CONF-960401--8

UCRL-JC-123480
PREPRINT

Structural Evolution in Carbon Aerogels as a Function of Precursor Material and Pyrolysis Temperature

J. Gross
C.T. Alviso
J.K. Nielsen
R.W. Pekala

This paper was prepared for submittal to the
Materials Research Society 1996 Spring Meeting
San Francisco, CA
April 8-12, 1996

April 1996

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED. 8

MASTER

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

STRUCTURAL EVOLUTION IN CARBON AEROGELS AS A FUNCTION OF PRECURSOR MATERIAL AND PYROLYSIS TEMPERATURE *

J. Gross, C.T. Alviso, J.K. Nielsen, and R.W. Pekala, Chemistry & Materials Science Department, Lawrence Livermore National Laboratory, Livermore, CA 94550

Abstract

Several organic reactions that proceed through a sol-gel transition have been identified at LLNL. The most-studied reaction involves the aqueous polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde. Recently, we have shown that phenol can be added to this polymerization as a comonomer. The resultant crosslinked gels are supercritically dried from carbon dioxide (T_c= 31°C, P_c = 7.4 MPa) to give resorcinol-phenol-formaldehyde (RPF) aerogels. Because RPF aerogels are composed of a highly crosslinked aromatic polymer, they can be pyrolyzed in an inert atmosphere to form vitreous carbon monoliths. The resultant aerogels are black in color and no longer transparent, yet they retain the high porosity (40-98 %), ultrafine cell/pore size (< 50 nm), high surface area (600-800 m^2/g), and interconnected particle (~10 nm) morphology of their organic precursors. In this study, we examine the acoustic and mechanical properties of these materials as a function of precursor material and pyrolysis temperature.

Introduction

One of the most serious drawbacks for applications of low density aerogels is their low elastic moduli and therefore difficult handling. Improvement of the elastic properties while retaining the low density is therefore an important goal. Another concern is the cost of producing aerogels; While the supercritical drying process can hardly be avoided, at least for target densities below 100 kg m^{-3}, one can try do use cheaper materials. This led to the introduction of phenol into the established resorcinol - formaldehyde (RF) [1] system for producing organic aerogels. While reducing cost, the elastic moduli of resorcinol - phenol - formaldehyde (RPF) aerogels were to be held at the level of pure RF aerogels or even higher. The ultimate goal is to arrive at carbon aerogels, produced by pyrolysis of the organic aerogels, of equal quality than the carbonized pure RF species. The present study is dedicated to evaluate the effect of several parameters during the production process on the elastic moduli of carbonized RPF (CRPF) aerogels, namely the gel density, the phenol content and the pyrolysis temperature. Like in many earlier publications, measuring the sound velocity is used as a convenient and accurate method to determine elastic properties [].

Experimental

Throughout this paper, the theoretical density of crosslinked polymer in a wet gel (excluding solvent) in untis of kg m^{-3} is used to designate the gel concentration (e.g. R100 for a gel containing 100 kg m^{-3} crosslinked polymer). Since a few percent of linear shrinkage is observed during supercritical drying, the density of the organic aerogels will be slightly higher than the R value. RPF gels were prepared by the method published earlier [2] for production of RF aeogels, with a [monomer] to [catalyst] molar ratio of R/C = 200; however, in addition to pure recorcinol a molar mixture of 75% resorcinol and 25% phenol, as well as a 50:50 mixture, was used. The resulting gels and aerogels will be named RPF100:0, RPF 75:25, RPF 50:50, respectively. The gels were cylinders of typically 24 mm diameter and 37 mm length. Gel concentrations from R100 to R500 were produced for pure RF (100:0) and R100 to R400 for the formulations containing phenol. Supercritical drying was achieved in the usual way. All aerogels were characterized with respect to mass, volume, density and elastic moduli, as described below, as dried and after each pyrolysis step. The pyrolysis was performed in an inert gas atmosphere at 600, 750, 900, 1050 and 1500 °C in this order for each sample; samples were loaded into the furnace, heated to the pyrolysis temperature with a heating rate of 10 K/min, remained at the designated temperature for 4 h and were allowed to cool within several hours; the samples pyrolyzed at 1500 °C were held only for

2.5 h. The pyrolyzed samples are black in colour and represent pure carbon aerogels[anything published about these yet?], designated as CRPF 100:0 etc. Between pyrolyzation steps samples were stored in a dessicator to prevent excessive moisture adsorption that would increase the density.

