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Ambient pressure drying of silica aerogels after hydrophobization with mono-, di- and tri-functional silanes and mixtures thereof

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Abstract

Aerogels are mesoporous materials with a rapidly growing thermal insulation market interest, partly because ambient pressure drying (APD) reduces cost. Silica gels must be hydrophobized to prevent condensation reactions and irreversible shrinkage during APD. Here, we study how hydrophobization with mono-, di-, and trifunctional organoalkoxysilanes (M, D, T) and their mixtures, affects spring-back, density, surface area, pore size and hydrophobicity. All aerogels were synthesized from a polyethoxydisiloxane precursor prepared from a tetraalkoxysilane (tetraethoxysilane, TEOS). Aged gels, hydrophobized with trimethylethoxysilane (M100), display the highest spring-back and lowest density

(0.100 g/cm³) upon APD drying. Hydrophobization with pure dimethyldiethoxysilane (D100) or methyltriethoxysilane (T100) leads to excessive shrinkage and respective densities of 0.440 and 1.450 g/cm³ due to the self-polymerization from the di- and trifunctional silanes: in the D100 material, the formation of polydimethyldisiloxane (PDMS) is evident in the ²⁹Si NMR spectra, whereas 3D silica structures (beads) are apparent for the T100 sample. Aerogels hydrophobized with binary and ternary mixtures of M, D and T display systematic variations in density: nearly constant (<0.12 g/cm³) values are obtained after replacing up to 20% of M, but the density increases rapidly upon further substitution. In contrast to the strong effects on density, the humidity uptake remains below 2 wt% for most samples and conditions. The possibility to use mixtures of hydrophobization agents, rather than pure compounds, may decrease the production costs of silica aerogels, and can be readily carried out for up to 20%, but would require further process optimization for higher degrees of substitution.

Keywords

Silica aerogel; Surface modification; Evaporative drying; Solid-state NMR

1. Introduction

Silica aerogels are amorphous, predominantly mesoporous materials with exceptional thermal and acoustic properties [1, 2] and are increasingly applied in industrial and building insulation [3, 4]. However, the production cost needs to be reduced in order to make them more competitive in the cost-sensitive building insulation market.

Silica aerogels are unique among aerogels because of the possibility to use ambient pressure drying (APD), which has a strong cost reduction potential. Classical aerogels are produced by supercritical drying (SCD) [5, 6], most often from supercritical CO₂ [7, 8], to eliminate the strong capillary forces and irreversible shrinkage that occur during evaporative drying. During APD, condensation reactions between surface silanol groups on adjacent particles of untreated silica gels lead to a permanent densification. Thus, an essential feature of the APD aerogel manufacturing process is the end-capping of reactive silanol groups to prevent unwanted condensation reactions. Such a hydrophobization treatment does not prevent a transient structural collapse during the initial stages of drying, but induces a spring-back effect towards the end of the drying process that enables the aerogel to recover most of the original pore volume and enables the production of low density, mesoporous aerogels by APD [9, 10].

The most common silylating strategy aims to cover the silica surfaces with trimethylsilyl (TMS) groups by soaking the gel in a solution containing a TMS precursor after gelation and aging. Trimethylchlorosilane (TMCS) [9-15] and hexamethyldisilazane (HMDZ) [11, 12, 16-20] both are characterized by a high reactivity that enables rapid hydrophobization, but release stoichiometric amounts of corrosive and/or toxic HCl or NH₃. In contrast, trimethyl(m)ethoxysilane (TMMS/TMES) [21-24] and hexamethyldisiloxane (HMDSO) [12, 13, 25-27] do not suffer from these drawbacks and are compatible with a wide variety of solvents, but have a lower reactivity compared to TMCS and HMDZ. Tri- and di-functional silanes, such as methyltri(m)ethoxysilane (MTMS/MTES), and dimethyldi(m)ethoxysilane (DMDMS/DMDDES) have been

widely described in the literature to lead to synthesize hydrophobic silica aerogels, typically by a coprecursor cogelation method but optionally also during a post-gelation treatment [24, 28-37].

All of the aforementioned silylating agents are ultimately derived from the Müller-Rochow process, where the reaction of methyl chloride with silicon metal forms a mixture of trimethylchlorosilane (TMCS, 2-4%), dimethyldichlorosilane (DMDCS, 70-90%) and methyltrichlorosilane (MTCS, 5-15%). The various hydrophobization agents are then produced through the isolation of the chlorosilanes and their optional conversion into the corresponding alkoxysilanes (TMMS, TMES, MTMS, MTES, DMDMS, DMDDES) or dimers (HMDZ, HMDSO). The low yield of the mono-functional chlorosilane (TMCS) in the Müller-Rochow process, which has been optimized to provide dialkyl-dichlorosilanes as raw materials for the silicone industry, thus represents a major availability challenge if the production volume of TMS-modified silica aerogels is to be increased substantially. In fact, even with the current demand, sourcing the hydrophobization agents constitutes a substantial fraction of the overall aerogel raw materials cost.

