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Aerogels from sodium silicate

Towards cost-effective mass production technologies



Increasing phase separation



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Zusammenfassung

Im Rahmen dieses Projekts wurden chemische Prozessverfahren zur Herstellung, mechanischen Verstärkung sowie chemischen Modifizierung (Hydrophobierung) von silikatbasierten Aerogelen ausgehend von Wasserglas entwickelt. Die Arbeiten sind nach Plan verlaufen und alle Projektziele wurden rechtzeitig erreicht. Als Highlight wurde eine neue Stoffklasse von Silikat-Pektin Aerogelen entwickelt, welche hervorragende mechanische Eigenschaften (staubfrei, kein Bruch bis >80% Kompression, Festigkeit >25MPa) bei tiefer Wärmeleitfähigkeit (<17mW/(m K)) aufweist. Gemäss unserer Prozessanalyse sind Herstellkosten im Bereich von 600EUR/m³ für Wasserglas-Aerogele denkbar, was Anwendungen im Bau massiv beschleunigen würde. Obwohl Wasserglas für die Massenproduktion zweifelsohne effizient ist, führten parallele Entwicklungen zur Entdeckung eines minimalen "Eintopf"-Verfahrens für Aerogele auf TEOS Basis, welches im Rahmen von ersten Gesamtkostenbetrachtungen (CAPEX und OPEX dominieren Rohstoffkosten) heute wohl der vielversprechendste Weg zur raschen Kommerzialisierung von Aerogelen darstellt. Die Wasserglas Technologie ist aber dennoch kompetitiv und bietet einzigartige Möglichkeiten im Bereich Biopolymer-Hybride und Membrantechnologien.

Résumé

Au cours de ce projet, des procédés chimiques de synthèse, des methods pour le renforcement structurel et la modification chimique (hydrophobisation) des aérogels de silice à base de silicate de soude ont été développés. Les travaux se sont deroulés comme prévu et tous les objectifs ont été atteints à temps. Comme aspect original dans ce projèt, une nouvelle classe d'aérogels hybrides pectine-silice a été inventé, qui ont d'excellentes propriétés mécaniques (sans poussière, compressibles jusqu'à > 80% sans fracture, compressibilité >25 MPa) et une faible conductivité thermique (< 17MW/(m K)). A partir d'une analyse détaillée, nous jugeons les coûts de production pour ces aerogels dans les environs de 600EUR/m³ comme réalistes, ce qui permettrait d'accélérer l'application dans la construction des bâtiments. Bien que le silicate de soude est sans doute éfficace pour la production d'aerogels au niveau industriel, des développements parallèles ont mené à la découverte d'une route minimale "one-pot" à base de TEOS. Ayant les coûts totales les plus bas (CAPEX et OPEX dominent les coûts des matières premières) cette route est la plus prometteuse pour la commercialisation rapide des aérogels. La technologie silicate de soude compétitive est uniques pour les hybrides biopolymères et les membranes.

Abstract

Within the scope of this project, chemical synthetic methods for gelation, aging, mechanical reinforcement and chemical modification (hydrophobization) of sodium silicate-based aerogels have been developed. The project work was completed according to plan and all goals and milestones were met in time. As a highlight, a new class of silica-pectin hybrid aerogels was developed, featuring excellent mechanical properties (dust free, no rupture until >80% strain, final strength >25MPa) combined with extremely low thermal conductivity values (<17mW/(m K)). Starting from a detailed analysis of the aerogel production process, a production cost on the order of 600EUR/m3 was predicted which could lead to a drastic acceleration of the use of aerogels in the building and construction sector Although the water glass process is undoubtedly efficient for mass production, parallel developments in our laboratory led to the discovery of a minimal solvent "one-pot" process for TEOS based aerogels, which in the context of initial total cost considerations (CAPEX and OPEX dominate raw material costs) today represent probably the most promising way for the rapid commercialization of aerogels. Water glass technology is yet competitive and offers unique opportunities in biopolymer hybrids and membrane technologies.

Summary deutsch

Ausgehend von ionengetauschtem Wasserglas wurden Aerogele erfolgreich hergestellt und deren Eigenschaften untersucht bzw. verbessert. Gelierung, Alterung, mechanische Verstärkung sowie Verbesserung der Lösemitteltrocknung und Kostenmodelle wurden systematisch untersucht und dokumentiert. In einem ersten Schritt wurden Gelierung und Alterung verbessert: der Gelierungsmechanismus wurde anhand von Partikelgrössenanalyse mittels dynamischer Lichtstreuung (DLS) untersucht; zudem wurde das Partikelwachstum auch mittels Theorie modelliert und die Resultate stimmten gut mit unseren Messungen überein. In einem zweiten Schritt wurde der Hydrophobierungsprozess optimiert. Eine ausreichende Belegung der inneren Oberflächen eines Silikatgels ist unabdingbar für die Lösemitteltrocknung und die Darstellung qualitativ hochstehender Aerogele. Unsere Resultate zeigen eine verbesserte Technologie zur Darstellung von Wasserglas-basierten Aerogelen mittels Lösemitteltrocknung.

Silica-Aerogele sind von Natur aus spröde, weshalb kommerzielle Produkte in der Regel eine mechanische Verstärkung erfordern. Diese basiert entweder auf makroskopischen (z.B. Fasermatten) oder mikroskopischen (z.B. chemische Vernetzung) Prinzipien. Mehrere unterschiedliche Routen zur mechanischen Verstärkung wurden im bis dato untersucht. **a)** Pektin und Chitosan Biopolymere zeigen gute Verträglichkeit mit wässrigen Wasserglas-Lösungen; in diesem System wurden die Eigenschaften der gebildeten Hybrid Aerogele in Funktion von pH Wert und Polymerbeladung systematisch untersucht. Die Gele wurden mittels Lösemittelaustausch und Hydrophobierung hergestellt und aus überkritischem CO₂ getrocknet. Mikrostruktur, hydrophobe Eigenschaften, Wärmeleitfähigkeit und mechanischen Eigenschaften wurden systematisch analysiert und die Resultate publiziert. **b)** Um die technische Machbarkeit für kommerziell attraktive Aerogel Isolationsprodukte aufzuzeigen, wurden Kompositematten ebenfalls ausgehend von kommerziell erhältlichen Polyester (PES) Fasermatten hergestellt. Nach umfangreichen Untersuchungen und Verbesserung der Lösemitteltrocknungsprozesse waren wir schliesslich in der Lage die ersten Wasserglas basierten Aerogelmatten zu produzieren. Diese Verbundwerkstoffe zeigen deutlich bessere Festigkeit im Vergleich zu reinen Silikat-Aerogelen, wobei die geringe Wärmeleitfähigkeit erhalten bleibt. Die Komposite zeigen vergleichbare thermomechanische Eigenschaften zu TEOS basierten.

Als letztes wurde eine Wirtschaftlichkeitsanalyse zur Herstellung von Wasserglas Aerogelen durch direkten Vergleich mit den bekannteren TEOS basierten Verfahren durchgeführt. Das Kostenmodell umfasst Rohstoffkosten, Abschreibungen auf Kapitalanlagen (CAPEX) und Betriebskosten (OPEX). Die Verwendung von Wasserglas senkt zwar die Rohstoffkosten im Vergleich zu TEOS-Vorläufer, aber dieser Vorteil Verstärkung wird durch höheres CAPEX aufgrund des aufwändigen Ionenaustauschprozesses teils kompensiert. Parallele Entwicklungsaktivitäten in unserer Gruppe auf TEOS Basis brachten die Entdeckung eines Ein-Topf-Verfahrens, das die Verwendung von Lösungsmitteln nahe an das theoretische Minimum (1m³ Lösungsmittel für 1m³ Aerogel) hervor. Das Ergebnis ist eine zusätzliche Reduzierung an CAPEX zusammen mit einer starken Verringerung der Betriebskosten weil durch weniger Lösungsmittel auch der Aufarbeitungsaufwand minimiert wird. Trotz attraktiver Ergebnisse in diesem Projekt mit Wasserglas (600 CHF/m³ für eine Kapazität >100'000m³/a) ist wohl das TEOS basierte Eintopfverfahren das im Moment günstigste und vielversprechendste Verfahren.

Zusammenfassend war das BFE Wasserglas Projekt ein voller Erfolg: i) Prozesse zur Gelierung/Alterung und Hydrophobierung von Wasserglas basierten Aerogelen wurden entwickelt und optimiert; ii) die Machbarkeit von Dämmplatten mit vergleichbaren thermomechanischen Eigenschaften bezogen auf den Stand der Technik wurde aufgezeigt; iii) Wasserglas ist der einzige Rohstoff zur Darstellung von Biopolymer-Silikat-Aerogelen; iv) Wasserglas Prozesse mit minimaler Schrumpfung erlauben spezielle Anwendungen (Membranen). Obwohl Wasserglas für die Massenproduktion zweifelsohne effizient ist, führten parallele Entwicklungen zur Entdeckung eines minimalen Lösungsverfahren für Aerogele auf TEOS Basis, welches im Rahmen von ersten Gesamtkostenbetrachtungen (CAPEX und OPEX dominieren Rohstoffkosten) heute wohl der vielversprechendste Weg zur raschen Kommerzialisierung von Aerogelen darstellt.

Summary français

Nous avons étudié des procédés pour la synthèse d'aerogels de silice à la base de silicate de soude par échange d'ions et achevé une amélioration de propriétés. Gélification, vieillissement, séchage ambient et renforcement de la structure mécanique ont été combinés une analyse de coûts de production. Dans une première étape, la gélification et le vieillissement ont été optimisés: le mécanisme de gélification suivant l'analyse de la taille des particules a été élucidé par diffusion de lumière dynamique (DLS). En outre, la croissance des particules a été modélisée et les résultats sont en bon accord avec nos experiments. Dans une seconde étape, le processus d'hydrophobisation a été analysé puisque un hydrophobization suffisante des surfaces internes d'un gel de silice est indispensable pour le séchage de solvant à pression ambiante. Nos résultats ont enfantés une technologie améliorée pour la production des aérogels à base de silicate de soude par séchage ambiant.

Les aérogels de silice sont fragiles ce qui nécessite un renforcement mécanique pour les produits commerciaux. Ceci est basé sur soit des objets macroscopiques (par exemple, des matelas de fibres) ou en utilisant des principes microscopiques (par exemple un modification chimique). Plusieurs voies différentes pour le renforcement mécanique ont été examinés au cours de nos travaux: **a**) les biopolymères pectine et chitosane ont démontrés une excellente compatibilité avec des solutions aqueuses de silicate de soude. Dans ces deux systèmes, les proprietés des aérogels hybrides formés ont été étudiés systématiquement en fonction du pH et du chargement du biopolymère. Les gels ont été préparés par échange de solvant et hydrophobizés et séchées par la méthode CO₂ supercritique. La microstructure, les propriétés hydrophobes, la conductivité thermique et les propriétés mécaniques ont été systématiquement analysées et les résultats ont étés publiées. **b**) Pour démontrer la faisabilité technique de solutions plus proches à des produits d'isolation à aérogel, des matelas fibreux avec aerogel de silics ont également été préparés à partir de matelas en polyester (PES). Après des developments persistants sur les procédés d'échange et de séchage de solvants, nous avons enfin pu produire des matelas composites à base de silicate de soude. Ces composites présentent une mécanique nettement meilleure par rapport à des aérogels de silice pure mais en même temps la faible conductivité thermique est maintenue. Ces composites présentent des propriétés thermomécaniques similaires à ceux produits à base de TEOS.

