack generation in silica gel and insufficient modification. Thus, IPA was used to inhibit the reaction of TMCS with pore water with $V_{\text{TMCS}}/V_{\text{IPA}}$ at 1. TMCS amount in this study was investigated in the range of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 times of pore water molar in wet gel, while the $V_{\text{n-hexane}}/V_{\text{TMCS}}$ was fixed at 10 (Samples were labeled as AE x-y with x as silica content in acid silicic; y from 1 to 6 related to molar ratio TMCS/pore water varied from 0.1 to 0.6). The surface modified wet gels were washed three times with a mixture of

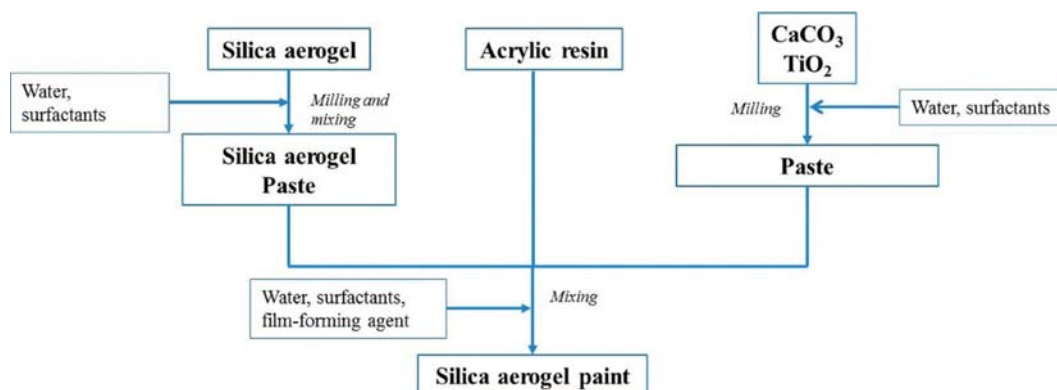


Fig. 2. Flowchart of silica aerogel water-based paint preparation.

reducing ratio IPA/n-hexane from 0.25 to 0 in 24 h. Surface modified wet gels then were dried at room temperature for 24 h, followed by heat drying at 50 °C in 3 h, 80 °C in 1 h, 150 °C in 1 h and 250 °C in 2 h. After drying, silica aerogels samples were obtained and the spring-back of volume was observed.

3. Silica Aerogel Water-based Paint Preparation

The flowchart in Fig. 2 shows the main steps of silica aerogel water-based paint preparation. Silica aerogel was milled and mixed in the presence of water and chosen surfactants to achieve a silica aerogel water-based paste. The silica aerogel paste then was mixed with prepared $\text{CaCO}_3/\text{TiO}_2$ paste and acrylic resin to obtain thermal insulation paint. The silica aerogel content in the paint was adjusted from 3-7% wt%. The paint was then coated onto cement board substrates with thickness of about $500 \pm 50 \mu\text{m}$ and a thermal insulation test was performed. The samples were marked as SA-added paint (zwt%) with z as silica aerogel content water-based paints. The pristine paint sample did not contain silica aerogel.

4. Characterization Methods

The surface area of the silica aerogel was measured using Nova 1000e-Quantachrome Instruments (USA), N_2 adsorption-desorption analysis of the samples outgassed at 300 °C for 2 h, bath temperature 77.3 K in the relative pressure range of $0.05 < P/P_0 < 0.35$. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. Apparent density was defined as weight of silica aerogel particle in a given volume. Porosity of silica aerogel was measured as follows: porosity (%) = $(1 - \rho/\rho_s) \times 100$,

where ρ is the apparent density of silica aerogel and ρ_s is the theoretical mass density SiO_2 (2.2 g/cm^3). FTIR was employed to observe the effect of surface modification on silica aerogel by using a Nicolet 6700 FTIR Spectrometer - Thermo Scientific (USA) within a range of $4,000\text{--}400 \text{ cm}^{-1}$ at a resolution of 1 cm^{-1} . To measure water contact angle of silica aerogel, one $1 \mu\text{L}$ drop and one $12 \mu\text{L}$ drop onto the aerogel powder paper coated surface and the water contact angle was measured by using OCA 20-DataPhysics (Germany). The surface morphology of the samples was investigated by field emission scanning electron microscope (FE-SEM) using a Hitachi S-4800 with accelerating voltage range at 10.0 kV. Thermal insulation testing device used an infrared lamp power of 275 W for a sun light simulation directly illuminated onto the top of sample, which was controlled of 45 °C. The temperature of the bottom sample was recorded every 10 min during 360 min. The heat transfer from the top to the bottom of sample was not affected by convection from the heat source.

