



AEROGELS FROM SODIUM SILICATE TOWARDS COST-EFFECTIVE MASS PRODUCTION TECHNOLOGIES

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Autor und Koautoren	Dr. Matthias M. Koebel; Dr. Shanyu Zhao
beauftragte Institution	Empa
Adresse	Überlandstrasse 129; 8600 Dübendorf
Telefon, E-mail, Internetadresse	+41 58 765 4780, matthias.koebel@empa.ch
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Sodium silicate based aerogels were successfully synthesized from using ion exchanged waterglass. The gelation process was investigated and we found rapid gelation for silicic acid (ion exchanged waterglass) and considerably slower gelation with commercial low-sodium silica sols did. Optimal gelation pH is between 4.5 and 5.5 with gelation times ranging from 40 to a few minutes at room temperature. After aging, the water inside the gels is replaced by removed by solvent exchange. Efforts directed at finding a simple and cost competitive hydrophobization process were very successful. At this point we are able to carry out drying of the gels under ambient pressure and obtain aerogels with quite intriguing properties. These new aerogels show comparable optical and mechanical properties to alkoxide (TEOS) based aerogels. Experiments to improve the mechanical strength by microfibrillated cellulose (MFC) modification were tried but only showed moderate success. In the coming year of 2013, improved ion exchange processing, gelation and aging conditions will be identified, supported by means of analytical methods, and polymer as well as fiber-reinforced aerogel composites will be systematically screened and characterized.

ZUSAMMENFASSUNG DEUTSCH

Ausgehend von Wasserglas wurden Aerogele im Labor hergestellt. Dabei wurde der Gelierungsprozess von ionengetauschtem Wasserglas und kommerziell erhältlichem Kieselsol untersucht. Ersteres System eignet sich prinzipiell besser und geliert deutlich rascher. Am besten wird bei pH 4.5 bis 5.5 geliert, wo die Gelierzeit bei Raumtemperatur zwischen 40 bis einige wenige Minuten variiert. Nach der Gelalterung wird das Wasser in den Poren mittels Lösemittelaustausch entfernt, dieser Prozess wurde zur Zufriedenstellung optimiert. Danach wurde ein kosteneffizientes und einfaches Rezept zur Hydrophobierung entwickelt, was wiederum die Trocknung der Gele bei Umgebungsdruck ermöglichte. Zum jetzigen Zeitpunkt ist es bereits möglich, neuartige Aerogele mit faszinierenden Eigenschaften ausgehend von Wasserglas herzustellen, deren Eigenschaften mit TEOS basierten übereinstimmen. Die mechanische Verstärkung mit Zellulose Mikrofasern zeigte bis dato nur wenig Erfolg. Im Jahr 2013 werden Gelierung, Alterung und Ionentausch im Detail untersucht, unter anderem mittels analytischer Methoden. Die Eigenschaften von Polymer- sowie Faserverstärkte Komposite werden zudem weiter verbessert.

Projektziele

Short background: Aerogels are among the most effective materials known for thermal insulation. With thermal conductivities as low as $13 \text{ mW m}^{-1}\text{K}^{-1}$, silica aerogels have the potential to significantly increase the energy balance of buildings, old and new, by drastically reducing the energy needed to maintain the constant temperatures (heating in winter) desired for comfortable living conditions. Despite the obvious advantages of aerogels, the market for aerogels as building isolation materials remains largely underdeveloped due to the high costs associated with industrial scale production. While small volumes of aerogels are currently produced for industrial applications, financial analysts at *Lux Research* forecast a ten-fold increase in total market size to \$230 million (USD) between 2011 and 2020 [1]. Most commercially available aerogels are derived from expensive silicon alkoxides such as tetraethylorthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) and require investment- and labour-intensive super critical drying in order to produce large monolithic boards [2-4]. Alternatively, sodium silicate has been identified as a cost effective silica source for aerogels [5-8].