Here, we investigate the possibility to hydrophobize silica aerogels by post-gelation modification with alternative hydrophobization agents and mixtures thereof. We carry out a parametric study with pure and mixed mono- (M), di- (D) and trifunctional (T) alkoxysilane precursors. We monitor the spring-back effect and the resulting aerogel properties, including microstructure, speciation, density, surface area, pore size and humidity uptake. We found that low density aerogels could only be produced using hydrophobization mixtures that contained at least 80% of the mono-functional silane because of the self-polymerization of the di- and tri-functional alkoxysilanes and the reduced surface selectivity it entails.

2. Experimental

2.1 Synthesis

All aerogels were prepared under identical conditions, apart from the composition of the hydrophobization liquid and the duration of the hydrophobization treatment. Silica gels (12 ml) were prepared from 4 ml of polyethoxydisiloxane (PEDS, P750E20, 20 wt% SiO₂ equivalent) as silica source [38], 8 ml ethanol as the gelation solvent, and 0.4 ml of distilled water and 0.1 ml of 5.5M ammonia as catalysts. After gelation, the gels were aged for 24 hours at 65°C to strengthen the silica particle network and maximize the spring-back effect [25]. Trimethylethoxysilane (M), dimethyldiethoxysilane (D) and methyltriethoxysilane (T) in volume ratios from 0 to 100% were used as hydrophobization agents. For gel modification, a constant volume (12 ml) of hydrophobization solution was used: 6 ml of ethanol (98%), 0.2 ml of HCl (37% in water) and 5,8 ml of the M/D/T mixtures. With this protocol, the hydrophobization agents are added in a large excess: between 27 and 35 molecules of hydrophobe are added for each nm² of silica gel surface area (assumed to be 800 m²/g for this calculation), compared to the ca. 5 silanol/ethoxy groups that are present for the same area. This study focusses on the type of hydrophobization agent needed, but not on the minimum amount required, which would need to be evaluated separately for each hydrophobization mixture. Four different modification times were used (24h, 48h, 72h and 168h), always at 65°C. The modification was performed in tight cylinders (12 mm diameter) during constant rotation at a rate of 10 turns per minute to improve the penetration of the agents into the gel pore network. No immiscibility was observed during any of the experiments. Finally, the gels were dried by APD at 150 °C for at least 3 hours. First, three gel series were functionalized by pure T, D and T alkoxysilanes. Since only one of the gels modified with pure M resulted in materials with aerogel like properties, such as densities around 0.100-0.120 g/cm³ and surface areas above 800 m²/g, we focused our subsequent samples on the systematic substitution of M by D, T, or mixtures thereof (Figure 1).

2.2 Characterization

The carbon and hydrogen content were determined by combustion and subsequent gas-phase FTIR analysis at the Laboratory for Organic Chemistry of ETH Zurich. The concentrations of carbon, hydrogen were determined by hot gas extraction on a LECO TrueSpec Micro and Oxygen analysis with a LECO RO-478 instrument. The combustion products of carbon (CO_2) and hydrogen (H_2O) were measured with infrared detectors. ^1H - ^{29}Si cross polarization (CP) magic angle spinning (MAS) solid-state NMR spectra were collected with a 7 mm CP MAS probe in a Bruker Avance III spectrometer equipped with a wide-bore 9.4 T magnet, corresponding to ^1H and ^{29}Si Larmor frequencies of 400.2 and 79.5 MHz for ^1H and ^{29}Si , respectively. The ^{29}Si chemical shift is referenced to tetramethylsilane at 0.0 ppm. The ^1H - ^{29}Si CP experiments were performed using the following parameters: 7.5 μs 90° excitation pulse on ^1H channel, 5 ms contact time with a ramp from 100 to 50% of power level on the proton channel (ramp from 33 to 23 kHz), 4'000 Hz MAS rate, 5 s relaxation delay, 33 kHz SPINAL 64 proton decoupling was applied during acquisition, and appropriate numbers of scans were recorded to yield reasonable signal-to-noise ratios.

Scanning electron microscopy (SEM) was performed on a SUPRA 50VP (Zeiss, Germany) instrument. Samples were sputtered with ~10 nm platinum (Bal-Tec SCD 500 Sputter Coater) and analyzed at 5 kV using SE2 detector or at 2 kV using In-lens detection. The envelope density was determined from the mass and volume determined by the powder displacement method (powder pycnometry, Micromeritics, GeoPyc 1360) with a low compression force of 4 N to minimize the compression of the aerogels during the analysis. The accuracy of the density measurements is on the order of 4% relative. The surface area (S_{BET}) was determined by the Brunauer–Emmett–Teller (BET) method [39], based on the amount of N_2 adsorbed at pressures $0.05 < P/P_0 < 0.3$ (Micromeritics, Triflex). The mesopore volume, pore size distribution and average pore diameter of the aerogels were analyzed by the BJH nitrogen adsorption and desorption method [40], despite the known limitations of pore size analysis of aerogel materials due to sample deformation during the nitrogen sorption analysis [41]. Alternatively, the pore volume (V_{pore}) and average pore size (D_{pore}) have been calculated from the envelope density (ρ_{envelope} from powder

