Thermal conductivity of epoxy adhesives filled with silver particles

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The thermal conductivity of a silver-filled epoxy adhesive has been measured with the transient hot wire technique at various temperatures and silver concentrations. Experimental results are compared with theoretical results for thermal conduction in two-phase materials. The results show that the thermal conductivity of silver-filled adhesives is higher than the theoretically expected values due to the formation of elongated agglomerates of silver particles.

Key words: metal/polymer composite; silver-filled epoxy adhesive; thermal conductivity; hot wire technique

Over the last two or three decades electrically conductive silver-filled epoxy adhesives have been in steadily increasing use in the microelectronics industry. Their primary application areas are the interconnection of electrical conductors, the attachment of passive electronic components such as resistors and capacitors, and the attachment of encapsulated active electronic components or bare silicon chips to substrates or packages. The primary physical property of these adhesives is high and stable electrical conductivity. Typically these adhesives have a specific electrical resistivity of 10^{-4} Ω cm or about two orders of magnitude higher than the best metallic conductors. This is appropriate for most applications.

One of the advantages of silver-filled epoxy adhesives is low processing temperature compared with alternative technologies such as soldering or silicon-gold eutectic bonding. In addition, there is no need for flux agents that have to be cleaned off as when soldering. This is currently an important aspect due to the prohibition in several countries of the frequently used chlorofluorocarbon (CFC) fluss cleaning agents. Also, the possible future prohibition against the use of lead could turn applications from solder to silver-filled adhesives.

Probably the most demanding application of silver-filled epoxy adhesives is the attachment of silicon chips to substrates, with high thermal conductivity as well as electrical conductivity being important properties in this regard. The reason for this is the rapid miniaturization of electronic devices. Power consumption density increases rapidly when the dimensions of the circuit elements shrink. Currently, advanced silicon chips approach 100 W cm^{-2} of heat dissipation; indeed, heat dissipation has already exceeded 100 W cm^{-2} in the field of power electronics where silicon chips are used to control heavy electrical machinery. Heat dissipation is a major technological problem in the application of these chips because they have a fundamental maximum operating temperature. In addition their reliability rapidly declines at increased operating temperatures. For these reasons the thermal conductivity of the silver-filled epoxy adhesives is a parameter of major importance.

This paper is concerned with measurement of the temperature-dependent bulk thermal conductivity of epoxy adhesives with different volume fractions of silver. Thermal conductivity measurements were carried out using the transient hot wire method. The results are compared with the theoretical results of Lewis and Nielsen[1] for thermal conduction in two-phase media.

Theory

The conductivity of a two-phase material depends on the conductivities of the matrix and filler, and the volume fraction and geometry of the filler material. In some cases the resistance in the interface between matrix and filler may be of significant influence. However, such a material may be considered to be a three-phase material with the interface as the third

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phase. The following review of theories will not include interface phenomena.

A particularly simple case is when the filler phase consists of fibres or rods arranged in the direction of conduction. The conductivity of such materials is described by a parallel coupling of the resistance in the matrix and the filler:

$$\frac{1}{\rho_C} = \frac{1-\phi_F}{\rho_M} + \frac{\phi_F}{\rho_F} \quad (1)$$

or, because conductivity is the reciprocal of resistivity:

$$\lambda_C = (1-\phi_F)\lambda_M + \phi_F\lambda_F \quad (2)$$

In these equations ρ is resistivity and λ is conductivity. The subscripts C, M and F refer to the composite, matrix and filler respectively. The volume fraction of filler material is ϕ_F. Slabs or plates arranged so that the direction of conduction is normal to their face is another equally simple case described by a series coupling of resistances:

$$\frac{1}{\lambda_C} = \frac{1-\phi_F}{\lambda_M} + \frac{\phi_F}{\lambda_F} \quad (3)$$

In the case of a general composite material these mixture rules represent the upper and lower limit of the conductivity. However, if the contrast of the composite material is large, the mixture rules converge to the conductivities of the filler and matrix materials respectively. In this case the equations are useless for the prediction of conductivity. The general case of a particulate filler of arbitrary size and shape is far more complex and no general theory has yet been developed.

