Mechanical and acoustical properties as a function of PEG concentration in macroporous silica gels

J. Martin, B. Hosticka, C. Lattimer, P.M. Norris *

Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, VA 22903, USA

Abstract

The pore size of macroporous silica aerogel can be controlled by varying the concentration of water-soluble organic polymers in the sol. These gels demonstrate a wide array of mechanical and acoustical properties in proportion to the organic polymer concentration in the sol. Presented in this paper are the resulting mechanical dependencies upon the concentration of high molecular weight polyethylene glycol (PEG) in the initial sol. Physical properties studied include density, surface area, pore structure, acoustic velocity, and mechanical strength. Most of these properties exhibited a large change when a small concentration of PEG was added to the initial sol, correlating with a strengthening of the solid matrix. Still higher concentrations of PEG progressively weakened the solid matrix. Through examination of the gels containing PEG, experiments have shown an inverse relation of acoustic velocity to PEG concentration while density remains relatively constant. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 62.65.+k; 62.20.-x; 62.20.Dc; 82.33.Ln

1. Introduction

The addition of water-soluble organic polymers to silica sol–gels provides the possibility of a bio-compatible production process [1]. This production route, presented by Conroy et al. [1], was initially developed for use with cell immobilization and colonization in the wet gels. The theory was that non-robust cells could be added to the sol prior to gelation without the threat of being harmed by harsh gelation conditions. Two requirements for a gel to support living cells are large pore size (providing control over the microstructure) and a non-toxic production process. Using high molecular weight polyethylene glycol (PEG) as the water-soluble organic polymer, gels are produced that satisfy both requirements. The addition of the PEG allows one to manipulate the size of the macropores present in the final gel.

Earlier work by Conroy et al. [1] explored the effects on microstructure caused by slight variances in the production methods at different concentrations of PEG in the initial sol. These investigations included effects of different hydrolysis ratios, temperature at gelation, and age of the pre-hydrolyzed sol. The study is continued here with a focus on the physical, mechanical, and acoustical properties of the resulting supercritically dried aerogels. The aerogels used in the present study vary only in the amount of PEG added to the initial sol. The properties of these aerogels show

*Corresponding author. Tel.: +1-804 924 6295; fax: +1-804 982 2037.
E-mail address: pamela@virginia.edu (P.M. Norris).
definite mechanical and acoustical trends that are directly related to the PEG concentration. Researchers have previously studied the mechanical properties of aerogel and have produced general compression curves. One method, employed by Scherer et al. [2], used a mercury porosimeter to compress aerogel samples hydrostatically. Three distinct regions were noted on a pressure–volume curve. For small increases in pressure, the volume of the aerogel decreased in a linear fashion. As pressure was increased beyond a yield point, the aerogel began to deform plastically. Still greater increases in pressure caused the material to harden such that the bulk modulus (K) changed with volume according to a power-law relationship

\[ K(V) = K_0 (V_0/V)^m, \]

where \( K_0 \) and \( V_0 \) are the bulk modulus and sample volume at the point where the compression curve changes to upward concavity [2]. The exponent, \( m \), was a constant on the order of 3.25 for the samples studied. A different method for determining mechanical properties, uniaxial compression testing, will be utilized in this paper. A qualitative similarity between the results obtained by the two methods is expected.

Acoustical techniques have also been used as a means of determining the material properties of aerogel such as porosity, density, mechanical strength, and attenuation [3–7]. Mechanical properties, such as the elastic coefficients, have been related to acoustic velocity using experimentally matched scaling laws [4]. Others have taken a more theoretical approach by using relationships for acoustic velocity in two component porous media [8]. The model of a two component system considers the interstitial gas as playing a non-negligible roll in material properties. The effect of gas pressure on the acoustic velocity has been studied through two different approaches. One approach assumed a relationship between the gas pressure, porosity, and density which is developed to fit the experimental data [4]. A more theoretical approach considered the mean free path of the interstitial gas, taking into consideration the heat transfer rates between the gas and solid phases [9]. Another interesting characteristic property of aerogel is that acoustic velocity decreases upon compression of the bulk material. Researchers have tried to model this phenomenon by a bent knee model presented by Gross et al. [10]. The dependence on compression is explained by modeling the links between the colloidal particles as stressed knees; as a knee is bent there is a decrease in the mechanical strength in the link, thus creating a slower propagation velocity [10].

