The Thermal Foaming of Solid Sodium Silicate for Thermo-Sensing Applications

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Abstract. *Sodium silicate solution is dried and slowly solidified in an amorphous phase. After heat is applied to the dried sodium silicate droplet, the solid sodium silicate droplet expands and becomes a foam. This ceramic foam formation occurs when ceramics are already in the solid state. During the foaming, the solid amorphous droplet is deformed and partially recrystallized. This transformation is anisotropic and depends on the heating rate. The residual water in the solid sodium silicate plays a major role in the foaming mechanism. By using the property of large volume expansion, solid sodium silicate is highly portable and functionalized for thermo-sensing applications such as fire alarm sensors and autovents.*

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1. Introduction

A large amount of sodium silicate has been produced and supplied to many industries in recent years. The main reason for the high consumption rate of sodium silicate is its versatility for many applications and its cost-effectiveness in terms of mass production. Sodium silicate is profitable for several businesses and has become a material of the millennium. In the past forty years, sodium silicate has been researched and used in several applications, such as adhesives, which was shown by Ref. [1]. It has also been applied as a drilling fluid, as mentioned in a book by Shaker [2]. Sodium silicate was also proposed as a fireproof material by Slimak [3]. Many applications, such as heat insulators or fireproof materials, rely on the foam structure, which encapsulates many small air cells inside. The closed foam cells can prevent the heat transfer between each cell. Therefore, sodium silicate foam has the potential to be an excellent heat insulator, which can be especially used at high temperatures, as presented by Gillilan [4]. Moreover, the strength and density of the foam are very low, which makes it suitable to be an air drop cushion, which was experimented and tested by Baker Jr, and Mallow [5]. With ongoing research on sodium silicate, there will be many other applications for this material in the near future.

Though there have been many research studies on the properties of sodium silicate, most of them were studied in the solution state. An example of a former study of sodium silicate solution is the work by Greenberg [6]. He studied the theory related to the silicate ion in solution. For sodium silicate in the solid phase, Acocella et al. [7] studied the optical properties of sodium silicate glass in terms of humidity and the fabrication of glass from a solution. However, the information about foaming in the solid state was still missing. Up until this point, the mechanism of foaming of solid state sodium silicate had yet to be clearly investigated. It is well known that sodium silicate is a material that has the property to generate foam after being subjected to heat. The mechanism behind this property is still a big mystery and has not been thoroughly studied. There are also several arguments regarding the mechanism of foaming. The mechanism of sodium silicate foaming can be discussed as hydro-bubbling during solidification of a silicate solution. Hoffman [8] showed that silicate solution also shows different structural transformations. A rapid heating usually yields the silicate foam, but a slow dehydration tends to soften sodium silicate. As a water-based solution, the bubbling of sodium silicate solution occurs at a temperature slightly higher than the water boiling point. Tsuyumoto [9] showed that the boiling and bubbling in sodium silicate solution can be generated from a chemical reaction between sodium silicate and a base or salt solution. The bubbling of sodium silicate is also used to assist the foam formation of ceramics foam made from quartz, as shown by Uribe et al. [10]. The bubble generation from a reaction is an important factor for foam formation in solution. On the other hand, Sams et al. [11] proposed that bubbling is, in fact, hydrogen gas, which is a product of a chemical reaction between silicon in solution, alkaline silicate, and water molecules. Considering a number of bubbles during the foaming, the hypothesis of hydrogen gas production is controversial for fireproof applications. Nevertheless, the structural investigation of solid sodium silicate has not been revealed and the mechanism of solid state foam formation is still unknown. The conclusion from the literature is still invalid due to different arguments. In general, the prior work on sodium silicate in literature has not provided sufficient knowledge on foaming. Therefore, in this work, we aim to obtain the additional knowledge on foaming of solid state sodium silicate. The external appearances, crystallinity, mechanical properties, and heating rate were observed and analyzed. In the last section, the knowledge of the foaming mechanism was applied to thermo-sensing devices.

