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2013

Sachithanadam, M., & Joshi, S. C. (2014). High strain recovery with improved mechanical properties of gelatin–silica aerogel composites post-binding treatment. *Journal of Materials Science*, 49(1), 163-179.

<https://hdl.handle.net/10356/104410>

<https://doi.org/10.1007/s10853-013-7690-1>

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Journal of Materials Science

Full Set - Includes 'Journal of Materials
Science Letters'

ISSN 0022-2461

Volume 49

Number 1

J Mater Sci (2014) 49:163-179

DOI 10.1007/s10853-013-7690-1

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High strain recovery with improved mechanical properties of gelatin–silica aerogel composites post-binding treatment

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Received: 8 April 2013 / Accepted: 21 August 2013 / Published online: 10 September 2013
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Abstract Silica aerogels are very light and highly porous materials that are intriguingly and complexly networked with large internal surface area, high hydrophobicity with extremely low density and thermal conductivity. These features make them ideal choice for applications as thermal and acoustics insulators or as optical, electrical, and energy storing devices. However, their exploitation for structural applications is primarily inhibited by their brittleness. The brittleness of the silica aerogels makes their processing and handling difficult. Volumetric shrinkage occurs, which becomes more apparent at elevated temperatures. While there are hybrid silica aerogels doped with materials such as polymer, ceramics, metals in the market, the improvements in the mechanical properties are compromised with tremendous increase in density and reduction in the insulation performance. Post-synthesis binding treatment of silica aerogels composites are not extensively explored due to the chemically inert trimethylsilyl (TMS) terminal groups on the surface of the hydrophobic silica aerogels. This paper discusses a unique fabrication method of developing a ductile silica aerogel composite solid via post-synthesis binding treatment. Gelatin–silica aerogel (GSA) and GSA–sodium dodecyl sulfate (SDS) composite blocks were produced by mixing hydrophobic aerogel granulates in a gelatin–SDS foamed solution by frothing method. The entire fabrication process and grounds for using a controlled % of gelatin as the main binder and SDS as an additive are explained. The compression testing of the blocks is presented. The associated strain recovery—an

unusual phenomenon with brittle silica aerogels, observed upon unloading is highlighted and studied. The micro-structure and surface characterization of these composites was examined via FESEM/EDX and XPS/ESCA, respectively. The dependency of process variables involved were analyzed through analysis of variance (ANOVA) model. Empirical models that relate the composition of gelatin, aerogel, and SDS to achieve the optimal strain recovery with the associated compressive modulus and strength and density are established. The transition from brittleness to ductility is measured in terms of compressive stress versus strain behavior for various mass fractions of gelatin and SDS. The test data presented indicate analogous behavior of these to creep-like behavior of a material typically identified as the primary, secondary, and tertiary stages. The rationale and mechanisms behind such creep-like three stages are explained using schematic diagrams.

Introduction

Since the discovery of silica aerogels in the 1930s by an American scientist Samuel Stephens Kistler, extensive research have been carried out to improve the mechanical, thermal, and acoustic properties of these materials. Gesser and Goswami [1] reviewed on the early developments of silica aerogels in the 1980s that have found applications mainly in catalysis, high-energy physics, passive solar energy uses and energy conversions, and low-temperature glass formation. Hunt et al. [2] revealed the potential use of silica aerogels as an alternative to chlorofluorocarbons (CFCs) in refrigerator thus reducing the CFC damage to the environment. The early production of low density silica aerogels developed by Lee et al. [3] involved expensive equipment and the highly dangerous super critical drying

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process using alcohols as the exchange solvent. Since then, extensive research to produce inexpensive silica aerogels using safer methodologies and syntheses have shown to produce better features and qualities when Lee et al. [4] investigated the properties of silica aerogels using inexpensive water–glass under ambient pressure drying and found them to have high porosities, specific surface areas, and hydrophobic. Similarly Rao et al. [5] produced the super hydrophobic silica aerogels under ambient pressure drying. Rapid synthesis of silica aerogels was achieved within 24 h using water–glass by Bhagat et al. [6]. The process refinements and key modifications of methods and synthesis reviewed by Soleimani Dorcheh and Abbasi [7] underlines the growing importance of silica aerogels as a commercial material. Currently, silica aerogels are available in different forms from monolithic to granules of regular shapes [8] and also in powder form [9] synthesized via sol–gel techniques. While the properties of the silica aerogels can be controlled, the material's major limitation of brittleness due to its porous and open structure hinders the use of the material for structural applications as concluded by Parmenter and Milstein [10]. Scherer et al. [11] investigated the bulk modulus of aerogels noting that the monolithic silica aerogels are linearly elastic under small strains. Thereafter, they exhibit yield followed by densification and subsequently brittle failure. Scherer et al. [11] evaluated that the bulk modulus of the aerogel has a power law dependence on density with an exponent of 3.2 in the plastic regime and on linear elastic modulus with an exponent of 3.6. Similarly, Moner-Girona et al. [12] investigated the compressive modulus and hardness via non-destructive methods and observed a transformation from elastic behavior to plastic that was largely dependent on the microstructure and ultimately the density that also followed a power law relationship. The power law relationship put forth clearly suggests that aerogels inherently possess low compressive modulus due to its low density and exhibit elasticity only at low strains.

To overcome this limitation, silica aerogels have since been added with another material such as polymers and metals prior to gelation stage of manufacturing before the drying process. Cross-linking of epoxies by modifying the surface groups on silica aerogels was reported to improve the modulus by 2 orders with corresponding 100 % increase in density as compared to native silica aerogels [13]. Meador et al. [14] further showed that epoxy cross-linked silica aerogels in ethanol exhibited strain recovery of up to 50 %. Katti et al. [15] experimented with polyurethane conformal coating on the silica framework and evaluated the compressive modulus to be 129 MPa, low thermal conductivity of 0.041 W/m K and exhibiting extended yield behavior till 40 % strain but with an increase in density by 0.40 g/cm³. Cross-linking of metals

such as silica–titania aerogels have also been known to improve the strength and essentially known to possess photo catalytic qualities in the degradation of organic pollutants [16]. However, the cross-linking route of improving mechanical properties has brought undesirable increase in density and drop in the performance of the thermal insulation.

