17. C. F. Baillie, D. A. Johnston, R. D. Williams, *ibid.* **335**, 469 (1990).
18. This result can be obtained by covering a sphere with equilateral triangles of side ℓ and taking the limit $\ell \rightarrow 0$. A similar procedure was followed in (*19*) for a cylindrical surface; in that case it was found that $\kappa = \sqrt{3}\lambda/2$.
19. H. S. Seung and D. R. Nelson, *Phys. Rev. A* **38**, 1005 (1988).
20. Unlike (*13*) (in which the maximum number of nearest-neighbor bonds was limited to eight), we do not explicitly restrict the maximum number of neighbors. We find, for example, that the average maximum connectivity of a monomer is ~12 for the largest systems studied (for $\lambda = 0$). We have checked, however, that restricting the maximum number of nearest neighbors as in (*13*) does not prevent the observed collapse to branched polymer behavior.
21. K. Fujikawa, *Nucl. Phys. B* **226**, 437 (1985).
22. G. Gompper and D. M. Kroll, *J. Phys. I France* **1**, 1411 (1991).
23. C. Itzykson, in *Proceedings of the GIFT Seminar, Jaca 85*, J. Abad *et al.*, Eds. (World Scientific, Singapore, 1986), pp. 130–188.
24. In evaluating $\bar{\kappa}$ we have used $\langle A\rangle \approx 2N_s(1 - 2/N)\langle A_\Delta\rangle$, with $\langle A_\Delta\rangle \approx 0.78$, where $\langle A_\Delta\rangle$ is the average area of an elementary triangle.
25. See (22) for a partial treatment of this problem for tethered membranes.
26. H. P. Duwe, J. Käs, E. Sackmann, *J. Phys. (Paris)* **51**, 945 (1990).
27. E. Evans and W. Rawicz, *Phys. Rev. Lett.* **64**, 2094 (1990).
28. M. Mutz and W. Helfrich, *J. Phys. (Paris)* **51**, 991 (1990).
29. J. M. Di Miglio, M. Dvolaitzky, L. Leger, C. Taupin, *Phys. Rev. Lett.* **54**, 1686 (1985).

30. Supported in part by the University of Minnesota Army High Performance Computing Research Center, U.S. Army contract DAAL03-89-C-0038, NATO grant CRG910156, and the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 266. D.M.K. has benefited from correspondence with M. E. Fisher and discussions with G. Grest.

30 September 1991; accepted 24 December 1991

Thermal Conductivity of Monolithic Organic Aerogels

X. LU, M. C. ARDUINI-SCHUSTER, J. KUHN, O. NILSSON, J. FRICKE, R. W. PEKALA

The total thermal conductivity λ of resorcinol-formaldehyde aerogel monoliths has been measured as a function of density ρ in the range from ρ = 80 to 300 kilograms per cubic meter. A record-low conductivity value in air at 300 K of λ ≈ 0.012 watt per meter per kelvin was found for ρ ≈ 157 kilograms per cubic meter. Caloric measurements under variation of gas pressure as well as spectral infrared transmission measurements allowed the determination of solid conductivity, gaseous conductivity, and radiative conductivity as a function of density. The development of such low conductivity materials is of great interest with respect to the substitution of environmentally harmful insulating foams made from chlorofluorocarbons.

OPACIFIED MONOLITHIC SILICA AEROgels (*1–3*) have smaller thermal conductivities than all other thermal insulants at ambient conditions (*4*). The reasons include: (i) the high porosity of the SiO_2 skeleton and thus the small solid conductivity (*5*); (ii) the extremely small pore sizes, typically 1 to 100 nm across, that cause a partial suppression of gaseous thermal conductivity (*4*); and (iii) a high specific extinction of thermal radiation if an opacifier (for example, carbon black) is integrated into the SiO_2 skeleton (*4*).

The smallest conductivity value for an opacified SiO_2 aerogel with $\rho = 120$ kg m^{-3} in air was measured to be $\lambda = 0.013$ W m^{-1} K^{-1} (*4*). Such aerogels thus have a large potential for applications in freezers and refrigerators as well as heat storage and transport systems. As nonporous organic materials in general have smaller solid thermal conductivities than nonporous inorganic materials under comparable conditions, we surmised that organic aerogels would provide an even higher thermal resistance than SiO_2 aerogels. In order to verify this assumption we performed caloric measurements on resorcinol-formaldehyde (RF) aerogels. In addition we quantified the radiative heat transfer by determination of the spectral infrared (IR) optical extinction.

