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Electrically Nonconductive Thermal Pastes with Carbon as the Thermally Conductive Component

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Electrically nonconductive thermal pastes have been attained using carbon (carbon black or graphite) as the conductive component and ceramic (fumed alumina or exfoliated clay) as the nonconductive component. For graphite particles (5 μm), both clay and alumina are effective in breaking up the electrical connectivity, resulting in pastes with electrical resistivity up to $10^{13}\Omega\cdot$cm and thermal contact conductance (between copper surfaces of roughness 15 μm) up to 9×10^4 W/m$^2\cdot$°C. For carbon black (30 nm), clay is more effective than alumina, providing a paste with resistivity 10^{11} $\Omega\cdot$cm and thermal contact conductance 7×10^4 W/m$^2\cdot$°C. Carbon black increases the thermal stability, whereas either graphite or alumina decreases the thermal stability. The antioxidation effect of carbon black is further increased by the presence of clay up to 1.5 vol.%. The addition of clay (up to 0.6 vol.%) or alumina (up to 2.5 vol.%) to graphite paste enhances the thermal stability.

Key words: Carbon black, graphite, clay, alumina, thermal paste, polyol ester, thermal conductance, electrical resistivity

INTRODUCTION

With the miniaturization and increasing power of microelectronics, heat dissipation has become critical to the performance, reliability, and further miniaturization of microelectronics. Heat dissipation from microelectronics is most commonly performed by thermal conduction. For this purpose, a heat sink, which is a material of high thermal conductivity, is commonly used. In order for the heat sink to be well used, the thermal contact between the heat sink and the heat source (e.g., a substrate with a semiconductor chip on it) should be good.

An important way to alleviate the overheating problem is to improve the thermal contact between the microprocessor and heat sink in the computer.[1–5] For this purpose, a material, known as a thermal interface material,[6] is placed at the interface. In the case of a microprocessor with an integrated heat spreader, a thermal interface material is also needed for the interface between the die and the heat spreader.

DESIGN OF THERMAL INTERFACE MATERIALS

The proximate surfaces involved in a thermal contact are never perfectly flat. There are hills and valleys in the surface topography, thus resulting in air pockets, which are thermally insulating, at the interface. Because air is a thermal insulator, it is important to displace the air by using an interface material that conforms to the topography of the mating surfaces. Therefore, conformability is an essential attribute of a thermal interface material.

A thermal interface material that is thick (i.e., the thickness above about 50 μm, typically above about 100 μm) is needed for filling the gap between the two proximate surfaces, in the case that the surfaces are not in direct contact (as encountered when each surface is curved, so that gaps exist at parts of the interface, or when the two surfaces are not exactly parallel). This category of thermal interface materials is known as gap filling materials. They are to be distinguished from thermal interface materials that are thin (i.e., the thickness below about 100 μm, typically below about 50 μm), ideally

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just thick enough to fill the valleys in the topography of the mating surfaces.

The thin type of thermal interface material is mainly in the form of a paste, which is known as a thermal paste.[7–17] This paste comprises a base medium (i.e., the vehicle) and a filler (a solid component) that is thermally conductive. The filler is typically in the form of particles, because it is more difficult to make a workable paste that contains fibers (discontinuous) instead of particles.

Workability is a commonly used attribute of a paste. The workability relates to the conformability, although the type of conformability required for a thermal paste is conformability to the surface topography in a fine (microscopic) scale, so that the extent of flow associated with the process of conforming is small. In contrast, workability usually refers to the ability to flow or deform in a relatively coarse scale. Conformability in a fine scale is more challenging than that in a coarse scale. The viscosity, which is a measure of the resistance to flow, is commonly used to describe the rheology of pastes. However, akin to the workability, the viscosity relates to the ability to flow in a relatively coarse scale.

For any thermal interface material, the thicker it is, the more thermal resistance it gives. Thus, a small thickness (ideally just enough to fill the valleys at the interface) is also important for a thermal interface material. For a thermal paste, a small thickness can be attained if the paste is highly spreadable. Hence, spreadability is the second criterion.

A thermal paste is preferably thermally conductive, in addition to being conformable and spreadable. In fact, it is customary to include in the formulation of thermal interface materials constituents that are high in thermal conductivity for the purpose of maximizing the thermal conductivity of the thermal interface materials.

For most electronic applications, a thermal paste is preferably not conductive electrically. This is because of the fear that the paste may seep out and cause short circuits.

Examples of constituents of high thermal conductivity are metal particles (e.g., nickel particles, zinc particles, copper particles, aluminum particles, and silver particles); ceramic particles (e.g., boron nitride particles, zinc oxide particles, and aluminum nitride particles); and carbon particles (e.g., carbon black, graphite particles, and diamond particles). Among these materials, carbon in the form of diamond is the most conductive thermally.

Graphite, diamond, and fullerenes are three categories of elemental carbon. Graphite and diamond differ in their chemical bonding, crystal structure, electrical conductivity, and thermal conductivity. Graphite has a hexagonal crystal structure, whereas diamond has a cubic crystal structure. The carbon atoms in graphite are sp^2 hybridized in their chemical bonding, whereas those in diamond are sp^3 hybridized. In other words, the chemical bonding in graphite is partly metallic and partly covalent, whereas that in diamond is totally covalent. Graphite is an electrical conductor as well as a thermal conductor, whereas diamond is an electrical insulator and an exceptionally good thermal conductor. The thermal conductivity of diamond is much higher than that of graphite. Fullerenes are different from both graphite and diamond in that they are in the form of molecules. The most common form of carbon is in the graphite category. Although ideal graphite is completely crystalline in its structure, carbons in the graphite category can have various degrees of crystallinity. The higher is the degree of crystallinity, the higher is the thermal conductivity. Irrespective of the degree of crystallinity, the chemical bonding in carbons in the graphite category involves sp^2 hybridization.

