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TRANSPARENCY AND THERMAL STABILITY OF SILICA AEROGEL SYNTHESIZED FROM SODIUM SILICATE USING AMBIENT PRESSURE DRYING

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Abstract
Silica aerogel is a special material due to its low density, high transparency, and high thermal stability. Producing silica aerogels in an inexpensive and environmentally friendly way is the focus of recent research. Here, silica aerogel is synthesized from sodium silicate as silica source and surface modification with organosilanes, followed by ambient pressure drying at various conditions. The resulting aerogels were analyzed for their density, transparency, and thermal stability. Silica aerogel with a low density of 0.4031 g/cm^3 was successfully synthesized with polydimethylsiloxane (PDMS) as modifying agent at 7:50 solvent ratio. The aerogel can withstand heat up to 400°C.This shows the potential of aerogel to be applied as thermal insulator in various fields.

Keywords:
Silica aerogel; sodium silicate; ambient pressure drying; thermal stability

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1. Introduction

Silica aerogel is a solid material that is lightweight, highly porous (nanoporous), non-flammable, and amorphous [1]. Aerogel has a high visual transmission up to 90-99%, low thermal conductivity of 0.004-0.03 W/m.K, low density of 0.01-0.35 g/cm³ and high surface area of around 1600 m²/g [2]. Due to its remarkable properties, silica aerogel has been applied as an adsorbent, catalyst, and thermal insulator [2]. Silica aerogel also has uses in other fields, such as aerospace. In 2005, NASA prepared the use of aerogel as a thermal protection system for Venus spacecraft [3]. Silica aerogel has been developed to be used as transparent window material and wall insulation [4].

Generally, there are two groups of material that are often used as silica aerogel precursors, alkoxide and sodium silicate. The types of alkoxides commonly used consist of Tetraethyl Orthosilicate (TEOS) and Tetramethyl Orthosilicate (TMOS). However, alkoxides are mostly expensive, difficult to obtain, and toxic [5]. Sodium silicate (waterglass) is an alternative raw material that can be used because it contains silica as much as 86.4% by mass [6]. Sodium silicate can produce silica aerogel with large porosity and is more readily available, environmentally friendly, cheaper and has almost the same level of stability as TEOS [7].

The basic technique of silica aerogel synthesis begins with the creation of sol from sodium silicate and an addition of acid or base catalyst. The sol is then aged to form a hydrogel and washed to remove contaminants that are still present. The hydrogel is then dried by the ambient pressure drying method to obtain aerogel [8]. There are several common methods that are often used in the silica aerogel drying process, such as supercritical drying, freeze drying, and ambient pressure drying. Supercritical drying is quite impractical due to its particular temperature and pressure, therefore it is difficult to apply commercially [9]. Freeze drying needs the addition of specific eutectics, solvents, and polymers [7]. Ambient pressure drying is safer because it operates at ambient pressure and low production costs [10]. Silica aerogel must go through a cationic exchange process as well as solvent exchange and surface modification before being dried at ambient pressure conditions.

Strengthening the gel structure beforehand to prevent cracking and rupture is important during the ambient pressure drying process. This can be achieved through surface modification with the help of silane compounds as silylating agents. The previous research which used Hexamethyldisilazane (HMDS), produced silica aerogel with a density 0.15 g/cm³, surface area of 746 m²/g, and porosity of 93% [11]. Whereas the use of Trimethylchlorosilane (TMCS) produces silica aerogel with a density of 0.071 g/cm³, a surface area of 945.8 m²/g and a pore size of 3.8

nm [8]. Polydimethylsiloxane (PDMS) can also be used as a modifying agent to produce silica aerogel with a density of 0.03099 g/cm³, a surface area of 574.38 m²/g, and high porosity [12].

In this study, we compare the effects of different silylating agents and its concentration on the yield, transparency, and thermal stability of silica aerogels synthesized from sodium silicate via sol-gel and ambient pressure drying. Through this research, we hope to investigate the optimum synthesize conditions as an effort to manufacture thermal insulators that have transparent optical properties.

2. Experimental Section

A. Resin activation

The resin was soaked in aquadest for 24 hours before being drained and then immersed in 37% HCl with a resin to HCl mass ratio of 1: 1 for 24 hours. Next, the resin was separated from the solution and washed with aquadest to remove excess HCl. The resin was patted using a tissue to make sure that there was no aquadest left.