Steady-state thermal conduction is described by the Laplace equation as:

$$a\nabla^2 T(x,y,z) = -q(x,y,z) \quad (4)$$

where a is the thermal diffusivity, $T(x,y,z)$ is the temperature at coordinates x, y, z and $q(x,y,z)$ is the heat dissipation density at coordinates x, y, z. The Laplace equation applies to widely different physical phenomena such as dielectrics, elasticity, diffusion and electrical conductivity. In these fields, theories of two-phase materials have been developed and some of these theories have been adopted by other fields of research to interpret experimental data. Maxwell[2] calculated the dielectric constant of a material consisting of spherical particles located at cubic lattice sites. The Maxwell equation was later used for the interpretation of thermal conductivity measurements of two-phase materials[3]. A major problem in the application of the Maxwell theory is that particles are normally not arranged in a regular lattice. They are randomly distributed with possibilities of percolation paths that will increase the conductivity, especially in high contrast composites. Tsao[4] developed a theory based on a parallel and series connection of resistances and a stochastic function describing the shape and distribution of the filler particles. The Tsao theory suffers from the difficulty of obtaining the stochastic function by experimental methods. Assumptions about this function have to be made, which limits practical applications of the theory.

Lewis and Nielsen[1] have presented a theory for thermal conduction in two-phase media without the disadvantages of the two previous theories:

$$\lambda_C = \lambda_M \frac{1 + AB\phi_F}{1 - B\psi\phi_F} \quad (5)$$

where $B = [(\lambda_F/\lambda_M) - 1]/[(\lambda_F/\lambda_M) + A]$, $\psi = 1 + [(1-\phi_m)/\phi_m^2]\phi_F$. A is a geometrical parameter reflecting the shape of the filler particles, see Table 1, and ϕ_m is the maximum packing fraction of the filler. The other notation is the same as in the previous equations.

A main achievement of the Lewis and Nielsen theory was the introduction of the geometry-dependent parameter A. This parameter takes care of the fact that elongated filler particles yield a higher conductivity than spherical particles if the volume ratio ϕ_F is equal. There is a relation between the aspect ratio of the particles and A. The Lewis and Nielsen theory also includes the concept of a maximum packing fraction of filler particles. The maximum packing fraction, ϕ_m, reflects that it is impossible to load more filler material into the matrix than ϕ_m. Tables 1 and 2 give some values of A and ϕ_m for particles of different shape.

The Lewis and Nielsen theory is mathematically simple and founded on quantities obtainable from experiment. Also the theory has been successfully employed to interpret experimental data on thermal conduction of two-phase materials[3]. These facts make it an attractive theory for practical work.

An interesting observation to be made from Equation (5) is that B is close to 1 for high contrast composites. Metal-filled epoxy is a high contrast composite. The thermal conductivity of the filler is typically two to three orders of magnitude larger than the thermal conductivity of the matrix. In the case of silver-filled epoxy the thermal conductivity of the matrix phase is 0.2 W m^{-1} K^{-1} and the thermal conductivity of the filler is 417 W m^{-1} K^{-1}. This implies that the conductivity of the filler has a negligible influence on the composite conductivity. The thermal conductivity of such composites is essentially

Table 1. Values for the shape parameter A in the Lewis and Nielsen theory of conduction in two-phase materials[9]

Particle shape	A
Cubes	1.5
Spheres	2.0
Randomly oriented rods:	
length/diameter = 4	2.1
length/diameter = 10	4.9
length/diameter = 15	8.4
length/diameter = 35	30

Table 2. Values for the maximum packing fraction ϕ_m in the Lewis and Nielsen theory[3]

Particle shape	Type of packing	ϕ_m
Spheres	Random close	0.601
Spheres	Hexagonal close	0.7405
Spheres	Cubic	0.524
Rods	Random	0.52

determined by the volume fraction ϕ_F, and the geometrical properties A and ϕ_m.