pycnometry) and skeletal density (ρ_{skeletal} , approximated here by 2.0 g/cm^3) assuming cylindrical pores:

$$V_{\text{pore}} = 1/\rho_{\text{envelope}} + 1/\rho_{\text{skeletal}}, D_{\text{pore}} = 4V_{\text{pore}}/S_{\text{BET}}.$$

The humidity uptake was determined using the following procedure: The weight of ~200 mg aliquots of aerogel was determined immediately after drying at 150°C for 24h. The samples were then placed in climate chambers at room temperature (25°C) with predetermined relative humidity (RH: 30, 50, 80, >90%). The humidity uptake was determined by weighing the samples after 5, 6 and 7 days of residence in the climate chambers. Additionally, selected samples were characterized by dynamic vapor sorption (DVS, TA Instruments VTI-SA+): 23°C isotherms were collected on 10 mg of sample and an equilibration criterion of 0.08% mass change per 5 minutes (Figure S3).

3. Results

3.1 Density

The composition of the hydrophobization solution has an extreme effect on the drying-induced shrinkage and aerogel density (Table S1, Figure 2). The sample hydrophobized with only the mono-functional hydrophobization agent (M100) has the lowest density of all samples ($0.100\text{--}0.105 \text{ g/cm}^3$), indicative of a nearly complete spring-back at the end of the evaporative drying process and true aerogel-like properties. In contrast, the samples hydrophobized with pure di- and tri-functional hydrophobization agents have much higher densities: 0.442 to 0.724 g/cm^3 for D100 and 1.231 to 1.454 g/cm^3 for T100, depending on the hydrophobization time. Because of the incomplete spring-back during drying, the D100 and T100 have xerogel-like properties. The densities of the samples hydrophobized with the mixed hydrophobization agents are not a simple linear function of the composition of the hydrophobization liquid. Instead, a plateau with densities below 0.120 g/cm^3 persists when up to 20% of

the mono-functional agent is substituted, followed by strong increase in density towards the D100 and T100 end-members for higher degrees of substitution. Consistent with the higher density of the T100 xerogel compared to that of the D100 end-member xerogels, increasing the fraction of tri-functional silanes has a more deleterious effect on density than substitution with the di-functional silanes (Figure 2, Figure S1). The densities of samples hydrophobized with a mixture of mono-, di- and tri-functional silanes, i.e. the M-D-T series, fall in between those of the M-D and M-T series. Increasing hydrophobization time generally decreases drying-induced shrinkage and density (Table S1), but these effects are small compared to those of the composition of the hydrophobization mixture.

3.2 Microstructure

The samples modified with pure mono-, di- and tri-functional silylating agents display clear differences in microstructure and only the sample modified with the mono-functional hydrophobization agent (M100) exhibits the typical mesoporous structure of silica aerogels with mesopores between the secondary silica particles (Figure 3). The sample prepared with only the di-functional silylating agent (D100) displays a more densely packed particle structure with larger secondary particles or aggregates. The structure of the sample functionalized with the pure tri-functional compound (T100) is strikingly different: in addition to a dense particle based structure, the growth of three dimensional silica structures such as 200-500 nm diameter beads, which are often empty and collapsed, is observed. The formation of these additional structures is consistent with previous publications [42-46] that highlighted the tendency of trifunctional silane precursors (MTCS, MTMS) to form complex nano- and microstructures on top of hydroxyl rich surfaces to impart superhydrophobic behavior.

The extreme differences in density and microstructure for the M100, D100 and T100 samples are also reflected in the nitrogen sorption isotherms (Figure 4). The M100 sample displays a typical type IV isotherm of silica aerogels, with a pronounced adsorption-desorption hysteresis and high quantity of adsorbed nitrogen at high relative pressure ($\sim 2400 \text{ cm}^3/\text{g}$ STP at $P/P_0=0.992$), consistent with a large mesopore volume. The samples modified with the pure di- and tri-functional silylating agents also display a type IV isotherm but with much lower quantities of adsorbed nitrogen (~ 550 for D100 and $\sim 260 \text{ cm}^3/\text{g}$ for T100, respectively, at $P/P_0=0.992$) because of their higher density. The BET and BJH derived properties verify these qualitative observations, with a surface area of 867, 334 and $412 \text{ m}^2/\text{g}$ and a BJH pore volume of 3.8, 0.7 and $0.3 \text{ cm}^3/\text{g}$ for the M100, D100 and T100 samples, respectively (Table S1). The nitrogen sorption isotherms and BET and BJH properties of the samples prepared from the mixed hydrophobization agents are consistent with the trends in density, and display a systematic decrease in maximum absorbed N_2 , surface area and pore volume as more of the mono-functional hydrophobization agent (M) is substituted by di- and/or tri-functional silanes (Figure 4, Figure 5, Table S1). Aerogels with high surface area (mostly above $>800 \text{ m}^2/\text{g}$) and a high fraction of mesopores ($V_{\text{BJH}} > 2.5 \text{ cm}^3/\text{g}$) can be prepared when up to 20% of the mono-functional silylating agent is substituted by di- and tri-functional precursors, but both mesoporosity and surface area decrease significantly for higher degrees of substitution (Figure 5, Table S1).

