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Effect of uni-axial loading on the nanostructure of silica aerogels

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ABSTRACT

Aerogels are unique materials offering a combination of remarkable properties that make them useful in a wide range of applications. However, aerogel materials can be difficult to work with because they are fragile. The intent of the work presented here was to study the relationship between axial loading and pore structure in aerogel material. Silica aerogel samples with a bulk density of 0.1 g/mL were compressed by uni-axial force loads from 1 to 5 kN which resulted in stress levels up to 23 MPa. The resulting change in the pore distribution was observed using nitrogen desorption analysis and scanning electron microscopy. Uncompressed aerogel samples exhibit peak pore volume at diameters of about 20 nm. As the aerogels are subjected to increased loading, the location of the peak volume moves to smaller diameters with a reduced volume of pores occurring above this diameter. The peak diameter, the average pore diameter and pore volume all decrease and scale with increasing maximum stress while the surface area of the aerogel samples remains unaffected at about 520 m^2/g. When combined with data from the literature, the relation between maximum pore diameter and applied stress suggests a failure mechanism dominated by bending induced fracture.

1. Introduction

Aerogels consist of an amorphous solid matrix surrounded by nano-scale sized pores, with porosities in the 90–99% range. This unusual structure gives silica aerogels a variety of unique properties including low density, good optical transparency, and high surface area. They also have extremely low thermal and electric conductivities and can be made super-hydrophobic. Considering their low density, aerogels are relatively strong but they exhibit somewhat complex mechanical behavior; they are brittle in tension yet plastic in compression [1].

A number of studies have been performed to characterize the mechanical properties of aerogels. These studies use a variety of techniques to determine the elastic or Young's modulus, including measuring the compression of the material due to mercury porosimetry [2–4], 3-point beam bending, [5], the measurement of sound velocity [7,8], and uni-axial loading [9]. Gronauer et al. [7] measured the sound velocity in aerogels and developed a power law relation between Young's modulus and aerogel bulk density. Although values vary depending on aerogel preparation, untreated silica aerogels with densities near 0.1 g/mL exhibit Young's moduli near 1.0 MPa. Studies by other groups have investigated the nature of the exponent in the power law (Woignier et al. [6], Scherer et al. [2], and Pirard and Pirard [10]). Significant work has also been done to strengthen aerogels using a variety of methods including aging (Einarsrud et al. [11]) the addition of fibers (Parmenter and Milstein [12]) and cross-linking (Leventis et al. [13], Meador et al. [14], and Boday et al. [15]).

Mercury porosimetry can be used to investigate the mechanical properties of aerogels [16]. Mercury does not penetrate the pores of an aerogel; it instead acts as a compaction medium. When subjected to mercury porosimetry, an aerogel structure experiences iso-static compression and the change in sample volume associated with increasing mercury pressure can be related to the volumetric strain. Scherer et al. [2] used mercury porosimetry to show that silica aerogel deforms elastically under small strains, yields at higher levels and then experiences plastic deformation. Woignier et al. [17] used mercury porosimetry to compress silica aerogel in the plastic regime and small angle X-ray scattering (SAXS) to study the evolution of the structure. The aerogel specimens shrank irreversibly and the SAXS data indicated that the mean particle size and cluster compactness were unaffected by compression but the cluster size decreased. These structural changes resulted in a change in the value of the elastic modulus.

Pirard et al. [4] observed the behavior of silica–zirconia aerogel material iso-statically compressed. They used mercury porosimetry to compact the samples and nitrogen adsorption to study the effects of this compaction on pore size. Using a simple failure model they concluded that the pores collapse due to buckling of the pore walls. Dieudonne and Phalippou [3] showed that compression by mercury porosimetry leads to a decrease in pore size and pore volume but does not affect surface area. They showed that this is in contrast to

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the effects of sintering where a decrease in surface area accompanies the decrease in pore size and volume. Pirard et al. [18] present a summary of the collapse and intrusion effects of mercury porosimetry on sol–gel materials.

While many studies have used the mercury porosimetry method only a few researchers have looked at the effects of uni-axial loading. Lemay et al. [9] performed a study on aerogel material using uni-axial loading but they did not study the pore size evolution under these conditions. Han et al. [19] studied the effect of uni-axial loading on nanoporous silica material that was fabricated by pelletizing silica particles into monolithic disks with densities of 0.7–1.1 g/mL. They found that the overall behavior of the material was ductile and, like Pirard et al. [4], they attributed the plastic deformation to buckling of the pore walls parallel to the external loading. They also found that the nanopore volume distributed over a broader range of smaller pore sizes after compression to stresses as high as 700 MPa, suggesting that the larger pores are broken down to smaller ones.

In the work presented here we have investigated the mechanisms of pore collapse in silica aerogels under uni-axial loading conditions. As described above, there are a number of studies that have used mercury porosimetry to do this. However, under these conditions the sample is compressed iso-statically. To our knowledge, there are no prior studies that have described the effect of uni-axial loading on the pore structure and pore distribution of silica aerogel material.

