Heterogeneous silica-polyimide aerogel-in-aerogel nanocomposites

Zuzanna Kantor a, b, 1, Tingting Wu a, 1, Zhihui Zeng c, Sabyasachi Gaan d, Sandro Lehner d, Milijana Jovic d, Anne Bonnin e, Zhengyuan Pan f, Zahra Mazrouei-Sebdani a, Dorina M. Opris g, Matthias M. Koebel a, Wim J. Malfait a, * , Shanyu Zhao a, *

a Laboratory for Building Energy Materials and Components, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland
b AGH University of Science and Technology, Aleja Adama Mickiewicza 30, 30-059 Kraków, Poland
c School of Materials Science and Engineering, Shandong University, Jinan 250061, PR China
d Laboratory for Advanced Fibers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Larchenfeldstrasse 5, 9014 St. Gallen, Switzerland
e Swiss Light Source, Paul Scherrer Institute, Forschungsstrasse 111, Villigen 5232, Switzerland
f State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510640 Guangzhou, PR China
g Functional Polymers, Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

* Corresponding authors.
E-mail addresses: wim.malfait@empa.ch (W.J. Malfait), shanyu.zhao@empa.ch (S. Zhao).
1 Z. Kantor and T. Wu contributed equally to this article.

A R T I C L E   I N F O
Keywords:
Polyimide aerogel
Silica aerogel
Dimensional stability
Dielectric constant
Thermal insulation

A B S T R A C T
Polymer aerogels are a promising, non-brittle alternative to silica aerogel, but are limited by their very poor high-temperature stability. Polyimide is widely known for its high heat-resistance, however, a high degree of volume shrinkage is common for polyimide aerogels after exposure to temperatures above 200 °C. Here, we present the aerogel-in-aerogel composites that comprise silica aerogel grains with a nanoparticulate microstructure embedded in a nanofibrous polyimide aerogel matrix. The mixing procedure and synthesis protocol were optimized to avoid excessive infiltration of the polyimide sol into the silica aerogel mesopores. The composites display a unique, heterogeneous structure with a high surface area, >600 m² g⁻¹, a low thermal conductivity down to 17.5 mW m⁻¹ K⁻¹, a very low dielectric constant (∼2.5 at 10⁻¹⁻⁰⁶ Hz, ∼1.2 at 8–12.5 GHz, ∼1.2 at 26.5–32 GHz) and dielectric loss (10⁻⁷ to 10⁻¹ at all studied frequencies). The hydrophobic silica aerogel component contributes a high water resistance, with high water contact angles (>150°) and a low humidity uptake (<4 wt% at 88% relative humidity), and a much-reduced volume shrinkage at high temperature. The polyimide component imparts excellent mechanical properties to the composites, including improved compressive modulus, compressive and bending strengths. The composite aerogels offer great potential for applications that require high mechanical strength, a low dielectric constant and/or thermal conductivity and/or high-temperature stability.

1. Introduction
Since the first development by S.S. Kistler in 1931, aerogel materials have generated great attention [1]. Over the years, many types of aerogel materials have been developed, e.g. inorganic (silica, titania, and alumina etc.), polysaccharides (cellulose, chitosan, and alginate etc.), synthetic polymers (polyurethane, polyimide, and resorcinol-formaldehyde, etc.), and carbon aerogels [2]. Today’s commercially available aerogel materials are primarily still of the silica variety: 98% of the aerogel revenue in 2019 was for silica-based materials [3]. However, the adoption of silica aerogel is still quite restricted for applications beyond oil and gas pipelines and industrial insulation (85% of the market). Aside from the cost, the poor mechanical properties and health concerns on released fine dust are major barriers. Hence, other aerogel variants, especially organic aerogels, hold great expectations for future market growth.

Polyimide aerogel is one of the most promising solutions among those organic candidates. Polyimides (PI) are high-performance engineering polymers with inherent high decomposition temperature, good mechanical property, chemical resistance, low refractive indices, and low permittivity. [4] They are widely used in optoelectronics, aviation, electronics, filtration, and aeronautics [5–7]. Polyimides are typically...
prepared by a step-growth condensation polymerization of diamines with dianhydrides, and the resulting poly(amic acid) is imidized thermally or chemically [8]. Polymide aerogels retain the intrinsic chemical composition and properties of polymides, and are prepared by the sol–gel process, followed by supercritical CO$_2$ drying [9,10], freeze-drying or ambient pressure drying [11]. To introduce a high porosity, the solid concentration in polyimide aerogels is controlled below 13 wt % (Figure S1).

The first reported route for synthesizing PI aerogel used pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) in N-methyl-2-pyrrolidone (NMP) and thermally imidized (190 °C). In the same work, 4,4'-methyleneedianiline and 4,4'-methylene di-isocyanate were also used [12]. However, this type of polymerization can only form linear chains, leading to a high degree of structure planarity and strong intermolecular forces, leading to bad volumetric stability during gelation and imidization. The shrinkage could be controlled by introducing amine-based crosslinkers, e.g. 1,3,5-tris(4-aminophenyl)benzene, 1,3,5-triaminophenoxybenzene (TAB) etc., which can form covalent bonds between the linear polymer chains [10]. The result is a 3D polymer network, which efficiently reduces shrinkage [13–15]. Moreover, the usage of an excess of acetic anhydride (AA) as the water scavenger enables the imidization at room temperature by pyridine [13] or TEA [10]. Since these groundbreaking studies, many other multifunctional crosslinkers, (di)amines and (di)anhydrides have been applied for the fabrication of PI aerogels, e.g. using 2,4,6-tris(4-aminophenyl)pyridine (dianhydride) crosslinked with bisphenol-A, 4,4'-tetracarboxylic dianhydride (BPDA) and rigid benzimidazole oligomers [16], amine end-capped oligomer (e.g. BPDA and DMBZ or ODA oligomer) crosslinked with triacidchlorides (e.g. 1,3,5-benzenetricarbonyl trichloride (BTC)) [9], and isocyanates, poly(maleic) anhydride as well as TAB [17].