The evolution of mass m, volume V and density ρ of the samples was followed by weighing and measuring the diameter and length of the cylinders. The relative mass and volume was calculated with respect to the non-pyrolyzed aerogels. Volume and density data are estimated to be accurate to within 2%. Sound velocities of shear and longitudinal waves, c_T and c_L, were measured along the axis of the cylinders using a pair of transducers for each mode. One transducer of each pair acted as transmitter and one as receiver. The center frequency of the transducers was 2.25 MHz. The travel time of the sound waves was measured using a digital oszilloscope with a precision of about 0.2 µs in the carbon aerogels, resulting in a relative error of the sound velocity of a few percent for the highest density samples and below 1% for low density samples. From the sound velocity and the density, the elastic moduli c_{11} and G were calculated according to

$$G = c_T^2\,\rho, \quad c_{11} = c_L^2\,\rho, \qquad (1)$$

where G is the shear modulus and c_{11} the longitudinal modulus. In general the behaviour of the shear modulus was very similar to that of c_{11}. Therefore we present data on c_{11} only and use the Poisson ratio ν to discuss the relative changes of the moduli. It was determined from the sound velocities by

$$\nu = (x^2/2 - 1) / (x^2 - 1), \quad x = c_L / c_T \quad . \qquad (2)$$

The Poisson ratio is rather sensitive to small errors in the sound velocities. Due to higher attenuation, the accuracy of the sound velocity measurement was considerably lower for the organic aerogels; therefore, no shear velocity measurement was attempted prior to pyrolysis, as this value was only needed to determine the Poisson ratio.
(BET, TEM for selected samples?).

Results

Elastic moduli of porous materials in general and of aerogels in particular are usually observed to obey a scaling relationship with density of the form

$$c_{11} / c_{11,0} = (\rho / \rho_0)^{\alpha} \quad , \qquad (3)$$

where α is called the scaling exponent [3,4,5]. For RF aerogels this scaling relationship was recently shown to merely an approximation for a limited density range [6]. On the other hand, since the scaling exponents are typically rather large (between 2 and 6 []) it is difficult to directly compare elastic moduli of different samples if their densities are not equal. To be able to compare elastic moduli, scaling law fits were applied to all series of samples discussed in this paper even though, as will be seen, sometimes a concave line would represent the data more accurately. The method is justified since we are mainly interested in observing trends, not absolute values.

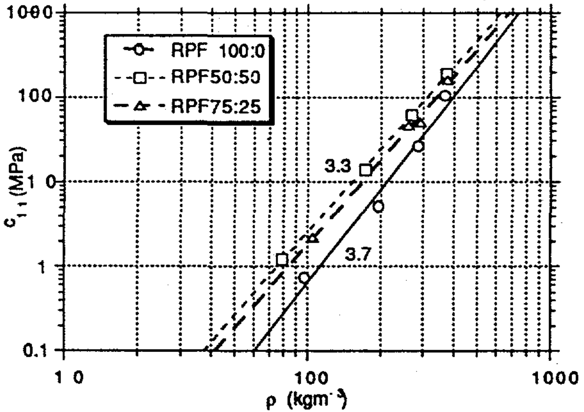

Figure 1: Elastic modulus c_{11} as function of density for unpyrolyzed RPF aerogels

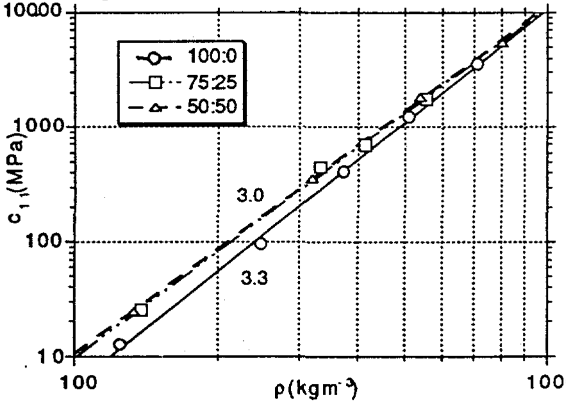

Figure 2: Elastic modulus c_{11} as function of density for CRPF aerogels pyrolyzed at 600 °C