Within this project we are aiming to develop an urgently needed route for obtaining monolithic aerogels from inexpensive sodium silicate precursors by means of an ambient pressure drying processes. A major challenge is that, based on previous experience, sodium silicate gels tend to be more fragile than those made from silicon alkoxide precursors. In order to develop a basic method for mass manufacturing mechanically robust aerogels from sodium silicate, several goals of the project have to be achieved as following.

Goal and Milestones: When targeting the development of an affordable method for manufacturing mechanically robust monolithic aerogels from sodium silicate solutions, one needs a solid understanding of sodium silicate chemistry, the effects of mechanical reinforcements, and the influence of drying parameters on the mechanical properties of the gels and aerogels. The system is complex because many of these processing parameters are limited by and dependent on the others. The milestone objectives (i) through (iv) define the aims associated with each phase of aerogel processing.

(i) *Understanding of Gelation & Aging Processes of Sodium Silicate:* This involves investigating the effects of acid catalysts on gelation kinetics through dynamic light scattering, and the effects of residual ions on gel strength through mechanical testing. One main aspect is the elimination of Na^+ ions from the gels.

Quantitative overall goal: substitution of TEOS or TMOS by ion exchanged waterglass to produce wet silica gels and to produce corresponding silica aerogels with identical physical properties.

(ii) *Mechanical Strengthening of Sodium Silicate Gels:* This involves investigating the possibilities of mechanically strengthening the gels through aging in different solutions, and reinforcement with polymerizable monomers and fibers. Improvements may be quantified using rheological studies in the wet state and mechanical testing of the dried aerogel materials.

Quantitative overall goal: modification of ion exchanged waterglass by addition of fibers, suitable polymer crosslinkers or biopolymers to produce wet silica gels and silica aerogels with mechanical fracture toughness 5 times higher and tensile strength 10 times higher than standard waterglass and / or TEOS based silica aerogels.

(iii) *Optimization of Solvent Exchanges and Ambient Pressure Drying:* This involves determining the required minimum times and volumes for complete solvent exchange using standard analytical chemistry techniques, and optimizing the hydrophobization and drying parameters.

Quantitative overall goal: To develop a production technology for silica aerogels by solvent exchange and hydrophobization based on waterglass based silica gels described under i) and ii) with minimal consumption of solvent exchange steps and consumption as well as minimal hydrophobization agent consumption.

(iv) *Cost performance analysis and optimization:* This involves determining the feasibility of large scale production based on the optimized process by calculating costs of raw materials, complexity of process, and related costs.

Quantitative overall goal: To carry out a preindustrial and industrial level cost analysis for the production of waterglass based silica aerogels based on i), ii) and iii) with a total cost 5 times lower than a comparable standard process (TEOS or TMOS based).

Durchgeführte Arbeiten und erreichte Ergebnisse

Similar to alkoxide precursor based silica gels, gelation of waterglass can be induced directly in a single step process by a simple neutralization or in a more elaborate two-step process (acidification / ion exchange followed by base addition). Figure 1 summarizes these similarities between waterglass and alkoxide chemistry.

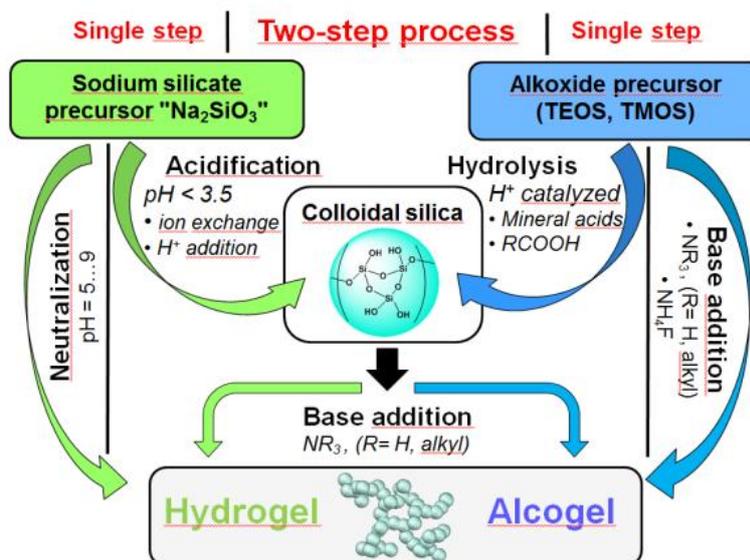


Figure 1: Schematic illustration describing the chemical mechanisms by which gel networks are formed from sodium silicate and alkoxide precursors.