2. Materials and Methods

A commercial grade sodium silicate solution was dropped as a sodium silicate droplet on a glass surface. The first sodium silicate droplet was dried at 90 ^{o}C for 40 h, as shown in Fig. 1.

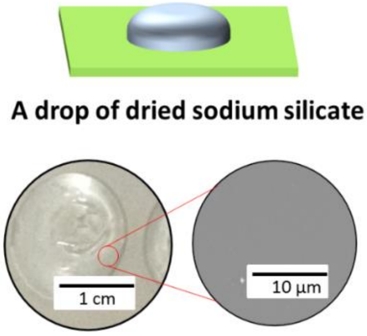

Fig. 1 Schematic of dried sodium silicate droplet and a dried sodium silicate droplet with different magnifications

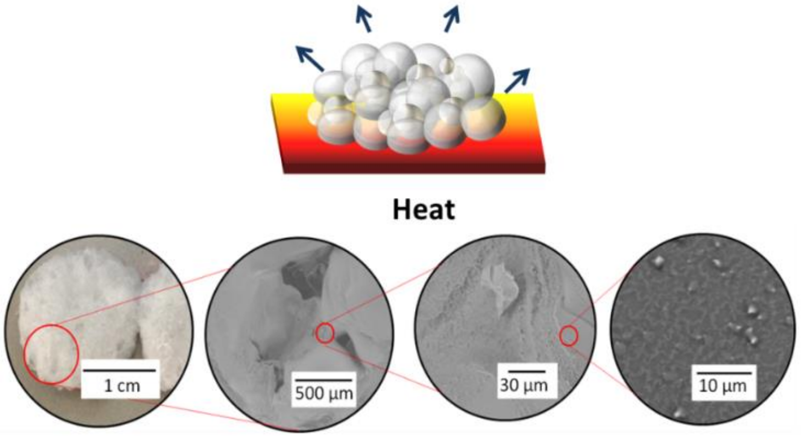

Fig. 2 Schematic of sodium silicate foaming by heating and a sodium silicate foam with different magnifications

The second sodium silicate droplet was dried at 90 ^{o}C for 40 h and annealed at 300 ^{o}C for 5 min to transform the structure into the sodium silicate foam, as shown in Fig. 2.

The external appearance of both glassy dried sodium silicate droplet and sodium silicate foam were observed by scanning electron microscopy (SEM). Then, the sodium silicate droplet and sodium silicate foam were investigated by X-ray diffractometry (XRD) and Fourier transform infrared spectroscopy (FTIR) to study crystal structure and bonding characteristics. Afterward, the sodium silicate droplet was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with different heating rates. Furthermore, mechanical shear stress and hardness were measured to determine the differences in mechanical properties. Later on, a fire alarm sensor and autovent were fabricated as examples of the thermo-sensing applications of sodium silicate.

3. Results and Discussion

From Fig. 1, a dried sodium silicate droplet on a glass slide appeared as a transparent glassy material. Basically, the transparency of dried sodium silicate droplet is related closely to crystallinity and particle size. In our work, transparency is the result of the amorphous structure, which was confirmed by XRD afterwards, as shown in Fig. 3 a).

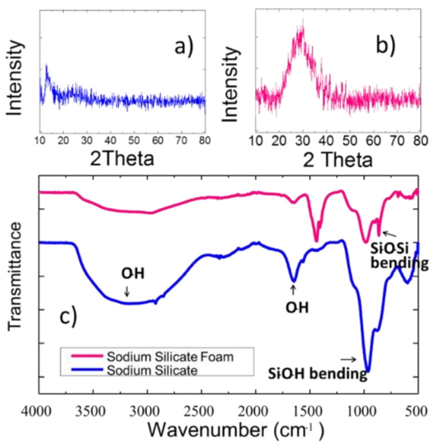

Fig. 3 a) XRD result of the dried solid sodium silicate droplet. b) XRD result of the sodium silicate foam. c) FTIR result of dried solid sodium silicate and sodium silicate foam.