Carbon black is a carbon in the graphite category. It can be partially crystalline, in contrast to ideal graphite (referred to as graphite), which is completely crystalline. Due to the low degree of crystallinity, carbon black is low in thermal conductivity compared to ideal graphite. However, carbon black is one of the most inexpensive forms of carbon, as it is akin to soot.

Graphite differs from carbon black in its higher degree of crystallinity, greater degree of preferred crystallographic orientation, larger crystallite size, larger particle size, and the absence of a porous agglomerate structure. These attributes make graphite a superior thermal conductor, at least in the in-plane direction of graphite (i.e., in the plane of the carbon layers). On the other hand, the absence of a porous nanostructure and the relatively large particle size (typically around 1 μm or more) make graphite much less conformable than carbon black.

Materials in the graphite category are conductive both thermally and electrically. In contrast, diamond and boron nitride are thermally conductive and electrically nonconductive, thus making them attractive for thermal pastes that are electrically nonconductive. However, diamond and boron nitride are expensive and are not available in the form of nanoparticles. Compared to boron nitride, zinc oxide (also electrically nonconductive) is less thermally conductive, though it is less expensive.

Because of the high cost and limited choice of thermal conductors that are electrically nonconductive, the combined use of a filler that is thermally and electrically conductive and a filler that is electrically nonconductive is investigated in this work for the purpose of attaining a thermal paste that is nonconductive electrically.

Due to its structure, a carbon nanotube is thermally conductive along the axis of each nanotube. The level of thermal conductivity depends on the degree of crystallographic order in the nanotube. The higher the degree of crystallographic order, the greater is the thermal conductivity. The thermal conductivity and the high aspect ratio (i.e., the ratio of the length to the diameter) of a nanotube are attributes that make the nanotubes attractive. The combined use of multiwalled carbon nanotubes (2%) and carbon black (10%) as thermally conductive constituents in a thermal interface material is recommended by Zhang et al.[15]

Because of the high thermal conductivity along the axis of a carbon nanotube, various forms of thermal interface materials involving carbon nanotubes have been reported.[18–22] The high cost of the carbon nanotubes, the high cost of making carbon nanotube arrays, the geometric limitations of the nanotube arrays, and the limited choices of array substrates are disadvantages that make practical use of these nanotube technologies difficult.

Of all the fillers mentioned above, carbon black, which is porous and nanostructured, is the only type that is itself squishable (i.e., highly compressible). Due to the squishability, carbon black is conformable to the topography of the mating surfaces and is spreadable. The conformability and spreadability are believed to be the reasons behind the superior performance of carbon black compared to the other fillers.[13–17] Furthermore, the porosity of a carbon black particle allows penetration of the vehicle into a carbon black particle, thereby enabling the resulting paste to have high fluidity.

For surfaces encountered in practical applications, such as the surfaces of heat sinks and microprocessors, the roughness is typically much more than the submicron level. The need for the thermal paste to fill deep valleys in the surface topography would make the thermal conductivity within the paste more important than when the valleys are shallow. Therefore, the relative performance of various thermal pastes can be different for rough mating surfaces and smooth mating surfaces.

The vehicle of a thermal paste is not a thermal conductor. Thus, the higher the proportion of thermally conductive constituent in a thermal paste, the higher is the thermal conductivity of the paste. For the purpose of maximizing the thermal conductivity of a thermal paste, it is conventional to use thermally conductive constituents at high proportions, e.g., zinc oxide in the amount of 72.8%.[23]

Both thermal conductivity and conformability help the performance of a thermal paste. The workability and conformability of a thermal paste diminish with increasing conductive filler content, although the thermal conductivity of the paste increases with increasing filler content. Thus, the use of an excessively high filler content results in low conformability, though the thermal conductivity is enhanced. Work on the development of thermal pastes has conventionally emphasized the attainment of a high thermal conductivity in the paste by using very high contents of conductive fillers. The low conformability that results from the high filler content has, until recently, been of relatively little concern. Thus, the emphasis has conventionally been on the development of a workable paste that has a high content of the conductive filler.

Thermal conductivity has long been assumed in the thermal interface material industry to be the key criterion in determining the effectiveness of a thermal interface material, but it is actually less important than conformability or spreadability, as unexpectedly found in the present invention. As long as the thermal interface material is more thermally conductive than air, its presence can improve the thermal contact. On the other hand, if the thermal interface material is relatively large in thickness, its thermal conductivity can be important. Thus, this paper emphasizes thermal pastes that are small in thickness (less than 50 μm, typically less than 25 μm) during use after application, in contrast to conventional prior work, which emphasizes thermal pastes that are much larger in thickness (above 50 μm, typically above 100 μm).

The conformability of a thermal paste also depends on the vehicle, i.e., the matrix. Silicone is the most commonly used vehicle, in spite of its high viscosity and the consequent low conformability and low spreadability.

During use, it is preferred that a thermal paste does not seep out of the interface, as the seepage can cause contamination and, in the case of an electrically conductive paste, short circuiting of the electronics around the thermal contact. Therefore, a thixotropic paste (a paste that flows only under an applied stress) is preferred to a fluidic paste (a paste that flows even in the absence of an applied stress). Silicone is thixotropic. Polyol ester can also be used to form a thixotropic paste.

Metal alloys with low melting temperatures (such as solders) applied in the molten state have long been used as thermal interface materials. However, they tend to suffer from the chemical reactivity of the liquid alloy with some metal surfaces (such as copper). The reaction products can interfere with the contact between the liquid alloy and a metal surface. Thus, although metals are high in thermal conductivity, they have limited conformability, thereby resulting in limited effectiveness as thermal interface materials. Furthermore, alloys suffer from the need to heat during their application. In contrast, thermal pastes do not require heating.