During the neutralization of a sodium silicate (Na_2SiO_3) solution, gelation happens typically rather quickly (seconds to minutes, depending on the solution pH and the type of acid used). However the residual sodium ions from the waterglass render the processing rather difficult. As part of a preliminary study, we found that sodium containing silica gels produce very brittle silica aerogel materials. This is why we chose the two-step route as the more promising alternative at the beginning of the project – and focused all our efforts on this technique.

In a two-step waterglass process, the sol used to prepare the gels consists of silicic acid (H_2SiO_3) and its oligomers polysilicic acids, which are produced by exchanging Na^+ ions from the sodium silicate with H^+ . To remove sodium ions in the sodium silicate solution, a dilute sodium silicate solution is passed through a strongly acidic, cationic ion-exchange resin (e.g. Amberlyst) as it is shown in Figure 2. The pH of the native sodium silicate solution is ~ 11.5 and but once passed through the ion exchange resin drops into the acidic range with typical values ~ 2.5 [9]. Following the ion exchange step, catalytic amounts of base e.g. ammonium hydroxide (NH_4OH) are added to induce gelation.

As obtained gels are then typically aged overnight and exchanged into ethanol four times and then into heptane thrice. At this point, the gels are hydrophobized (HMDS, HMDSO or TMCS) and then dried in an oven at 150°C . In the following, the ongoing work is briefly discussed in the context of the milestones i) through iv).

i) *Understanding Gelation & Aging Processes of Sodium Silicate:*

Background

For the preparation of sodium silicate based aerogels, the $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio and the silica content ($\text{Na}_2\text{SiO}_3/\text{H}_2\text{O}$ ratio) are important parameters for the preparation of sodium silicate gels. Rao et al. [10] reported that, with $\text{Na}_2\text{SiO}_3/\text{H}_2\text{O}$ molar ratios $> 8 \times 10^{-3}$, aerogels have optimum hydrophobicity and physical properties. Hwang et al. [11] found that, the best value of $\text{Na}_2\text{O}/\text{SiO}_2$ in the starting waterglass solution is 1:3.3 and the best aerogels are obtained with silica contents in the solution between 4 and 8% by weight.

During the gelation and aging steps, syneresis of wet gels is generally observed and the linear shrinkage of wet gel caused by syneresis was determined by Hwang et al. [11] to be about 10%. According to references [9, 12], the optimum pH, gelation temperature, and aging time were 3.5, 60°C , and 24 h, respectively. Rao et al. [13] and Shi et al. [14] found that at pH 4-5, the gels show the best optical and mechanical properties. Lee et al. [9] found that porosities, densities, and surface areas tended to decrease with the increase of the sol pH. Based on this brief literature survey, the various processing parameters such as acid type, precursor concentration, and the presence of residual ions will largely affect the microstructure of the gel and with it the final properties of the aerogel.



Figure 2: Photograph of the ion exchange process of sodium silicate to produce a silicic acid sol