RESULTS AND DISCUSSION

1. Influence of Silicic Acid Concentration on Aerogel Characteristics

Silica aerogel often contains lower than 10 wt% of solid SiO_2 . Therefore, this study investigated the silica content from 4 to 9 wt% in silicic acid at fixed molar ratio of TMCS/pore water of 0.3 that was measured by the ASTM D501 - 03 (2016) Standard Test

Table 1. Properties of the silica aerogels with different SiO_2 content of silicic acid

Sample*	SiO_2 (wt%)	Surface area (m^2/g)	V_{RT} (mL)	m_a (g)	V_a (mL)	ρ (g/mL)	Porosity (%)	η (%)
AE4	4.005	628.5	5.75	1.4982	10.25	0.146	93.36	34%
AE5	5.012	646.7	7.25	1.9315	13.25	0.146	93.37	44%
AE6	6.093	791.6	17.75	2.2981	22.75	0.101	95.41	76%
AE7	7.011	914.4	22.50	2.6411	31.25	0.085	96.16	104%
AE8	8.005	690.0	23.50	2.8998	29.50	0.098	95.53	98%
AE9	9.031	647.6	23.75	3.2769	29.25	0.112	94.91	98%

*Samples were labeled as AEx with x as silica content in acid silicic varied from 4 to 9 wt%, V_{RT} is apparent volume of silica aerogel after drying 24 h at room temperature, m_a , V_a , ρ and η are total weight, apparent volume, apparent density and spring-back efficiency of silica aerogel, respectively.

Methods of Sampling and Chemical Analysis of Alkaline Detergents [11]. Silica aerogel was achieved in the particle form with diameter around 1-5 mm. Further, the surface area, pore volume, apparent density, and porosity of silica aerogel were measured. Pore water molar was calculated by the different of water molar in original gel and the amount of water leak out the gel during aging.

The result in Table 1 showed that surface area of silica aerogels increased from $628.5 \text{ m}^2/\text{g}$ to $914.4 \text{ m}^2/\text{g}$ with the increasing of SiO_2 content in silicic acid from 4% to 7% wt%. However, at higher content of SiO_2 in the range of 8-9%, the surface area of silica aerogels decreased to $690.0\text{--}647.6 \text{ m}^2/\text{g}$. It could be visibly observed that during surface modification with TMCS, the volume of silica wet gels reduced, after 24 h solvent evaporation at room temperature, the volume of gels was shrunk or collapsed and more reduced. When heat was applied, the gels could show spring-back effect of volume as illustrated in Fig. 3 due to the hydrophobic of trimethyl silanol group on the surface of aerogel. However, the extent of spring-back depends on silica content in those gels [12]. The sample AE4 and AE5 showed the strong shrinkage after modification and violent collapse in the gel structure. When the solvent was evaporated, less spring-back of volume during heating was noticed caused of the lower surface area and porosity of those sample. AE4 and AE5 samples reached only 34 and 44% of original volume. Less silica content, the gel structure was not strong enough for bearing the shrinkage due to bi-products seeping out and solvent extraction/exchange during modification and solvent evaporation during drying also. The volume of AE4 and AE5 was only 5.75

mL and 7.25 mL, respectively after 24 h drying at room temperature. Even though heating was applied, the gels structure could not recover because of breaking the crosslinking of gel skeleton. The sample AE6 and AE7 showed less shrinkage volume after modification and solvent evaporation. The volume of gels after shrinkage was 17.75 mL and 22.5 mL for AE6 and AE7, respectively. The AE7 was less shrinkage and more spring-back that lead highest surface area. Apparent volume of AE7 after drying was 31.25 mL which is 104% of original volume of gel while AE6 reached 76% of original volume. In AE7 structure, silica gel network was not collapse due to modification and solvents vapor but strong recover. Sample AE8 and AE9 had lowest shrinkage among 6 samples because of the higher density of silica in gel structure. However, AE8 and AE9 did not show spring-back as strong as AE7 which was 98% of original volume. The more density in AE8 and AE9 lead to the lower surface area.