B. Silica sol-gel formation

The sodium silicate solution (4%, 6%, and 8%) was mixed with an activated cationic resin with a mass ratio of 1: 2 accompanied by stirring to carry out the ion exchange process. The H^+ ion of the activated cationic resin replaces the Na^+ ion so that the pH of the solution becomes 1-2. Ammonium hydroxide 1 M was then added to the solution dropwise until a stable silica colloid is formed at pH 5. For another mass concentration of 6%, without the addition of resin, HCl as an acid catalyst was added to reach a specified pH. After that, the colloids were poured into silicone molds. Then ethanol was added to a total of 15 ml. When a cloud had formed in the center of the solution, it indicated that sol had been reached. Then it was tightly closed using parafilm paper for 12 h aging process at 45°C in the incubator shaker to form a solid hydrogel.

C. Surface modification and ambient pressure drying

After 12 h of aging, hydrogel was obtained. First, the hydrogel should be soaked with pure n-hexane solvent for 12 h inside the silicone mold to stimulate the formation of pore. The solvent exchange process was carried out 2 times. Then, the silylating agent (TMCS, HMDS, and PDMS) that had been dissolved in n-hexane with volume variations of 4:50 and 7:50 were mixed with hydrogel to be sonicated for 12 hours. The resulting gels were then dried with a gradual heating temperature of 60°C for 2 h followed by 100°C for the next 2 h.

D. Characterization

Tapped density measurements were performed using measuring glass. The transparency of silica aerogels was analyzed using Jasco V-750UV-Visible (UV-Vis) Spectrophotometer. Thermal stability was investigated using SDT650 TA Instruments Thermogravimetric analyzer (TGA). Yield of silica aerogels was calculated using the following equations:

$$\%\ yield\ silica\ aerogel = \frac{silica\ aerogel\ mass}{(sodium\ silicate\ mass + silylating\ agent\ mass)}\ x\ 100\% \tag{1}$$

3. Result and Discussion

The yield of silica aerogel at various synthesis conditions are shown in Table 1. The volume of silylating agent is directly proportional to the yield of silica aerogel. The yield of silica aerogel with TMCS 7:50 is higher than TMCS 4:50, which are 12.946 % and 14.306%. At the same ratio of silylating agent, HMDS has a higher yield (17.249%) compared to TMCS and PDMS due to the larger number of alkyl groups that can be substituted. The yield of silica aerogel is also directly proportional to the mass concentration of sodium silicate. However, without resin the yield drops because there are still sodium ions inside the solution during sol-gel process which hinder the formation of silica hydrogel.

Table 1. Yield of silica aerogel at various synthesis conditions

Silylating agent	Silylating agent to n-hexane ratio	Sodium silicate concentration	Yield
TMCS	4:50	6 %	12.946 %
TMCS	7:50	4%	3.060 %
TMCS	7:50	6 %	14.306%
TMCS	7:50	6 % without resin	6.379 %
TMCS	7:50	8%	23.720 %
HMDS	7:50	6 %	17.249%

PDMS	7:50	6 %	8.651%

Table 2. Density of silica aerogels at various synthesis conditions

Silylating agent	**Silylating agent to n-hexane ratio**	**Sodium silicate concentration**	**Density (g/cm^3)**
TMCS	4:50	6 %	0.4760±0.010
TMCS	7:50	4%	1.174±0.100
TMCS	7:50	6 %	0.7631±0.211
TMCS	7:50	6 % without resin	0.480±0.1
TMCS	7:50	8%	0.579±0.1
HMDS	7:50	6 %	0.5445±0.011
PDMS	7:50	6 %	0.4031±0.002

Silica aerogel is a solid with low density characteristics, between 0.032- 1.154 g/cm^3 [1][2]. From Table 2, it can be concluded that silica aerogels with low density have successfully synthesized, except the one obtained from 4% sodium silicate concentration. At the same silylating agent ratio and sodium silicate concentration, PDMS produces the lowest density (0.4031±0.002 g/cm^3) compared to HMDS (0.5445±0.011 g/cm^3) and TMCS (0.7631±0.211 g/cm^3), although the values are not significantly different. Alkyl ($-CH_3$) groups in the silylating agents will modify the surface of aerogel to be superhydrophobic. Therefore, it will experience less shrinkage during ambient pressure drying which results in lower density.

