



# Hybrid silicone aerogels toward unusual flexibility, functionality, and extended applications

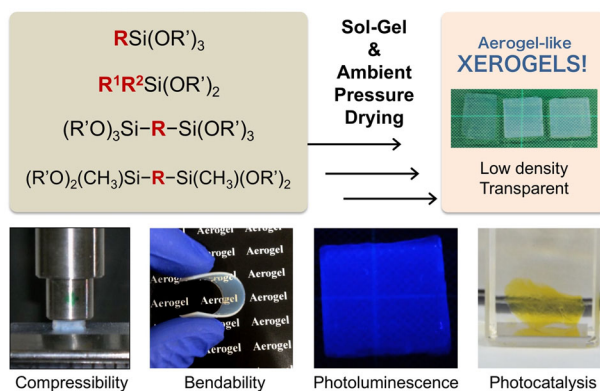
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## Abstract

Here, we overview the developments in the past decade made on organic–inorganic hybrid aerogels and xerogels based on silicone (polyorganosiloxanes) through persistent works by the authors to increase the mechanical strength and flexibility and add functionality. Polymethylsilsesquioxane (PMSQ,  $\text{CH}_3\text{SiO}_{3/2}$ ) has been found to show unusual strength and flexibility against compression, and their bending properties can also be improved by several strategies. Silicone-based networks with organic bridges between inorganic moieties are also beneficial for these improvements. In particular, organic bridges with a higher fraction and more extended length have been found to allow higher durability against large deformations. In addition, functional groups such as vinyl, chloromethyl, and amino can readily be introduced by starting from organoalkoxysilanes with these functional substituents (e.g.,  $\text{FG-Si(OR)}_3$  or  $(\text{RO})_3\text{Si-FG-Si(OR)}_3$ , where **FG** shows an organic substituent containing functional groups and R is typically methyl or ethyl), and other functional groups such as carboxyl can be introduced by post-gelation modifications on the pre-installed **FG** in the network. Possibilities in applications such as thermal insulators, photoluminescent media, and photocatalysts are also discussed.

## Graphical Abstract



## Highlights

- Silicone-based organic–inorganic hybrid aerogels developed by the authors are overviewed.
- Improved mechanical flexibility allows ambient pressure drying to yield aerogel-like xerogels.
- Reactive organic functional groups can be introduced in the hybrid networks.

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**Keywords** Organic–inorganic hybrid · Silicone · Aerogel · Xerogel · Mechanical property · Functionality

## 1 Introduction

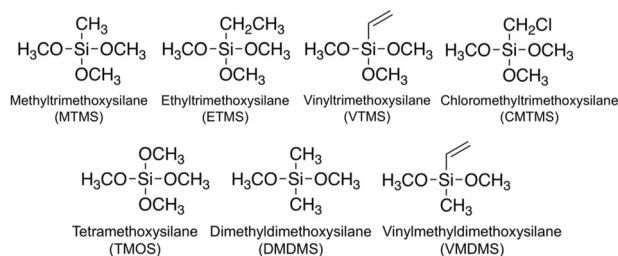
Aerogels are a class of low-density materials especially derived from a supercritical drying (SCD) process [1, 2]. Although aerogels can show unique and attractive properties such as visible-light transparency and low thermal conductivity, it has been difficult to industrialize mainly due to the high-pressure SCD process, which suffers from high cost and the difficulty in scaling up. Preparation of aerogel-like materials without SCD has therefore been studied extensively, in which improvements in mechanical properties such as strength and elasticity are the main issues to target, because these improvements would lead to successful ambient pressure drying (APD) by simple evaporation of the solvent [3] and easier handling. Incorporation of organic moieties/materials has been regarded as one of the most promising methods for this purpose [4–8]. Among different strategies, we have been trying to develop silicone-type organic–inorganic hybrid aerogels (from SCD) and xerogels (from APD) using organometallic alkoxysilanes such as organoalkoxysilanes  $R_n\text{Si}(\text{OR}')_{4-n}$  and organo-bridged alkoxysilanes  $(\text{R}'\text{O})_3\text{Si}-\text{R}-\text{Si}(\text{OR}')_3$  and  $(\text{R}'\text{O})_2(\text{CH}_3)\text{Si}-\text{R}-\text{Si}(\text{CH}_3)(\text{OR}')_2$ , where R and R' are organic groups [9, 10]. In this paper, we overview the improvements in the mechanical properties and functionalization through this hybridization strategy based on a carefully designed sol–gel chemistry, and discuss the further desired developments for future applications on an industrial scale. Schemes 1 and 2 show the alkoxysilane precursors discussed in this paper, and Table 1 summarizes the obtained materials and structural/physical properties. All the acronyms of chemical name of the precursors/networks used in the following section can be referred in these schemes and table.

