Elastic nonlinearity of aerogels

J. Gross and J. Fricke

Physikalisches Institut der Universität Würzburg, Am Hubland, D-8700 Würzburg, Germany

R. W. Pekala and L. W. Hrubesh

Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, California 94550

We have investigated the sound propagation in SiO_2 aerogels and three types of organic aerogels: resorcinol formaldehyde, melamine formaldehyde, and vitreous carbon. The main parameter determining the sound velocity is the aerogel density; however, the bond strength and cross linking also influence the stiffness of these materials. Furthermore, we show that at least two types of low-density aerogels become less stiff and consequently the sound velocity is lowered when the specimens are uniaxially compressed. We explain this in terms of a model for the internal structure.

I. INTRODUCTION

Aerogels are sol-gel-derived supercritically dried materials with extraordinarily large porosity, i.e., low density.[1-3] Typical densities are around 100 $kg\,m^{-3}$, corresponding to porosities of 95%. Recently, silica aerogels with densities as low as 5 $kg\,m^{-3}$ (porosity 99.8%) were produced.[4] High densities are often achieved in these materials via sintering of the silica matrix. Although most aerogels are made of SiO_2 or other metal oxides,[5] the synthesis of organic or organic-based aerogels has been reported.

Two features regarding the elastic properties of aerogels are especially interesting: first, the scaling of the sound velocity with density,[6,7] which is often discussed in terms of percolation theory or fractal structures; second, the decrease of elastic moduli of silica aerogels with increasing compressive stress.[8]

A "normal" solid body, on the contrary, shows increased stiffness if compressively stressed. This is understandable as the interatomic potential energy curves are brought into their repulsive branch, where they generally rise faster than proportional to $(x - x_0)^2$, where $x - x_0$ is the deviation from the equilibrium distance x_0 of the building units. Nonporous vitreous silica is one of the rare exceptions. Recently the elastic nonlinearity of silica aerogels with densities between 180 and 360 $kg\,m^{-3}$ was satisfactorily explained in terms of the nonlinear scaling of vitreous silica.[9]

In this work the decrease of elastic moduli is reported for low-density aerogels made of resorcinol formaldehyde (RF), melamine formaldehyde (MF), and vitreous carbon (C).[10] The latter were made by pyrolysis of RF aerogels at 1050 °C in an inert atmosphere. Furthermore the range of densities covered for silica aerogels in this study is extended over more than one order of magnitude toward lower densities.

II. EXPERIMENTAL TECHNIQUES

Sound velocities of aerogels are conveniently measured with two piezoelectric transducers for signal transmitting and receiving, respectively.[8] As aerogels are generally destroyed when brought into contact with a wetting liquid, no contact agent could be used. This required parallel, flat surfaces of the specimens in order to couple a sufficient amount of ultrasonic energy into and out of the samples. The whole apparatus was mounted in a vacuum vessel. Thus sound velocities could be measured under variation of air pressure. This is of importance especially for the low-density silica aerogels. Typical sample dimensions were 10 mm in diameter and 30 mm in length. Generally the two transducers are used as pistons in order to improve the acoustical contact. Depending on the specimen, i.e., their sound velocity and attenuation, frequencies between 5 kHz and 5 MHz were chosen.

The variation of the sound velocity with external load was measured at 180 kHz using the transducers to apply uniaxial stress. A special technique was used to automatically record small changes of the sound velocity.

The transmitting transducer was excited with 300 V ac pulses at approximately 1000 repetitions/s. After preamplification the receiver signal was fed into a boxcar averager triggered by the transmitter pulse. The gate of the boxcar averager was adjusted to a zero of the receiver signal with negative slope. Using the input offset control, the averaged output was matched to the gate delay control voltage. Connecting the averaged output to the delay control input then caused the boxcar averager to track the selected zero of the received signal. The delay control voltage is directly proportional to the time delay between trigger pulse and gate position and is recorded with a computer controlled digital voltmeter.