2. Experimental techniques

2.1. Production

The aerogels used for this experiment were made using hydrolyzed tetraethyloxysilicate (TEOS) in a two-step gelation process. TEOS was added to a water/nitric acid solution that had reached 60°C at a molar ratio of 1/33/0.02 (TEOS/water/nitric acid). The solution was refluxed for one hour at a temperature of 80°C. Upon cooling, the solution was divided into five separate flasks containing varying amounts of carbowax xentory polyethylene glycol (PEG) MW 3350. Once the PEG was dissolved, the sol was chilled using an ice water bath to slow down the final gelation reaction. The sol was then catalyzed with one molar KOH at a molar ratio of 1/0.035 (TEOS/KOH) causing a swing in pH from acidic to basic. The mixture was then poured into 20 ml naphthylene molds. Seven samples of each were made from the five PEG concentrations listed in Table 1. The gels were decast three days after gelation and then placed together in an ethanol bath. All of the gels were washed, supercritically dried with CO₂, and treated under identical conditions so the only variable is the concentration of PEG in the initial sol.

2.2. Aerogel characterization

Static properties of the aerogel that were studied included density, pore structure, and surface area. Three gels from each of the five groups were randomly selected and their dimensions were measured. Assuming that the aerogels were tapered cylinders, several dimensional and mass
measurements were recorded and averages were taken. Using the averaged weight and volume, the densities were calculated.

The microstructure of the aerogel was compared in two ways, through scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area analysis. A JOEL™ JXA-840A SEM was used to view the microstructures of the differing groups of aerogels. Samples were coated with gold and SEM imaging was performed under the same conditions for each sample. The photos were taken at a working distance of about 14 mm using a magnification of 8500x.

A BET analysis was performed on the aerogels to find the total surface area per gram of gel. After degassing at 150°C under vacuum for 24 h to evaporate any residual water or other volatile contaminants, they were analyzed with a Micrometrics™ 2010 Surface Area Analyzer.

### 2.3. Mechanical strength characterization

Mechanical testing was performed using a specially designed uniaxial compression test stand, shown in Fig. 1. The stand consisted of a rigid rectangular frame and a floating top platen. Since the aerogel samples were subjected to low stresses and deformations, it was important to begin the experiment with no preload applied to the samples. The platen was supported by three vertical springs to allow the test to begin with zero deadweight force applied to the aerogel. Force was applied to the movable platen by three Airpax™ anti-stiction gas cylinders configured in parallel. The cylinders were rated to 690 kPa, producing 136 N apiece. Pressure was measured by an Ashcroft™ K17M0215F2200# pressure transducer. The displacement of the movable platen was measured by an Omega™ LD300-15 Linear Variable Differential Transformer (LVDT) with an LDX-3A signal conditioner. The output signals from the LVDT and pressure transducer were sent to a MetaByte™ DAS-16G2 computer data acquisition card. The data acquisition equipment was able to measure pressure from 0 to 690 kPa with an accuracy of ±0.1 kPa and displacement ranging from 0 to 19 mm with an accuracy of ±0.01 mm.

Pressurization of the air cylinders was controlled by manual operation of a needle valve. The instantaneous pressure and displacement rates were constantly displayed on the computer monitor, allowing the operator to adjust the needle valve to maintain a constant strain rate on the sample. The force of the springs supporting the movable platen was subtracted from the raw data to reveal the behavior of the aerogel under loading.

Uniaxial mechanical testing was performed on three samples chosen from each group. Every
effort was made to select samples that contained few, if any, surface or internal cracks. Parallel, horizontal faces were produced through sanding. Each sample was tested using an initial strain rate of 0.0015 s⁻¹.