Preparation and gelation of pure silicic acid sols

The first step in the synthesis of waterglass based silica aerogels is to remove sodium ions. This is achieved by passing a dilute sodium silicate solution (approximately 8-9% SiO_2 by weight) through a cation exchange resin (Amberlyst 15) which was packed inside a chromatography column as shown in Figure 2. The pH of the effluent (silicic acid sol) was changed from 11.95 (commercial waterglass) to around 2.5 – 3.5. The extent of Na^+ removal will be confirmed later on by elemental analysis. The so-obtained silicic acid sol will form a gel by itself when left idle, however gelation at $\text{pH} < 4$ is requiring quite a long time. Henceforth we shall adhere to the use of the term “silicic acid” or “silicic acid sol” to describe such an ion-exchanged sodium silicate solution. To understand the effect of the sol pH on the gelation kinetics, several sol samples were adjusted to different pH values with dilute ammonium hydroxide solution and the corresponding gelation times recorded. Figure 3, shows the gelation time of an ion exchanged silica sol at different pH values. An ideal range of pH for real-life applications is between pH 4.5 and 5.5 with gelation times ranging from 40 to just a few minutes at room temperature. By heating the solutions to 45°C , gelation is much faster: at pH 4.5 it occurs in less than 5 minutes. The effect of temperature on the gelation times will be studied in detail over the course of a more detailed study which will continue.

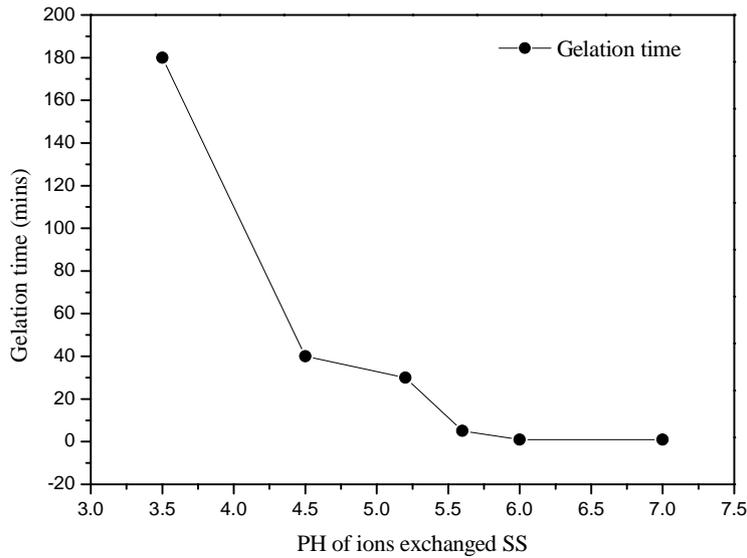


Figure 4: gelation times of ion exchanged sodium silicate at various pH values

Preparation and gelation of mixed silicic acid and Betol KS 307 sols

One important aspect, when developing a new technology, is to consider the most economical source of raw materials. In this case, commercial waterglass or sodium silicate is certainly one of them, however as mentioned earlier, we are required to remove the sodium ions first to produce the silicic acid sol which requires an extra processing step.

Commercial silica sols with very low sodium contents are readily available from a number of different suppliers, with the advantage that they can be used as received. For comparison and performance assessment, we started by comparing a low-sodium commercial silica sol (Betol KS 307, Woellner Silikate, Germany) with ion exchanged sodium silicate. Pure Betol KS 307 sols with a silica content of 9% took around 40 minutes to gel at 40°C and pH 4.5. This seemed in fact rather long and we attempted to speed up the gelation by mixing in ion exchanged waterglass as prepared in the lab. Figure 4 below shows the effect of adding ion exchanged sodium silicate (silicic acid) to Betol KS 307 in different amounts.

