



Improving Elastic Properties of Polymer-Reinforced Aerogels

30

Mary Ann B. Meador and Baochau Nguyen

Contents

30.1	Introduction	791
30.2	Hexyl-Linked Polymer-Reinforced Silica Aerogels	793
30.2.1	Di- and Tri-isocyanate-Reinforced Aerogels	793
30.2.2	Styrene-Reinforced Aerogels	794
30.2.3	Epoxy-Reinforced Aerogels from Ethanol Solvent	796
30.3	Alkyl Trialkoxysilane-Based Reinforced Aerogels	798
30.4	Future Directions	800
30.5	Conclusions	804
	References	807

Abstract

Monolithic aerogels provide superior thermal insulation compared to other forms of aerogel (composites, particulate, etc.). It has also been demonstrated that monolithic aerogels can be made mechanically stronger and more durable by incorporating a conformal polymer coating on the skeletal nanostructure. However, for many applications, it would be most desirable to have monolithic aerogels in a more flexible form, for example, as insulation in deployable and inflatable structures or space suits or to wrap around a structure needing insulation. To this end, it has been found that by incorporating organic linking groups or alkyl trialkoxysilanes into the silica backbone, elastic recovery and/or flexibility is improved, while strength is increased by the use of polymer reinforcement.

Keywords

Polymer reinforced aerogels · Elastic recovery · Insulation

30.1 Introduction

Due to their combination of low density, high porosity, high surface area, and nanoscale pore sizes, silica aerogels are of interest for many applications including thermal and acoustic insulation, optics, catalysis, and chromatographic systems [1–3] (see ► Chap. 13). However, potential applications of aerogel monoliths in aerospace, industry, and daily life have been restricted due to their poor mechanical properties and their extreme fragility [4]. Hence, in aerospace, especially (see ► Chaps. 60 and ► 61), aerogel monoliths have been limited to a few exotic applications such as collecting hypervelocity particles from the tail of the comet Wild 2 in the Stardust Program [5] and as thermal insulation on the Mars Rover [6].

It has been shown that reinforcing silica aerogels by reacting polymer with the silanol surface to create a conformal coating over the silica skeleton is an effective way to increase mechanical strength by as much as two orders of magnitude while only doubling the density over those of native or non-reinforced aerogels [7–9] (see ► Chap. 29). In addition, the mesoporosity of these polymer-reinforced aerogels, and hence, their superior insulation properties among other things, is only marginally affected. Incorporating an amine onto the surface of the silica gel particles by coreacting the tetraalkoxysilane with 3-aminopropyltriethoxysilane (APTES), as shown in Fig. 30.1, allows for reinforcement with epoxy-terminated oligomers [10, 11] or cyanoacrylates [12] and also improves the reactivity of the silica surface toward isocyanates [13–15]. Expanding the silica surface chemistry to include styrene groups [16], free radical initiator [17], or vinyl [18] permits the use of polystyrene as a crosslinker. Other approaches to strengthening the silica aerogel structure by incorporation of a polymer include

M. A. B. Meador (✉)
Materials and Structures, NASA Glenn Research Center, Cleveland,
OH, USA
e-mail: mmeador@uakron.edu

B. Nguyen
Ohio Aerospace Institute, NASA Glenn Research Center, Brookpark,
OH, USA
e-mail: baochau.n.nguyen@nasa.gov

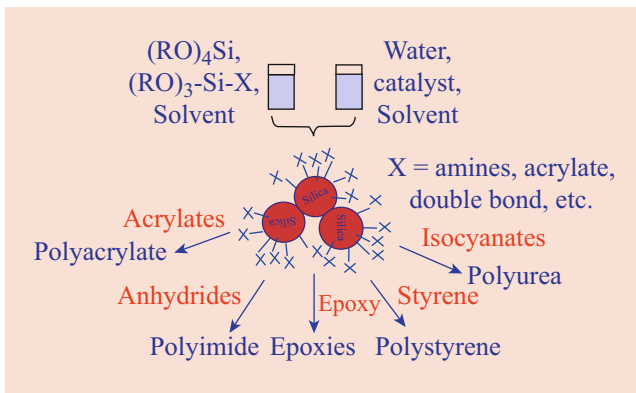


Fig. 30.1 Concept of polymer reinforcement using reactive groups on the silica surface

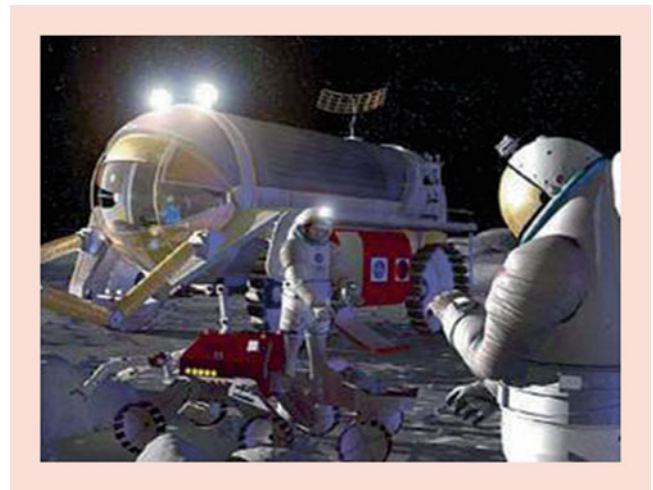


Fig. 30.2 NASA vision of manned mission to Mars surface activities. (Reprinted from [22], Copyright 2011 American Chemical Society)

dispersing functionalized polymer nanoparticles in a silica network [19] (see ► Chap. 7) and copolymerization of silica precursors with poly(methylmethacrylate) or poly(dimethylacryl-amide) [20] or poly(vinylpyrrolidone) [21].

Improvements to mechanical properties (see ► Chap. 8) seen by reinforcing aerogels with polymer enable a whole host of weight-sensitive aerospace applications, including thermal and acoustic insulation for habitats, extravehicular activity (EVA) suits, launch vehicles, cryotanks, and inflatable decelerators for planetary reentry, as well as lightweight, multifunctional structures (including insulation, sound dampening, and structural support) for aircraft or rotorcraft. In addition, if manufacturing costs of polymer-crosslinked monolithic aerogel can be decreased, down to earth applications, including insulation for refrigeration, building and construction, and industrial pipelines, can be realized.

In particular, manned Mars surface applications shown in Fig. 30.2 absolutely require a new insulation system. Multi-layer insulation (MLI), usually consisting of many thin layers of polymer such as Kapton or Mylar metalized on one side with aluminum or silver, requires a high vacuum to be effective. In evacuated conditions, contact points between the separate layers in MLI are reduced. Hence, conduction and convection are minimized. The multiple layers reduce the last form of heat transfer, radiation, by radiating and absorbing heat from each other, effectively trapping most of the thermal energy (see ► Chap. 9). The high vacuum required for MLI to be an effective insulation is abundantly available in the lunar environment and earth orbit. Mars, on the other hand, has an atmosphere consisting of mostly CO_2 with an average surface pressure of 6 torr [23]. The target thermal conductivity of materials for Mars EVA suits is 5 mW/m-K. Of a variety of composite materials considered in a recent study, only aerogel fiber composites come close to meeting that goal [24]. A monolithic polymer-reinforced aerogel may meet this goal, but insulation for EVA suits should also be durable and flexible to accommodate as much freedom of movement

for the astronaut as possible. Flexible fiber-reinforced silica aerogel composite blankets were recently evaluated using thermal and mechanical cycling tests for possible use in advanced EVA suits [25]. During testing, thermal conductivity did not change much, but the composite aerogels were found to shed silica dust particles at unacceptable levels. Polymer reinforcement may also be a means to reduce shedding.

A flexible form of polymer-reinforced aerogel would also be desirable for wrapping around structures that need to be insulated, such as cryotanks or cryogenic transfer lines. Currently, expendable cryotanks, such as the Space Shuttle's external liquid oxygen/hydrogen tank, use spray-on polyurethane foam to insulate the tank on the launch pad. Cryogenic tanks employed in space generally utilize the same MLI as space suits but require additional insulation while on the launch pad since the MLI is not an effective insulator under ambient pressure as discussed previously. An aerogel insulation system can function reliably in both ambient pressure and high vacuum, making foam insulation unnecessary [26]. However, molding a net shape aerogel to fit around a structure can be difficult since complex molds need to be devised and the gels before polymer crosslinking can be quite fragile.

Another use for flexible durable aerogels could be as part of an inflatable decelerator used to slow spacecraft for planetary entry, descent, and landing (EDL) as shown in Fig. 30.3 [27]. EDL systems used to successfully land six robotic missions on Mars from 1976 to 2008 employed a hard aeroshell heat shield and parachutes of 12–16 m in diameter. Future robotic and manned missions are much heavier and will require more drag for landing. Hence, new designs with much larger diameters (30–60 m) will be required [28]. Inflatable decelerators would stow in a small space and deploy into a large area lightweight heat



Fig. 30.3 Inflatable decelerator concepts. (Courtesy of the Inflatable Re-entry Vehicle Experiment (IRVE) Project)

shield to survive reentry [29]. Minimizing weight and thickness of the system and providing suitable insulation are important considerations.

Polymer-reinforced aerogels are somewhat flexible at densities below 0.05 g/cm^3 , but mechanical strength is reduced at these densities [14]. However, much more flexibility can be obtained in aerogels by altering the silica backbone in some significant way. For example, Kramer et al. [30] demonstrated that including up to 20 w/w% polydimethylsiloxane (PDMS) in tetraethyl orthosilicate (TEOS)-based aerogels resulted in rubbery behavior with up to 30% recoverable compressive strain. More recently, Rao et al. [31] have demonstrated that utilizing methyltrimethoxysilane (MTMS) as the silica precursor and a two-step synthesis imparts extraordinary flexibility to the aerogels. The MTMS-derived aerogels are more flexible largely because of the resulting lower cross-link density of the silica (three alkoxy groups that can react vs. four in rigid TMOS- or TEOS-derived aerogels). Kanamori et al. [32], using a surfactant to control pore size and a slightly different process, have shown that MTMS-derived gels demonstrate reversible deformation on compression. In fact, some formulations were able to be dried ambiently. Initially, the gels shrink about 65% but spring back to nearly their original size, resulting in nearly the same density and pore structure as those dried supercritically.

Though the MTMS-derived aerogels are very flexible and elastic, it does not take much force to compress them. For example, Rao [31] reports a Young's modulus of only 0.03–0.06 MPa for the flexible MTMS-derived aerogels ranging in density from 0.04 to 0.1 g/cm^3 . Kanamori [32] does not report Young's modulus, but stress-strain curves indicate that stresses of less than 1 MPa are sufficient to compress samples with bulk densities around 0.2 g/cm^3 to 25% strain. Hayase [33] also later described versions of MTMS- and dimethyldimethoxysilane (DMDS)-derived aerogels and xerogels as marshmallow-like.

Shea and Loy have employed bridged bis(trialkoxysilyl) monomers as precursors for silsesquioxane-derived aerogels and xerogels [34, 35]. Typically, this allowed for control of

pore size directly related to the size of the bridge, with the best results obtained using a stiffer structure such as an arylene chain. More flexible bridges such as alkyl chains resulted in more compliant aerogels but tended to shrink more, reducing porosity. Other examples of aerogels derived from bridged silsesquioxanes with sulfur-sulfur links reported by Yun [36] and Guo [37] demonstrate ability to recover from large deformation but again have low modulus. The latter also have a marshmallow-like consistency.

More recently, we have been combining the notion of altering the underlying silica structure to add flexibility and elastic behavior and the notion of polymer reinforcement to add strength and durability. This is accomplished by substituting some of the TEOS or TMOS with organic bridged bis(trialkoxysilanes) or with MTMS. This work, which has been shown to be a versatile method of imparting more elastic behavior and flexibility to the aerogels, is summarized herein.