One total loading cycle lasted typically 200 s. At least three cycles were performed to characterize one speci-
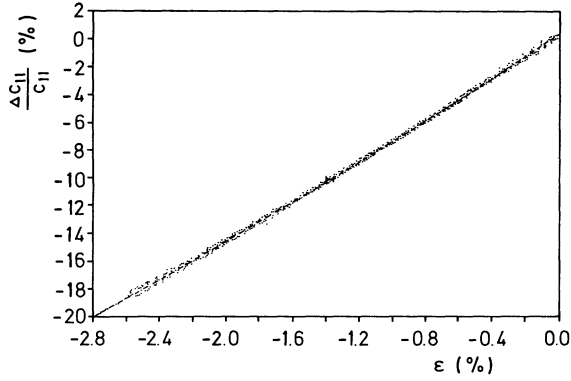

FIG. 1. Relative change of the elastic constant c_{11} as a function of strain ε for a SiO$_2$ aerogel ($\rho = 48$ kg m^{-3}). The slope S_c is 8.0 ± 0.4 for this specimen.

men. The typical strain was a few percent. All of the samples exhibited more than 98% recovery of the maximum applied strain per cycle; for most samples the recovery was better than 99.5%.

The accuracy was limited by the following effects: First, the sample thickness was measured to about $\pm$ 5 μm. Second, the jitter is about 0.1 μs for times above 100 μs and 0.01 μs for times shorter then 100 μs. Third, the time delay of the boxcar averager does not only vary with the traveling time of the sound wave, but to a minor degree also with the amplitude of the received signal. The latter may change drastically at low stresses due to improved acoustical coupling. This error does not show in the spread of individual data points, however, it can be estimated to be < 1 μs.

From the change in sample thickness and time measurements the sample strain ε and sound velocity c_l were calculated. From the sound velocity and the density ρ_ε at strain ε the elastic constant c_{11} was derived according to

$$c_{11} = c_l^2 \rho_\varepsilon .$$

The data are plotted as $(c_{11} - c_{11.0})/c_{11.0}$ vs ε, where $c_{11.0}$ is the value of c_{11} for $\varepsilon = 0$, and are fitted to second-order polynomials (Fig. 1). The second order was included as a control value only. Normally the zero- and second-order coefficients are negligible; here the first-order coefficient S_c is of interest. It represents the slope in Fig. 1.

III. EXPERIMENTAL RESULTS

A. Sound velocities

The sound-velocity data collected in this work are compared with earlier data on untreated and sintered aerogels[11,12] (Fig. 2). In general, the sound velocity varies greatly with density. However, if aerogels of a given density with different chemical and microstructural composition are compared a large velocity spread is observed which is not due to experimental errors: e.g., at $\rho \approx 100$ kg m^{-3} for carbon aerogels $c_l \approx 500$ ms^{-1} and for RF
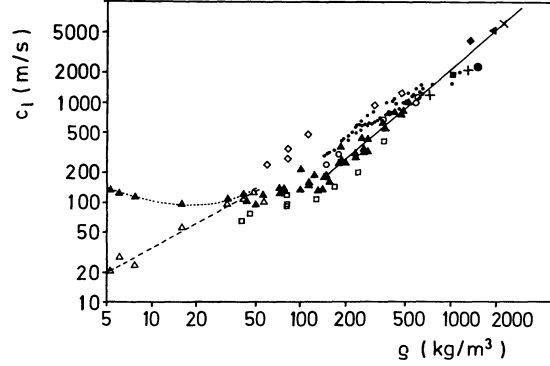

FIG. 2. Measured sound velocities c_l of various aerogels and related materials as a function of density ρ. The materials are: $\times$, vitreous silica; ◀, opal; $+$, SiO$_2$ xerogels; ·, sintered SiO$_2$ aerogels; ▲, SiO$_2$ aerogels in air; $\triangle$, SiO$_2$ aerogels evacuated; □, RF aerogels; ■, RF xerogels; ○, MF aerogels; ●, MF xerogels; ◇, carbon aerogels; ◆, carbon xerogels. The dashed and solid lines represent scaling laws $c_l \propto \rho^{0.8}$ and $c_l \propto \rho^{1.3}$, respectively; the dotted curve is calculated according to the theory for aerogels in air assuming isothermal compression Ref. (11).

aerogels $c_l \approx 100$ ms^{-1} results. Heat-treated aerogels in general show higher sound velocities than untreated aerogels of the same density. The heat treatment reduces the number of dangling bonds and improves the binding between neighboring sites.