Fig. 4 shows the SEM micrographs obtained of AE7 sample in different magnification. It is noticed from Fig. 3 that the surface of silica aerogel had cluster structure. The cluster structure of silica aerogel led to the present of a number of micropores and mesopores also in AE7 sample that lead to highest surface area. The study of Feng et al. [13] showed the similar results when the SiO_2 content increased in water glass that lead to increasing surface area and porosity of aerogel samples. However, the precursor water glass from rice husk ash was limited modulus thus the effect of silica content to aerogel properties was not significantly showed. In the study of Hwang et al. [14], silica aerogel showed smooth struc-

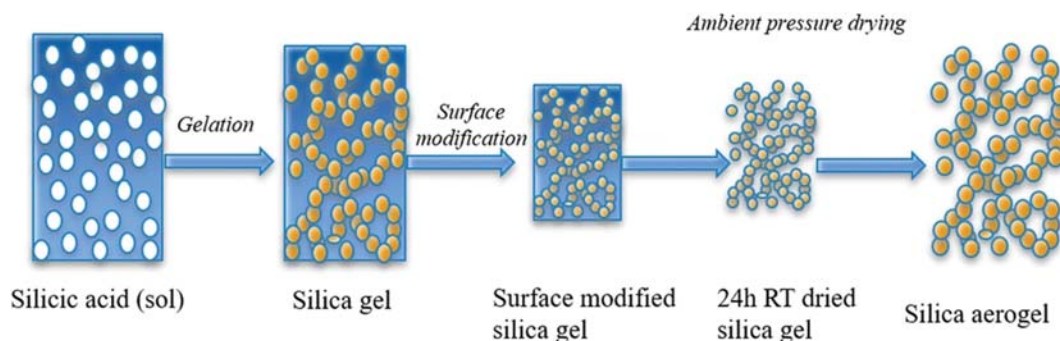


Fig. 3. Representation of volume change during aerogel synthesis.

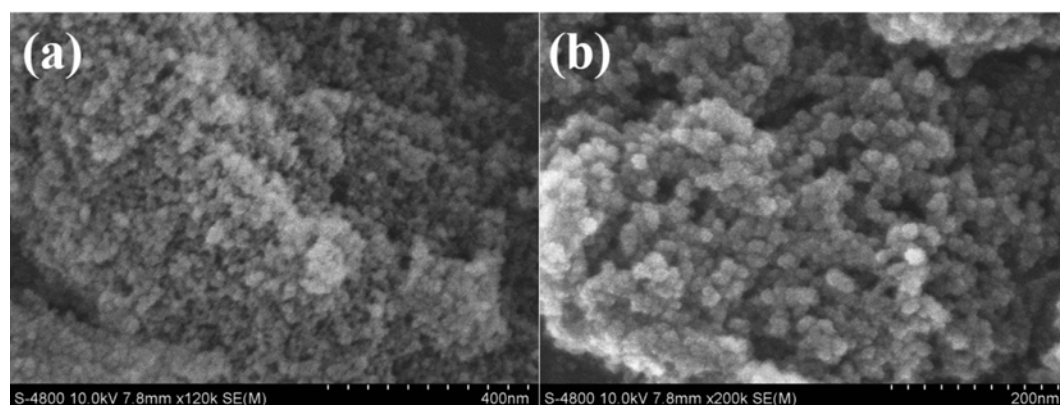
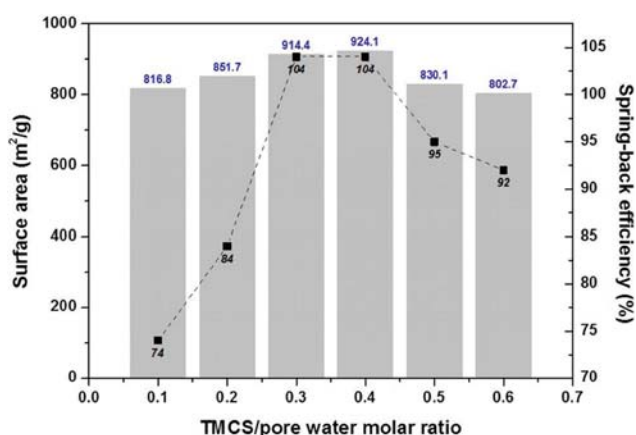


Fig. 4. SEM micrographs of sample AE7 with different magnification (a) 120k and (b) 200k.

Table 2. Properties of the silica aerogel samples with various TMCS/pore water molar ratio

Sample*	Molar ratio TMCS/pore water	Surface area (m ² /g)	V _a (mL)	ρ (g/mL)	Porosity (%)	η (%)
AE7-1	0.1	816.8	22.25	0.106	95.17	74%
AE7-2	0.2	851.7	25.25	0.098	95.56	84%
AE7-3	0.3	914.4	31.25	0.085	96.16	104%
AE7-4	0.4	924.1	31.25	0.085	96.14	104%
AE7-5	0.5	830.1	28.75	0.092	95.80	96%
AE7-6	0.6	802.7	27.50	0.096	95.62	92%