These RF aerogels were made by base-catalyzed aqueous polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde (*6, 7*). In this polymerization, resorcinol serves as a trifunctional monomer capable of adding formaldehyde in the 2-, 4-, and 6-ring positions. This monomer is especially reactive because of the attached hydroxyl groups. The substituted resorcinol rings agglomerate to form clusters 3 to 20 nm across in solution. The cluster size is regulated by the concentration of the catalyst (for example, sodium carbonate). The clusters have surface groups, such as $-CH_2OH$, that react further to form a dark red gel. The solution (basically water) in the pores of the RF gel is exchanged with an organic solvent (for example, acetone) and then with CO_2. Supercritical drying with respect to CO_2 (temperature $T \approx 31°C$, critical pressure $p_c \approx 74$ bar) was performed. The resulting RF aerogels show a considerable mechanical flexibility in contrast to their SiO_2 counterparts, which in general are brittle.

Aerogels of RF that are 1 cm thick provide enough IR absorption to be treated as optically thick. Thus radiative transport is a local phenomenon that can be described by the thermal conductivity λ_r:

$$\lambda_r = (16/3)n^2\sigma T_r^3/[e(T_r)\rho] \qquad (1)$$

where n is the mean index of refraction of the insulation (for low-density insulations, n is close to 1), σ is the Stefan-Boltzmann constant, T_r is the radiative temperature [calculated from the boundary temperatures T_1 and T_2 (*1*, p. 96) as $T_r^3 = (1/4)(T_1^2 + T_2^2)(T_1 + T_2)$], and the product $e \cdot \rho = E$ is the extinction coefficient, which is equal to $1/l_{photon}$, where l_{photon} is the photon mean free path. In optically thick insulations the photon mean free path is very small compared to the thickness of the specimen. The temperature-dependent specific extinction coefficient $e(T_r)$ is derived from the spectral specific extinction (Fig. 1) by proper spectral averaging (Rosseland mean) (*8*).

The solid conductivity λ_s of monolithic aerogels strongly depends on the density. For silica aerogels, the relation is (*9*)

$$\lambda_s \propto \rho^\alpha, \text{ where } \alpha \approx 1.5 \qquad (2)$$

in the density range 70 to 230 kg m^{-3}. The conductivity λ_{evac} for evacuated opacified and thus optically thick aerogels can be approximated by the arithmetic sum of the solid and the radiative conductivity:

$$\lambda_{evac} = \lambda_s + \lambda_r \qquad (3)$$

In general λ_s is much less temperature-dependent than λ_r. If the specific extinction shows only a weak temperature dependence, an approximate value for e can thus be derived from the slope of the $\lambda_{evac}(T_r)$ versus T_r^3 curve. The extrapolation $\lambda_{evac}(T_r^3 \rightarrow 0)$ yields an estimate for the solid conductivity. As the organic aerogels cannot withstand temperatures above ~80°C, the available temperature range is too small to allow an accurate determination of e. In this case the specific extinction in the IR infrared must be derived from the specific spectral extinction (absorption) with subsequent Rosseland averaging (*8*).

If air or any other gas is introduced into the porous aerogel, the conductivity increases due to the gaseous conductivity as (*10*):

$$\lambda_g = \frac{\lambda_{g0}\Pi}{1 + 2\beta Kn} \qquad (4)$$

X. Lu, M. C. Arduni-Schuster, J. Kuhn, O. Nilsson, J. Fricke, Physikalisches Institut, Universität, Am Hubland, D-8700 Würzburg, Germany.
R. W. Pekala, Chemistry and Materials Research Science Department, Lawrence Livermore National Laboratory (LLNL), Livermore, CA 94550.

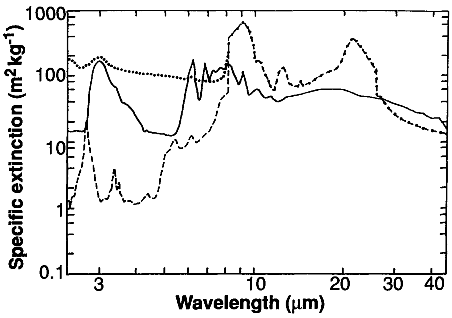

Fig. 1. Spectral specific extinction (absorption) $e(\Lambda)$ of organic RF aerogel (—), inorganic pure SiO_2 aerogel (- - -), and opacified (5% carbon black) SiO_2 aerogel (· · ·).