Even though the selection of the right polymeric crosslinker can strongly reduce the shrinkage of the PI aerogel during the synthesis, a common problem for PI aerogels remains: the high degree of volume shrinkage and structural collapse when exposed to moderately high temperatures, well below the thermal decomposition temperature of the polyimide itself, for example, 26% linear shrinkage at 150 °C for 24 h and 40% linear shrinkage at 200 °C for 24 h [18], which result in their underutilization for high-temperature applications. However, even the addition of nanofillers, e.g. cellulose nanocrystals [19] and attapulgite [18], were reported to stabilize the polyimide composite aerogels to some extent at a use temperature of 200 °C, the samples are still not stable when the use temperature is over 200 °C. Silica/silanes have been introduced to form rigid networks, e.g. 3-aminopropyltrimethoxysilane (APTES), bis(trimethoxysilylpropyl) amine (BTMSA) and octa (aminopropyl)silsesquioxane (OAPS) [13–15,20]. Silica aerogel fillers were also reported to stabilize the PI aerogels [21,22]. After adding the silica or even silica aerogel fillers, the shrinkage during the synthesis was improved. Still, the PI-silica composite aerogel’s properties are not as good as either silica aerogel or PI aerogel, with surface areas up to 450 m$^2$ g$^{-1}$ and a thermal conductivity around 28.3–37.1 mW m$^{-1}$K$^{-1}$, and the high-temperature stability was barely examined [22]. The less than optimal properties of the PI-silica composite, compared to pure polyimide and pure silica aerogel counterparts, are most likely related to the long mixing time of the silica aerogel powder with the poly(amic acid) solution, which may have degraded the silica aerogel mechanically and/or caused infiltration of the poly(amic acid) into the silica aerogel mesopores.

In the present study, high-temperature, low shrinkage heterogeneous polyimide-silica aerogel composites were prepared by incorporating micrometer-sized silica aerogel particles into a polyimide sol. By controlling the mixing process to avoid excessive infiltration of sol into the silica aerogel mesopores, the polyimide-silica aerogel composites display a unique heterogeneous structure. The composites display a high surface area, an ultra-low thermal conductivity, and a very low dielectric constant and loss. Besides, the composites are superhydrophobic with a low humidity uptake which is beneficial to maintain the low dielectric constant in humid conditions. The composites with loadings of silica aerogel display a low volume shrinkage and maintain moderately high surface areas after exposure to high temperature, in stark contrast to pure polyimide aerogels.

2. Experimental

2.1. Chemicals

4,4'-oxydianiline (ODA, 97%) and biphenyl-3,3',4,4'-tetracarboxylic dianhydride (BPDA, 98%) were provided by Sigma-Aldrich. The imidization agents pyridine (≥99%) and acetic anhydride (≥98%) were purchased from Sigma-Aldrich. The crosslinker 1,3,5-benzene tricarboxylic acid (BTC, 98%) was purchased from Sigma-Aldrich. N-methyl-2-pyrrolidone (NMP, 98%, Chemie Brunschwig AG) was used as a solvent for polyimide synthesis, and acetic anhydride (99%, Thomen Furler) was used as a solvent for the solvent exchange and supercritical CO$_2$ drying. Silica aerogel powder (amorphous, 5–20 μm) is obtained from Cabot Aerogel (ENOVA IC3100). All reagents were used without further purification.

2.2. Preparation of polyimide aerogels

The biphenyl-3,3',4,4'-tetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) were mixed with a molar ratio of respectively n: n + 1 in a N-methyl-2-pyrrolidone (NMP) solvent, the concentration of the polymeric polymer in the solution is 7 wt%. And the repeating units n varied from 20 to 40, but with the same amount of crosslinker 1,3,5-benzene tricarboxylic acid (BTC), which is designed to stoichiometrically crosslink with the end oligomer amino group in the n = 40 samples. After 30 min of polymerization at room temperature (S.T.P.), acetic anhydride was added slowly to the solution, followed by pyridine, and the whole mixture was stirred for 5 to 15 min. In the meantime, BTC was dissolved in the NMP, which was subsequently added to the polymer solution, and stirred for 5 more minutes. What we added here the sequence is different from the typical polyimide aerogels (typically step of adding crosslinker precedes step pyridine and acetic anhydride), the new sequence provides more time flexibility for silica aerogel addition in the following composite samples. The mixture was transferred into silicon molds and the gelation occurs within 5 to 15 min, depending on the number of units and the imidization process. Samples were aged 24 h at room temperature (S.T.P.), and the solvent was exchanged with 75/25, 25/75, and 0/100 NMP/acetone in 24 h intervals. The composites were finally dried under supercritical CO$_2$. The pure polyimide aerogels with different repeating units were named Pyr$_{20}$, Pyr$_{30}$, and Pyr$_{40}$, respectively.