OBJECTIVE AND SCOPE

This paper separately uses two materials in the graphite category, namely, carbon black (30 nm) and graphite flakes (5 μm), as fillers that are both thermally and electrically conductive. In addition, it separately uses fumed alumina and exfoliated clay as nanosize fillers that are electrically nonconductive and low in thermal conductivity. Different combinations of a conductive filler and a nonconductive filler in various proportions are used in this work to formulate thermal pastes, with the objective of attaining effective thermal pastes that are nonconductive electrically. Due to the very small particle size of carbon black compared to graphite, the microstructure needed to avoid formation of a conductive network is expected to be different between a carbon black paste and a graphite paste.

The comparative evaluation described in this paper for the various formulations of thermal paste pertains to the effectiveness of the thermal interface material, the temperature resistance (i.e., the thermal stability), the conformability, and the viscosity, as these attributes are relevant to the thermal interface material application. In particular, evaluation of the effectiveness of the thermal interface material is conducted by measuring the thermal contact conductance across two copper mating surfaces with a controlled surface roughness.

This paper uses thermal contact conductance (in units of $W/m^2 \cdot °C$) to describe the quality of the thermal contact. An alternate description is the thermal resistivity (in units of $m^2 \cdot °C/W$), which is defined as the reciprocal of the thermal contact conductance. The thermal resistivity is the product of the thermal resistance (in unit of °C/W) and the contact area. The thermal resistance depends on the contact area, whereas the thermal resistivity does not. For a thermal contact conductance of 3×10^5 $W/m^2 \cdot °C$ (best case in prior work[10–12]) and for a circular contact area of diameter 12.6 mm, the thermal resistance is 0.026°C/W.

Due to variability in the testing conditions (e.g., roughness and thermal conductivity of the mating surfaces) and methods (e.g., positions relative to the thermal interface of the temperature measurement), the relative performance of various thermal interface materials should be evaluated by using the same testing method and condition. Comparative evaluation in this work uses the guarded hot plate method, which involves measurement of the heat flux in the steady state (ASTM method D5470).[16]

EXPERIMENTAL METHODS

Materials

This section describes the formulation of thermal pastes. Two types of thermally conductive solids are used, namely, carbon black and graphite. In addition, two types of electrically nonconductive solids are used, namely, fumed alumina and exfoliated clay.

The vehicle consists of polyol esters, which are attractive for their ability to resist elevated temperatures. The polyol esters in the vehicle were pentaerythritol ester of linear and branched fatty acids and dipentaerythritol ester of linear and branched fatty acids. The polyol ester mixture was Hatcol 2372, as provided by Hatco Corp. (Fords, NJ).[12] The specific gravity was 0.97. No solute is used.

The carbon black is a type for electrical conductivity and easy dispersion (Vulcan XC72R GP-3820; Cabot Corp., Billerica, MA). It consists of porous agglomerates of carbon particles of particle size 30 nm, density 1.7–1.9 g/cm^3, nitrogen specific surface area 254 m^2/g, and maximum ash content 0.2%. It is used in the amount of 2.4 vol.%, which is the optimized amount used in prior work.[12]

The graphite is natural crystalline graphite flakes, Grade Micro 850 (Asbury Graphite Mills, Inc., Asbury, NJ), with 98.5% minimum carbon content, 5-μm typical size, and specific gravity 2.25. It is used in the amount of 10.7 vol.%, which is an effective amount used in prior work.[12]

The fumed alumina (SpectrAl, Cabot Corp., Billerica, MA) is synthetic aluminum oxide nanoparticles, with BET surface area 55 m^2/g, pH 4.7, specific gravity 3.6, >99.8% Al_2O_3, crystallinity, and positive surface charge. Information on the particle size is not provided by the manufacturer. The material is a light, fluffy powder that is white in appearance. It is used in amounts ranging from 1.0 to 2.5 vol.% of the resulting paste.

The exfoliated clay is obtained by subjecting the clay to an exfoliation-adsorption process.[24–30] It is used in amounts ranging from 0.1 vol.% to 3.0 vol.% of the resulting paste. The clay prior to exfoliation-adsorption processing is nanoclay (Cloisite 25A, from Southern Clay Products, Inc., Gonzales, TX), which is a natural montmorillonite phyllosilicate intercalated with a dimethyl, dihydrogenated tallow, 2-ethylhexyl quaternary ammonium chloride salt. Its specific gravity is 1.87. It is made of layered magnesium aluminum silicate platelets of thickness 1 nm and size 70–150 nm. The interlayer spacing is 18.6 Å, based on x-ray diffraction. The mean particle size is 6 μm. Phyllosilicates are inherently hydrophilic, but ion exchange involving the cations in the silicate and the ammonium salt renders the clay more hydrophobic. The modified clay has a lower surface energy, which is well suited for use with organic matrices.

The exfoliation-adsorption processing process[24–30] refers to a process that combines exfoliation (separation of the silicate platelets) and adsorption (adsorption of an organic material, i.e., the vehicle of the thermal paste, on the surface of the platelets). This process involves dissolving the polyol ester vehicle in a solvent, which is chlorobenzene (Mallinckrodt Baker Inc., Phillipsburg, NJ, with assay 100.0% and specific gravity 1.11).[25] Interaction of the solution with the ammonium salt in the silicate, along with sonication,[25] causes exfoliation of the silicate and adsorption of the polyol ester solution on the exfoliated silicate platelets. The sonication is conducted by using a 100 W ultrasonic cleaner (Fisher Scientific International Inc., FS60H, Hampton, NH). Subsequent evaporation of the solvent allows the vehicle to adsorb onto the exfoliated silicate layers, thereby rendering a nanocomposite.

The specific procedure of the exfoliation-adsorption process of this work is described below. The solvent and clay are mixed in a 70:1 mass ratio and vigorously hand mixed to fully disperse the clay in the solvent. The clay dispersion is then placed in a water bath in the ultrasonic cleaner and sonicated for 2 h. Next the vehicle is added, vigorously hand mixed to achieve a homogeneous dispersion, and then sonicated for an additional 15 min. During sonication, the temperature of the water bath is held between 35°C and 45°C. A large portion of the solvent is then removed by evaporation using a hot plate held at 100°C for 4 h. Any remaining solvent is then removed by placing the samples in a vacuum chamber and heating to 85°C for 24 h.