Finalement, nous avons éffectué une analyse des coûts pour la production d'aérogels à base de silicate de soude et compare cette méthode à ceux connue à base de TEOS. Ce modèle prend en cômpte les coûts des matières premières, l'amortissement des investissements (CAPEX) et des dépenses d'exploitation (OPEX). Bien que l'utilisation de silicate de soude réduit les coûts des matières premières par rapport au précurseur TEOS, cet avantage est compensé par un CAPEX plus élevé suite à une complication du procédé de l'échange d'ions. Des activités de développement parallèles dans notre groupe à base de précurseurs TEOS ont fait émerger la découverte d'un procédé "one-pot" qui limite l'utilisation de solvants proche au minimum théorique (1m³ de solvant pour 1m³ d'aérogel). Le résultat est une réduction drastique de CAPEX en combinaison avec une forte réduction des coûts de retraitement des solvants et de travail mauel. Malgré des résultats intéressants dans ce projet avec le silicate de soude (600 CHF/m³ pour une capacité> 100'000m³/a), la méthode "one-pot" à base de TEOS est probablement la moins chère au moment et la méthode la plus prometteuse.

En résumé, le projet BFE "aerogels à base de silicate de soude" a été un succès complet: i) les procédés de gélification / vieillissement et hydrophobization d'aérogels à base de silicate de soude ont été développés et optimisés; ii) des matelas superisolants avec des propriétés thermo-mécaniques comparables à l'état d'art ont été produits; iii) le silicate de soude est un précurseur ideal pour la préparation d'aérogels hybrides biopolymère-silicate; iv) la synthèse de ces aerogels avec un retrait minimal permet des applications spécifiques (membranes). Bien que pour la production de masse le silicate de soude est sans doute éconimique, des développements parallèles ont produit une méthode "one-pot" pour aerogels à base de TEOS de qui minimize l'utilization de solvants. Selon une première modelisation de coûts totals (CAPEX et OPEX dominent les coûts des matières premières) cette route semble la plus prometteuse aujourd'hui pour la commercialisation rapide des aérogels.

Summary english

Sodium silicate based aerogels were successfully synthesized by using ion-exchanged water glass. The gelation & ageing, mechanical reinforcement, ambient pressure drying optimization and cost performance analysis were systematically studied and well documented. The gelation and aging of waterglass based gels has been optimized: the relating mechanism has been systematically studied by analysing colloid size distribution and growth with a dynamic light scanning (DLS) method, and the pH dependant colloids formation and growth were analysed theoretically, which shows good consistency with the experiments results. The hydrophobization process has been optimized. The sufficient hydrophobization of the silica surfaces is a requirement for successful ambient pressure drying. With the optimized hydrophobization process, the feasibility for ambient pressure drying of waterglass based silica aerogel has been demonstrated.

Silica aerogels are inherently brittle materials and commercial products typically require mechanical reinforcement either on the macroscopic (e.g. fiber blankets) or the microscopic (e.g. chemical cross-linking). Several different routes for mechanical reinforcement have been investigated. **a)** Biopolymers of pectin and chitosan display good compatibility with aqueous waterglass solutions, the pH & polymer loading dependent properties of silicabiopolymer hybrid aerogels were systematically investigated. The gels were produced by optimized solvent exchanges, hydrophobization and dried under supercritical and ambient conditions. The microstructural morphology, hydrophobicity, thermal conductivity and mechanical properties were analysed systematically. Two publications correlating to this work were accepted for publication. **b)** In order to determine the technical feasibility for commercially attractive waterglass based aerogel insulation products, commercial available polyester (PES) fibrillary blankets were used for preparing the monolithic aerogel composites. After extensive investigations on the feasibility of ambient drying, PES-silica composites have been successfully produced under ambient condition. These composites achieve improvements in strength compared to pure silica aerogel, whilst retaining the low thermal conductivity typical of silica aerogel. The produced blankets show comparable thermo-mechanical properties to commercially available TEOS based aerogel blankets.

A cost performance analysis is presented in this report by comparing the sodium silicate based and typical TEOS based composite blankets taking into account raw materials cost, depreciation of capital investments (CAPEX) and operation costs (OPEX). The use of waterglass as silica source reduces the raw materials costs compared to TEOS precursors, but this gain is partially offset by the increase in CAPEX by 20-30% due to the necessity for elaborate ion-exchange facilities. In addition, parallel R&D activities at Empa on TEOS based aerogel production processes culminated in the discovery of a one-pot process that minimizes the solvent use to close to the theoretical minimum (1m³ of solvent for 1m³ of aerogel). The result is an additional reduction in CAPEX together with a strong reduction in OPEX as the amount of solvent workup is minimized. Despite a promising economic cost analysis of water glass based aerogels (600 EUR/m³ for a production volume of >100'000 m³/a), our cost model predicts even lower manufacturing cost for the one-pot TEOS which today makes it the most promising way forward towards cost-effective mass production of silica aerogel.

In summary, the BFE Waterglass project has been a full success in may key aspects: i) optimization of gelation and hydrophobization chemistries; ii) demonstrated feasibility of waterglass based insulation composites with thermos-mechanical properties comparable to commercially available TEOS based aerogel blankets; iii) waterglass is an essential silica source for biopolymer-silica hybrid materials; iv) waterglass aerogels can be synthesized with minimal shrinkage, enabling speciality applications (e.g. Knudsen pumps). On the other hand, although waterglass is considered viable for mass production compared to the current state of the art, parallel developments lead to the discovery of a minimal solvent process for TEOS based aerogels that is considered to be of higher commercial viability than waterglass based aerogels (importance of CAPEX and OPEX over raw materials cost) and this route is selected for further optimization.

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2. Executive Summary

Within this project we have developed new reinforced strategies in order to produce mechanically strong super-insulating monolithic aerogel composites from inexpensive sodium silicate precursors by means of an ambient pressure drying processes. The main approaches are based on the sol-gel chemistry of sodium silicate, and the impregnation of 2 bio-derived polysaccharides: chitosan and pectin and 1 commercial polymer blanket: polyester. The gelation and aging, mechanical strengthening, solvent exchange and ambient drying as well as cost performance analysis have been systematically studied. In order to develop a strategy for mass manufacturing mechanically robust aerogels from sodium silicate, several goals of the project have to be achieved.

Goal and Milestones: Four scientific and technical objectives (S&T O) have been defined in the original project application and the aims associated with each phase of chemical & process engineering related aspects were well defined. These general objectives have been achieved through focused development efforts which were also described successively in the corresponding annual reports. This final report contains a collective summary and detailed description of the progress made throughout the project in light of the S&T Objectives / Milestones.

S&T O1. 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.

Milestone 1. The pH influence experiments and relating gelation time and the DLS investigation of the kinetics of the gelation and aging processes are described in this report. The mechanism of the colloids' formation and growth can be explained based on these findings, which provides important insight for improving the practical preparation of sodium silicate based gels. This milestone has been completed as planned (100%).

S&T O2. 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.

Milestone 2. Modification of ion exchanged waterglass by addition of bio- polymer pectin and chitosan to produce silica aerogel composites with high final compressive strength (4 - 35 MPa), high stiffness (2-10 MPa of elastic modulus) and minimal dust release without compromising the thermal superinsulating properties. The bio-polymer silica composites still have to be dried using supercritical CO₂ drying. Ambient drying of biopolymer reinforced waterglass hybrid aerogels dried was also developed, however they are still cracking / breaking upon drying. So far, quasimonolithic blocks / boards cannot be obtained from these materials yet by ambient drying which need further work. For comparison, a silica aerogel composite using a commercially available polyester blanket as a mechanical support based on the sol-gel & silylation chemistry optimized from the S&T O1 and S&T O3 is described in this report. **S&T O3**. Optimization of Solvent Exchange 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.

Milestone 3. A first study on the influence of solvents and silvlation agents on the appearance and properties of ambient dried sodium silicate based aerogels is presented below. A faster and more economical method based on a Single-step Solvent Exchange/ surface Modification (SISEM) process is presented as the most promising route in this report.

S&T O4. 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.

Milestone 4. As planned in the project proposal workplan, cost analysis of the final processing technologies was carried out in the final project year and a summary and comparison of these results with other process chemistries is presented here.



3. Starting point

Aerogels are among the most effective materials known for thermal insulation. With thermal conductivities as low as 13 mW m⁻¹K⁻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 2020¹. Most commercially available aerogels are derived from expensive silicon alkoxides such as tetraethylorthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) and require investment- and labour-intensive supercritical 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. At the time of the project start, our laboratory was focusing exclusively on TEOS based aerogels.

Scheme 1 below summarizes the chemistry of waterglass based gel preparation in comparison with their alkoxide precursor based gel counterpart. Waterglass can be gelled either directly in a single step process by simple neutralization or in a more elaborate two-step process (acidification / ion exchange followed by base addition). In our work we focused primarily on the second route because of the greater freedom processing and morphological control of the resulting gels. Following a necessary solvent exchange into a suitable solvent system, the aged gels are further silylated and dried using either ambient (pure waterglass based aerogel composites) or supercritical drying (monolithic specimens).



Scheme 1: Schematic illustration describing the chemical mechanism of gel network formation using commonly used sodium silicate and alkoxide precursors.

4. Project aims

The main motivation of using waterglass as a raw material is its significantly lower cost when compared with alkoxide based precursors such as TEOS or TMOS. However the use of aqueous waterglass gel systems requires one additional solvent exchange step which is also time and cost intensive. Thus the central development goal of this work is to simplify the solvent exchange and hydrophobization chemistry of waterglass based gels and to improve the resulting aerogel properties by means of parameter optimization studies and mechanical reinforcement.

Four <u>scientific and technical objectives (S&T O)</u> have been defined in the original project application and the aims associated with each phase of chemical & process engineering related aspects were well defined.

S&T O1. 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.

S&T O2. 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.

S&T O3. Optimization of Solvent Exchange 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.

S&T O4. 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.



5. Boundary conditions

With a unique combination of properties such as its ultra-low thermal conductivity, low flammability and vapour open structure, silica aerogel is a very attractive material for building insulation. However, until now, the high manufacturing cost and the brittle nature of silica aerogels have prevented their widespread adoption in the construction sector. As detailed above, the main goal of this project was to investigate the use of waterglass for the production of silica and reinforced silica-polymer hybrid aerogels to alleviate these problems.

It is of critical importance that the hoped for reduction in cost and the improvement in the mechanical properties do not detract from silica aerogel's unique properties. In other words, the unique selling point of silica aerogels should not be compromised by the project developments. Thus, the development of new production routes and new hybrid materials can only lead to commercially viable materials if they fulfil the following criteria:

- Low flammability
- Ultra-low thermal conductivity, below 15 mW/(m K)
- No deleterious effects on the materials toxicity
- Good mechanical stability, ideally with reduced dust release
- Hydrophobic materials to ensure good long term stability in the built environment

6. Concept and Facilities

This work comprises mostly of R&D at the laboratory scale with two major components: i) basic R&D for a gain in know-how on the systems and processes and ii) applied materials and process development for the production of materials with improved properties through a production process that has the potential to be economically viable.