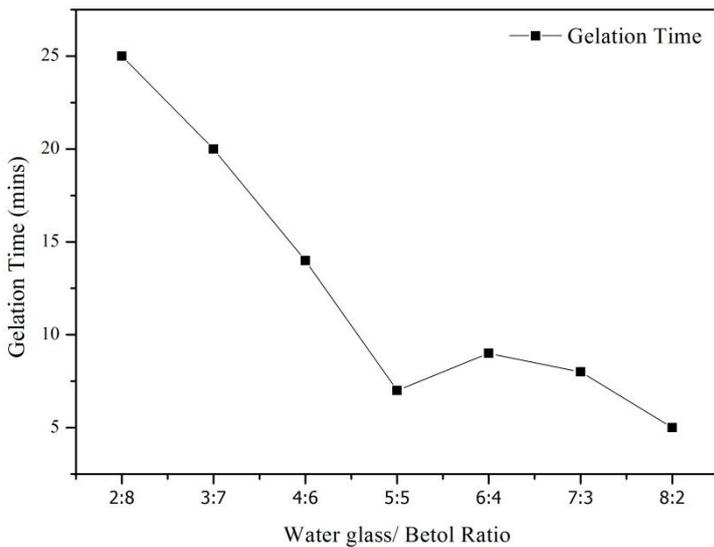


Figure 4: The gelation time of sodium silicate / Betol mixtures at 40°C with a total silica content of 9%

Mixed silicic acid / Betol sols were obtained by mixing a dilute silicic acid sol (sodium silicate solution passed through Amberlyst 15 as described above) with the desired quantity of Betol 307. The pH was then adjusted to 4.5 to initiate gelation and the samples were kept at 40°C. The so observed gelation times were between 5 and 30 minutes, with higher Betol 307 concentration resulting in lower gelation times, as expected. With silicic acid contents above 50%, gelation times below 10 minutes are achieved which are ideal for practical use.

During initial test with Betol and mixed silicic acid / Betol KS 307 gels, we discovered, however that after completing drying and solvent exchange steps, even using an optimized procedure described below, the resulting materials exhibited far larger shrinkage than standard silicic acid gels without Betol. In conclusion, we found that even though commercial sodium free silica sols can be gelled nicely, they are not particularly well suited for the preparation of silica aerogels. We believe that the rather large size of the colloids (7nm according to manufacturer's specifications for KS307) result in an altogether different gel structure than with pure silicic acid or alkoxide based two-step gel preparations. Because the initial gel structure determines also the final properties of the aerogel, this type of commercial silica sol is not a valid replacement for a freshly ion exchanged sodium silicate solution.

ii) *Surface modification and ambient pressure drying*

Background

Replacing water as the pore fluid from the gels is indispensable for further processing and ambient drying. This is normally done by solvent exchange into a suitable aprotic solvent such as alkanes or acetone or acetonitrile. To prepare the gels for ambient drying, hydrophobization of surface modification with a “waterproofing agent” such as trimethylchlorosilane, dimethyldichlorosilane, or hexamethyldisilazane is necessary. These compounds are known to diffuse into the pores of the gel and spontaneously react with the hydroxyl groups on the surface, thus substituting them with non-polar chemical functionalities such as trimethylsilyl or dimethylsilyl groups. For further information on the hydrophobization chemistry, the reader is referred to [15,16]. Alternatively, one could make the gel with a silicon alkoxide such as methyltrimethoxysilane (MTMS) that introduces hydrophobic surface groups to start with, eliminating the need for post-gelation modification of the gel. The resulting aerogels are generally white and not transparent but remarkably elastic–marshmallow-like–and can thus be dried subcritically [17]. However, this method is not well compatible with waterglass and thus will not be pursued within this project. X-aerogels, which are aerogels that have a conformal polymer skin applied over their skeletal surface, are frequently both hydrophobic and incredibly stiff and so they can also be subcritically dried [18].

Gel preparation and solvent exchange

In the previous section we had described the preparation of silica gels from silicic acid sols. Before solvent exchange, gels are typically kept in a sealed container at moderate temperature (40-50°C) for up to 24h. During this process, the interparticle necks will be strengthened by deposition of silica. Hence, aged gels generally become stiffer and tougher. As part of ongoing research efforts, silicic acid gels were aged overnight in water and then solvent exchanged into ethanol. During aging and ethanol exchange, some shrinkage occurs (about 10-15% by volume, depending on the recipe). This allows for easy removal of the gels from the mold (containers). The alcogels were then washed with ethanol three times more to make sure most of the water is replaced/exchanged by ethanol and then three times with heptane.