In general, the thermal paste preparation in this work involves mixing followed by placing the paste in a vacuum chamber (which involves a mechanical vacuum pump) for the purpose of air bubble removal.

Testing

Thermal contact conductance measurement

A steady-state method known as the guarded hot plate method (ASTM method D5470) is used to measure the thermal contact conductance for various thermal contacts. Various thermal pastes are sandwiched between the 1 in. × 1 in. (25 mm × 25 mm) proximate surfaces of two copper blocks (both 1 in. × 1 in. surfaces of each block having roughness around 15 μm, as attained by mechanical polishing). Each copper block has a height of 35 mm. The roughness of 15 μm is the same as that used and referred to by Leong and Chung[10,12,13] as the "rough" case. The "smooth" case (roughness 0.05 μm) of Leong and Chung[10,12,13] is not addressed in this work, though prior work[10,12,13] indicates that the relative performance of various thermal pastes depends on the roughness of the mating surfaces and that pastes containing carbon black are particularly effective compared to other pastes when the surfaces are smooth.

The heat in this test is provided by a 3 in. × 3 in. (76 mm × 76 mm) copper block that has two embedded heating coils (top block in Fig. 1). During the period of temperature rise, the heating rate is controlled at 3.2°C/min by using a temperature controller. This copper block is in contact with one of the 1 in. × 1 in. copper blocks that sandwiched the thermal interface material. The cooling in this test is provided by a second 3 in. × 3 in. copper block, which is cooled by running water that flowed into and out of the block (bottom block in Fig. 1). This block is in contact with the other of the two 1 in. × 1 in. copper blocks that sandwich the thermal paste. A 100-Ω resistance temperature detector probe was inserted in four holes (T_1, T_2, T_3, and T_4 in Fig. 1, each hole of diameter 3.2 mm). Two of the four holes are in each of the 1 in. × 1 in. copper blocks. The temperature gradient is determined from $T_1 - T_2$ and $T_3 - T_4$. These two quantities should be equal at equilibrium, which is attained after holding the temperature of the heater at the desired value for 30 min. Equilibrium is assumed when the temperature variation is within ± 0.1°C in a period of 15 min. At equilibrium, the temperature of the hot block is in the range 70–80°C, that of the cold block is in the range 60–40°C, while that of the thermal paste is in the range 60–70°C. The pressure in the direction perpendicular to the plane of the thermal interface is controlled by using a hydraulic press at pressures of 0.46 MPa, 0.69 MPa, and 0.92 MPa. The system is thermally insulated by wrapping laterally all the copper blocks with glass fiber cloth.

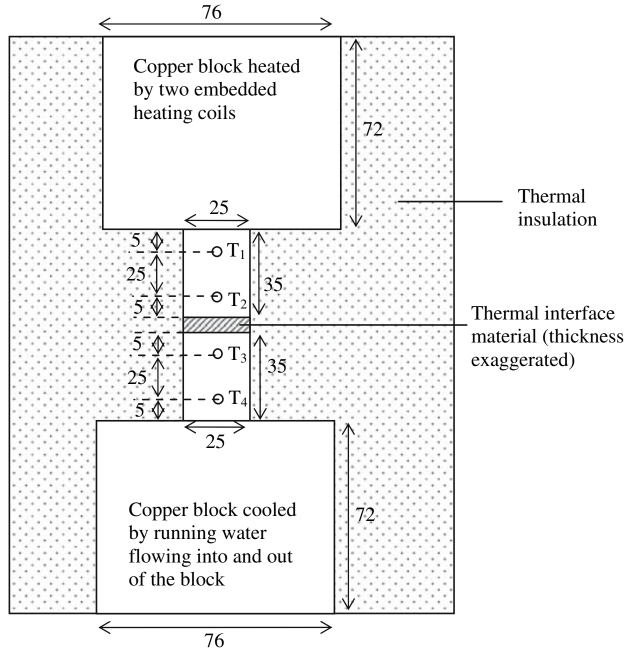

Fig. 1. A schematic representation of the steady-state method (guarded hot plate method) of thermal contact conductance measurement. T_1, T_2, T_3, and T_4 in the drawing are holes of diameter 2.4 mm. A thermocouple (type T) is inserted in each hole. All dimensions are in millimeters.

In accordance with ASTM method D5470, the heat flow Q is given by

$$Q = \frac{\lambda A}{d_A} \Delta T \tag{1}$$

where $\Delta T = T_1 - T_2 = T_3 - T_4$, λ is the thermal conductivity of copper, A is the area of the 1 in. × 1 in. copper block, and d_A is the distance between thermocouples T_1 and T_2 (i.e., 25 mm).

The temperature at the top surface of the thermal interface material is T_A, which is given by

$$T_A = T_2 - \frac{d_B}{d_A}(T_1 - T_2) \tag{2}$$

where d_B is the distance between thermocouple T_2 and the top surface of the thermal interface material (i.e., 5 mm). The temperature at the bottom surface of the thermal interface material is T_D, which is given by

$$T_D = T_3 + \frac{d_D}{d_C}(T_3 - T_4) \tag{3}$$

where d_D is the distance between thermocouple T_3 and the bottom surface of the thermal interface material (i.e., 5 mm) and d_C is the distance between thermocouples T_3 and T_4 (i.e., 25 mm).

The thermal resistivity θ is given by

$$\theta = (T_A - T_D)\frac{A}{Q} \tag{4}$$

Note that insertion of Eq. 1 into Eq. 4 causes cancellation of the term A, so that θ is independent of A. The thermal contact conductance is the reciprocal of θ.

