

# NANOSTRUCTURED CARBON PASTES AS THERMAL INTERFACE MATERIALS

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## Abstract

Thermal pastes are needed for improving thermal contacts. The structure of carbon black, as described by the DBP value, governs the effectiveness of the black as a thermally conductive solid component in a thermal paste, as shown for pastes with a polyol-ester vehicle. Carbon black with a lower DBP value (i.e., a lower structure) is more effective, as shown by a higher value of the thermal contact conductance measured across copper surfaces of roughness 15  $\mu\text{m}$ . This is because a carbon black with a lower structure gives a smaller bond-line thickness, which is preferably less than 3  $\mu\text{m}$ . In addition, this is because a lower structure gives a lower viscosity for the paste, thereby promoting conformability. The carbon black volume fraction has an optimum value for attaining maximum thermal conductance. A lower structure results in a higher value of the optimum carbon black volume fraction, due to the viscosity effect. By using Tokaiblack #3800 carbon black (with DBP value 60 ml/g and optimum carbon black content 15 vol.%), a thermal paste that is more effective than the previously reported paste with Vulcan XC72 carbon black (with DBP value 188 ml/g and optimum carbon black content 2.4 vol.%) has been attained.

## Introduction

Thermal interface pastes are applied at the interface between a heat source and a heat sink in order to improve the thermal contact, thereby promoting the heat flow from the heat source to the heat sink (Chung, 2006, 2001). Thermal pastes are critically needed by the electronic industry.

The performance of a thermal paste depends on the conformability, spreadability and thermal conductivity. Conformability is important, as the mating surfaces are never perfectly smooth and the paste needs to fill the microscopic valleys in the surface topography for the purpose of displacing the air from the interface (Xu et al., 2000, 2002). Spreadability is important, as the thermal resistance increases with the thickness of the paste, whatever is the thermal conductivity of the paste. Ideally the paste is just enough to fill the valleys, since this corresponds to the smallest thickness. For mating surfaces that are rough, curved or misaligned, the quantity of paste needed to fill the interface is larger, so that the thickness of paste for the heat to flow through is larger. Under this situation, the thermal conductivity of the paste is important. For mating surfaces that are smooth, flat and parallel, the conformability and spreadability can be even more important than the thermal conductivity in governing the effectiveness of the thermal paste.

Carbon black is thermally conductive, though it is less conductive than silver, which is commonly used in formulating thermal pastes. However, carbon black is in the form of porous agglomerates of nanoparticles. This microstructure makes carbon black highly compressible (i.e., squishable). As a consequence of the squishability and nanostructure of carbon black, pastes with carbon black as the solid component are highly effective as thermal pastes, as shown for one particular type of carbon black (Howe et al., 2006; Leong and Chung, 2003, 2004; Leong et al., 2005, 2006), which outperforms silver (Leong and Chung, 2004), boron nitride (Leong and Chung, 2004) and carbon nanotube (Hu et al., 2004; Lee et al., 2005; Xu et al., in press) as the thermally conductive component of a thermal paste. In addition, the carbon black paste outperforms solder (Leong and Chung, 2003) and carbon nanotube arrays (Chuang et al., 2004; Desai et al., 2004; Ngo et al., 2004; Sample et al., 2004; Wu et al., 2005) as thermal interface materials.

There are numerous types of carbon black that differ in structure and in their interaction with various materials (Bishai et al., 2003; Choi, 2004; Nasr et al., 1995). Examples of structural attributes are the agglomerate size, the nanoparticle size and the degree of crystallinity. The structure may affect the squishability, which is valuable for the conformability. The compressed state is also attractive for its enhanced thermal conductivity (Khizhnyak et al., 1979). As different types of carbon black may have different degrees of effectiveness for providing thermal pastes, it is important to compare the effectiveness

of different types of carbon black. Moreover, this comparison is expected to shed light on the factors that govern the effectiveness of a solid for forming thermal pastes.

The main objective of this paper is to investigate the effect of the structure of carbon black on the performance of carbon black thermal pastes. A second objective is to improve the previously reported carbon black thermal paste by using a more effective type of carbon black. A third objective is to understand the factors that govern the effectiveness of carbon black for use in a thermal paste.