Most of the proposed work was conducted at the laboratory scale within the wet chemistry laboratories at Empa Dübendorf, supplemented with existing characterization methods present at Empa:

- Thermal conductivity measurements using a custom-built guarded hot-plate device
- Particle size distributions using dynamic light scattering (DLS, Malvern Zetasizer)
- Surface area and pore size distribution analysis using nitrogen sorption (BET, Mircromeritics)
- Microstructural characterization using scanning electron microscopy (SEM, FEI Nanosem)
- Spatially resolved elemental analysis with EDX
- Microstructural characterization using transmission electron microscopy (TEM)
- Elemental mapping with EELS
- Humidity uptake in climatic chambers
- Water contact angle measurement device
- Thermogravimetric analysis
- Compressive strength measurements with a Zwick press
- Solid-state NMR spectroscopy for surface chemistry and speciation analysis



7. Methodology

7.1. Understanding gelation and aging of sodium silicate aerogels

The development of waterglass based aerogels requires a fundamental understanding of the colloid formation in waterglass. For the preparation of sodium silicate based aerogels, the Na2O/SiO2 molar ratio, and the silica content (Na₂SiO₃/H₂O ratio) are important parameters as they determine the final silicate and sodium contents of the resulting gels. Based on an initial literature survey, various processing parameters such as acid type, precursor concentration, and perhaps most importantly the presence of residual ions will largely affect the final properties of the aerogel. A first experimental study on the acid type and the concentration of precursors and their influence on the gelation kinetics was performed. A more detailed analysis of colloid formation and growth using dynamic light scattering (DLS) analysis was also undertaken. Finally, we develop and escribe the main results of the 2-step (sodium free, "ion exchanged") waterglass gelation process.

7.2. Mechanical strengthening of sodium silicate gels

We undertook systematic studies on the strengthening of silica aerogel by hybridization with biopolymers. Series of samples with different biopolymer/silica ratios were prepared, in addition to systematic parameter studies related to the gelation pH. The results from the fundamental studies described in 7.1 guide the selection of the chemical and parameter space to be investigated. Produced materials are characterized with a wide range of analytical techniques (see section 6).

7.3. Surface modification and ambient pressure drying

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, alcohols, ketones or acetonitrile. To prepare the gels for ambient drying, hydrophobizytion of surface modification with a "waterproofing agent" such as trimethylchlorosilane, dimethyldichlorosilane, or hexamethyldisilazane is necessary. Within this project, we have optimized the surface modification and ambient pressure drying process for the production of aerogel granulate and also applied to the manufacturing of aerogel boards through systematic parameter studies.

7.4. Cost performance analysis and optimization

For the cost modelling we have developed a simple parameter based model which takes into account the main cost drivers of the aerogel production process which are:

- Raw materials cost
- Write-off / depreciation of capital investment (CAPEX)
- Operation cost (OPEX)
 - o Operating cost of key technical modules (see below)
 - o Solvent recycling cost
 - o Equipment maintenance
 - o Manpower needed for operation
 - o Overhead cost

8. Results and Discussion

8.1. Understanding gelation and aging of sodium silicate aerogels

Adoption of precursors

Two sodium silicate precursors have been used in this work: a commercial available silica sol "Betol KS 307[®] "(Woellner Silikate, Germany) and homemade ion exchanged sodium silicate solution.

The pH of the silicic acid sol (ion exchanged sodium silicate) was around 2.5 - 3.5. As expected, the gelation time of the silicic acid sol was strongly influenced by the pH of the sol. An ideal range of pH for industrial applications, where short processing times are important, is between pH 4.5 and 5.5 with gelation times ranging from just a few minutes to 40 minutes at room temperature. By heating the solutions to 45° C, gelation is much faster, taking less than 5 minutes at pH 4.5 (Figure 1.a).

Betol KS 307 sol with a silica content of 9% takes a very long gelation period, around 40 minutes to gel at 40°C and pH 4.5. This seemed in fact rather long, especially for the further scale-up and production. And we attempted to speed up the gelation by mixing in ion exchanged waterglass. Betol KS 307 gelation could be speeded up with a doping of ion-exchanged sodium silicate (Figure 1.b).



Figure 1: a). The gelation time of ions exchanged sodium silicate b). The gelation time of sodium silicate / Betol mixtures at 40°C with a total silica content of 9%

The most important findings of this study was that Betol KS 307 containing gels exhibited far larger shrinkage than standard silicic acid gels. Although the commercial, sodium-free silica sol Betol KS307 produces nice gels of high transparency, this precursor is not particularly well suited for the preparation



of silica aerogels. We believe that the larger size of the colloids (7nm for KS307) and perhaps the presence of additives lead to a significant alteration in the gel structure when compared to pure silicic acid or alkoxide based two-step gel preparations. As a result, the use of freshly prepared ion-exchanged sodium silicate solution was used as the precursor material of choice for the continuation of this work.

Gel preparation and aging

After gelation and before solvent exchange, gels are typically kept in a sealed container at moderate temperature (40-50°C) for up to 24h for aging. During this process, the gel network will be strengthened by deposition of dissolved silica species from solution which happens preferably in areas of high curvature i.e. at the interparticle necks. As a result, aged gels generally become stiffer and tougher. The systematic optimization of individual process parameters led to an optimized aging protocol for silicic acid based gels which involved aging overnight (12 hours) in water followed by solvent exchanged into ethanol. During aging and ethanol exchange, a typical shrinkage on the order of 10-15% by volume is observed, allowing for easy removal of the gels from the respective molds (containers).

Kinetics analysis of gelation & aging of pure silicic acid sols monitored by DLS

The kinetics of the gelation and aging of ion-exchanged sodium silicate was analyzed by DLS. First off, 3 parallel experiments were carried out by analysing the initial colloid size distribution at different pH values. This proved an effective method for understanding and monitoring the sol-gel process of the silica sols and for optimizing the synthesis strategies in an effort to minimize the thermal conductivity and maximize the mechanical strength of waterglass based silica aerogels and their corresponding composite materials.

Silicic sol samples were adjusted to different pH from 0.5 to 5.0 with dilute ammonia and then instantly measured in the DLS spectrometer (Malvern Zetasizer Nano ZS). Looking at the effect of the sol pH on the particle size distribution of the silica colloids, we can clearly see a continuous shift from small sizes at low pH of 0.5 (Figure 2A) to larger particles at an intermediate pH of 5.0 (Figure 2D). This means that the initial pH of the sol strongly affects the colloid size of the silicic acid solution, but also their aggregation dynamics, which in turn influences the gelation of the silica sol and the final structures of the gels.



Figure 2: Gelation kinetics of silicic acid sol at varying pH values: (A) 0.5, (B) 2.98, (C) 3.9 and (D) 5.0

16/65

From experimental trials, gelation at pH 5.0 always takes about 10 min at room temperature. A further analysis of the structural evolution of the colloidal sol at pH 5 provides valuable insight into the gelation process. After base addition, the colloidal size distribution does not change much in the beginning: Compared with Figure 3A (0 min), there is just a slight redistribution (coalescence) in the trimodal silica sol size distribution. After 10 min, there is a significant increase of the colloid size, which clearly indicates the formation of a larger "superstructure" by aggregation of smaller particles. At this point, the mean particle size is around 500nm and when checking the cuvette, one notices that gelation has already occurred. If we leave the gel inside the cuvette for an additional 10min, (Figure 3D, 20 min), structural features (average hydrodynamic radius) have again grown quite substantially (6000nm).



Figure 3: The gelation kinetics of ions exchanged sodium silicate with varying time of (A) 2 mins, (B) 4 mins, (C) 10 mins, and (D) 20min at PH 5.0

The same gelation study was repeated at pH 3.9. From gelation tests, pH 3.9 sols took a lot longer to gel than their pH5.0 analogs. Looking at the temporal evolution of the particle size distribution (PSD) in the case of a pH 3.9 silicic acid solution, first off, a similar similar trend compared to pH 5 can be detected. Figure 4 again reveal an initial "incubation period", meaning that from 0 to 37 mins, the colloids are quite stable and there is little change in the PSD. At 120 mins, more of the larger clusters or superstructure features become visible (> 1000nm features) but, the sol is still liquid although visibly more viscous. When the sol is kept for 720mins, one notices that the sample now has gelled. As a result, the >1000nm scattering feature increases. In comparison to the pH 5.0 case, we still observe a large fraction of smaller silicate species, indicating that not only gelation but more importantly also silica deposition and aging at pH 3.9 is a lot slower. At pH 5.0, after 20 min most colloidal silica particles were no longer visible in the DLS spectra, which does not mean that they are no longer present but they are masked by the much stronger scattering of the larger structural features. Average particle sizes taken from DLS spectra are also reported in Table below. They indicate a large change in average scatterer size once the sol-gel transition is crossed. Also the numbers indicate that the average colloidal size in a silica sol increases upon neutralization which is common knowledge in sol-gel chemical processes.





Figure 4: Gelation kinetics of Silicic acid sol (ion exchanged sodium silicate) with varying time of (A) 0 mins, (B) 10 mins, (C) 20 mins, (D) 37mins, (E) 120mins ,and (F) 720mins at pH 3.9

Series	PH	Time(min)	Average(nm)
1	0.5	0	24.85
2	2.98	0	38.40
3	3.9	0	39.60
4	3.9	10	36.27
5	3.9	20	35.46
6	3.9	37	38.23
7	3.9	120	44.41
8	3.9	720	237.6
9	5.0	0	228.8
10	5.0	2	395.2
11	5.0	4	342.9
12	5.0	10	456.8
13	5.0	20	6416

Table 1: DLS results of the ion exchanged sodium silicate by varying PH and time



8.2. Mechanical strengthening of sodium silicate gels

The structure of silica aerogels is quite fragile and yet, due to the strong and rigid bonding of the amorphous colloidal SiO_2 building blocks combined with their weaker interparticle necks, the fracture mechanics of silica aerogel materials at higher density tend to exhibit brittle characteristics. Consequently it is generally rather tricky to prepare monolithic gels and aerogels, particularly because of the high strains acting on the gel network during the drying step. When comparing two-step, alkoxide and waterglass based aerogels, the latter are generally weaker. Within this project, the main focus was on preparing biopolymer reinforced hybrid aerogels:

Chitosan / silicic acid composite materials

Low density mesoporous chitosan/silica nanocomposite aerogels were first prepared by cogelation of a chitosan biopolymer in an aqueous silicic acid solution. Waterglass is an ideal precursor for the preparation of biopolymer hybrid gels and aerogels because of the excellent solubility and chemical compatibility of the silica sol and common biopolymers in aqueous solutions. Depending on the gelation pH of the silicic acid sol, the physical properties of the resulting aerogels can be tuned to differ significantly. A silica aerogel reference material which was synthesized at a low pH of 2.5 for example features a very low density and high porosity. Accordingly, this material also shows highly elastic behavior but a comparatively weak skeletal structure (final strength < 1MPa). This is in agreement with our previous DLS study which suggests that even after long aging times, a large fraction of the silica used in the sol is still present in the form of colloidal silica and thus does not contribute to the buildup of a strong network structure. This of course then explains the low density of the resulting materials and also their poor mechanical properties. However by compounding a pH 3-4 gelled silica sol with a chitosan coprecursor, an inorganic-organic nanocomposite aerogel is formed, exhibiting still high mechanical flexibility (strain at rupture >80%) but with greatly increased yield strength (> 7MPa, shown in Figure 7) and without a significant increase in density and thermal conductivity (< 19 mW⁻¹ ·K⁻¹, shown in Figure 9) when compared to the native silica aerogel reference materials. In the presence of chitosan, the gelation times are also significantly reduced and the density of the material is much higher which suggests that the biopolymer effectively traps colloidal silica particles and helps to integrate them into the gel network structure during gelation. In that sense one could speak of a true co-gelation mechanism. The resulting silica-chitosan composites display excellent mechanical and thermal properties which are summarized below:

Influence of the gelation pH on the structure of aerogels.