3.3 Carbon and hydrogen content, speciation and humidity uptake

The samples display a combined carbon and hydrogen content between 15 and 27 wt%, with molar hydrogen/carbon ratios of 2.8 to 3, consistent with methyl groups as the dominant organic functional group, as expected from the synthesis protocol (Section 2.1, Table S1). The carbon and hydrogen contents are lowest for the M100 sample and systematically increase with increasing substitution of the mono-functional with di- and trifunctional precursors in the hydrophobization solution. All samples display a low humidity uptake of typically less than 2 wt%, even at 90% relative humidity, regardless if

humidity uptake is evaluated by the protocol with the climate chambers or DVS (examples shown in Figure S3).

The ^1H - ^{29}Si solid-state NMR spectra (Figure 6) can be divided into four main regions, corresponding to Si atoms coordinated by 4 oxygens (Q), 3 oxygens and 1 methyl group (T), 2 oxygens and 2 methyl groups (D) and 1 oxygen and 3 methyl groups (TMS), derived from the TEOS based PEDS precursor and the tri-, di- and mono-functional silylation agents, respectively [47, 48]. The Q, T, and D species can further be described in terms of their number of bridging oxygens or Si next-nearest-neighbors: a Q^n species is a Si atom coordinated by n bridging oxygen atoms (BO) and $4-n$ non-bridging oxygen atoms (NBO), a T^n species is a Si atom coordinated by n BO, $3-n$ NBO and 1 methyl group, and a D^n species is a Si atom coordinated by n BO, $2-n$ NBO and 2 methyl groups. The TMS, D and T peak areas approximate the composition of the hydrophobization mixture for all investigated samples, although it is clear that the signal enhancement during cross-polarization increases the relative intensities of the Si sites bearing methyl groups (Figure S2). The signal enhancement also affects the apparent degrees of polymerization derived from the cross polarization spectra, but qualitative observations can still be derived. The Q^n speciation is dominated by Q^4 with smaller contributions of Q^3 and Q^2 . Such a high degree of polymerization of the Q^n species is typical for silica aerogels as the primary particles consist of an SiO_2 -like interior (i.e. Q^4) with a Q^3 rich surface [48]. For nearly all samples, also the T^n and D^n speciation is dominated by the most polymerized species, i.e. T^3 and D^2 . One notable exception is the T100 sample, where T^2 is by far the most intense peak, possibly related to the beads observed in the SEM images (Figure 3). The T100 sample also has a more prominent Q^2 shoulder compared to the other samples. The spectrum of the D100 sample displays a narrow, liquid-like signal in addition to the expected peaks for D^1 , D^2 , Q^3 and Q^4 . This narrow resonance likely corresponds to a homopolymer of polydimethylsiloxane (PDMS) with sufficient flexibility of the polydimethylsiloxane chains to the narrow the peak. Finally, a second, smaller TMS peak is present for the samples hydrophobized with mixtures relatively rich in di- and tri-functional silylating agents. Based on the relative intensities, we tentatively assign the main

resonances to TMS groups connected to Q species, and the smaller ones to TMS groups connected to T or D species.

4. Discussion

The main objective of this study was to investigate if, and how much, mono-functional silylating agents can be substituted by better available di- and tri-functional silylating agents during post-gelation hydrophobization of silica aerogels produced by ambient pressure drying. A complete substitution with either the di- or tri-functional hydrophobization agent lead to a large increase in density and is clearly not possible, at least not without a comprehensive process optimization project.

The NMR data (Figure 6) clearly point to the self-polymerization of the di-functional silanes and the occurrence of polydimethylsiloxane (PDMS) in the D100 sample, presumably through hydrolysis (reactions 1-2) followed by condensation (reaction 3). The resulting homopolymer of PDMS is not removed from the sample during the drying procedure at 150°C.

Self-polymerization of the tri-functional silanes is also evident for the T100 sample in the form of rounded, hollow or collapsed beads in the SEM image (Figure 3). Given the high peak intensity of T² in the ¹H-²⁹Si CP MAS NMR spectrum of this, and only of this, sample, it follows that these structures consist predominantly of partially self-polymerized tri-functional silanes, through similar hydrolysis and condensation reactions that occur for the di-functional silanes (1-3).

