The effects of ambient humidity on the mechanical properties and surface chemistry of hygroscopic silica aerogel

M.R. Miner, B. Hosticka, P.M. Norris *

Department of Mechanical and Aerospace Engineering, University of Virginia, 122 Engineer’s Way, Charlottesville, VA 22904, USA

Abstract

The stress vs. strain relation of hygroscopic aerogels was tested in a controlled humidity chamber to study how the Young’s modulus and non-recoverable strain are affected by the adsorption of water in the gel. Mass gains over desiccated conditions varied from 4% at 32% relative humidity (RH) to 12% at 70% RH. Above 70% RH, the samples failed catastrophically. The Young’s modulus increased from 0.51 to 0.70 MPa and non-recoverable strain increased from 0.047 to 0.059 over the same humidity range. Yield stress did not show significant changes. The samples were also studied with near-infrared transmission measurements to determine if the adsorbed water was chemically as well as physically bound to the surface. Several absorption lines indicative of hydrogen bonding between water and silica were seen to increase with increasing humidity while surface silanol lines decreased.

© 2004 Elsevier B.V. All rights reserved.

PACS: 62.20.Fe; 81.05.Rm; 81.70.Bt

1. Introduction

Hygroscopic silica aerogels deteriorate with time when exposed to normal ambient humidity by adsorbing water from the air. This deterioration is manifested by clouding of the samples, shrinkage, cracking, and under extreme cases, catastrophic failure reducing a clear monolithic sample to a pile of opaque fragments. This property necessitates that in actual use for insulation, aerogels must be encapsulated or the surfaces rendered non-active by the attachment of hydrophobic tails to cap the open silanol sites. However, it is these same open sites that can be utilized directly or indirectly as chemical absorbers for detection or cleanup that also make them hygroscopic [1]. Understanding how exposed aerogels behave with respect to water adsorption under actual use is important in engineering suitable supports and structures for the aerogels as well as ascertaining their expected longevity. At humidities lower than those leading to catastrophic failure, we study the strength, density, and changes to the near infra red (NIR) transmission spectrum of the samples. Water can be adsorbed both physically as well as chemically [2]. The change in mass of the sample is caused by both means of water uptake but the changes in the NIR absorption yield information on the surface chemistry of the gels [3,4].

2. Experimental

Aerogel samples were prepared using Silbond H5™ as a silica source, ammonium hydroxide as a base catalyst, and ethanol plus water as the solvent. The overall volume ratio of Silbond:30%NH₄OH:EtOH:H₂O was 480:3.3:800:333. After gelling in 20 ml molds the samples were decast, aged in a slightly basic ethanol solution, and rinsed in ethanol to remove residual water. The wet gels were dried supercritically following CO₂ replacement of the liquid phase. This yielded clear
aerogel samples with a density of about 80 kg/m$^3$ and a
surface area determined by nitrogen absorption of about
1000 m$^2$/g. No heat treating or passivation was per-
fomed to reduce the hygroscopic nature of the samples.

After drying, the samples were stored over desiccant
to establish a starting point for further studies under
controlled humidity. All samples were made at the same
time. Twenty out of the 32 samples were found to be free
of physical defects such as cracks or broken surfaces and
were divided into five groups of four samples each for
testing under differing humidities. The samples with de-
cfects were used to establish the range of humidities
where valid measurements could be made as well as
for destructive testing for surface area.

To establish a fixed humidity environment for
mechanical testing, dry air and water saturated air were
mixed in a sealed glove box containing a compression
tester [5], scale, and electronic humidity sensors. The
humidity was monitored over time and it was found that
after an hour had passed to allow the chamber to come
to equilibrium, it would maintain the desired humidity
for greater than one day. The samples to be tested at a
given humidity were left sealed in small desiccators until
the desired humidity in the chamber was established
then they were removed from the desiccator and allowed
to come to equilibrium with the humidity in the cham-
ber. This equilibrium took approximately 20 h as deter-
mined by observing the increase in weight of the samples
in the chamber.

Once the samples were at equilibrium with the test
humidity, compression tests and weight gain determina-
tions were performed inside the chamber and the sam-
ples were sealed with chamber air for transport to the
NIR spectrometer.