Electrical resistivity measurement

The DC volume electrical resistivity of the thermal pastes is conducted by filling a mold cavity of size 70 mm × 10 mm × 10 mm with the paste, such that the top surface of the paste is flush with that of the mold. The two-probe method is used for films of resistivity above 10^5 Ω·cm, whereas the four-probe method is used for films of resistivity below 10^5 Ω·cm. Electrical contacts are in the form of silver paint in conjunction with tin-coated copper wires (diameter = 0.13 mm), which are parallel to one another, extending across the entire 10-mm width of the mold cavity, at a distance of 10 mm from one another. Silver paint was used to fix the wires at the bottom of the mold and to improve the electrical contact between the wires and the thermal paste to be poured into the mold. Each wire droops down from the mold wall into the shallow mold cavity. Thus, each wire is immersed in the paste, though it protrudes out of the paste on both sides of the mold. Each specimen is measured for three times, using a picoammeter system, which consists of a Keithley (Keithley Instruments, Inc., Cleveland, OH) 617 programmable electrometer, a Keithley 230 programmable voltage source, and a computer.

Viscosity measurement

The viscosity describes the resistance to shear deformation. It is a commonly used attribute for describing pastes. The viscosity of various pastes is measured by using a viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA, model LVT dial-reading viscometer, with model SSA-18/13R small sample adaptor). In addition, the viscometer is used to measure the thixotropic index, as explained below.

Thixotropy refers to the rheological behavior in which a material flows only under a stress. An example of a thixotropic paste is Ketchup. The thixotropic index is a time-dependent rheological property that describes the extent of thixotropic behavior. A range of rotational speeds are selected. The apparent viscosity is measured while the shear rate is progressively increased to the maximum and then progressively decreased to the minimum at constant time intervals. After the last viscosity measurement, the viscometer is turned off for 10 min. After this rest period, a measurement of the viscosity at the lowest rate is taken again. Two methods can be used to calculate the thixotropic index. Method A is the ratio of the increasing speed viscosity to that of the decreasing speed viscosity. Method B is the ratio of the lowest speed viscosity taken after the rest period to that before the rest period. The higher either ratio, the greater is the thixotropy.[31]

Thermal stability testing

The thermal stability refers to the ability to resist elevated temperatures. It is necessary for a thermal paste to be able to resist the elevated temperatures involved in the particular application environment. The thermal stability is evaluated by measurement of the weight loss due to heating in air in a furnace at 200°C for 24 h. The specimens are contained in aluminum weighing dishes. Three specimens of each type are tested. The heating and cooling rates are 3°C/min.

RESULTS AND DISCUSSION

Thermal Conductance and Electrical Resistivity

Figure 2 shows the thermal contact conductance and electrical resistivity for the combined use of carbon black and various volume fractions of clay. Figure 3 shows these quantities for the combined use of graphite and various volume fractions of clay. Figure 4 shows these quantities for the combined

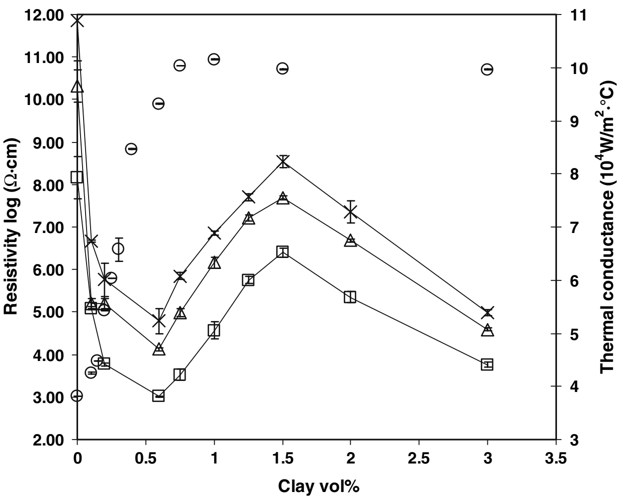

Fig. 2. Effect of the clay volume fraction on the electrical resistivity (○) and the thermal contact conductance (0.46 MPa: □; 0.69 MPa: Δ; and 0.92 MPa:×) of carbon black thermal pastes.

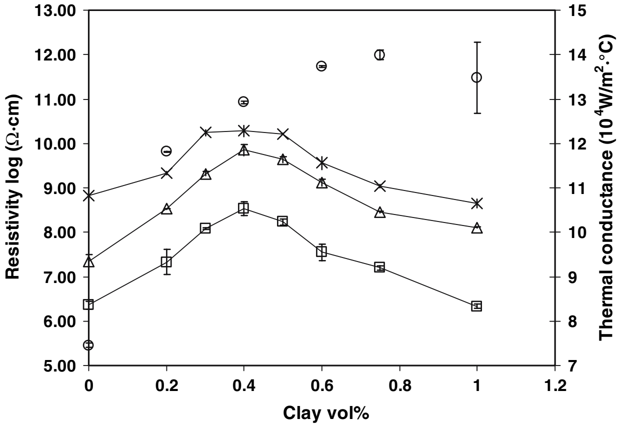

Fig. 3. Effect of the clay volume fraction on the electrical resistivity (○) and the thermal contact conductance (0.46 MPa: □; 0.69 MPa: Δ; 0.92 MPa: ×) of graphite thermal pastes.

