Organic–inorganic hybrid aerogels with high mechanical properties via organotrialkoxysilane-derived sol–gel process

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A brief overview of siloxane-based low-density aerogels and aerogels-like xerogels is presented. Aerogels are highly porous solids composed of inorganic oxides, metals, cross-linked polymers and carbons, and are known to possess a number of excellent physical properties such as high visible-light transparency with low refractive index, low dielectric properties, and extremely-low thermal conductivity. Aerogels are therefore regarded as a promising candidate for applications such as superinsulators; however, a mass production and applications of aerogels have been significantly discouraged due to the lack of mechanical properties since the first invention in 1931. This review introduces the substantial effort to improve the mechanical properties of aerogels with particularly highlighting our recent findings on elastic organic–inorganic hybrid aerogel monoliths obtained from methyltrimethoxysilane (MTMS) using the controlled sol–gel chemistry.

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1. Introduction

Various porous solids such as silica gels, zeolites, charcoals and polymer foams, are utilized in daily life and industries for desiccation, cushioning, insulation, filtration, adsorption, separation, catalysis, etc. To meet various requirements, material shapes (particles, films or monoliths) and chemical compositions must be adequately controlled. Physical properties including mechanical and high-temperature stabilities and chemical resistivity should also be high enough to ensure the long-lasting stability in a given environment. Besides, a precise control over pore size, pore volume (porosity) and morphology is particularly desirable for effective application to above-mentioned purposes. Inorganic, organic, or organic–inorganic hybrid porous materials are vigorously studied to establish the wide control of these properties and to open up the new possibilities for a broad range of applications.

Based on gas adsorption behaviors, porous materials are classified into three groups in pore size; microporous (pore size <2 nm), mesoporous (2–50 nm), and macroporous (>50 nm).¹) Within inorganic-based porous materials, zeolites²) are typical microporous materials consisting of molecular-sized micropores embedded in aluminosilicate or silicate crystalline frameworks. Activated carbons with huge surface areas are another well-known instance for microporous materials. Mesoporous materials are represented by ordered mesoporous silicates³) originally developed by Yanagisawa et al. (FSM series)⁴ and Kresge et al. (MCM series).⁵) Macropores are imparted in inorganic materials by phase separation,⁶ replication, sacrificial templating, and foaming.⁷ In general, micropores are expedient for increasing surface area, and meso- and macropores take advantage in enhancing the mass transport in the material.

Amongst the actively studied porous materials, aerogels⁸⁾ are a particular class of porous solids with unique physical proper-



Fig. 1. Nanometer-sized porous structure and its two-dimensional representation of a commercial silica aerogel. Each silica nanoparticle, which is typically $\sim 10 \text{ nm}$ in size, connects to form tenuous porous architectures.

ties.9)-15) The representative silica aerogels with controlled porosity possess disordered open mesopores with a few tens nanometers and high porosity (typically >90%). The typical structure of commercial silica aerogels is shown in Fig. 1, in which nano-sized silica particles are weakly linked together to form the mesopores. As a result, aerogels show high visible-light transparency, low refractive index, low thermal conductivity, and low-k properties, all of which make aerogels be differentiated from other porous materials. In particular, thermal conductivity is the lowest among all solid materials on earth; thermal conductivity can be decreased down to $\sim 8 \,\text{mW}\,\text{m}^{-1}\,\text{K}^{-1}$ at ambient pressure, which is only a third of air ($\sim 25 \text{ mW m}^{-1} \text{K}^{-1}$) and is equivalent to vacuum insulation in the order of 1 Pa.¹⁶) Heat transfer through an aerogel is highly limited due to the small pores shorter than the mean free path of air (ca. 70 nm), which fact highly restricts the heat conduction by the gaseous momentum transfer. Note that convection of air is of course impossible due to the small pore sizes and conduction is only the way for the gaseous heat transfer. Besides, low fraction of solid phase due to the high porosity decreases the heat transfer through solid phase as well. Silica aerogel is therefore a promising candidate for transparent thermal insulators that can be used for windows¹⁷⁾⁻¹⁹ and solar heat collectors.^{20),21)}

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However, vigorous research has not been done due to the difficulty in preparation and handling of aerogels as described below.