## 2 Progresses made in the PMSQ system

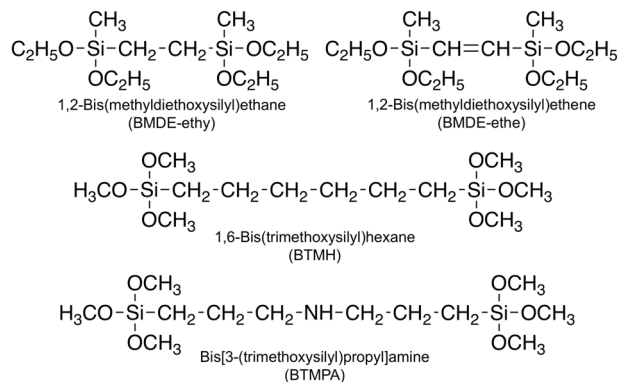
In 2007, we first reported monolithic PMSQ aerogels and xerogels with high transparency and low density [11]. It has been known that a hydrophobic co-precursor impacts phase separation tendency in the sol–gel system, which generally results in more coarsened pore structures with decreased or completely lost transparency [7, 12]. Here, it should be emphasized that transparency for visible light, resulted from a highly homogeneous pore structure in the length scale of  $\sim 10^1$  nm, is important for applications of aerogels. In addition to optical applications such as Cherenkov counters and photocatalysis, the fine, homogeneous pore structure in transparent aerogels is desirable to reduce thermal

conductivity, in which pore sizes should be shorter than the mean free path of gas molecules ( $\sim 68$  nm in the typical case of nitrogen at an ambient condition) in the pores. In the studies by the authors, a lot of efforts have therefore been paid to make the materials transparent by effectively suppressing phase separation and promoting three-dimensional gelation.

In the case of PMSQ, we have developed a modified synthesis protocol based on two-step acid–base sol–gel, a combination of acid-catalyzed hydrolysis of MTMS and the following base-catalyzed polycondensation, under the presence of a surfactant. The base ammonia was in situ generated from urea, which was included in the starting solution, by hydrolysis at moderately high temperature such as  $>60$  °C. Macroscopic phase separation of the hydrophobic PMSQ network from the aqueous solution was suppressed in the co-presence of an adequate surfactant such as cationic *n*-hexadecyltrimethylammonium bromide/chloride (CTAB/CTAC,  $\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3\text{Br}^-/\text{Cl}^-$ ) [13] and nonionic Pluronic F127 or P105 ( $\text{HO}(\text{C}_2\text{H}_4\text{O})_m(\text{C}(\text{CH}_3)\text{CH}_2\text{O})_n(\text{C}_2\text{H}_4\text{O})_m\text{H}$ ) [14]. After gelation and successive aging, the resultant gel was washed with alcoholic solvents



**Scheme 1** Organoalkoxysilane precursors focused in this paper



**Scheme 2** Organo-bridged alkoxysilane precursors focused in this paper

**Table 1** Various polyorganosiloxane aerogel/xerogel materials and their typical structural/physical properties obtained from research by the authors

Network	Precursor <sup>a</sup>	Catalysts <sup>b</sup>	$\rho_b^c/g\text{ cm}^{-3}$	$S_{\text{BET}}^d/m^2\text{ g}^{-1}$	Transparency	$\lambda^e/mW\text{ m}^{-1}\text{ K}^{-1}$
Polymethylsilsesquioxane (PMSQ) $\text{CH}_3\text{SiO}_{3/2}$	MTMS	AB2	0.04– 0.45	575– 622	++	>14.9
Polyethylsilsesquioxane (PESQ) $\text{CH}_3\text{CH}_2\text{SiO}_{3/2}$	ETMS	AB2	0.24– 0.57	201– 383	±	NA
Polyvinylsilsesquioxane (PVSQ) $\text{CH}_2=\text{CHSiO}_{3/2}$	VTMS	AB2	0.14– 0.17	334– 541	+	>15.3
Polychloromethylsilsesquioxane (PCMSQ) $\text{ClCH}_2\text{SiO}_{3/2}$	CMTMS	A1	0.17– 0.28	NA	+	NA
Hexylene-bridged polysilsesquioxane (HBPSQ) $\text{O}_{3/2}\text{Si}-(\text{CH}_2)_6-\text{SiO}_{3/2}$	BTMH	B1	0.13– 0.22	874– 924	+	NA
Ethylene-bridged polymethylsiloxane (Ethy-BPMS) $\text{O}_{2/2}(\text{CH}_3)\text{Si}-(\text{CH}_2)_2-\text{Si}(\text{CH}_3)\text{O}_{2/2}$	BMDE-ethy	AB2	0.15– 0.51	599– 797	+	NA
Ethenylene-bridged polymethylsiloxane (Ethe-BPMS) $\text{O}_{2/2}(\text{CH}_3)\text{Si}-\text{CH}=\text{CH}-\text{Si}(\text{CH}_3)\text{O}_{2/2}$	BMDE-ethe	AB2	0.053– 0.15	946	++	NA
Polyvinylpolymethylsiloxane (PVPMS) $[\text{CH}_2\text{CH}(\text{Si}(\text{CH}_3)\text{O}_{2/2})]_n$	VMDMS	B1	0.16– 0.31	903– 950	±	>15.0