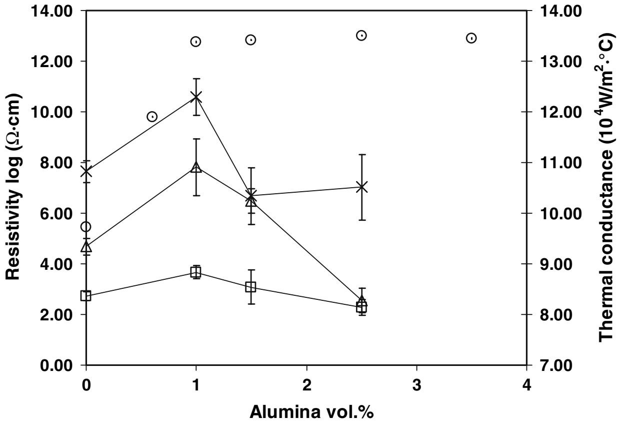

Fig. 4. Effect of the alumina volume fraction on the electrical resistivity (○) and the thermal contact conductance (0.46 MPa: □; 0.69 MPa: Δ; and 0.92 MPa: ×) of graphite thermal pastes.

use of graphite and various volume fractions of fumed alumina. Figure 5 shows the resistivity for the combined use of carbon black and various volume fractions of fumed alumina. Figure 6 shows these quantities for various volume fractions of clay in the absence of conductive fillers. Table I shows a compilation of all the data, including the data scatter.

The resistivity is greatly increased by the addition of clay to pastes containing carbon black (Fig. 2) or graphite (Fig. 3) and by the addition of fumed alumina to the paste containing graphite (Fig. 4). However, it is much less significantly increased by the addition of alumina to the paste containing carbon black (Fig. 5). The effectiveness of both clay and alumina in increasing the resistivity of graphite pastes is due to the large size of the graphite particles compared to the clay or alumina particles and the consequent ability of the clay or alumina to break up the electrical connectivity of the graphite particles. The effectiveness of both clay and alumina in increasing the resistivity of carbon black pastes is smaller than that for graphite pastes. This is due to the small size and squishability of the carbon black particles and the consequent difficulty of breaking up the electrical connectivity of the carbon black particles. The effectiveness of alumina in increasing the resistivity of carbon black paste is lower than that of clay. This is probably due to the platelike shape of the clay particles and the equiaxed shape of the alumina particles. The platelike shape is more effective for breaking up the electrical connectivity of the carbon black than the equiaxed shape. Due to the particularly low effectiveness of alumina for increasing the resistivity of carbon black paste, the thermal contact conductance of pastes containing alumina and carbon black has not been measured in this work.

The thermal contact conductance is decreased by the addition of clay to carbon black paste up to

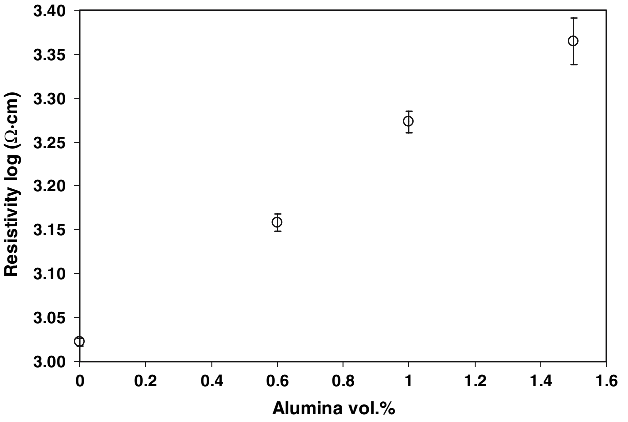

Fig. 5. Effect of the alumina volume fraction on the electrical resistivity of carbon black thermal pastes.

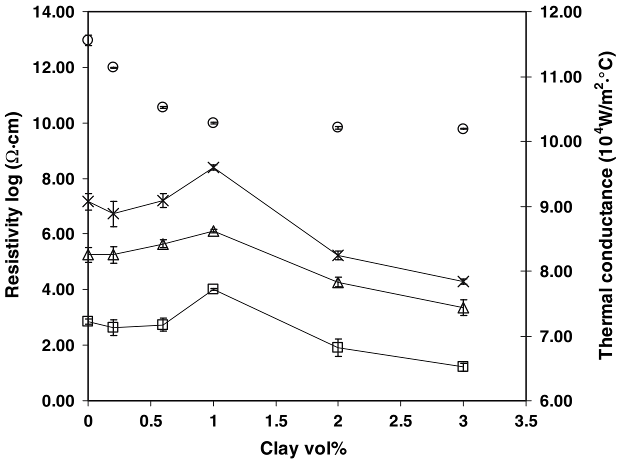

Fig. 6. Effect of the clay volume fraction on the electrical resistivity (○) and the thermal contact conductance (0.46 MPa: □; 0.69 MPa: Δ; and 0.92 MPa: ×) in the absence of a conductive filler.

Table I. Thermal Stability of Various Thermal Pastes, as Shown by the Residual Mass Excluding/Including the Solid Component after Heating; CB = Carbon Black (2.4 Vol.%), and G = Graphite (10.7 Vol.%)

			Residual Wt.%	
Line	Conductive Filler	Nonconductive Filler Vol.%	Excluding the Solid Component	Including the Solid Component
1	None	None	31.2 ± 1.0	31.2 ± 0.7
2	None	0.20% clay	31.4 ± 0.1	31.7 ± 0.1
3	None	0.60% clay	32.0 ± 0.1	32.8 ± 0.1
4	None	0.75% clay	32.8 ± 0.3	33.8 ± 0.2
5	None	1.00% clay	33.6 ± 0.4	34.9 ± 0.3
6	None	1.00% alumina	22.4 ± 1.5	25.9 ± 1.5
7	CB	None	47.0 ± 0.7	44.5 ± 0.7
8	CB	0.60% clay	59.7 ± 1.0	52.1 ± 0.5
9	CB	1.50% clay	62.4 ± 1.8	65.1 ± 1.7
10	CB	3.00% clay	57.7 ± 0.9	60.6 ± 0.8
11	G	None	12.0 ± 2.1	38.5 ± 1.8
12	G	0.20% clay	14.6 ± 1.3	41.2 ± 1.1
13	G	0.40% clay	21.0 ± 1.9	45.2 ± 2.3
14	G	0.60% clay	29.5 ± 0.6	52.1 ± 0.5
15	G	1.00% clay	28.0 ± 0.1	51.5 ± 1.1
16	G	1.0% alumina	18.9 ± 1.5	48.5 ± 1.0
17	G	2.5% alumina	21.7 ± 3.1	56.6 ± 2.7
18	G	3.5% alumina	19.9 ± 1.2	58.9 ± 1.0

0.6 vol.%, but it is increased by the addition of clay or alumina to graphite paste. This is because of the inherently high conformability of the carbon black paste (due to the squishability and small particle size) and the inherently low conformability of the graphite paste (due to the nonsquishability and large particle size). The addition of fine particles (clay or alumina) to graphite paste increases the conformability, thereby improving the thermal contact conductance, in spite of the increase in resistivity. However, the addition of clay to carbon black paste decreases the thermal contact conductance, possibly due to the decrease in thermal conductivity within the paste, as suggested by the observed increase in resistivity and possibly also due to the minor decrease in the conformability.

