Letters

Thermal conductivity of epoxy–aluminium powder mixtures

The following symbols are used in this letter:

A = area normal to heat flow (cm^2)
C = specimen conductance (cal sec^{-1} $°C^{-1}$)
C_a = conductance of aluminium (cal sec^{-1} $°C^{-1}$)
C_c = conductance of aluminium–epoxy (cal sec^{-1} $°C^{-1}$)
C_e = conductance of epoxy (cal sec^{-1} $°C^{-1}$)
C_w = conductance of water films (cal sec^{-1} $°C^{-1}$)
C_{air} = conductance of air films (cal sec^{-1} $°C^{-1}$)
C_{dry} = conductance of dry specimen (cal sec^{-1} $°C^{-1}$)
C_{wet} = conductance of wet specimen (cal sec^{-1} $°C^{-1}$)
d = thickness of epoxy shell around aluminium (cm)
f = fractional increment of radius (dimensionless)
g = fractional decrement of radius (dimensionless)
k = thermal conductivity of specimen (cal sec^{-1} cm^{-1} $°C^{-1}$)
k_a = thermal conductivity of aluminium (cal sec^{-1} cm^{-1} $°C^{-1}$)
k_c = thermal conductivity of composite (cal sec^{-1} cm^{-1} $°C^{-1}$)
k_e = thermal conductivity of epoxy (cal sec^{-1} cm^{-1} $°C^{-1}$)
k_h = thermal conductivity for hexagonal packing (cal sec^{-1} cm^{-1} $°C^{-1}$)
k_k = thermal conductivity for cubic packing (cal sec^{-1} cm^{-1} $°C^{-1}$)
k_{dry} = thermal conductivity of dry specimen (cal sec^{-1} cm^{-1} $°C^{-1}$)
k_{wet} = thermal conductivity of wet specimen (cal sec^{-1} cm^{-1} $°C^{-1}$)
n = number of spheres or cubes per cubic centimetre (cm^{-3})
P = vol % of aluminium (dimensionless)
R = effective radius (cm)
r = radius from the centre of a particle (cm)

In a variety of industrial applications epoxy adhesives are required to have an enhanced thermal conductivity. The normal method for changing this physical property is to add to the epoxy a filler of higher conductivity than the continuous phase. Prediction of the thermal conductivity of such resin-filler composites has become the object of a number of theoretical and experimental investigations.

In 1961 Tsao [1] reviewed the literature and proposed a two-phase statistical model. His analysis was a departure from early work which was based on an analogy with electrical conductivity. Some of the more recent investigations such as Garrett and Rosenberg [2], Meredith and Tobias [3], and Hamilton and Crosser [4] still used electrical analogy, however, with good results. Cheng and Vachon [5] obtained a solution to Tsao's equation and concluded that this gave better results than the older approach. Sundstrom and Chen [6] and Sundstrom and Lee [7] confirmed this finding by applying Cheng and Vachon's equation to polystrene and polyethylene containing, as a filler, very small glass spheres or powdered oxides of aluminium, calcium, or magnesium. Nielsen [8, 9] has obtained even better correlation by modifying earlier equations dealing with the elastic moduli of composite materials. Because high concentrations of metallic powders in an epoxy matrix pose somewhat of a special problem still another approach was tried.

In the present work a model is proposed based on particle-to-particle heat transfer between aluminium particles in an epoxy matrix. In the absence of typical shape, each powder particle is assumed initially to be spherical. This assumption is later modified. A diagram of the model is shown in Fig. 1.

The aluminium has such a high conductivity (roughly 1500 times that of the epoxy) that we may safely presume no significant temperature gradients exist within the metal particle. While this property promotes a heat flux normal to the surface, such flux lines are quickly bent into the shape of a flux cylinder between two aluminium

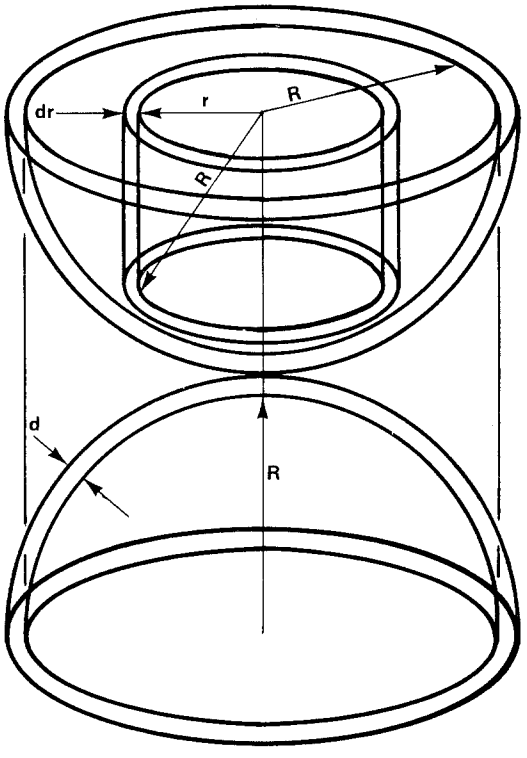

Figure 1 Model of aluminium spheres in an epoxy matrix.

hemispheres by reason of neighbouring aluminium particles and their attendant fluxes. The same argument dictates that the transfer of heat must be between two metallic hemispheres only, and not with other neighbouring particles.