2.3. Preparation of polyimide-SiO$_2$ composite aerogels

The polyimide sol preparation follows the scheme in Fig. 1. After the addition of BTC solution, silica aerogel powders were added into the solution, all reactants were transferred into a polypropylene container, and speed mixing with 2000 r.p.m. for 2 min. The mixture was transferred into silicon molds and the gelation occurs within 5 to 15 min, depending on the number of units and the imidization process. Samples were aged 24 h at room temperature (S.T.P.), and the solvent was exchanged with 75/25, 25/75, and 0/100 NMP/acetone in 24 h intervals. The composites were finally dried under supercritical CO$_2$. The preparation of the polyimide-SiO$_2$ composite aerogels as described in Fig. 1a,b. The n = 40 polyimide composite aerogels with different amounts of silica aerogels were named Pyr$_{40}$, Pyr$_{40}$, and Pyr$_{40}$; respectively. Moreover, the corresponding silica fractions in the dried composite aerogels are 23.0, 28.2, and 35.2 wt%, respectively.

3. Characterizations

Density determination. The bulk density was calculated from the
mass and volume of the rectangular and cylindrical samples. The skeletal density was measured by means of a helium pycnometer (AccuPyc II 1340, Micromeritics, USA).

**Microstructural analysis.** SEM images were recorded on a FEI Nova NanoSEM 230 (FEI) at an accelerating voltage of 10 kV and a working distance of ~5 mm. Nominal 15 nm of Pt (measured with a flat piezo detector) was coated to avoid charging, but the effective thickness on the aerogels, with their extreme topography and surface area, will be much lower.

**Nitrogen sorption analysis** was carried out on a TriFlex nitrogen sorption analyzer (Micromeritics) after prior degassing for 20 h at 100 °C and 0.02 mbar. The specific surface areas ($S_{BET}$, uncertainty ~ 50 m$^2$/g) were obtained using the BET method (10). The pore volume ($V_{pore}$) and average pore diameter ($d_{pore}$) were calculated from the
density of the aerogels and their $S_{BET}$ using Equations 1 and 2, respectively (11).

\[
V_{\text{pore}} = \frac{1}{\rho} - \frac{1}{\rho_{\text{skeletal}}} \tag{S1}
\]

\[
d_{\text{pore}} = \frac{4V_{\text{pore}}}{S_{\text{BET}}} \tag{S2}
\]

where $\rho$ is bulk density, $\rho_{\text{skeletal}}$ is skeletal density, and $S_{\text{BET}}$ is specific surface area.

**Thermal stability.** Thermogravimetric analysis was conducted on a TGA7 analyzer (Perkin Elmer, USA) with the aim to identify the onset temperature to the degradation / loss of hydrophobic TMS groups, which represents an upper boundary for operation temperature. High-temperature shrinkage experiments were conducted by placing square samples in a kiln (Pyrotec Brennofenbau Osnabrück). The linear shrinkage (S) was calculated by $S = (L_0 - L_f)/L_0$, where $L_0$ and $L_f$ are the lengths of the samples before and after heat treatment. Limiting oxygen index (LOI) was measured according to ASTM D 2863 using the device from Fire Testing Technology (UK). The samples (60 mm $\times$ 15 mm $\times$ 15 mm) were conditioned for at least 40 h at 23 ± 2 °C and 50 ± 5% relative humidity (RH) before the measurements.

**Thermal conductivity.** Thermal conductivities were determined from separately prepared square plate specimens (around 48 $\times$ 48 $\times$ 7 mm$^3$, cast simultaneously from the same sols) of monolithic aerogels using a custom-built guarded hot plate device (guarded zone: 50 $\times$ 50 mm$^2$, measuring zone: 25 $\times$ 25 mm$^2$) designed for small samples of low thermal conductivity materials with a 10 °C temperature difference. In order to be consistent with measurements according to European Standards [23], calibration measurements were carried out using conventional expanded polystyrene samples measured once in a 50 cm $\times$ 50 cm $\times$ 50 cm device, which was then calibrated and validated for the smaller testing equipment. The small guarded hot plate measurement data was then again measured for the same EPS sample in the smaller scale tested device.

**Mechanical test.** Uniaxial compression tests of the composites were performed on a cylindrical sample using a universal material testing machine (Zwick/Z010, Zwick/Roell, Germany), equipped with a 10 kN force transducer (KAP-S, AST Gruppe GmbH, Germany) in a controlled environment (23 °C, 50% relative humidity). Elastic moduli (E) were calculated from the initial linear region of the stress–strain curves, which typically occurred at 3 ± 2% strain. A constant deformation rate of 1 mm/min was used and compressive strength values were taken at the first noticeable sign of cracking or until reaching 80% strain. Tensile tests were also performed on the Zwick/Z010 device equipped with a 2 kN force transducer, five dog-bone-shape specimens were prepared in accordance with ASTM D 6363, and the size was shown in Figure S10. A constant deformation rate of 5 mm/min was used and the elongation of the specimen were monitored by a Laser extensometer. A universal testing machine (Zwick/Z010, Zwick/Roell, Germany) was used to measure the bending properties of the PI aerogels with a three-point bending method based on standard test method of ASTM C203-05a, as support span length was 10 times of the sample thickness. The bending modulus is calculated from the slope of the first linear part of the load-deformation curves. The crosshead rate was 5 mm/min and 3 specimens for sample n40 were measured. Flexural stress and strain at any point can be calculated from a known dimension of the sample, deflection and force needed for the deflection.