Experimental method

Measurements of thermal conductivity generally require careful consideration. Available techniques may be divided into steady-state or transient methods. Steady-state methods usually measure the temperature at two different positions in the sample and the heat flow between the positions. This enables calculations of the thermal resistance, from which the thermal conductivity is obtained if the geometry of the sample is known. These methods are conceptually simple but they suffer from inaccuracies due to use of two or more temperature measurement devices, uncertainty of geometry and heat loss to the surroundings. Surface effects, such as thermal contact resistance, may also affect the measurements. If heaters and temperature measurement devices are not attached properly to the sample, erroneous results may appear due to thermal resistances in the interfaces. The steady-state methods are also time consuming, especially on large samples with relatively low thermal conductivity. This is due to the time it takes to reach thermal equilibrium.

In transient methods, the temperature change as a function of time is measured. Normally only one temperature measurement device is used and the methods are generally less geometry-dependent. By careful experimental design, the influence of interface resistances between the experimental apparatus and the sample may be eliminated[5]. These methods are usually fast to perform, but the instrumentation is often more complex than for steady-state methods.

In this study the transient hot wire (THW) technique was used. This method was first described by Van der Held and Van Drunen[6]. Basically, the THW method utilizes a metal wire embedded in the material to be measured. Heat is dissipated in the wire from an electrical current. The current is switched on by a relay at the start of the measurement. If the boundary effect at the ends of the wire is neglected, the temperature on the wire increases with the logarithm of time and is given by:

$$T(t) = C + \frac{Q}{4\pi h\lambda}\ln t \qquad \text{for } t > \tau \tag{6}$$

where the time $t = 0$ at the onset of heat dissipation. $T(t)$ is the temperature in the wire, C is a constant depending on the initial temperature, Q is the total heat dissipation in the wire, h is the length of the wire, λ is the thermal conductivity of the material surrounding the wire and τ is a characteristic time usually of no practical importance. Because the current through the wire is constant, the voltage drop across the wire increases due to the temperature coefficient of resistance (TCR). The voltage drop may be written as:

$$V(t) = a + b\ln t \tag{7}$$

where a and b are constants. Using the definition of TCR

$$\alpha = \frac{\partial R}{\partial T}\frac{1}{R} \tag{8}$$

where α is TCR, T is temperature and R is the electrical resistance in the wire, and substituting

$$Q = RI^2 \tag{9}$$

in Equation (6) where R is the resistance of the wire, I the electrical current and h the length of the wire, one obtains the THW equation for thermal conductivity:

$$\lambda = \frac{\alpha R^2 I^3}{4\pi h}\frac{1}{b} \tag{10}$$

A least-squares fit to a logarithmic function is performed on the experimental data, $V(t)$. By using Equation (7), the parameter b is found, and then the thermal conductivity is calculated from Equation 10.

The experimental set-up is shown in Figs 1 and 2. A relay is used to switch on the current. The series resistor, about 100 times larger than the wire resistance, ensures a constant current. A manganin reference resistor, with TCR ≈ 0, is used as series resistor to avoid resistance change due to heating of the series resistor. The voltage drop across the wire is measured at 15 ms intervals with a Keithley 199 programmable multimeter that is triggered by the relay. A total of 200 voltage measurements are recorded during a period of 3 seconds. Data are then transferred to an IBM personal computer over the IEEE-488 databus for the least-squares calculations.

A 50 μm diameter nickel wire is used in the measurements because of its high TCR and good mechanical strength. Separate current and voltage connections were made in order to avoid problems with electrical contact resistance. In the case of electrically conductive silver-filled epoxy, the wire had to be electrically insulated from the epoxy. This was done by growing a thin oxide layer on the wire by heating it to roughly 600–700°C for 15 min. Samples were placed inside a Weiss Tecnik thermal chamber in order to measure the temperature-dependent thermal conductivity from −30°C to 120°C. The electrical

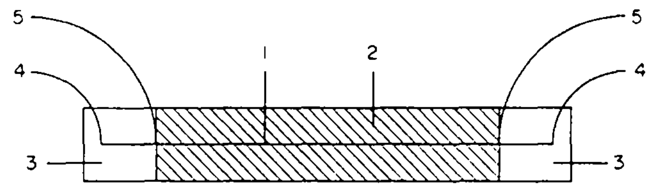

Fig. 1 Preparation of silver-filled epoxy samples for transient hot wire measurement of thermal conductivity: 1—nickel wire; 2—silver-filled epoxy; 3—unfilled epoxy; 4—current supply leads; 5—voltage measurement leads