In the model, heat flows from the upper to the lower hemisphere through a set of concentric epoxy cylinders of radius r, thickness dr, and length $2(R+d)-2\sqrt{(R^2-r^2)}$. The parameter d is the thickness of a spherical shell of epoxy, identical in all respects to the remainder of the epoxy, which surrounds each aluminium sphere. The conductance then, between two hemispheres is

$$C_e = \pi k_e \int_0^R \frac{r\,dr}{R+d-\sqrt{(R^2-r^2)}}, \quad (1)$$

while the conductance through either aluminium hemisphere is

$$C_a = 2\pi k_a \int_0^R \frac{r\,dr}{\sqrt{(R^2-r^2)}}. \quad (2)$$

The composite cylinder consisting of two hemispherical aluminium ends plus intervening epoxy has the conductance

$$C_c = \frac{1}{\frac{2}{C_a}+\frac{1}{C_e}} = \frac{\pi R k_a k_e \left[(R+d)\ln\left(\frac{R+d}{d}\right)-R\right]}{R k_a + k_e\left[(R+d)\ln\left(\frac{R+d}{d}\right)-R\right]}. \quad (3)$$

If we let d be a fraction of R, say fR, and multiply C_c by the cylinder length, $2R(1+f)$, and divide by the cross-sectional area, πR^2, we get the thermal conductivity of the composite cylinder.

$$k_c = \frac{2(1+f)k_a k_e\left\{(1+f)\ln\left(\frac{1+f}{f}\right)-1\right\}}{k_a + k_e\left\{(1+f)\ln\left(\frac{1+f}{f}\right)-1\right\}}. \quad (4)$$

If the aluminium spheres and their surrounding spherical shell of epoxy are stacked in hexagonal close-packed symmetry, we may pass a horizontal plane through the equators. An equilateral triangle joining the centres of three circles in this plane will then represent one unit of cross-sectional area normal to the heat flow. The area of this triangle is

$$A = \sqrt{3}(R+d)^2 = \sqrt{3}R^2(1+f)^2 \quad (5)$$

The fraction of this area occupied by aluminium is

$$\frac{\pi R^2/2}{\sqrt{3}R^2(1+f)^2} = \frac{\sqrt{3}\pi}{6(1+f)^2}, \quad (6)$$

which is transmitting heat with the conductivity k_c, while the remainder is transmitting heat with the conductivity k_e. Also, in hexagonal symmetry the aluminium spheres are not aligned in the precise direction of net heat flow, so that the downward component is only $\sqrt{\frac{2}{3}}$ times the sphere-to-sphere flow. The resulting thermal conductivity for hexagonal packing is

$$k_h = \frac{\sqrt{2}\pi}{6(1+f)^2}[k_c - k_e] + k_e. \quad (7)$$

A relationship can be obtained between the vol% of aluminium and the factor $(1+f)$. The tetrahedron joining the centres of three spheres in one plane and one sphere centrally nested in the

plane above represents one unit volume of the system. The vol% of aluminium inside this tetrahedron is then

$$P = \frac{50\sqrt{2}\pi R^3}{3(R+d)^3} = \frac{50\sqrt{2}\pi}{3(1+f)^3}. \quad (8)$$

Obtaining the value of $(1+f)$ from Equation 8, Equation 7 becomes

$$k_h = 0.04199P^{2/3}[k_c - k_e] + k_e. \quad (9)$$

For simple cubic packing of aluminium spheres, the unit of volume is a cube containing exactly one sphere. With cubic geometry the number of spheres (and the number of cubes) per cm^3 is

$$N = \frac{P/100}{(4/3)\pi R^3} = \frac{3P}{400\pi R^3} \quad (10)$$

The edge dimension of each cube is

$$N^{-1/3} = R\left(\frac{400\pi}{3P}\right)^{1/3}. \quad (11)$$

The fraction of the cross-sectional area normal to heat flow which is occupied by aluminium is

$$\frac{\pi R^2}{R^2\left[\frac{400\pi}{3P}\right]^{2/3}} = \left[\frac{3\sqrt{(\pi)}P}{400}\right]^{2/3} \quad (12)$$

This fraction is conducting with the conductivity k_c and the remainder conducts with k_e, so that the resulting equation for cubic packing is

$$k_k = 0.05612P^{2/3}[k_c - k_e] + k_e. \quad (13)$$

A series of six specimens was prepared ranging from 0 to 37.73 vol% of aluminium powder. The matrix, or continuous phase, was Epon 828 epoxy resin marketed by Shell Chemical Company with Epon curing agent D, cured at 150° C for 1 h. The powder was a nominal 2 μm aluminium, the particles of which appeared under the microscope to be spherical, but variable in size. Specimens were machined from the cured composite to conveniently fit the contact pads of the Cenco-Fitch thermal conductivity apparatus.

