Organic aerogels: microstructural dependence of mechanical properties in compression

R.W. Pekala, C.T. Alviso and J.D. LeMay

Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

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Aerogels are a unique class of ultrafine cell size (<1000 Å), low-density foams. These materials have continuous porosity and a microstructure composed of interconnected colloidal-like particles or chains with characteristic diameters of 100 Å. Traditional aerogels are inorganic, made via the hydrolysis and condensation of metal alkoxides (e.g. tetraisopropoxy titanate). Recently, the authors reported the development of organic aerogels from the sol–gel polymerization of resorcinol with formaldehyde. Because these new aerogels are composed of a highly crosslinked aromatic polymer, they can be pyrolyzed in an inert atmosphere to form vitreous carbon aerogels. This work describes how the microstructure of these organic aerogels can be manipulated and controlled. The microstructural dependence of the compressive mechanical properties of both resorcinol–formaldehyde and carbon aerogels is examined in detail.

1. Introduction

Porous solids such as wood, coral, and bone are common structural materials in nature. These cellular materials have apparently evolved because they provide high stiffness and strength at remarkably low densities. In many cases, nature has engineered these materials so that they have an anisotropic cell structure which maximizes stiffness and strength in a particular direction. For example, many types of wood are 10 times stiffer along the grain as compared to across it [1,2].

Synthetic foams can be prepared from a wide variety of metals, glasses, and polymers [3–9]. Production processes for these materials often utilize (1) phase separation, (2) blowing agents, (3) sacrificial substrates, (4) microemulsions, or (5) sol–gel technology. The resultant foams can be either closed-cell or opened-cell depending upon the production process. In general, synthetic foams are isotropic, meaning that their structure and properties have no directionality.

In order for engineers successfully to design load-bearing structures from foams, it is important to understand how mechanical properties scale with density and microstructure. Our research has focused on a special class of opened-cell foams referred to as aerogels. These materials have a cell/pore size of less than 1000 Å and a microstructure composed of interconnected particles or chains with characteristic diameters of 100 Å. Because their cell/pore size is several orders of magnitude smaller than conventional foams, aerogels can be prepared as transparent, porous solids.

Inorganic aerogels are usually formed from the hydrolysis and condensation of metal alkoxides (e.g. tetramethoxy silane) [10–14]. The structure and properties of silica aerogels, in particular, have been studied in great detail [15–20]. Recently, we reported that organic aerogels could be formed from the aqueous, sol–gel polymerization of resorcinol (1, 3 dihydroxy benzene) with formaldehyde [21–24]. The microstructure of the resorcinol–formaldehyde (RF) aerogels is largely controlled by the [resorcinol]/[catalyst] ratio in a particular formulation. In addition, the RF aerogels can be pyrolyzed in an inert atmosphere to
form vitreous carbon aerogels. The mechanical structure–property relationships of both RF and carbon aerogels are described in this paper.

2. Experimental methods

2.1. Aerogel preparation

RF gels were prepared from aqueous solutions containing various percentages of solids at fixed molar ratios of [formaldehyde]/[resorcinol] equal to 2.0. Sodium carbonate was used as a base catalyst in all formulations. The RF solutions were poured into glass molds, sealed, and cured for a maximum of 7 d at 85–95°C. Gel times were as short as 2 h for solutions containing 20% solids and as long as several days for solutions with 3% solids.

Upon completion of the cure cycle, the gels were dark red in color but transparent. All gels were then placed in a dilute acid solution to aid in further crosslinking through the condensation of hydroxymethyl groups present in the gels. A noticeable increase in modulus occurred for gels prepared at low solids contents.

In order to preserve the gel structure and obtain a low-density foam, it was necessary to dry the gels under supercritical conditions. In this operation, the RF gels were first exchanged with an organic solvent (e.g. acetone) and then placed in a pressure vessel (Polaron®, Watford, UK). The pressure vessel was filled with liquified carbon dioxide which was completely exchanged over several days for the organic solvent present in the pores of the RF gels. The pressure vessel was then heated above the critical point of carbon dioxide ($T_c = 31°C; P_c = 7.6 MPa$). After slowly venting the pressure vessel, the RF aerogels were removed and further characterized.