**Hydrophobicity.** The surface wettability of samples was evaluated by water contact angle measurement using a Contact Angle System OCA (Dataphysics TBU 90E, Germany), combined with a high-speed camera. Water droplets were deposited directly on the top or bottom surfaces of the samples. Three measurements were performed per sample and averaged. The volume of the water droplet was 10 μl, and the tip was a precision stainless steel tip (Gauge 32, EFD). Dynamic water vapor sorption (DVS) isotherms were obtained using a DVS Endeavour 5X Parallel Gravimetric Sorption Analyzer (Surface Measurement Systems, UK). Around 50 mg aerogels were put onto the high-precision microbalance, allowing continuous monitoring of the amount of adsorbed water vapor, and exposed to stepwise increasing humidity levels (0–88%) in 5% increments in a controlled flow of a mixture of nitrogen and water. Before recording the isotherm curves, the aerogels were heated up to 80 °C for 2 h to remove the potential absorbed humidity under nitrogen atmosphere. The resulting mass was taken as the dry reference mass. Afterwards, the chamber cooled to 25 °C for the collection of the mass change at different humidity levels.

**Heat treatment.** The volumetric shrinkage of the pure polyimide aerogels and polyimide silica composite aerogels were evaluated after exposure to 200 °C, 300 °C, and 400 °C, respectively, for 1 h.

**Fourier transform infrared (FT-IR) spectra** were recorded with a FT-IR spectrometer (Bruker, Tensor 27 FTIR) by means of attenuated total reflectance (ATR) using a diamond crystal.

**Solid-state NMR spectra** were acquired with a Bruker, Avance III spectrometer equipped with a wide-bore 9.4 T magnet, corresponding to Larmor frequencies of 400.2 MHz for 1H and 100.6 MHz for 13C. The aerogels were loaded in 4 mm diameter ZrO$_2$ rotors and MAS at 13 kHz. Spectra were acquired with $^1$H–$^1$C cross-polarization (CP) with a recycle delay of 2 s, and a rather long contact time of 2 ms. The spectral intensities not only depend on the species abundance but also on the CP and relaxation dynamics.

**Dielectric properties.** The waveguide transmission technique was employed for testing the dielectric properties of the polyimide aerogels. Three different frequency ranges were studied. For low-frequency measurements ($10^3$–$10^6$ Hz), the sample measurement was performed on a parallel plate capacitor using a Novocontrol impedance Alpha Analyzer combined with a Quatro temperature controller. Two stainless steel discs with a diameter of 20 mm served as electrodes. In the gigahertz frequency, the X-band (8–12.5 GHz) and Ka-band (26.5–32 GHz) were performed using a vector network analyzer (VNA, Agilent PNA N5244A) and in the waveguide mode. The sizes of the tested samples are 22.8 mm $\times$ 10.2 mm for X-band and 15.8 mm $\times$ 8.0 mm for Ka-band. Three samples were tested for each component. The S parameters were recorded and used to calculate power transmissivity.

**Synchrontron X-ray tomographic microscopy analysis.** $3 \times 3 \times 10$ mm$^3$ rectangular polyimide samples were cut and measured by synchrotron X-ray tomography. Imaging was performed at the TOMCAT beamline of the Swiss Light Source, situated on a 2.9 T bending magnet, and equipped with a multilayer monochromator. X-ray images were acquired at 12 keV and a propagation distance of 50 mm. The X-ray indirect detector comprised a LSO:Tb 5.8 $\mu$m scintillator, a $\times 40$ optical objective, and a scCMOS pco.EDGE camera (6.5 $\mu$m pixel size, 2560 $\times$ 2160 pixels), resulting in an effective pixel size of 0.162 $\mu$m. During the continuous tomography scan, 1501 projections were collected over 180° with an exposure time of 500 ms per projection as well as two series of 50 flats and a series of 20 dark projections. The data were reconstructed using the Gridrec algorithm (8) with and without prior phase-retrieval (Paganin, delta = 0.2e$^3$, beta = 3.6e$^3$ with unsharp mask of 0.3 width and sigma = 1).

**3D image analysis.** X-ray images were imported into ImportGeo-Vol (Geodict, Math2Market) for reconstructing the samples. The voxel sizes were 0.1625 $\mu$m, corresponding to the effective pixel sizes used during the tomography scan. After a series of image processing steps, the Otsu Single Threshold method was used for segmenting silica aerogel from the background polyimide. Then volume fractions of two aerogel materials were calculated based on the reconstructed samples.

4. Results and discussion

The microstructure and properties of polyimide aerogels are influenced by many factors, i.e. the diamines and dianhydrides precursors, the crosslinkers, imidizers, the gelation, drying solvents, and imidization conditions. In this study, the most popular diamine (ODA) and
dianhydride (BPDA) were selected as the precursors, while BTC was used to crosslink the amino terminated oligomers (Fig. 1a). The poly (amic acid) was chemically imidized by pyridine and acetic anhydride. The oligomer chain length was adjusted by varying the number of repeat units n of 10, 20, 30, and 40. The stoichiometric amount of BTC was calculated based on the n = 40 formulation, but kept constant for n = 20 and n = 30 samples (Table S1). As a result, there are 0.24 and 0.08 mmol excess amino groups for the n = 20 and n = 30 samples. The N$_2$ sorption isotherms and pore size distribution of the silica aerogel particles used to make the composite shows a typical mesoporous structure with the peak of pore size at 7 nm (Fig. 1c). The full imidization with our protocol is confirmed by the $^{1}$H-$^{13}$C cross-polarization NMR spectra (Fig. 1d). The pure polyimide aerogel spectrum is virtually identical to that from the literature for polyimide aerogels prepared with a very similar formulation [9], and no peak related to non-imidized poly(amic acid) is present. The spectrum of the polyimide-silica aerogel composite is very similar, but with an added resonance near zero ppm from the trimethylsilyl hydrophobic groups present on the silica aerogel.