The nomenclature of the samples is as follows: RefS-X denotes the Reference Silica aerogels gelled at pH=X, ChiS-X-Y stands for the Chitosan-Silica hybrids with chitosan:silica weight ratios of Y:100 and gelled at pH=X.

Sample	SiO ₂ in the sol (w/w%)	Chitosan content (w/w%) ^a	Gelation pH	Gelation time	Density g/cm ³	Skeleton density g/cm ³	Linear shrinkage, Ls (%)	Porosity (%)
RefS_2.5		0	2.5	~160 hrs	0.07	2.12±0.02	18.92	96.7
RefS_6		0	6	1-2 mins	0.13	2.12±0.03	33.24	94.1
ChiS_3_2	6	2	~3-4	12hrs	0.09	2.12±0.07	14.53	96.0
ChiS_3_5		5	~3-4	10hrs	0.08	2.05±0.04	14.45	94.4
ChiS_3_10		10	~3-4	7hrs	0.11	2.01±0.02	15.08	93.8

Table 2: Nomenclature and characterization of aerogels prepared from varying precursors and pHs

a) Expressed in terms of SiO₂ weight loading in the silicic acid sol.

Furthermore, for the silica/chitosan composite aerogels we observe a reduced shrinkage compared to both pH 2.5 and pH 6 reference silica aerogels. This is attributed to a stabilizing effect of the polymer chains which are believed to adsorb onto the silica network structure and increase its strength. The densities of the composites are higher with increasing weight loading of chitosan, but still lower than the pH 6 pure silica aerogel reference sample.

Evidence for the incorporation of the chitosan in the composites was obtained from FT-IR spectroscopic analysis. The spectra of the composite in Figure 5b, show typical amide II region signatures which come from the acetylated residual groups on the chitosan and which are obviously absent in the pure silica spectra. There are seen peaks at 1546 and 1595 cm⁻¹ for protonated and free amine groups on the backbone of chitosan⁹, and in the fingerprint region, the peak in the range of 1100-1150 cm⁻¹ can be assigned as C-N, which is belong to the stretching vibration from amine group of chitosan.





Figure 5: FT-IR spectra (2000-1000 cm⁻¹) for (a) $RefS_{2.5}$ (b) sodium silicate based composite $ChiS_{3.5}$, inset image is a zoomed range of 1400-2000 cm⁻¹

The pH dependent morphology of TEOS based aerogel/composites is well documented in the literature reported¹⁰ and the influence of acidic/basic catalysis on the growth kinetics rather well understood. Transmission Electron Microscopy of the different materials are shown in Figure 6. In agreement with a 'Cluster-Cluster' type growth which is favored under acidic condition¹¹, RefS_2.5 shows a rather highly branched "polymer-like" particle network structure which is consistent with a solgel process controlled by hydrolysis. In the case of RefS_6, the gelation is carried out at higher pH (catalyzed by NH₄OH addition) and the structure formation is governed by condensation reactions, thus following a 'Monomer-Cluster' aggregation mechanism which leads to generally more dense structures. As mentioned before, the difference in the apparent densities of the two reference materials is attributed to a more complete deposition of the silica onto the network in the base catalyzed case (Ref_6) but which is also promoted by the biopolymer phase. In the acid catalyzed analogue RefS_2.5, significant amounts of silicic acid must still remain dissolved (in the form of colloids) at low pH and are hence removed from the system during the solvent exchange step after gel aging. The difference in shrinkage alone does not explain the factor of two differences in density of the two reference silica aerogels. RefS_6 is mechanically much stronger but also more brittle (higher E-modulus, lower strain at rupture, see Figure 7). With addition of 5% w/w chitosan to the silicic acid, the final pH of the sol mixture is around 3.7 – in this case a highly regular structure with rather small pores (TEM, Figure 6c), indicating the formation of a SiO₂ clusters that are nanoscopically linked with the biopolymer.



Figure 6: TEM images and BET isotherm curve for (a) (b) silica aerogel, RefS_2.5 (c) (d) silica aerogel, RefS_6.3 (e) (f) SiO₂-chitosan composite aerogel, ChiS_3_5

The surface area and average pore sizes of the aerogel/composites were obtained by BET analysis. Due to the mechanical deformation experienced by the aerogel samples in the desorption branch of the capillary condensation range¹², which is effectively a second drying of the gel from the liquid nitrogen pore fluid including a deformation with "springback" ¹³, volume (V_{pore}) and average pore diameter (D_{pore}) values determined for silica aerogels using the Barret-Joyner-Halenda (BJH) or density functional theory (DFT) cannot be trusted. Nevertheless, those values are given in Table 3 for comparison. Average values for V_{pore} and D_{pore} were calculated from the density and specific surface area of the respective aerogel materials (see equations 1 and 2). *RefS_2.5* has almost half the density and thus twice the pore volume and more than three times the average pore size (D_{pore}) when compared with the pH 6 gelled *RefS_6*.



$$V_{pore} = \frac{1}{\rho} - \frac{1}{\rho_{skeleton}}$$
(1)

$$D_{pore} = \frac{4V_{pore}}{S_{BET}}$$
(2)

	Nitrogen Adsorption	Porosity analysis based on Nitrogen Adsorption							
Samples	BET	microporosity		mesoporosity		Macroporosity		Total	
	surface area (m²/g)	ml of N ₂ /g	%	ml of N ₂ /g	%	ml of N ₂ /g	%	porosity ml of N ₂ /g	
RefS_2.5	441	0.129	5.5	0.813	34.6	1.408	59.9	2.349	
RefS_6	745	0.124	4.1	2.229	74.4	0.641	21.4	2.994	
ChiS_3_5	530	0.178	10.9	1.402	85.8	0.054	3.3	1.634	

Table 3: NL-DFT analysis of the pore structure of silica aerogels and composite

The N₂ adsorption–desorption isotherms are shown in Figure 6. The isotherm of RefS_2.5 is close to a type 4 isotherm, however the amount adsorbed around a relative partial pressure of 0.1 is only around 20% of the total uptake, being consistent with the micropores being the minority species in both the silica and the hybrid aerogels. The majority of the uptake takes place between relative pressures of 0.1 and 0.95, indicating a majority of mesopores. RefS_6 features a similar adsorption curve but a more narrow hysteresis loop (less deformation during liquid N₂ evaporation in the desorption branch) which is directly connected to the smaller pore sizes and higher rigidity distributed pore sizes in the gel structure. The 5% w/w chitosan loaded silica nanocomposite shows a significantly higher (around 40% of the total) uptake at 0.1 and still a majority of mesopores (uptake between 0.1 and 0.95). This increase in early nitrogen sorption is attributed to the direct interaction adsorption onto the biopolymer phase. More importantly, the composite material, despite its lower density compared to RefS_6, displays virtually no hysteresis which suggests that it can resist the internal forces during the "liquid nitrogen drying" rather effectively. The hysteresis for a pure silica aerogel of density around 80-120 g/cm³ would, in a first approximation, be expected to lie somewhere in-between the ones of the silica reference materials shown in Figure 6b and 6d. The significantly reduced hysteresis can thus be taken as indirect evidence for the strengthening of the silica aerogel structure by the chitosan biopolymer.

Sample ID	BET surface area	V _{pore}	D _{pore}
	(11179)	(cm³/g)	(nm)
RefS_2.5	441	13.91	126.2
RefS_6	745	6.71	36.0
ChiS_3_5	530	8.30	62.6

Table 4: BET specific surface area, pore volume and average pore diameter of aerogels.

Structure-property effects in SiO₂-chitosan nanocomposite aerogels.

The nanocomposite obtained from a sol containing 5% w/w chitosan (gelation at pH 3.7) displayed a comparable but higher V_{pore} and D_{pore} than the *RefS_6*, in agreement with the porosity discussed previously (see Table 4). The D_{pore} of *RefS_2.5* is 126.2 nm, and thus already above the mean free path of ambient air, underlined by both, the extremely weak network structure and rather high thermal conductivity of the sample. The pore size of *RefS_2.5* also agrees qualitatively with the SEM images Figure 8a. The average pore diameter (D_{pore}) of the *RefS_6* and composite *ChiS_3_5* is about half of that of *RefS_2.5* and thus remains well below the mean free path of the air under ambient conditions (70 nm @1 atm, 298K ¹⁴), suggesting that the materials should display a very low gas conductivity ¹⁵.

The mechanical properties of the aerogel materials were measured by uniaxial compression testing of cylindrical samples. Typical stress (σ) – strain (ϵ) curves are shown in Figure 7a. When comparing the two silica aerogel reference materials prepared from identical sols but at different pH values, the lower density, acid catalyzed gel (pH 2.5) analogues show a very low elastic modulus (E) but a very high compressibility, which is in qualitative agreement with our previous study on polyethoxydisiloxane based aerogels¹⁶. Corresponding elastic moduli / compressive strength / strain at rupture values for RefS_2.5 and RefS_6 are 0.15 MPa/ 1.40 MPa / 76 % and 1.57 MPa/ 0.68 MPa / 35%. While the reference silica materials gelled at a higher pH of 6.3 exhibited a roughly 10 times higher elastic modulus, the improvement of the stiffness led to a decreasing of strain at fracture to 35%. The evolution of σ_{max} and E of the composites reinforced with varying amounts of chitosan polymers are plotted in comparison with the reference materials in Figure 7b. The 2% and 5% w/w chitosan nanocomposites show lower elastic moduli (the materials are more brittle) and fracture strengths compared to the plain RefS_6 aerogel. However at 10% w/w chitosan content, one observes a dramatic increase in all mechanical properties: ChiS_3_10 resists up to 7.3 MPa at 80% strain. In the magnified $\sigma - \varepsilon$ curve (Figure 7a, insert) one notices that the composite keeps its elastic behaviour for ε < 30 %. The significant improvement in fracture strength with rather high stiffness again corroborates the function of a network strengthening agent of the chitosan biopolymer.





Figure 7: Mechanical properties of the reference aerogels and composites with 2%, 5% and 10% w/w of chitosan: (a) compressive stress (ϵ) versus compressive strain (σ) for the reference and composite aerogels (b) compressive modulus (E) and compressive strength (σ_{max}), Red solid-line with • compressive strength, Blue dotted-line with • elastic modulus.

Electron microscopy was used for a qualitative discussion of the gel structures of silica aerogel and nanocomposite materials. In agreement with the BET average pore size value of 125nm, *RefS_2.5* displays a significant number of macropores (up to several 100nm) and smaller silica building blocks, whereas *RefS_6* is composed of rather large size silica clusters. The silica-chitosan nanocomposite aerogels all feature similar and rather dense particle aggregate textures but with very small cluster sizes (even smaller than in the case of the *RefS_2.5*) which is consistent with a gelation triggered in a more the acidic sol. However, despite the higher gelation pH of 3.7, the chitosan nanocomposites have smaller cluster sizes than even the pH 2.5 silica aerogel which suggests that the chitosan sensibly affects the structure formation of the gel structure at the nanoscopic level. Furthermore, from the SEM images in Figure 8 c, d, and e, the cluster size seems rather independent of chitosan loading. With only 2% chitosan loading, *ChiS_3_2* shows still rather large pores between the network clusters but with increasing amounts of polymer, the chitosan-silica aerogel develops a denser and more fused particle network morphology. Those combied findings suggest the following gelation mechanism for the nanocomposite materials:

- At the sol stage, the colloidal silica primary particles are stabilized / coated by the chitosan biopolymer which acts as some sort of capping agent and is active already at lower weight loadings (2%) and further controls the structure formation of the secondary particles / clusters. The interaction between silica and chitosan chemistries at the particle surfaces is most likely mediated through a siloxane adsorption layer on the biopolymer but requires additional clarification.
- ii) During gelation, a network secondary particles / is forming which is effectively 'glued' together by the chitosan biopolymer and the amount controls the packing density of the clusters. There is a minimal amount of chitosan needed (10% w/w) to produce a mechanically robust silicachitosan percolation network.