Silica aerogels are generally prepared by the liquid-phase synthesis from water glass, tetraalkoxysilanes or its derivatives with a large amount of solvent (usually alcohol) to decrease bulk density. The typical synthesis uses sol-gel chemistry of tetraalkoxysilanes such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). It is well-known that tetraalkoxysilane [Si(OR)₄] undergoes hydrolysis and condensation to form colloidal particles consisting of siloxane networks dispersed in the solution (termed as sol). The sol becomes gel when forms linkage throughout the sol and loses fluidity. The hydrolysis and condensation behaviors are largely influenced by the solution pH, resulting in "polymeric" gels and "colloidal" gels in acidic and basic conditions, respectively, as schematically shown in Fig. 2.²²⁾ In general, the base-catalyzed process is favored in tetraalkoxysilane-derived systems because of the resultant coarser and more distinct pore structure in colloidal gels, which are easier to be dried than polymeric gels, as a result of reactionlimited monomer-cluster aggregation (RLMCA).²²⁾ The polymeric gels are typically composed of less-branched chain-like polymers derived from reaction-limited cluster-cluster aggregateion (RLCA)²²⁾ and the solvent in polymeric gels is more difficult to be removed without contracting the existing networks because of the narrower interstices and low diffusion of solvent, resulting in aerogels with higher density. The acid/base two-step process,²³⁾ which is a combination of acid-catalyzed hydrolysis and base-catalyzed condensation, is believed to be more advantageous in widely controlling aerogel properties²⁴⁾ as described later in detail.

In the final drying step, solvent in the wet gel must be removed and replaced with air to attain porosity. Since the resultant wet gels are highly friable because of the low solid fraction and weak linkage of the silica particles, one needs a special care in drying. Evaporation of the liquid will cause serious shrinkage and cracking due to the high capillary pressure at the menisci of the



Fig. 2. A typical reaction scheme of the alkoxide-derived sol–gel process. In this instance, tetraalkoxysilane [Si(OR)₄] undergoes hydrolysis and condensation in acid- or base-catalyzed conditions. Depending on the pH conditions, "colloidal gel" or "polymeric gel" will be obtained as a result of different reaction mechanisms. Aerogels are generally obtained from supercritical drying (SCD) of low-density wet gels to prevent shrinkage and collapse of pores, and colloidal gels are usually favorable to obtain low-density aerogels. Simulated structures of condensates from RLMCA and RLCA are also presented (adopted from Ref. 22, see text for details).

solid-liquid-vapor interfaces inside the drying gel body, and porosity will not remain accordingly.^{25),26)} To avoid this, drying with a supercritical fluid is often employed. In this process, called as supercritical drying (SCD), the porous networks are not contracted owing to the virtually no capillary pressure of the supercritical fluid, resulting in highly porous aerogels (Fig. 2). However, SCD must be performed in an autoclave because high pressure (and sometimes high temperature) is needed to transform the pore liquid into its supercritical state. Supercritical fluids such as water (critical point is 374.1°C and 22.0 MPa), methanol (239.4°C and 8.1 MPa) and ethanol (243.0°C and 6.3 MPa) have been used for this purpose, and recently carbon dioxide (31.0°C and 7.4 MPa)²⁷⁾ is more widely used because of the low critical point, no flammability, low toxicity, and low environmental damage (note that the commercially available carbon dioxide is the reuse of exhausts from industries). However, a huge cost has to be paid to build and run the autoclave in an industrial scale. In addition, a continuous production is impossible by SCD because of the prolonged batch process. A process which does not rely on SCD has therefore been awaited for long time as mentioned in the following section.