The pure polyimide aerogels display a nanofibrous 3D network with apparent fiber diameters in the 20-50 nm range, regardless of oligomer chain length (Fig. 1e-g). The PI aerogel with n = 20 displays a denser structure likely due to easier pore collapse during drying for these shorter, only partially cross-linked oligomers. The silica composites in this paper were all prepared from n = 40 PI formulation. We have developed a fast mixing process (Fig. 1b), to promote the dispersion of the particles in the viscous PI sol, prevent the break of silica aerogel particles and limit the infiltration of the sol in the silica aerogel’s mesopores. In the following discussion, Pyr$_{x}$y stands for the polyimide aerogel imidized by pyridine and acetic anhydride, with a repeat unit $\times$ and y wt.% silica aerogel particles in the sol.

The size of the silica particles in the composite ranges from 5 to 30 $\mu$m (Fig. 1h-j), consistent with the particle size distribution analysis of the silica aerogel starting powder in the gelation solvent NMP (Figure S2). The addition of the crosslinker (BTC) induces the quick gelation of the polyimide phase, fixes the silica aerogel granulates and stops full infiltration of the oligomers/polymer into the silica pores (EDX map and line scan shown in Figure S3). Consequently, a two-phase aerogel composite formed with silica aerogel grains embedded in a polyimide aerogel matrix (Fig. 1j-h). The high magnification images from the polyimide phase (Fig. 1k) and silica phase (Fig. 1i) display well-maintained fibrous polymer aerogel and particulate silica aerogel microstructures, respectively. No obvious polyimide infiltration could be identified at the silica aerogel granulate surface. The bulk density of the composites does increase with the increased loading of silica aerogel particles (Table 1), but not to a lesser extent than expected just from the increased solid content, e.g. the addition of 4 wt% silica aerogel increases density by 0.025 g/cm$^3$ rather than the theoretically expected 0.040 g/cm$^3$. This lower than expected increase in density reflects the decreased drying-induced shrinkage upon the addition of the silica aerogel filler. The bright interfacial sections around the silica aerogel grains in the tomographic slices (Fig. 1m) confirm locally higher density areas at the silica and polymer interface, presumably due to a filtering effect at the silica aerogel-polyimide sol interface, where NMP infiltrates the silica aerogel pores, but the polyimide chains do not. The 3D volume rendering indicates well-distributed silica aerogel particles in the polyimide aerogel matrix (Fig. 1 n-p, S4 and S5). The volumetric image analysis for this sample results in 46.0 vol% silica aerogel and 54.0 vol% PI aerogel. The silica volume fraction is higher than the theoretical value, calculated from the 4 wt% loading and a silica aerogel and sol density of 0.100 and 1.03 g/cm$^3$ (41.2 vol% silica aerogel), due to the shrinkage of the PI phase in the composite.

As a high-performance polymer, polyimide is well-known for its excellent high-temperature and chemical stability. However, in the form of aerogels, the pore structure and physical properties are not stable for the high-temperature applications. Hence, for polyimide aerogels, we should not just consider the chemical decomposition, but also the deterioration of physical properties and pore structure stability. TGA results of pure polyimides and polyimide-silica composites are shown in Fig. 2a. The onset temperatures (95% mass loss) of the polyimide aerogels are all above 560 °C (Table 1), which is higher than most organic materials [24]. After the addition of silica aerogels, the onset temperature was reduced to around 520 °C, which is induced by the low decomposition temperature of the surface trimethylsilyl (TMS) group of silica aerogels (Fig. 2a) [25]. The TG analysis ended at 900 °C, where polyimides were completely decomposed, only a few percent of the weight remained. PI-silica composites show 50.6, 44.1 and 37.7 wt% remaining weights for Pyr$_{40}$, Pyr$_{40}$, and Pyr$_{40}$, respectively. In comparison with the start materials composition (Table S1), some parts of the polyimide preserved even at 900 °C, indicating the polyimide silicon interactions in the composites. The chemical structures of the pure polyimide (Figure S6a) and polyimide-silica aerogels (Figure S6b) were analyzed by FTIR. The bands around 1720 and 1780 cm$^{-1}$ attributed to the symmetrical and asymmetrical stretching vibration of carbonyl groups on the imide ring and 1380 cm$^{-1}$ peculiar to the C-N stretching could be clearly observed in all samples before and after treatments at 200 and 400 °C, reflecting the chemical stability. Regarding the silica component, to avoid numerous polyimide peaks in the background, we have subtracted the spectra of the silica-free aerogel out from the composite spectra and then compared them with the spectra collected from hydrophobic and hydrophilic reference silica aerogels (the hydrophobic silica aerogels were treated at 400 °C for 1 h to become the hydrophilic ones) (Fig. 2d-f). We could identify all the chemical signatures of the trimethylsilyl groups of the hydrophobic silica aerogel in the untreated and, surprisingly, heat-treated composite samples (Fig. 2d-e, bands near 700, 2900, and 2960 cm$^{-1}$), even though the trimethylsilyl groups are considered to be unstable above 300 °C at air atmosphere [25,26]. Thus, the polyimide matrix helps retain the hydrophobic groups of the silica aerogel upon heat treatment.

