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A New Phenomenon of Compressive Strain Recovery in Gelatin-Silica Aerogel Composites with SDS

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Abstract

Silica aerogels are nano-structured, highly porous solids with extremely low density but fragile and brittleness. To enhance the applicability of aerogels, gelatin-silica aerogel (GSA) composite blocks were produced by mixing the hydrophobic aerogel-granules in a gelatin-SDS (sodium dodecyl sulfate) foamed-solution by frothing method. Gelatin essentially acts as binder whereas SDS enhances the foaming capacity of the mixture to the overall binding of the aerogels. The characteristics of these blocks depend on fabrication process and the gelatin-SDS composition. Especially, the strain recovery exhibited after compression is an unusual phenomenon observed with brittle silica aerogels.

This paper discusses the effects of SDS on the density and the strain recovery of GSA composites. The fabrication process is explained; compression testing of these blocks is presented and associated strain recovery observed upon unloading is studied. The process variables such amount of gelatin/aerogel/SDS mix; compressive strain; and strain rates were analysed through Analysis of Variance (ANOVA). An empirical model that relates these variables to achieve the optimal strain recovery is established. In addition, the rule of mixture model with a correction factor was developed to estimate the densities of GSA-SDS composites. These composites can be used for heat protection, sound barrier, impact-resistance and shock-absorption.

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Nomenclature

SR	Strain Recovery	CS	Compressive Strain (mm)
ΔL	Change in length of specimen (mm)	LSZ	Low Strain Zone
HSZ	High Strain Zone		
<i>Greek symbols</i>			
β, μ, γ, ϕ	Coefficients of main effects and interactions in ANOVA model		
ρ_o	Density of GSA composites	ρ_i	Density of GSA-SDS composites

1. Introduction

Aerogels was first discovered by an American scientist Samuel Stephens Kistler in the 1930s [1] but the interest in these materials was renewed in the last four decades in the fields of engineering [2, 3]. Silica aerogels are very light and highly porous solids, and possess significant thermal insulation properties [4]. They

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appear as translucent substance referred to as “Frozen Smoke” with large internal surface area [5, 6]. These features make aerogels an ideal material for applications as thermal and acoustics insulators or in the areas of optical, electrical and energy storing devices [1-5]. The current commercial synthesis of silica aerogels are brittle and exhibit volumetric shrinkage [4, 8] at elevated temperatures [7] that hinders processing and handling of these materials [5, 9]. As such, there is a need for a better and simpler way to produce stable solids of the aerogels to enhance their applicability. In the current work, GSA and GSA-SDS composite blocks were produced by mixing the hydrophobic aerogel granules in a gelatin and gelatin-SDS foamed solution respectively by frothing method. 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 [10] and in pharmaceutical industry as a suspending agent, encapsulating agent, and a tablet binder [11]. 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; has the ability to foam and form micelles and known to denature proteins [12] without breaking the peptide bonds [13].

In this research, gelatin acts as binder whereas SDS enhances foaming capacity of the gelatin to the overall binding of the aerogels for producing solid blocks. The effects of SDS on the GSA composites, in particular, the strain recovery upon unloading after compression loading is an unusual phenomenon to occur with brittle silica aerogels are presented. Statistical design methodology (ANOVA) was used to derive empirical models to establish relationships between significant variables.

2. Materials and Experimental Methods

2.1. Materials

Hydrophobic silica Aero gel translucent granulates, with bulk density of 0.08-0.10, porosity of >90%, pore diameter ~ 20nm, surface area of 600-800m²/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.

2.2. Instrumentation

Sonication of gelatin solution was carried out on Fisher Scientific FB15051. Materials were weighed on a 4-decimal accurate weighing balance, AB201-S Mettler Toledo, USA. The compression testing of all the specimens was carried out on Universal Testing Machine, INSTRON 4459 load frame with a calibrated 500N ±4% load cell. Statistical design analyses were carried out using MATLAB 2009a.

2.3. Fabrication of GSA and GSA-SDS Composites

Various aqueous solutions with 2.0 to 50.0 wt% of gelatin in 12 ml water were prepared at 35^oC and 70^oC via sonication for 1 hour to dissolve the gelatin granulates. The solution is then stirred gently to achieve homogeneous mix. SDS from 0 to 0.66wt% were then dispersed into the solution and frothed into foam before adding 50.0 to 98 wt% of silica aerogels.

2.4. Experimental Techniques

2.4.1. Density

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

2.4.2. Compression Test

Square specimens of x-y dimensions of 17.5mm±2.5mm with 27.5mm±1.5mm height were compression tested in their z-direction at three strain rates, via; 0.8/min, 1.0/min with the preload of 25% of the nominal strain, and at 1.2/min at the nominal strain up to 44.4%. Tests are conducted using 500N±4% load cell. The amount of strain recovery was measured after 1 minute upon unloading. The expression for strain recovery (SR) is shown in Eq. (1).