The effect of high thermal resistance at the interface between the contact pads and the specimen was minimized in the following manner. Each specimen was run in two ways: dry, and with both specimen surfaces painted with water. The results were treated as follows.

$$\frac{1}{C_w} + \frac{1}{C} = \frac{1}{C_{wet}} \quad (14)$$

$$\frac{1}{C_{air}} + \frac{1}{C} = \frac{1}{C_{dry}}.$$

Noting that $C_w = 23.419\ C_{air}$, and that the geometry is constant,

$$k = \frac{k_{wet}k_{dry}}{k_{wet} - 1.0446(k_{wet} - k_{dry})}. \quad (15)$$

Thermal conductivity k versus vol% aluminium is shown in Fig. 2.

If we choose an equation for thermal conductivity with a coefficient midway between that of Equation 9 and that of Equation 13, the fit of these data is not good because of the aluminium particle shape. Photomicrographs show that the aluminium, once incorporated into the matrix, agglomerates into much larger, very irregularly shaped particles. These aggregates approach each other more rapidly than spheres of the same volume, as the vol% of metal is increased. Thus there is much bridging or near-bridging between particles which behave similar to a higher concentration of spheres. In the model of hexagonal symmetry or of the cubic symmetry the increase of aluminium concentration is represented by an increase in the particle radius relative to a unit of volume (a tetrahedron or cube). So the irregular aggregates may be said to have an effective radius which is larger than the equivalent radius of such a particle.

If, in the various equations we let R be an effective radius, then the equivalent radius of a particle will be somewhat less, R-gR, and that Equation 8 becomes

$$P = \frac{50\sqrt{2}\pi(1-g)^3}{3(1+f)^3}, \quad (16)$$

that is,

$$1 + f = 3.9702P^{-1/3}(1-g). \quad (17)$$

An experimental point from Fig. 2 must be chosen

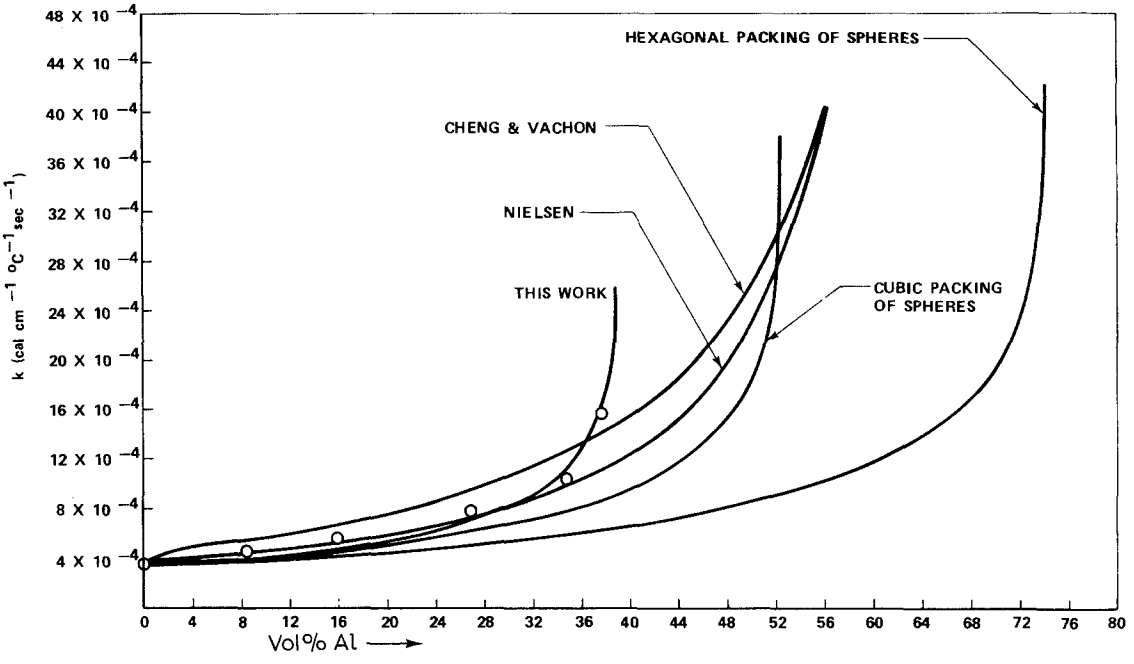

Figure 2 Thermal conductivity versus vol% of aluminium powder.

($P = 37.73\%$) to calculate $(1 + f)$ from a mean of Equation 9 and Equation 13. The $(1 - g)$ may be obtained from Equation 17. With this value the theoretical curve in Fig. 2 may be plotted.

Thus the following conclusions may be drawn:

(1) A particle-to-particle heat transfer model may be used to fit the experimentally determined thermal conductivities of epoxy-aluminium powder mixtures.

(2) Lower concentrations of aluminium powder in epoxy pose no difficulty to predicting thermal conductivities, however, higher concentrations in the vicinity of the maximum packing density present a more difficult case.

(3) Because the size and shape of the aluminium particle aggregates are indeterminate, data from one experimental point are needed to determine the remainder of the curve.

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