Attempts to bind the aerogels similar to traditional composites have yielded little success. Dry binding systems such as epoxy and ethylene vinyl acetate (EVA) resins are some of the commonly used binders for composites leveraging on the tackiness of the binding materials to promote physical adhesion. However, resins being much denser tend to settle at the bottom of the hot plate during the curing stage thus resulting in non-uniform mixture and distinct separation of the constituent materials. This is a major limitation in using resin binder systems although Ge et al. [17] managed to fabricate a composite using epoxy resins primarily because aerogels were grounded, technically crushing them into smaller fragments. Gupta and Ricci [18] used acetone for the composite fabrication which resulted in collapsing of the aerogel structure when mixed with epoxy reporting a compressive modulus of 1800 MPa due to the infiltration of the epoxy mixture through the pores of the aerogels thus increasing the density making it heavier than copper. Post-binding treatment of silica aerogels were not reported extensively primarily due to the possible collapse of the “pearl necklace” like structure of the silica aerogels by infiltration of the binding material into the pores by displacing the air inside. The silica aerogel granules used in this study are surface functionalized with inert oxy-trimethylsilyl (TMS) terminal groups that gives its hydrophobic properties [6]. Being hydrophobic, these inert groups prevent water from entering the nano-pores and at the same time, offer little reaction with most compounds and organic solvents such as acetone and toluene tend to deteriorate the hydrophobic property and ultimately collapsing the aerogels into powder. Thus, a feasible and simple post-binding treatment method is needed to produce a composite with improved mechanical properties while retaining unique features of aerogel, such as low density and low thermal conductivity.

One possible route of binding treatment is the use of water soluble polymers (WSP). Water can be evaporated or sublimed from an aqueous solution via heating through controlled pressure and temperature making it a desirable solvent to be used. WSP are ideal constituent as a binder but they must be able to covalently bind with the oxy-TMS groups of the aerogels or at least be physically adsorbed via their charges.

WSPs are hydrophilic and bonding is achieved through hydrogen bonds and weak Van Der Waals' interaction between the material and water [19] and are ideal class of

materials due to their wide range of applications and their properties [20–23].

One of the WSP materials that could bind with the hydrophobic silica aerogels is gelatin. Gelatin, as a biocompatible polymer, has been used as a delivery vehicle for the release of bioactive molecules and in the generation of scaffolds for tissue engineering applications as gelatin foams using freeze drying technique [24] and in pharmaceutical industry as a suspending agent, encapsulating agent, and a tablet binder as revealed by Aristippos [25]. Gelatin has both polar and non-polar side chains. This is very desirable as a binding agent for the aerogels because it offers more than one reactive sites due to its numerous amine and carboxyl sites that offers cross-linking, functionalization, and even grafting of hydrophobic materials onto its peptide chain. Fidler and Thomas [26, 27] have patented an aerogel insulated foam using gelatin as a main binding material with additives from inorganic and organic materials. Their works involved blending the aerogels and gelatin together into a foam and curing it under ambient conditions.

In the current work, gelatin–silica aerogel (GSA) composite blocks via post-synthesis binding treatment by mixing the hydrophobic aerogel granule particles in a gelatin–sodium dodecyl sulfate (SDS) foamed solution by frothing method was investigated. SDS is anionic surfactant consisting of a 12-carbon tail attached to a sulfate group, giving the material the amphiphilic properties

required of a detergent. As a detergent, SDS has the ability to foam and form micelles and known to denature proteins as described by Mo and Sun [28] without breaking the peptide bonds [29]. Thus, gelatin essentially acts as binder whereas SDS enhances the foaming capacity of the gelatin solution to improve the overall binding of the aerogels for producing solid blocks. The effects of SDS on the GSA composites were investigated and reported.

Materials and experimental methods

Materials

Hydrophobic Silica Aerogel translucent granulates, with bulk density of 0.08–0.10 g/cm³, porosity of >90 %, pore diameter ~20 nm, surface area of 600–800 m²/g were purchased from Cabot Corp[®](USA). High Strength Gelatin from porcine skin (bloom strength 240–270; density ~1.043 g/cm³) and SDS (density = 0.37 g/cm³) were purchased from Sigma Aldrich.

Instrumentation

Sonication of gelatin solution was carried out on Fisher Scientific FB15051. The gelatin, GSA, and GSA–SDS composite blocks were weighed on a 4-decimal accurate

Fig. 1 Median density factor. **a** 95 % confidence of experimental data with fitted curve for density factor, **b** reduced density due to SDS addition

weighing balance, AB201-S Mettler Toledo, USA. The compression testing of all the specimens was carried out on Universal Testing Machine, INSTRON 5569 load frame with a calibrated $500 \text{ N} \pm 4 \%$ load cell. Microstructure investigations were carried out using JSM7600 Field Emission Scanning Electron Microscopy with EDX. Surface characterizations were carried out using XPS/ESCA on aerogels, gelatin, and GSA composites.

Fabrication of GSA and GSA–SDS composites

Various aqueous solutions with 2.0–50.0 wt% quantities of gelatin in 12 ml water were prepared at 35 and 70 °C via sonication for 1 h to dissolve the gelatin granulates. The solution is then stirred gently to achieve homogeneous mix. Quantities of SDS from 0.0 to 0.66 wt% were then dispersed into the solution and frothed into foam before adding 50.0–98.0 wt% of silica aerogel granules. The foamed solution of gelatin was then mixed carefully with silica aerogels with a stirrer with a relatively slow motion for 10 min until the silica aerogels binds for various quantities with SDS and without it. The mixture is then cast as blocks of 75 mm by 50 mm by 25 mm on a metal dish laid with a porous sheet. The composites were left to cure

at room temperature with a relative humidity of 60 %. A total of 3 sets of GSA and GSA–SDS composite blocks comprising 172 specimens were fabricated.

Experimental techniques

Density

The foamed GSA and GSA–SDS composite blocks were removed after curing at room temperature at the relatively humidity of 60 % and weighed. The densities of the various composite blocks of GSA and GSA–SDS were determined from the known dimensions of those block samples.