2. Historical strategy for improvement of mechanical properties of aerogels

In the history of aerogels starting from the imaginative invention by Kistler in 1931,^{28),29)} much effort has been paid to improve the low mechanical properties and to avoid dangerous and costly SCD. Most of the effort can be classified into three groups. In the first group, as-prepared wet gels are extensively aged in a mother solution, a monomer solution, or water.^{30)–33)} It is naturally expected that silica backbones are reinforced through the neck growth by Ostwald ripening, additional condensation of monomers onto the preformed networks, and/or by rearrangement of the as-formed networks. This method, however, works well only to a limited extent and more extensive reinforcement is usually required. The second group includes hybridization with organic polymers that will not be washed out during solvent exchange and/or SCD processes. Novak et al.³⁴⁾ used an approach to prepare interpenetrating networks with preformed polymers or in-situ polymerizing species to enhance the compressive strength of aerogels. A significant improvement in mechanical properties upon compression was found. Later, Mackenzie et al. employed poly(dimethylsiloxane) with both ends terminated with silanol (Si-OH) groups to enhance the flexibility of TEOS-derived aerogels and termed as AEROMOSIL after the name of ORMOSIL (organically modified silicates).^{35),36)} Leventis et al. cross-linked organic polymers using surface reactive groups of aerogels with di-isocyanates,³⁷⁾ epoxies,³⁸⁾ and styrenes.³⁹⁾ to enhance the mechanical properties and hydrophobicity to be suitable for robust applications. Some other groups also report the strengthening of aerogels using organic polymers.⁴⁰⁾⁻⁴²⁾ Although all these efforts work well to improve the brittleness and enhance the strength which allows drying under ambient conditions in some cases, hybridization with polymers in general more or less sacrifices optical transparency and porosity because the polymers coated on the silica backbones partially fill the pores of the aerogels.

The third group relies on inclusion of trifunctional silanes with organic substituent. Schubert and Hüsing studied monolithic aerogels utilizing TMOS and a broad range of organotrialk-oxysilanes including methyltrimethoxysilane (MTMS), 3-mer-captopropyltrimethoxysilane (MPTMS), 3-glycidoxypropyltrimethoxysilane (GLYMO), 3-methacryloxypropyltrimethoxysilane



Fig. 3. The new acid/base two-step sol-gel synthesis of aerogels used in our study. Methyltrimethoxysilane (MTMS) and other constituents are mixed in a single reaction vessel and MTMS is allowed to be hydrolyzed in an acidic condition. In the following condensation step, temperature is increased to promote hydrolysis of urea, which results in gradual and homogeneous pH increase. Employment of surfactant is another important idea to suppress macroscopic phase separation.

(MAPTMS).⁴³⁾⁻⁴⁵⁾ They observed higher shrinkage and longer gelation time with increasing organotrialkoxysilanes/TMOS ratio due to the less effective and incomplete hydrolysis and condensation of organotrialkoxysilanes. In the case of MTMS reacted in basic media, gels were not obtained with higher MTMS ratio (e.g. MTMS/TMOS > 0.4). Moreover, in all cases, aerogels became turbid with increasing fractions of trifunctional monomers due to macroscopic phase separation. It is actually known that there is an inherent difficulty in forming homogeneous gels from organotrialkoxysilanes because of enhanced cyclization and phase separation in a large amount of polar solvent.46)-48) The former prevents sols from forming welldeveloped three-dimensional (3-D) random networks and the latter forms micron or submicron-sized large domains which lower the visible-light transmittance. These problems should be overcome to obtain monolithic aerogels with high transparency as described later in our approach.

Rao et al. also used the mixture of tri- and tetraalkoxysilanes to improve mechanical properties and to gain superhydrophobicity.49)-52) They also found decreases in transparency and specific surface area with increasing MTMS/TMOS ratio and an increase in pore size due to the more enhanced phase separation. However, it is noteworthy that contact angle of water droplet reached 175° and showed superhydrophobicity.⁵¹⁾ Since silica aerogels are believed to be sensitive even to the moisture in the air, the surface modification using such as hexamethyldisilazane (HMDS) is required to increase the long-lasting stability.⁵³⁾ Hydrophobic aerogels derived from organotrialkoxysilanes are therefore advantageous especially for commercial productions because there is no need for such a time- and cost-consuming derivatization process. When employing MTMS as the single precursor, flexibility against shear or tensile stress is also noteworthy,⁵²⁾ though these aerogels are also opaque due to macroscopic phase separation. The resultant product is termed as poly(methylsilsesquioxane) (PMSQ) because the gels are mostly composed of polymeric random networks with the ideal chemical formula CH₃SiO_{1.5}.