RF aerogels consist of a highly crosslinked aromatic polymer, and they can be pyrolyzed in an inert atmosphere to produce pure vitreous carbon aerogels. Pyrolysis was conducted in a 3-zone Lindberg furnace using nitrogen as the purge gas. Samples were heated from room temperature to 1100°C at a rate of 1°C/min. Samples were held at 1100°C for 4 h before the furnace was allowed to cool back to room temperature overnight. The carbon aerogels were totally amorphous as evidenced by X-ray diffraction. Elemental analysis showed that the aerogels had an empirical formula of $C_{99}N_1$. Because of the visible absorption properties of carbon, these aerogels were black and no longer transparent.

2.2. Mechanical property measurements

Aerogels at moderate densities ($> 0.15 g/cm^3$) are relatively robust, but at lower densities they are inherently soft and weak. Consequently, mechanical characterization of low-density aerogels is difficult; specimens cannot be gripped or bonded to fixtures without being damaged, and they are difficult to machine into complex shapes (e.g. tensile dog bones). Therefore, it is desirable to employ a test method that utilizes simple specimen shapes and does not require that specimens be gripped.

In this study, the modulus and strength of aerogels were measured in uniaxial compression with an Instron tester (model #1125). The tests were performed at an initial strain rate of 0.1%/s. All measurements were made under ambient conditions at about 22°C and 50–70% relative humidity. No precautions were taken to prevent moisture adsorption by the aerogels.

The specimens were machined as $1 \times 1 \times 1 \text{cm}^3$ cubes (approximate) with a high speed circular saw. Great care was exercised to ensure that the specimens were machined with flat, smooth faces and plane-parallel opposing faces. Machining was performed with a modified end mill employing a specially designed vacuum chuck to hold the aerogel. The small specimen size was necessitated by the small size of the as-produced bulk aerogel samples. The surfaces of the as-produced aerogel samples were totally removed to eliminate possible contributions of surface skins. Since the mechanical properties were expected to be strongly dependent on the density, each test specimen was weighed and measured dimensionally prior to testing. Even specimens machined from the same bulk aerogel sample showed slight variations in density. Each specimen tested represents a single data point.
Figure 1 shows typical uniaxial compression stress–strain curves obtained for RF and carbon aerogels. The modulus was determined from the slope of the linear region of the curve. We call this value a compressive modulus instead of Young's modulus because the latter connotes a property of a linear-elastic material which the aerogels are not. The stress–strain curves do not exhibit a well-defined yield point; therefore the strength was determined at the point where the curve deviates from linearity by 0.2% strain. Although no fundamental reason exists for choosing this offset value, we have found it convenient for comparing the ‘strength’ of many different low-density materials that exhibit dissimilar responses at high compressive strains. In cyclic tests, the RF aerogels showed a little hysteresis at stresses below the offset value, but significantly more pronounced hysteresis at higher stresses. Carbon aerogels, on the other hand, showed virtually no hysteresis even at stresses well above the offset value, and appeared to be reversibly elastic at compressive strains approaching 10%.

3. Results and discussion

3.1. Resorcinol–formaldehyde chemistry

The sol–gel polymerization of resorcinol with formaldehyde is depicted in fig. 2. Because of the electron donating and ortho, para directing effects of the attached –OH groups, resorcinol is a trifunctional monomer capable of electrophilic aromatic substitution in the 2, 4 and/or 6 ring positions. Resorcinol reacts with formaldehyde under alkaline conditions to form mixtures of addition and condensation products. These intermediate products react further to form a tightly crosslinked polymer network. The principal reactions include (1) the formation of hydroxymethyl (–CH₂OH) derivatives of resorcinol, and (2) the condensation of the hydroxymethyl derivatives to form methylene (–CH₂–) and methylene ether (–CH₂OCH₂–) bridged compounds [25,26].

During the sol–gel polymerization, the low-viscosity sol state is populated with many RF ‘clusters’. These ‘clusters’ are crosslinked colloidal-like particles with diameters ranging from 30–200 Å, depending upon the catalyst concentration. Because resorcinol is totally consumed at an early point in the polymerization, the surface of the RF ‘clusters’ is covered with hydroxymethyl groups. Eventually, inter-cluster crosslinking takes place through these surface groups, leading to aggregation and eventual gel formation.

The size and number of RF clusters generated during the polymerization is controlled by the
Fig. 2. A schematic diagram of (a) the sol–gel polymerization of resorcinol with formaldehyde and (b) the structure of the crosslinked polymer network.