Compression tests

Each sample block was then cut into a square specimen of x – y dimensions of $17.5 \pm 2.5 \text{ mm}$ with $27.5 \pm 1.5 \text{ mm}$ height (in z -direction) using razor blades. The GSA and GSA–SDS specimens were compression tested in the z -direction at three strain rates, via; 0.8/min, 1.2/min at the nominal strain up to 44.4 % and at 1.0/min. Each specimen was loaded in compression using $500 \text{ N} \pm 4 \%$ load cell with the initial load of 25 % of the nominal strain for 1 min and, thereafter was unloaded. The amount of strain recovery was measured after 1 min upon unloading. The expression for strain recovery is shown in Eq. (1). Compressive Strength and Modulus values were taken directly from the in-built software of the tester. Total of 172 specimens were tested for strain recovery at various strains, of which, 17 specimens had zero strain recovery. “Failed Specimen Analysis” was carried out to purge out the redundant data, which is defined as a specimen already failing at first level but having duplicate data at higher levels

$$\text{SR} = \left(1 - \frac{\Delta L}{\text{CS}} \right) \times 100\%, \quad (1)$$

Fig. 2 Composites stress–strain response

Fig. 3 Strain recovery in terms of % gelatin

where SR is the strain recovery, CS is compressive strain (mm), and ΔL is the change in length of specimen due to compression (mm).

Statistical analysis: ANOVA

Full factorial ANOVA design methodology was used via MATLAB R2009a to evaluate the effects of each process

Fig. 4 SEM pictures of **a** silica aerogel granules; **b** single silica aerogel granule under SEM; **c** chemical structure of aerogel; **d** pearl-like necklace structure of the aerogel with clear visualization of nanopores (boxed in red); **e–f** GSA–SDS composite showing the retention

of the silica aerogel pearl-like necklace structure suggesting non-penetration of gelatin into pores and binding of gelatin onto the hydrophobic surface

variable on the measured properties for all types of test studies. A full quadratic empirical model including all main effects, second order effects, two and three way interactions were accounted via multiple linear regression analysis to determine the properties. Terms that were not significant in the model (<95 % confidence) were eliminated one at a time. The general empirical model for all the properties evaluated is given in Eq. (2)

$$Y = \beta_0 + \beta_1 G + \beta_2 S + \beta_3 Sr + \beta_4 C + \mu_1 G^2 + \mu_2 S^2 + \mu_3 C^2 + \gamma_1 (G * S) + \gamma_2 (G * Sr) + \gamma_3 (G * C) + \gamma_4 (S * Sr) + \gamma_5 (S * C) + \gamma_6 (C * Sr) + \varnothing_1 (S * Sr * G) + \varnothing_2 (S * C * G) + \varnothing_3 (C * Sr * G) + \varnothing_4 (S * Sr * C) + \varnothing_5 (S * Sr * G * C), \quad (2)$$

where Y is the response of the property, G is gelatin, S is SDS, Sr is strain rate, C is compressive strain on the specimen, and β , μ , γ , $\varnothing$ are the coefficients of main effects and interactions.

Results and discussion

Experiment data

The experimental data median values for density, strain recovery, compressive modulus, and compressive strength are shown in Appendix (Tables 5, 6).

General trend of density

The addition of SDS into the solution of gelatin increases the foaming capacity significantly as seen in Fig. 1b. As a result, the volume of the foamed solution increases and thus reducing the density of the composite when compared

with those without SDS additive. The density factor (d_i) is expressed as shown in Eq. (3)

$$d_i = \frac{\rho_i}{\rho_o}, \quad (3)$$

where ρ_i density of GSA–SDS and ρ_o density of GSA.

The d_i is greatly influenced by the %SDS added to the solution. The box plot in Fig. 1 shows the Median d_i as a function of %SDS (α) after removing the single point observations and the outliers. In the experiments, the maximum amount of SDS used is 0.66 %. Ideally, the d_i should not exceed the limiting value of 1. With this boundary condition, a natural logarithm function will be ideal to express d_i in terms of α as follows, where C_i and B_i are %SDS constant and limiting constant, respectively.

$$d_i = \frac{\rho_i}{\rho_o} = C_i \ln \alpha_i + B_i \quad (4)$$

Median points were curve fitted to establish d_i as a function of α as shown in Fig. 1. The established equation for the above expression is:

$$d_i = \frac{\rho_i}{\rho_o} = 0.1122 \ln \alpha_i + 0.9003. \quad (5)$$

The data points are within 95 % confidence interval which shows that the equation is a good fit; the R^2 is approximately 0.79. The d_i in Fig. 1 approaches the limiting value of 1 with increasing %SDS.

General trend of compressive strength and strain

The experimental stress–strain curves in Fig. 2a, b show transformation of brittle to ductile behavior with the addition of SDS (max 0.66 wt%) exhibiting 3 distinct regions analogous to creep curve as annotated as low strain zone (LSZ), high strain zone (HSZ) and densification. LSZ

Fig. 5 Existence of air pockets in the GSA and GSA–SDS composite blocks

Table 1 EDX data

Specimen	Wt%		
	Carbon	Silicon	Oxygen
10 % Gelatin–0 % SDS	51.30	12.29	35.84
10 % Gelatin–0.66 % SDS	12.3	35.14	52.07

is defined as the region under less than 20 % compressive strain whereas HSZ refers to the region where the composites were subjected to 20–50 % compressive strain. Generally, beyond 50 % compressive strain, densification of the composites follows. Most of the analyses in this paper are restricted to the LSZ and HSZ regions.

General trend of strain recovery

In Fig. 3, the addition of %SDS improves the strain recovery to approximately 10 % over the range of gelatin

mass fraction in LSZ thus sustaining high % strain recovery of between 80 and 95 %. This range is wider in HSZ as %SDS has more significance in the strain recovery when subjected to high compressive strain when the strain recovery is only observable at above 10 % gelatin in GSA composites. In contrast, the addition of SDS shows that the GSA–SDS composites is able to sustain good recovery of 70–90 % when subjected to high compressive strain for all mass fractions of gelatin setting up a converging envelope of strain recovery in the HSZ toward higher mass fractions of gelatin.