When the structure was amorphous, the light scattering inside the material was negligible and the material became transparent. Under electron microscopy, the surface of the dried sodium silicate droplet was flat down to the micrometer scale. For the droplet physical condition after applying heat at 300 °C, the dried droplet was swollen and became a bubble crust (foaming), as shown in Fig. 2. The bubble crust was fragile and the overall volume expanded. The density of the foam was 0.6116 g/cm^3. The structure at higher magnification was very rough and wavy, and the color of the foam was white and opaque. The physical appearance of the solid state sodium silicate had drastically changed after foam formation. One can conclude that the structure had completely undergone a transformation down to the microscopic level. Furthermore, the transparent property disappeared after foam formation. This phenomenon is the result of light scattering due to a large number of micro air-encapsulated cells inside the foam structure. The example of light scattering inside foam was explained by Durian et al. [12]. The change in optical property by thermal activation might possibly lead to useful applications in the future.

In Fig. 3 a), XRD of dried sodium silicate droplet indicated a completely amorphous structure with a very small broad peak at 15°. After the droplet had been heated and the foaming had occurred, XRD was observed and shown in Fig. 3 b).

The peak at 2 theta of 15° had become a minor peak, and a major peak at 2 theta of 30° appeared. When compared to the XRD peak from Subasri and Näfe [13], the XRD peaks in this work demonstrate an amorphous structure with a single broad peak. The overall XRD peaks before and after foaming were shifted. We expected that the original dried sodium silicate was completely disordered amorphous, and once the foaming occurs, the structure turned to amorphous with a fragment of crystallinity. When sodium silicate was foaming, the structure permanently changes its shape, which can be considered as plastic deformation. The plastic deformation can induce recrystallization in many materials. For example, Wang et al. [14] showed crystallization of Ni-W-P film from the amorphous phase was related to plastic deformation. The same mechanism also occurs in ceramic materials, which was discussed in detail by Oleinik and Danilenko [15]. When the sodium silicate foam expands, a plastic deformation was created on the bubble crust. The deformation induced an internal stress, and the internal stress causes a recrystallization in the sodium silicate structure. A fragment of recrystallization can be observed in the difference of XRD peaks before and after foaming. It is possible that the deformed amorphous on the bubble crust tried to align itself into a new preferential orientation. Based on the atomic structure of β-Na_2Si_2O phase reported by Pant [16], β-Na_2Si_2O is a two-dimensional atomic network composed of Si-O covalent bonding and ionic Na-O bonding. This structure also has a crystal peak at the 2Theta = 30° [17]. Apparently, this effect can be considered as a semi-phase transformation between solid sodium silicate and foam sodium silicate because both crystal orientation and external appearance have changed.

In Fig. 3 c), FTIR of dried sodium silicate droplet was investigated. Although annealed at 90 °C for 40 h in the oven, a signal of water inside a droplet was still shown as an O-H vibration at 1640 cm^{-1} and 2500–4000 cm^{-1}. Si-O-H was also another evidence of residual water at 960 cm^{-1}. The existence of water after annealing at 90 °C for 40 h illustrated the nature of dried sodium silicate as an excellent water re-adsorption material. The peaks associated with water drastically decreased after a dried sodium silicate droplet transformed into foam. Because water usually vaporizes at 100 °C, FTIR peaks of water could be evidence that water vapor pressure takes part in the foam formation and initiates a tension force on the bubble crust afterwards. It is important to realize that the foam also had a lower IR transmittance because the structure was white and opaque. After the foam formation, the FTIR result showed an obvious Si-O-Si bending peak at 860 cm^{-1}. This peak implies that the signal of Si-O-Si bonding becomes comparatively stronger after the foam formation. This bond could be the fragment of a two-dimensional network structure of amorphous silicate in foam, which was not prominent in the completely amorphous structure of the dried sodium silicate droplet.