30.2 Hexyl-Linked Polymer-Reinforced Silica Aerogels

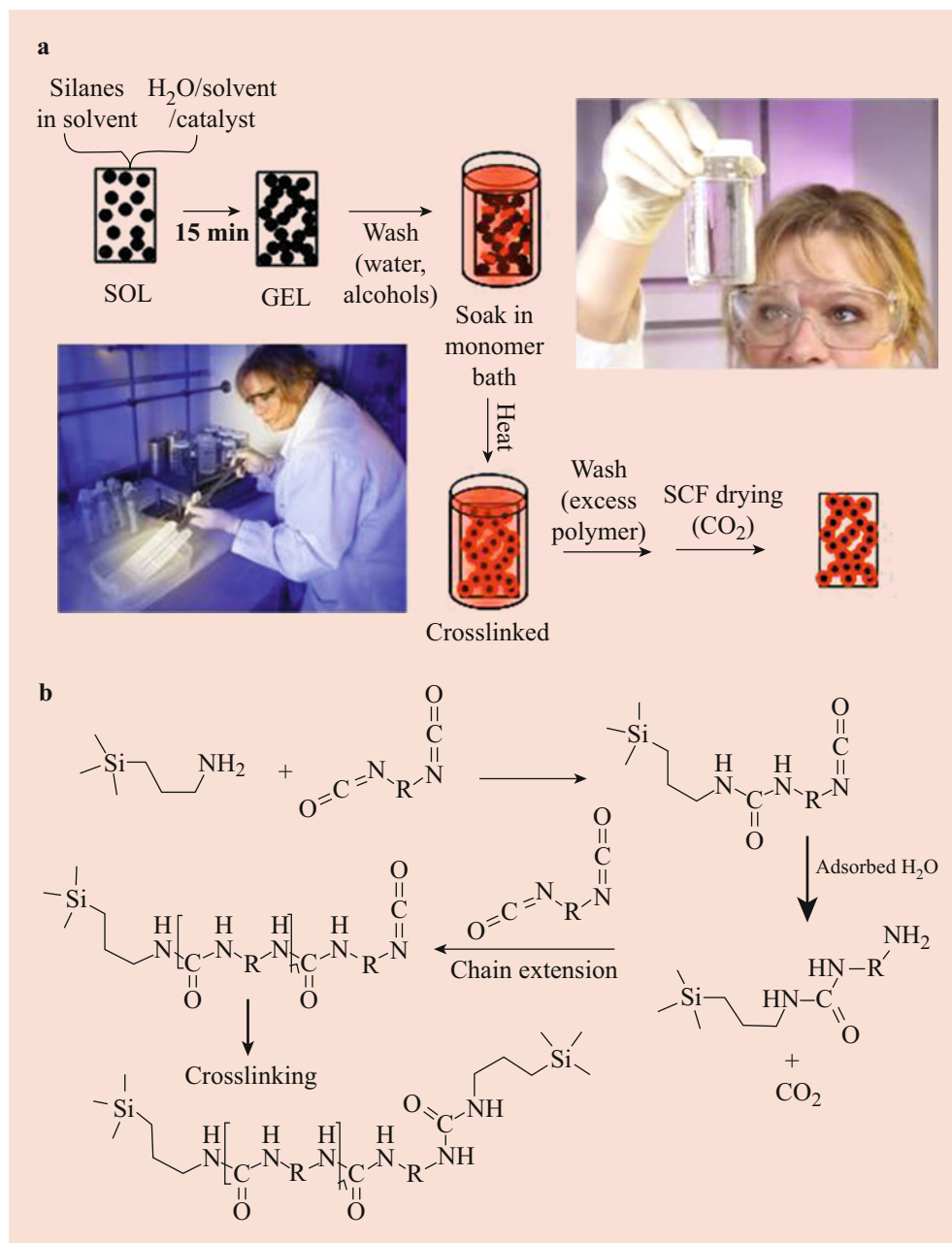
30.2.1 Di- and Tri-isocyanate-Reinforced Aerogels

Silica aerogels reinforced with diisocyanate through aminopropyl groups on the silica surface are made as shown in Fig. 30.4, where APTES and TMOS or TEOS are coreacted in acetonitrile to form a wet gel [13]. After being washed several times to remove water and alcohol by-products of gelation, the wet gel is subsequently soaked in a solution of di- or tri-isocyanates. Heating causes reaction of the isocyanates with surface amines as shown in Fig. 30.4b. The length of the polyurea crosslinks depends on both the diisocyanate concentration in the soak solution and the amount of residual water from the hydrolysis left in the gels. This is because isocyanate reacts with water to generate an amine that can react with other isocyanates to cause chain extension.

Hexyl linkages can be incorporated into the wet gels by replacing some of the TMOS or TEOS with 1,6-bis(trimethoxysilyl)hexane (BTMSH), noting that each BTMSH molecule contributes two atoms of Si [38]. Figure 30.5 shows a comparison of the silica gel structure (a) with 20 mol% APTES-derived Si and no hexyl linkages incorporated and (b) with about 40 mol% Si derived from BTMSH. A comparison of the silica gel structure with and without hexyl links is shown in Fig. 30.5. Note that the hexyl linkages serve to open up the structure and effectively reduce in size the regions of rigid silica.

Wet gels prepared with BTMSH are more resilient and easier to handle than those containing no BTMSH even at

Fig. 30.4 Fabrication of polymer-reinforced aerogels (a) and mechanism of diisocyanate crosslinking (b)



low silane concentrations, bending as they come out of a mold instead of breaking. Hence, the use of BTMSH can possibly improve the manufacturability of the aerogels. After reaction with diisocyanate, the wet gel is resilient enough to be bent and manipulated to a great extent without breaking as shown in Fig. 30.6. The resulting aerogels after drying with supercritical CO_2 can also be bent without breaking, but not to the same extent as the wet gels. This is due to a reduced plasticization of the silica/polymer network by the removal of the solvent.

30.2.2 Styrene-Reinforced Aerogels

Several approaches to reinforcing silica aerogel with styrene have been studied, including incorporation of styrene [16], a free radical initiator [17], or a vinyl [18] on the silica surface. All of these approaches result in greater hydrophobicity (see ► Chap. 14) and improvements in mechanical strength over non-crosslinked silica aerogels. A series of vinyl decorated silica gels have been fabricated by coreacting vinyltrimethoxysilane (VTMS), BTMSH, and TMOS in alcohol

Fig. 30.5 Underlying silica backbone structure made using (a) 20 mol% APTES and (b) 20 mol % APTES with 40 mol% BTMSH-derived Si. (Reprinted from [22], Copyright 2011 American Chemical Society)

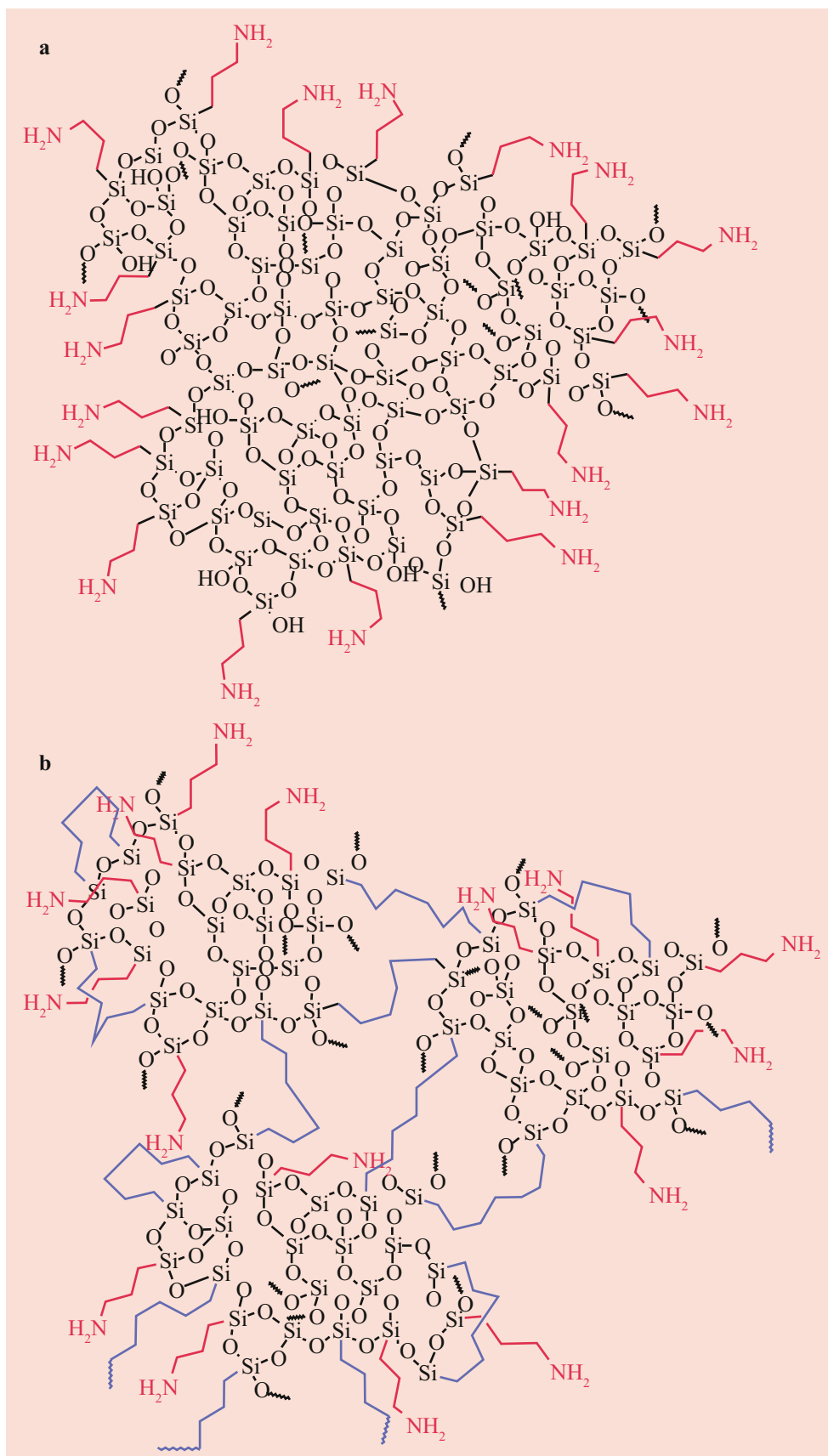




Fig. 30.6 A diisocyanate-reinforced wet gel with 35 mol% BTMSH-derived Si and 30 mol% Si from APTES is shown to be flexible and resilient before drying

solution. Up to 50% of the TMOS-derived Si atoms are replaced with BTMSH-derived Si, noting again that each BTMSH contributes two atoms of Si. As shown in Fig. 30.7a, the proposed silica gel structure is similar to that previously shown for the APTES-derived structure except with a vinyl decorated surface. Crosslinking with styrene is carried out as shown in Fig. 30.7b after exchanging solvent from methanol or ethanol to chlorobenzene and soaking the wet gels in a solution of styrene monomer and radical initiator.

As a way of characterizing elastic properties (see ► Chap. 8), styrene-reinforced aerogel monoliths are taken through two successive compression cycles to 25% strain. Stress-strain curves of successive compression tests of polymer-reinforced aerogels without hexyl-linking groups in the underlying silica typically look like that shown in Fig. 30.8a. The first compression is taken to 25% strain and released and followed immediately by a second compression to 25% strain. Between the first and second compression, about 13% of the length of the sample is not recovered. In contrast, Fig. 30.8b shows repeat compression tests of a styrene-reinforced aerogel made with 49 mol% of Si derived from BTMSH, 29 mol% from VTMS, and 22 mol% from TMOS. In this case, the first and second compression curves almost overlap. Nearly, all the length (99.5%) is recovered within 30 min after the second compression as shown in Fig. 30.10c. Note that the compressive modulus of this hexyl-linked aerogel is over 3 MPa.

Interestingly, hexyl-linking groups also improve the hydrophobicity of the polystyrene-reinforced aerogels. Water droplet contact angles of styrene-reinforced aerogels have been reported to be in the range of 112–120° for samples containing no BTMSH [16]. Samples with at least 29 mol% BTMSH-derived Si had water droplet contact angles ranging from 127° to 138°. This indicates that the hexyl group from BTMSH is also present on the silica surface and has a significant effect on the hydrophobic nature of the aerogels above and beyond the simple polystyrene crosslinking.