Hybridization with bis(trialkoxysilane)s with organic bridging groups such as α, ω -bis(trimethoxysilyl)alkanes is not advantageous to increase the mechanical properties.^{54),55)} Since the surface of the gels derived from these precursors is highly hydrophilic, the organic bridging groups are deduced to be embedded inside the rigid siloxane networks resulted from hexafunctionality, and do not contribute to the mechanical properties and hydrophobicity. Flexible networks with low crosslinking density, low residual silanol groups density, and the presence of dangling hydrophobic groups are highly important factors to increase the mechanical properties and hydrophobicity of siloxane-based aerogels.

3. Our approach to improve the mechanical properties

In the aforementioned approaches, organotrialkoxysilane or its mixture with tetraalkoxysilane was reacted in a similar way as in the typical preparation of silica aerogels, though the reaction behavior is far different. Namely, the base-catalyzed one-step reaction in a large amount of alcoholic solvent was employed. In these systems, heterogeneous hydrophobic colloidal gels with highly branched siloxane networks are expected due to the rapid base-catalyzed condensation after slow hydrolysis of organotrialkoxysilanes. Clearly, this situation is highly disadvantageous to facilitate homogeneous poly(silsesquioxane) gel formations with high transparency. Meanwhile, in the acid-catalyzed one-step process with limited amount of water and solvent (molar ratios ~ 2 with respect to MTMS), we have reported that well-defined macroporous PMSQ gels with relatively high density (0.4- $0.5 \,\mathrm{g}\,\mathrm{cm}^{-3}$) are obtained as a result of moderate phase separation.^{56)–58)} Only precipitates or stable sols are obtained in the more dilute conditions because of the enhanced phase separation and cyclization as mentioned above. It is accordingly not suitable for low-density gel preparations. Dong et al. also reported the similar tendency with various sol-gel systems containing MTMS.⁵⁹⁾⁻⁶¹⁾ They also observed that the acid/base two-step process favorably gives gels rather than precipitates or resins.48),59) A complete hydrolysis in acidic conditions and subsequent rapid condensation both at cyclic or linear sites in basic conditions readily lead to gels prior to enhanced phase separation.

In pursuit of aerogels with improved mechanical properties, we employed MTMS as a sole precursor in a modified acid/base two-step sol-gel process to overcome these difficulties (cyclization and phase separation).^{58),62)-64)} Figure 3 represents the typical scheme for the process; starting from the mixture of all constituents in one pot, the two-step process undergoes acidcatalyzed hydrolysis at room temperature by dilute aqueous acetic acid and base-catalyzed condensation by in-situ generated ammonia from hydrolysis of urea at 60°C. Although the conventional two-step process requires the addition of aqueous base in the second step, our process does not require such delicate and problematic process which may impair the homogeneity and reproducibility. The hydrolysis of urea is used for the pH increase in a similar way to the "homogeneous precipitation method" widely used to obtain well-defined inorganic precipitates, and more homogeneous growth of PMSQ networks is expected compared to the conventional two-step process, in which the sudden local increase of pH would result in heterogeneity. Urea-assisted gelation in silica aerogels are also employed to generate well-dispersed magnetic nanocrystals in the silica matrix.65)

The other important aspect is to use surfactant to effectively suppress phase separation. While we observed that the two-step process even with a large amount of water (water/MTMS ~ 10 in molar ratio) gives low-density monolithic gels,⁶⁶⁾ the gels are opaque due to macroscopic phase separation. In order to suppress phase separation, we employed surfactant, and two kinds of surfactant are found to be effective; cationic n-hexadecyltrimethylammonium salts (bromide denoted as CTAB and chloride as CTAC) and nonionic surfactant nonionic poly(ethylene oxide)*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (EO₁₀₆-PO70EO106, EO and PO denote ethylene oxide and propylene oxide units, respectively) called as the product name Pluronic F127. The obtained wet gels are subsequently washed with solvent (water or methanol) and then replaced with 2-propanol to obtain alcogels. Finally, the alcogels are supercritically-dried with CO2 (80°C, 14 MPa) to transform into aerogels. In the case of evaporative-drying at ambient conditions, the washed samples are solvent-exchanged with the solvent with low surface tension such as hydrofluorocarbons or non-polar organic solvent (e.g. hexane). Finally, the solvent is allowed to slowly evaporate in ambient temperature and pressure conditions (typically, 30°C, 0.1 MPa).