2. Methods and materials

2.1. Aerogel synthesis

We use a rapid supercritical extraction (RSCE) process to make aerogels (see Gauthier et al. [20, 21], Roth et al. [22], and Anderson et al. [23]). This technique uses a hydraulic hot press to bring the solvent within the pores of the sol–gel to high temperature and pressure so that it can be directly extracted as a supercritical fluid in a three- to eight-hour process without the need for solvent exchange.

The aerogels were made using a recipe based on tetramethylorthosilicate (TMOS, CAS 681-84-5). We used TMOS:methanol:water:ammonia in a molar ratio of 1:12:4:7.4×10^{-3}. The TMOS was acquired from Sigma Aldrich at 98+% purity. Reagent-grade methanol, acquired from Fisher Scientific, and laboratory quality deionized water were used without further treatment. The 1.5-M ammonia catalyst was prepared by dilution of concentrated ammonia (Fisher Scientific, Reagent A.C.S. grade) with deionized water. A single batch required 80 mL of the precursor mixture, which was obtained by mixing 17 mL of TMOS, 55 mL of methanol, 7.2 mL of water and 0.27 mL of 1.5-M ammonia. The precursors were mixed in a beaker, which was placed in an ultrasonic bath for 2 min for additional mixing before processing in the hot press.

The gels are processed in a 76 by 76 by 19 mm high steel mold with nine 23-mm diameter holes. This mold is placed on a high temperature Kapton®/graphite gasket located on the bottom platen of the hydraulic hot press and the precursor solution is poured into the nine 23-mm-diameter holes. Another piece of gasket material is placed on top of the mold and the press is closed. The hydraulic press undergoes five steps in the processing of the aerogels. They are: (1) heating: the restraining force is set to 214 kN while temperature increases linearly to 290 °C over 4 h; (2) dwell: the press conditions are held constant at 214 kN and 290 °C for 1 h, allowing for thermal equilibration; (3) release: the restraining force is lowered to 9 kN at a rate of 9 kN/min (23 min); (4) dwell: the press conditions are held constant at 9 kN and 290 °C for 15 min to allow the supercritical fluid to escape from the mold chambers; (5) cooling: in the last step, the press platens cool down to 32 °C over a 70-minute period. When the processing is complete, the mold is taken from the hot press and the aerogel samples are removed. The entire process takes approximately 7 h to complete. Four batches of silica aerogel samples were fabricated over a 48-hour period. Each batch consisted of nine monolithic aerogel samples, which yielded a total of 36 samples for testing.

2.2. Compression tests

The best monolithic aerogel samples, those with the fewest chips or cracks, were selected for mechanical testing. The aerogel samples were compressed using an MTS Insight 5 mechanical tester, which has an axial loading capability of up to 5 kN and is capable of constant speed compression. The load cell is calibrated to within 1.5 N and the displacement sensor on the platens is accurate to within 0.01 mm. Each sample was massed and photographed before and after compression. During sample compression the lower plate was fixed and the upper plate was connected to the load cell and allowed to move axially. The plate speed was set to 2.54 mm/min. Data recording started once the sample made contact with the upper plate and the load cell reading exceeded 1 N. The top plate stopped moving down when the terminal load was reached. Each sample was compressed to 1, 2, 3, 4 or 5 kN.

2.3. Characterization

The bulk density of each sample was calculated prior to compression testing using the initial volume and mass of the sample. Load and extension measurements were converted to stress and strain by dividing the applied force by the initial cross-sectional area of the sample and dividing displacement by the initial height of the sample. The elastic modulus was then computed by estimating the slope of the stress strain curve at strain levels from 10 to 20%.

Some of the aerogel samples were imaged using a Zeiss EVO-50XVP scanning electron microscope. Samples were attached to round metal stages using 12-mm carbon adhesive tabs and sputter coated with a mixture of gold and palladium in a Denton Desk IV sputter coater. The aerogels were imaged at a working distance of 6 to 9 mm. A relatively low beam voltage of 3.5–7.5 kV was used to reduce charging.

Each sample was analyzed in a Micromeritics ASAP 2010 gas adsorption analyzer. Samples were crushed prior to analysis and 0.1–0.35 g of aerogel material was placed in a sample tube. Each sample was then degassed at 90 °C for 1 h and then at 200 °C for a minimum of 4 h. The BET surface area analysis was performed using nitrogen at five relative pressure values between 0.05 and 0.25. Then nitrogen was adsorbed at thirteen relative pressures from 0.1

Table 1
Estimates of measurement uncertainty.

Measurement	Typical value	Uncertainty estimate	Source of uncertainty estimate
Density (g/mL)	0.1	7%	Calculated from mass, volume measurement uncertainty
Load (kN)	0–5	0.001	Load cell calibration
Extension (mm)	0–16	0.01	Sensor accuracy
Modulus (MPa)	0.55–0.90	12%	Calculated from load, extension, area uncertainty
BET surface area (m^2/g)	500	20	Mass measurement, instrument precision
Peak diameter (nm)	10–20	2	Instrument precision
BJH avg diameter (nm)	10–20	2	Instrument precision, repeatability
Pore volume (cm^3/g)	0.1–4	0.3	Mass measurement, instrument precision