Optimization of the hydrophobization treatments

In a preliminary study, different hydrophobization agents were compared and for reasons of cost efficiency, ease of handling and lack of toxic or corrosive byproducts, we opted for HMDSO (Hexamethyldisiloxane) as a standard silylation agent. In order to react properly, HMDSO requires small amounts of a hydrochloric acid catalyst. Two methods of introducing HCl to the hydrophobization solutions were tested, namely the direct addition of hydrochloric acid solutions and the use of Trimethylchlorosilane in small amounts. The latter is a commonly used hydrophobization agent which also releases stoichiometric amounts of HCl during its reaction according to:



In order to determine the best conditions for hydrophobization, heptane-exchanged gels were immersed in 6%, 8%, 10%, 15% HMDSO/heptane solutions at 65°C, respectively. 0.2mL of concentrated HCl were used in all samples as an acid catalyst. Figure 5 reveals the highest optical transparency of the ambient-dried aerogel material in the case of a gel modified in 10% HMDSO (sample C), probably representing the best case conditions. At 6% HMDSO (sample A) there is considerable shrinkage, indicating the amount of HMDSO is not sufficient for a complete hydrophobization. At 15% HMDSO, surprisingly, the resulting aerogels are breaking up into smaller pieces and the material is again more opaque. The results of this series of experiments are listed in Table 1.

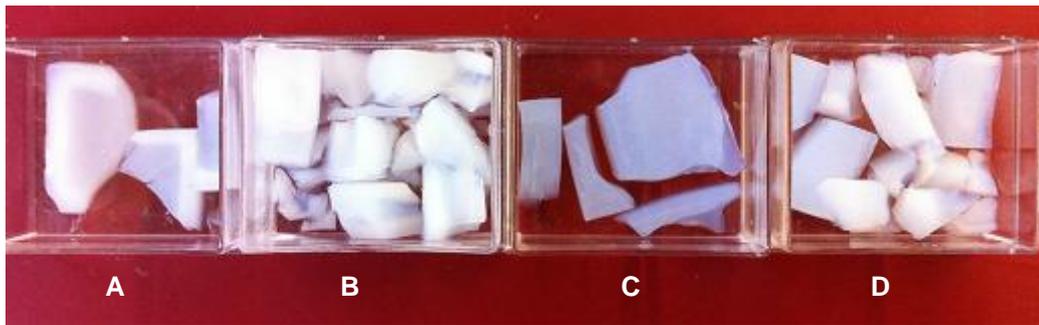


Figure 5: Silicic acid sol aerogels modified with different amounts of HMDSO: A. 6% B. 8% C. 10% D. 15%

Samples	Silylation agents	Density g/cm ³	Appearance
A	6%HMDSO/HCl	0.286	Considerable shrinkage during drying, incomplete hydrophobization
B	8%HMDSO/HCl	0.155	Cracked, smaller, whitish fragments
C	10%HMDSO/HCl	0.140	Large almost monolithic blocks, very transparent
D	15%HMDSO/HCl	0.141	Cracked, whitish fragments

Table 1: Density of ion exchanged sodium silicate based aerogels modified with HMDSO/TMCS

In conclusion, 10% HMDSO seems ideal for the hydrophobization of waterglass gels, the use of higher concentration solutions does not seem to yield better results. Ambient drying at 150°C yields low density aerogel materials with excellent optical transparency. Future investigations are going to focus on the preparation of lower density materials and monolithic specimens with larger dimensions, ideally 5cm x 5cm. Such blocks are required for thermal conductivity measurements.

In a second series of experiments we attempted to introduce HCl in the form of TMCS as described previously. Since only small amounts of HCl are needed, the TMCS concentration in the hydrophobization solution was varied between between 0.04% and 0.2%. From the photographic images in Figure 6, a 10% HMDSO/ 0.06% TMCS (sample F) modified aerogel exhibits the lowest amount of shrinkage. At the same time this material is almost perfectly monolithic, highly translucent and has the same density as sample C from the previous series. Sample G with (0.08% TMCS) is rather similar to sample F, also combining low density with good optical transparency and almost monolithic character. Table 2 shows the most striking characteristics of samples E through G.