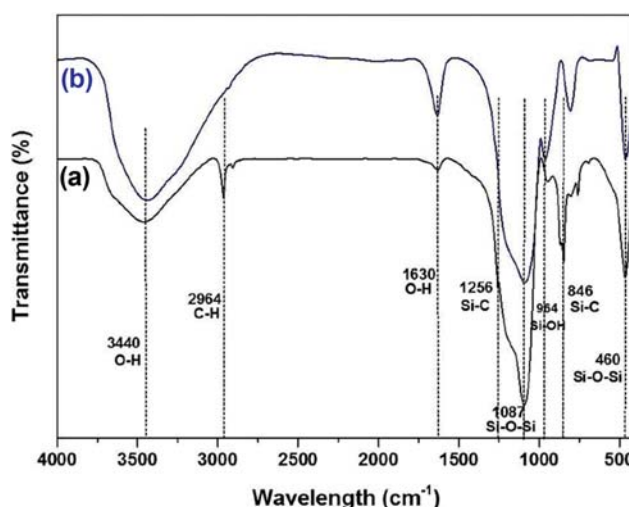
*Samples were labeled as AEx-y with x as silica content in acid silicic; y from 1 to 6 related to molar ratio TMCS/pore water varied from 0.1 to 0.6, V_a, ρ and η are apparent volume, apparent density and spring-back efficiency of silica aerogel, respectively.

**Fig. 5. The effect of TMCS/pore water molar ratio on the specific surface area and spring-back efficiency of silica aerogel.**

ture at 4-8% SiO₂ of silicic acid concentration, lower or higher SiO₂ content could cause the crack in aerogel. But Hwang study did not mention about the surface area of silica gel at each silicic content because the focused topic was uncrack aerogel. The study also investigated the effect of SiO₂ content of precursor TEOS, and the similar trend was showed [15].

2. Influence of TMCS/Pore Water Molar Ratio on Aerogel Performance

During the investigation of TMCS/pore water molar ratio, the silicic acid concentration was fixed at 7 wt.% SiO₂. The detail results are listed in Table 2 and briefly shown in Fig. 5. When TMCS/pore water molar ratio increased from 0.1 to 0.3, the surface area of silica aerogel increased from 816.8 m²/g to 914.4 m²/g (Sample AE7-1, AE7-2, and AE7-3). At a TMCS/pore water ratio of 0.4, the surface area of silica aerogel was only slightly increased to 924.1 m²/g. The present of low TMCS in modification solution could cause insufficient silica gel surface modification. It was observed that sample AE7-1 was not really homogeneous which a part of xerogel in aerogel. Thus, AE7-1 reached 74% of original volume. The surface area of aerogel was reported as a highest of 924.1 m²/g using industrial sodium silicate as material and APD technic along with porosity higher than 96%. For further increasing of TMCS amount for modification, the surface area of silica aerogel unfortunately decreased. A similar behavior was also reported by Hwang et al. [16,17]. This could be attributed by the high amount of TMCS could violently form HCl and HMDSO (Eq. (4)) caused of

**Fig. 6. FTIR spectra of silica aerogel: (a) AE7-7 sample and (b) silica gel.**

crack in gel. Hence, a part of silica sol condensation linking network of in gel was fractured that lead to decrease the efficiency of spring-back. A larger amount of visible crack could be observed during surface modification on the sample AE7-5 and AE7-6 compared with AE7-3 and AE7-4. Silica aerogel AE7-3 and AE7-4 samples obtained in this study were transparent light blue color caused by Rayleigh scattering [8]. To study the modification, FT-IR was used and FT-IR spectra of silica aerogel AE7-4 sample (line a) and pure dried silica gel (line b) are shown in Fig. 6.

The peaks of transmittance at 470 cm⁻¹ and 1,060 cm⁻¹ were attributed by Si-O-Si asymmetric stretching and bending vibration which were both observed in aerogel and silica gel sample. However, the peaks of Si-C at 1,260 cm⁻¹ and 846 cm⁻¹; and the peak of C-H at 2,964 cm⁻¹ were only showed in silica aerogel sample which demonstrated that aerogel particle surface was modified by TMCS. It could be observed that the intensity peak of Si-OH at 958 cm⁻¹ of aerogel sample was lower than silica gel samples at 964 cm⁻¹, and peak of O-H at 1,650 cm⁻¹ showed in both samples but the transmission intensity in aerogel sample was much lower than unmodified sample which indicated that Si-OH group was almost absence. The peak of O-H at 3,450 cm⁻¹ showed in both samples but the transmission intensity in aerogel sample was lower than unmodified sample, due to the humidity in aerogel pore compared silica gel. The modified surface of silica wet gel was low surface