<sup>a</sup>Acronyms of precursors are defined in Schemes 1 and 2

<sup>b</sup>Types of sol–gel system classified by catalysts employed for hydrolysis and polycondensation: AB2 stands for two-step acid–base, A1 for one-step acid, and B1 for one-step base processes

<sup>c</sup>Bulk density

<sup>d</sup>BET-specific surface area

<sup>e</sup>Thermal conductivity at ambient condition

(typically methanol and 2-propanol) followed by solvent exchange with supercritical carbon dioxide (for aerogel) or a solvent with low surface tension (e.g., *n*-hexane, for xerogel). Especially in ambient pressure drying, the solvent in the wet gel should be carefully removed by slow, controlled evaporation to allow temporal, isotropic shrinkage and spring back without cracking. Additionally, a solution containing a small amount (~0.3%) of hydrolyzed and oligomerized MTMS can be used for extended aging, which was effective in decreasing cracks during washing and drying [15].

The resultant PMSQ aerogels and xerogels show similar properties in bulk density, transparency, pore size and volume, specific surface area, and thermal conductivity, which are also comparable with conventional silica aerogels. Comparison of other features between PMSQ xerogel and silica aerogel is given in Fig. 1. Although it had been difficult to realize monolithicity, transparency, and low thermal conductivity in a single xerogel material in spite of the efforts and progresses in a hydrophobized silica system [16], it is now facilitated in the PMSQ network. Other material formats such as granules/powders, sheets/films, and composites can also be prepared by APD. However,

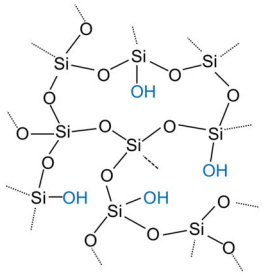
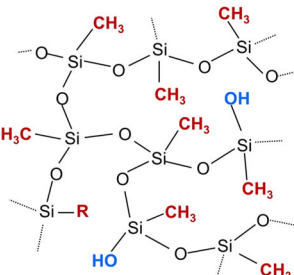
since some issues still remain in the PMSQ material, further extended research is ongoing as mentioned in the following section.

### 3 More strength and flexibility for easier drying and better handling

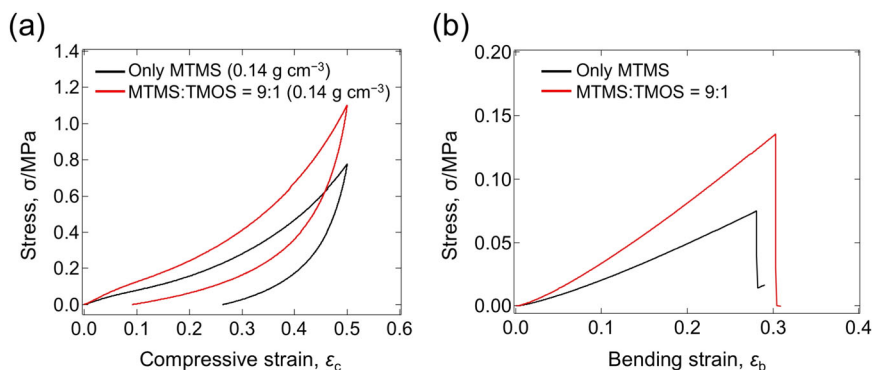
#### 3.1 PMSQ-based systems

Although the PMSQ network solely from MTMS gives significant improvements especially in compressive strength and flexibility, further improvements are possible by adding an inorganic silica component in the network. Aerogels obtained from a mixed alkoxysilane system consisting of MTMS and TMOS have been prepared and the compressive and bending behaviors are compared in Fig. 2. Replacing 10% of MTMS with TMOS increased both compressive and bending stresses during the tests. In addition, resilience immediately after the 50% compression test increased from 75 to 91%, which allows a more efficient, reliable ambient pressure drying process. The higher bending strength is also beneficial in handling.