For attaining high values of both the thermal contact conductance and the electrical resistivity, graphite paste containing 1 vol.% alumina is recommended, as it provides the highest resistivity (close to 10^{13} Ω·cm) and almost the highest thermal contact conductance (8.83×10^4 W/m^2·°C). Almost as attractive is the graphite paste containing 0.6 vol.% clay, because it provides resistivity close to 10^{12} Ω·cm and thermal contact conductance 9.50×10^4 W/m^2·°C. The pastes containing carbon black and clay are inferior in both the thermal contact conductance and the resistivity.

Figure 6 shows that, in the absence of a conductive filler, the electrical resistivity decreases slightly and monotonically with increasing clay content. The decrease occurs up to a clay content of 1 vol.%, beyond which the resistivity does not change with increasing clay content. The thermal contact conductance increases slightly with increasing clay content up to 1 vol.% and decreases as the clay content further increases. The increase in thermal contact conductance in the range of low clay content is due to the slight thermal conductivity of the clay nanoplatelets. The decrease in the conductance in the range of high clay content is probably partly due to the decrease in conformability. It may also be partly due to the increase in viscosity and the consequent increase in bondline thickness of the paste. The monotonic decrease of the electrical resistivity with increasing clay content is due to the slight electrical conductivity of the clay.

Viscosity

The viscosity of a paste without a conductive filler is increased by the addition of clay, as shown in Fig. 7. The higher the volume fraction of clay, the higher is the viscosity. At the same content of 1 vol.%, clay gives much higher viscosity than alumina (Fig. 8), probably because of the high surface area of the clay allowing interaction between clay and the vehicle. The further addition of graphite to the paste with alumina greatly increases the viscosity (Fig. 8).

The thixotropic index, as shown in Fig. 9, Fig 10, decreases monotonically with increasing clay content. It is also decreased by the addition of alumina. This decrease is attributed to the nonclassical thixotropy of montmorillonite clay suspensions.[29] This behavior is associated with a slow recovery process after the application of shear, although the breakdown upon shear is rapid. Figure 9 shows that the thixotropic index determined by using method A is slightly higher than that determined by using method B.

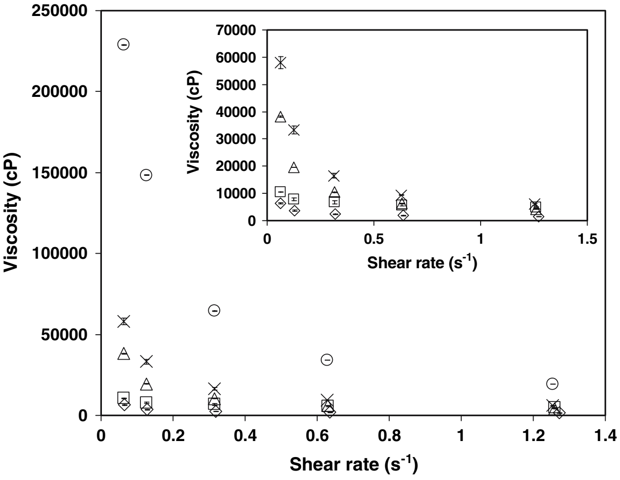

Fig. 7. Effect of shear rate on the viscosity for pastes with various volume fractions of clay in the absence of a conductive filler. 0 vol.%: ◇; 0.20 vol.%: □; 0.60 vol.%: Δ; 0.75 vol.%: ×; and 1.00 vol.%: ○. The inset shows a magnified view of the regime of low viscosity.

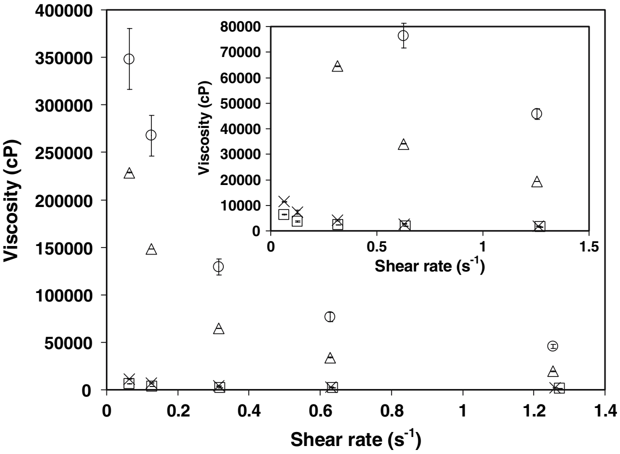

Fig. 8. Effect of shear rate on the viscosity for paste with alumina and of paste with alumina and graphite. Without any filler: □; 1.0 vol.% clay: Δ; 1.0 vol.% alumina: ×; 1.00 vol.% alumina and 10.7 vol.% graphite: ○. The inset shows a magnified view of the regime of low viscosity.