Figure 8: SEM images of the Chitosan-SiO₂ hybrid aerogels, (a) silica aerogel, $RefS_{2.5}$ (b) silica aerogel, Ref_{6} (c) composite aerogel with 2% chitosan, $ChiS_{3.2}$ (d) composite aerogel with 5% chitosan, $ChiS_{3.5}$ (e) composite aerogel with 10% chitosan, $ChiS_{3.10}$

Thermal conductivity of SiO₂-chitosan nanocomposite aerogels.

If one is to envision applications of hybrid silica biopolymer aerogel composites for thermal insulation, their thermal transport properties are of great importance. Ambient thermal conductivities of square shaped monolithic specimens of 5cm × 5xm × 0.8 cm were measured on a custom built guarded hot plate device at 25°C and 50 % R.H. ¹⁷. RefS_2.5 reveals a rather high thermal conductivity of 17.4 × 10^{-3} W/(m K) when compared to the RefS_6 with an customary 14.2×10^{-3} W/(m K), which is consistent with the study of density versus lambda reported in the literature¹⁶. As for the composites, the hybridization with chitosan causes a moderate increase in thermal conductivity, but with increasing chitosan loading, there is no significant effect on the measured thermal conductivities. In conclusion, even the very robust composite aerogels ChiS_3_10 retain their super-insulating properties. Given the fact that all silica-chitosan nanocomposites have moisture uptake at 50 % R.H. between 2 and 3 %, which is roughly ten times higher than that of the hydrophobic silica reference materials (see Figure 10), it seems likely that the increase in thermal conductivity is to a large extent due to a higher solid conductivity hybrid network structure due to the adsorbed water.





Figure 9: Thermal conductivity of the aerogels, from left to right: silica aerogel, RefS_2.5; silica aerogel, RefS_6.3; composite aerogel with 2% chitosan, ChiS_3_2; composite aerogel with 5% chitosan, ChiS_3_5; composite aerogel with 10% chitosan, ChiS_3_10.

Humidity-uptake and thermal stability of the SiO₂-chitosan aerogels.

When used in thermal insulation, durability is a key feature. If the material is not hydrophobic enough or absorbs too much water during service, this can lead to chemical degradation, structural changes, finally leading to loss of insulation performance and even disintegration of an installed component. For this reason the relative moisture uptake of previously oven dried samples was measured by reweighing them after exposure to 30, 50, 80 and 98 % relative humidity at 25°C for 7 days, respectively. The sample weight was repeatedly monitored at days 5, 6 and 7 counting from the first exposure inside the high humidity climate chamber.



Figure 10: Humidity uptake of the (a) silica aerogel, *RefS_6* (b) composite aerogel with 2% chitosan, *ChiS_3_2* (c) composite aerogel with 5% chitosan, *ChiS_3_5* (d) composite aerogel with 10% chitosan, *ChiS_3_10*. Reaching of equilibrium conditions were verified by reweighing the samples once daily during the last three days.

Because chitosan is a hydrophilic polymer, decorated with polar -OH and -NH₂ surface functional groups on the backbone, one certainly expects a significantly higher water uptake when compared to a hydrophobic silica aerogel reference materials. Furthermore, chitosan cannot be directly hydrophobized during the HMDZ modification step. Nevertheless, in comparison with the nonhydrophobized, supercritically dried hydrophilic silica aerogel (almost 100% moisture at 98 % RH) and commercial chitosans (in high humidity conditions (RH > 60%), water molecules were found to penetrate very intensively through chitosan chains, the reported water binding capacity ranging from 355 to 805 % ¹⁸⁻¹⁹), the composite aerogels show much lower and no remarkable difference in humidity uptake at 98 % RH (14.0 % for the 2 %, 16.1 % for the 5% and 20.3% for the 10% chitosan loading composites). The weak dependence of humidity uptake on the chitosan loading can be explained by two hypotheses, namely: i) the chitosan itself is hydrophobized effectively (most probably through a conformal SiO₂ layer deposited from silica species in the solution during gelation / aging) and does itself not contribute significantly to the water uptake but rather inhibits the complete hydrophobization of the silica network structure by the HMDZ through polar interactions with the silica network or ii) that the chitosan is not hydrophobized very effectively and is in fact responsible for the increased water uptake but with increasing concentration forms thicker hydrogen bonded chitosan "nanoglue phases" which are conformally covering the silica structure. At higher biopolymer content, one expects a significant loss of polar character (large hydrogen bonded biopolymer network, reduced dipole moment through extensive H-bonding) when compared with a "monolayer type adsorption layer on silica at low loadings where the biopolymer -OH and -NH₂ groups are more readily accessible for moisture uptake.

Clearly, the humidity uptake behavior and its connection to the observed thermal conductivities must be further investigated. Comprehensive dynamic vapor sorption studies covering also higher relative humidity will be the topic of a follow-up project.





Figure 11: Contact angle of the (a) silica aerogel, Ref_6 (b) composite aerogel with 2% chitosan, $ChiS_3_2$ (c) composite aerogel with 5% chitosan, $ChiS_3_5$ and (d) composite aerogel with 10% chitosan, $ChiS_3_10$.

The results from the water uptake studies were also directly compared with water contact angle measurements. The pristine silica aerogel and composite aerogels with 2 % w/w chitosan show very high water contact angles of 134.5° and 134.1°, respectively. With further increase in chitosan loading, the 5% and 10% composites are significantly losing their hydrophobic surface properties with respective contact angles of 105.8° and 63.5°. This result is at first rather surprising because nanoscale roughness effects alone cannot explain such a sizeable difference between contact angle and water uptake. However it supports the hypothesis ii) of poor hydrophobization and the formation of thicker nanoglue layers at higher loadings which was discussed above.



Figure 12: TGA of the (a) silica aerogel, $RefS_{2.5}$ (b) composite aerogel with 2% chitosan, $ChiS_{3_2}$ (c) composite aerogel with 5% chitosan, $ChiS_{3_5}$ and (d) composite aerogel with 10% chitosan, $ChiS_{3_10}$.

The thermal stability of both aerogel and nanocomposite samples was analyzed by thermogravimetric analysis (TGA). A distinct weight loss in the reference *Ref_2.5* can be observed around 500°C, which is consistent with the deterioration of the hydrophobic sites (loss of methyl / trimethylsilyl groups) from the silica aerogel backbone which is well documented in the literature ²⁰⁻²¹. This suggests that hydrophobic silica aerogels have an upper bound service temperature around 500°C. The corresponding chitosan hybrids *ChiS_3_2*, *ChiS_3_5* and *ChiS_3_10* on the other hand show a second peak around 330°C, which is attributed to the degradation of the chitosan biopolymer itself. Hence service temperature above 300°C are not recommended for the silica chitosan nanocomposite materials.



Pectin / silicic acid superinsulating hybrid aerogels

After the reinforcement of chitosan, the hybrids display a promising thermo-mechanical performance, but the serious deformation of the hybrid, which was mostly led by the intensive H-bonds formed between $-NH_2$ of chitosan and -OH of silica aerogels, motivate us to use polymers from the same family but less active functional groups.

Using one-pot mixing of dissolved pectin with silicic acid, we have prepared monolithic, lightweight $(0.12 - 0.18 \text{ g/cm}^3)$ silica-pectin hybrid aerogels that display versatile morphologies and properties as a function of the sol pH. The hybrids synthesized at pH=1.5 exhibit minimal dust release (Figure 25.c), a high plastic deformation range with no rupture until at least 80% strain, and a greatly increased compressive strength (up to 27.5 MPa, Figure 25.a) and Young's modulus (up to 9.4 MPa, Figure 25.b). In contrast to other reinforcement strategies, the improved mechanical performance does not come at the cost of an increased thermal conductivities (λ =14.2-17.0 mWm⁻¹K⁻¹, Figure 25.d). The details have been presented in the annual report of 2013 and 2014.

Influence of silica and pectin concentration on the properties of SiO₂-pectin aerogels

The first experiment was carried out to figure out the influence of the silica and pectin concentration on the structural characteristics and properties of the hybrids, the gelation pH was around 5, the nomenclature of the samples is as follows: RS-Z denotes the Reference Silica aerogels with silica concentration of Z%, PecS-Z-Y stands for the Pectin-Silica hybrids with silica concentration of Z% and pectin:silica weight ratios of Y:100.

Silica concentration (w/w %)	Pectin concentration of the SiO ₂ (wt %)	Nomenclature
5	0	RS-5
8	0	RS-8
10	0	RS-10
8	5	PecS-8-5
8	10	PecS-8-10
8	20	PecS-8-20
10	5	PecS-10-5
10	10	PecS-10-10
10	20	PecS-10-20

Table 5: The nomenclature used for the pectin-silica aerogel composites



Figure 13: Pectin reinforced sodium silicate based aerogel composites, from left to right RS-10 reference, PecS-10-5, PecS-10-10, PecS-10-20

SEM images of the hybrid aerogels are given in Figure 14 and show the nanometer sized silica particles and nanoporous structure variation of the samples with different amounts of pectin, the silicic sol RS-10 with 10% silica has more dense structure, the pectin polymer structures cannot be detected in the images, but RS-8 silicic sol has porous and loose structure, the cross-linked pectin polymers can be detected, which are embedded in the silica structure and hold the silica colloids forming a whole composite.





Figure 14: SEM of sodium silicate based aerogels composites reinforced with varing amount of pectin (a) RS-10 (b) PecS-10-5 (c) PecS-10-10 (d) PecS-10-20 (e) RS-8 (f) PecS-8-5 (g) PecS-8-10 (h) PecS-8-20

In order to check the pectin dispersion in the aerogel composite samples, the EDS-X spectra was used to check the carbon and silicon elements dispersion. The samples were analyzed by energy diffractive spectroscopy coupled with SEM in back-scattered electrons mode. The spectra are extremely similar for all samples: the Silicon K α peak at 1.74 Kev and the oxygen K α peak (0.525 keV) are of high intensity, and a smaller carbon peak at 0.277 Kev shows the presence of the organic phase. The relative intensity of the silicon peak as compared to the carbon peaks means that the pectin is mostly coated by silica, and it accounts for the low concentration of pectin. We can also notice traces of NaCI. The localized nature of the analysis and the low variation in pectin concentration does not allow for precise characterization of pectin contents with this method, as shown by the large difference observed between measured and theorectical carbon wt% in Table 6.



Figure 15: EDS spectra of pectin-sodium silicate based aerogels, (a) PecS-10-5 (b) PecS-8-5 (c) PecS-10-10 (d) PecS-8-10 (e) PecS-10-20 (f) PecS-8-20. Scale bar (in red) is 900µm.