**Fig. 1** A comparison between a typical silica aerogel and PMSQ xerogel. Both materials can be prepared in different formats such as monoliths, granules, and composites

Silica aerogel		PMSQ xerogel	
TMOS Water glass	Precursor	MTMS	
	Network structure & properties		
Low strength Hydrophilic (silylation required)		Flexible, high strength Hydrophobic	
Supercritical (> 100 atm)	Drying	Ambient (1 atm)	
>12 mW m <sup>-1</sup> K <sup>-1</sup>	Thermal conductivity	>13 mW m <sup>-1</sup> K <sup>-1</sup>	

**Fig. 2** Stress–strain curves obtained from **a** uniaxial compression and **b** three-point bending tests. Although the aerogel sample only from MTMS springs back almost completely from compression with a longer time or under a higher temperature such as 100 °C, the sample from MTMS:TMOS = 9:1 shows more prompt spring-back

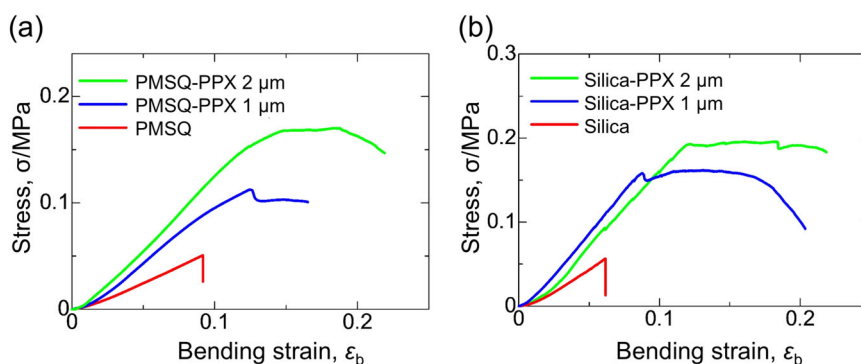


In another strategy for strengthening, the as-prepared aerogels and xerogels can be reinforced via a vapor-phase reaction of *p*-xylylene to form a thin crystalline layer of poly(*p*-xylylene), which is known as parylene (PPX) especially in electronics [17], on the surface of the gel body. Figure 3a compares stress–strain behaviors of an uncoated PMSQ aerogel (0.14 g cm<sup>-3</sup>) and those coated with poly(monochloro-*p*-xylylene) (Parylene C) with thicknesses of 1 and 2 μm. For these three samples, respectively, the Young's modulus increased from 0.57 to 1.0 and 1.2 MPa, and bending strength from 0.050 to 0.11 and 0.16 MPa. Bending strain at break increased and there was no distinct collapse in the sample with a PPX layer of 2 μm. This strengthening strategy also works for conventional silica aerogels as shown in Fig. 3b. Since aerogels and other highly porous materials in general have low durability against liquids, vapor-phase coating techniques such as PPX are useful and effective for mechanical reinforcement and functionalization, although this technology is not widely applied to porous materials [18].

Further advanced flexibility can be achieved by introducing difunctional alkoxy silanes such as DMDMS in place of a part of MTMS in the starting solution [19]. While the pore structure induced by phase separation developed into micrometer scale due to the higher hydrophobicity of the resultant network, the resultant aerogels and xerogels were imparted with significant bending flexibility. These soft, flexible gels (marshmallow gels) showed characteristics such as superhydrophobicity and flexibility at low temperatures and would find applications such as oil–water separation and potentially thermal insulation at low temperatures [20]. The marshmallow gels prepared from a mixture of vinyltrimethoxysilane and vinylmethyldimethoxysilane can be functionalized with a thiol molecule via the thiol-ene reaction. By employing a perfluoroalkyl thiol as a reactant, oleophobic (amphiphobic) marshmallow gels can be obtained [21].

Fibrous materials are also promising for improving mechanical flexibility. In an example of a composite of PMSQ and cellulose nanofibers (CNFs), low-density aerogels with higher bendability have been reported [22].

**Fig. 3** Stress–strain curves obtained from three-point bending tests of **a** uncoated PMSQ aerogel and those coated with PPX, and **b** uncoated silica aerogel and those coated with PPX. Bending strength and strain at break (or yield) significantly increased with a PPX layer with 1- or 2- $\mu\text{m}$  thickness, which did not give a large impact on transparency



Although light transmittance decreased due to the presence of aggregated structures to some extent, thermal conductivity did not increase due to the low fraction of CNFs. This strategy is propitious to obtain mechanically robust aerogels for thermal insulators. As well-tailored nanofiber dispersions were found to form transparent aerogels by themselves [23, 24], future developments in the dispersion and interactions of multiple networks in the molecular scale will allow more advanced controls over transparency and mechanical properties in these composites, while maintaining the low thermal conductivity of the original aerogel.

### 3.2 Organo-bridged polysiloxanes (HBPSQ, Ethy-BPMS, and Ethe-BPMS systems)

Organic bridges in the polysiloxane network can also increase the strength and flexibility both in compression and bending [8]. The hexylene-bridged precursor BTMH has been reacted in a one-step base process using an organic base tetramethylammonium hydroxide (TMAOH,  $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ ) in a solvent *N,N*-dimethylformamide (DMF) to yield transparent HBPSQ aerogels [25]. In particular, wet gels hydrophobized with trimethylsilyl  $(\text{CH}_3)_3\text{Si}-$  groups can be dried via APD from *n*-hexane and the resultant xerogels showed significantly higher compressive and bending strength and flexibility compared to silica and PMSQ aerogels.