Fig. 1 (a) shows the effect of silylating agent type and ratio on silica aerogel transmittance. The addition of silylating agent aims to maintain the integrity of pore structure when the drying process takes place. The more alkyl groups substituted, the less shrinkage happens. Thus, silica aerogel will be filled with air which makes it has a high transmittance [13]. The transmittance of aerogels in UV-Visible spectrum increases as the volume of the silylating agent increases. It can be proven by comparing the maximum transmittance value at 4:50 and 7:50 ratios which are 6.4531% and 13.8877% at a wavelength of 420 nm, respectively. HMDS and TMCS aerogels show better performance than PDMS. The transmittance of HMDS is higher due to its slow reaction rate with the silica surface which leads to the formation of aerogels with small pore size [14].

In terms of sodium silicate concentration, 6% with resin addition also gives better transmittance compared to 4% and 8% as can be seen in Fig. 1 (b). At the same concentration of 6%, silica aerogel without resin exchange has lower transmittance due to the presence of sodium ions which remain trapped in the structure. However, the transmittance of all aerogel samples is generally still low (<20%), therefore optimization in the synthesis parameters is needed if they are going to be applied as transparent insulation material.

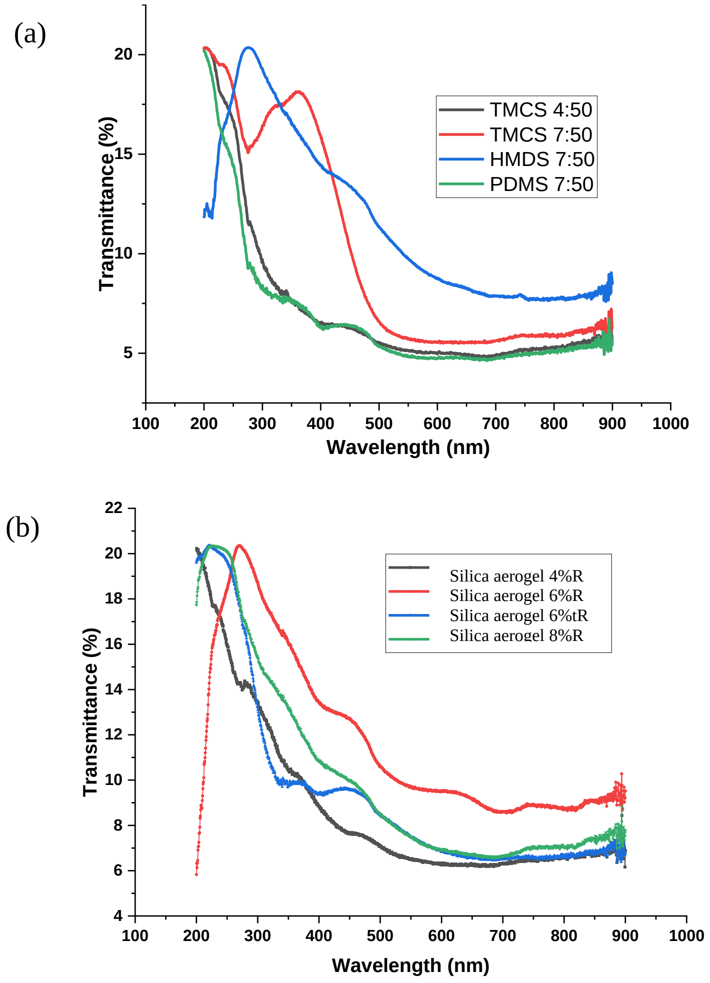

Figure 1. Transmittance of aerogels synthesized with (a) various silylating agents; (b) various sodium silicate mass concentration.

Fig. 2 shows the results of thermal stability measurement of aerogels at various synthesis condition. There are two steps of thermal degradation in the aerogel structure as indicated by the loss of mass. First, the evaporation of the remaining n-hexane solvent and water molecules below 100°C, followed by Si-CH_3 oxidation or the degradation of aerogel at higher temperature. The thermal stability of aerogel reflects its density (Table 2). Based on Fig. 2 (a), aerogel which was modified by TMCS at 4:50 performs better than 7:40 because it has lower density. In Fig. 2 (b), TMCS aerogel has more drastic loss of mass in the first step because there is still water or solvent inside the structure, as indicated by its higher density compared to HMDS and PDMS aerogels. HMDS aerogel is thermally stable up to 350°C. And although PDMS has some initial loss of mass due to solvent evaporation, it can be considered more stable for high temperature application, which is up to 400°C. From Fig. 2 (c), it can be concluded that resin exchange contributes significantly to the formation of aerogel. When the solvent exchange process occurs in hydrogels that still contain salt, n-hexane cannot replace water in the pores which results in poor thermal stability.