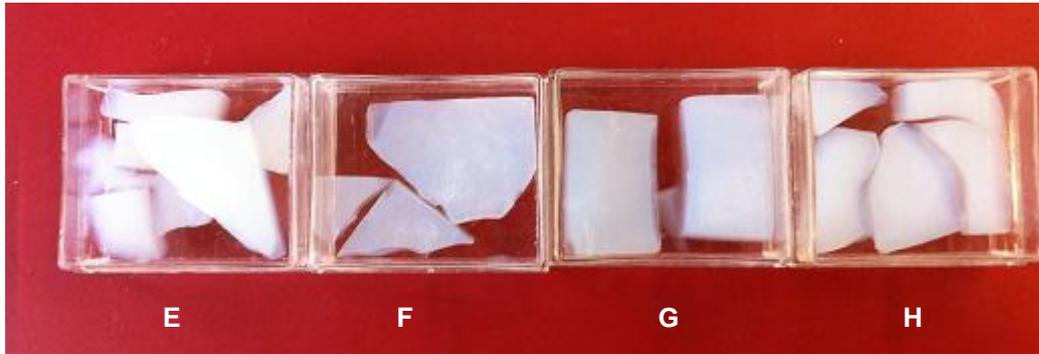


Figure 6: Sodium silicate based aerogels modified with different amounts of TMCS: E. 0.04%TMCS F. 0.06% TMCS G. 0.08% TMCS H. 0.2% TMCS

Samples	Silylation agents	Density g/cm ³	Appearance
E	10%HMDSO,0.04%TMCS	0.161	Whitish rather large fragments
F	10%HMDSO,0.06%TMCS	0.140	Almost monolithic & transparent
G	10%HMDSO,0.08%TMCS	0.145	Almost monolithic & transparent
H	10%HMDSO,0.2%TMCS	0.143	Whitish rather large fragments

Table 2: Density of ion exchanged sodium silicate based aerogels modified with HMDSO/TMCS

In conclusion, HCl can be introduced in the form of TMCS. In doing so, one can avoid bringing additional water into the system, which as it turns out is not as critical as we had initially expected: Both aqueous HCl and 0.06% to 0.08% TMCS are producing good quality almost monolithic aerogels. An additional optimization of the drying must be pursued in order to produce perfect monoliths.

iii) *Mechanical Strengthening of Sodium Silicate Gels:*

Background

The structure of silica aerogels is quite fragile and yet, due to the rigid bonding of the fourfold coordinated Si-O bonds, silica aerogel materials also show a brittle characteristic. Consequently it is generally rather tricky to prepare monolithic gels and aerogels. When comparing two-step, alkoxide and waterglass based aerogels, the latter are generally weaker. For practical applications, additional strengthening of silica aerogels is always useful, no matter what the source of silica [18]. Generally one can add fibrous or polymerizable monomers to improve the mechanical properties of aerogels. X-aerogels, which are aerogels that have a conformal polymer skin applied over their skeletal surface, are frequently both hydrophobic and incredibly stiff and so they can also be subcritically dried [19]. Regenerated cellulose can also be combined with inorganic silicates to produce composites with quite astonishing properties [20]. Unfortunately, such modifications also lead to a drastic deterioration of the insulation performance. With thermal insulation markets in mind, we are going to focus on minimizing the amounts of strengthening agents used. The work described here is centered on cellulose base fibers (MFC).

MFC cellulose / silicic acid composite materials

Several formulations of silicic acid gels with aqueous dispersion of microfibrillated cellulose (MFC) have been prepared in an attempt to understand the change of mechanical properties that arises from such modifications. The main advantage of using this combination is that both silicic acid and MFC are water-based systems and thus perfectly compatible and miscible.