4. Physical properties of PMSQ aerogels

In Fig. 4, some of the obtained aerogels dried by SCD are shown with starting compositions and some properties (Table 1). The water/MTMS molar ratio is increased to ~ 16 (volume ratio



Fig. 4. Appearance of typical poly(methylsilsesquioxane) (PMSQ) aerogels obtained with different kinds of surfactant. See text and Table 1 for abbreviations and starting compositions.

 Table 1. Fundamental properties of aerogels obtained from typical starting compositions

Code	$ ho_{ m b}$ /g cm ^{-3 b}	\mathcal{E}_{p} $(\%)^{c}$	$T \ (\%)^d$	$a_{\rm BET}$ $/{ m m}^2{ m g}^{-1e}$	$a_{\rm m} / {\rm m}^2 {\rm g}^{-1f}$	$\frac{W_0}{/\mathrm{cm}^3\mathrm{g}^{-1g}}$	$\frac{V_{\rm p}}{/{\rm cm}^3{\rm g}^{-1h}}$
CTAB-1	0.13	91	89	601	148	0.080	6.9
CTAC-1	0.14	90	87	618	141	0.074	6.4
F127-1	0.17	88	39	528	220	0.11	5.0

^{*a*}Starting compositions are; MTMS 10 mL, aqueous acetic acid 20 mL, Urea 6.0 g and surfactant. The amounts of surfactant are; CTAB 0.80 g (CTAB-1), CTAC 0.80 g (CTAC-1) and F127 2.0 g (F127-1). Note that the concentration of acetic acid is 1 mM for CTAB-1 and CTAC-1, and 5 mM for F127-1. ^{*b*}Bulk density. ^{*c*}Porosity. ^{*d*}Light transmittance at 550 nm through a 10 mm-thick-equivalent sample. ^{*c*}BET total surface area determined by nitrogen adsorption/desorption at 77 K. ^{*f*}Micropore surface area determined by α_s -plot. ^{*g*}Micropore volume by α_s -plot. ^{*h*}Total pore volume determined from the true density (1.41 g cm⁻³, by He pycnometry) and bulk density.

 \sim 2) in order to decrease bulk density. No other diluting solvents such as alcohols are added. In CTAB/CTAC systems, highly transparent (~90% at 550 nm through 10 mm-thick-equivalent samples) and high porosity (~90%) are confirmed, which are comparable to silica aerogels. To the best of our knowledge, this is the first example of transparent PMSQ aerogels. Although the PMSQ aerogels CTAB/CTAC-1 are friable when handled with hand, the mechanical properties are largely improved compared to silica aerogels as described in the next section. In F127 system, though visible-light transmittance reaches only $\sim 60\%$ at most (39% in the case of sample F127-1), the sample is not highly friable and has better stiffness against stresses when treated with hand or a knife. These differences can be understood on the basis of pore structures. According to the field emission SEM (FE-SEM) micrographs shown in Fig. 5, CTAB (and CTAC) system gives a finer porous structure with weakly linked PMSQ nanoparticles. On the other hand, F127 system leads to a coarser porous structure with more strongly linked nanoparticles. The difference in size of the porous structures mainly reflects the difference in light transmittance, and the smoother and more continuous linkage of nanoparticles in F127-1 improves the stiffness.