In a different type of bridged precursors having a methyl group on each silicon, e.g., BMDE-ethy and BMDE-ethe, aerogels have been prepared in a two-step process consisting of a strong acid (nitric acid) and a strong base (TMAOH) in a surfactant solvent polyoxyethylene 2-ethylhexyl ether (EH-208,  $\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{H}$  with HLB = 14.6 and melting point  $\sim -10^\circ\text{C}$ , a viscous liquid at room temperature) [26, 27]. Since the obtained Ethy-BPMS and Ethe-BPMS networks were intrinsically hydrophobic, these aerogels showed improved strength and flexibility without a post-gelation hydrophobization process. In addition, among the PMSQ, Ethy-, and Ethe-BPMS aerogels, higher stress relaxation was observed in the Ethy-BPMS aerogel. This viscoelasticity should be derived from

the higher mobility of the network with lower cross-linking density. Xerogels were also successfully obtained in this system via APD. Besides the higher cost of these precursors, these systems also afford an attractive platform to obtain mechanically improved aerogels and xerogels.

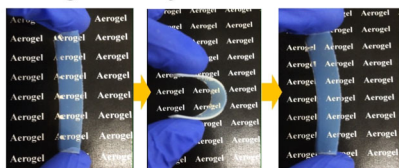
### 3.3 Polysiloxane network bridged with extended hydrocarbon chains (PVSQ and PVPMS systems)

Organotrialkoxysilanes with two carbons in the substituent group, e.g., ETMS and VTMS, are another attractive class of precursors for transparent aerogels. Employing a similar two-step process consisting of a strong acid and a strong base in the solvent EH-208 gave rise to transparent, low-density PVSQ aerogels from VTMS, while it was difficult to obtain transparent, low-density aerogels from ETMS [28]. We found that hydrocarbon chains grew in the PVSQ network when the wet PVSQ network reacted with a radical initiator azobisisobutyronitrile (AIBN) in a solvent 2-propanol at  $60^\circ\text{C}$ . The resulting network having both hydrocarbon chains and polysiloxane has been found to show higher compressive stress and resilience, which makes the PVSQ materials suitable for APD.

On the other hand, when a radically polymerizable precursor (typically VMDMS) was first polymerized with a radical initiator followed by hydrolysis and polycondensation using a one-step base process using TMAOH in a solvent benzyl alcohol, PVPMS aerogels and xerogels with unusual mechanical properties have been obtained [29]. In addition to the transparency/translucency, low density ( $>0.16\text{ g cm}^{-3}$ ), and low thermal conductivity ( $>15.0\text{ mW m}^{-1}\text{ K}^{-1}$ ), the aerogels and xerogels showed multicycle compressive flexibility and significantly improved bending flexibility (Fig. 4). Due to this unusual flexibility, the once-dried xerogels could be immersed in a solvent such as *n*-hexane without damage and redried via APD. The xerogels could also be formed in a desirable shape with a simple cutting tool, which has not been observed in aerogels and xerogels so far. Moreover, since APD from 2-propanol or even from the mother pore liquid gave xerogels comparable with the corresponding aerogels in



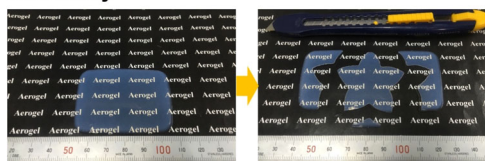
### Bending flexibility of a thick film



### Durability against solvents



### Formability



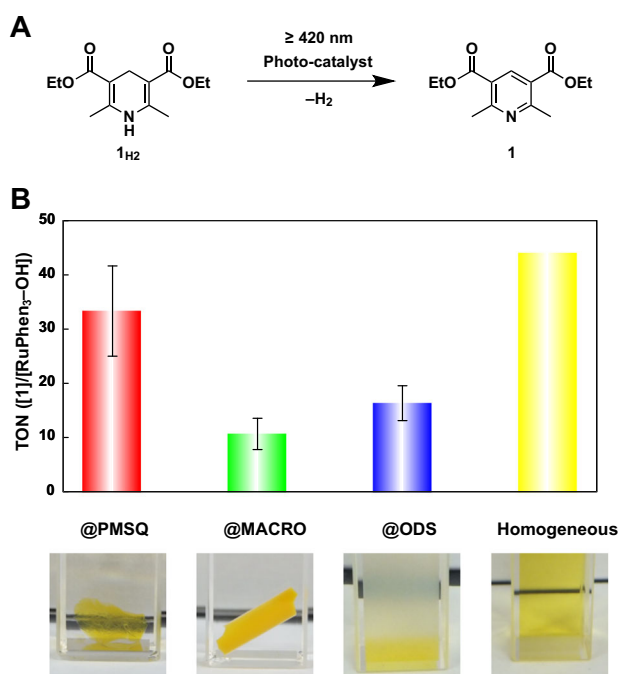
**Fig. 4** Outstanding bendability, durability against solvents, and formability of doubly cross-linked PVPMS xerogels

the PVPMS system, it is possible to significantly reduce the time and cost of the solvent exchange process, which shows considerable advantage toward an industrial process. A similar process, a combination of radical polymerization and hydrolytic polycondensation, was also reported to be beneficial to control the thermal and mechanical durability in dense, free-standing films [30, 31]. Since the precursor system can be extended to any molecules having radically active double bonds such as vinyl- and allyltrialkoxysilanes [32], aerogels and xerogels with more extended mechanical and functional properties would be obtained in future research.