2.4. Acoustic characterization

Acoustic measurements were made through the use of two Panametrics™ 5 MHz contact mode transducers set up as pulse and receive. The pulse consisted of five-cycle sinusoidal pulses created using a Hewlett Packard™ 8165A Programmable Signal Source triggered by a Hewlett Packard 8003A Pulse Generator. This pulse was then amplified by an EIN 325 LA RF 50 dB Power Amplifier before entering the first transducer. The second transducer received the signal, after which it was amplified by a Panametrics Ultrasonic Preamp before being sent to a Lecroy™ 9324 Oscilloscope. Output scans were summed anywhere from 250 to 1000 times depending on the amount of background noise present.

Two pulse transit time experiments were performed. The first showed the dependence of pulse transit time through the aerogel on gas pressure. Two samples were randomly chosen from each group and were prepared by sanding each side to produce two parallel faces for the transducers. The sample was placed between the two transducers before the entire test stand was sealed in a vacuum chamber. Measurements were taken at pressures ranging from atmospheric to two inches of mercury. Each sample was evacuated for 12 h before the first pulse transit time was recorded. The pressure was then increased and the aerogel was allowed to come into equilibrium before another transit time was recorded. Measurements were taken at 6.7, 37, 71 kPa, and atmospheric pressure.

The second pulse transit time experiment showed the dependence of pulse transit time through the aerogel on the stress applied to the gel. For this experiment, the transducers were attached to the mechanical testing device shown in Fig. 1. The sample was prepared as before and placed between the two transducers. The aerogel was compressed while pulse transit times were recorded. With this device, the force exerted on the material could be accurately monitored simultaneously with the deformation of the aerogel. To determine the maximum level of stress that could be applied to the aerogels, a transparent sample containing zero PEG was observed through a circular polariscope while being compressed. When birefringent patterns began to emerge, the applied force was noted. It was known from previous experience that this level of stress was well inside the elastic region of the aerogel sample. All measurements were then taken at stresses below the critical stress to ensure elastic behavior.

Using the recorded acoustic velocities (longitudinal and shear) from the second pulse transit time experiment, the Lamé constants were calculated. Once found, these values were applied to known mechanical formulas to determine various material properties, one of which is the Young’s modulus [11].

3. Results

3.1. Physical properties

During the supercritical drying process, the gels shrank linearly by differing amounts according to their PEG concentration. As shown in Table 1, the most shrinkage was observed in aerogels with low amounts of PEG while the density of all aerogels listed in Table 1 averaged out to be around 115.7 g/cm³. The error shown in Table 1 represents ± one standard deviation as determined by the propagation of error technique described by Bevington and Robinson [12]. This technique takes into consideration errors in dimensional measurements of the samples, systematic errors of the apparatus transducers, and the sampling accuracy of the data acquisition card. A statistical analysis was performed on the density data to show that there was no linear trend for the density of the aerogels just after supercritical drying. Using a two-sided hypothesis test, it was found that a null hypothesis of zero slope could not be rejected with a confidence level greater than 80%. Density and percent shrinkage measurements were again taken about two months after supercritical drying. It was found that the aerogels continued to shrink and densify
and the trends of percent shrinkage seemed to change. The aerogels with a low PEG concentration shrank more than the gels containing zero PEG. The percent shrinkage then decreased monotonically in the aerogels containing increasing PEG concentrations (Table 1).

The aerogels of differing PEG concentrations can be easily distinguished by visual observations. Gels with no PEG were transparent and felt rigid when touched. With increasing amounts of PEG, the aerogels became more opaque, white, and soft. The BET surface area of these gels ranged from 850 to 550 m²/g with the highest PEG concentration reporting the lowest surface area (Table 1).

In SEM photographs, an obvious increase in the macro-pore regime can be noted along with an increase in the thickness of the solid skeleton. It can be seen in Fig. 2 that the feature sizes (pores and solid structures) increase linearly with increasing PEG concentration.