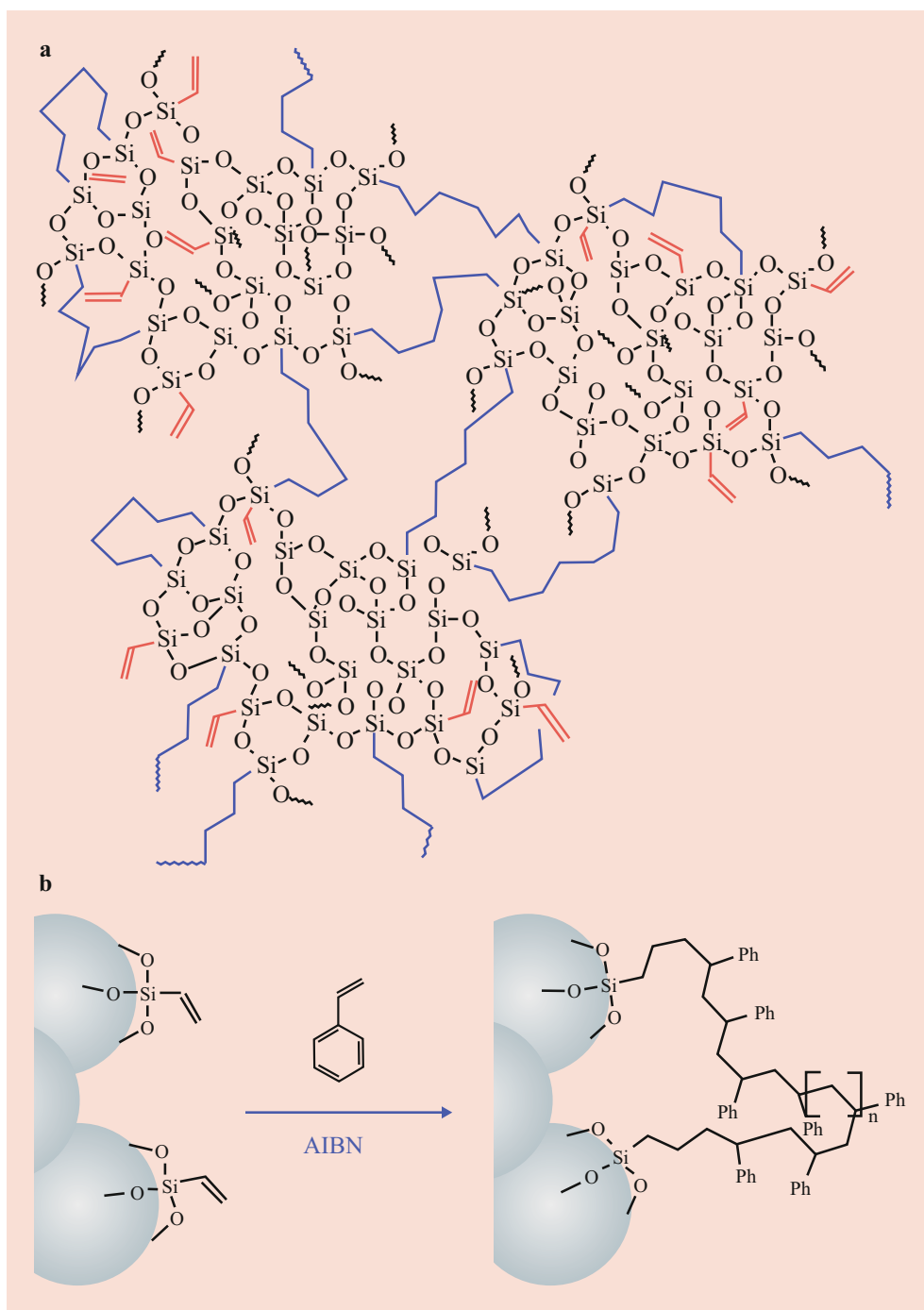
30.2.3 Epoxy-Reinforced Aerogels from Ethanol Solvent

Previously, the type of polymer reinforcement has dictated the solvent choice based on the solubility of the monomers and cure temperature of the crosslinking chemistry. In order to scale up manufacturing processes for crosslinking aerogels, it is desirable to adopt a more industrially friendly solvent. It has been demonstrated that less toxic TEOS and ethanol can be used to synthesize polymer-reinforced silica aerogels by crosslinking ethanol-soluble epoxies with APTES-derived amine groups (Fig. 30.9). In this manner, similar increases in mechanical properties were achieved in comparison with previously studied isocyanate crosslinked aerogels [11]. The use of ethanol as solvent in particular improves the viability of large-scale manufacturing of the polymer-crosslinked aerogels since large amounts of solvent (from initial gelation through diffusion of monomer into the alcogels and additional rinsing steps) are used in the production.

Varying total silane concentration and the mole fraction of APTES and BTMSH leads to aerogels with different pore structures as seen with both the styrene- and diisocyanate-reinforced aerogels. Figure 30.10 shows scanning electron micrographs of four aerogel monoliths made using 15 mol% APTES. The top samples (Fig. 30.10a, b) are made using 1.6 mol/l total silicon. The sample shown on the left (Fig. 30.10a) is made using no BTMSH, while the right-hand sample (Fig. 30.10b) is made using 40 mol% of Si derived from BTMSH. Both samples show a fine distribution of similar size particles, but in the sample containing hexyl links (Fig. 30.10b), pores appear to be larger. The density of the hexyl-linked samples is also smaller, though the two samples are made with the same total moles of silicon, the same amount of amine, and the same concentration of epoxy. The density difference is due to the fact that hexyl-linked samples tend to shrink less during processing. A similar but more pronounced effect is seen for samples made using 0.8 mol/l total silicon (Fig. 30.10c, d). Again, the particle sizes are similar between the two samples, but larger pores are evident in the hexyl-linked sample shown in Fig. 30.10d and the density is lower. However, BET surface areas are fairly constant for all four samples – only the distribution of pore sizes changes with BTMSH concentration.

Empirical models were generated for predicting properties of the epoxy-crosslinked aerogels over a wide range of densities as well as to identify and understand significant relationships between the processing parameters and final properties. Figure 30.11 exhibits empirical models for (a) density, (b) Young's modulus from compression tests, and (c) amount of recovery after compression to 25% strain. As seen in Fig. 30.11a, highest density is seen when using 1.6 mol/l total Si and APTES-derived Si is 45 mol%. At the

Fig. 30.7 Silica structure incorporating hexyl links and vinyl groups for reinforcement with polystyrene. (Reprinted from [18], Copyright 2009 American Chemical Society)



same time, Fig. 30.11b shows that highest modulus (95 MPa), when no BTMSH is used, is achieved with APTES-derived Si at about 30 mol%.

Using BTMSH does appear to lower modulus with optimum modulus in this system (~40 MPa) being produced in combination with 45 mol% APTES. However, this change in modulus is at least in part due to the decrease in shrinkage (and concomitant decrease in density) using higher BTMSH concentrations.

It is possible to achieve good, i.e., nearly complete, recovery after compression with epoxy-reinforced aerogels using 15 mol% APTES, 40 mol% Si from BTMSH, and 15% (w/w) epoxy in the soaking solution; this is illustrated in Fig. 30.11c. In fact, across the whole range of total Si concentration (densities ranging from 0.1 to 0.23 g/cm³ and modulus as high as 10 MPa), the monoliths prepared using these conditions recover nearly their full length after deformation to 25% strain. Similar modulus and recovery after compression is obtained in

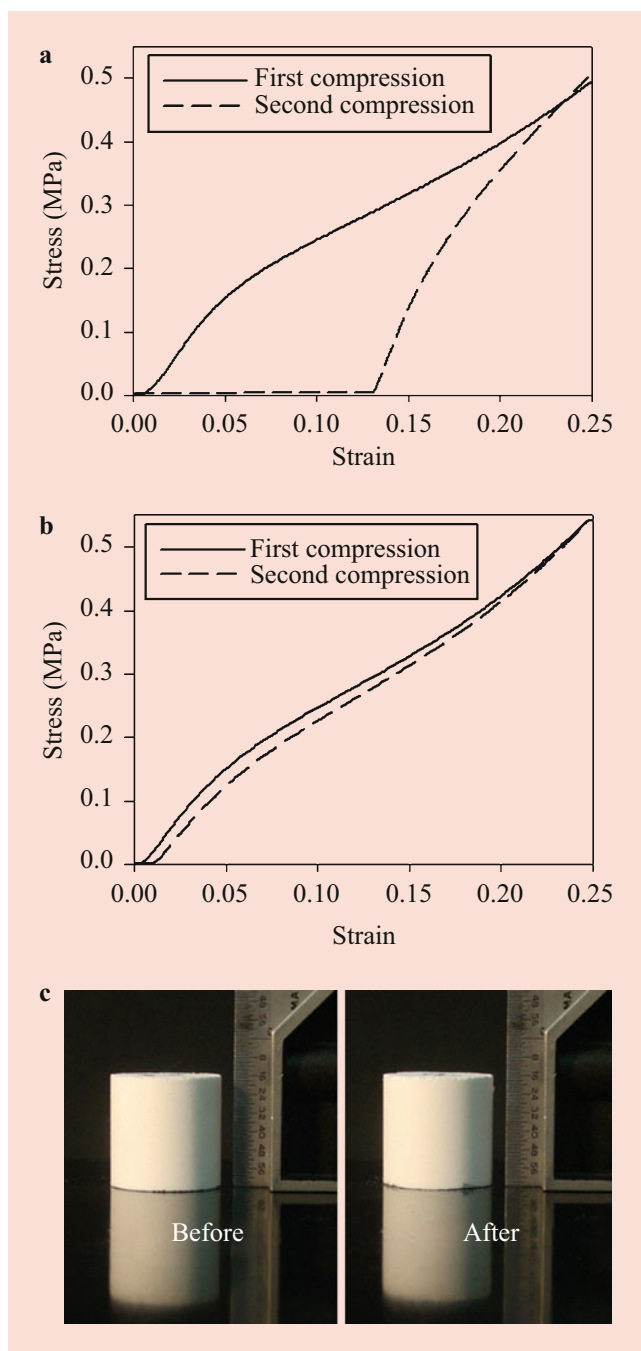


Fig. 30.8 Repeat compression cycles of (a) a styrene-reinforced aerogel monolith without flexible linking groups (density = 0.122 g/cm³; surface area = 366 m²/g); (b) a styrene-reinforced aerogel monolith with 49 mol% Si derived from hexyl-linked BTMSH (density = 0.232 g/cm³; surface area = 158 m²/g); and (c) the monolith from (b) before and after two compressions. (Reprinted from [18], Copyright 2009 American Chemical Society)

epoxy-reinforced aerogels using ethyl-linked or octyl-linked bis-silanes in place of BTMSH [22].

If more flexible monoliths are desired, vastly improved elastic recovery from compression at up to as much as 50%

strain can be obtained using even lower total Si concentration (0.4 mol/l total Si, 45 mol% derived from APTES, and 40 mol% derived from BTMSH). As shown in Fig. 30.12, a 2.3 cm monolith made using this formulation after two compression cycles to 50% strain loses only 2.6% of initial length. At 25% strain, the sample demonstrates complete recovery after two compression cycles. However, with a density of 0.047 g/cm³ and porosity greater than 96%, the modulus of this monolith decreases to 0.05 MPa and surface area is also low (54 m²/g).