## 4 Functionalization of aerogels

### 4.1 Functionalization of PMSQ by hydrogen bonding

Functionalization of aerogels and xerogels has been demonstrated by post-gelation modification and precursor strategies. On the pore surface of a PMSQ aerogel ( $0.14 \text{ g cm}^{-3}$ ), metal complexes that show catalytic activity by absorbing visible light have been “softly” attached via hydrogen bonding between the polar groups (such as carboxyl) on the complexes and silanol groups [33]. One of the loaded samples bearing Ru(II) tris-phenanthroline complex showed photocatalytic activity in the dehydrogenation of a dihydropyridine (Hantzsch ester) with a high turnover number (TON) comparable with a homogeneous catalytic system in solution (Fig. 5). The incorporated catalysts could be removed from the aerogel by immersing in a solvent having stronger elution tendency, because of the non-covalent attachment on the surface. The visible-light

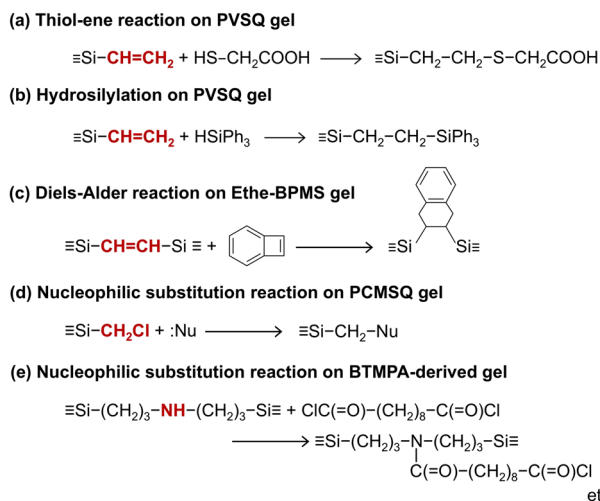


**Fig. 5** a Photocatalytic dehydrogenation reaction of a dihydropyridine (Hantzsch ester) and b turnover numbers (TON) of the reaction in the presence of Ru(II) tris-phenanthroline complex loaded to PMSQ aerogel (PMSQ), macroporous silica monolith (MACRO), and octadecylsilylated porous silica particles (ODS). The TON of a homogeneous solution of the catalyst is also shown for comparison [33]

transparency and high specific surface area ( $\sim 800 \text{ m}^2 \text{ g}^{-1}$ ) contributed to the high catalytic activity, together with a certain mobility of catalyst on the pore surface.

### 4.2 Functionalization of PVSQ, Ethe-BPMS, and CMTMS using functional groups

The above-mentioned PVSQ is also meaningful in terms of introducing functionality in the aerogel. The vinyl groups on the pore surface have been used to attach different functional groups on the PVSQ aerogel; carboxyl groups were introduced via the thiol-ene reaction between thio-glycolic acid and vinyl groups in the presence of AIBN (Scheme 3a) [34]. The resultant aerogel turned from hydrophobic to hydrophilic with accessible carboxyl groups on the pore surface. Hydrosilylation between triphenylsilane and PVSQ (Scheme 3b) was also possible in the presence of the Karstedt’s catalyst, but required a longer reaction time (7 days, as compared to 1 day in thiol-ene) and the loading mostly occurred in the outer part of a monolithic sample. Although some reports are available [35], it is still difficult to effectively attach guest molecules on vinylsiloxane surfaces by the hydrosilylation reactions, while hydrosilylation on hydride-modified surfaces such as hydrogen-terminated silicon is widely investigated [36]. The double bond in the network from BMDE-ethe has also

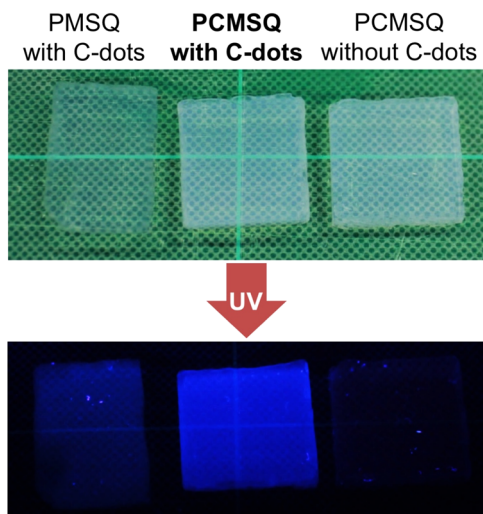


**Scheme 3** Reactions between functional substituents and guest molecules to modify the networks of aerogels

been successfully modified by the Diels–Alder reaction using a diene benzocyclobutene in a solvothermal condition (Scheme 3c) [27].