### Table 1

<table>
<thead>
<tr>
<th>Samples$^a$</th>
<th>Physical properties</th>
<th>$N_2$ sorption</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure$^b$</td>
<td>Mixted$^c$</td>
<td>Porosity</td>
</tr>
<tr>
<td></td>
<td>g cm$^{-3}$</td>
<td>g cm$^{-3}$</td>
<td>%</td>
</tr>
<tr>
<td>Silica aerogel</td>
<td>0.120</td>
<td>0.200</td>
<td>94</td>
</tr>
<tr>
<td>Pyr$_{10}$</td>
<td>0.141</td>
<td>1.45</td>
<td>90</td>
</tr>
<tr>
<td>Pyr$_{20}$</td>
<td>0.139</td>
<td>1.45</td>
<td>90</td>
</tr>
<tr>
<td>Pyr$_{30}$</td>
<td>0.135</td>
<td>1.47</td>
<td>91</td>
</tr>
<tr>
<td>Pyr$_{40}$</td>
<td>0.132</td>
<td>1.46</td>
<td>91</td>
</tr>
<tr>
<td>Pyr$_{40}$</td>
<td>0.137</td>
<td>1.54</td>
<td>91</td>
</tr>
<tr>
<td>Pyr$_{40}$</td>
<td>0.150</td>
<td>1.55</td>
<td>90</td>
</tr>
<tr>
<td>Pyr$_{40}$</td>
<td>0.157</td>
<td>1.58</td>
<td>90</td>
</tr>
</tbody>
</table>

$^a$ Pyr$_{x}$y denotes polyimide aerogel imidized by pyridine and acetic anhydride, with repeat unit $\times$ and y wt.% silica aerogel particles in the sol. PI content in the sol is constant (6.5 wt%) for all samples.

$^b$ Uncertainties: $\rho_{\text{bulk}}$ 1% relative, $\rho_{\text{skeletal}}$ 0.1% relative, SBET around 50nm2 g$^{-1}$, Dpore 5% relative, Vpore 5% relative.
Chemical Engineering Journal 443 (2022) 136401

polyimide features at 1380, 1730, and 1780 cm\(^{-1}\) cannot be subtracted out completely, both before and after heat treatment, indicating that the polyimide component is affected, to a minor extent, by the inclusion of the silica aerogel powder in the sol and by the heat treatment.

Even though the polyimide is chemically stable at elevated temperatures, its pore structure is not. For treatment temperatures below 200 °C (for 1 h), the shrinkage between pure polyimide and the composite aerogels is similar (Fig. 2b). Increasing the treatment temperature above 300 °C results in an 80% porosity reduction of pure polyimide aerogels and almost no mesoporous structures are preserved after treatment (Fig. 2c). However, we could observe a significant reduction of shrinkage upon the addition of silica aerogel. At 3 wt% loading of silica aerogel in the sol (28 wt% in the dried composite), the volumetric shrinkage was reduced by 40% due to the high shape preservation capability of the silica aerogel (Fig. 2b and Figure S9). To understand the pore structure change after the heat treatments, the \(\text{N}_2\) sorption isotherms and surface area (Fig. 2c, S7) and SEM images (Fig. 2g) of the pure polyimide and composites were compared. Without heat treatment, all samples display type IV isotherms with H3 hysteresis. The composites show much higher \(\text{N}_2\) sorption volume, specific surface area,
and mesopore volume (Table 1), which indicate a great mesoporosity contribution of silica aerogel. After heat treatment, the surface area of the pure polyimide aerogel was reduced strongly, to 118 m$^2$ g$^{-1}$ after 200 °C and below the limit of detection after treatment at 400 °C (Table S2). In contrast, the composites with silica aerogel could maintain over 200 m$^2$ g$^{-1}$ surface area even after 400 °C treatment. These changes in pore structure are also visible in the SEM images (Fig. 2g). The nanofibrous structure is still visible, albeit with densified pores, after 200 °C treatment, but completely disappears after 400 °C treatment for the pure polyimide aerogels. This effect also occurs for the composites, but the mesoporous structure of silica aerogel components remains, which contributes to the partial retention of porosity and surface area after heating.

Due to their unique chemical structures and high porosity, polyimide aerogels typically have a very low relative dielectric constant ($\epsilon$) and dielectric loss tangent (tan$\delta$) [18,27]. To study the dielectric properties of the silica-polyimide composites, the $\epsilon$ and tan$\delta$ of the pure and composite polyimide aerogels (Pyr_40 and Pyr_40_3) were measured at three different frequency ranges (Fig. 3a). In the X band (8 GHz to 12 GHz) of the microwave region of the electromagnetic spectrum, the $\epsilon$ of the pure and composite aerogels (Pyr_40 and Pyr_40_3, respectively) are stable and very low, around 1.1 to 1.4, and the tan$\delta$ is in a super low range from $10^{-3}$ to $10^{-1}$ (Fig. 3a2), comparable to reported polyimide aerogels of similar density [27]. In the Kα band (26.5 GHz to 32 GHz), the $\epsilon$ of the pure and composite aerogels are stable between 1.0 and 1.3. And the tan$\delta$ values are in the range of $10^{-2}$ to $10^{-1}$ (Fig. 3a3). Such high-frequency ranges are representative for the frequencies used for high Mach number aircraft aeronautics and aerospace communications, which is one possible application of polyimide aerogels. However, in order to comprehensively understand the overall dielectric performance of our polyimide composites, a low frequency range of $10^{1}$ to $10^{6}$ Hz (radio wave and sub-microwave regions) was also studied (Fig. 3a1), which are critical for communication with submarines. In this frequency range, both pure and composite aerogels show slightly higher $\epsilon$ (2.4 for Pyr_40, and 2.5 for Pyr_40_3), however, they are still lower than reported PI films, which are in a range of 2.7 to 3.6 [28–32]. Additionally, the corresponding tan$\delta$ are stable around $10^{-3}$.