Interestingly, epoxy-crosslinked aerogels can also be produced using a one-pot reaction scheme using ethanol as the solvent [39]. The typical process for making the aerogels can be quite long, involving production of the gel, solvent exchanges, and diffusion of monomer, followed by more solvent exchanges and supercritical fluid extraction. The one-pot reaction scheme shortens the process to make epoxy-reinforced aerogels by eliminating monomer diffusion, and half of the solvent washes to the previously described diffusion-controlled process as shown in Fig. 30.13. The ethanol-soluble epoxy monomers are included in the initial step of the sol-gel process without interfering with gelation of the starting silanes. Notably, properties of aerogels made using a low amount of amine reactive sites have properties similar to those previously reported that used the longer diffusion controlled process, whereas higher amounts of amine sites produce less desirable monoliths with much higher density and lower surface areas. Also noteworthy, although aerogels made using 40% BTMSH had better elastic recovery, even those made using no BTMSH and 15% APTES recover almost completely from 25% compression. Clearly, epoxy is contributing more to elastic recovery when included in the initial sol in the one-pot reaction scheme. This may be due to the presence of epoxy inside of the secondary particles, whereas these smallest pores may not be accessible to epoxy in the diffusion controlled process.

30.3 Alkyl Trialkoxysilane-Based Reinforced Aerogels

As pointed out in Sect. 30.1 of this chapter, MTMS-based aerogels have been synthesized with a surprising amount of flexibility [31, 32]. It is of interest then to see if strength and durability of the MTMS aerogels can be improved by introducing the notion of polymer reinforcement. In preliminary studies, formulations with MTMS coreacted with APTES to provide a reactive site for polymer crosslinking tend to gel in only a narrow range of total Si concentration, and they shrink much more than their TEOS- or TMOS-based counterparts [40]. In contrast, MTMS coreacted with bis(trimethoxysilylpropyl) amine (BTMSPA) readily gels across a wide range of

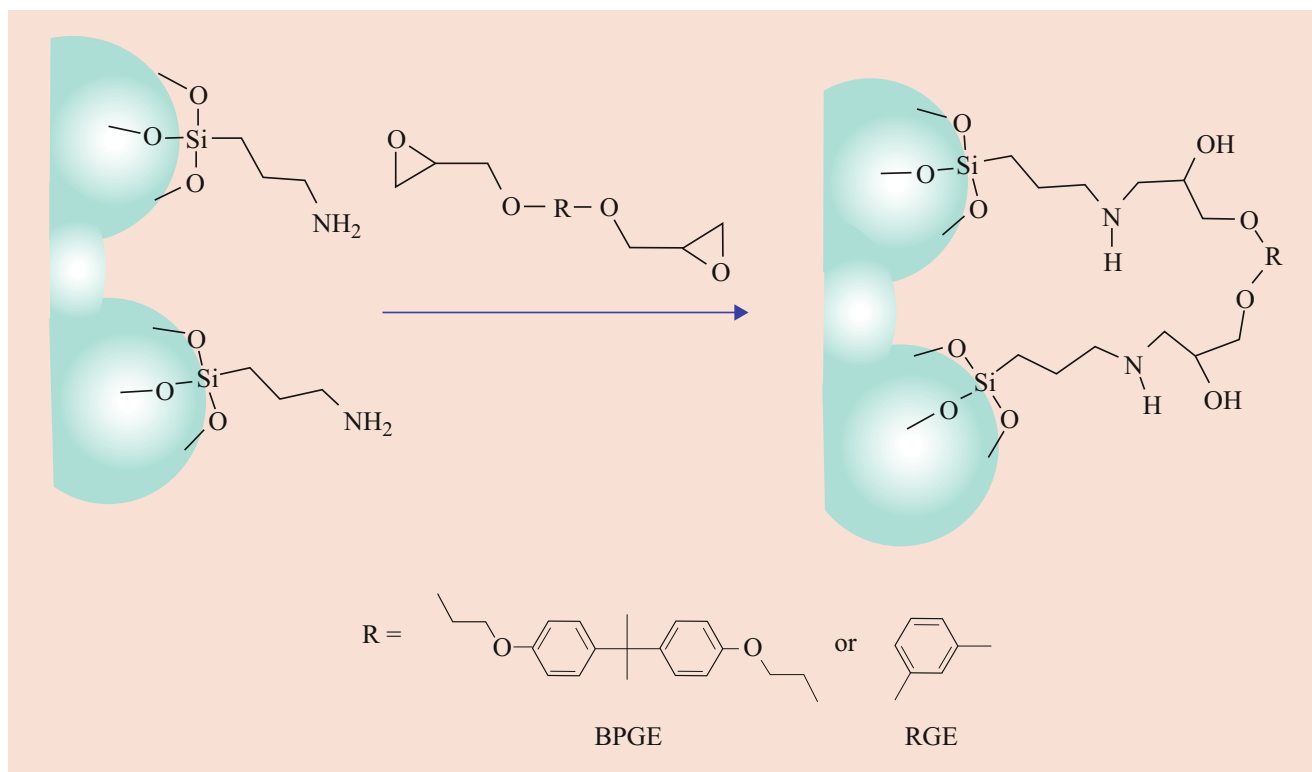


Fig. 30.9 Typical reaction scheme for crosslinking silica gels with epoxy through surface amine groups. (Reprinted from [11], Copyright 2009 American Chemical Society)

total Si concentration [41]. The secondary amine of BTMSPA provides a ready reactive site for Desmodur N3300A [42], a tri-isocyanate crosslinker, as shown in Fig. 30.14.

Since only a small excess of water (ratio of water to Si ranging from 2 to 5) was used to make the aerogels in this study, chain extension of the polyurea was minimized. NMR analysis indicated that the polymer-reinforced structure is as shown with approximately a one-to-three ratio between each amine and each tri-isocyanate for samples where total Si ranged from 1.2 to 1.65 mol/l and 40 to 80 mol% of the Si from BTMSPA. For gels made in acetonitrile with lower total Si and 40 mol% BTMSPA, it was found that very little isocyanate crosslinking occurred. Monoliths made using these formulations also exhibited very low BET surface areas ($<10 \text{ m}^2/\text{g}$), most likely due to solvent interactions between acetonitrile and polar surface groups. With methyl groups in greater abundance on the surface of the developing gel, this leads to collapse of the gel structure. Such low surface area would lead to very little secondary amine available to react with isocyanate. Using a less polar solvent such as acetone for gelation reverses this trend, leading to higher surface areas and better crosslinking.

Figure 30.15 shows a side-by-side comparison of unreinforced monoliths (left) and polymer-reinforced monoliths (right) produced using the same initial gelation

conditions. All four monoliths pictured were prepared using 1.65 mol/l total Si. Figure 30.15a, b is of aerogel monoliths produced using 80 mol% Si derived from BTMSPA. As illustrated, particle sizes are very similar in appearance; however, the pores appear slightly reduced in size in the reinforced structure (Fig. 30.15b). This accounts in part for the relatively large differences in density, porosity, and surface areas between the two samples. When BTMSPA mole fraction is reduced to 40 mol% (Fig. 30.15c, d), both uncrosslinked and polymer-reinforced aerogels exhibit a larger distribution of pore sizes than seen in Fig. 30.15a, b, probably due to the different spacing formed from the connecting group in BTMSPA vs. the nonreactive methyl groups contributed by MTMS. Notably, the uncrosslinked monolith in Fig. 30.15c has a much finer particle structure and larger surface area compared to the reinforced aerogel shown in Fig. 30.15d (smoother, larger particles).

Compression testing of the monoliths made from MTMS and BTMSPA was carried out as previously described on both the unreinforced and polymer-reinforced aerogels. Though there is usually a trade-off between modulus and elastic recovery as seen with the hexyl-linked aerogels, in this study, the trade-off is very small, with even the highest modulus (84 MPa) of crosslinked aerogels exhibiting only about 3% unrecovered strain. To illustrate, stress-strain curves for repeat compression tests to 25% strain of four

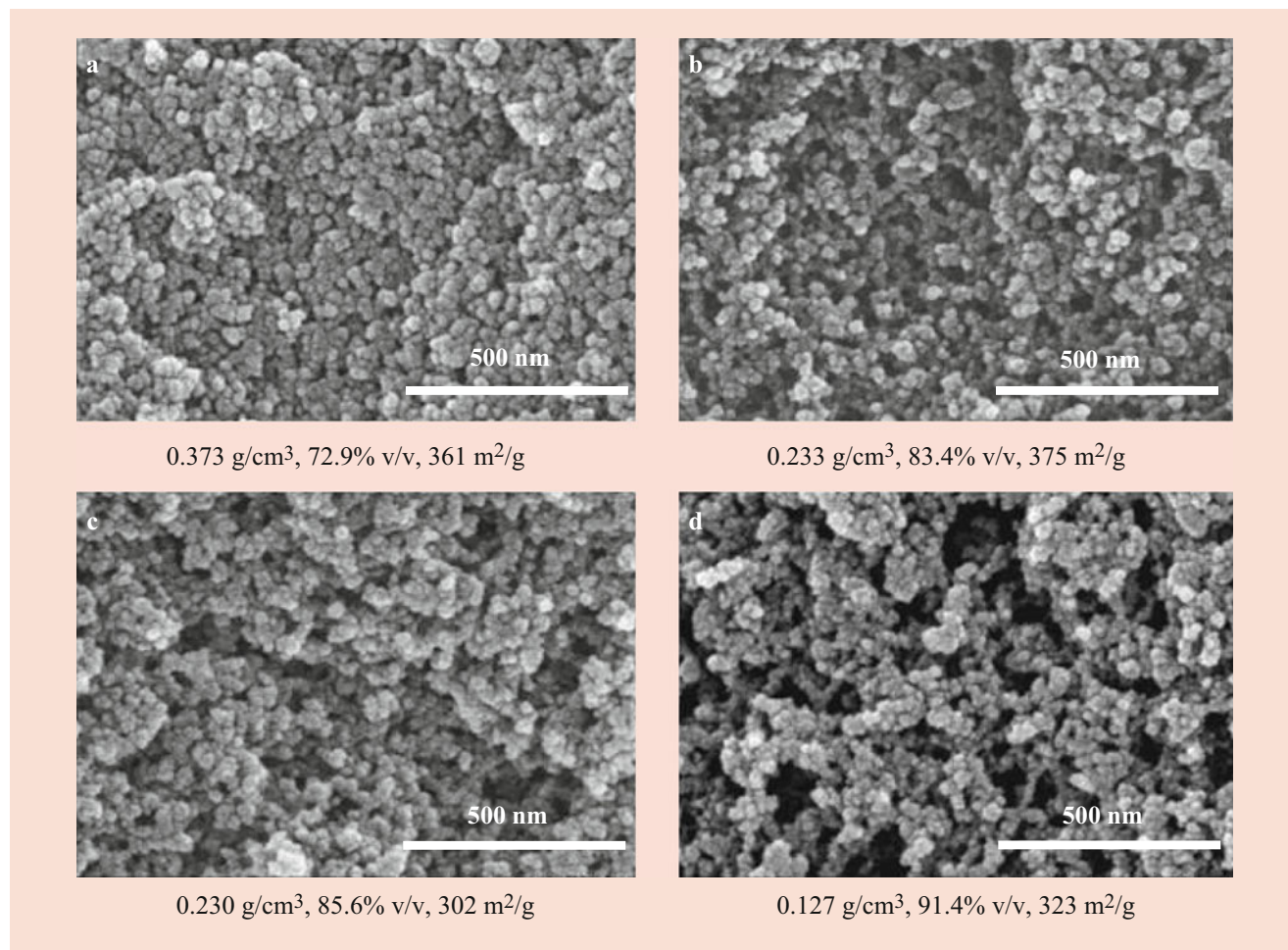


Fig. 30.10 Side-by-side comparisons of micrographs of samples with (left) no BTMSH and (right) 40 mol% BTMSH-derived Si, including samples prepared with 1.6 mol/l total Si (15 mol% APTES) (a and b)

and with 0.8 mol/l total Si (15 mol% APTES) (c and d). (Adapted from [11], Copyright 2009 American Chemical Society)