Detailed pore characteristics are also somewhat different between two systems. Since F127 system undergoes shrinkage during aging and SCD in $\sim 8\%$ in linear in total while CTAB/ CTAC-1 shrinks only $\sim 1\%$, specific pore volume and porosity are accordingly lower (Table 1). This is attributed to a slight hindrance of silanol groups by hydrogen bonding with F127 molecules at ether oxygen in EO units during polycondensation.67),68) As a result, the amount of unreacted silanol groups is larger at the onset of gelation in F127 system, and local condensation in-between remaining silanol groups continues after gelation, resulting in higher shrinkage during aging. The F127 molecules were washed out by the washing process after aging, and the remaining silanol groups are exposed, which further continue to react during SCD at 80°C. Micropore volume W_0 and micropore surface area a_m are also larger for F127-1 because the removal of F127 molecules which had penetrated in the PMSQ networks leaves interstices with the size of micropores.^{69),70)} In contrast, there is no strong specific interaction other than hydrophobic interaction between MTMS-derived condensates and CTAB/CTAC because of the negativelycharged condensates at pH > IEP (isoelectric point \sim 4.5) and the neutral polar head group of CTAB/CTAC, which in a large part is not dissociated in the aqueous solution. The condensates/ surfactant complex therefore takes the favorable conformation to reduce the enthalpic interaction in a way that polar head groups are exposed toward the solvent. In this case, silanol groups are not hindered, and, moreover, repulsive interaction in-between polar head groups prevents shrinkage during aging.⁷¹)



Fig. 5. Porous structures of CTAB-1 and F127-1 samples. The sample CTAB-1 consists of nano-sized particles weakly linked together to form tenuous networks similar to the conventional silica aerogels. By contrast, F127-1 consists of fibrous skeletons with larger structural size.



Fig. 6. An example of temporal shrinkage and reexpansion ("spring-back") of PMSQ aerogel during uniaxial compression. The optimized aerogels undergo as high as 80% strain and 9 MPa stress upon compression, and recover nearly the original size.

The obtained PMSQ aerogels are thermally stable up to 300°C. Above this temperature, vigorous thermal decomposition of methyl groups starts at 400°C.⁷²⁾ Between these temperatures, several events including additional condensation and redistribution reactions of cyclic species into branched siloxane networks may proceed, which cause densification and the partial collapse of pores.⁶¹⁾

5. Mechanical properties of PMSQ aerogels

The most important feature of these PMSO aerogels is the elastic property and high compressive mechanical strength as shown in Fig. 6. The low cross-linking density derived from the trifunctional precursor allows a high deformability, and the methyl groups promote "spring-back" by repelling each other after the stress is removed. In addition, the low remaining silanol density, which has been confirmed by infrared absorption spectra,⁶³⁾ prevents permanent irreversible shrinkage. The irreversible shrinkage due to the formation of new siloxane bonds upon compression in silica gels is universally observed.73),74) This unfavorable phenomenon leading to the collapse of pores was successfully avoided in the PMSQ networks. The stressstrain curves obtained from uniaxial compression tests on optimized samples prepared in CTAB and F127 systems demonstrate that the PMSQ aerogel can be compressed up to 80% with a stress of >9 MPa and recovers to its original size after removing the load; resilience (h/h_0) , see in Fig. 6) for the optimized gels reaches as high as 98%.

A small difference between samples prepared with CTAB/ CTAC and F127 systems should be noted. Since aerogels from F127 system possess the larger amount of silanol groups on the surfaces, irreversible shrinkage upon compression is generally larger. Instead, surface cracking due to anisotropic tensile or shear stresses during a compression test is considerably suppressed (but still occurs) because of the more continuous gel networks as shown in Fig. 5. As a general trend, these PMSQ aerogels are highly deformable against the compressive stress; however, they are friable against the tensile and shear stresses. Further improvement by post-treatment and/or co-gelation with other network-forming precursors may be required to tailor truly flexible and bendable aerogels. However, the deformability against compressive stress is readily enough for drying under ambient conditions as follows.