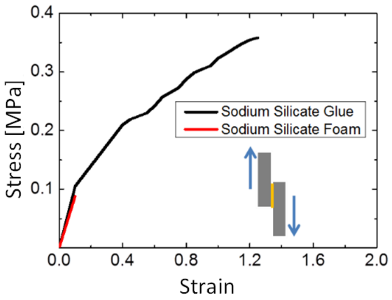

Fig. 4 Shear stress and strain curve of solid sodium silicate and sodium silicate foam.

Because the appearance of sodium silicate before and after foaming is very different, the mechanical properties of both solid sodium silicate and sodium silicate foam were measured. Shear stress and shear strain was reported in Fig. 4. The test was performed based on ASTM D1002 standard using a universal testing machine with a single lab joint.

The shear stress of solid sodium silicate is 0.35 MPa with a strain of 1.2. On the other hand, sodium silicate foam has much less ultimate shear stress, which is only 0.1 MPa with a strain of 0.1. In terms of ultimate shear stress, dried (glued) solid sodium silicate was much stronger than sodium silicate foam. This was not far from what was expected because the dried sodium silicate had a very dense, compact, and rigid structure, but sodium silicate foam composed of a thin bubble crust was a natural stress concentration area. The hardness of solid sodium silicate and sodium silicate foam at 5 different positions is shown in Table 1.

Material	Hardness Shore D (Position)					Average	Standard Deviation
	1	2	3	4	5		
Sodium Silicate	48.5	49.0	51.0	50.5	51.5	50.1	1.29
Sodium Silicate Foam	12.5	10.5	11.5	9.5	13.0	11.4	1.43

Table 1 Hardness of solid sodium silicate and sodium silicate foam

There was a large variation in the hardness of sodium silicate foam. This effect was the result of a large void size distribution in the foam. During the foaming, the bubble size of the entire sodium silicate foam is far from homogeneous. When the hardness was tested, the local deformation occurs on different bubble voids. Therefore, different positions yield a variation in hardness. Furthermore, the average hardness of solid sodium silicate is approximately 5 times higher than that of sodium silicate foam. These results indicated that solid sodium silicate was much stronger than sodium silicate foam. The difference in terms of strength between both structures can be used in the detachable adhesive application. If we consider sodium silicate as a glue, this special glue is very strong and the instrument is firmly attached to the surface. By applying heat to the glue, the instrument can be easily detachable from the surface due to the foaming mechanism of sodium silicate.

Although sodium silicate foam could be fabricated by heating and boiling a sodium silicate solution, at this point, foam formation itself does not need to start from a solution at all because foam was fabricated from a solid state sodium silicate in this work. With the previous result, the foaming involves water vapor, a transformation between a completely amorphous to an amorphous with a fragment of preferential orientation. A small part of the amorphous structure has transformed into a short range order, which was a planar sheet structure. Therefore, the foam occurred with a semi two-dimensional sheet structure, which is constructed into the thin bubble wall. Because the foaming process is an anisotropic growth of the planar structure, the degree of transformation was also observed as a function of heating rate. Therefore, DSC and TGA measurements are needed to determine the foaming interaction in terms of energy, temperature, mass, and the heating rate, as shown in Fig. 5 a) with the heating rate of 20 ^{o}C/min, Fig. 5 b) with the heating rate of 10 ^{o}C/min, and Fig. 5 c) with the heating rate of 5 ^{o}C/min As expected, the transformation was heating rate dependent.

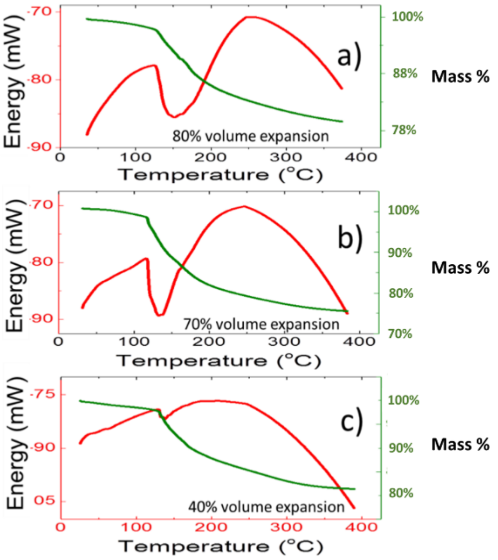

Fig. 5 DSC (red line) and TGA (green line) of sodium silicate droplet, a) at 20 ^{o}C per minute, b) at 10 ^{o}C per minute, c) at 5 ^{o}C per minute