Brittle to ductile behavior

The experimental densities recorded in Appendix (Table 5) suggest that the gelatin foamed solution was able to bind with the hydrophobic coated surface of the silica aerogels without penetrating into the pores. Figure 4a, b shows the

Fig. 6 Schematic of the networked aerogel particles bonded with gelatin (orange) and linkages developed due to SDS polar and non-polar groups

silica aerogel granules and visual examination of a single aerogel granule under SEM. Figure 4c shows the chemical structure and Fig. 4d, the microstructure of the magnified region where the “pearl necklace” like structure and the nano-pores are visibly seen as reported by Guo et al. [30] and Zhong et al. [31]. The SEM pictures in Fig. 4e, f clearly show the GSA–SDS composite where retention of the “pearl necklace” like structure and visibility of nano-pores suggesting that gelatin had bonded onto the hydrophobic surface and there is negligible penetration of the gelatin. Hence, there exists a possible reaction or physical adsorption between the carboxyl and amides functional groups of the gelatin with the oxy-TMS groups of the silica aerogel.

This was verified when the same silica aerogels failed to bind with gelatin foamed solution when it was heated at

350 °C before the mixing phase indicating that the oxy-TMS ($\text{Si-O-Si}(\text{CH}_3)_3$) groups had reverted to hydroxyl (Si-OH) groups by oxidation as reported previously by Rao et al. [32]. The foamed solution of gelatin and SDS induces large amount of air from the surrounding forming bubbles. This action enables air to be trapped between the aerogel granules during mixing.

While some of the trapped air escape via differential gas pressure inside the bubbles, some may not thus, remaining trapped during the curing stage. The introduction of SDS into the foamed gelatin solution increases the amount of bubbling and therefore trapped air volume. This can be observed from Fig. 1b where the volume of the composite block increased significantly for the same amount of gelatin and hence reducing the density. The binding was further aided by adding the SDS having both the polar and

Fig. 7 Silica aerogel elemental peaks

non-polar groups was able to bridge the hydrophobic groups of silica aerogel with polar groups of gelatin giving the added springiness in the interface between the aerogels and the foamed solution. SEM picture in Fig. 5 shows a comparison between two specimens of GSA and GSA–SDS. It is clear that with GSA–SDS, there are more air pockets between the aerogel particles. The EDX data in Table 1 shows reduction of C but increase of Si and O elements on the surfaces of composites at the regions of air pockets between both specimens because of re-distribution of the gelatin content throughout the composite mix due to increased volume with the addition of SDS. This observation concludes that for composites having same gelatin content, the binding between the aerogel particles has significant amount of trapped air in the form of “air pocket” when added with SDS that simultaneously increases its flexibility due to the pockets of trapped air in the dried foam. Thus the ability of these “air pockets” to withstand the compressive load during testing result in a lower strength, higher strain recovery, and therefore transforming into a ductile polymer behavior [33] as shown in Figs. 2b and 3. A simplified schematic on the mechanism of the behavior is shown in Fig. 6. The linkages represented by SDS, together with the gas pressure within the dried foam enables the gelatin–silica aerogel composite particles to resist compressive load. During initial loading in LSZ, the pressure within the foam provides resistance that causes steep slope in the stress–strain curve up to <20 %CS. Then the slope becomes more gradual with increasing %CS indicating that the pressure within the dry foam is decreasing as annotated by HSZ in Fig. 2b.

Upon unloading, the air re-enters the dried foam and thus resulting in strain recovery. Figure 2a shows that without SDS, the composites fail prematurely in HSZ due to the de-bonding of the aerogel from gelatin and Fig. 2b shows sustained gradual increase of strength in HSZ with SDS. However, further loading beyond HSZ will fully compress the dried foam expelling all the trapped air but having densification as seen in Fig. 2b thus preventing de-bonding of the particles from the gelatin network.

Chemical surface characterization

XPS characterization was carried out on selected specimens of GSA and GSA–SDS composites to determine the chemical states of the elements. In Fig. 7, there are two carbons peaks, 284.0 and 284.6 eV, with an atomic concentration of 0.75 and 20.4 %, respectively, on the silica aerogels. The peak at 284.6 eV is assigned to the methyl groups ($-\text{CH}_3$) from the oxy-TMS groups on the surface of aerogels [34]. The oxygen peak at 532.8 eV is assigned to the oxygen bonds in the SiO_2 clusters and the peak at 532.2 eV is assigned to the oxy-TMS groups [35]. Similarly, the peak at 103.4 eV is assigned to the silicon content in SiO_2 aerogel cluster and 103.9 eV is assigned to Si–C bonds in oxy-TMS groups [36–38].

In Table 2, the loss of N 1s peaks in the composites suggest that the free $-\text{NH}_2$ groups have undergone hydrogen bonding with the aerogels aided by the reducing elemental ratio Si:C shown in Table 3. This indicates that the some of the oxy-TMS groups would have participated in the reaction with $-\text{NH}_2$ groups. At the same time, the lower Si:O ratio of composites with SDS indicates that not all of the oxy-TMS groups on the aerogel bond due to increase in O 1s with the addition of SDS.

Figure 8a shows the breakdown of the Si 2p peaks in aerogels and the various compositions of composites. Si–O peaks at 103.4 eV were relatively constant at 20 ± 2 % for the aerogels and the composites. The aerogels has another small peak at 103.9 eV which was identified as the Si– OR_3 ($\text{R} = \text{CH}_3$). However, this peak shifted to 101.5 eV for the composites which has been identified as Si– OR_x suggests possible reduction of methyl groups or a loss of hydrogen

Table 3 Elemental ratio of composites

Sample	Calculated elemental ratio					
	N/C	O/C	N/O	Si/C	Si/O	Si/N
GSA	0.019	1.751	0.011	0.988	0.564	51.049
GSA–SDS	0.019	2.092	0.009	1.038	0.496	55.283
Aerogel	–	2.548	–	1.196	0.470	–
Gelatin films	0.214	0.304	0.678			

Table 2 Binding energy position and percentage atomic concentration of composites