### 3.2. Mechanical results

When the stress–strain curves of the various samples were analyzed, classic yield strength behavior was noted. The aerogel initially deformed following a linear-elastic trend, followed by a smooth transition to plastic deformation. The Young’s modulus of the aerogel was significantly affected by the presence of PEG as shown in Fig. 3. The aerogel samples without PEG had a Young’s modulus of approximately 4.4 MPa. With the addition of a small amount of PEG to the sol, the Young’s modulus increased to 6.5 MPa. However, as PEG concentration subsequently increased, Young’s modulus (Eₘₑᶜʰ) decreased monotonically to a value of 0.9 MPa in the final group (Table 2). It should be noted that these samples were roughly of equal density. The errors presented in Table 2 are computed using the error propagation technique described above [12].

The stress at which the samples yielded to plastic deformation followed a trend much like that of the Young’s modulus. The yield stress was defined as the stress at which the stress–strain curve deviated from the initial linear behavior. The samples without PEG yielded at 0.20 MPa. The addition of PEG caused the elastic limit to peak at about 0.25 MPa, as seen in Table 2. As PEG

![Fig. 2. SEM micrographs show an increase in feature size with increasing PEG concentration.](image)

![Fig. 3. Young’s modulus determined through both acoustical and mechanical methods demonstrate similar trends with increasing PEG concentration.](image)
Table 2
Parameters obtained through mechanical and acoustic testing. Elastic limit, non-recoverable strain, and \( E_{\text{mech}} \) were determined using the uniaxial compression device. \( E_{\text{acous}} \) and acoustic velocity were the results of acoustic testing.

<table>
<thead>
<tr>
<th>Group</th>
<th>Elastic limit (MPa)</th>
<th>Non-recoverable strain</th>
<th>( E_{\text{mech}} ) (MPa)</th>
<th>( E_{\text{acous}} ) (MPa)</th>
<th>Acoustic velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.205 ± 0.001</td>
<td>0.047 ± 0.002</td>
<td>4.41 ± 0.17</td>
<td>6.85 ± 0.01</td>
<td>241.0 ± 0.5</td>
</tr>
<tr>
<td>B</td>
<td>0.245 ± 0.002</td>
<td>0.038 ± 0.003</td>
<td>6.46 ± 0.34</td>
<td>10.30 ± 0.02</td>
<td>272.1 ± 0.8</td>
</tr>
<tr>
<td>C</td>
<td>0.171 ± 0.001</td>
<td>0.037 ± 0.003</td>
<td>4.70 ± 0.35</td>
<td>6.43 ± 0.03</td>
<td>225.7 ± 1.1</td>
</tr>
<tr>
<td>D</td>
<td>0.079 ± 0.001</td>
<td>0.035 ± 0.003</td>
<td>2.34 ± 0.20</td>
<td>4.12 ± 0.02</td>
<td>176.2 ± 0.6</td>
</tr>
<tr>
<td>E</td>
<td>0.033 ± 0.001</td>
<td>0.037 ± 0.003</td>
<td>0.92 ± 0.07</td>
<td>1.27 ± 0.03</td>
<td>103.2 ± 2.4</td>
</tr>
</tbody>
</table>

Concentration increased further, the yield stress decreased monotonically to a value of 0.03 MPa.

Linear recoverability of a sample was demonstrated using uniaxial compression. The aerogel was cyclically loaded to a value approximately 75% its elastic limit and unloaded to zero three times. It was then loaded to approximately 150% of its elastic limit. The aerogel was seen to retrace its linear loading curve below the elastic limit. Above the elastic limit, the aerogel was permanently deformed and followed a different unloading curve. Non-recoverable strain appeared to be greatest in the samples without PEG, averaging 0.047. Samples containing PEG showed a lower value. This value was fairly constant with PEG concentration, ranging from 0.035 to 0.038 (Table 2).

Due to the non-catastrophic failure of the aerogels tested, it was difficult to determine the exact point of failure. However, it may be inferred by inspecting the stress–strain curves that the ultimate strength of the aerogels decreases with increasing PEG concentration.

3.3. Acoustic propagation results

Acoustic velocity is strongly dependent on the concentration of PEG in aerogels. A pronounced trend can be seen in Table 2 which follows the trend noted during mechanical testing. There was a slight increase in acoustic velocity between the aerogels with no PEG and those with a low concentration, followed by a decrease in acoustic velocity with an increase in PEG concentration. The studies on acoustic velocity with respect to gas pressure showed that there was minimal change in the acoustic velocity as the pressure is raised from 6.7 kPa to atmospheric pressure.