where Π is the porosity and λ_{g0} is the gaseous conductivity of a free gas. The parameter β takes into account the energy transfer between gas molecules and the limiting structure. For air in aerogel $\beta \approx 2$ (*10*). The Knudsen number *Kn* is

$$Kn = l_g/\varnothing \tag{5}$$

where l_g describes the mean free path of the gas particles and ∅ the pore diameter. Because *Kn* is of the order of 1 for aerogels at atmospheric pressure (p_g = 1 bar and $l_g \approx$ 70 nm), the gaseous conductivity λ_g remains considerably below the value λ_{g0}. As a rule of thumb $\lambda_g < 0.01$ W m^{-1} K^{-1} at 1 bar for aerogels. The total conductivity of air-filled monolithic aerogels thus becomes

$$\lambda_t = \lambda_s + \lambda_r + \lambda_g = \lambda_{evac} + \lambda_g \tag{6}$$

Equation 6 can only be used for systems in which the coupling between the different heat transfer modes is negligible.

We measured λ_t by squeezing a Pt hot wire between a pair of identical aerogel blocks, each 2 cm by 3 cm by 10 cm in size. In order to reduce contact resistances the surfaces adjacent to the wire were diamond-turned. The elasticity of the organic aerogel then allows proper embedding of the wire into the aerogel, and virtually no slit between the blocks remained. The conductivity of the specimens is derived in the usual way (*11*) by feeding a constant power per unit length into the wire and evaluating the increase of the wire temperature with time. In addition, IR optical transmission measurements were performed in order to determine the specific spectral extinction (absorption) of the specimens over the wavelength range from 2.3 to 45 µm.

The spectral specific absorption of RF aerogels was drastically different from that for pure and opacified SiO_2 aerogels (*4*) in the near IR (Fig. 1). By Rosseland averaging, we derived the temperature-dependent specific extinction *e* needed for Eq. 1 (Fig. 2). Typically *e* was 50 m^2 kg^{-1} at 300 K for RF aerogels, 20 m^2 kg^{-1} for pure SiO_2 aerogels, and 80 m^2 kg^{-1} for the opacified SiO_2 aerogels. For RF aerogels the estimated radiative conductivity at room temperature was 0.001 W m^{-1} K^{-1} for $\rho \approx 250$ kg m^{-3}.

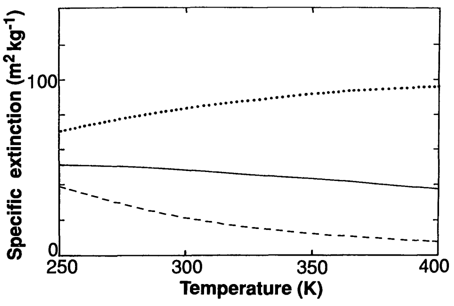

Fig. 2. Rosseland-averaged specific extinction $e(T)$ of RF aerogels (—) versus *T*; for comparison, data for pure SiO_2 aerogels (- - -) and opacified (5% carbon black) SiO_2 aerogels (· · ·) are also depicted.

The thermal conductivity of the RF aerogels varied with gas pressure (Fig. 3). At 300 K and atmospheric pressure, total conductivities were between λ_t = 0.012 and 0.018 W m^{-1} K^{-1} but were between λ_{evac} = 0.004 and 0.014 W m^{-1} K^{-1} for the evacuated samples. A plot of λ as a function of density ρ (Fig. 4), shows that λ_t undergoes a flat minimum of ~0.012 W m^{-1} K^{-1} around $\rho \approx 160$ kg m^{-3}. The various conductivity components λ_r, λ_s, and λ_g also varied as a function of density; λ_s increased from about 0.002 to 0.014 W m^{-1} K^{-1}, whereas λ_g decreased from about 0.010 to 0.003 W m^{-1} K^{-1} as the density increases from 80 to 300 kg m^{-3}. The accuracy of λ_t is about ± 0.5 × 10^{-3} W m^{-1} K^{-1}; the components λ_g and λ_s are reliable within ±1 × 10^{-3} W m^{-1} K^{-1} and the relative error of λ_r is estimated to be ±15%.