Sample	Position BE (eV)				Atomic concentration (%)			
	O 1s	N 1s	C 1s	Si 2p	O 1s	N 1s	C 1s	Si 2p
GSA	532.4 $\pm$ 0.2	400.5 $\pm$ 0.6	284.5	103.7 $\pm$ 0.1	46.6 $\pm$ 0.7	0.5 $\pm$ 0.3	26.6 $\pm$ 0.9	26.3 $\pm$ 0.6
GSA–SDS	532.4 $\pm$ 0.1	399.8 $\pm$ 0.4	284.5	103.6 $\pm$ 0.2	51.3 $\pm$ 0.5	0.5 $\pm$ 0.2	24.5 $\pm$ 0.4	25.4 $\pm$ 0.6
Aerogel	532.5	–	284.5	103.7	53.7	–	21.1	25.2
Gelatin films	530.7 $\pm$ 0.2	399.3 $\pm$ 0.1	284.5		20.1 $\pm$ 0.1	14.0 $\pm$ 0.1	65.8 $\pm$ 0.2	–

Fig. 8 Comparison of carbon and silicon chemical states in silica aerogels, GSA, GSA–SDS, and gelatin

that reacted with the free $-\text{NH}_2$ groups of the gelatin resulting in the lower binding energy. The reduction in the atomic concentration from 6.44 to 3.75 % on the oxy-TMS groups also points to the above postulation.

The C 1s peaks in Fig. 8b showed that the COO^- and C–N peaks had disappeared and a new C–X at 283.6 eV appeared in the composites. The new peak has 1.1–1.9 % atomic concentrations which could be hydrocarbon or carbon–carbon bond. Similarly, the O 1s(2) composition in the composites showed a reduced percentage level as compared to aerogels. The XPS data affirmed the initial postulation that there is some reaction between the aerogels and the gelatin as seen from the shift on the Si-OR_3

binding energy of the composite and as well as the disappearance of the C–N and COO^- peaks that were distinct in the gelatin films but not in the composite. Essentially, for a material to bind with aerogels, it must possess free $-\text{NH}_2$ groups in more than 14 % concentration and with COOH groups.

Empirical analysis

ANOVA

Full factorial design based on ANOVA was carried out and Table 4 below summarizes the significant effects of the

Table 4 Summary of main effects and interactions

Properties	Significant terms	R^2
Density	G, S, G^2 , S^2	0.9519
Strain recovery	G, S, C, S^2 , C^2 , (G*S)	0.8385
Compressive modulus	G, S, G^2 , S^2	0.9815
Compressive strength	G, S, G^2 , S^2	0.9804

main and interactive terms. ANOVA showed that strain rate does not have any effect on any of the mechanical properties, thus the %SR data were normalized at 1.0/min by averaging the response. However, it is noted that %CS is a significant term for strain recovery but not for the others. Therefore, the empirical analysis of strain recovery involves three variables whereas the others involve only the mixing ratio of the constituents. The co-efficient terms were solved using the regress analysis in MATLAB by tabulating the variables. Six empirical models were developed to capture the trend-lines observed in the experimental data minus the redundant data. Figure 9 shows the comparison of the experimental and empirical data for both, the low and the high, compressive strains. The empirical model trend-line correlates well with the experimental data providing reasonable estimation of strain recovery for gelatin content of 2–50 % and SDS content between 0 and 0.66 %. Similarly, surface response fitting was carried out to plot the behavior of density, compressive strength and compressive modulus in terms of the constituents' mass fraction as shown in Fig. 10.

Discussion

Since the interest is on strain recovery of the composite at high compressive strain, the empirical models to validate the effect of SDS were plotted as shown in Fig. 11 at compressive strain of 45 % using empirical models from Table 4 and the coefficients derived from the experimental data. The best strain recovery of 86 % is achieved when Gelatin is 50 % at 0.41 % SDS. The optimal strain recovery 0.74 is achieved for all the five variations of gelatin content when SDS is at 0.56 %. Figure 12 shows a comparison of recovery with increasing gelatin content at 45 % compressive strain with 0 %SDS and 0.56 %SDS, respectively, achieving consistently high strain recovery. Figure 12 shows the response with the empirical density and the analytical density from Eqs. 2 and 5. Increasing the gelatin content from 2 to 50 % generally result in an increase of density by 55.5 % for empirical and 42.3 % for analytical with a decrease of strain recovery of 6 %. The optimal behavior of strain recovery with respect to compressive strength and modulus as a function of density was

Fig. 9 Empirical and experimental data and trend-lines for **a** low compressive (LC: <20 %) strain and **b** high compressive (HC: >20 %) strain: (thick lines show experiment trend-line while dotted and dashed lines indicate empirical trend-line)

plotted in Fig. 13. Both the compressive modulus and strength show similar behavior. The lighter GSA–SDS composites eventually reach the modulus and strength that is comparable to the brittle GSA composite and at the same time exhibiting significant strain recovery. The optimal combination for 0.56 % SDS is when gelatin is approximately 45 % with strain recovery of 0.70, strength of 0.42 MPa and modulus of 3.2 MPa with the density of 0.107 g/cm³. The optimal combination for 0.41 %SDS is when gelatin is approximately 50 % with strain recovery of 0.84, strength of 0.53 MPa, and modulus of 3.6 MPa with the density of 0.115 g/cm³. The observation reveals a power law dependence of the mechanical properties on density.

It was evaluated that an exponent of 2.87–3.27 for modulus and 3.16–4.00 for strength, respectively. The evaluated values incidentally agree well with the works of Woignier et al. [39] who concluded that the process parameters such as concentration of silicon compounds, catalytic conditions, and the preparation conditions affects an aerogel prepared via sol gel technique affects the modulus of the aerogel that obeys the power law dependence relative to its density with the exponent of 3.7.

Fig. 10 Surface response fitting of **a** strength, **b** density, **c** modulus with gelatin and SDS contents

Conclusions

A new phenomenon of strain recovery was observed in GSA–SDS composites. A new fabrication method has been proposed revealing a unique phenomenon of high strain recovery following a transformation of brittle to ductile behavior in silica aerogels. This unusual phenomenon was explained via microstructure analysis and simple schematic diagrams explaining the brittle to ductile behavior of the GSA composites with SDS. Experiments conducted show the strain recovery of 70 % or more when loaded up to 45 % of the compressive strain. ANOVA statistical analysis performed on the experimental data to derive empirical models to determine the trends in the response of strength, modulus and strain recovery as a function of the density carried out revealed a power law dependence of the modulus and strength with density.