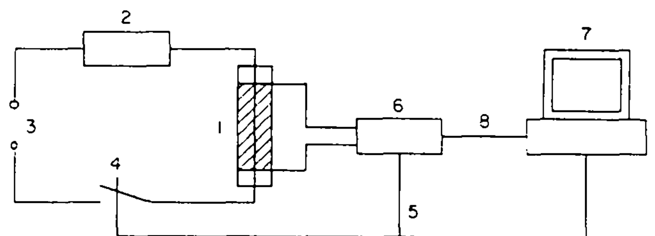

Fig. 2 Instrumentation for the transient hot wire technique: 1—epoxy sample; 2—reference resistor; 3—voltage supply; 4—relay; 5—relay/trigger line; 6—Keithley 199 multimeter; 7—IBM PC; 8—IEEE-488 databus

current was selected so that the total temperature increase in the wire during the measurement was 3–5°C. Thermal contact resistance between the wire and the epoxy was not a problem in these measurements. If this problem arises the first few data points may be omitted, see the work of Gustafsson *et al.*[5].

Materials and preparation

Two different commercially available epoxy adhesives were used in the experiments, Araldite Standard and Epo-Tek 353ND. Seven different samples with weight percentages of silver from 0 to 75% were prepared from each of the two adhesives. Silver powder and adhesive were mixed together by weight and then stirred until a homogeneous mixture was obtained. Before curing, the silver-filled adhesive was placed into a 50 mm long, 10 mm wide and 10 mm deep tray made from a sheet of polyester. The tray was prepared with narrow slots in the end walls to allow the nickel wire for the THW measurements to pass through the tray. The adhesive was then cured. Standard Araldite was cured at room temperature for 24 h and then for 2 h at 120°C to prevent any residual cure taking place during the THW measurements at elevated temperature. Epo-Tek 353ND was cured at 120°C for 1 h. The glass transition temperature, T_g, of Araldite Standard is reported to be 35°C[7]. For Epo-Tek 353ND the T_g is 124°C if cured at 150°C (manufacturers' data), but the T_g will probably be a little less when cured at 120°C as in this study.

After curing, leads were soldered to the nickel wire (the solder flux dissolved the nickel oxide). The voltage measurement leads were connected to the nickel wire as close as possible to the end walls of the tray. Any part of the nickel wire between the voltage measurement leads that was not embedded in the silver-filled adhesive would represent an error in the measurements. The current supply leads were then connected some few millimetres outside the voltage leads and all the leads were secured by unfilled epoxy adhesive. Before THW measurements, the electrical resistance of the wire was checked to see if it was consistent with the length of the wire. If the resistance was too small, some current was transported in the silver-filled adhesive. In such cases the nickel oxide insulation was defective and the sample was rejected.

Fig. 3 shows an optical micrograph of the silver particles as they appeared prior to mixing with epoxy adhesive. The larger particles are certainly agglomerates of smaller particles. This fact was established by lightly grinding the particles between two pieces of glass: after this treatment the larger particles were divided into smaller ones. Some particles were barely visible in the optical microscope, indicating a size less than 0.5 μm. Due to the agglomeration no attempt was made to measure the average size of the particles. The shape of the particles appeared to be essentially spherical with some edges indicating crystallites. Three samples were sectioned and polished after the THW measurement for inspection by optical microscopy. Figs 4–6 show micrographs of these samples.

The volume fractions of silver in the samples, needed for the theoretical evaluation of the THW measurements, were calculated from the specific density of silver and the epoxy adhesives (manufacturers' data).