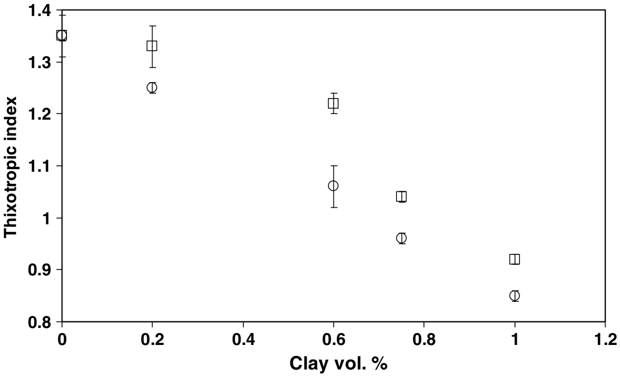

Fig. 9. Effect of clay volume fraction on the thixotropic index in the absence of a conductive filler. Method A: □; and method B: ○.

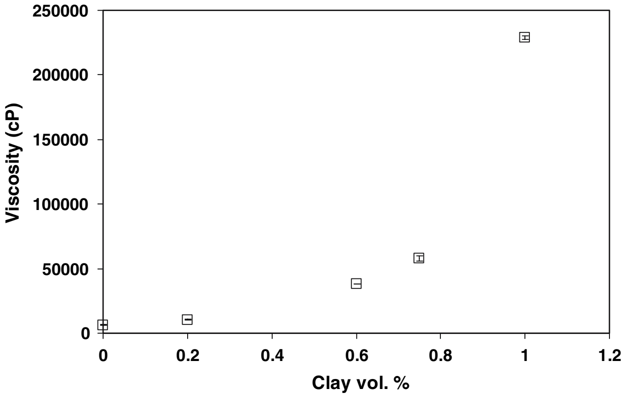

Fig. 10. Effect of clay volume fraction on the viscosity for a shear rate of 0.3 s^{-1}.

Thermal Stability

Lines 1–5 of Table I show that, in the absence of a conductive filler, the addition of clay has negligible effect on the thermal stability of the paste, whether one considers the overall paste or the liquid portion of the paste. Comparison of the data in line 1 (the blank vehicle), line 6 (1.0% alumina), line 7 (2.4 vol.% carbon black), and line 11 (10.7% graphite) of Table I shows that carbon black increases the thermal stability, whereas either graphite or alumina decreases thermal stability. These effects occur, whether one considers the overall paste (including the solid component) or the liquid portion of the paste (excluding the solid component). The positive effect of carbon black is probably because of the large surface area of nanostructured carbon black and the surface functional groups, such as phenolic groups, on the carbon serving as a primary antioxidant, and quinone[31] and lactone functional groups on the carbon serving as a scavenger of alkyl-free radicals. The origin of the negative effects of graphite and alumina is presently not clear.

In Table I, lines 7–10 show that the antioxidation effect of carbon black is further increased by the presence of clay, and lines 11–15 show that the addition of clay to a graphite paste enhances the thermal stability, though lines 1–5 show that the clay by itself essentially does not affect the thermal stability. The synergistic effect of carbon black and clay and that of graphite and clay may be due to the interaction between functional groups on the surface of carbon black or graphite and those on the clay surface.

Comparison of lines 11 and 16–18 of Table I shows that addition of alumina to graphite paste helps the thermal stability, though comparison of lines 1 and 6 shows that alumina by itself degrades the thermal stability. This means that there is a synergistic effect involving graphite and alumina.

Comparison of lines 9 and 10 of Table I shows that a clay content beyond 1.5 vol.% slightly degrades the thermal stability of carbon black paste.

Similarly, comparison of lines 14 and 15 shows that a clay content beyond 0.6 vol.% slightly degrades the thermal stability of graphite paste. These effects may be due to the high viscosity of both the carbon black paste with 3.0 vol.% clay (line 10) and the graphite paste with 1.0 vol.% clay (line 15) and the consequent difficulty of complete removal of the solvent from these pastes during the preparation of the pastes. The residual solvent may volatilize during thermal stability testing, thereby decreasing the thermal stability.

All levels of thermal stability shown in Table I are low compared to levels attained by commercial thermal pastes that are similarly tested.[32] However, they can be significantly improved by the use of antioxidants. Commercial thermal pastes tend to contain antioxidants. Nevertheless, the results in Table I are valuable for showing the effects of the various components on the thermal stability.

CONCLUSIONS

Electrically nonconductive thermal pastes have been attained using carbon as the thermally conductive solid component. The concept involves the breaking up of the electrical connectivity of the carbon in the paste by using electrically nonconductive fine particles (either fumed alumina or exfoliated clay). In the case that the carbon is graphite particles of size 5 μm, both clay and alumina are effective in breaking up the electrical connectivity. By using 1 vol.% alumina in paste containing 10.7 vol.% graphite, a paste that provides resistivity close to 10^{13} Ω·cm and thermal contact conductance (between copper surfaces of roughness 15 μm) 8.83×10^4 W/m^2·°C has been attained. By using 0.6 vol.% clay in paste containing 10.7 vol.% graphite, a paste that provides resistivity close to 10^{12} Ω·cm and thermal contact conductance 9.50×10^4 W/m^2·°C has been attained. In the case that the carbon is carbon black, both clay and alumina are relatively ineffective, although clay is more effective than alumina. The use of 1.5 vol.% clay in paste containing 2.4 vol.% carbon black provides resistivity 10^{11} Ω·cm and thermal contact conductance 6.52×10^4 W/m^2·°C. These results reflect the greater ease of breaking up the electrical connectivity of graphite particles than that of carbon black particles.

In the absence of a conductive filler, clay up to 1 vol.% slightly decreases the electrical conductivity. The thermal contact conductance increases with increasing clay content up to 1 vol.% and decreases with increasing clay content beyond 1 vol.%. These effects are due to the slight electrical and thermal conductivity of the clay.

In the absence of a conductive filler, the addition of clay has negligible effect on the thermal stability. Carbon black increases the thermal stability, whereas either graphite or alumina decreases the thermal stability. The antioxidation effect of carbon black is further increased by the presence of clay. The addition of clay or alumina to graphite paste enhances the thermal stability.

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