To show a direct advantage of using polyimide-silica aerogels for thermally agnostic application scenarios, it is critical to understand the fire resistance behavior. Both pure polyimide and silica composites show very high limiting oxygen indices (LOI > 43%), which is consistent with the reported high fire-resistance of polyimide [33]. Even though the polyimide samples can still be carbonized by fire, the actual behavior is rather glowing than burning (Fig. 3b). Interestingly, the silica loading lowers the onset decomposition temperature in the TGA (Fig. 2a), but not the LOI values.

Polyimide aerogels prepared from the precursors selected here (Fig. 1) are generally hydrophilic. Particularly samples with sub-stoichiometric crosslinkers ($n < 40$) are super-hydrophilic because of residual amino groups, and no contact angle can be measured because the water droplets were absorbed immediately (Figure S8). For fully crosslinked Pyr_40, the water contact angle on the surface and fresh cross-section can reach up to 80° and 110° during a short period of measurement, but this is mostly due to the surface roughness, and the water droplet is absorbed in seconds, leading to irreversible structural damage (Fig. 3d and S6). The addition of silica aerogel increases the water contact angle, but the samples with 2 wt% silica in the sol (Pyr_40_2) still quickly absorb the water during the measurement. Samples that contain a large amount of silica aerogel particle (Pyr_40_3 and Pyr_40_4) display hydrophobic behavior with stable WCA>150°, and the water droplet is no longer absorbed (Fig. 3d). Furthermore, dynamic water vapor sorption (DVS) was carried out in the humidity range from 5 to 88% R.H. The decreases of humidity uptake confirm the contribution of silica aerogels to the hydrophobicity of composites.

Better mechanical properties, and a reduction in brittleness in particular, is one of the main selling points of polymer aerogels (including polyimide). Typical stress ($\sigma$) – strain ($\varepsilon$) curves of uniaxial compression, flexural bending and tensile testing, and the corresponding Young’s modulus, strains (or elongation) at break and maximum strength are shown in Fig. 4. During uniaxial compression, both polyimide and composite aerogels display a linear viscoelastic regime at low strain (up to 5%), followed by plastic deformation. Additionally, there is no fracture/yield point up to at least 80% strain. The composite with 28 wt% silica shows 1.4 times higher compressive Young’s modulus $E_c$, and

![Fig. 3](image_url)
three times higher $\sigma_c$ than pure polyimide aerogel. All samples are compressible but not elastic: there is very limited shape recovery after compression to strain values into the plastic deformation regime. The maximum elongation $\varepsilon_t$ during the tensile test is not very impressive, the pure polyimide aerogel only shows 14% elongation, and the addition of silica aerogel further degrades the tensile properties. The tensile modulus $E_t$ of pure and composite PI aerogels are identical. During the flexural bending test, the silica addition shows neither a positive nor negative effect, the Young’s modulus $E_b$, strain at break $\varepsilon_b$ and maximum stress $\sigma_b$ are similar, while the yield regime is much higher in the composite material. In summary, the composite aerogels have good mechanical properties. The addition of silica aerogel moderately improves the Young’s modulus and significantly improves the final compressive strength of the composites, but the bending and tensile strength show limited improvements or a deterioration in properties, mainly induced by the brittleness of the silica aerogel (Fig. 2).

Aside from the increase in high temperature dimensional and structural stability (Fig. 2), the most impressive improvement upon silica addition is decreased thermal conductivity. Polyimide aerogel generally has very good mechanical properties, but its thermal conductivity is always higher than silica aerogel (Table S3). In this study, the pure polyimide aerogels display a thermal conductivity between 22.0 and 24.0 mW m$^{-1}$K$^{-1}$, among the best reported for polyimide aerogels (Table S3, Fig. 5), and below that of standing air (26.0 mW m$^{-1}$K$^{-1}$) due to the Knudsen effect in the polyimide aerogel mesopores. The addition of silica aerogel reduces the thermal conductivity to below 20.0 mW m$^{-1}$K$^{-1}$, with the lowest value of 17.5 mW m$^{-1}$K$^{-1}$ with 35 wt% silica loading (relative to the total dry mass). The thermal gradient of the aerogel samples was evaluated on a high temperature (240 °C) hot plate (Fig. 4f-h): after one-hour equilibration, the composite aerogel displays a ~ 60 °C lower surface temperature compared to the pure polyimide aerogel (Fig. 4f). After the hotplate test, the pure polyimide aerogel deformed substantially, while the composite aerogels had almost no shape change (Fig. 4h).