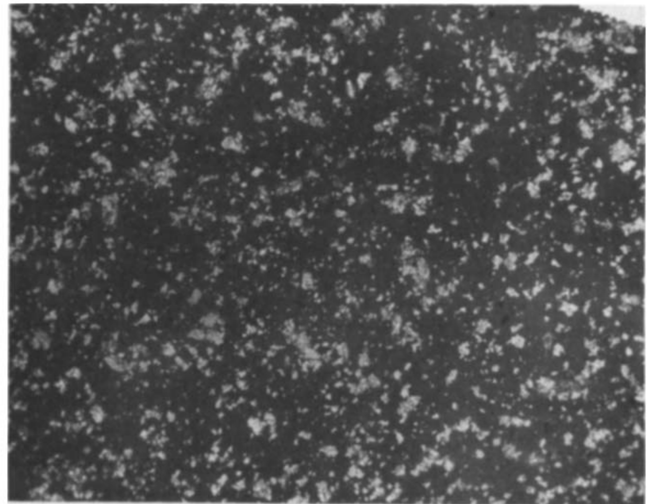

Fig. 3 Micrograph of the silver particles before mixing with the epoxy adhesive. Magnification 550×

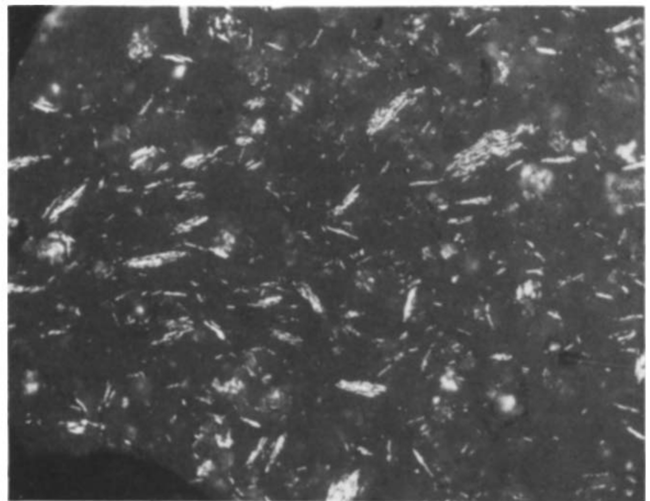

Fig. 4 Micrograph of sectioned sample of silver-filled epoxy. The volume fraction of silver is 0.0376 and the magnification is 550×

Results and discussion

THW results for thermal conductivity of the epoxy adhesives at different volume fractions of silver and at different temperatures are shown in Figs 7 and 8. The thermal conductivity increases with increasing temperature less than T_g and decreases with increasing temperature above T_g except for the Araldite Standard samples with highest volume fraction of silver. For comparison, commercially available silver-filled epoxies do typically have a volume fraction of silver from 0.25 to 0.3 and thermal conductivities from approximately 1.5 to 4 W m^{-1} K^{-1}. The temperature dependency of thermal conduction is usually not measured by the manufacturers of silver-filled epoxy, but Araujo *et al.*[8] have measured the thermal conductivity of epoxy resin filled with metal particles. Their data extend from 1 to 300 K. The thermal conductivity was found to increase with increasing

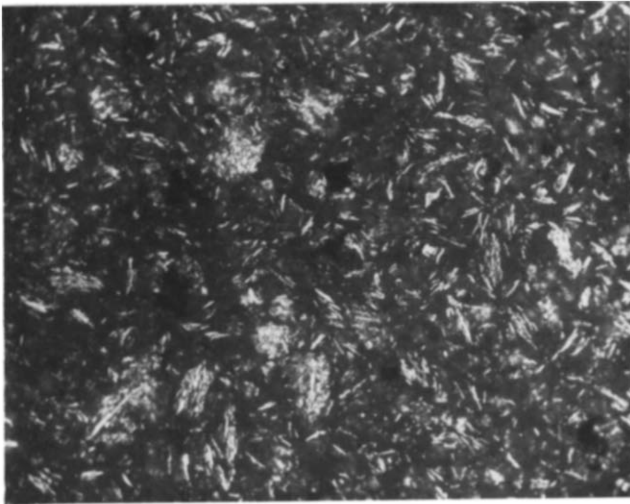

Fig. 5 Micrograph of sectioned sample of silver-filled epoxy. The volume fraction of silver is 0.125 and the magnification is 550×