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

2.4.3. Statistical Analysis: ANOVA

Full factorial ANOVA design methodology was used via MATLAB R2009a to evaluate the effects of each process variable on the measured strain recovery and density 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 strain recovery and density is given in Eq. (2).

$$Y = \beta_0 + \beta_1 G + \beta_2 S + \beta_3 Sr + \beta_4 C + \mu_1 G^2 + \mu_2 S^2 + \mu_3 C^2 + \gamma_1(G * S) + \gamma_2(G * Sr) + \gamma_3(G * C) + \gamma_4(S * Sr) + \gamma_5(S * C) + \gamma_6(C * Sr) + \phi_1(S * Sr * G) + \phi_2(S * C * G) + \phi_3(C * Sr * G) + \phi_4(S * Sr * C) + \phi_5(S * Sr * G * C) \tag{2}$$

where, *Y* = Response of the property, *G* = gelatin, *S* = SDS, *Sr* = StrainRate, *C* = Compressive Strain on the Specimen

3. Results and Discussion

3.1. Experimental Data

A 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 1st level but having duplicate data at higher levels.

3.1.1. General Trend on Strain Recovery

Fig. 1 shows two distinct behaviours of the GSA and GSA-SDS composites. LSZ is defined as the region where the % SR achieved under less than 20% CS. HSZ refers to the region where the composites were subjected to 20-50% CS. In the LSZ, the addition of %SDS improves the SR to ~10% over the range of gelatin mass fraction. In HSZ, %SDS has more significance in the SR when subjected to high CS. HSZ shows significant improvement in SR at lower mass fraction of gelatin followed by a converging envelope towards higher mass fractions. Fig.1 also shows that in LSZ, the composite is able to sustain high %SR of between 80 to 95%. However, at high CS, the SR is only observable at above 20% gelatin in GSA, whereas, GSA-SDS composite is able to sustain good recovery of 70% to 90% when subjected to high CS.

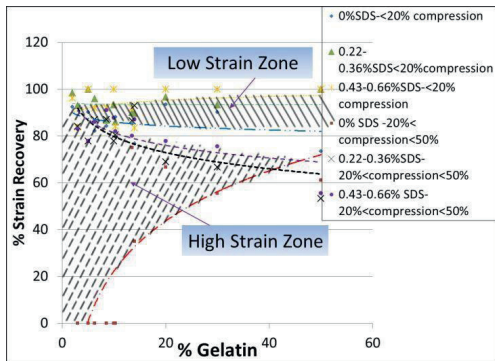


Fig. 1 – Strain Recovery under LSZ and HSZ regions at various %Gelatin, %SDS and %CS

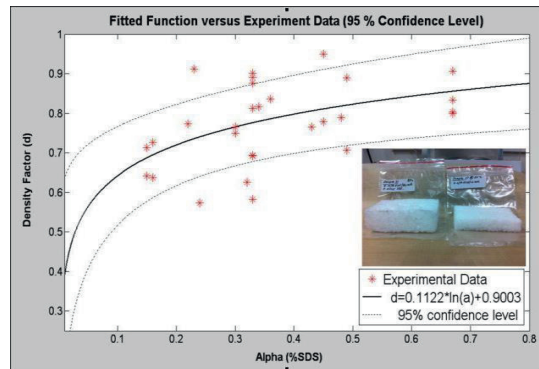


Fig. 2 - 95% Confidence of Experimental Data with Fitted Curve for Density Factor; ([insert] Reduced Density due to SDS addition)

3.1.2. General Trend on Density

The addition of SDS into the solution of gelatin increases the foaming capacity significantly as seen in Fig. 2(insert). As a result, it reduces the density of the GSA-SDS composite when compared with GSA composite. The density factor (*d_i*) is expressed as shown in Eq. (3). The *d_i* is greatly influenced by the %SDS added to the solution. 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 shown in Eq. (4).

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

$$d_i = \frac{\rho_i}{\rho_o} = 0.1122 \ln \alpha_i + 0.9003 \quad (4)$$

Median points were curve fitted to establish d_i as a function of α as shown in Fig. 2. 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. 2 approaches the limiting value of 1 with increasing %SDS. This essentially shows that the density of the composite with %SDS will ultimately reach the density of composite without SDS but with higher strain recovery.