For densities below 50 kg m^{-3} the elastic properties of the enclosed air contribute significantly to the sound propagation; therefore we also performed measurements on evacuated specimens in this density range.

B. Elastic nonlinearity

In Fig. 3 the slopes S_c are shown versus density for aerogels made of different materials (SiO$_2$, RF, MF, and C). SiO$_2$ aerogels of low densities ($\rho < 60$ kg m^{-3}) exhibit the most pronounced nonlinearity, i.e., the largest slopes. Typically $S_c = 6$–10 is obtained, which means that for a
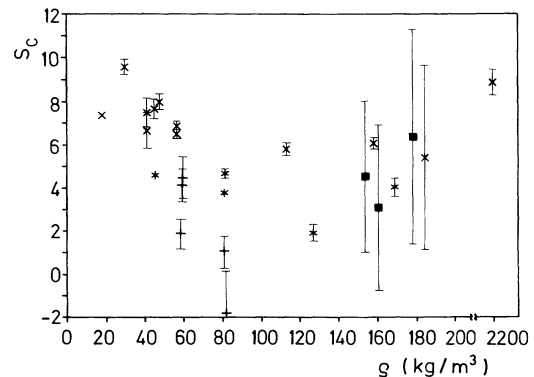

FIG. 3. Slopes $S_c = d[(c_{11} - c_{11.0})/c_{11.0}]/d\varepsilon$ as a function of density for low-density aerogels made of SiO$_2$ ($\times$), RF ($*$), MF (■), and C ($+$). For nonporous vitreous silica the value is $S_c = 10.8 \pm 0.6$ Ref. (13).

strain $\varepsilon = -1\%$ the elastic modulus c_{11} decreases by 6–10%. For increased density $(60 < \rho < 180$ kg m$^{-3})$ $S_c \approx 6$ is observed, while for nonporous vitreous silica $S_c = 9.0 \pm 0.6$ holds.[13]

The carbon aerogels show a positive S_c only for $\rho < 80$ kg m^{-3}. Typical S_c values for RF aerogels are 2–5, with no significant ρ dependence. For MF aerogels the error bars (due to small sample sizes) are too large to allow a definite conclusion.

IV. DISCUSSION

From the variation of S_c with ρ in Fig. 3 we can conclude that the explanation for the nonlinearity of SiO$_2$ aerogels given in Ref. 9 is not appropriate for low densities: A pure scaling of material properties ought to result in a constant S_c equal to that of vitreous silica. Obviously, the observed density variation of S_c must therefore be related to an influence of the microstructure of the aerogels on the elastic nonlinearity. Although the higher-order elastic moduli of the skeleton material of the carbon aerogels are not known up to now, the fact that S_c varies with density, too, allows us to draw the same conclusion for the carbon aerogels. For the RF aerogels a similar conclusion would require the knowledge of the higher-order elastic moduli of nonporous RF, as S_c for the RF aerogels is approximately independent of density. The same argument holds for the MF aerogels because of the large experimental uncertainties in the S_c values. However, as negative higher-order elastic moduli (which lead to positive S_c) are quite rarely found in nonporous materials, the behavior of all of the aerogels studied may be at least regarded as unusual.

The explanation we give to explain the low-density nonlinearity is the model proposed earlier.[12] It makes use of the fact that highly porous aerogels are composed of chain- or barlike structures. Due to the statistical growth process of the gel these bars are normally not straight but rather are bent like "knees." When stressed, the knee angles are decreased and thus the bar becomes weaker even if the material it is made of is elastically linear. The longer the bars or chains are, the more easily they can be bent, which causes the observed density dependence of the elastic nonlinearity. The model thus does not rely on special material properties. It seems suitable to describe the special elastic behavior of low-density aerogels in which the length of the nanometer-sized bars is large enough compared to their diameter to be significantly bent under compression. For larger densities the bending

becomes insignificant and thus material properties determine the elastic behavior, in agreement with the results in Ref. 9. This breakoff point does not necessarily occur at the same volume fraction for different materials because the bars themselves might also exhibit a nonuniform substructure. For example, they might be porous themselves or show varying cross sections (i.e., consist of spheres connected by necks of smaller diameter). Porosity of the bars would result in shorter and thicker bars at a given volume fraction and thus shift the breakoff point to lower densities. On the contrary, necks reduce the effective cross section for bending of the bars without major effects on the density. Consequently, the breakoff point would occur at a higher volume fraction. This is probably the case in silica aerogels.[14,15]