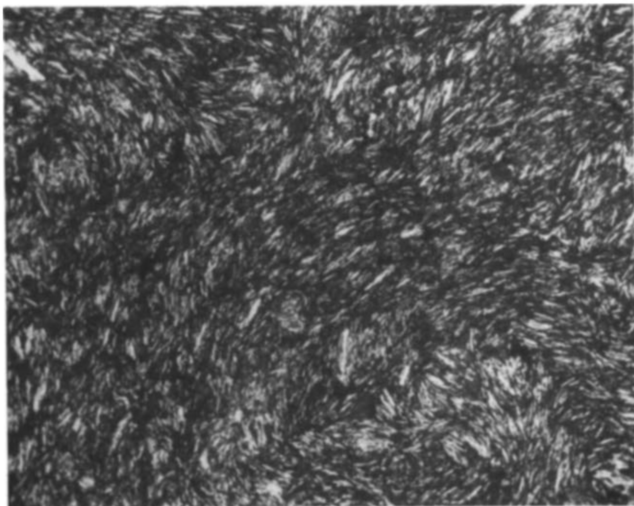

Fig. 6 Micrograph of sectioned sample of silver-filled epoxy. The volume fraction of silver is 0.260 and the magnification is 550×

temperature over the entire range of temperatures. The T_g was not included in their paper.

Figs 9 and 10 show the thermal conductivity as a function of the volume fraction of silver. The dotted lines are predictions from the theory of Lewis and Nielsen with a maximum packing fraction $\phi_m = 0.6$ and shape parameter $A = 1.75$. The maximum packing fraction of randomly packed spheres was chosen, see Table 2. However, ϕ_m has only a minor influence on the theoretical conductivity, Equation (5), for filler fractions considerably less than ϕ_m which is the case for the experimental data. The shape parameter A was set to 1.75 or midway between spheres and cubes. The essentially spherical silver particles with some edges shown in Fig. 3 led to the value 1.75 for A.

It is clear from Figs 9 and 10 that the theory of Lewis and Nielsen fails to explain the experimental data. The only way to adapt the theory is to increase the shape parameter A considerably. This corresponds to elongated particles. The continuous lines in Figs 9 and 10 are the theoretical conductivites with values for A calculated from a least-squares approximation of theoretical to experimental data. The optimal value for A is 24.4 for the Araldite Standard samples and 27.5

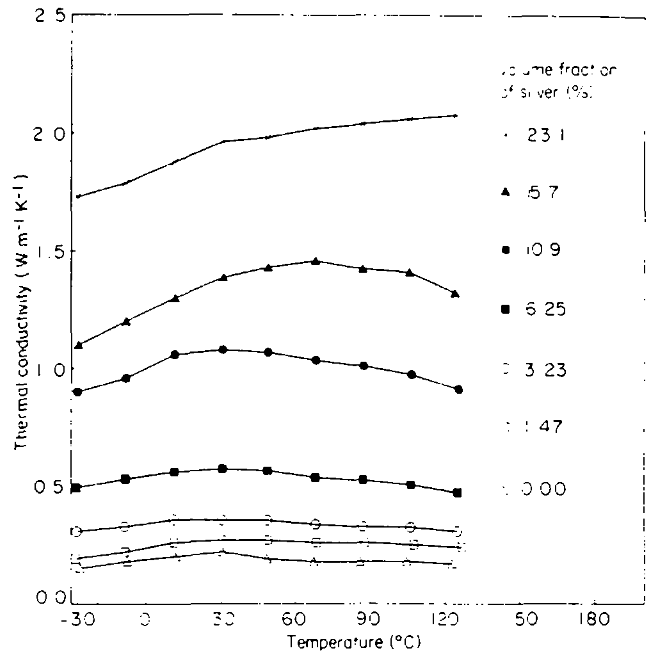

Fig. 7 Thermal conductivity of silver-filled Araldite Standard epoxy adhesive as a function of temperature, measured with the transient hot wire technique