3.2. Empirical Results

3.2.1. ANOVA

Full factorial design based on ANOVA was carried out. ANOVA showed that strain rate does not have any effect on SR, thus the %SR data were normalized at 1.0/min. The SR of the composites is influenced by the mixing ratio of the constituents as well as % CS. It was also observed that addition of negligible amount of SDS (max of 0.66Wt%) had tremendous effect on the SR in all the datasets. After eliminating the insignificant terms, the final empirical model derived is shown in Eq. (5) with G- Gelatin, S -SDS, C-% Compressive Strain, and, D - density.

$$SR = \beta_0 + \beta_1 G + \beta_2 S + \beta_4 C + \alpha_2 S^2 + \alpha_3 C^2 + \gamma_1 (G * S) \quad (5)$$

$$D = \beta_0 + \beta_1 G + \beta_2 S + \alpha_1 G^2 + \alpha_2 S^2 \quad (6)$$

The model only has one linear term for gelatin even though it is a main factor because it was only significant in the study at 1.0/min strain. Similarly, the empirical model arrived at for the density is shown in Eq. (6).

3.2.2. Empirical Strain Recovery

Given that the empirical model for SR is a function of 3 variables, 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. Fig.3 shows the comparison of the experimental and empirical trendlines for both, the low and the high, compressive strains. In Fig. 3(a), the upper and lower bounds of SR are within 15% range for both, the experiment and empirical data, when the CS is less than 20%. In Fig. 3(b), the empirical and experimental data for shows good co-relation as well for composites subjected to CS between 20 to 50%. Thus, the empirical models provide reasonable estimation for SR for gelatin content of 2 to 50% and SDS content between 0 to 0.66%.

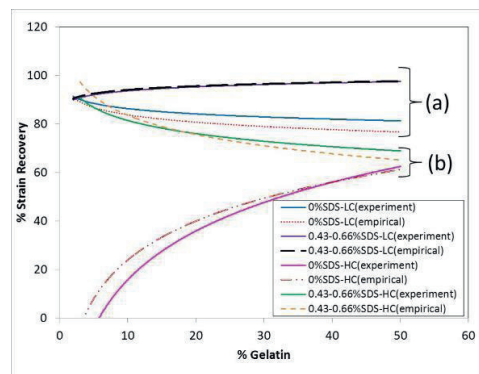


Fig. 3 - Empirical and experimental trend lines for (a) Low compressive (LC: < 20%) strain and (b) High compressive (HC: > 20% < 50%) strain: (thick lines show experiment trend-line while dotted and dashed lines indicate empirical trend-line)

3.2.3. Relationship between Strain Recovery and Density Empirical Models

Since the interest is on SR of the composites at high CS, the empirical models to validate the effect of SDS were plotted as shown in Fig. 4 at 45%CS using Eq. (6). The maximum SR of 86% is achieved when gelatin is 50% at 0.4%SDS. The optimal SR 0.74 is achieved for all the five variations of gelatin content when SDS is at 0.56%.

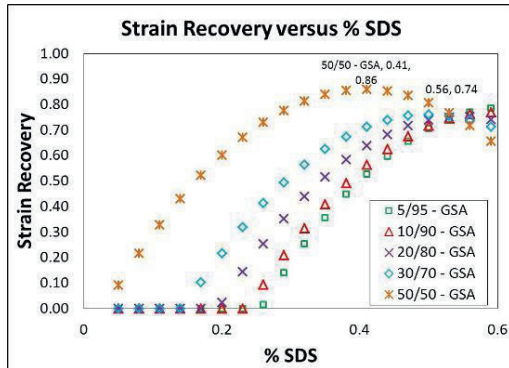


Fig. 4 - Graphs showing Empirical Compressive Strain Recovery with increasing %SDS at 45% Compressive Strain

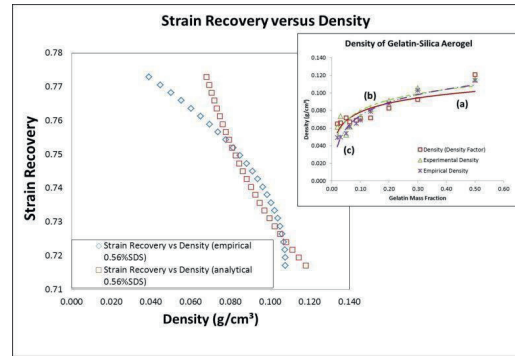


Fig. 5 - SR versus Density (empirical and analytical). [Insert : (a) Density(analytical);(b) Density (experiment); (c) Density (empirical) vs % Gelatin]

Fig. 5(insert) shows the various density models with increasing gelatin content. The empirical model and experimental data have better correlation than the density factor model. Fig. 5 shows the SR response with the empirical density and the analytical density from Eqs. (4) and (6) at 45%CS with 0.56%SDS. It is observed that 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% empirically. Therefore, a median value of 25% gelatin at 0.56%SDS will be able to achieve approximately 75% SR at 45%CS.

4. Conclusions

A new phenomenon of strain recovery was observed in GSA-SDS composites. Experiments conducted show the strain recovery of 70% or more when loaded up to 45%CS. Empirical models agree well with the experiment as explained above. SDS added in negligible amount (<1.00%), aids in the recovery of the composite and is the key element. 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.

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