Up to now, our model has been described in a merely qualitative manner. In a former study,[16] a quantitative approach was tried to evaluate the mean knee angle that is needed to explain the nonlinear behavior of silica aerogels. Although it seems that the result (knee angle $\approx 120°$) was quite realistic, that approach was far too simple to account for the numerous effects that have to be explained. For example, the bending was restricted to the knee itself, whereas the rest of the bar was assumed to be totally stiff; the higher-order elasticity of the skeleton material was not taken into account; no shear deformation was allowed for; the problem was restricted to one dimension. All these features are needed, however, to model theoretically the density dependence of S_c. This is currently under study. The scope of this paper is to cover the experimental data. A more quantitative theoretical model will be published in the near future.

V. OUTLOOK

In general it would be helpful to have lower densities available for C and MF aerogels in order to confirm the trends shown in Fig. 3. A definite decision for or against our model for organic aerogels also requires the knowledge of the higher-order elastic constants for nonporous MF and RF. To our knowledge, these have not yet been measured.

[1] *Aerogels*, edited by J. Fricke (Springer, Berlin, 1986).

[2] *2nd International Symposium on Aerogels* (ISA 2), edited by R. Vacher, J. Phalippou, J. Pelous, and T. Woignier (Les Editions de Physique, Les Vlis CEDEX, France, 1989) [Rev. Phys. Appl. **24**, C4 (1989)].

[3] J. Fricke and A. Emmerling in *Chemistry, Spectroscopy and Applications of Sol-Gel Glasses*, edited by R. Reisfeld and C. K. Jorgensen, Springer Series in Structure and Bonding Vol. 77 (Springer, Berlin, 1992), pp. 37–87.

[4] L. W. Hrubesh, T. M. Tillotson, and J. F. Poco, in *Better Ceramics through Chemistry III*, edited by C. J. Brinker, D. E. Clark, D. R. Ulrich, and B. J. Zelinski, MRS Symposia Proceedings No. 180 (Materials Research Society, Pittsburgh, 1990), pp. 315–319.

[5] S. J. Teichner, G. A. Nicolaon, M. A. Vicarini, and G. E. E. Gardes, Adv. Colloid Interface Sci. **5**, 245 (1976).

[6] T. Woignier, J. Pelous, J. Phalippou, R. Vacher, and E. Courtens, J. Non-Cryst. Solids **95&96**, 1197 (1987).

[7]E. Courtens, J. Pelous, J. Phalippou, R. Vacher, and T. Woignier, Phys. Rev. Lett. 58, 128 (1987).

[8]J. Gross, G. Reichenauer, and J. Fricke, J. Phys. D 21, 1447 (1988).

[9]P. Xhonneux, E. Courtens, J. Pelous, and R. Vacher, Europhys. Lett. 10, 733 (1989).

[10]R. Pekala, in Fifth International Conference on Ultrastructure Processing, Orlando, 1991, edited L. Hench, (in press).

[11]J. Gross, J. Fricke, and L. W. Hrubesh, Acoust. Soc. Am. (to be published).

[12]J. Gross, R. Goswin, R. Gerlach, and J. Fricke, in 2nd International Symposium on Aerogels (ISA 2), edited by R. Vacher, J. Phalippou, J. Pelous, and T. Woignier [Rev. Phys. Appl. 24, C4-185 (1989)].

[13]E. H. Bogardus, J. Appl. Phys. 36, 2504 (1965).

[14]A. Emmerling, J. Gross, R. Gerlach, R. Goswin, G. Reichenauer, and J. Fricke, J. Non-Cryst. Solids 125, 230 (1990).

[15]T. Woignier and J. Phalippou, J. Non-Cryst. Solids 100, 404 (1988).

[16]J. Gross, Diploma thesis, Physikalisches Institut der Universität Würzburg, Würzburg, Germany, 1987 (unpublished).