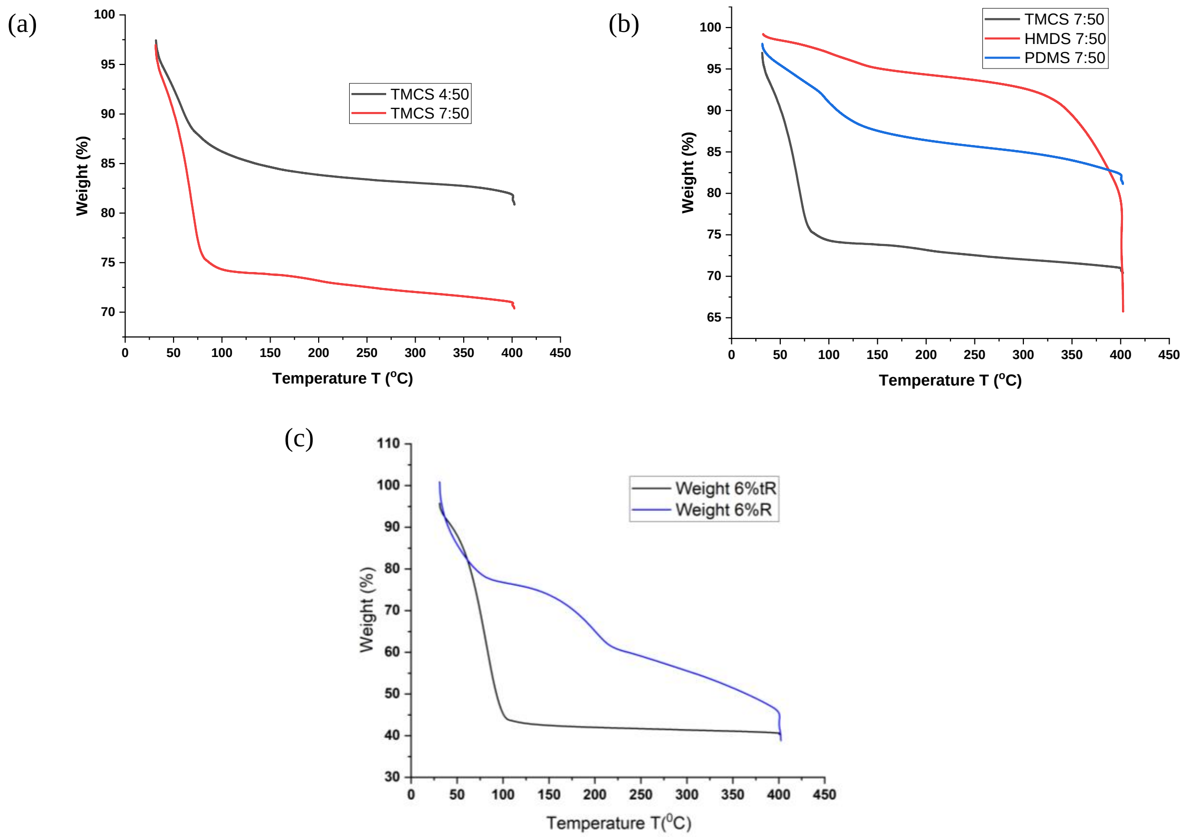

Figure 2. Thermal stability of the as-synthesized aerogels at (a) silylating agent volumetric ratio; (b) silylating agent type; (c) resin addition; and (d) sodium silicate mass ratio variations.

4. Conclusion

Silica aerogel with low density and high thermal stability are successfully synthesized from natrium silicate through sol-gel, surface modification, and ambient pressure drying. Overall, PDMS as silylating agent performs better than HMDS and TMCS in terms of thermal stability and density. Resin exchange is also proven as an important part to synthesize xerogel without impurities, However, the transparency of the aerogel still needs to be improved. Different synthesis conditions, silylating agents, or solvents should be considered in the future in order to produce transparent silica aerogel as thermal insulator.

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