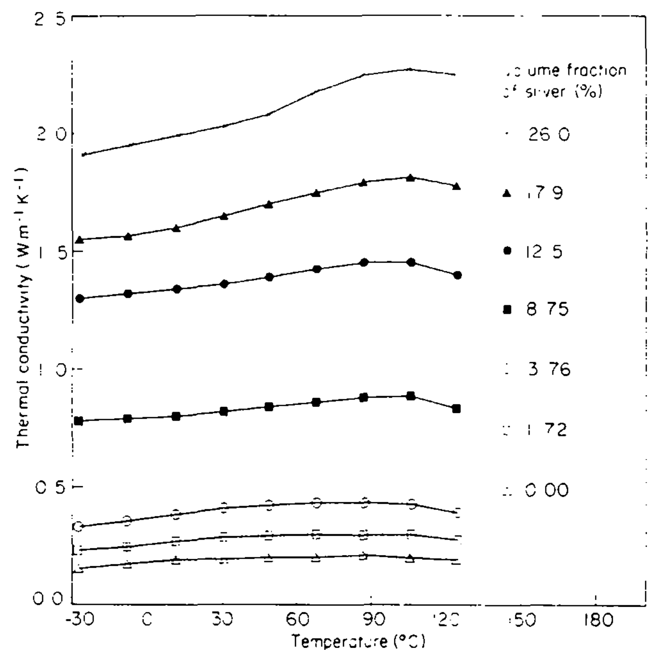

Fig. 8 Thermal conductivity of silver-filled Epo-Tek 353ND epoxy adhesive as a function of temperature, measured with the transient hot wire technique

for the Epo-Tek 353ND samples. These values for A correspond to particles with a length-to-diameter ratio of about 29 and 33 respectively, see Table 2. The maximum packing fraction ϕ_m is still 0.6.

Our suggestion for explanation of the results is as follows. The silver particles, essentially spherical before mixing with the epoxy adhesive, become agglomerated into elongated clusters of particles during the mixing or curing. This hypothesis is supported by the fact that micrographs from sectioned samples show typically elongated particles or clusters of particles, see Figs 4–6. It is well known that small particles agglomerate into clusters in order to minimize the surface energy.

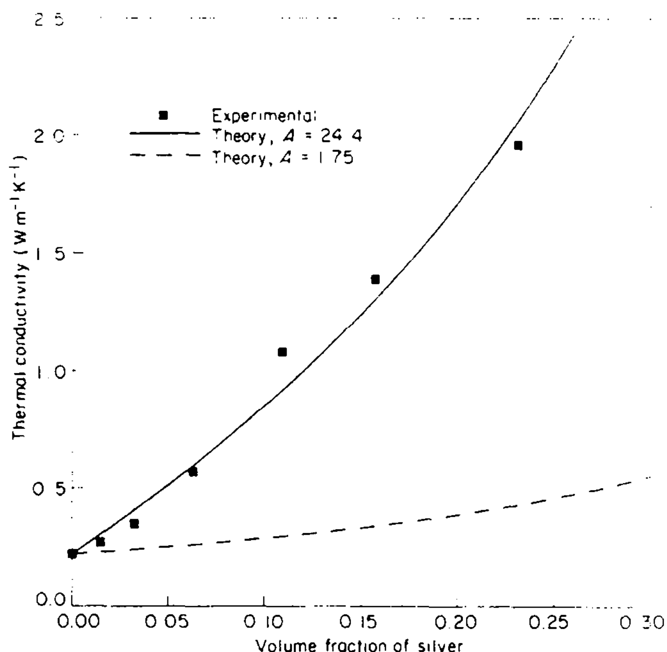

Fig. 9 Thermal conductivity of silver-filled Standard Araldite epoxy at 30°C and different volume fractions of silver. Conductivities from the theory of Lewis and Nielsen are plotted for shape parameter values of A = 1.75 and A = 24.4