At a very high heating rate, as shown in Fig. 5 a), the transformation started from 105 ^{o}C until 250 ^{o}C. This large broad energy peak corresponded to big foam formation of approximately 80 % volume expansion. The semi-phase transition between amorphous structures at a high heating rate did not show a sharp transition. There were two small minimum points within a big peak, implying the multistep transformation during the foaming. Decreasing mass of sodium silicate during the transformation was due to the evaporation of water during the foaming process. This result indicated that a high heating rate gave rise to a rapid vaporization of water, yielding a high tension force on the silicate bubble surface. The result was connected to a recrystallization, which was shown in Fig. 3 a) and b). When compared with different heating rates, though the mass reduction characteristic during the foaming was still the same, the broad peaks of the DSC at 110 ^{o}C were smaller with reduction of heating rate lower in Fig. 5 b) and c). When the heating rate is only 5 ^{o}C/min, foaming expansion is the least at 40 % expansion. These results indicated that, when mass loss is not fast enough, the vaporization rate was less and foaming of sodium silicate was also less. In conclusion, the water vapor and recrystallization effect might play a major role in foam formation of solid state sodium silicate. The DSC and TGA results confirm that the temperature gradient was a driving force for the anisotropic growth of partial-crystalline amorphous phase during the foam formation.

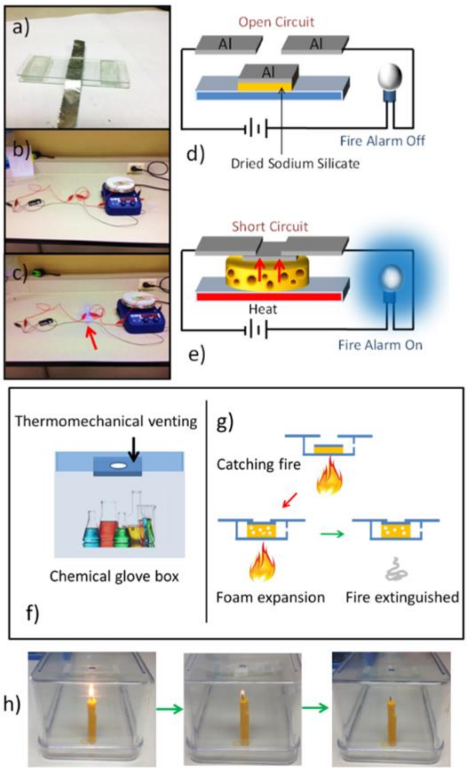

Fig. 6 a) Heat switch using sodium silicate as a sensing material. b) A circuit setup driven by batteries before applying heat. c) A circuit setup driven by batteries after applying a temperature of 250 °C, blue light turned on. d) A schematic of heat detector circuit before applying heat. e) A schematic of heat detector circuit after applying heat. Dried sodium silicate droplet turned to a foam. f) A schematic of a chemical glove box with an autovent from sodium silicate, g) after chemical catches fire, the sodium silicate expands and closes the venting hole. The oxygen inside the box is consumed and fire is extinguished. h) The experiment of the autovent when subjected to a flame.

With a large number of air encapsulations, sodium silicate foam could be used to prevent heat diffusion. The thermal conductivity of foam measured by a standard cut-bar method is approximately 0.33 $\mathrm{W\ m^{-1}\ K^{-1}}$, which is low compared to other ceramics. However, another simple application has been proposed in this paper. Because sodium silicate is now in a solid state, it can be fabricated as a heat detector or a thermal switch for several applications, such as a fire alarm, by using the property of large volume expansion during the foam formation at high temperatures. Two sections of aluminum (Al) film were separately placed next to each other, as shown in Fig. 6 d).