Partial substitution of up to 20% of the mono-functional by di- and tri-functional silanes is possible, but higher substitution degrees negatively affect spring-back, density and surface area. The root cause of these deleterious effects is not directly obvious from our dataset. In theory, the use of tri- and di-functional silanes can lead to the addition of additional hydrophilic ethoxy or silanol groups in the form of unreacted or hydrolyze ethoxy groups from the D and T precursors. However, this effect is limited because most of the D and T species are present as D^2 and T^3 , with the T100 sample as the sole exception (Figure 6). All samples display moderate to high contents of methyl groups (Table S1) and all samples are very hydrophobic with a low humidity uptake (typically below 2 wt%), both of which are indicative of a low fraction of free silanol groups. Thus, permanent densification through condensation of silanol groups during evaporative drying, the dominant densification mechanism for non-hydrophobized silica xerogels, is not the major or only cause of the densification of some samples. The self-polymerization reactions detected for the two fully substituted samples (D100 and T100) may also be active for the mixed samples (M-D, M-T, M-D-T), but due to the high load of methyl-silyl groups and resulting low humidity uptake of these samples, it is unlikely that self-polymerization reactions negatively affected the hydrophobization and elimination of the surface silanol groups. An alternative hypothesis is that the densification of samples prepared with higher fractions of D and/or T precursors is related to the physical processes during the ambient pressure drying step. During evaporative drying, strong capillary forces at the solvent-gas interface within the gels mesopores cause the sample to shrink. When ambient pressure drying from ethanol is carried out, it is our experience that fast drying, for example through the use of elevated temperature, is essential for a strong spring-back effect. The presence of e.g. PDMS oligomers with high boiling points will slow down the evaporation substantially, and in fact, the drying process may not have been completed for the D100 sample as indicated by the presence of PDMS in the final xerogel. Alternatively, the presence of larger structures of self-polymerized silylating agent may reduce the permeability of the silica particle network and slow down the drying process in this way. In the case of liquid-like PDMS polymers, one also expects that these polymers are trapped within the pores given their

high solubility in the hydrophobic aerogel matrix and high boiling point which renders them unlikely to dry completely under the condition used. Finally, it is also possible that the grafted, partially self-polymerized di- and tri-functional silanes reduce the elastic response of the aerogels and reduce the spring-back effect through a purely mechanically assisted mechanism.

Regardless of the mechanism, the strong negative effects of di- and tri-functional silanes on aerogel density and surface area preclude their use for post-gelation hydrophobization at substitution degrees well above 20%, unless the encountered problems can be resolved within a further, successful process optimization study. Some key challenges of such an optimization program include avoiding excessive self-polymerization of the di- and tri-functional silanes and insuring that the silica gels have the appropriate mechanical properties to enable a spring-back after drying. If these challenges are not met, substitution of the silylating agent is feasible up to 20%, which only brings about a minor advantage in terms of availability and cost, has no advantages in terms of material properties (density, surface area, mesoporosity), and may negatively affect the fire properties through the somewhat higher organic content.

Note that this study exclusively deals with silica aerogel synthesis by ambient pressure drying, for which the appropriate surface modification is a critical pre-requisite to limit drying shrinkage. For production by supercritical drying, surface modification is not essential for the production process, but hydrophobization is carried out to increase the (long-term) stability during service life. Hence, much wider tolerances exist for synthetic protocols of hydrophobic silica aerogels which are employing supercritical drying.

The limited potential for di- and trifunctional silanes for post-gelation modification, as described in this study, contrasts with their exceptional potential as (co-)precursors into the sol where they can impart flexibility to silica-like aerogels and foams [31, 37]. Note that this flexibility typically comes at the cost of

a more macroporous structure and a subsequent penalty in thermal conductivity, although transparent mesoporous aerogels have been derived from tri-functional precursors through the generous use of surfactants [35].

5. Conclusions

The effect of replacing mono-functional by di- and tri-functional silylating agents on silica aerogel properties was systematically evaluated for aerogel production by ambient pressure drying. Aerogel properties are unaffected for low degrees of substitution (up to 20%), but deteriorate markedly when more di- and tri-functional silanes are added, with a strong increase in drying-induced shrinkage and envelope density and a strong decrease in surface area. The complete substitution by di- and tri-functional silanes leads to self-polymerization of the hydrophobization agents in the form of polydimethylsiloxane and beads, respectively, and similar processes most likely occur for the mixed systems. Although the replacement of 20% of the mono-functional silylating agent may be economically favorable by itself, such a low degree of substitution will not alleviate possible shortages in the supply chain of the trimethylsilyl based, mono-functional raw materials.