## Experimental methods

### Materials

Except for the choice of carbon black, the formulation, ingredients and preparation method of the thermal pastes are identical to those in prior work on carbon black thermal paste with a polyol ester vehicle (Leong et al., 2005). The vehicle used consists of polyol esters, which are attractive for their thixotropic behavior and ability to resist elevated temperatures. The polyol esters in the vehicle are pentaerythritol ester of linear and branched fatty acids and dipentaerythritol ester of linear and branched fatty acids. The polyol ester mixture is provided by Hatco Corp., Fords, NJ. The specific gravity is 0.97.

In prior work (Howe et al., 2006; Leong and Chung, 2003, 2004; Leong et al., 2005, 2006), the carbon black is Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. Besides this type (denoted as Type III), four other types of carbon black are used in this investigation. Two of them are Tokaiblack #3800 (denoted as Type I) and Tokaiblack #3845 (denoted as Type II), which are graphitized carbon black supplied by Tokai Carbon Co., Ltd (Tokyo, Japan). Other types of carbon black are Ketjenblack EC300J (denoted as Type IV) and Ketjenblack EC600JD (denoted as Type V), which are both supplied by Akzo Nobel (Chicago, IL, USA). The properties of the five types of carbon black are listed in Table 1. These properties are the particle size, BET specific surface area, DBP (defined below), pH and  $\Phi$  (defined below).

Carbon black consists of nearly spherical primary particles, which are fused together to form aggregates. The degree of aggregation of the particles is known as the “structure”. A carbon black with aggregates that are composed of many primary particles, such that there is considerable branching and chaining within an aggregate, is referred to as a high-structure black. If an aggregate consists of relatively few primary particles, the carbon black is referred to as a low-structure black.

The structure of carbon black is conventionally analyzed by a method based on the amount of dibutyl phthalate (DBP) absorbed by the carbon black. The result is expressed in terms of the volume of DBP absorbed per gram of carbon black. A greater amount of absorption indicates a higher structure.

The carbon black structure is related to the maximum packing fraction, which is defined as the maximum fraction of particles in a given matrix. Thus, the DBP value allows one to calculate the maximum carbon black volume fraction ( $\Phi$ ) in random media according to the relation (Mallete et al., 2001)

$$\Phi = (1 + \rho D)^{-1}, \quad (1)$$

where  $\rho$  is the density of the black and  $D$  is the DBP value. A higher DBP value gives a higher value of  $\Phi$ , which is related to the yield stress of the carbon black suspension (Shenoy, 1999). The yield stress is relevant to the thermal paste performance. The values of  $\Phi$ , based on Eq. (1), are listed in Table 1. All the pastes, regardless of the type of carbon black, are prepared by ultrasonic dispersion of the carbon black in the vehicle for 15 min. A solvent is added for the purpose of decreasing the viscosity of the paste during the dispersion. After the ultrasonic dispersion, the paste is placed in a rough vacuum chamber at 70°C for 24 h for the purpose of solvent removal. Acetone is used as solvent because it greatly reduces the viscosity of the paste and can be evaporated rapidly.

Table 1 Characteristics of the five types of carbon black used in this comparative study.  $\Phi$  relates to DBP.

	DBP (ml/g)	pH	Specific surface area (m <sup>2</sup> /g)	Particle size (nm)	$\Phi$
I: Tokaiblack #3800	60	--	27	70	0.481
II: Tokaiblack #3845	161	--	57	40	0.257
III: Vulcan XC72	188	4-11	254	30	0.238
IV: Ketjenblack EC300J	310~345	8-10	929	30	0.145
V: Ketjenblack EC600JD	480~510	8-10	--	6-7	0.101