Aerogels functionalized with chloromethyl groups have been obtained by using CMTMS as the single precursor [37]. The resultant PCMSQ aerogels derived from one-step acid process in the presence of a surfactant *n*-dodecyltrimethylammonium chloride ( $\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ ) showed transparency and low density ( $>0.17 \text{ g cm}^{-3}$ ). Using the chloromethyl functional groups, it was successful to embed photoluminescent carbon dot (C-dot) derived from citric acid and polyethyleneimine (Fig. 6) [38]. Additionally, since the  $\text{S}_{\text{N}}2$  reaction (Scheme 3d, with Nu such as amine) on the chloromethyl in the CMTMS precursor was found to change the equilibrium between the formation and dissociation of a polysiloxane network, an in situ functionalization of the chloromethyl groups during sol–gel process has been developed. A diamine, diethylene glycol bis(3-aminopropyl) ether ( $\text{H}_2\text{N}-\text{C}_3\text{H}_6\text{OC}_2\text{H}_4)_2\text{O}$ , has been introduced to the network, which increased resilience against uniaxial compression. Our preliminary experiments in the preparation of PCMSQ-based xerogel resulted in a high-density ( $0.27 \text{ g cm}^{-3}$ ) sample, but this strategy based on in situ hybridization would be an interesting alternative tool for altering the mechanical properties and adding different functionalities. The chloroalkyl groups on pore surfaces were reported to be useful for surface modification via a click reaction, and more extended works are desired for these unexplored networks [39].

In our more recent study, aerogels with amino groups, which are useful for cross-linking organic polymers [40] or adsorption of acidic compounds such as  $\text{CO}_2$  [41], have been prepared from a different organo-bridged precursor BTMPA. Aerogels with low density ( $>0.10 \text{ g cm}^{-3}$ ) and transparency have been derived from a one-step base



**Fig. 6** Fluorescent behaviors of three samples with or without an embedment of carbon dots (C-dots). While PMSQ with C-dots does not show intense photoluminescence, the sample PCMSQ with C-dots shows because the larger amounts of C-dots remain in the gel through attractive interactions between PCMSQ and C-dots [37]



**Fig. 7** Examples of transparent aerogels from BTMPA prepared through a one-step base process in different solvents; DMF, EH-208, DMSO, and *N,N*-dimethylacetamide (DMAc)

process using TMAOH in solvents such as DMF and dimethylsulfoxide (DMSO, Fig. 7). Although resilience against uniaxial compression tends to be lower (80% or less), the resultant network with amino groups is available for reactions with guest molecules such as sebacyl chloride (Scheme 3e) and 4-(chloromethyl)styrene ( $\text{CH}_2=\text{CH}-\text{Ph}-\text{CH}_2\text{Cl}$ ). In this system, however, it was difficult to increase the mechanical flexibility since both the remaining silanol groups and amino groups hindered the spring-back behavior. Decreasing the silanol groups by silylation or starting from a more hydrophobic precursor such as bis[3-(methyldimethoxysilyl)propyl]amine or a mixed precursor system with, for instance, MTMS was successful to concomitant the amino functionality and flexible mechanical nature, which will be reported elsewhere.

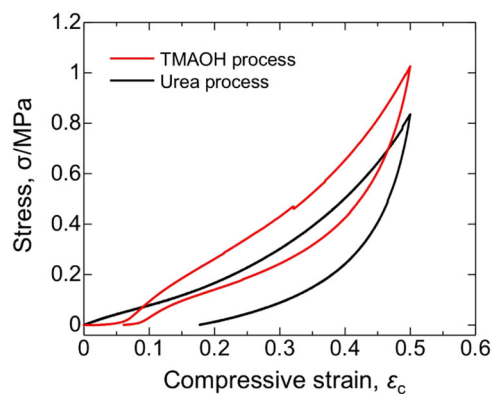
## 5 Remaining issues for further developments in PMSQ

Since the first preparation of PMSQ aerogels and xerogels, a number of developments have been made. Aerogels/

xerogels with improved mechanical properties and functionalities described in the previous sections have high potential for extended applications. When focusing on, however, one of the most promising applications of aerogels, i.e., thermal superinsulation for windows, the PMSQ system is currently the most powerful solution because of the high transparency and low enough thermal conductivity, which can be down to  $\sim 13 \text{ mW m}^{-1} \text{ K}^{-1}$  at an ambient condition if optimized. Although the PMSQ system has already been established for industrialization, several future developments will further help the industrialization and application as follows.