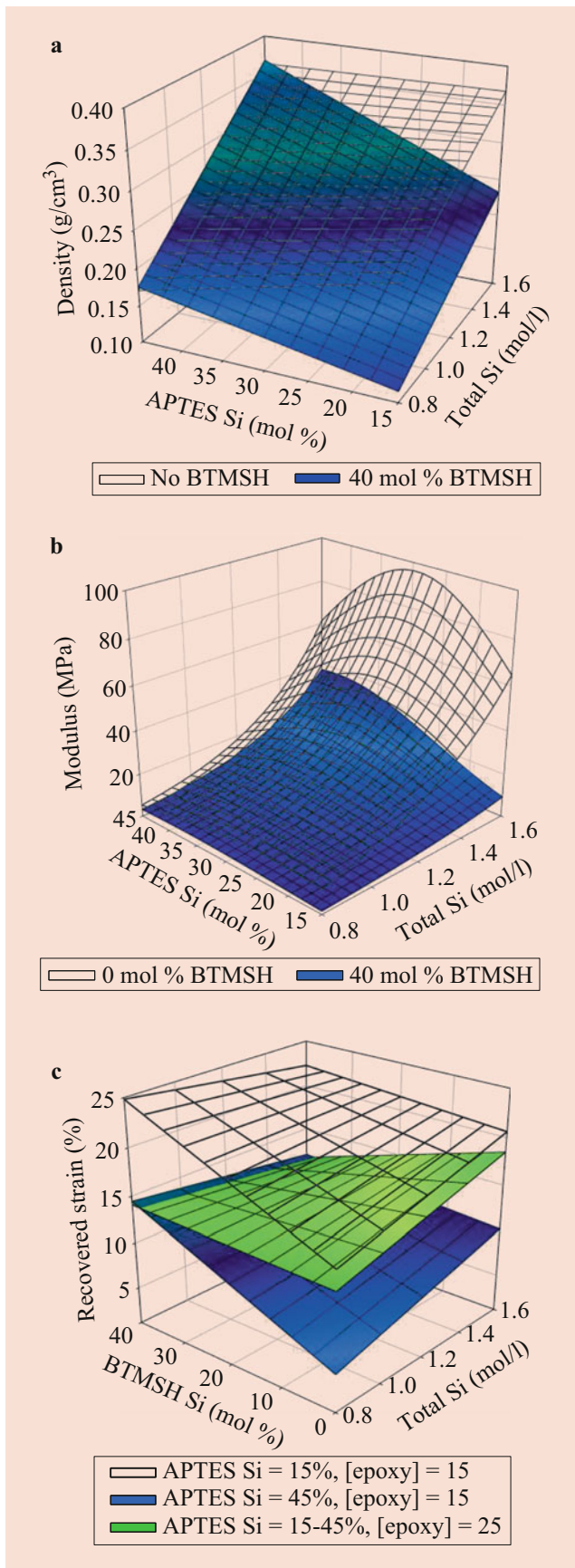
different polymer-reinforced aerogels are compared in Fig. 30.16 (both graphs show the same four monoliths at different scales). The pairs of lines represent two subsequent stress-strain curves for each of the monoliths. The green curve labeled Test 1 is the first compression, and Test 2 is the second compression for a formulation from 1.65 mol/l total Si (80 mol% from BTMSPA), with about 3% strain not recovered. In contrast, the red lines show repeated compression cycles from a formulation, made using 1.2 mol/l total Si but 80 mol% BTMSPA-derived Si. In this case, unrecovered strain is <2% (the sample recovers almost completely). Hence, a high degree of elastic recovery is present using a combination of MTMS-derived Si and the organic linking groups from BTMSPA. Unreinforced aerogels from the same study have about the same degree of recovery as the cross-linked aerogels shown.

Typical compressive stress-strain curves taken to failure are shown in Fig. 30.17a. For unreinforced aerogels, the Young's modulus taken from the initial slope of the stress-

strain curve is typically about half of that for the reinforced aerogels. In addition, the unreinforced aerogels break at about half the value of strain, and the maximum stress at break is an order of magnitude lower. Hence, as seen in the graph of the response surface model shown in Fig. 30.17b, the toughness, calculated from the area under the stress strain curve, is as much as an order of magnitude higher for polyurea-reinforced aerogels made from MTMS and BTMSPA. Thus, while elastic recovery is about the same for reinforced and unreinforced aerogels using MTMS and BTMSPA, the polymer-reinforced aerogels are much more robust.

30.4 Future Directions

Incorporating flexible links in the silica backbone or using MTMS in place of TEOS in polymer-reinforced aerogels has been shown to be an effective way to introduce flexibility and good elastic recovery. In most cases, increasing the amount of



polymer crosslinking does reduce flexibility. Thus, it stands to reason that in these cases the use of a more flexible polymer in combination with alterations made to the silica structure should increase flexibility even more. Taking this notion one step further, use of a shape memory polymer as reinforcement may give rise to a shape memory aerogel [43]. A shape memory polymer, such as a polyurethane block copolymer, is capable of changing its shape in response to a set of external stimuli, for example, pH, electric current, and heating. Usually, one or more polymer blocks respond to external stimuli, while others contribute to the desired properties. The synthesis of flexible aerogels reinforced with shape memory polyurethane crosslinkers should give rise to a shape memory effect as shown in Fig. 30.18, offering the advantage of storage of the aerogel in a deformed state for transport aboard a spacecraft where storage is at a premium. Alternatively, the shape memory aerogel could be inserted into a cavity needing insulation in its deformed shape and made to recover to fill the cavity. Monolithic thermally responsive shape memory polymer aerogels have been reported [44–46], but as of yet no shape memory polymer-reinforced silica aerogels are known.

Flexible monolithic aerogels could have wide applications in various thermal insulation systems for space as previously discussed. For structures that need to be folded in a compact space for transport before deploying, such as the inflatable decelerators or habitats for the Moon or Mars, the thinner and more flexible the insulation system, the better. In such a thin form, even polymer-reinforced aerogels with flexible linking groups as described in this chapter would probably be too fragile to stand on their own. Use of a continuous nonwoven fiber batting to further reinforce the flexible aerogels, such as in the aerogel blankets produced by Aspen Aerogels, is one approach but may still not result in a thin enough insulation for such deployable structures.

Carbon nanofiber-reinforced silica aerogel composites can be made by incorporating up to 5% (w/w) of the nanofibers into the initial sol [47]. Tensile strength of the composite aerogels using diisocyanate as a polymer crosslink was improved by as much as a factor of 5 over diisocyanate-crosslinked aerogels with no carbon nanofibers. In addition, the nanofiber-containing gels were also easier to handle before crosslinking. Incorporating carbon nanofibers into a flexible reinforced aerogel matrix may allow the formation of thinner, more flexible aerogel sheets with improved durability (see ► Chap. 35).

Fig. 30.11 Empirical models of (a) density and (b) modulus from compression graphed vs. total Si concentration and fraction of APTES-derived Si and (c) recovered strain graphed versus total Si concentration and BTMSH fraction. (Reprinted from [11], Copyright 2009 American Chemical Society)

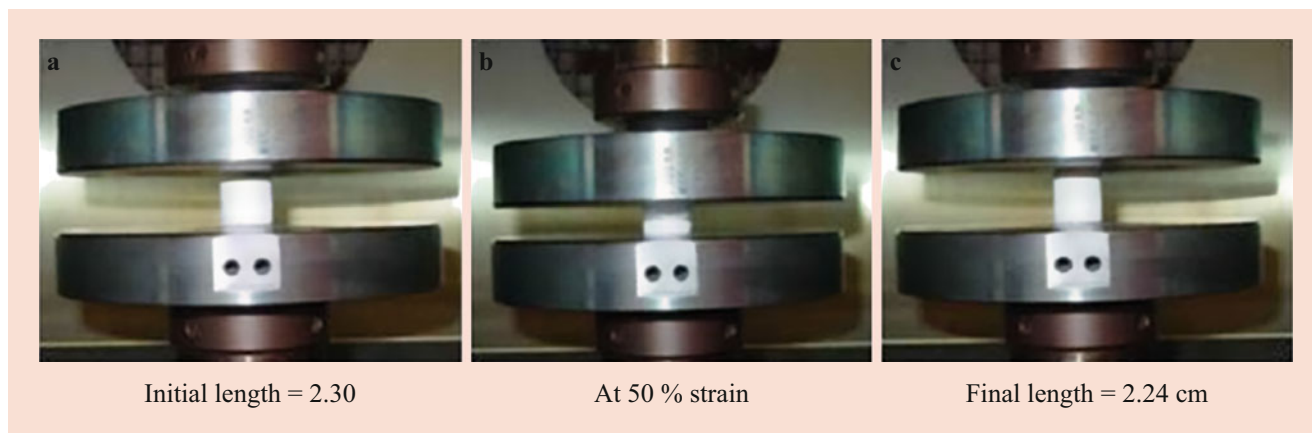


Fig. 30.12 Repeat compression test to 50% strain of epoxy-reinforced monolith made using 0.4 mol/l total Si (40 mol% from BTMSH and 45 mol% from APTES). (Reprinted from [11], Copyright 2009 American Chemical Society)

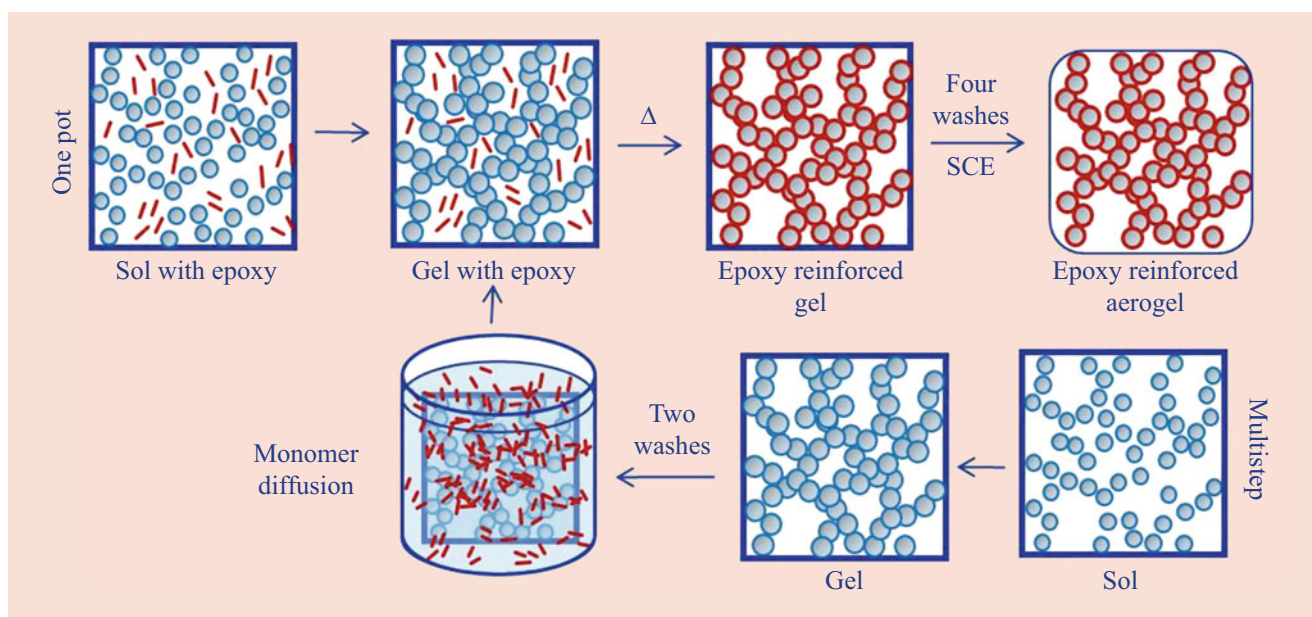


Fig. 30.13 Comparison of one-pot with multistep diffusion process for fabricating epoxy-reinforced aerogels. (Reprinted from [39], Copyright 2010 American Chemical Society)

Another way to form a thin aerogel composite is to incorporate electrospun polyurethane nanofibers into a cast sol film prior to gelation of the silica-based sol [48]. By precisely controlling the gelation kinetics with the amount of base present in the formulation, nanofibers are electrospun into the sol before the onset of the gelation process and uniformly embedded in a silica network made flexible by incorporating low molecular weight oligomers of silanol-terminated PDMS. The final composite films, which have been fabricated to be 0.5–2 mm in thickness, are pliable and flexible.