The compression tester in Fig. 1 uses a compressed
nitrogen system to apply force to the sample through
three Airpel$^\text{TM}$ low friction cylinders. These use graphite
pistons running on glass cylinders so that the area of the
piston and the pressure of the gas define the force on the
sample stage. Prior to applying gas pressure to the tes-
ter, the stage is held above the sample with springs that
must be compressed before any stress is actually applied
to the sample. This prevents the dead weight of the
apparatus from defining the minimum stress on the sam-
ple. A ballast tank in the gas system slows the response
of the apparatus such that loading and unloading rates
can be managed with manual valves. The displacement
of the stage is measured with a linear variable differen-
tial transformer (LVDT). The gas pressure and displace-
ment data along with time are collected directly into a
computer for further analysis. A typical run consists of
slowly increasing the gas pressure on the air cylinders
while monitoring the position of the stage and the gas
pressure. The force of the springs and apparatus weight
is known or independently measured and the force on
the tester is corrected accordingly to give the stress
strain curve for the sample alone. Prior to testing, the
samples were ground flat on two parallel surfaces to as-
sure pure compression and the dimensions were meas-
ured for normalization. This apparatus is described in
greater detail in Ref. [4].

A resultant stress strain curve with the sample under-
going loading and unloading is shown in Fig. 2. The off-
set in strain between the zero stress point on the loading
and the unloading legs of the curve is the non-recovera-
ble strain. The slope of the linear portion of the loading
curve is the Young's modulus and the stress where the
curve departs from a linear relation is the yield stress.
The samples were compressed to 90% of their original
length (strain of 0.1) at a rate no greater than
0.01 mm/s.

![Fig. 1. The low range compression tester used in this study. The three
air cylinders are of a special low break-away friction design so that the
stress on the samples is proportional to the gas pressure. Springs
support the weight of the movable portions of the apparatus to allow
test runs to start and end at zero stress.](image)

![Fig. 2. Typical compression run showing both the loading and
unloading legs of the test. The spring loading is stripped from each
data point. The difference in strain between zero stress at the beginning
and end of the run is the non recoverable strain.](image)
Transmission NIR spectra were collected on each sample at three times during testing using a Cary 5E UV–Vis-NIR spectrophotometer. These time stages were: (1) while desiccated, (2) after reaching equilibrium with the humidity before compression testing, and (3) after compression testing. Spectra were also collected on the wet reagents used to make the samples.

3. Results

The samples failed catastrophically above 70% RH without being compressed. They crumbled, shrank, and became opaque. This physical instability limited results to tests performed at lower humidities. The mass and non-recoverable strain increased significantly as a function of humidity as shown in Table 1 and Figs. 3 and 4. The reported Young’s modulus is the minimum sum of squares straight line fit to the elastic portion of the stress–strain curve for each sample. The plot of Young’s modulus as a function of relative humidity in Fig. 5 suggests a correlation, which can be testing using Analysis of Variance (ANOVA). Starting with the null hypothesis that Young’s modulus is independent of relative humidity, the ANOVA test resulted in rejection of this null hypothesis, confirming this correlation with greater than 99% confidence. The yield stress is the transition point from elastic to non-elastic behavior. This transition is determined from the stress–strain data by offsetting the Young’s modulus line by 1.002 and determining the point at which this offset line intersects the measured stress–strain curve. As can be seen in Fig. 2, the transition from elastic to inelastic behavior is not abrupt, which introduces compounding errors into yield stress determination. The yield stress determined from the experimental data showed even less correlation with relative humidity than the Young’s modulus and when analyzed by the ANOVA method, the null hypothesis that the yield stress is independent of relative humidity could not be rejected with any reasonable degree of confidence. Table 2 summarizes the results of the ANOVA analysis.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Summary of mechanical results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity</td>
<td>Gain in mass (%)</td>
</tr>
<tr>
<td>32%</td>
<td>4.15%</td>
</tr>
<tr>
<td>41%</td>
<td>5.32%</td>
</tr>
<tr>
<td>52%</td>
<td>6.72%</td>
</tr>
<tr>
<td>62%</td>
<td>9.98%</td>
</tr>
<tr>
<td>70%</td>
<td>11.7%</td>
</tr>
</tbody>
</table>

Fig. 3. Percent mass gain as a function of humidity. Clear correlation is seen.