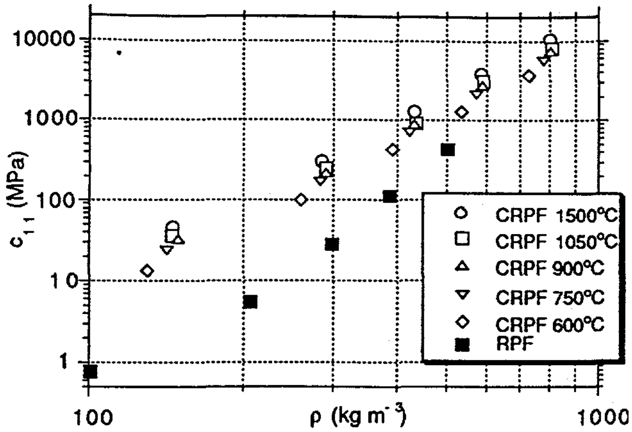

Figure 3: Modulus c_{11} vs. density for CRF (100:0) aerogels pyrolyzed at various temperatures

Figure 1 shows a comparison of the elastic moduli of the unpyrolyzed, organic aerogels. The data for pure RF aerogels do indeed not fall on the fit line very well; it seems like the lowest density sample lies considerably above a scaling line established by the rest of the samples. The pure RF samples obviously exhibit the lowest elastic moduli as compared to the series containing phenol. In addition, the scaling exponent is much smaller for the latter series, and the scaling line better describes the data. The elastic moduli of the samples after the first pyrolysis treatment at 600 °C are shown in Fig. 2. In all three series the scaling exponent is lower after pyrolysis, however the differences between the samples containing phenol and the pure RF samples has become smaller.

Note also that the density was increased and that the elastic moduli are almost an order of magnitude higher after pyrolysis. As an example for the influence of pyrolysis at successively higher temperature, Fig. 3 shows the evolution of elastic moduli for the pure RF (RPF100:0) series. Subsequent pyrolysis steps at higher temperatures are seen to cause only minor change of the densities and moduli. In order to directly compare the influence of the pyrolysis at various temperatures on the scaling behaviour, the scaling exponent α and the value of the modulus $c_{11,1}$ at a given density $\rho_1 = 300$ kg m^{-3} was determined for each series of samples. This value for ρ_1 waschosen because it lies approximately in the center of the density range covered by samples and thus the influence of the variation of α is minimized. The results of this procedure are depicted in Figs. 4 a and b. Higher pyrolysis temperatures are seen to still increase the moduli slightly, however the effect becomes smaller with every step. Also, the difference between CRPF 75:25 and CRPF 50:50 deminishes after the first pyrolysis treatment. The scaling exponent does not significantly vary after pyrolysis at 600 °C.

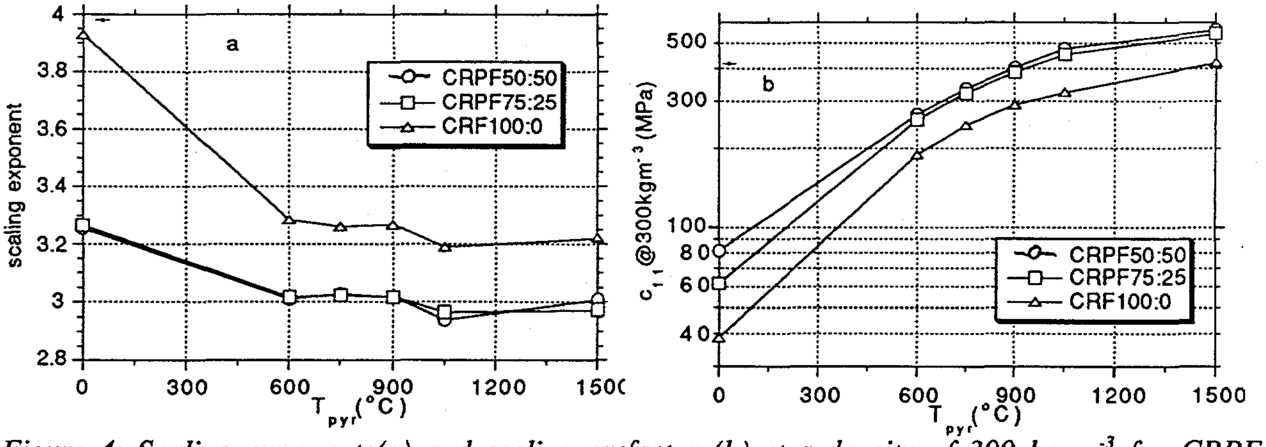

Figure 4: Scaling exponent (a) and scaling prefactor (b) at a density of 300 kg m^{-3} for CRPF aerogels as function of pyrolyzation temperature