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References

- [1] V. Arrighi, S. Gagliardi, C. Zhang, F. Ganazzoli, J.S. Higgins, R. Ocone, M.T.F. Telling. A Unified Picture of the Local Dynamics of Poly(dimethylsiloxane) Accross the Melting Point, *Macromolecules* 36 (2003) 8738-8778.
- [2] N. Hüsing, U. Schubert. Aerogels-Airy Materials: Chemistry, Structure, and Properties, *Angewandte Chemie International Edition* 37 (1998) 22-45.
- [3] R. Baetens, B.P. Jelle, A. Gustavsen. Aerogel Insulation for Building Applications: a State-of-the-art Review, *Energy and Buildings* 43 (2011) 761-769.
- [4] M.M. Koebel, A. Rigacci, P. Achard. Aerogel-Based Thermal Superinsulation: an Overview, *J. Sol-Gel Sci. Tech.* 63 (2012) 315-339.
- [5] S.S. Kistler. Coherent Expanded Aerogels and Jellies, *Nature* 127 (1931) 741-741.
- [6] S.S. Kistler. Coherent Expanded Aerogels, *J. Phys. Chem.* 36 (1932) 52-64.
- [7] P.H. Tewari, A.J. Hunt, K.D. Lofftus. Ambient-Temperature Supercritical Drying of Transparent Silica Aerogels, *Mat. Lett.* 3 (1985) 363-367.
- [8] M.J. van Bommel, A.B. de Haan. Drying of Silica Aergel with Supercritical Carbon Dioxide, *J. Non-Cryst. Solids* 186 (1995) 78-82.
- [9] S.S. Prakash, C.J. Brinker, A.J. Hurd, S.M. Rao. Silica Aerogel Films Prepared at Ambient Pressure by Using Surface Derivatization to Induce Reversible Drying Shrinkage, *Nature* 374 (1995) 439-443.
- [10] S.S. Prakash, C.J. Brinker, A.J. Hurd. Silica Aerogel Films at Ambient Pressure, *Journal of Non-Crystalline Solids* 190 (1995) 264-275.
- [11] D. Mahadik, A.V. Rao, A.P. Rao, P. Wagh, S. Ingale, S.C. Gupta. Effect of Concentration of Trimethylchlorosilane (TMCS) and Hexamethyldisilazane (HMDZ) Silylating Agents on Surface Free Energy of Silica Aerogels, *Journal of Colloid and Interface Science* 356 (2011) 298-302.
- [12] A.V. Rao, E. Nislen, M.-A. Einarsrud. Effect of Precursors, Methylation Agents and Solvents on the Physicochemical Properties of Silica Aerogels Prepared by Atmospheric Drying Method, *J. Non-Cryst. Solids* 296 (2001) 165-171.
- [13] F. Schwertfeger, D. Frank, M. Schmidt. Hydrophobic Waterglass Based Aerogels without Solvent Exchange or Supercritical Drying, *Journal of Non-Crystalline Solids* 225 (1998) 24-29.
- [14] L.-J. Wang, S.-Y. Zhao, M. Yang. Structural Characteristics and Thermal Conductivity of Ambient Pressure Dried Silica Aerogels with One-Step Solvent Exchange/Surface Modification, *Materials Chemistry and Physics* 113 (2009) 485-490.
- [15] S.-W. Hwang, T.-Y. Kim, S.-H. Hyun. Effect of Surface Modification Conditions on the Synthesis of Mesoporous Crack-free Silica Aerogel Monoliths from Waterglass via Ambient-Drying, *Microporous and Mesoporous Materials* 130 (2010) 295-302.
- [16] A.M. Kartal, C. Erkey. Surface Modification of Silica Aerogels by Hexamethyldisilazane–Carbon dioxide Mixtures and their Phase Behavior, *The Journal of Supercritical Fluids* 53 (2010) 115-120.
- [17] H. Yokogawa, M. Yokoyama. Hydrophobic Silica Aerogels, *J. Non-Cryst. Solids* 186 (1995) 23-29.
- [18] S.D. Bhagat, Y.-H. Kim, K.-H. Suh, Y.-S. Ahn, J.-G. Yeo, J.-H. Han. Superhydrophobic Silica Aerogel Powders with Simultaneous Surface Modification, Solvent Exchange and Sodium Ion Removal from Hydrogels, *Microporous and Mesoporous Materials* 112 (2008) 504-509.
- [19] A.V. Rao, M.M. Kulkarni, D. Amalnerkar, T. Seth. Surface Chemical Modification of Silica Aerogels using Various Alkyl-Alkoxy/Chloro Silanes, *Applied Surface Science* 206 (2003) 262-270.
- [20] J.C.H. Wong, H. Kaymak, S. Brunner, M.M. Koebel. Mechanical Properties of Monolithic Silica Aerogels Made from Polyethoxydisiloxanes, *Micropor. Mesopor. Mat.* 183 (2014) 23-29.
- [21] N.D. Hegde, H. Hirashima, A.V. Rao. Two Step Sol-Gel Processing of TEOS based Hydrophobic Silica Aerogels using Trimethylethoxysilane as a Co-precursor, *Journal of Porous Materials* 14 (2007) 165-171.