The addition of SDS in negligible amounts (0.66 wt% max) has significantly contributed to the improved performance of the aerogel composites. Optimal values of strain recovery, compressive strength, and modulus were determined without compromising the insulation properties of the aerogels.

Fig. 11 Graphs showing empirical compressive strain recovery with increasing %SDS at 45 % compressive strain

It was observed through XPS investigation of the chemical states of the composites in comparison with gelatin films and neat aerogels proved that certain degree of bonding existed between the surface of the aerogels and gelatin. Free —NH_2 groups were responsible for the binding but not all oxy-TMS groups were bonded due to lower concentration levels of the —NH_2 groups in gelatin. The carboxyl groups in gelatin aided in the hydrogen bonding with water and with

Fig. 12 Strain recovery versus density (empirical and analytical)

Fig. 13 Empirical response on compressive strength, compressive modulus and strain recovery as a function of density

the aerogels, while SDS ensures uniformity in binding by bridging the polar and non-polar groups.

The consequence of such a phenomenon has several advantages. Firstly, the behavior of the composite changes from brittle–elastic to elastomeric material. Secondly, the addition of SDS delays the onset of a complete composite failure due to compressive force. Thirdly, the addition of SDS shows the capacity of the composite to absorb large amount of compression (almost half the length) and still exhibit recovery, thus making it an ideal candidate as an energy absorbing material. Fourthly, it is shown that water soluble polymers with adequate free $-NH_2$ groups could be

the possible binders for the hydrophobic silica aerogels. Lastly, our preliminary findings indicate that thermal conductivity of these composites is low enough to make them to be promising thermal insulators. However, further studies are needed and are being carried out.

Acknowledgements The first author gratefully acknowledges Nanyang Technological University (NTU) for financial and other support.

Appendix

See Tables 5 and 6

Table 5 Experimental data for density GSA and GSA–SDS composite blocks

Sample no.	Mass fraction			Density	Density factor
	Gelatin	Aerogel	SDS	ρ (g/cm ³)	d_i
GA1	0.05	0.95	0.0000	0.090	
GA2	0.10	0.90	0.0000	0.083	
GA3	0.20	0.80	0.0000	0.100	
GA4	0.30	0.70	0.0000	0.118	
GA5	0.50	0.50	0.0000	0.131	
GA6	0.05	0.95	0.0033	0.052	0.583
GA7	0.10	0.90	0.0033	0.067	0.812
GA8	0.20	0.80	0.0033	0.091	0.902
GA9	0.30	0.70	0.0033	0.105	0.891
GA10	0.50	0.50	0.0033	0.115	0.877
GA11	0.05	0.95	0.0066	0.046	0.517
GA12	0.10	0.90	0.0066	0.069	0.834
GA13	0.20	0.80	0.0066	0.091	0.906
GA14	0.30	0.70	0.0066	0.094	0.799
GA15	0.50	0.50	0.0066	0.105	0.803
GS1	0.02	0.98	0.0000	0.076	
GS2	0.02	0.98	0.0024	0.055	0.726
GS3	0.02	0.98	0.0036	0.053	0.692
GS4	0.02	0.98	0.0048	0.068	0.889
GS5	0.06	0.94	0.0000	0.088	
GS6	0.06	0.94	0.0023	0.056	0.637
GS7	0.06	0.93	0.0034	0.061	0.693
GS8	0.06	0.93	0.0046	0.062	0.707
GS9	0.10	0.90	0.0000	0.095	
GS10	0.10	0.90	0.0022	0.061	0.641
GS11	0.10	0.89	0.0032	0.073	0.766
GS12	0.10	0.89	0.0043	0.074	0.778
GS13	0.14	0.86	0.0000	0.094	
GS14	0.14	0.86	0.0024	0.067	0.713
GS15	0.14	0.86	0.0036	0.071	0.750
GS16	0.14	0.86	0.0048	0.090	0.950
S11	0.03	0.97	0.0000	0.090	
S12	0.03	0.97	0.0024	0.052	0.573
S13	0.03	0.97	0.0036	0.076	0.836
S14	0.03	0.97	0.0048	0.071	0.789

Table 5 continued

Sample no.	Mass fraction			Density	Density factor
	Gelatin	Aerogel	SDS	ρ (g/cm ³)	d_i
S15	0.09	0.91	0.0000	0.109	
S16	0.09	0.91	0.0023	0.100	0.912
S17	0.09	0.91	0.0034	0.089	0.817
S18	0.09	0.91	0.0046	0.100	1.005
S41	0.14	0.86	0.0000	0.106	
S42	0.14	0.86	0.0022	0.082	0.773
S43	0.14	0.86	0.0032	0.066	0.626
S44	0.14	0.86	0.0043	0.081	0.766

Table 6 Experimental data for strain recovery, compressive strength, and compressive modulus GSA and GSA–SDS composite blocks

Sample no.	Compressive strain (%)	Strain recovery (%)	Compressive modulus (MPa)	Compressive strength (MPa)	Compressive strain (%)	Strain recovery (%)	Compressive modulus (MPa)	Compressive strength (MPa)
S11	7	100	0.529	0.031	16	25	0.388	0.041
S12	7	100	0.031	0.001	16	92.5	0.048	0.005
S13	7	93.4	0.222	0.012	16	86.3	0.179	0.022
S14	7	86.7	0.152	0.009	16	83.8	0.22	0.026
S15	7	80	0.957	0.052	16	85	0.987	0.093
S16	7	83.4	0.962	0.048	16	85	0.764	0.081
S17	7	90	0.504	0.029	16	87.5	0.562	0.062
S18	7	93.4	0.647	0.042	16	91.3	0.782	0.074
S41	7	90	1.171	0.057	16	85	1.184	0.115
S42	7	93.4	1.212	0.044	16	88.8	0.746	0.064
S43	7	100	0.681	0.027	16	90	0.52	0.043
S44	7	93.4	0.693	0.031	16	86.3	0.677	0.054
S11	11	84	0.517	0.039	21	0	0.44	0.029
S12	11	94	0.034	0.003	21	86	0.039	0.005
S13	11	80	0.236	0.016	21	82	0.187	0.026
S14	11	80	0.186	0.016	21	83	0.216	0.024
S15	11	84	0.899	0.077	21	0	0.832	0.088
S16	11	86	0.995	0.065	21	86	0.656	0.098
S17	11	88	0.717	0.051	21	88	0.581	0.068
S18	11	92	0.692	0.051	21	91	0.655	0.074
S41	11	84	1.435	0.089	21	75	1.193	0.137
S42	11	84	1.016	0.056	21	85	0.724	0.073
S43	11	90	0.564	0.037	21	88	0.483	0.052
S44	11	92	0.658	0.039	21	80	0.541	0.062
GS1	6	100	0.225	0.019	17	0	0	0
GS2	6	100	0.115	0.006	17	92	0.102	0.008
GS3	6	100	0.141	0.009	17	94.5	0.107	0.011
GS4	6	99	0.149	0.009	17	95.25	0.124	0.011
GS5	6	96.65	0.61	0.045	17	81.25	0.727	0.065
GS6	6	100	0.187	0.017	17	88.75	0.189	0.021
GS7	6	100	0.369	0.018	17	87.5	0.247	0.031
GS8	6	100	0.256	0.012	17	87.5	0.216	0.025
GS9	6	93.35	0.842	0.048	17	83.75	0.943	0.093
GS10	6	100	0.473	0.018	17	88.75	0.358	0.034