The variation of the scaling exponent implies that the pyrolysis treatment has different effects on samples of different densities. This is examined in more detail for the pure RF series in Figs. 5 a - d. The equivalent plots for the phenol containing series look very similar, so they can be omitted. Figure 5a shows the evolution of the relative elastic modulus for each of the RPF100:0 samples as function of the pyrolysis temperature. In order to distingiush the curves, the common point $c_{11}/c_{11,0} = 1$ for the non pyrolyzed samples was suppressed. The modulus increases more drastically for the lower density samples. In Fig. 5b the change of relative density is plotted in the same manner, calculated from the relative volume change (Fig. 5c) and relative mass change (Fig. 5d) of the

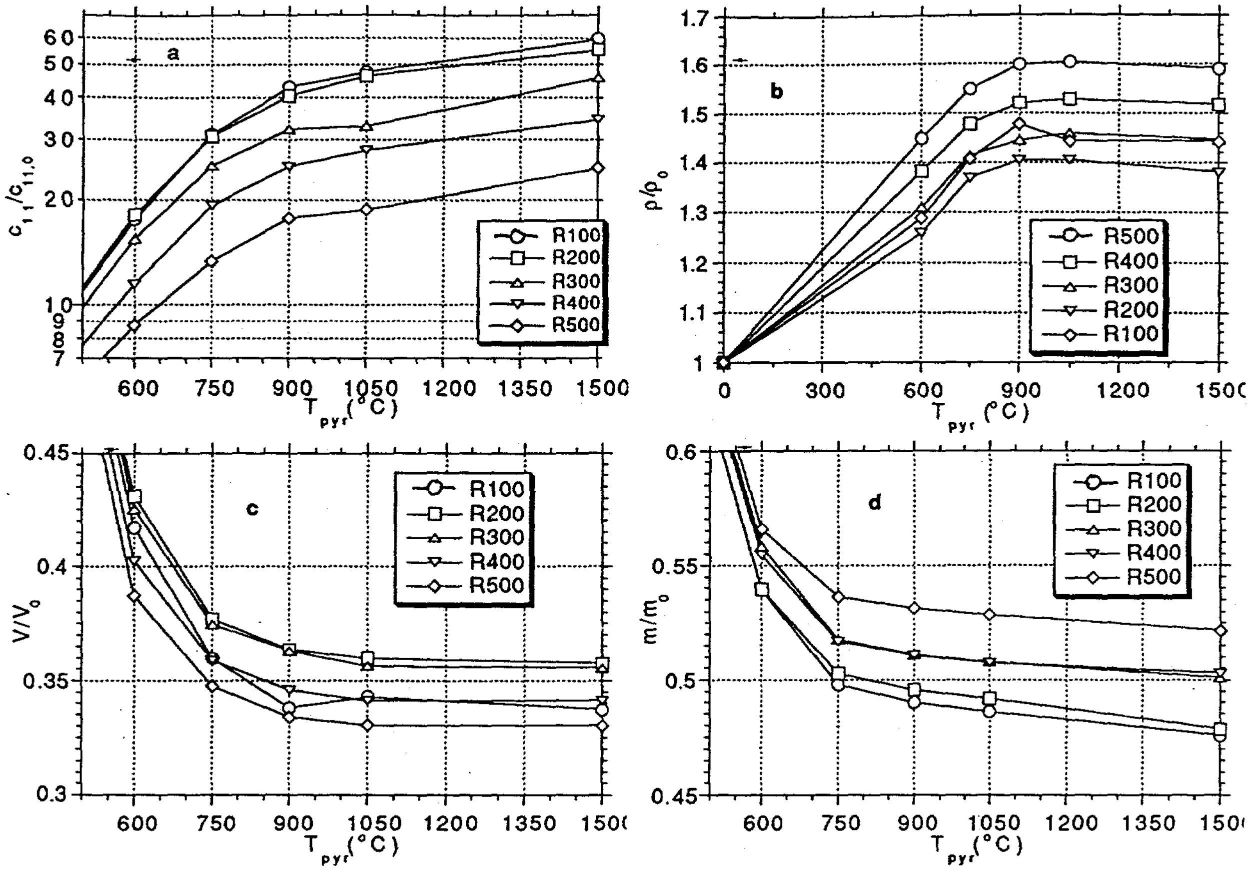

Figure 5: Relative change of (a) modulus, (b) density, (c) volume and (d) mass of pure RF aerogels during pyrolysation as function of pyrolyzation temperature samples.