6. Drying under ambient conditions

With the aid of the spring-back phenomenon, the wet PMSQ gels can be dried from solvent with low surface energy simply by evaporation in ambient conditions with undergoing temporal



Fig. 7. The concept of ambient pressure drying by solvent evaporation exploiting temporal shrinkage and reexpansion (spring-back). The drying gel undergoes shrinkage due to the capillary pressure of solvent exerted on the gel, followed by spring-back to the original size upon emptying the pores. Pores are mostly preserved in this way, and aerogel-like xerogels are obtained.

shrinkage and reexpansion as schematically shown in **Fig. 7**. In a typical example of ambient pressure drying, as large as 64% shrinkage in volume was observed at maximum shrinkage (leatherhard point, the onset the menisci start to recede into the gel^{25),26)}) at 38 h, and the volume gradually recovered the original size in concert with emptying the pores, resulting in aerogel-like xerogel in 60 h. Bulk density, light transmittance, porous and mechanical properties are almost equivalent between supercritically-dried aerogels and evaporatively-dried xerogels. **Figure 8** shows an example of PMSQ aerogel and xerogel with comparable pore structures and physical properties.

During evaporative drying, compressive stress is exerted on the drying gels due to the capillary pressure at the menisci.^{25),26)} Since the capillary pressure is inversely proportional to the pore size, and since the pore liquid must flow toward the gel surface, pore size should not be too small. Also, pore size distribution should be as narrow as possible; otherwise stress develops as a result of inhomogeneous pressure gradient throughout the gel. In practice, ambient pressure drying becomes easier with slow



Fig. 8. An example of aerogel and xerogel with comparable pore structures and physical properties. Starting composition: MTMS 5 mL, 10 mM acetic acid aq. 7 mL, F127 1.1 g, and urea 0.5 g. The sample thickness is ca. 10 mm.

evaporation rate, larger pores (such as >50 nm, note that too large pores reduce transparency), high homogeneity in pore size, and with drying solvent with low surface tension such as hydrofluorocarbons or low-molecular-weight organic solvents. Nevertheless, one may observe surface cracking during drying, which propagates from flaws or micro cracks naturally formed on the gel surfaces, similar to the failure of inorganic glasses (Griffith flaws). These flaws or micro cracks can be filled with oligomeric species of MTMS as a post treatment to obtain crackand shrinkage-free aerogel-like xerogels. In this way, huge PMSQ aerogel tiles with a few thousands square centimeters and 10 mm thick can be obtained. Details will be reported elsewhere.

In the previous literatures, Prakash et al. obtained low-density silica xerogel films (porosity 98.5%) by dip-coating of homogenized wet gels.⁷⁵⁾ The TEOS-derived silica gels were derivatized with trimethylchlorosilane to eliminate surface silanol groups for promoting spring-back. While this method is not very successful in large monoliths where 3-D temporal shrinkage and reexpansion occur, the surface modification takes advantage in preparing small-sized low-density xerogels such as films and granules.^{76)–78)} Although the aerogel granules obtained from SCD⁷⁹⁾ were not very commercially successful (e.g. Basogel by BASF), their equivalent obtained from ambient pressure drying using this technique is presently available as a commercial product (Nanogel by Cabot), from which fact we can learn the importance of cost-effective process without SCD. Up to now, no transparent and low-density xerogel monoliths with aerogel-like features have been reported except for those obtained by us.

Summary and future perspectives

This review gives a brief overview of strengthened siloxanebased aerogels (and aerogel-like xerogels) developed using various techniques such as hybridization with organic polymers and surface modifications. A special emphasis is put on the organic–inorganic hybrid aerogels prepared using organotrialkoxysilanes. We for the first time found that compressible and mechanically strong aerogels with high transparency and low density can be obtained solely from MTMS by a modified twostep sol-gel route in the co-presence of appropriate surfactant. Owing to the elastic properties against compressive stress, the PMSQ wet gels can be dried by evaporation of solvent at ambient conditions. The obtained xerogels with aerogel-like properties are promising for cost-effective industrial production and various applications such as to (transparent) thermal insulators.

To attain further versatility, mechanical properties should be improved in terms of strength against tensile and shear stresses, which will give bendable and flexible aerogels and xerogels. It is actually difficult to balance transparency and excellent mechanical properties because number density of neck between particles, at which breakage tends to occur, in a unit volume becomes higher with decreasing structural size. Bendable aerogels reported so far therefore possess large structural sizes such as microns and are consequently opaque. In addition, a shape control of materials to films, particles, granules, and composites is desirable to acquire more broadened opportunities for low-cost and largescale applications. We believe a great progress will be made out of active research both in academic and industrial fields.

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