Table 6 continued

Sample no.	Compressive strain (%)	Strain recovery (%)	Compressive modulus (MPa)	Compressive strength (MPa)	Compressive strain (%)	Strain recovery (%)	Compressive modulus (MPa)	Compressive strength (MPa)
GS11	6	83.35	0.706	0.031	17	82.5	0.589	0.062
GS12	6	93.35	0.972	0.04	17	82.5	0.625	0.068
GS13	6	76.65	1.389	0.067	17	81.25	1.316	0.121
GS14	6	93.35	0.827	0.036	17	91.25	0.654	0.059
GS15	6	96.65	1.003	0.039	17	87.5	0.561	0.059
GS16	6	83.35	0.889	0.041	17	83.75	0.87	0.08
GS1	10	92.25	0.218	0.019	21	a^	a^	a^
GS2	10	98	0.119	0.009	21	a^	a^	a^
GS3	10	98.75	0.125	0.01	21	a^	a^	a^
GS4	10	96.15	0.133	0.01	21	a^	a^	a^
GS5	10	82	0.782	0.046	21	0	0.341	0.031
GS6	10	100	0.174	0.014	21	90	0.187	0.024
GS7	10	92	0.233	0.022	21	84	0.292	0.04
GS8	10	92	0.243	0.017	21	86	0.188	0.03
GS9	10	88	1.181	0.075	21	0	0.437	0.049
GS10	10	94	0.337	0.023	21	78	0.35	0.041
GS11	10	80	0.657	0.042	21	83	0.515	0.06
GS12	10	84	0.819	0.058	21	82	0.765	0.087
GS13	10	74	1.401	0.081	21	35	1.132	0.053
GS14	10	82	0.668	0.042	21	95	0.607	0.064
GS15	10	88	0.811	0.043	21	91	0.792	0.073
GS16	10	82	0.989	0.061	21	87	0.759	0.091
GA1	11.4	90	0.706	0.053	33.3	a^	a^	a^
GA2	11.4	93.3	0.779	0.069	33.3	a^	a^	a^
GA3	11.4	93.3	1.615	0.119	33.3	66.7	1.389	0.213
GA4	11.4	90	2.251	0.156	33.3	55.6	1.576	0.244
GA5	11.4	73.3	3.675	0.236	33.3	61.1	1.921	0.176
GA6	11.4	100	0.05	0.005	33.3	77.8	0.076	0.013
GA7	11.4	93.3	0.443	0.029	33.3	77.8	0.35	0.077
GA8	11.4	96.7	1.201	0.092	33.3	68.9	1.311	0.109
GA9	11.4	93.3	1.841	0.14	33.3	66.7	2.164	0.306
GA10	11.4	100	6.541	0.466	33.3	53.3	4.583	0.485
GA11	11.4	100	0.039	0.003	33.3	77.8	0.044	0.011
GA12	11.4	100	0.515	0.03	33.3	87.8	0.375	0.068
GA13	11.4	100	1.782	0.094	33.3	77.8	1.15	0.13
GA14	11.4	100	2.599	0.122	33.3	75.6	1.717	0.23
GA15	11.4	100	5.007	0.352	33.3	55.6	4.919	0.532
GA1	24	a^	a^	a^	44.4	a^	a^	a^
GA2	24	a^	a^	a^	44.4	a^	a^	a^
GA3	24	75	1.043	0.171	44.4	0	1.149	0
GA4	24	66.7	2.371	0.242	44.4	0	1.421	0
GA5	24	66.7	2.794	0.306	44.4	41.7	2.541	0.59
GA6	24	83.3	0.063	0.01	44.4	66.7	0.064	0.008
GA7	24	83.3	0.333	0.051	44.4	67.7	0.301	0.111
GA8	24	78.3	1	0.104	44.4	41.7	0.798	0.271
GA9	24	70	2.017	0.231	44.4	54.2	1.724	0.569
GA10	24	58.3	6.992	0.534	44.4	50	3.562	0.55

Table 6 continued

Sample no.	Compressive strain (%)	Strain recovery (%)	Compressive modulus (MPa)	Compressive strength (MPa)	Compressive strain (%)	Strain recovery (%)	Compressive modulus (MPa)	Compressive strength (MPa)
GA11	24	100	0.05	0.008	44.4	66.7	0.041	0.016
GA12	24	91.7	0.361	0.049	44.4	75	0.324	0.1
GA13	24	80	1.134	0.107	44.4	74.2	0.769	0.195
GA14	24	76.7	2.283	0.181	44.4	67.5	1.436	0.35
GA15	24	66.7	4.787	0.554	44.4	35	3.132	0.998

Note a[^] Failed Specimen-Test not carried out as sample blocks were too fragile during handling