- [22] A.V. Rao, M. Kulkarni, G. Pajonk, D. Amalnerkar, T. Seth. Synthesis and Characterization of Hydrophobic Silica Aerogels using TRimethylethoxysilane as a Co-precursor, *Journal of Sol-Gel Science and Technology* 27 (2003) 103-109.
- [23] A.V. Rao, M.M. Kulkarni. Hydrophobic Properties of TMOS/TMES-based Silica Aerogels, *Materials Research Bulletin* 37 (2002) 1667-1677.
- [24] A.M. Anderson, M.K. Carroll, E.C. Green, J.T. Melville, M.S. Bono. Hydrophobic Silica Aerogels Prepared via Rapid Supercritical Extraction, *Journal of sol-gel science and technology* 53 (2010) 199-207.
- [25] S. Iswar, W.J. Malfait, S. Balog, M. Lattuada, M.M. Koebel. Effect of Aging on Silica Aerogel Properties, *Micropor. Mesopor. Mat.* 241 (2017) 292-302.
- [26] S. Iswar, G.M.B.F. Snellings, S. Zhao, R. Erni, Y.K. Bahk, J. Wang, M. Lattuada, M.M. Koebel, W.J. Malfait. Mechanically Reinforced Silica Aerogel with Low Thermal Conductivity by Co-gelation with Silane Terminated Prepolymers. , *Acta Materialia* 147 (2018) 322-328.
- [27] L. Huber, S. Zhao, W.J. Malfait, S. Vares, M.M. Koebel. Fast and Minimal-Solvent Production of Superinsulating Silica Aerogel Granulate, *Angewandte Chemie International Edition* 57 (2017) 4753-4756.
- [28] S. Yun, H. Luo, Y. Gao. Superhydrophobic Silica Aerogel Microspheres from Methyltrimethoxysilane: Rapid Synthesis via Ambient Pressure Drying and Excellent Absorption Properties, *RSC Advances* 4 (2014) 4535-4542.
- [29] A.V. Rao, M.M. Kulkarni, D. Amalnerkar, T. Seth. Superhydrophobic Silica Aerogels based on Methyltrimethoxysilane Precursor, *Journal of Non-Crystalline Solids* 330 (2003) 187-195.
- [30] D.Y. Nadargi, A.V. Rao. Methyltriethoxysilane: New Precursor for Synthesizing Silica Aerogels, *Journal of alloys and compounds* 467 (2009) 397-404.
- [31] A.V. Rao, S.D. Bhagat, H. Hirashima, G. Pajonk. Synthesis of Flexible Silica Aerogels using Methyltrimethoxysilane (MTMS) Precursor, *Journal of Colloid and Interface Science* 300 (2006) 279-285.
- [32] S.D. Bhagat, C.-S. Oh, Y.-H. Kim, Y.-S. Ahn, J.-G. Yeo. Methyltrimethoxysilane Based Monolithic Silica Aerogels via Ambient Pressure Drying, *Microporous and Mesoporous Materials* 100 (2007) 350-355.
- [33] A.V. Rao, D. Haranath. Effect of Methyltrimethoxysilane as a Synthesis Component on the Hydrophobicity and some Physical Properties of Silica aerogels, *Microporous and Mesoporous Materials* 30 (1999) 267-273.
- [34] T. Shimizu, K. Kanamori, K. Nakanishi. Silicone-Based Organic-Inorganic Hybrid Aerogels and Xerogels, *Chemistry-A European Journal* (2017).
- [35] K. Kanamori, M. Aizawa, K. Nakanishi, T. Hanada. New Transparent Methylsilsesquioxane Aerogels and Xerogels with Improved Mechanical Properties, *Advanced Materials* 19 (2007) 1589-1593.
- [36] G. Hayase, K. Kugimiya, M. Ogawa, Y. Kodera, K. Kanamori, K. Nakanishi. The Thermal Conductivity of Polymethylsilsesquioxane Aerogels and Xerogels with Varied Pore Sizes for Practical Application as Thermal Superinsulators, *Journal of Materials Chemistry A* 2 (2014) 6525-6531.
- [37] G. Hayase, K. Kanamori, K. Nakanishi. New Flexible Aerogels and Xerogels Derived from Methyltrimethoxysilane/Dimethyldimethoxysilane Co-precursors, *Journal of Materials Chemistry* 21 (2011) 17077.
- [38] G.M. Pajonk, E. Elaloui, P. Achard, B. Chevalier, J.-L. Chevalier, M. Durant. Physical Properties of Silica Gels and Aerogels Prepared with New Polymeric Precursors, *Journal of Non-Crystalline Solids* 186 (1995) 1-8.
- [39] S. Brunauer, P.H. Emmett, E. Teller. Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.* 60 (1938) 309-319.
- [40] E.P. Barrett, L.G. Joyner, P.P. Halenda. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, *J. Am. Chem. Soc.* 73 (1951) 373-380.