Spectre	C (wt%)	Ctheor (wt%)	O (wt%)	Na (wt%)	Si (wt%)	Sitheor (wt%)	CI (wt%)
PecS-10-5	13,85	4,84%	48,11	0,12	37,62	40,48%	0,3
PecS-8-5	8,47	6,12%	47,59	0,27	41,86	38,76%	1,8
PecS-10-10	15,05	8,51%	45,85	-	38,9	35,55%	0,2
PecS-8-10	13,93	10,42%	46,24	-	39,14	32,98%	0,7
PecS-10-20	14,78	13,68%	35,37	-	49,03	28,58%	0,83
PecS-8-20	12,34	16,05%	56,59	0,23	30,35	25,40%	0,49

Table 6: wt% of each element present in the samples, as evaluated by EDS. C_{theor} and Si_{itheor} are calculated from the known pectin and Si concentrations in the system

The Hydrophobicity analysis of pectin / silicic acid composite materials was shown in Figure 16. The physical properties of the hybrids were listed in the Table 7.



Figure 16: Contact angle test for pectin-sodium silicate based aerogels, (a) RS-10 (b) RS-8 (c) PecS-10-5 (d) PecS-8-5 (e) PecS-10-10 (f) PecS-8-10 (g) PecS-10-20 (h) PecS-8-20

Sample	Pectin concentration, wt%	Densityª (g/cm3)	Density ^b (g/cm3)	Water contact angle (°)	water uptake (%wt)
RS-10	0	0.110	0,1011	141,3	1,25%
RS-8	0	0.099	0,1025	137,4	0,47%
PecS-10-5	0.61	0.109	0,1110	148	1,36%
PecS-8-5	0.61	0.106	0,1143	139,1	1,12%
PecS-10-10	1.22	0.126	0,0977	150	0,70%
PecS-8-10	1.22	0.107	0,1129	139	0,96%
PecS-10-20	2.4	0.131	0,1820	146,7	1,95%
PecS-8-20	2.4	0.124	0,1103	136,2	6,26%

Table 7: Densities, water contact angles, and water uptake (in %wt) for Pectin-sodium silicate hybrid gels

a. Density measured by volume and mass of the gels

b. Density measured by powder pycnometer

The results of the mechanical tests including compressive strength, elastic modulus and fracture strain are shown in Figure 17.



Figure 17: Mechanical testing of the NCS scaffold supported aerogel hybrids. The series containing from left to right: (A) E modulus and compressive strength, and (B) Fracture strain and density of the composites.

Ion exchanged sodium silicate aqueous solutions of 10%, 8% and 5% silica concentrations (represented as w/w of SiO₂ to solution). Various amounts of pectin, from 0% (reference) to 20%, represented as %wt of the mass of sodium silicate in the solution. As compared with RS-8 reference, the hybrids reinforced



by pectin presents no improvement or even negative affections. While for RS-10 samples, the pectin reinforced composites shows a promoted compatibility with silica, an improvement can be observed for the hybrids with pectins, which have elastic moduli (1.45 MPa of the PecS-10-20) and compressive strength (1.8 MPa of the PecS-10-20) greatly increased over those of plain silica aerogel (0.34 MPa and 26.05 kPa), and relating properties can be found to increase exponentially with cellulose loading. Moreover, an enhancement of flexibility can be detected as well, when combined with increasing amount of pectins, which can withstand increase amounts of fracture strain without failure.

The thermal conductivities of samples are presented in Figure 18.



Figure 18: Thermal conductivity of the sodium silicate and relating pectin reinforced aerogel hybrids measured by guarded hotplates.

For both RS-10 and RS-8 samples, with the addition of 5% pectin, lambda is going down, which means the gas conductivity is reduced, because from the SEM, we can see pure waterglass aerogel normally has big pores formed inside, the small amounts of polymer can make more dense of the structure, then with increasing amounts of pectin, the lambda is going up, which might be explained as skeletal conductivity begin to dominate, introducing more pectin can form a more dense structure.

Influence of sol pH and pectin concentration on the performance of the aerogel hybrids

After a systematical research on the silica and pectin concentration, it was found that the gelation pH plays a significant role on the structure and final performance of the silica – pectin hybrids. Then further study was put on the cogelation pH. The nomenclature of the samples is as follows: RS-X denotes the Reference Silica aerogels gelled at pH=X, PecS-Z-X stands for the Pectin-Silica hybrids with pectin:silica weight ratios of Z:100 and gelled at pH=X.

Ion exchanged sodium silicate solutions (silicic acid) is stable at pH < 3 (gelation time at pH = 1.5 is about 14 days), but gels within minutes at pH > 4. HM pectin solutions with a degree of esterification of $_{38/65}$

72 to 74 % require an acidic medium ($2 \le pH \le 3$) to gel in about 3 - 7 minutes²²; no gelation occurs above pH 3.5 and gelation is very slow below pH 2.0. In this study, we prepared hybrid pectin-silica gels at pH 1.5, with very slow gelation for both components, pH 3.0 with gelation of HM pectin within 10 minutes followed by slower gelation of the silicic acid phase²², and at pH 5.0 with no gelation of pectin but rapid gelation of the silica sol within 10 minutes²³. The nomenclature and physical properties of the hybrids were listed in Table 8.



Table 8: Bulk (ρ_{bulk}) and skeleton ($\rho_{skeleton}$) density, porosity (ε %, Eq. S1), specific surface area (S_{BET}), pore diameter $D_{pore, BJH}$, pore volume V_{pore} , pore diameter D_{pore} and water contact angle of the synthesized aerogels.

Sample	Cpectin	ъЦ	Gelation	ρ _{bulk}	$ ho_{skeleton}$	c%	S_{BET}	D _{pore, BJH}	V _{pore}	D _{pore}	Contact
Sample	(wt %)	рп	time (min)	(g/cm ³)	(g/cm ³)	(g/cm ³)		(nm)	(cm ³ /g)	(nm)	angle
RS-1.5	0	1.5	19340	0.10±0.03	2.12±0.04	95	597	14	9.5	64	148
RS-2.5	0	2.5	11520	0.11±0.03	2.12±0.04	95	583	14	8.6	59	148
RS-5	0	5	20	0.13±0.02	2.12±0.03	94	745	11	7.2	39	142
PecS-5-1.5	5	1.5	7200	0.13±0.01	1.95±0.03	92	827	11	5.9	29	135
PecS-5-3	5	3	600	0.13±0.02	1.89±0.02	93	796	12	7.5	38	146
PecS-5-5	5	5	15	0.13±0.02	2.06±0.03	94	766	16	7.2	37	131
PecS-10-1.5	10	1.5	4320	0.16±0.01	1.74±0.01	91	837	11	5.7	27	130
PecS-10-3	10	3	510	0.13±0.05	1.94±0.02	92	835	13	7.1	34	74
PecS-10-5	10	5	12	0.14±0.05	2.05±0.02	93	749	13	6.7	36	73
PecS-20-1.5	20	1.5	1728	0.19±0.01	1.87±0.03	90	763	10	4.8	25	134
PecS-20-3	20	3	300	0.16±0.03	2.05±0.03	92	772	12	6.0	31	40
PecS-20-5	20	5	5	0.14±0.05	2.04±0.04	93	752	14	6.7	35	25

Scanning electron microscopy (SEM) reveals a 3D open-porous network consisting of particle aggregates of tens of nanometers in size; fibrous structure can also be detected for some formulations (Figure 19). Neat silica aerogels are composed of aggregates of colloidal silica particles linked together in a pearl necklace type network structure²⁴. Pure pectin aerogels display a network of polymer "strands" or "nano-fibers" of a few tens of nanometers diameter with primarily mesopores and small macropores^[19]. The hybrids gelled at pH 1.5 do not show evidence of visible pectin "fibers" at all studied pectin concentrations (Figure 19 a, d, g). It should be noted that at this pH pectin most probably did not completely gel within the preparation time. Hybrid aerogels prepared at pH 3 and pH 5 show a coarser microstructure compared to that of aerogels prepared at pH 1.5 for a given pectin loading. Aerogels with pectin concentrations above 10 wt% at pH 3 and 5 exhibit pectin "nano-fibers". At the highest pectin concentrations and pH, the material segregates into biopolymer-rich and silicarich domains (compare Figure 19 b and c). For all investigated acidities, increasing the pectin content leads to finer microstructures with smaller silica secondary particles and pores, in agreement with the pore size analysis (Table 8, Figure 21).



Increasing phase separation

Figure 19: SEM images of the reference silica (0 wt% pectin) and pectin-silica hybrid aerogels prepared at various pH and pectin concentrations (scale bar: 500 nm, inset numbers are water contact angles).









Figure 20: Nitrogen sorption isotherms for the reference silica and pectin-SiO₂ hybrid aerogels (a) RS-2.5, PecS-20-1.5, PecS-10-1.5 and PecS-5-1.5, (b) PecS-20-3, (c) PecS-20-5, (d) PecS-10-3, (e) PecS-10-5, (f) PecS-5-3 and (g) PecS-5-5.



Figure 21: (a) Specific surface area, (b) pore volume (Eq. S2) and (c) average pore diameter (Eq. S3) versus pectin loading under different pH.



The differences in microstructure of the neat silica versus hybrid aerogels are clarified by highresolution transmission electron microscopy (HRTEM). Pure silica aerogel displays a typical pearlnecklace structure with distinct quasi-spherical silica nanoparticles of 2-5 nm in diameter (Figure 22d1d3). The co-gelation with pectin at pH 1.5 leads to a drastic morphological change of the network structure (Figure 22 a1-a3) towards a structure free of necks and with thicker and continuous struts. As it will be shown later, the formation of a polymer-silica hybrid with such a microstructure leads to a mechanically strong hybrid aerogel. The hybrid gelled at high pH displays an inhomogeneous microstructure (Figure 22 b and c), consistent with the phase separation observed by SEM (Figure 19 c).The PecS-20-1.5 hybrid aerogel features pore sizes on the order of a few tens of nanometers with pore wall thicknesses around 10 nm.



Figure 22. HRTEM images of (a1-a3) PecS-20-1.5 hybrid aerogel, (b1-b3) PecS-20-3 hybrid aerogel, (c1-c3) PecS-20-5 hybrid aerogel and (d1-d3) RS-5 reference silica aerogel.



Figure 23: HRTEM and EFTEM images of (a) reference silica aerogel and its corresponding elemental maps of (b) Si and (c) C, and (d) PecS-20-1.5 hybrid aerogel and its corresponding elemental maps of (e) Si and (f) C. The carbon signal observed in (c) arises from the carbon film rather than from the silica aerogel.

The reference silica aerogel sample displays strong Si signals (Figure 23 b) and a weak but homogeneous C signal, which could be from trimethylsilyl (TMS) group and surface ethoxy groups (\equiv Si-O-CH₂-CH₃) ²⁵. The pectin-silica composite displays a much stronger, homogeneously distributed C signal arising from pectin, ethoxy and TMS (Figure 23 f).

We employ ${}^{1}\text{H} - {}^{29}\text{Si}$ hetero-nuclear correlation (HETCOR) solid-state NMR spectroscopy to confirm the homogenous distribution of silica and pectin in the PecS-20-1.5 sample (Figure 24). The spectrum displays the typical peaks of silylated silica aerogel 25 . In addition, there is a correlation between the pectin protons (at 5 to 7 ppm) and Q³ (Qⁿ is a tetrahedral Si atom with n bridging oxygen). The relative intensity of pectin protons is higher in the ${}^{1}\text{H}$ projection of the ${}^{1}\text{H}$ - ${}^{29}\text{Si}$ HETCOR spectrum compared to the quantitative ${}^{1}\text{H}$ spectrum. This is similar to the ethoxy (CH₂) protons where a covalent \equiv Si-O-CH₂bond exists. Compared to the spectrum of the pH 1.5 hybrid, these pectin-Q³ cross peaks are less intense and absent in the spectra of the pH 5 hybrid and a macroscopic pectin-silica mixture, respectively. Thus, although the ${}^{1}\text{H}$ - ${}^{29}\text{Si}$ HETCOR spectrum cannot, by definition, provide direct evidence for covalent silica-pectin bonds, it does provide unambiguous evidence that pectin and silica are interspersed on the molecular scale for samples gelled at low pH. The fine dispersion of pectin and silica is also evident from the TEM element maps (Figure 23).