The practical preparation of the composite gels was as described above. In addition, 2-8% of MFC (with respect to the total silica contents) were mixed into the sols. The hydrogels were equally exchanged with ethanol and heptane and then hydrophobized in 10% HMDSO/heptane solutions with 0.2mL HCl. Drying was done at 50°C for 2 hours and 150°C for 2 hours to reduce the time exposed to high temperature. High temperature treatments during drying lead to darkening (charring) of the cellulose phase. This becomes increasingly more apparent with increasing MFC concentrations. The compatibility of the sodium silicate solution and MFC is quite good as seen from a rather homogeneous dispersion in both the gels and the aerogel composites as can be seen from the images in Figure 7. Unfortunately, all ambient dried samples are prone to cracking during drying at 150°C. All aerogels' densities are below 0.1g/mL (see Table 3). After silylation, there may still be substantial amounts of water trapped inside the gel, particularly the cellulose part, which can cause cracking and a "softer" structure of the aerogel composites. Shrinkage of composites is effectively suppressed by addition of MFC, which is seen both in the large filling levels of the containers (large total volume) and the low densities.

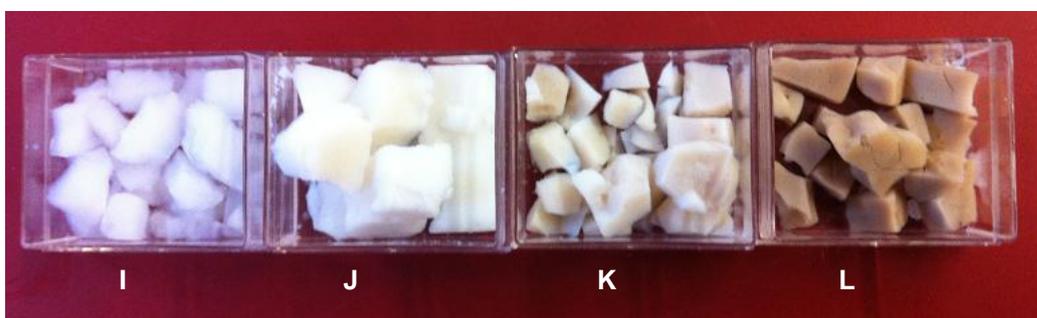


Figure 7: MFC fiber-reinforced sodium silicate based aerogel composites I. 2%MFC J. 4%MFC K. 6%MFC L. 8%MFC added to the silicic acid sol prior to gelation

Table 3: Density of silicic acid aerogel composites with varying amounts of NFC fibers

Samples	Percentage of MFC	Density g/cm ³
I	2%	0.079
J	4%	0.085
K	6%	0.069
L	8%	-

The addition of MFC also seems to weaken the silica structure rather than to strengthen it. When crushed by hand, the composites seem even more fragile than pure silica aerogels. This effect will be investigated and if necessary other strengthening techniques pursued over the course of the project.

Internationale Zusammenarbeit

This work is a complementary approach to the 7th framework project „AeroCoins“ (www.aerocoins.eu) where alternative cost efficient production technologies for aerogels based on standard alkoxide basis are investigated. Here we are focusing on substituting alkoxide precursors by waterglass which is by far cheaper but more difficult to handle. In the case of a successful completion of AeroCoins and the desired upscaling into an industrial production setting, the waterglass-based chemistry can bring additional cost-savings, thus making the production of aerogel insulation materials even more competitive.

Bewertung 2012 und Ausblick 2013

Sodium silicate based aerogels were successfully prepared by removing sodium by ion exchange and water by solvent exchange. Optimized procedures for the preparation and hydrophobization of gels were determined in a first step. The gels can easily be dried under ambient pressure. These new aerogels show comparable optical and mechanical properties to TEOS based aerogels.

The study of gelation kinetics and the gelation mechanism will be pursued by means of analytical methods (DLS). In this way, improved ion exchange processing, gelation and aging conditions will be identified. The solvent exchange and hydrophobization steps will only need minor adjustments, as these processes are already highly optimized. In order to improve mechanical strength, MFC modification was tried but with moderate success. In 2013, chitosan, polymer and cellulose fiber reinforced aerogel composites will be systematically improved and characterized.

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