References

- Gesser HD, Goswami PC (1989) Chem Rev 89(4):765. doi:10.1021/Cr00094a003
- Hunt AJ, Jantzen CA, Cao W (1991) Insulation materials: testing and applications. ASTM, Gatlinburg, p 455 ASTM Special Technical Publication
- Lee K-H, Kim S-Y, Yoo K-P (1995) J Non-Cryst Solids 186:18. doi:10.1016/0022-3093(95)00066-6
- Lee CJ, Kim GS, Hyun SH (2002) J Mater Sci 37(11):2237. doi:10.1023/a:1015309014546
- Rao AP, Pajonk GM, Rao AV (2005) J Mater Sci 40(13):3481. doi:10.1007/s10853-005-2853-3
- Bhagat SD, Kim Y-H, Ahn Y-S, Yeo J-G (2007) Appl Surf Sci 253(6):3231. doi:10.1016/j.apsusc.2006.07.016
- Soleimani Dorcheh A, Abbasi MH (2008) J Mater Process Technol 199(1–3):10. doi:10.1016/j.jmatprotec.2007.10.060
- Alnaief M, Smirnova I (2011) J Supercrit Fluids 55(3):1118. doi:10.1016/j.supflu.2010.10.006
- Bhagat SD, Kim Y-H, Moon M-J, Ahn Y-S, Yeo J-G (2007) Solid State Sci 9(7):628. doi:10.1016/j.solidstatesciences.2007.04.020
- Parmenter KE, Milstein F (1998) J Non-Cryst Solids 223(3):179. doi:10.1016/s0022-3093(97)00430-4
- Scherer GW, Smith DM, Qiu X, Anderson JM (1995) J Non-Cryst Solids 186:316. doi:10.1016/0022-3093(95)00074-7
- Moner-Girona M, Roig A, Molins E, Martinez E, Esteve J (1999) Appl Phys Lett 75(5):653. doi:10.1063/1.124471
- Meador MAB, Fabrizio EF, Ilhan F, Dass A, Zhang G, Vassilaras P, Johnston JC, Leventis N (2005) Chem Mater 17(5):1085. doi:10.1021/cm048063u
- Meador MAB, Weber AS, Hindi A, Naumenko M, McCorkle L, Quade D, Vivod SL, Gould GL, White S, Deshpande K (2009) ACS Appl Mater Interfaces 1(4):894. doi:10.1021/am900014z
- Katti A, Shimpi N, Roy S, Lu H, Fabrizio EF, Dass A, Capadona LA, Leventis N (2006) Chem Mater 18(2):285. doi:10.1021/cm0513841
- Xu Z, Gan L, Jia Y, Hao Z, Liu M, Chen L (2007) J Sol-Gel Sci Technol 41(3):203. doi:10.1007/s10971-006-1500-z
- Ge DT, Yang LL, Li Y, Zhao JP (2009) J Non-Cryst Solids 355(52–54):2610. doi:10.1016/j.jnoncrysol.2009.09.017
- Gupta N, Ricci W (2008) J Mater Process Technol 198(1–3):178. doi:10.1016/j.jmatprotec.2007.06.084
- Veronica V, Adrian T (2010) Water and life. CRC Press, Boca Raton, p 235. doi:10.1201/EBK1439803561-c16
- Schweitzer PA (2006) Corrosion of polymers and elastomers. CRC Press, Boca Raton, p 147. doi:10.1201/9780849382468.ch3
- Chanda M, Roy SK (2008) Industrial polymers, specialty polymers, and their applications. CRC Press, Boca Raton, p 1. doi:10.1201/9781420080599.ch1
- Boris D, Anatoliy Z, Elena Y (2001) Smart Polymers. CRC Press, London. doi:10.1201/NOE0415267984.ch10
- Gary C, Mikhail F, Parminder S (2008) Technology of pressure-sensitive adhesives and products. CRC Press, Boca Raton, p 71. doi:10.1201/9781420059410.ch7
- Frydrych M, Wan C, Stengler R, O'Kelly KU, Chen B (2011) J Mater Chem 21(25):9103. doi:10.1039/C1jm10788g
- Aristippos G (2002) Protein-based films and coatings. CRC Press, Boca Raton. doi:10.1201/9781420031980.ch16
- Fidler C, Simonton TC (1996) Aerogel-in-foam thermal insulation and its preparation. US Patent, 5569513, 29 Oct 1996
- Fidler C, Simonton TC (1996) Aerogel-in-foam thermal insulation and its preparation. US Patent, 6136216, 24 Oct 2000
- Mo X, Sun X (2000) J Polym Environ 8(4):161. doi:10.1023/a:1015241609497
- Ruiz CC, Díaz-López L, Aguiar J (2008) J Dispers Sci Technol 29(2):266. doi:10.1080/01932690701707571
- Guo J, Nguyen BN, Li L, Meador MAB, Scheiman DA, Cakmak M (2013) J Mater Chem A 1(24):7211. doi:10.1039/C3TA00439B
- Zhong Y-H, Zhou B, Gui J-Y, Li Y-N, Du A, Shen J, Wu G-M, Zhang Z-H (2011) At Energy Sci Technol 45(10):1170
- Rao AV, Kulkarni MM, Pajonk GM, Amalnerkar DP, Seth T (2003) J Sol-Gel Sci Technol 27(2):103. doi:10.1023/a:1023765030983
- Ashby MF, Gibson LJ (1997) Cellular solids-structure and properties. 2nd edn. Cambridge university Press, Cambridge
- Moulder JF, Chastain J, King RC (1995) In: Chastain J, King RC Jr (eds) Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data. Physical Electronics, Eden Prairie, MN
- Wang S-J, Jin I-S, Park H-H (1998) Surf Coat Technol 100–101:59. doi:10.1016/S0257-8972(97)00588-4
- Yang H-S, Choi S-Y, Hyun S-H, Park C-G (1999) Thin Solid Films 348(1–2):69. doi:10.1016/S0040-6090(99)00016-4
- Jo M-H, Hong J-K, Park H-H, Kim J-J, Hyun S-H, Choi S-Y (1997) Thin Solid Films 308–309:490. doi:10.1016/S0040-6090(97)00437-9
- Mazur JH (1984) High resolution electron microscopy study of silica aerogel transparent insulation. In: Proceedings of SPIE vol 502
- Wojniew T, Phalippou J, Vacher R (1989) J Mater Res 4(03):688. doi:10.1557/JMR.1989.0688