Figure 24: ¹H-²⁹Si hetero-nuclear correlation NMR spectrum for PecS-20-1.5.

The pronounced alteration of the microstructure with pectin addition dramatically changes the physical and mechanical properties (Figures 25 and 26). In contrast to reference silica aerogels, hybrid aerogels prepared at pH 1.5 can sustain uniaxial compression to at least 80% strain without rupture. The compressive elastic modulus (*E*), final strength (σ_{max}) and fracture strain (ε_i) strongly depend on pectin loading and gelation pH, with the most significant improvement at pH 1.5 (Figure 25a, b). The mechanical reinforcement at pH 1.5 is also evident from the BET isotherms (Figure 20): the hybrid materials present almost no mechanical deformation induced hysteresis, which indicates that the hybrids maintain their morphological integrity during the liquid nitrogen desorption ¹⁶.

Another major advantage of the pectin-silica hybrids is their limited dust release, lower by a factor 2-10 compared to reference silica aerogel (Figure 25c). The mechanical reinforcement and minimal dust release correlate well with the microstructural observations, with the best properties for the pectin-rich, homogeneous, neck-free hybrids synthesized at pH 1.5 (Figures 19 and 22). In addition to this morphological change, well dispersed pectin molecules may strengthen the material through hydrogen bonding to silanol groups. Hybridization at higher pH does not improve the mechanical properties because of pectin aggregation and formation of fibrous network structures (Figure 19).



Figure 25: (a) Final compressive strength. (b) Compressive modulus (E). (c) Submicron (< 500nm) particle dust release during mechanical grinding of RS-2.5 and PecS-20-1.5. (d) Thermal conductivity.



Figure 26: Compression test of PecS-10-1.5 aerogel



One of the main applications of aerogel is high-performance thermal insulation. The thermal conductivity (λ) was measured on monolithic 48×48×(6-8) mm³ tiles at 25°C and 50 % relative humidity (RH) ¹⁷. At pH 1.5, the sample with a minimal pectin loading of 5 wt% shows the lowest conductivity of the whole series, 14.2 mW·m⁻¹·K⁻¹. Increasing the pectin content increases thermal conductivity due to the higher solid conductivity and water uptake (Figure 27), but this increase is very minor and all hybrid aerogels are superinsulating with λ between 15 and 17 mW·m⁻¹·K⁻¹ ²⁶. This outstanding thermal performance places this new class of hybrids amongst the best thermal insulators under ambient condition, but with drastically improved mechanical properties. Thus, pectin-silica hybrids prepared at pH 1.5 present a unique combination of very low thermal conductivity and superior final compressive strength.



Figure 27: (a) Humidity uptake by hybrid aerogels after 7 days as a function of pectin concentration and (b) humidity uptake by the pure pectin and non-hydrophobised silica aerogels prepared at the same condition as RS-5 as a function of relative humidity.



Figure 28: DTGA of the silica reference aerogel (a) RS-2.5 and pectin-silica hybrid aerogels (b) – (d) with 5 - 20 wt% pectin loadings and gelled at pH 1.5 and (d) – (f) with 20 wt% pectin loading and gelled at pH 1.5 – 5.0.



The thermal stability of both reference silica aerogel and pectin–silica hybrids was analyzed by DTGA, shown in Figure 28. A distinct weight loss in the reference RS-2.5 can be observed around 580°C, which is consistent with the decomposition of the hydrophobic sites (loss of methyl/trimethylsilyl groups) on silica aerogel backbone which is well documented in the literature ²⁰⁻²¹. This suggests that hydrophobic silica aerogels have an upper bound service temperature around 550°C. The corresponding pectin hybrids PecS-Y-X all show a lower-temperature peak around 280°C, which is attributed to the degradation of the pectin biopolymer itself. Hence service temperature above 250°C is not recommended for the hybrid aerogel materials.

Overall, after a systematic study of the reinforcement of silica aerogel using biopolymer aerogels, we have found that samples with the best performance were all dried under supercritical condition. So far, ambient drying attempts in analogy to pure silica aerogel did only produce granular materials but no monolithic samples. The results of these studies have been accepted by high-peer scientific publications. Additional efforts were spent on ambient pressure drying of work was put on improving the surface modification of silica aerogels and their ambient drying process.

8.3. Surface modification and ambient pressure drying

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, alcohols, ketones or acetonitrile. To prepare the gels for ambient drying, hydrophobizytion of surface modification with a "waterproofing agent" such as trimethylchlorosilane, dimethyldichlorosilane, or hexamethyldisilazane is necessary. Within this project, an optimized surface modification and ambient pressure drying process has been developed and applied in the manufacturing of aerogel boards. The main results of this optimization can be summarized as follows:

Optimization of the hydrophobization treatments

Different hydrophobization agents (hexamethyldisilazane, HMDZ; hexamethyldisiloxane, HMDSO; and trimethylchlorosilane, TMCS) were compared and for reasons of cost efficiency, ease of handling and lack of toxic or corrosive by-products, we opted for HMDSO as a standard silylation agent. In order to react properly, HMDSO requires small amounts of a hydrochloric acid catalyst. Two methods of introducing HCI to the hydrophobization solutions were tested, namely the direct addition of hydrochloric acid solutions and the use of trimethylchlorosilane in small amounts (which when in contact with a protic solvent releases quantitative amounts of HCI but is soluble in organic solvents).

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 HCI was used in all samples as an acid catalyst (Figure 29). From this work, a 10% HMDSO heptane solution was found ideal for the hydrophobization of waterglass gels. More concentrated solutions do not seem to yield better results. Ambient drying at 150°C produces low density aerogel materials with excellent optical transparency (sample C).



Figure 29: Socium silicate based ærogels modified with different amounts of HMDSO: A. 6% B. 8% C. 10% D. 15%

Samples	Silylation agents	Density g/cm3	Appearance
A	6%HMDSO/HCI	0.286	Considerable shrinkage during drying, incomplete hydrophobization
В	8%HMDSO/HCI	0.155	Cracked, smaller, whitish fragments
С	10%HMDSO/HCI	0.140	Large almost monolithic blocks, very transparent
D	15%HMDSO/HCI	0.141	Cracked, whitish fragments

Table 9: Density of ions exchanges sodium silicate based aerogels modified with HMDSO/TMCS

We have also attempted to introduce HCl in the form of TMCS as described previously. The TMCS concentration in the hydrophobization solution was varied between between 0.04% and 0.2% (Figure 30), 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 one could assume: Both aqueous HCl and 0.06% to 0.08% TMCS are producing good quality almost monolithic aerogels.



Figure 30: Sodium silicate based aerogels modified with different amounts of TMCS: A. 0.04%TMCS B. 0.06% TMCS C. 0.08% TMCS D. 0.2% TMCS

Samples	Silylation agents	Density g/cm3	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
н	10%HMDSO,0.2%TMCS	0.143	Whitish rather large fragments

Table 10: Density of ion exchanged sodium silicate based aerogels modified with HMDSO/TMCS

A further optimization of the hydrophobization has been done in 2014 to simplify the cumbersome solvent exchange/hydrophobization process and promote the scale-up possibility of the mass production of waterglass based aerogel materials. The process is named 'SISEM' (SIngle-step Solvent Exchange/surface Modification), the target is to synthesize waterglass based aerogel in simple/ straightforward one step by using the recipe above-mentioned (HMDSO/HCI/ethanol), and the novelty as compared with our previous studies²⁷⁻²⁸ is no expensive aggressive chemical, e.g. trimethylchlorosilane, have to be used, which is much more efficient and cost-saving for future large scale production, shown in Figure 31.



Figure 31: Sodium silicate based aerogels modified from SISEM with different volume ratios of HCI/ethanol: A. 1:1 B. 1:5 C. 1:10 D 2:1.

Ambient pressure drying of PES reinforced silicic acid based aerogel composites

After a systematical study of the solvent exchange and surface modification, and the failure attempts of ambient drying with biopolymer chemistry (see part ii. *Mechanical Strengthening of Sodium Silicate Gels*), a commercial available polyester (PES) blanket was adopted for reinforcing the silicic acid based aerogel materials. A successfully prepared monolithic aerogel mats with the size of $\sim 50\times50\times10$ mm and $\sim 100\times100\times10$ mm are shown in Figure 32. The densities of the monolithic pieces were on the order of 0.08 g/cm³ to 0.11 g cm⁻³ and the final compressive strength is 7 MPa with a high plastic deformation range up to 80% strain, shown in Figure 33. The thermal conductivity of such ambient



dried composite retaining low of $\lambda = 17.6-18.5 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, listed in Table 11. Comparing the supercritical dried sample and ambient dried sample, no difference was observed for macroscopic appearance.



Figure 32: PES-silicic acid based aerogel composites, from left to right 24x22x10 mm supercritical dried sample, 24x22x10 mm ambient dried sample, 49x49x10 mm supercritical dried sample, 49x49x10 mm ambient dried sample and 108x103x10 mm ambient dried sample



Figure 33: Mechanical properties of PES- silicic acid based aerogel composites

The thermal conductivities of the waterglass-based silica aerogels are presented in Table 11 on the next page. In the aerogels studied here, λ reaches a minimum value of 17.0 mW/m·K around a density of 0.109 g/cm³. And comparing the composites dried by ambient and supercritical methods, there is little difference in their respective density and thermal conductivity values.

Samples	Drying method	Size (mm)	Density (g/cm3)	[Si] (M)	Linear shrinkage %	Thermal conductivity (mW/mK)
WGPA-1	APD	49×49×10	0.109	1.55	2	17.0
WGPS-2	CO ₂ SCD	49×49×10	0.083	1.55	2.3	17.6
WGPA-3	APD	108×103×10	0.089	1.55	2.2	18.0
WGPA-4	APD	108×102×10	0.089	1.55	2.2	17.6

Table 11: Thermal conductivity of waterglass based PES aerogel composites

In the meantime, we have tried to optimize the composite production by using the novel SISEM route, however, there are still problematic for PES/waterglass composite, which shows a relative high thermal conductivity of 26 mW·m⁻¹·K⁻¹, shown in Figure 34, and the poor thermal resistant performance probably dues to the trapped water in the PES foam. Further studies need to be done to further optimize this process. Analysis of process parameters suggested an incomplete exchange /removal of the water from the pore fluid which is known to cause structural collapse during both ambient an supercritical drying.



Figure 34: PES-waterglass based aerogel composites (60×60×15 mm) made using the SISEM route

Before a successful transfer of the waterglass based chemistry from the lab-scale to a small pilot scale, we need to conduct a further optimization of the SISEM route (Figure 34). As a second prerequisite we woud need to scale up the ion exchange process of the waterglass solution to a larger exchange column in order to be able to fabricate sufficient quantities of the silicic acid raw materials.



However, the lab scale results combined with previous scale up experience with TEOS based 480×480×20 mm PES-silica aerogel composites (Figure 35, part of the EU-FP7 project "AeroCoins"), suggest that after optimization, the SISEM recipe could indeed be developed further to allow cost effective for mass production of sodium silicate based quasimonolithic aerogel composite blankets.