After much bending and pulling on the films by hand, small cracks develop, but the film holds together by the nanofibers knitted together and bridging the crack. The room temperature thermal conductivity of the composite aerogels ranges from 13 mW/m-K for samples with bulk density of 0.17 g/cm³ to 50 mW/m-K for samples with bulk density of 0.08 g/cm³.

Zu et al. have recently reported flexible silica-based aerogel thin films by radically polymerizing vinylmethyl-dialkoxysilanes followed by hydrolytic polycondensation

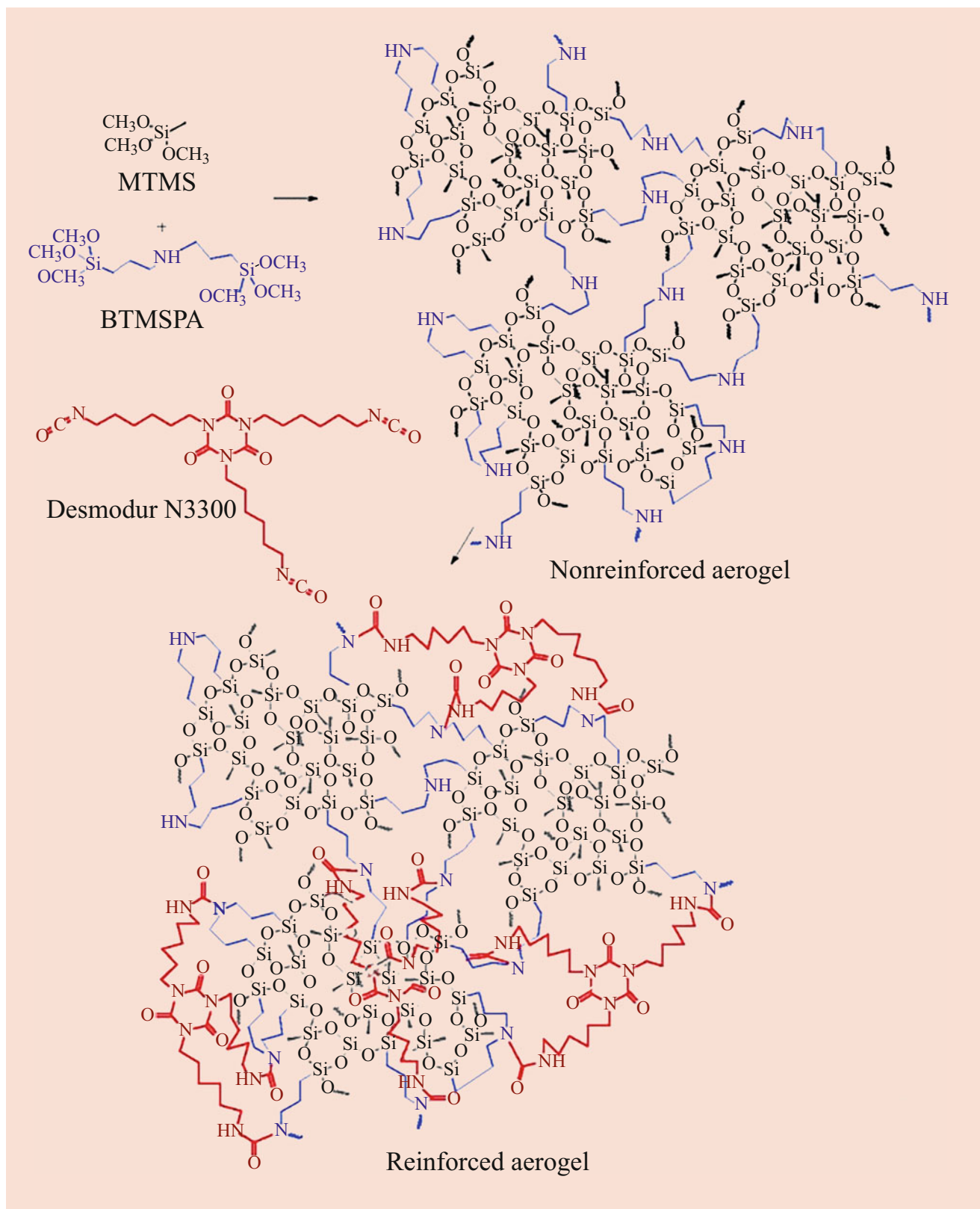


Fig. 30.14 Synthesis of MTMS-based aerogels with BTMSPA used as both a flexible linking group and site for tri-isocyanate crosslinking. (Reprinted from [41], Copyright 2010 American Chemical Society)

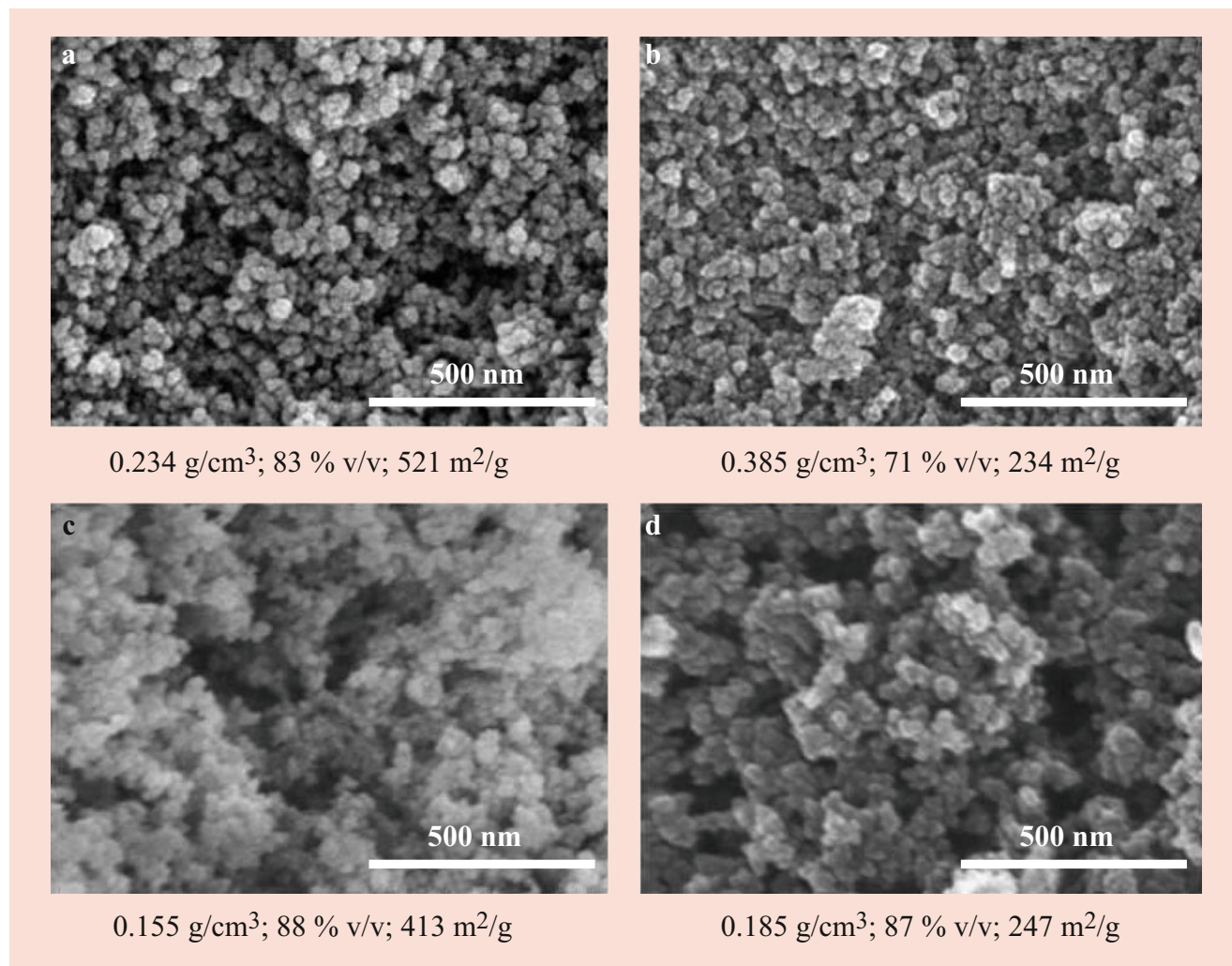


Fig. 30.15 SEM images of aerogel monoliths made using 1.65 mol/l total Si: (a) uncrosslinked and (b) polymer-reinforced aerogels prepared using 80 mol% Si from BTMSPA and (c) uncrosslinked and (d)

polymer-reinforced aerogels prepared using 40 mol% Si from BTMSPA. (Adapted from [41], Copyright 2010 American Chemical Society)

of the silicate groups [49]. A surprising degree of flexibility is obtained in the highly transparent thin film aerogels without any reinforcement as shown in Fig. 30.19, while cylinders of the aerogel could be compressed up to 500 times with near full recovery. Still, greater flexibility can be achieved in thin film monolithic polymer aerogels such as polyimide [50–52].

30.5 Conclusions

Incorporating short, flexible, organic linking groups into the silica backbone of polymer-reinforced aerogels has been shown to be a versatile way to improve elastic properties of

the aerogels. The aerogels can recover from compression up to as much as 50% strain and in some cases are even flexible. The flexible linking groups may also result in greater hydrophobicity especially when combined with hydrophobic polymer crosslinkers such as polystyrene (see ► Chap. 14) and also provide a means to alter pore structure, although the relationship between different pore structure and molecular building blocks is not well understood.

While there is a trade-off between modulus and elastic recovery in polymer-reinforced aerogels using flexible linking groups, the combination of MTMS and BTMSPA used in the silica backbone provides enhanced elastic properties almost independent of modulus. These aerogels, across a wide range of density and modulus, can be compressed to

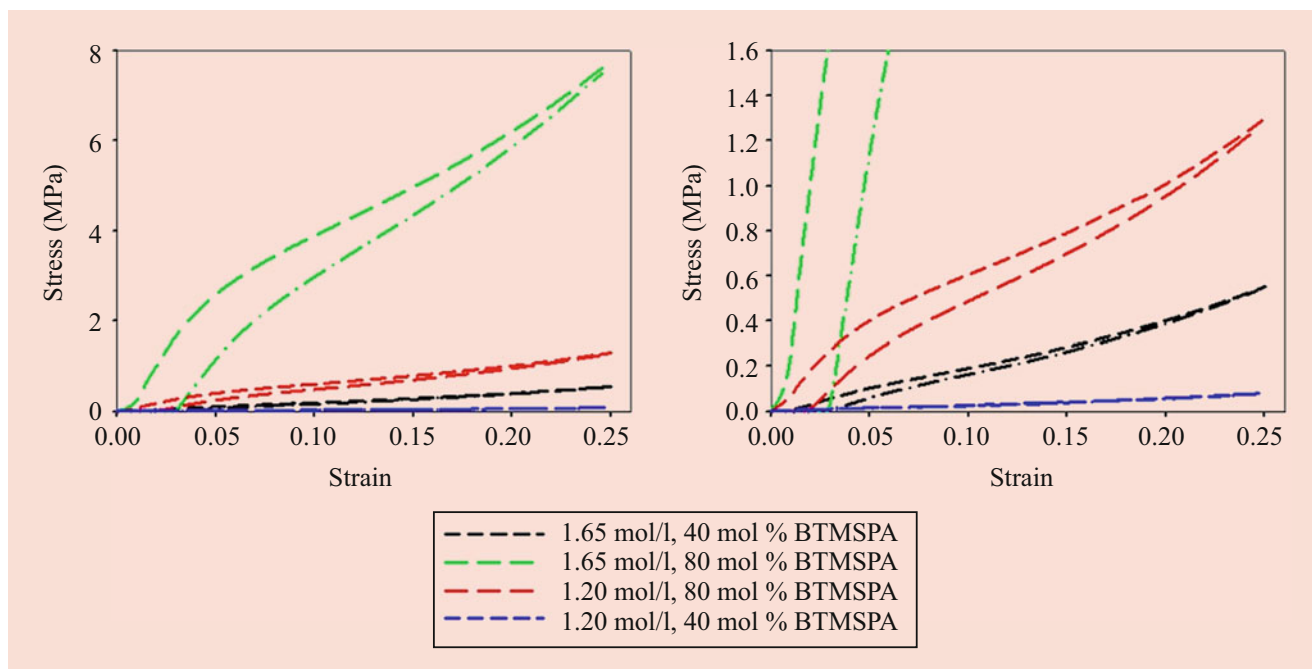


Fig. 30.16 Typical stress-strain curves for a repeat compression tests on MTMS aerogels reinforced with Desmodur N3300A tri-isocyanate at different total silicon concentration and mol fraction of BTMSPA. The graphs are the same curves shown at different y-scales. Densities and

surface areas of the monoliths made in acetonitrile are shown in *parentheses*. (Reprinted from [41], Copyright 2010 American Chemical Society)