A comprehensive dataset of density, modulus, specific surface area, and thermal conductivity of polyimide and polyimide composite aerogels was compiled (Table S3) to benchmark the PI-silica aerogel composites developed here (Fig. 5). In this dataset, the polyimide composite aerogels cover a wide variety of nanofillers, e.g. clay, silica, graphene oxide, cellulose, and glass fibers etc. The first Ashby plot describes the density dependence of the compressive modulus $E$ (Fig. 5a). Most aerogel materials display a strong, power-law dependence, $E \propto \rho^\alpha$, which appears as a straight line on a log–log plot [61]. However, the properties of polyimide aerogel are influenced by many factors, i.e. a wide variety of starting precursors, crosslinkers, and imidizers, as well as gel formation and gel drying solvents [9]. These variations mask the density dependence of the $E$ modulus when combining data from different studies and no clear trend is discernible in the log–log plot. For their
density, our polyimide and polyimide-silica composite aerogels display a moderate E modulus, which is not surprising considering it is prepared from a ‘soft’ ODA chain, which according to the literature, results in a relatively low Young’s modulus [9]. The density dependence of thermal conductivity (λ) (Fig. 5b) displays a very broad positive correlation. Perhaps most relevant are the lowest thermal conductivity samples. Only a few polyimide and composite aerogels are reported with thermal conductivity below 20.0 or even 25.0 mW m⁻¹K⁻¹. Still, the best performing samples for a given density, i.e. the low λ boundary of the dataset, describe a U-shaped dependence on density, with the lowest λ values around 0.150 g/cm³. While this dataset is both too sparse and not sufficiently systematic to draw stringent conclusions, a similar U-shaped dependence is observed for most aerogel systems [62]. Among all reported polyimide and polyimide composite aerogels, the heterogeneous aerogel-in-aerogel composites presented here display the lowest λ of 17.5 mW m⁻¹K⁻¹. In terms of application, a simultaneously low λ and high E modulus is optimal: the composite aerogel Pyr_40_3 is in one of the best scenarios for thermal insulation applications, with a very low λ at intermediate Ec (Fig. 5c). The dependence of thermal conductivity on the surface area is highly scattered (Fig. 5d), most likely because many of the materials have thermal conductivities well above 30.0 mW m⁻¹K⁻¹, and in this range, any possible reductions of gas phase conduction through the Knudsen effect, which correlates with mesoporosity and surface area, are masked by the high solid, hence high overall conductions. As expected, λ values well below that of standing air are only reported for materials with relatively large surface areas, most notably the samples presented in this study.

5. Conclusions

This study reports the development of heterogeneous polyimide-silica aerogel composites by compounding micrometer-sized silica aerogel particles into the polyimide aerogel by using an efficient mixing manor that prevents excessive infiltration of polyimide into the silica aerogel filler. This approach with silica aerogel fillers can be extended to other polyimide aerogels, provided that the polyimide chemistry (monomers and cross-linkers) impart sol viscosities and gelation times compatible with the mixing process. Using a silica aerogel powder filler is not problematic from a cost perspective given the comparative costs of the polyimide precursors and the targeted high-performance applications. The heterogeneous polyimide silica aerogel composite displays a unique two-phase, aerogel-in-aerogel) structure (particulate silica and fibrous polyimide aerogel). The best performing composites display a high specific surface area of 609 m² g⁻¹, an ultra-low thermal conductivity of 17.5 mW m⁻¹K⁻¹ and low dielectric constant and loss over a wide range in frequency. Benefiting from high silica aerogel particle loadings, the composites show superhydrophobicity and very low water vapour sorption. Most importantly, the composites with sufficiently high silica aerogel display a low volume shrinkage and maintain a high surface area after high temperature exposure. Compared to state-of-the-art polyimide materials, the composite aerogels developed in the current study show great potential for applications where a (very) low dielectric
constant and high-temperature stability are required. Aside from the ultra-low thermal conductivity and low dielectric constant, the applications benefit from the high-temperature stability (chemical and dimensional) and the improved mechanical properties imparted by the polyimide matrix.

Author Contributions

Z.K., T.W., M.M.K., W.J.M. and S.Z. designed the experiments, Z.K. synthesized the polyimide aerogels and their SiO$_2$ composites with the support from S.Z. and T.W., and measured the thermal stability of the samples. S.Z. conducted SEM, EDX mapping, N$_2$ sorption, mechanical tests (compression, tensile) of aerogels. Z.M.S. carried out the fluorescence bending test. S.L., M.J. and S.G. managed the TGA and LOI fire tests. T. W. tested the water contact angle, and high-temperature insulation (via IR image). W.J.M. carried out the solid-state NMR measurements. D.O. characterized dielectric constant and dielectric loss at frequencies between 0.1 and 10$^6$ Hz, and Z. Z. measured the samples at microwave frequencies X band (8 GHz to 12 GHz) and Ka band (26.5 GHz to 32 GHz). A.B. collected and Z.P. processed the X-ray tomography data, S.Z. wrote the manuscript with the support of T.W. and W.J.M. All authors have approved the final version of the manuscript.

Funding information

The NMR spectrometer was funded in part by grant 150,638 from the Swiss National Science Foundation. The authors acknowledge the Paul Scherrer Institut, Villigen, Switzerland, for the provision of synchrotron radiation beamtime at the TOMCAT beamline X02DA of the SLS.

Data and materials availability

All data are included in the manuscript and supporting information are available from the corresponding authors on request.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: This work is original and has not been published elsewhere, nor is it currently under consideration for publication elsewhere. All co-authors agree with its submission to Chemical Engineering Journal. We consulted the Guide for Authors, and we confirm that the paper is prepared in compliance with the Ethics in Publishing Policy. All authors reviewed the manuscript. The data that support our findings are available from the corresponding authors, Wim Malfait or Shanyu Zhao, upon request. A patent for the polyimide-silica aerogel composites (EP21172334) has been filed on behalf of Empa. K.Z., S.Z., W.J.M. and M.M.K. are inventors on the patent application.

Acknowledgments

The authors thank Beatrice Fischer for assistance with the tensile tests, Snigdha Nitin Burklate for the help with N$_2$ sorption analysis and Stefanie Beatrice Hauser for the FTIR measurements, Sam Bodry and Joshua Yip for the help with supercritical CO$_2$ drying, Ekaterina Filimonova for the help with DVS test. The NMR spectrometer was funded in part by grant 150638 from the Swiss National Science Foundation. The authors acknowledge the Paul Scherrer Institut, Villigen, Switzerland, for the provision of synchrotron radiation beamtime at the TOMCAT beamline X02DA of the SLS.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2022.136401.