In our current model, the resorcinol anions which are generated quickly add formaldehyde in up to 3 positions on the ring. Electrostatic repulsion retards interaction between the charged, substituted resorcinol molecules. Nevertheless, additional uncharged monomers (formaldehyde and resorcinol) are able to add to these clusters. Because the functionality (i.e. number of available reactive sites) of the clusters increases as more resorcinol is covalently attached, the probability of additional monomers reacting with the clusters...
also increases and leads to their preferential growth.

Titration, chromatography, and NMR data show that resorcinol is the first monomer to be completely consumed [22,27]. As a consequence, only formaldehyde is available to react with sites at the surface of the RF clusters, forming numerous hydroxymethyl groups. In many ways, RF cluster formation is similar to the synthesis of 'starburst' polymers [28–30].

3.2. Organic aerogel microstructure

Based upon the above model, formulations prepared at the same percentage of solids with different catalyst concentrations should have clusters with different average diameters. For example, under high catalyst conditions (i.e. low R/C ratios), many clusters are generated in solution but they cannot grow very large in diameter before all available resorcinol is consumed. Under low cata-

Fig. 3. Transmission electron micrographs of RF and carbon aerogels prepared at 5% solids with different [resorcinol]/[catalyst] (R/C) ratios.
lyst conditions (i.e. high R/C ratios), fewer clusters are generated but they grow larger in diameter than their high catalyst counterparts. R/C ratios of 50–300 provide an acceptable range in which transparent gels are formed.

The dependence of cluster size upon the R/C ratio manifests itself in a number of ways in the dried aerogels. Density, surface area, and cell/pore size of both RF and carbon aerogels depend upon the synthetic conditions used in the sol–gel polymerization. Figure 3 shows TEMs of RF aerogels made at the extremes of our catalyst conditions. Each aerogel is composed of interconnected spherical particles which are derived from the clusters generated in solution. At R/C = 300 (i.e. low catalyst conditions), the particles have diameters of 160–200 Å and are lightly fused together giving a 'string-of-pearls' appearance. At R/C = 50 (i.e. high catalyst conditions), the particles have diameters of 30–50 Å and are joined together with large necks between particles. In fact, it is often difficult to visualize individual particles since they have a fibrous appearance. As expected, the surface areas of these aerogels also differ. The surface area of the high catalyst aerogel (small particle size) is ~ 900 m²/g while the low catalyst aerogel (large particle size) is ~ 400 m²/g. A linear relationship between surface area and the R/C ratio has been observed for a series of aerogels prepared at 5% solids [23].

The carbonized versions of the above aerogels are also shown in fig. 3. During pyrolysis, all samples undergo a 50% mass loss; however, the aerogels synthesized under high catalyst conditions experience much greater volumetric shrinkage. Interestingly, the particle size for the high catalyst aerogel is slightly larger in the carbonized state when compared to the initial RF material. We believe that the small, individual particles of the RF aerogel fuse together during pyrolysis leading to slightly larger particles in the carbonized state. Such ‘healing’ phenomena have been observed in the pyrolysis of other polymers [31,32]. Under low catalyst conditions, the particle size in the carbonized state is slightly smaller than in the corresponding RF aerogel. The change in particle size after carbonization is reflected in the BET adsorption data for these aerogels [23].

3.3. Mechanical behavior

The microstructural differences of aerogels prepared under various catalyst conditions are apparent in their mechanical properties. Figure 4 shows the compressive modulus of both RF and carbon aerogels as a function of density and R/C ratio. As expected, the modulus increases as a function of bulk density. The linear log–log plot in each case demonstrates a power–law density dependence that has been observed in many other low-density materials. This relationship is expressed as

\[ E = c \rho^n \]  

where \( \rho \) is the bulk density, \( c \) is a constant (prefactor), and \( n \) is a non-integer exponent that usually ranges from 2–4. For highly regular opened-cell foams, the exponent usually falls very close to 2.0 while ideal closed-cell foams give an exponent of 3.0 [2,33–35]. Foams with irregular, fractal type morphologies generally have a value which exceeds 3.0.