The density of the R500 sample increases most strongly, which is observed to be a result of this sample exhibiting the least mass loss and the most shrinkage. Except for the R100 sample, which is not the one to shrink to the largest extent, the trends are consistent throughout the series. Finally, Fig. 6 shows the relative change of modulus, density, volume and mass, averaged over each series and over all pyrolysis temperatures, as well as the slopes of the relative modulus and the relative mass versus the gel concentration averaged over the pyrolysis temperatures, as a function of phenol content. While most of the values just confirm that the relative changes already discussed hold for the phenol series as well, there are a few significant and consistent variations with phenol content. These are, first, the relative density change, which is much larger for higher Phenol concentrations; the effect is obviously due to a considerably higher amount of shrinkage in the higher phenol series. And, second, the average slope of relative modulus is negative for the pure RF series (100:0), almost zero for the 75:25 and distinctly positive for the 50:50 series. This means that for pure RF the relative modulus is higher for the lower gel concentrations, while for the 50:50 the modulus increases more strongly at higher gel concentrations.

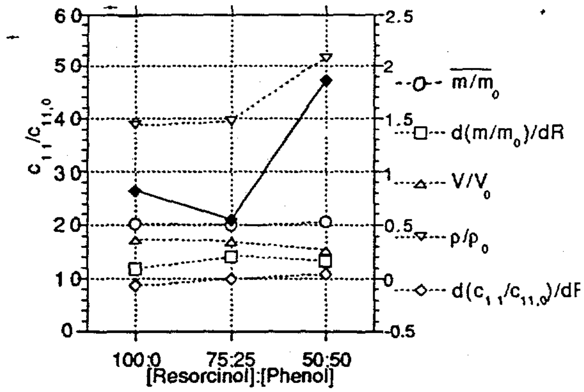

Figure 6: Average change of relative quantities during pyrolyzation as function of phenol content in the RPF aerogels

Discussion

The variation of elastic moduli with density of porous materials can be related to structural efficiency of the material. For example, most low density foams are deformed by bending of their structural entities. Since in conventional foams all material contributes to the elastic network, the structural efficiency is close to optimal; a scaling law of the moduli is observed and the scaling exponent equals 2 [7]. Aerogels, on the other hand, were shown to be less structural efficient and have higher scaling exponents - which means that with decreasing density the elastic moduli decrease much faster [3]. There are several possible ways to account for the reduced structural efficiency of aerogels. They typically deviate from an ideal, optimally efficient material in that the diameter of the bending structures is not constant (neck radii between particles), the beams are not straight (tortuosity) and not all the beams are connected to the network on both sides (dead ends). The neck radii can be assumed to be independent of density at a given R/C ratio [8], therefore they will not alter the scaling exponent. No reliable information is available for the tortuosity; however it is believed that it is only weakly density dependent. In addition, it enters into the modulus only with the first power, so only a minor error will result in neglecting this factor. We are thus left with the connectivity of the skeleton as the factor that has the largest influence on the scaling exponent. More specifically, the connectivity of the gel network has to increase with increasing density in order to produce a scaling exponent in excess of 2. Since the phenol containing aerogels exhibit consinstently higher moduli, the addition of phenol has to increase the structural efficiency somehow.