## Testing

**Thermal contact conductance measurement** The testing method (guarded hot plate method, i.e., ASTM Method D5470) is the same as that in prior work (Howe et al. 2006), which shows that this method gives results that are consistent with those obtained by measuring the temperature rise in an operating computer that uses the thermal paste at the interface between the microprocessor and the heat sink. In the guarded hot plate method, various thermal pastes are sandwiched between the 1 x 1 inch (25 x 25 mm) surfaces of two copper blocks (both 1 x 1 inch surfaces of each block having a controlled degree of roughness). Each copper block has a height of 35 mm. The thermal contact conductance between two 1 x 1 in (25 x 25 mm) copper blocks with a thermal paste between them is measured. The heat is provided by a 3 x 3 in (76 x 76 mm) copper block that has two embedded heating coils (top block in Fig. 1). The heating rate is controlled at 3.2°C/min. This copper block is in contact with one of the 1 x 1 in copper blocks that sandwich the thermal interface material. The cooling is provided by a second 3 x 3 in copper block, which is cooled by running water that flows into and out of the block (bottom block in Fig. 1). This block is in contact with the other one of the two 1 x 1 in copper blocks that sandwich the thermal paste. The two mating surfaces of the two 1 x 1 in copper blocks are either “rough” (15  $\mu\text{m}$  roughness, as attained by mechanical polishing) or “smooth” (0.009  $\mu\text{m}$  roughness and 0.040 – 0.116  $\mu\text{m}$  flatness, as attained by diamond turning). Four thermocouples (Type T) are inserted in four holes ( $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  in Fig. 1, each hole of diameter 2.4 mm). Two of the four holes are in each of the 1 x 1 in copper blocks. The temperature gradient is determined from  $T_1 - T_2$  and  $T_3 - T_4$ , which should be equal at equilibrium, which is attained after holding the temperature at the desired value for 30 min. Equilibrium is assumed when the temperature variation is within  $\pm 0.1^\circ\text{C}$  in a period of 15 min. At equilibrium, the hot block is at 75 - 80°C, while the cold block is at 10 - 15°C, while that of the thermal paste is in the range 40-50°C. The pressure in the direction perpendicular to the thermal interface is controlled by using a hydraulic press at 0.46, 0.69 and 0.92 MPa. The system is thermally insulated with glass fiber cloth.

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

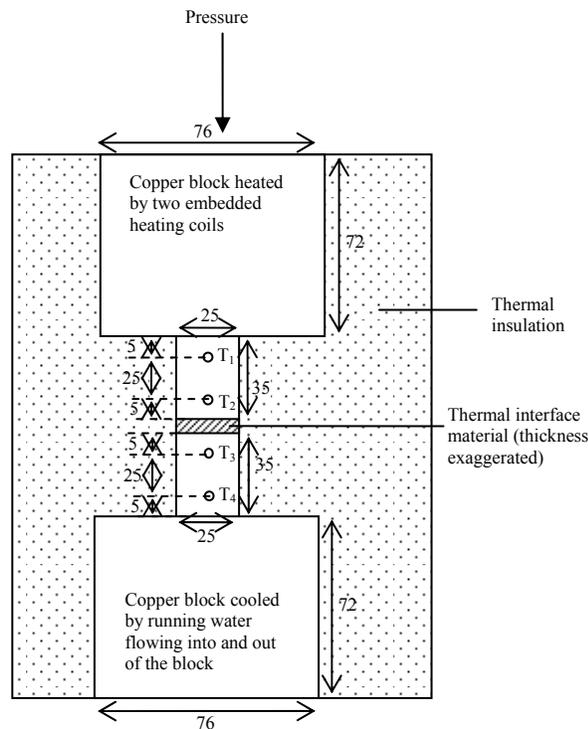


Fig. 1 Experimental set-up of the guarded hot plate method of thermal contact conductance measurement.  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  are holes of diameter 2.4 mm. A thermocouple (Type T) is inserted in each hole. All dimensions are in mm.

$$Q = \frac{\lambda A}{d_A} \Delta T \quad (2)$$

where  $\Delta T = T_1 - T_2 = T_3 - T_4$ ,  $\lambda$  is the thermal conductivity of copper,  $A$  is the area of the 1 x 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

$$T_A = T_2 - \frac{d_B}{d_A} (T_1 - T_2), \quad (3)$$

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

$$T_D = T_3 + \frac{d_D}{d_C} (T_3 - T_4), \quad (4)$$

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  $\theta$ , which is the thermal resistance multiplied by the area, is given by

$$\theta = (T_A - T_D) \frac{A}{Q} \quad (5)$$

Note that insertion of Eq. (2) into Eq. (5) causes cancellation of the term  $A$ , so that  $\theta$  is independent of  $A$ . The thermal contact conductance is the reciprocal of  $\theta$ .

*Bond-line thickness measurement* The bond-line thickness refers to the thickness of the thermal interface material between the 1 x 1 in copper blocks under the condition of the thermal contact conductance measurement. It is measured at room temperature by sandwiching the thermal paste at a pressure of 0.46 MPa with the “rough” copper surfaces that are used for thermal contact conductance measurement. A strain gage is mounted on a stainless steel spring which is fastened to an aluminum support. This support is adhesively bonded to the top of a copper bar, which is fastened to the lower one of the two copper blocks that serve to sandwich the thermal interface material. The steel spring is in contact (without bonding) with the bottom of another copper bar, which is fastened to the upper one of the two copper blocks. This design allows the distance between the proximate surfaces of the two copper blocks to affect the output of the strain gage. Through calibration, this output can be related to the bond-line thickness. This calibration is conducted prior to the experiment by sandwiching copper foils of known thicknesses by the copper blocks. The accuracy of this testing method is verified by testing copper foils of thickness 15  $\mu\text{m}$  and 25  $\mu\text{m}$ . This copper foil test shows an error of 15% in the thickness measurement.