Another Al film was placed underneath two separated Al films. There was a dried sodium silicate film under the Al film. Al films and sodium silicate were compacted within a set of glass slides, as shown in Fig. 6 a). A test circuit was established, as shown in Fig. 6 b) and d). The overall setup before giving heat to the sensor was an open circuit. After heat was applied to the sensor, sodium silicate transformed to a foam. The volume of foam expanded and pushed the Al film upward. The Al film was now a closed circuit and the current ran. The blue fire alarm lit up, as shown in Fig. 6 c) and e). This simple setup is a sensor that detects heat and fire directly. It detects heat at high temperatures, which is suitable in a kitchen, in a manufacturing facility, or in any place where it is always subjected to a high temperature process. There is no false alarm from a temperature below 125 °C, which could occur without a fire in a kitchen, and it can be used in a place where smoke is common and false alarms happen occasionally. The sensor can be repeatably functional because the foam is slightly extracted by absorbing the humidity after a couple of hours, which makes it a reusable thermal switch. This is the result of the nature of sodium silicate, which is a good water absorber. The best evidence of water reabsorption in sodium silicate foam is the result from FTIR in Fig. 3 c). Even at a long annealing time, water can still be reabsorbed and the water peak is still shown in the FTIR spectrum. Sodium silicate is a water soluble material, and once it is subjected to water, the structure can turn back to a non-foaming structure. However, humidity in the air is not enough to transform the foam to a liquid or dried droplet. Hence, the sodium silicate foam was merely slightly retracted from the contacting position after a while. With this simple setup, the sensor can be produced at an extremely low cost as a disposable sensor. Hence, it can be attached to many places in a building with a lower installation cost. Another application from the expansion of sodium silicate foam is the autovent. Considering a closed system such as a glove box in Fig. 6 f), this glove box is attached with the autovent on the top of the box, which allows air exchange between the inside and outside. When the chemical inside the glove box catches fire, the solid sodium silicate in the autovent transforms to sodium silicate foam, as shown in Fig. 6 g) and h). The foam pushed the tap up and closed the air gap between the inside and the outside. When the air gap was closed, the oxygen inside the box was depleted and the fire was extinguished. The system is suitable for a non-living closed system to prevent flame propagation.

4. Conclusions

Sodium silicate solution was dropped and dried on a glass surface. The dried sodium silicate droplet on glass was heated and transformed to a sodium silicate foam. The foam formation had been observed by optical microscopy, SEM, XRD, FTIR, DSC, and TGA. The dried sodium silicate droplet was transparent under the optical microscope, and the XRD signal indicated that it was amorphous. FTIR results depicted the remnant water inside a dried sodium silicate droplet. The foam formation was heating rate dependent, which could be observed by DSC and TGA. This heating rate dependence implied that the temperature gradient is a driving force for foam formation of solid state sodium silicate. The foaming mechanism was related to the water vaporization, which leads to a tension force in the bubble. The residual stress induces the recrystallization effect, which was shown in XRD. Water plays a major role in the foaming mechanism based on the results from DSC and TGA. In order to set an example of an advanced application of sodium silicate foam, a fire alarm sensor and autovent were fabricated by using the concept of a great volume expansion of sodium silicate foam. The alarm sensor started with a open circuit of 3 separated Al pieces. After heat was applied, the middle Al piece moved up and bridged the gap between 2 top Al pieces. Then, the circuit was closed and current ran. The sensor is very simple and cheap, and detects fire directly. It can be repeatedly used and can be easily installed in several places. Another example of a thermo-sensing application is the autovent. The autovent uses the same concept as the fire alarm sensor, by using a tap to close the air gap between the inside and outside. When the oxygen inside the glove box is depleted, the fire is extinguished. This work proves that foam formation of sodium silicate does not need to start from a solution, but that the solid state material can foam as well. Therefore, it can be applied in many applications in the future.

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