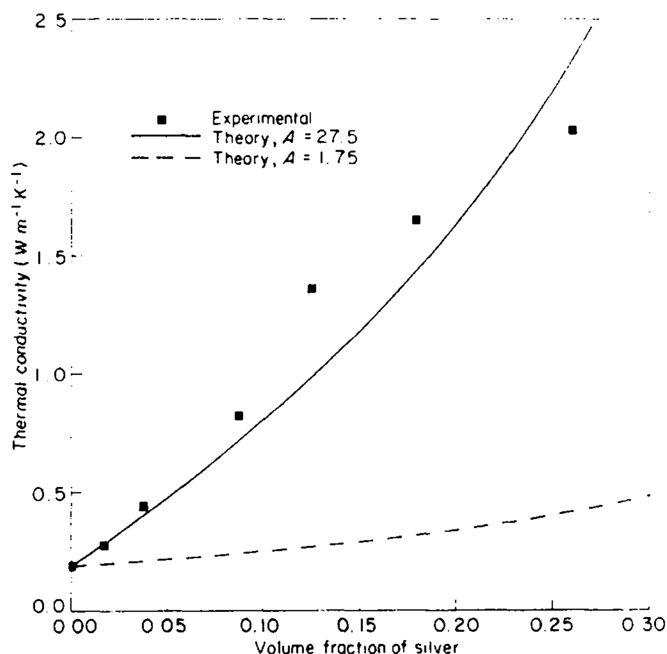

Fig. 10 Thermal conductivity of silver-filled Epo-Tek 353ND epoxy at 30°C and different volume fractions of silver. Conductivities from the theory of Lewis and Nielsen are plotted for shape parameter values of A = 1.75 and A = 27.5

Spherical clusters should be expected from purely energetical reasons because spheres yield the largest surface-to-volume ratio and they therefore minimize the surface energy. However, the kinetics of cluster formation may lead to different shapes. In metallurgy, whisker or lamella shaped precipitates from solid solutions are often seen[10]. These shapes may form because of the enhanced surface energy at the tip of an elongated precipitate, due to the higher curvature at the tip. Similarly, in silver-filled epoxy, small particles may be attracted to the tip of the larger particles thereby promoting the growth of elongated clusters.

Conclusions

The thermal conductivities of epoxy adhesives filled with different volume fractions of silver particles have been measured by the transient hot wire technique. Measurements were carried out at temperatures from −30°C to 120°C. The transient hot wire technique was found to be a simple and reliable method for thermal conductivity measurements both for electrically conductive and non-conductive adhesives.

Results show that the thermal conductivity increases up to the glass transition temperature. At temperatures above the glass transition the thermal conductivity decreases. The thermal conductivity increases with increasing volume fraction of silver. A higher thermal conductivity than expected from theory was measured, which is due to clustering of the initially spherical particles into elongated clusters of particles in the adhesive.

The implications of these results when regarding design and development of high thermal conductivity adhesives is that the shape and arrangement of the filler particles in the adhesive are of high importance. The volume fraction of filler is also of high importance. According to the theory, but not experimentally verified in this paper, the thermal conductivity of the filler is less important.

Acknowledgements

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References

1 **Nielsen, L.E.** 'The thermal and electrical conductivity of two-phase systems' *Ind Engng Chem Fundam* **13** No 1 pp 17-20
2 **Maxwell, J.C.** *'A Treatise on Electricity and Magnetism', 3rd ed* (Dover, New York, 1954) ch 9
3 **Progelhof, R.C., Throne, J.L. and Ruetsch, R.R.** 'Methods for predicting the thermal conductivity of composite systems: a review *Polym Engng and Sci* **16** No 9 (September 1976) pp 615-625
4 **Tsao, G.T.N.** 'Thermal conductivity of two-phase materials' *Ind Engng Chem* **53** No 5 (May 1961) pp 395-397
5 **Gustafsson, S.E., Karawacki, E. and Cohan, M.A.** 'Thermal transport studies of electrically conducting materials using the transient hot strip technique' *J Phys D, Appl Phys* **19** (1986) pp 727-735
6 **Van der Held, E.F.M. and Van Drunen, F.G.** *Physica* **15** (1949) pp 865—881
7 **Remskar, M. and Rocak, D.** 'Characterisation of die attach adhesives' *Hybrid Circuits* No 20 (September 1989) pp 14-17
8 **Araujo, F.F.T., Garrett, K.W. and Rosenberg, H.M.** 'The thermal conductivity of epoxy-resin/powder composites and of indium/glass composites from liquid helium to room temperature' *Proc Int Conf on Composite Materials, Geneva, April 1975*
9 **Bigg, D.M.** 'Conductive polymeric compositions' *Polym Engng and Sci* **17** No 12 (December 1977) pp 842-847
10 **Verhofen, J.D.** *'Fundamentals of Physical Metallurgy', 1st ed* (John Wiley & Sons, Inc, New York, 1975) ch 11

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