*Optical microscopy* The microstructure of the carbon blacks is observed with a reflected light microscope using carbon blacks that have been dispersed in the polyol ester vehicle at a volume fraction of 0.1 %.

*Viscosity measurement* 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).

## Results and discussion

### *Optical microscopy*

Optical microscopy is used to observe the structure of dispersions with 0.1 vol. % carbon black. Types IV and V exhibit relatively long branches and large agglomerates. This is characteristic of a highly structured carbon black. On the other hand, Types I and III exhibit relatively short branches and small agglomerates, indicating a low structure. Type II exhibits an intermediate level of structure.

The small agglomerate size of Type I is consistent with its low DBP value (Table 1). The large agglomerate size of Types IV and V is consistent with their high DBP values. The medium agglomerate size of Type II is consistent with its medium DBP value. However, the small agglomerate size of Type III is apparently inconsistent with its medium DBP value. This apparent inconsistency reflects the fact that the absorption degree indicated by the DBP value depends not only on the agglomerate size, but also on the specific surface area, which is indeed quite high for Type III (Table 1).

### ***Thermal contact conductance***

Table 2 and Fig. 2 give the thermal contact conductance of all the carbon black pastes studied. All types of carbon black except Type V show that the highest conductance is attained at an intermediate content of carbon black when the contact conductance is measured using rough copper surfaces at a pressure of 0.46 MPa. That an intermediate content of carbon black gives the highest conductance is because of the compromise between the thermal conductivity of the paste itself (a property that increases with increasing carbon black content) and the viscosity (which also increases with increasing carbon black content). A high viscosity degrades the conformability. Type I carbon black reaches a conductance of  $(11.27 \pm 0.34) \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  at 15 vol.%; Type II reaches a conductance of  $(8.68 \pm 0.07) \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  at 4.8 vol.%; Type III reaches a conductance of  $(8.72 \pm 0.07) \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  at 2.4 vol.%; Type IV reaches a conductance of  $(7.83 \pm 0.12) \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  at 1.2 vol.%. For Type V, the conductance monotonically decreases with increasing carbon black content, so that the highest conductance  $(6.24 \pm 0.05) \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  is attained at the lowest carbon black content of 0.3 vol.%. The optimum carbon black content of 2.4 vol.% for Type III is consistent with prior work (Leong and Chung, 2003).

The dependence of the thermal contact conductance (as measured at 0.46 MPa using rough surfaces) on the carbon black content for each of the five types of carbon black is shown more clearly in Fig. 2. Type I gives the highest conductance; Type V gives the lowest conductance. Types II and III give similar values of the conductance. Type IV gives conductance that is higher than that given by Type V, but is lower than those given by Types II and III. The relative performance among these types of carbon black is the same for the higher pressures (0.69 and 0.92 MPa), as shown in Table 2.

For each of the pastes, the thermal contact conductance increases with increasing pressure (Table 2). This trend is consistent with prior work (Leong and Chung, 2004) and is possibly due to one or more of the following: (i) the pressure helping the filling of the valleys by the paste and (ii) the pressure helping to increase the thermal conductance across the microscopic interface between the paste and the copper. In case of smooth surfaces, the investigation is limited, particularly in relation to the small number of carbon black contents studied for each type of carbon black (Table 2). Thus, the trends reported for the case of the rough surfaces may or may not apply in case of smooth surfaces. For the same composition, the conductance is higher for the smooth case than the rough case, as previously reported for Type III carbon black (Leong and Chung, 2003). The higher conductance for the smooth case is due to the smaller depth of the valleys for the smooth case and the consequent lower thickness of the thermal interface material inside the valleys. Due to the fact that carbon black is not high in the thermal conductivity, the thermal resistance within the carbon black paste becomes more important as the paste thickness increases.