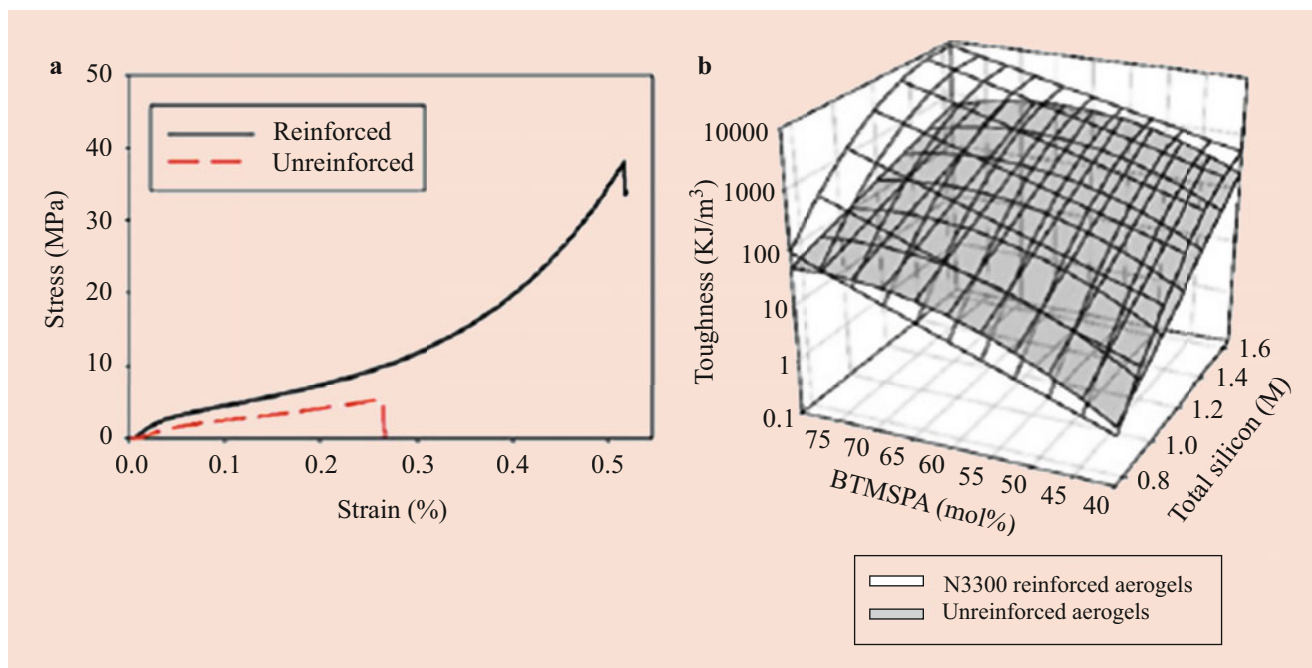


Fig. 30.17 (a) Typical stress-strain curve for compression to break and (b) the response surface model of toughness calculated from the stress-strain curves for both crosslinked and uncrosslinked aerogel monoliths. (Reprinted from [41], Copyright 2010 American Chemical Society)

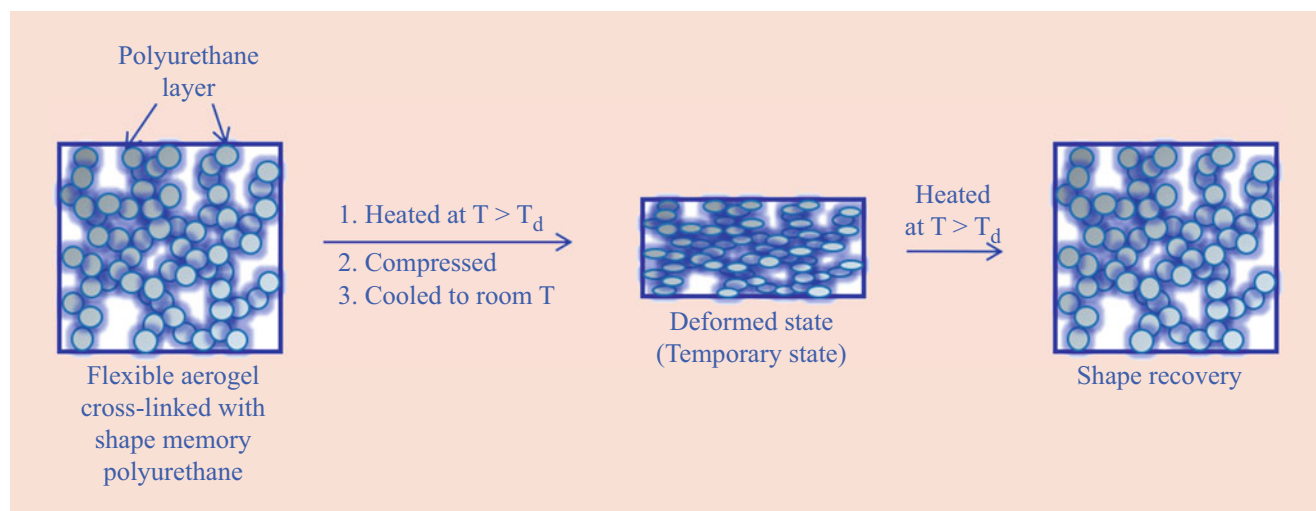


Fig. 30.18 Proposed scheme to deploy a flexible aerogel reinforced with a shape memory polyurethane

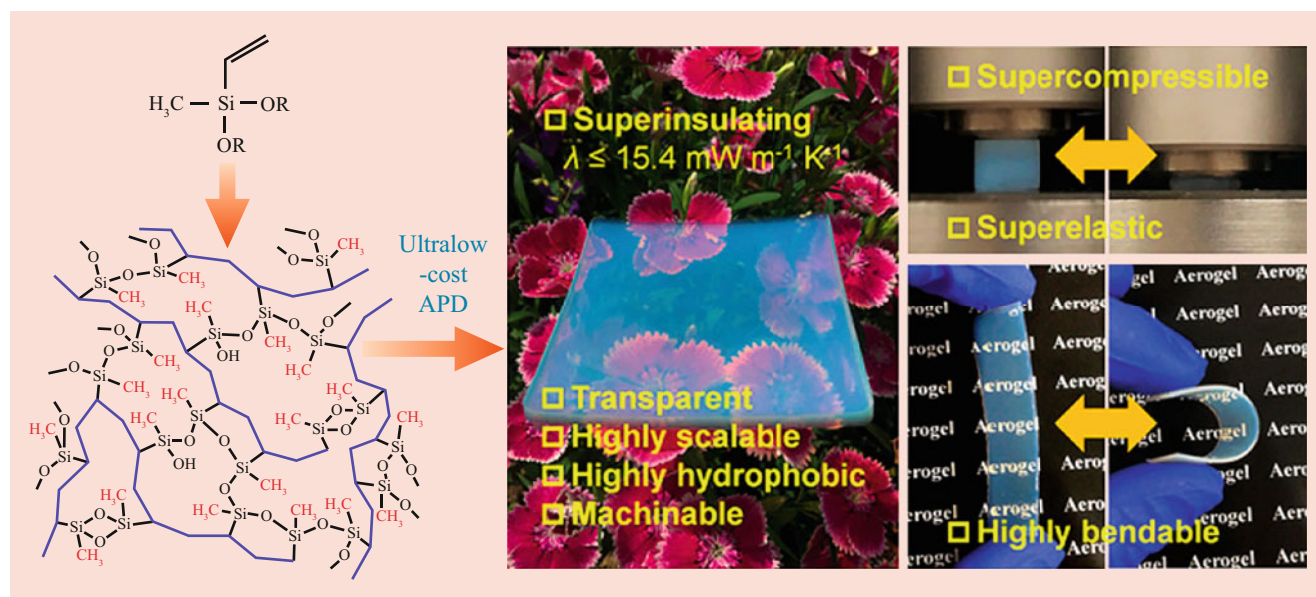


Fig. 30.19 Flexible silica-based aerogel thin films produced by radically polymerizing vinylmethylalkoxysilanes followed by hydrolytic polycondensation of the silicate groups. (Reprinted from [49], Copyright 2018 American Chemical Society)

25% strain and recover almost completely. Reinforcing these aerogels with tri-isocyanate oligomers reacted through the secondary amine of BTMSPA results in up to an order of magnitude increase in compressive strength and toughness of the aerogel monoliths, while the overall elastic properties arising from the underlying silica structure is maintained. Use of flexible polymer-crosslinked aerogels, especially in combination with nanofiber reinforcement, is a promising route to making robust aerogel thin films and sheets, enabling

a multitude of aerospace and other high performance applications.

Of course, fabrication of polymer-reinforced aerogels is somewhat complex, involving multiple steps of gelation, solvent exchange, monomer infiltration, and heat treatment. This may hinder scale-up and commercialization compared to more recently discovered polymer aerogels, which can be simpler to fabricate in one step under ambient conditions. Relevance of these materials will depend on the ability to

create polymer aerogels with the combination of properties these materials afford, such as hydrophobicity combined with elastic recovery and high modulus.