The data show that monolithic organic aerogels at ambient temperatures have low conductivities in air. The lowest value measured was 0.012 W m^{-1} K^{-1} at a density of 157 kg m^{-3}, which is slightly lower than conductivities of opacified SiO_2 aerogels, for which the smallest measured conductivity was 0.013 W m^{-1} K^{-1} for ρ = 120 kg m^{-3} (*4*). The low conductivity values achieved open a vast potential for practical applications if such aerogels can be produced cheaply. Evacuation to 10 mbar is sufficient to suppress gaseous thermal conduction and to achieve thermal conductivities as low as 0.006 W m^{-1} K^{-1} for the 80-kg m^{-3} specimen.

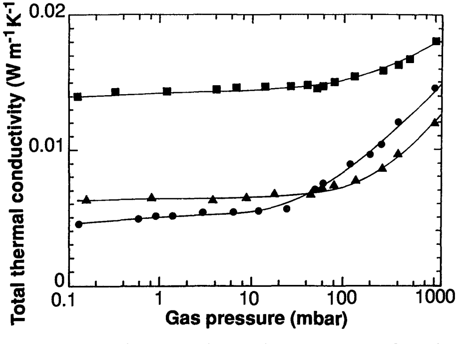

Fig. 3. Total thermal conductivity λ_t of various RF aerogels versus gas (air) pressure p_g at room temperature; (●), 82 kg m^{-3}; (▲), 157 kg m^{-3}; and (■), 303 kg m^{-3}. The solid lines through the points are guides to the eye.

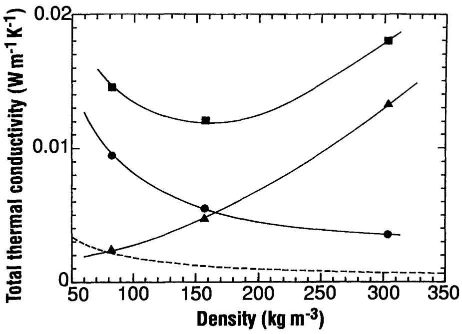

Fig. 4. Total conductivity λ_t (■), calculated radiative conductivity λ_r (- - -), gaseous conductivity λ_g (●), and solid conductivity λ_s (▲) of RF aerogels as a function of density ρ at ambient conditions. The solid lines through the points are guides to the eye.

Similar λ_s values have been determined for SiO_2 aerogels as for RF aerogels (Fig. 4), although the thermal conductivities of the nonporous basic material is much higher than that for RF aerogels. For vitreous silica, λ_s = 1.4 W m^{-1} K^{-1} and for organic polymers it lies between 0.15 and 0.3 W m^{-1} K^{-1} (*12*). An explanation may be the lower porosity and thus the larger solid-volume fraction of RF aerogels compared to SiO_2 aerogels at the same density.

REFERENCES

1. J. Fricke, Ed., *Aerogels* (Springer Verlag, Heidelberg, 1986).
2. R. Vacher, J. Phalippou, J. Pelous, T. Woignier, Eds., *Rev. Phys. Appl.* **24**, C4 (1989).
3. J. Fricke and A. Emmerling, in *Structure and Bondings*, R. Reisfeld and C. K. Jørgensen, Eds. (Springer Verlag, Heidelberg, 1991), vol. 77, pp. 37–87.
4. X. Lu *et al.*, *High Temp. High Pressures*, in press.
5. P. Scheuerpflug, H.-J. Morper, G. Neubert, J. Fricke, *J. Phys. D* **24**, 1395 (1991).
6. R. W. Pekala, *J. Mater. Sci.* **24**, 3221 (1989).
7. J. D. LeMay, R. W. Hopper, L. W. Hrubesh, R. W. Pekala, *Mater. Res. Soc. Bull.* **15** (no. 12), 19 (1990).
8. R. Caps and J. Fricke, in (*1*), pp. 110–115.
9. J. Fricke, X. Lu, P. Wang, D. Büttner, U. Heinemann, *Int. J. Heat Mass Transfer*, in press.
10. M. G. Kaganer, *Thermal Insulation in Cryogenic Engineering* (Israel Program for Scientific Translations, Jerusalem, 1969).
11. O. Nilsson, G. Rüschenpöhler, J. Groß, J. Fricke, *High Temp. High Pressures* **21**, 267 (1989).
12. Y. S. Touloukian, R. W. Powell, C. Y. Ho, P. G. Klemens, *Thermal Conductivity: Nonmetallic Solids*, vol. 2 of *Thermophysical Properties of Matter* (Plenum, New York, 1970).

17 September 1991; accepted 24 December 1991