In the two-step sol–gel process reported in the MTMS system, urea is used as an in situ base generator. This process is reasonable to maximize the homogeneity of pH throughout the reaction time in the whole solution/gel, which leads to the higher homogeneity in the resultant material as well. The use of urea, however, causes an issue in the gelation and aging processes, because the pH increase is slow and shows a limitation because a weak base ammonia is gradually generated. Instead, it is also possible to employ the classical two-step process, in which a base is separately added to a hydrolyzed solution. As in some of the previous examples, it has been found in the PMSQ system as well that a strong organic base such as TMAOH leads to transparent, low-density aerogels similar to those obtained with the urea-based two-step process. Although the typical gelation time is 2–3 h in the original recipe (MTMS, aqueous acetic acid, urea, and CTAB) at the moderate gelation temperature of 60 °C, it can be reduced to several minutes at room temperature in a modified recipe with TMAOH instead of urea. The shorter gelation time at lower temperature is beneficial to reduce the process time and cost, and further, will increase the formability (such as films) because the chance of evaporation of the solvent during gelation will be decreased. The use of TMAOH or other bases instead of urea in the two-step reaction also simplifies the washing process as mentioned below, because only a catalytic amount (e.g.,  $[\text{OH}^-]/[\text{Si}] \sim 10^{-2}$ ) is necessary for gelation and aging, while an excess amount (e.g.,  $[\text{urea}]/[\text{Si}] \sim 1.4$ ) is desirable in the case of urea. The starting composition and the whole process should be instead carefully designed in order not to sacrifice the homogeneity and transparency of the gels.

The use of adequate surfactant is necessary in the preparation of hydrophobic networks in an aqueous solution in order to avoid macroscopic phase separation that leads to opaque gels or precipitation [9]. However, since the surfactant in turn burdens an extended washing process to be removed, an alternative way is under development. The surfactant EH-208 has been described to effectively suppress the phase separation of hydrophobic networks such as PVSQ, and it is more easily removed in the washing process



**Fig. 8** Comparison between the stress–strain curves obtained from uniaxial compression tests on the PMSQ aerogels derived from the original process using urea as the base source and the modified process using TMAOH as the base. The sample from the modified process showed higher stress and more prompt spring-back. The density of both samples is  $0.14 \text{ g cm}^{-3}$

because it is a liquid surfactant that is miscible with a wide variety of solvents. In a system consisting of MTMS, aqueous acetic acid, aqueous TMAOH, and EH-208, transparent wet gels have been obtained with optimized starting compositions. Although exhaustive washing with methanol and solvent exchange with 2-propanol (typically  $>6$  times in total) were required in the original system, only three-time washing and solvent exchange was found to give an aerogel with good transparency and monolithicity.

In this modified system, moreover, there is a possibility to improve the mechanical elasticity against compression in the PMSQ aerogels. Figure 8 compares the stress–strain curves obtained from uniaxial compression tests on aerogels from the original recipe (MTMS, aqueous acetic acid, CTAB, and urea) and a modified recipe (MTMS, aqueous acetic acid, EH-208, and aqueous TMAOH). The aerogel from the modified recipe showed higher elasticity (spring-back) after compression of 50%, while the perfect spring-back occurred after a longer time or a heat treatment  $>100^\circ \text{ C}$  in the case of the aerogel from the original recipe. This instant spring-back behavior will be beneficial both for APD and handling. In the near future, changes in bending deformation behaviors will be evaluated to discuss the effects of strong bases in greater detail.

## 6 Concluding remarks

Organic–inorganic hybridization, which is one of the most prominent benefits of the sol–gel process, is a classical method to improve the mechanical properties and add functionality to inorganic-based materials derived from gels [42]. As far as aerogels are concerned, the sol–gel hybridization approach has demonstrated mechanical flexibilities



[7, 43] and functionalities [44] by controlling the cross-linking density and introducing organoalkoxysilanes with functional groups. To the best of our knowledge, however, there have been no reports on flexible/functional aerogels with transparency derived only from organoalkoxysilane precursors without an aid of tetraalkoxysilanes.

In this paper, we have shown the drastic improvements in mechanical properties and extensions of functionalities using our new aerogels and xerogels, derived from different organoalkoxysilane precursors through a rather classical organic–inorganic hybridization strategy, as examples. In particular, such improvements and extensions with maintaining the transparency are highly important to distinguish aerogels from other porous materials. The silicone-type organic–inorganic hybridization approach shown here has provided new opportunities in the flexible mechanical properties and different functionalities, and will continue to provide a promising basis for such developments, since it is capable to precisely design rational structures from the molecular scale to mesoscale using various techniques in organosilicon, polymer, and sol–gel chemistries. We believe that the bottlenecks of aerogels such as low mechanical strength and the associated low productivity would be solved by further developing the organic–inorganic hybridization strategy, and through a more extended functionalization, aerogels would become an easily available choice in various applications in the near future.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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