Figure 35: Prototype of TEOS based ambient pressure dried PES-silica composite blankets produced by EMPA as part of the AeroCoins project.

8.4. Cost performance analysis and optimization

Synthesis

Ambient pressure dried (APD) waterglass based aerogel samples reinforced with polyester blankets are a very promising candidate as an inexpensive superinsulation material. The details of the synthesis of Aerogel-based boards and reionforced aerogel materials was described in section 8.2 and 8.3. To assess volume dependent production cost of such materials in an industrial process, we first need to elucidate the different fabrication steps and try to address the main costdrivers for the industrial process. A blackbox schematic illustrating the aerogel synthesis is presented below in Figure 36.



Figure 36: Flow diagram showing the preparation of a hydrophobized silica gel from waterglass

<u>Gel Drying</u>

As mentioned before, ambient drying of aerogels makes is nowadays regarded as the most cost effective drying method for aerogel manufacture. A typical APD process involves evaporation of a gels pore fluid followed by condensation of the solvent vapor. Complete recuperation of all solvents is essential for keeping the overall process cost at tolerable levels. The condensate mixture then must be separated into its pure compounds or suitable mixtures by distillation, exctraction and /or mechanical separation in order to be fed back into the production stream.





Figure 37: Ambient pressure drying process flow diagram.

Cost Modelling

For the cost modelling we have developed a simple parameter based model which takes into account the main cost drivers of the aerogel production process which are:

- Raw materials cost
- Write-off / depreciation of capital investment (CAPEX)
- Operation cost (OPEX)
 - Operating cost of key technical modules (see below)
 - o Solvent recycling cost
 - o Equipment maintenace
 - Manpower needed for operation
 - Overhead cost

The cost model predicts materials cost based on raw materials pricing and consumption using process data from pilot scale studies from previous projects (<u>www.aerocoins.eu</u>). We also try to predict economy of scales aspect of the materials pricing by employing a volume dependent power law scaling for CAPEX (investment cost) and OPEX (manpower only).

Design aspects of the different components needed for a completely closed cycle aerogel manufacturing process were worked out with the assistance of a chemical engineering firm as part of own ongoing efforts to improve aerogel manufacturing process efficiency. The total CAPEX was calculated as the sum of the key modules which are:

The key modules are:

- Solvent and product storage infrastructure
- Ion-exchange system,
- Reactors
- Dryer
- Solvent recycling technology
- Process control system



Figure 38: Simplified production of aerogel blankets based on waterglass

The reactor and dryer design which match corrosion, hygiene safety and environment toughest standards are the most challenging and costly tasks which involve a high level of industrial expertise.

CAPEX

Cost estimates for a waterglass based production processare were calculated using our current state of process knowledge combined with cost estimates from chemical engineering experts. The different module components are presented below in Figure 39:



Figure 39: Key modules and their relative contribution to total CAPEX cost

Looking at the relative contributions, it becomes apparent that the main investments are in the sol gel and hydrophobization reactors (22% each) as well as the ambient drying oven. The remaining 30% are spent on process control (14%), solvent recycling (9%) and solvent and materials storage infrastructure (6%). If we look at the production volume dependence of CAPEX, we notice that a large industrial facility requires a very substantial initial investment.





The total CAPEX investment for a waterglass production line is estimated 20-30% higher than for a similar installation which uses TEOS as a raw material due to the more complex solvent exchange and solvent workup efforts which are necessary to ensure satisfactory product quality and reproducibility. Furthermore, the exact cost of the setup strongly depends on the specific reactor and process design, so the numbers reported here should be regarded as guideline values.

OPEX

OPerating EXpenses (OPEX) for the aerogel board production of this study are comprised of the cost of the raw materials, processing of the raw materials (preparation of the silica sol by ion exchange of the sodium silicate solution), and process media and energy cost. On the operator side we include manpower and overhead cost, which was estimated as percentage fractions of the respective personnel and infrastructure costs.

Three different scales were considered in this work to describe the economy of scale laws of the production price with increasing capacity namely industrial pilot scale (1'000 m³/a), small (10'000 m³/a) and medium (100'000 m³/a) sized industrial production lines.

Special attention must be paid to the raw materials cost which are the main contribution for any large scale industrial materials or semi-finished product manufacturing process. For simplicity, we assume that all raw materials (sodium silicate and hydrophobe) will be completely integrated into the solid 60/65

backbone of the aerogel material, i.e. that there are no losses of by washing out, precipitation etc. For an ideal process this is a safe assumption but in reality washing out of soluble silicates during solvent exchange is known to complicate the design of the solvent recycling module. The cost of the waterglass / hydrophobe for a cubic meter of silica aerogel is on the order of about EUR 80 each. Their relative mass fraction in the final aerogel product are roughly 75% / 25% according to solid state NMR analysis²⁹.

Total Manufacturing cost

The total predicted manufacturing cost of the aerogel-based component is presented in Figure 41 below. One notices that the raw materials cost at around 200EUR/m³ for waterglass based aerogels are extremely low in light of the astronomically high aerogel materials prices (2500-5000 EUR/m³) which are commonly accepted today. An unknown factor on the raw materials cost side is the price for the ion exchange process of the sodium silicate and the selloff of the resulting large volumes of salts (e.g. sodium chloride) which is left behind as a waste product.



Figure 41: Various contributions to the total manufacturing cost per cubic meter of aerogel at three different scales

Cost for solvent workup and processing of HMDSO / ethanol mixtures is the smallest contribution to the overall cost. CAPEX amortisation and operational (without materials) OPEX cost shows a very high volume dependence on the pricing. This is qualitatively explained simply by a lower relative contribution of an initial investment of the production plant due to economy of scale laws and by a reduction of operating staff on a per capacity basis for larger installations due to a higher degree of process automation. Despite the low raw materials cost, waterglass based aerogels cannot be produced cost effectively in low volumes: given a 1'000m³/a capacity, we predict overall production cost on the order of 1800 EUR/m³. However above 10'000m³/a capacity, the production becomes 61/65



competitive in comparison with today's market prices but also the demand of customers / end users for cheaper aerogels. At larger production volumes >100'000 m³/a, the price of aerogel will become rather competitive with predicted manufacturing cost below EUR 600/m³. Not also that the relative fraction of raw materials for very large production volumes becomes the primary cost driver in the production of the silica aerogels. This is in line with a commonly used rule of thumb in chemical engineering that for mature markets (commodities), the contribution of the raw materials is typically between 65 and 80% of the total production cost.

In conclusion, we have been able to create a simple economy of scale model to predict aerogel manufacturing cost as a function of production volume. Although this model is based on a number of assumptions about the detailed process engineering steps, it is a useful benchmark to compare different technologies. The biggest uncertainty in this model is linked to properly accounting for the detailed process complexity in each detail. To fill in lacking information here can only come from real scale-up and industrial manufacturing test plants and studies.

9. Conclusions

Within this project, we have systematically studied the feasibility of cost-effective mass production technologies for waterglass based aerogel composites by i) optimizing the sol-gel system up to the point of the gelation, ii) aging and reinforcement strategies of the resulting hydrogels, iii) demonstrating the feasibility for ambient drying of these materials and iv) carrying out an economy of scale based cost performance analysis.

In conclusion, we were able to demonstrate an industrially viable route for the mass production of quasimonolithic (e.g. fiber-reinforced boards), mechanically strong waterglass based aerogel composites by ambient drying. Furthermore, we were able to significantly enhance the mechanical properties of waterglass based silica aerogels through aqueous cogelation with biopolymers such as pectin and chitosan. This opens up a number of promising avenues to create next generation smart, multifunctional aerogel hybrid materials through cogelation of silicic acid sols with a range of water soluble organic polymer systems. Such second generation hybrid aerogels will feature improved mechanical properties and reduced dust evolution while maintaining their superior thermal insulation performance. This work led to two publications in very high peer scientific journals. From an academic and fundamental research perspective, the project was a great success. All in all, this project has opened-up new possibilities and methodologies and brought a significant advancement in understanding which will serve as the basis for new research activities

From an industrial perspective, the work has allowed a clear description of the chemical process steps and a much clearer understanding of the overall process cost. The work has clearly shown, that silica aerogels can be obtained at very low cost if they are produced at a significantly large scale (>100'000m³/a). The use of waterglass as silica source reduces the raw materials costs compared to TEOS precursors, and although this gain is partially offset by the increase in CAPEX by 20-30% due to the necessity for elaborate ion-exchange facilities, waterglass based silica aerogels have the potential to be cost-competitive with current production processes. However, parallel R&D activities at Empa on TEOS based aerogel production processes culminated in the discovery of a one-pot process this process is considered the most promising way forward towards cost-effective mass production of silica aerogel (See Section 10.1). With respect to commercialization and mass production, the work carried out during the cost evaluations enabled a more robust estimation of aerogel manufacturing costs and the developed cost models are directly applicable not only to waterglass, but also to other silica aerogel systems. Although waterglass is no longer considered the optimum silica precursor (see section 10.1), the developed methodologies will directly impact the commercialization of next generation aerogel materials as superinsulators for the built environment. In short, the project must be regarded as a success also from the industrial perspective.

10. Outlook and next steps

10.1. Towards mass production of silica aerogel building insulation

R&D activities at Empa in parallel to the BFE Waterglass project on TEOS based aerogel production processes culminated in the discovery of a one-pot process that minimizes the solvent use to close to the theoretical minimum (1 m³ of solvent for 1 m³ of aerogel). The result is an additional reduction in CAPEX together with a strong reduction in OPEX as the amount of solvent workup is minimized and this process is considered the most promising way forward towards cost-effective mass production of silica aerogel. This process has been demonstrated both at the lab and pilot-scale with a total production time of 4 hours, including gelation, aging, hydrophobization and ambient pressure drying, and production of aerogel in 40 L batches. This technology has been patented by Empa and will be the core technology of the Empa spin-off nexAero. Many of the engineering challenges with respect to gelation, aging and hydrophobization have been solved and a full engineering layout of the production plant is now in design. Some engineering challenges related to the drying and solvent recycling remain open, but will be solved through dedicated R&D on the topic. NexAero will be foremost a producer of silica aerogel granulate as a semi-finished product that will be further processed to insulation boards, renders etc. by various (predominantly Swiss) industry partners and clients. The availability of silica aerogel granulate at a much reduced cost will enable silica aerogel to break out of its niche in the building insulation market.

10.2. Reinforced silica aerogels

This project resulted in the development of reinforced biopolymer-silica aerogel hybrids with superior thermos-mechanical properties compared to silica aerogel. At the moment, these materials still require supercritical drying and as a result, they still have a significant time to market. Empa is currently conducting a feasibility study for the production of biopolymer-silica aerogels in collaboration with a Swiss producer of polysaccharides (name not disclosed at their request). This feasibility study builds directly on the developments during the BFE Waterglass project and provides a first stepping stone towards the commercialization of this second generation aerogel materials.

10.3. Exotic applications of waterglass aerogels

One attractive feature of waterglass aerogels is that they experience minimal to no shrinkage during supercritical drying, whereas TEOS based aerogels always display some shrinkage, even during supercritical drying. This enables dimensional and structural control of silica aerogels for various applications and enabled us to produce waterglass aerogel membranes for miniaturized motionless gas pumps with unprecedented efficiency ²⁹. Empa recently was part of a consortium that submitted an EU H2020 proposal for the production of thermos-acoustic speakers. Empa's role in the project is to provide an aerogel thermal insulation layer to improve the speaker efficiency. This project directly builds on the know-how gain achieved during the BFE Waterglass project.

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