To explain the influence of precursor material on the elastic moduli we have to adress the chemical differences of phenol and resorcinol first. Both monomers are trifunctional, but the phenol is much ive less react~~ant~~. While the particle growth mechanism is totally different for the present organic system [8], the strong difference in monomer reactivity reminds of a silica system with TMOS (tetramethoxysilane) and MeTMOS (Methyl-Trimethoxysilane), where the latter monomer is reacting slower [9]. In that work is was found that due to the difference in reactivity the slower reacting monomer predominantly condensed onto the surface of primary particles that mainly consisted of TMOS. Due to the reduced functionality of MeTMOS and its blocking of surface reactivity of the primary particles, however, the elastic moduli of the mixed aerogels were lower than for the pure TMOS aerogels [10]. Both effects are not expected to occur in a resorcinol phenol system. However, if we assume that the resorcinol is able to build up a continuous gel before large parts of the phenol can react, this will lead to a surface layer of polymer that can produce a structurally more efficient gel. The measurable effects expected to arise from a model like this are increased relative neck radii between particles and a reduction of dead ends (part of whom have been connected by the phenol surface layer). Since increased connectivity can also be obtained by increasing the density at a given monomer composition, similar effects are expected from higher density (gel concentration) and higher phenol content. This has already been shown to be the case (trivially) for the modulus (Fig.1); however, it is also true for the shrinkage during pyrolysis, as can be seen from comparison of Figs. 6 and 5c: higher phenol content as well as higher gel concentration lead to more shrinkage during pyrolysis. Now it is not straightforward to explain why the shrinkage during pyrolysis should be stronger for higher concentration gels; in fact, if the shrinkage was closely linked to the stiffness of the aerogel the opposite effect would be expected. The third systematically varying quantity in Fig. 6 is the slope of relative modulus increase vs. gel concentration. Two effects contribute to this slope: first, at higher density there is also a higher relative increase of density, so the modulus varies stronger at higher gel concentrations, as is indeed observed for the RPF 50:50 series; on the other hand, at lower densities there is more poorly connected mass that can be attached to the load bearing network. The latter effect dominates for pure RF (100:0), therefore the slope ends up to be negative.

With increasing amount of phenol the connectivity is improved especially at low densities, leaving less opportunity for improvement during pyrolysis. Note that these arguments hold independent of any explanation for the increased connectivity of RPF aerogels - they are only based on measured data.

In contrast to the variation of shrinkage with density, the larger relative mass loss at low concentrations during pyrolysis is reasonable. One possibile explanation is the decreased permeability of the pore space in higher density aerogels, which causes a higher resistance to gaseous species formed during pyrolysis to escape the aerogel. It is reasonable to assume a higher chance of readsorption and chemical reaction with the network.

A general observation may be added at this point: the elastic moduli of carbon aerogels at a given density obviously are enhanced by higher pyrolysis temperatures. On the other hand, the longer heating and cooling times needed and the more expensive equipment would probably be a drawback in commercial applications. Figure 4b shows that pyrolysis at 1050 °C is a good compromise since this temperature is reached with common furnaces.

Conclusion

We have shown in this paper that it is possible to include phenol into the sol-gel polymerization of resorcinol with formnaldehyde. The elastical properties of the resulting aerogels are superior to the pure resorcinol formaldehyde aerogels. This advantage is preserved during the pyrolysis of the organic aerogels. The phenol containing gels are shown to exhibit higher structural efficiency especially at low densities. Higher pyrolysis temperatures always lead to increased elastic moduli, however the gain tends to level off above 1050 °C. Some of the more subtle changes, especially of shrinkage during pyrolysis, are not yet fully understood. A preliminary model is presented to account for the increased connectivity of RPF aerogels, but more information is needed to support it.

---

1 R.W.Pekala, C.T.Alviso, J.D.LeMay, Ultrastructure Processing conference, Orlando, Florida, Feb 1991

2 R.W. Pekala, J. Mat. Sci 24, 3221 (1989)

3 J.D.LeMay, R.W.Hopper, L.W.Hrubesh, R.W.Pekala, MRS Bulletin **15**(12), 30-36 (1990)

4 J.Gross, J.Fricke, J. Non-Cryst. Solids **145**, 217-222 (1992)

5 T.Woignier, J.Pelous, J.Phalippou, R.Vacher, E.Courtens, J. Non-Cryst. Solids **95/96**, 1197-1202 (1987)

6 J.Gross, G.W.Scherer,C. Alviso, R. Pekala, "Elastic properties of crosslinked Resorcinol-Formaldehyde gels and aerogels", to be published

7 L.J.Gibson, M.F.Ashby, Proc. R. Soc. London A 382, 43-59 (1982)

8 D.W.Schaefer, R.W.Pekala, G.Beaucage, J. Non-Cryst. Solids 186, 159-167 (1995)

9 F.Schwertfeger, W.Glaubitt, U.Schubert, J. Non-Cryst. Solids 145, 85-89 (1992)

10 F.Schwertfeger, A.Emmerling, J.Gross, U.Schubert, J.Fricke, in: Sol-Gel Processing and Applications, ed. by Yosry A.Attia, Plenum Press, New York 1994, 343-349

*This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.