Correlation of the trends among the types of carbon black for the conductance and for the DBP value (Table 1) shows that a high conductance correlates with a low DBP value. Type I exhibits the lowest DBP value and gives the highest conductance. Type V exhibits the highest DBP value and gives the lowest conductance. Types II and III exhibit close and intermediate DBP values and give close and intermediate conductance values. Type IV exhibits DBP intermediate between Types III and V and gives conductance between Types III and V. This correlation is more clearly shown in relation Fig. 3, which shows that the thermal conductance decreases with increasing DBP value for each volume fraction of carbon black. Although Type I gives the best thermal paste performance, it has the highest particle size (Table 1). Type V gives the worst thermal paste performance, but it has the lowest particle size (Table 1). From the point of view of the ease of thorough filling of the valleys in the surface topography, a lower particle size is preferred. This correlation of the conductance trend with the particle size trend means that the structure of the carbon black, as described by the DBP number, is a much more significant factor than the particle size in governing the performance of the carbon black thermal paste.

Table 1 shows that Types II and III are quite different in the specific surface area, but Table 2 shows that they are similar in the thermal paste performance. Table 1 also shows that they are similar in the DBP value. This implies that the specific surface area is not a significant factor compared to the DBP value in governing the effectiveness of a carbon black for use in a thermal paste.

Information on the pH is insufficient in Table 1. Nevertheless, the pH does not seem to vary significantly among the different types of carbon black. As a result, the pH is probably not a significant factor in governing the effectiveness of a carbon black for use in a thermal paste.

The degree of crystallinity of the carbon black is a factor that has not been investigated in this work. Types I and II are both described by the manufacturer as graphitized carbon black, but Type I is more

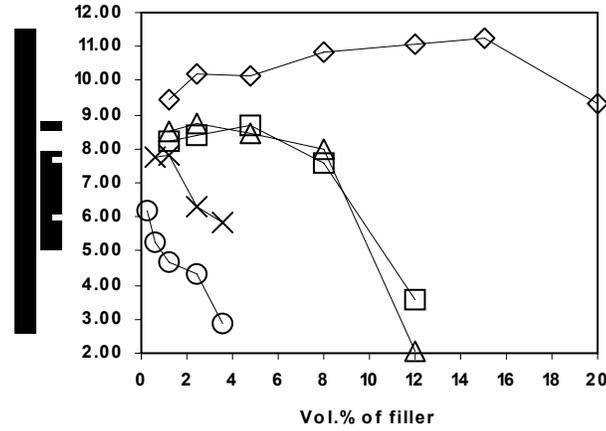


Fig. 2 Dependence of the thermal contact resistance on the carbon black volume fraction. ◇: Type I, □: Type II, △: Type III, ×: Type IV, ○: Type IV.

effective than Type II for use in thermal pastes (Table 2). Although the crystallinity may contribute to the high effectiveness of Type I, it appears that the crystallinity is a minor factor compared to the DBP value in governing the effectiveness of a carbon black for use in a thermal paste. The relatively small role of the crystallinity is consistent with (i) the fact that carbon black in general is not high in the thermal conductivity compared to many conductive materials (such as silver), and (ii) the notion that the high effectiveness of carbon black paste (compared to silver paste) is due to its conformability rather than its thermal conductivity (Howe et al., 2006; Leong et al., 2006).

Based on the data in Table 2, the relation between bond-line thickness and carbon black volume fraction is obtained and shown in Fig. 4. The bond-line thickness increases as the carbon black volume fraction increases, as shown for Types I, II and III. At the same volume fraction (2.4 vol. %), a higher DBP value corresponds to a higher bond-line thickness.

The relation among the thermal contact conductance, bond-line thickness and DBP value, as described above, is explained below. Consider a filled polymer system that exhibits a yield stress. If the electrostatic interaction between the filler particles is negligible compared to the van der Waals interaction between them, the yield stress  $\tau$  may be expressed as (Shenoy, 1999)

$$\tau = B \cdot \left[ \frac{1}{(\Phi/\varphi)^{1/3} - 1} \right]^2 \quad (6)$$

where  $B$  is a positive constant that depends on the particle size,  $\Phi$  is the maximum filler volume fraction and  $\varphi$  is the filler volume fraction.

The bond-line thickness  $h$  of a thermal interface material can be expressed as (Prasher et al., 2001)

$$h = C \left( \frac{\tau}{P} \right)^m, \quad (7)$$

where  $C$  and  $m$  are empirical constants, and  $P$  is the pressure.