Fig. 4. Percent non-recoverable strain as a function of humidity. Clear correlation is seen.

Fig. 5. Young’s modulus as a function of humidity. The ANOVA test gives a greater than 99% confidence of correlation.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Results of ANOVA statistical tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
<td>F-Statistic</td>
</tr>
<tr>
<td>Non-recoverable strain</td>
<td>33.5</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>10.5</td>
</tr>
<tr>
<td>Yield stress</td>
<td>0.890</td>
</tr>
</tbody>
</table>
The NIR lines attributed to hydrogen bonded surface water at wave numbers 5280, 6884, and 7117 cm\(^{-1}\) showed consistent increase with relative humidity while the free silanol lines at 4566 and 7320 cm\(^{-1}\) decreased with increasing relative humidity as indicated in Fig. 6. There was no observable change in the NIR spectra caused by the mechanical compression of the samples.

4. Discussion

Capillary condensation of water onto the highly curved surfaces of the hygroscopic aerogel sample can cause catastrophic failure as the smaller pores fill with water [6]. The Kelvin equation can be used to relate the size scale and relative humidity at which water will condense on a surface, as given by:

\[
\ln \frac{p}{p_s} = \frac{-2\gamma V_m}{RT} \frac{1}{r_m},
\]

where \(p/p_s\) is the relative vapor pressure in equilibrium with a meniscus having a radius of curvature \(r_m\), and \(\gamma\) and \(V_m\) are the surface tension and molar volume of the liquid adsorptive, respectively, and \(R\) and \(T\) are the universal gas constant and temperature, respectively. Solving this equation for surfaces with a radius of curvature of 2 nm, which is typical of the cluster size of silica aerogels [7], indicates that condensation at 300 K will occur at about 60% RH. We observed total failure of the aerogel samples at 70% RH, which is consistent with water condensing on the surface and resulting capillary forces collapsing the pore structure. Thus if structural integrity is required of hygroscopic samples the radius of curvature of the porous structure must be kept above the point at which Kelvin condensation occurs.

The NIR absorption lines at 4566 cm\(^{-1}\) and 7320 cm\(^{-1}\) are associated with the stretching-bending combination and to the first overtone of the free silanol groups, respectively [3]. The line located near 5280 cm\(^{-1}\) is the stretching-bending combination of hydrogen-bonded water. The lines at 7110 cm\(^{-1}\) and 6884 cm\(^{-1}\) are due to silanol groups that are hydrogen bonded to molecular water [4]. As water is taken up from the air, an increasing number of the free surface silanol groups are bound to water causing the peaks associated with them to fall as the peaks associated with the bound water increase.

The Young's modulus is an elastic measure of the stiffness of the sample and its recoverable strain. Surface water at the flexing knees causes the knees to resist bending by introducing material within the knee [8]. The overall effect is seen as an increase in the Young's modulus. Once bent, the weakening of the Si–O–Si bond by adsorbed surface water causes more of the knees to be broken at a given stress than in the absence of water [9,10]. This enhanced breaking of Si–O–Si bonds in the presence of surface water leads to an increase in non-recoverable strain. The total energy deposited in the form of non-recoverable strain was determined from the open area of the loop in the stress–strain curve between the loading and unloading portions with the strain expressed in total volume change. This determination yielded an energy deposition of \(~0.05\,\text{Jg}^{-1}\). If the surface silanol groups in the pores cross link and condense to absorb this energy, the population of surface silanol would drop by about \(1.5 \times 10^{17} \,\text{g}^{-1}\). Given that the initial population was on the order of \(5 \times 10^{21}\) for the entire sample, the change in the silanol population would only represent \(3 \times 10^{-5}\) of the total. This amount is much too small to be seen with any available instrumentation.

5. Conclusions

The observed behavior of hygroscopic aerogels is consistent with the bulk of the water being physically adsorbed but some water chemically absorbs and enhances condensation of residual silanol groups. Any possible change in surface silanol concentration due to cross linking while under compression is too small to be detected. When aerogel material is to be used in a manner where its physical integrity is important while in humid environments, either passivating the surface...
to make it hydrophobic or encapsulating the aerogel is imperative.

References