Under uniaxial compression, the acoustic velocity through the aerogels was observed to decrease with increasing stress. As previously noted, this trend is common in most aerogels and was seen in all of the gels tested. The total change in the acoustic velocity upon compression varied from around 3% to 17%, the latter of which was observed in the aerogels which contained the highest PEG concentrations. The percent change in the acoustic velocities between applied stresses of 0 and 25 kPa for aerogels labeled A–E are 1.7%, 1.5%, 1.8%, 3.9%, 16.5%, respectively.

The acoustically determined Young’s modulus that was calculated using Lamé constants, which can be seen in Table 2 labeled as \( E_{\text{acous}} \) and in Fig. 3, also follows the same hump-like trend as the modulus found by mechanical testing.

4. Discussion

The amount of shrinkage after supercritical drying was nearly linear with PEG concentration. With this linear trend it is surprising to find that there is relatively no variance in the density of the aerogels just after supercritical drying, giving rise to the suggestion that the solid matrix is changing. When the same measurements were taken two months later, they showed the first sign of a hump-like trend, where there is an initial increase in a property with low concentrations of PEG and then a drop as the PEG concentrations increase beyond a certain level.

As PEG concentration increases, so does the pore size of the gel. This is manifested by changes in the BET surface area and in optical clarity. The decrease in BET surface area can most likely be
attributed to the transition from the meso-pore to the macro-pore regime. The increased opacity of the aerogels can also be attributed to the increasing pore size. Gels with pore sizes smaller than the wavelength of light will seem clear, whereas aerogels with large pores will reflect and scatter the light.

The Young’s modulus obtained in both experiments, mechanical and acoustic, demonstrates a hump-like trend that shows an initial increase in mechanical strength with the addition of a small concentration of PEG and then a decrease in strength at higher concentrations. The similar results presented by both of these methods creates a greater confidence that this hump-like anomaly occurs within the material and is not an experimental artifact. In the acoustic experiments, it was shown that evacuating the gels caused little change in the acoustic velocity. This lack of dependence on gas pressure shows that the acoustic pulse travels primarily through the skeleton of the aerogel at these pressures; hence there is an acoustic dominance of the solid phase in this two-phase system. In the mechanical tests, the strain rates were slow enough that there was no increase in pressure or stress caused by the fluid in the pores. We are therefore confident that both the acoustical and mechanical techniques test the integrity of the solid matrix. In Fig. 3, it is apparent that the acoustical test produced a higher result for Young’s modulus than the uniaxial compression test. This discrepancy was likely due to shrinkage of the aerogels between the time when the mechanical tests and acoustic velocity tests were performed. It is interesting to note that the aerogels with zero PEG (group A) and the aerogels with a medium PEG concentration (group C) have approximately the same mechanical strengths even though their microstructures are obviously different (Table 2, Fig. 2).

The observed hump-like characteristic may indicate that there is an optimal amount of PEG for structural integrity. A stronger argument for this hump is that it may be occurring due to the effect of PEG on the microstructure. This hump-like behavior has been observed in previous studies by Nakanishi et al. [13] when the addition of just a minute amount of organic polymer caused a large change in the gelation time, which was then recovered at higher concentrations of that same organic.

5. Conclusion

By adding organic polymers (PEG) to the initial sol of sol–gel derived silica aerogels, gel properties can be manipulated to achieve desirable values of static properties such as pore size, clarity, and surface area per gram. These properties decrease monotonically with increasing PEG concentration. The mechanical strength and pulse transit time increase when comparing aerogels containing no PEG to aerogels with a low PEG concentration. By structurally changing the solid component of the gel, PEG increases mechanical stability and acoustic velocity at low concentrations and then weakens the solid matrix at higher concentrations resulting in slower acoustic velocities.

Acknowledgements

We thank DARPA and Veridian-PSR for their financial support of this work and Professor William Walker at the University of Virginia for the use of his equipment.

References