In the case of both RF and carbon aerogels, the above exponent equals 2.7 ± 0.2. In comparison, the modulus of silica aerogels has been reported to show a power–law dependence with an exponent equal to 3.7 ± 0.3 [36–40]. Recent data from our
Table 1
Scaling exponents and prefactors for the compressive mechanical properties of organic aerogels

<table>
<thead>
<tr>
<th>R/C</th>
<th>Compressive modulus</th>
<th>Compressive strength</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Prefactor</td>
<td>Exponent</td>
</tr>
<tr>
<td>RF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$10^{3.211} \pm 0.033$</td>
<td>2.87 $\pm$ 0.04</td>
</tr>
<tr>
<td>200</td>
<td>$10^{2.350} \pm 0.041$</td>
<td>2.48 $\pm$ 0.08</td>
</tr>
<tr>
<td>300</td>
<td>$10^{2.133} \pm 0.058$</td>
<td>2.65 $\pm$ 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$10^{4.043} \pm 0.028$</td>
<td>2.77 $\pm$ 0.05</td>
</tr>
<tr>
<td>200</td>
<td>$10^{3.550} \pm 0.053$</td>
<td>2.53 $\pm$ 0.06</td>
</tr>
<tr>
<td>300</td>
<td>$10^{3.504} \pm 0.056$</td>
<td>2.76 $\pm$ 0.06</td>
</tr>
</tbody>
</table>

All data $\pm 1$ standard deviation.

laboratory show that silica aerogels prepared from base catalyzed TMOS (tetramethoxy silane) have an exponent equal to $2.8 \pm 0.2$ [41]. In contrast to the silica aerogels, SAXS data show that RF and carbon aerogels are not mass or surface fractals. Nevertheless, the correlation functions of the organic aerogels agree more closely with the base catalyzed silica aerogels than the acid catalyzed silica aerogels [42].

Although the scaling exponents are the same for both RF and carbon aerogels, the prefactors differ as a function of the matrix material and the R/C ratio. We find that the prefactors scale inversely with the R/C ratio for either type of organic aerogel. As the R/C ratio and the interconnected particle size decrease, the modulus actually increases due to an apparent improvement in particle interconnectivity. At equivalent densities, RF aerogels prepared at R/C = 50 are $\sim 7 \times$ stiffer than RF aerogels prepared at R/C = 300. A comparison of RF and carbon aerogels prepared under identical catalyst conditions show that the prefactors are an order of magnitude larger for the carbonized materials. Thus, carbon aerogels are $\sim 10 \times$ stiffer than their RF analogs at equivalent densities. The prefactors and scaling exponents for the modulus data are listed in table 1. The $\pm$ values are the standard deviations determined by linear least-squares fitting of the data.

The compressive strength of these aerogels as a function of density are shown in fig. 5. The scaling exponents are the same for all materials with a value of $2.4 \pm 0.3$. Once again, the prefactors vary as a function of material and R/C ratio with the strongest aerogels being prepared in carbon at low R/C ratios. The prefactors and scaling exponents for the strength data are listed in table 1.

To ascertain the effects of pyrolysis upon the aerogel microstructure, it is helpful to examine the reduced modulus as a function of reduced density, i.e. $E/E_s = f(p/p_s)$ where the subscript 's' designates a property of the solid material from which the aerogel is composed. This analysis permits a comparison of the structural efficiency of foams made from different materials. Figure 6 shows the above relationship for carbon and RF aerogels prepared at R/C = 200. From this plot, we conclude that the degree of interconnection between particles is improved after carbonization. Al-

![Fig. 5. A log-log plot of compressive strength vs. density for RF and carbon aerogels synthesized at [resorcinol]/[catalyst] ratios equal to 50, 200, and 300.](image-url)
Fig. 6. A log–log plot of reduced compressive modulus vs. reduced density for RF and carbon aerogels prepared at a [resorcinol]/[catalyst] ratio equal to 200. Calculations were based upon: (1) a density of 1.3 g/cm$^3$ and modulus of 3.5 GPa for crosslinked resorcinol–formaldehyde, and (2) a density of 1.5 g/cm$^3$ and a modulus of 24 GPa for glassy carbon.

Differences in microstructure are reflected in the compressive properties of the organic aerogels. In all cases, the aerogels exhibit a power–law relationship between modulus or strength and bulk density. The scaling exponents were found to be $2.7 \pm 0.2$ for the modulus and $2.4 \pm 0.3$ for the strength, independent of the matrix material or the synthetic conditions under which the aerogels were formed. The latter variables directly affected the magnitude of the prefactors in the scaling law relationships. The magnitude increases with decreasing particle size, increasing degree of particle interconnectivity, and improved properties of the matrix material.

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References