References

- Pierre, A.C., Pajonk, G.M.: Chemistry of aerogels and their applications. *Chem. Rev.* **102**, 4243–4265 (2002)
- Fricke, J.: Aerogels – highly tenuous solids with fascinating properties. *J. Non-Cryst. Solids.* **100**, 169–173 (1998)
- Husing, N., Schubert, U.: Aerogels – airy materials: chemistry, structure and properties. *Angew. Chem. Int. Ed.* **37**, 22–45 (1998)
- Parmenter, K.E., Milstein, F.: Mechanical properties of silica aerogels. *J. Non-Cryst. Solids.* **223**, 179–189 (1998)
- Tsou, P., Brownlee, D.E., Sandford, S.A., Hörz, F., Zolensky, M.E.: Wild 2 and interstellar sample collection and Earth return. *J. Geophys. Res.* **108**(E10), 8113 (2003)
- Jones, S.M.: Aerogel: space exploration applications. *J. Sol-Gel Sci. Technol.* **40**, 351–357 (2006)
- Zhang, G., Dass, A., Rawashdeh A-M, M., Thomas, J., Council, J. A., Sotiriou-Leventis, C., Fabrizio, E.F., Ilhan, F., Vassilaras, P., Scheiman, D.A., McCorkle, L., Palczar, A., Johnston, J.C., Meador, M.A.B., Leventis, N.: Isocyanate-crosslinked silica aerogel monoliths: preparation and characterization. *J. Non-Cryst. Solids.* **350**, 152–164 (2004)
- Leventis, N., Sotiriou-Leventis, C., Zhang, G., Rawashdeh, A.-M. M.: Nanoengineering strong silica aerogels. *Nano Lett.* **2**, 957–960 (2002)
- Boday, D.J., Stover, R.J., Muriithi, B., Keller, M.W., Wertz, J.T., Obrey, K.A.D., Loy, D.A.: Formation of polycyanoacrylate–silica nanocomposites by chemical vapor deposition of cyanoacrylates on aerogels. *Chem. Mater.* **20**, 2845–2847 (2008)
- Meador, M.A.B., Fabrizio, E.F., Ilhan, F., Dass, A., Zhang, G., Vassilaras, P., Johnston, J.C., Leventis, N.: Cross-linking amine modified silica aerogels with epoxies: mechanically strong lightweight porous materials. *Chem. Mater.* **17**, 1085–1098 (2005)
- Meador, M.A.B., Weber, A.S., Hindi, A., Naumenko, M., McCorkle, L., Quade, D., Vivod, S.L., Gould, G.L., White, S., Deshpande, K.: Structure property relationships in porous 3D nanostructures: epoxy cross-linked silica aerogels produced using ethanol as the solvent. *ACS Appl. Mater. Interfaces.* **1**, 894–906 (2009)
- Boday, D.J., Stover, R.J., Muriithi, B., Keller, M.W., Wertz, J.T., Obrey, K.A.D., Loy, D.A.: Strong, low-density nanocomposites by chemical vapor deposition and polymerization of cyanoacrylates on aminated silica aerogels. *ACS Appl. Mater. Interfaces.* **1**, 1364–1369 (2009)
- Meador, M.A.B., Capadona, L.A., Papadopoulos, D.S., Leventis, N.: Structure property relationships in porous 3D nanostructures as a function of preparation conditions: isocyanate cross-linked silica aerogels. *Chem. Mater.* **19**, 2247–2260 (2007)
- Capadona, L.A., Meador, M.A.B., Alumni, A., Fabrizio, E.F., Vassilaras, P., Leventis, N.: Flexible, low-density polymer crosslinked silica aerogels. *Polymer.* **47**, 5754–5761 (2006)
- Katti, A., Shimpi, N., Roy, S., Lu, H., Fabrizio, E.F., Dass, A., Capadona, L.A., Leventis, N.: Chemical, physical and mechanical characterization of isocyanate cross-linked amine modified silica aerogels. *Chem. Mater.* **18**, 285–296 (2006)
- Ilhan, U.F., Fabrizio, E.F., McCorkle, L., Scheiman, D.A., Dass, A., Palczar, A., Meador, M.A.B., Johnston, J.C., Leventis, N.: Hydrophobic monolithic aerogels by nanocasting polystyrene on amine-modified silica. *J. Mater. Chem.* **16**, 3046–3054 (2006)
- Mulik, S., Sotiriou-Leventis, C., Churu, G., Lu, H., Leventis, N.: Cross-linking 3D assemblies of nanoparticles into mechanically strong aerogels by surface-initiated free-radical polymerization. *Chem. Mater.* **20**, 5035–5046 (2008)
- Nguyen, B.N., Meador, M.A.B., Tousley, M.E., Shonkwiler, B., McCorkle, L., Scheiman, D.A., Palczar, A.: Tailoring elastic properties of silica aerogels cross-linked with polystyrene. *ACS Appl. Mater. Interfaces.* **1**, 621–630 (2009)
- Fidalgo, A., Farinha, J.P.S., Martinho, J.M.G., Rosa, M.E., Ilharco, L.M.: Hybrid silica/polymer aerogels dried at ambient pressure. *Chem. Mater.* **19**, 2603–2609 (2007)
- Novak, B.M., Auerbach, D., Verrier, C.: Low-density mutually interpenetrating organic–inorganic composite materials via supercritical drying techniques. *Chem. Mater.* **6**, 282–286 (1994)
- Wei, T.Y., Lu, S.Y., Chang, Y.C.: Transparent, hydrophobic composite aerogels with high mechanical strength and low high-temperature thermal conductivities. *J. Phys. Chem. B.* **112**, 11881–11886 (2008)
- Randall, J.P., Meador, M.A.B., Jana, S.C.: Tailoring mechanical properties of aerogels for aerospace. *ACS Appl. Mater. Interfaces.* **3**, 613–626 (2011)
- Essex Corporation, Extravehicular Activity in Mars Surface Exploration, Final Report on Advanced Extravehicular Activity Systems Requirements Definition Study (1989) NAS9-17779
- Paul, H.L., Diller, K.R.: Comparison thermal insulation performance of fibrous materials for the advanced space suit. *J. Biomech. Eng.* **125**, 639–647 (2003)
- Tang, H.H., Omdoff, E.S., Trevino, L.A.: Thermal performance of space suit elements with aerogel insulation for Moon and Mars exploration. In: 36th International Conference on Environment Systems, July 17–20, 2006, Norfolk, Virginia AIAA 2006-01-2235 (2006)
- Fesmire, J.E.: Aerogel insulation systems for space launch applications. *Cryogenics.* **46**, 111–117 (2006)
- Braun, R.D., Manning, R.M.: Mars exploration entry, descent and landing challenges. *J. Spacecr. Rocket.* **44**, 310–323 (2007)
- Brown, G.J., Lingard, J.S., Darley, G.D., Underwood, J.C.: Inflatable aerocapture decelerators for Mars Orbiters. In: 19th AIAA Aerodynamic Decelerator Systems Technology Conference and Seminar, 21–24 May 2007, Williamsburg, VA, AIAA 2007-2543 (2007)
- Reza, S., Hund, R., Kustas, F., Willcockson, W., Songer, J.: Aerocapture Inflatable decelerator (AID) for planetary entry. In: 19th AIAA Aerodynamic Decelerator Systems Technology Conference and Seminar, 21–24 May 2007, Williamsburg, VA, AIAA 2007-2516 (2007)
- Kramer, S.J., Rubio-Alonso, F., Mackenzie, J.D.: Organically modified silicate aerogel: aeromosil. *Mater. Res. Soc. Symp. Proc.* **435**, 295–299 (1996)
- Rao, A.V., Bhagat, S.D., Hirashima, H., Pajonk, G.M.: Synthesis of flexible silica aerogels using methyltrimethoxysilane (MTMS) precursor. *J. Colloid Interfaces Sci.* **300**, 279–285 (2006)
- Kanamori, K., Aizawa, M., Nakanishi, K., Hanada, T.: New transparent methylsilsesquioxane aerogels and xerogels with improved mechanical properties. *Adv. Mater.* **19**, 1589–1593 (2006)
- Hayase, G., Kanamori, K., Nakanishi, K.: New flexible aerogels and xerogels derived from methyltrimethoxysilane/dimethyldimethoxysilane co-precursors. *J. Mater. Chem.* **21**, 17077–17079 (2011)
- Shea, K.J., Loy, D.A.: Bridged polysilsesquioxanes. Molecular-engineered hybrid organic–inorganic materials. *Chem. Mater.* **13**, 3306–3319 (2001)
- Loy, D.A., Shea, K.J.: Bridged polysilsesquioxanes. Highly porous hybrid organic–inorganic materials. *Chem. Rev.* **95**, 1431–1442 (1995)
- Yun, S., Luo, H., Gao, Y.: Low-density, hydrophobic, highly flexible ambient-pressure-dried monolithic bridged silsesquioxane aerogels. *J. Mater. Chem. A.* **3**, 3390–3398 (2015)
- Guo, H., Nguyen, B.N., McCorkle, L.S., Shonkwiler, B., Meador, M.A.B.: Elastic low density aerogels derived from bis[3-(triethoxy)]

- silylpropyl]disulfide, tetramethylorthosilicate and vinyltrimethoxysilane via a two-step process. *J. Mater. Chem.* **19**, 9054–9062 (2009)
38. Vivod, S.L., Meador, M.A.B., Nguyen, B.N., Perry, R.: Di-isocyanate cross-linked silica aerogels with hexyl links incorporated in the underlying silica backbone. *Polym Prepr.* **50**, 119–120 (2009)
 39. Meador, M.A.B., Scherzer, C.M., Vivod, S.L., Quade, D., Nguyen, B.N.: Epoxy reinforced aerogels made using a streamlined process. *ACS Appl. Mater. Interfaces.* **2**, 2162–2168 (2010)
 40. Meador, M.A.B., Nguyen, B.N., Scherzer, C.S.: Unpublished results
 41. Nguyen, B.N., Meador, M.A.B., Medoro, A., Arendt, V., Randall, J., McCorkle, L., Shonkwiler, B.: Elastic behavior of methyltrimethoxysilane based aerogels reinforced with tri-isocyanate. *ACS Appl. Mater. Interfaces.* **2**, 1430–1443 (2010)
 42. Supplied by Bayer Corporation
 43. Jana, S.C., Meador, M.A.B., Randall, J.P.: Process for forming shape-memory polymer aerogel composites. US Patent Application, 2006–854838P (2008)
 44. Michal, B.T., Brenn, W.A., Nguyen, B.N., McCorkle, L.S., Meador, M.A.B., Rowan, S.J.: Thermoresponsive shape-memory aerogels from thiol–ene networks. *Chem. Mater.* **28**, 2341–2347 (2016)
 45. Donthula, S., Mandal, C., Schisler, J., Leventis, T., Meador, M.A.B., Sotiriou-Leventis, C., Leventis, N.: Nanostructure-dependent Marcus-type correlation of the shape recovery rate and the Young's modulus in shape memory polymer aerogels. *ACS Appl. Mater. Interfaces.* **10**, 23321–23334 (2018)
 46. Donthula, S., Mandal, C., Leventis, T., Schisler, J., Saeed, A.M., Sotiriou-Leventis, C., Leventis, N.: Shape-memory poly(isocyanurate-urethane) (PIR-PUR) aerogels for deployable panels and biomimetic applications. *Chem. Mater.* **29**, 4461–4477 (2017)
 47. Meador, M.A.B., Vivod, S.L., McCorkle, L., Quade, D., Sullivan, R. M., Ghosn, L.J., Clark, N., Capadona, L.A.: Reinforcing polymer cross-linked aerogels with carbon nanofibers. *J. Mater. Chem.* **18**, 1843–1852 (2008)
 48. Li, L., Yalcin, B., Nguyen, B.N., Meador, M.A.B., Cakmak, M.: Nanofiber reinforced aerogel (xerogel): synthesis, manufacture and characterization. *ACS Appl. Mater. Interfaces.* **1**, 2491–2501 (2009)
 49. Zu, G., Shimizu, T., Kanamori, K., Zhu, Y., Maeno, A., Kaji, H., Shen, J., Nakanishi, K.: Transparent, superflexible doubly cross-linked polyvinylpolymethylsiloxane aerogels superinsulators via ambient pressure drying. *ACS Nano.* **12**, 521–532 (2018)
 50. Guo, H., Meador, M.A.B., McCorkle, L., Quade, D.J., Guo, J., Hamilton, B., Cakmak, M., Sprowl, G.: Polyimide aerogels cross-linked through amine functionalized polyoligomeric silsesquioxane. *ACS Appl. Mater. Interfaces.* **3**, 546–552 (2011)
 51. Meador, M.A.B., Malow, E.J., Silva, R., Wright, S., Quade, D., Vivod, S.L., Guo, H., Guo, J., Cakmak, M.: Mechanically strong, flexible polyimide aerogels cross-linked with aromatic triamine. *ACS Appl. Mater. Interfaces.* **4**, 536–544 (2012)
 52. Meador, M.A.B., Alemán, C.R., Hanson, K., Ramirez, N., Vivod, S.L., Wilmoth, N., McCorkle, L.: Polyimide aerogels with amide cross-links: a low cost alternative for mechanically strong polymer aerogels. *ACS Appl. Mater. Interfaces.* **7**, 1240–1249 (2015)



Dr. Mary Ann Meador has a B.S. from Duquesne University (1979) and a Ph.D. from Michigan State University (1983). She joined NASA in 1983. Her research interests have focused on development of polymers and polymer aerogels for future NASA missions. She is also an ACS Fellow, an Executive Editor for ACS Applied Materials and Interfaces, and Adjunct Professor in Polymer Engineering at the University of Akron.



Dr. Baochau Nguyen received her Ph.D. from the University of Akron in 2000. She has worked on synthesizing and processing different types of polymers including unsaturated polyesters, sheet molding compounds, water-based polyurethane adhesives, high temperature polyimides, polyimide composites, and aerogels. Her current focus is on developing organic aerogels for additive manufacturing at the NASA Glenn Research Center.