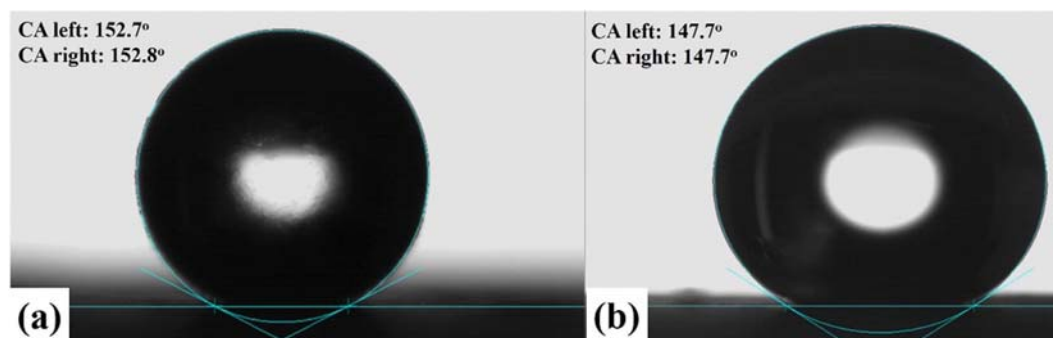


Fig. 7. Water contact angle of silica aerogel with (a) drop volume 1 μL and (b) drop volume 12 μL .

tension which not only led silica aerogel being spring-back to the original gel volume, but also caused hydrophobic property of aerogel. Silica aerogel AE7-4 sample was measure water contact which show contact angle 152.7° with drop volume 1 μL and 147.7° with drop volume 12 μL (Fig. 7).

3. Thermal Insulation Performance of Silica Aerogel Water-based Paint

Adding hydrophobic silica aerogel into water-based paint is complicated which was solved by a siloxane-based wetting agent. The wetting agent help modified the silica aerogel powder surface to hydrophilic. However, due to low density of silica aerogel, the volume of added silica aerogel was limited by 7 wt%. Fig. 8 shows that by adding silica aerogel particles into paint, the thermal conduction and convection of paint was reduced. When the content of silica aerogel increased from 3 to 6 wt% of volume, the paint's insulation performance was enhanced. With 6 wt% silica aerogel content in paint (sample marked SA-added Paint (3 wt%)), the coating has the best thermal insulation with the difference temperature compared with un-coated sample of 1.2 °C under the surrounding temperature of 45 °C. When the content of the used silica aerogel is up to 7 wt%, the heat insulation ability of coating is reduced due to the dried coating defect which was cracks and small size lumps.

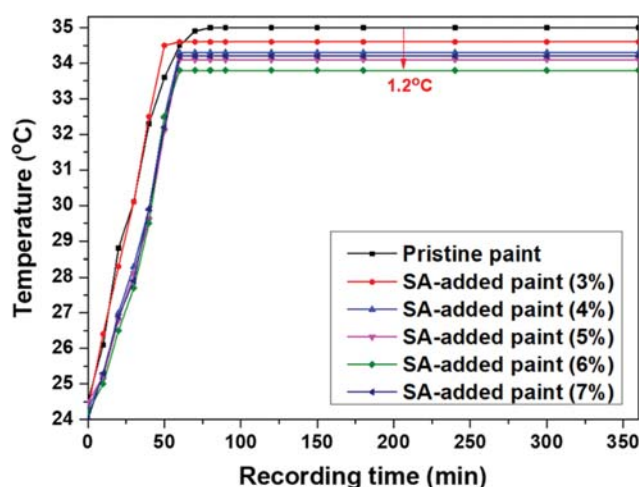


Fig. 8. Thermal insulation performance of silica aerogel water-based paint with different aerogel content.

CONCLUSIONS

Silica aerogel particles were prepared and characterized and had an surface area of 924.1 m^2/g , apparent density of 0.085 g/ml , and porosity of 96.14% with the silicic acid concentration 7.011 wt% and TMCS/pore water molar ratio 0.4. Skeleton of silica network in aerogel structure was strongly decided by shrinkage ratio and spring-back efficiency of silica aerogel, which was demonstrated by different silica content in wet gel. TMCS could react violently with Si-OH on the surface of wet gel and water in the wet gel caused a crack in the gel structure. A sufficient amount of TMCS was 0.3 and 0.4 times of pore water molar, which was enough for silica gel modification and gel structure preservation. The thermal insulation of the water-based paint with silica aerogel (6 wt%) was improved (reduced about $\sim 1.2^\circ\text{C}$) under the surrounding temperature of 45 °C.

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