- [41] G. Reichenauer. Structural Characterization of Aerogels. in: Aegerter MA, Leventis N, Koebel MM, (Eds.). *Aerogels Handbook*. Springer, New York, 2011. pp. 449-498.
- [42] G.R. Artus, S. Seeger. One-Dimensional Silicone Nanofilaments, *Advances in Colloid and Interface Science* 209 (2014) 144-162.
- [43] L. Gao, T.J. McCarthy. $(\text{CH}_3)_3\text{SiCl}/\text{SiCl}_4$ Azeotrope Grows Superhydrophobic Nanofilaments, *Langmuir* 24 (2008) 362-364.
- [44] H.S. Khoo, F.-G. Tseng. Engineering the 3D Architecture and Hydrophobicity of Methyltrichlorosilane Nanostructures, *Nanotechnology* 19 (2008) 345603.
- [45] P. Orsolini, C. Antonini, A. Stojanovic, W.J. Malfait, W.R. Caseri, T. Zimmermann. Superhydrophobicity of Nanofibrillated Cellulose Materials through Polysiloxane Nanofilaments, *Cellulose* 25 (2018) 1127-1146.
- [46] A. Stojanovic, S. Oliveira, M. Fischer, S. Seeger. Polysiloxane Nanotubes, *Chemistry of Materials* 25 (2013) 2787-2792.
- [47] W.J. Malfait, R. Verel, M.M. Koebel. Hydrophobization of Silica Aerogels: Insights from Quantitative Solid-State NMR Spectroscopy, *Journal of Physical Chemistry C* 118 (2014) 25545-25554.
- [48] W.J. Malfait, S. Zhao, R. Verel, S. Iswar, D. Rentsch, R. Fener, Y. Zhang, B. Milow, M.M. Koebel. The Surface Chemistry of Hydrophobic Silica Aerogels, *Chemistry of Materials* 27 (2015) 6737-6747.

Figure captions

Figure 1. Ternary plot of the investigated hydrophobization mixtures of trimethylethoxysilane (M), dimethyldiethoxysilane (D) and methyltriethoxysilane (T).

Figure 2. Density as a function of the fraction of trimethylethoxysilane (M) has been substituted by dimethyldiethoxysilane (D) and/or methyltriethoxysilane (T). All plotted data is for samples that were hydrophobized for 24 hours.

Figure 3. SEM images of the samples prepared with pure hydrophobization agents (M100, D100 and T100).

Figure 4. a) Nitrogen sorption isotherms of the samples from the M-T series, i.e. hydrophobized with mono-functional silanes, tri-functional silanes, or mixtures thereof. b) Nitrogen sorption isotherms of the samples from the M-D series, i.e. hydrophobized with mono-functional silanes, di-functional silanes, or mixtures thereof. All plotted data is for samples that were hydrophobized for 24 hours.

Figure 5. Surface area as a function of the fraction of trimethylethoxysilane (M) has been substituted by dimethyldiethoxysilane (D) and/or methyltriethoxysilane (T). All plotted data is for samples that were hydrophobized for 24 hours.

Figure 6. ^1H - ^{29}Si cross polarization NMR spectra of silica aerogels hydrophobized with various hydrophization agents.

Figures

Figure 1. Ternary plot of the investigated hydrophobization mixtures of trimethylethoxysilane (M), dimethyldiethoxysilane (D) and methyltriethoxysilane (T).

Figure 2. Density as a function of how much trimethylethoxysilane (M) has been replaced by dimethyldiethoxysilane (D) and/or methyltriethoxysilane (T) during sample preparation. All samples were hydrophobized for 24 h.

Figure 3. SEM images of the samples prepared with pure hydrophobization agents (M100, D100 and T100). All samples were hydrophobized for 24 h.

Figure 4. Nitrogen sorption isotherms of samples from the M-T series (top) and the M-D series (bottom), hydrophobized with mono-, di- or tri-functional silanes, or mixtures thereof. All samples were hydrophobized for 24 h.

Figure 5. Surface areas as a function of how much trimethylethoxysilane (M) has been replaced by dimethyldiethoxysilane (D) and/or methyltriethoxysilane (T) during sample preparation. All samples were hydrophobized for 24 h.

Figure 6. ^1H - ^{29}Si cross polarization NMR spectra of silica aerogels hydrophobized with various hydrophobization agents. The sharp resonance at -22 ppm for the D100 sample (*) can be assigned to PDMS.

Ambient pressure drying of silica aerogels after hydrophobization with mono-, di- and tri-functional silanes and mixtures thereof

- Up to 20% trimethylsilyl can be substituted without compromising aerogel density
- Higher degrees of replacement not possible without further optimization
- Self-polymerization of dimethyldiethoxysilane into polydimethylsiloxane
- Self-polymerization of methyltriethoxysilane into 100-200 nm large beads