Combination of Eq. (1), (6) and (7) gives

$$h = C \left( \frac{B}{P} \right)^m \cdot \left[ \frac{1}{(1 + \rho D)^{-1/3} \cdot \varphi^{-1/3} - 1} \right]^{2m} \quad (8)$$

Eq. (8) also shows that the bond-line thickness ( $h$ ) increases with the filler volume fraction ( $\varphi$ ), as indeed shown in Fig. 6 for Types I, II and III.

Table 2 Thermal contact conductance and bond-line thickness of carbon black pastes, as measured at various pressures applied perpendicular to the plane of the thermal contact. Negative values of the bond-line thickness are not really negative, as they are merely due to the substantial error in measuring small thickness values.

Carbon black		Thermal conductance ( $10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ )					Bond-line thickness ( $\mu\text{m}$ )
		Rough surfaces			Smooth surfaces		
Type	Vol.%	0.46 MPa	0.69 MPa	0.92 MPa	0.46 MPa	0.69 MPa	0.46 MPa
I	1.2	9.45 ± 0.02	9.59 ± 0.09	9.89 ± 0.02	/	/	/
I	2.4	10.20 ± 0.20	11.01 ± 0.05	11.87 ± 0.08	24.23 ± 0.17	27.75 ± 0.11	-1.2 ± 1.4
I	4.8	10.12 ± 0.16	11.10 ± 0.10	11.59 ± 0.15	/	/	/
I	8.0	10.85 ± 0.20	11.39 ± 0.10	11.64 ± 0.12	/	/	1.8 ± 1.1
I	12.0	11.06 ± 0.27	11.71 ± 0.12	12.57 ± 0.28	/	/	/
I	15.0	11.27 ± 0.34	12.41 ± 0.22	13.18 ± 0.11	25.58 ± 0.35	27.86 ± 0.10	8.7 ± 2.6
I	20.0	9.34 ± 0.21	9.86 ± 0.11	11.11 ± 0.13	/	/	13.7 ± 3.2
II	1.2	8.20 ± 0.15	9.41 ± 0.12	10.28 ± 0.04	/	/	/
II	2.4	8.40 ± 0.12	9.44 ± 0.15	9.89 ± 0.17	25.31 ± 1.12	29.05 ± 1.22	0.6 ± 0.8
II	4.8	8.68 ± 0.07	9.41 ± 0.10	10.72 ± 0.15	/	/	/
II	8.0	7.56 ± 0.06	9.00 ± 0.11	9.36 ± 0.10	/	/	3.3 ± 0.9
II	12.0	3.58 ± 0.04	4.45 ± 0.05	5.12 ± 0.02	/	/	/
III	1.2	8.50 ± 0.16	9.39 ± 0.11	10.36 ± 0.20	/	/	/
III	2.4	8.72 ± 0.07	10.18 ± 0.20	11.12 ± 0.12	25.91 ± 0.16	27.75 ± 0.14	-1.4 ± 2.6
III	4.8	8.45 ± 0.11	9.39 ± 0.15	10.58 ± 0.11	/	/	/
III	8.0	7.96 ± 0.08	8.71 ± 0.10	8.78 ± 0.09	/	/	2.2 ± 0.9
III	12.0	2.05 ± 0.02	2.28 ± 0.03	2.49 ± 0.02	/	/	/
IV	0.6	7.75 ± 0.13	7.98 ± 0.08	8.45 ± 0.11	/	/	/
IV	1.2	7.83 ± 0.12	8.22 ± 0.10	8.51 ± 0.09	/	/	/
IV	2.4	6.28 ± 0.14	7.15 ± 0.12	7.49 ± 0.14	14.40 ± 0.17	17.20 ± 0.26	2.8 ± 1.1
IV	3.6	5.82 ± 0.05	6.45 ± 0.05	6.99 ± 0.09	/	/	/
V	0.3	6.24 ± 0.05	7.07 ± 0.07	7.50 ± 0.18	/	/	/
V	0.6	5.25 ± 0.05	5.83 ± 0.05	6.08 ± 0.06	/	/	/
V	1.2	4.65 ± 0.22	5.13 ± 0.13	5.40 ± 0.05	/	/	/
V	2.4	4.33 ± 0.15	5.03 ± 0.06	5.51 ± 0.06	8.81 ± 0.10	9.75 ± 0.07	7.5 ± 1.8
V	3.6	2.88 ± 0.05	3.42 ± 0.05	3.69 ± 0.03	/	/	/

The thermal resistance of a system consisting of a thermal paste sandwiched by a heat source and a heat sink can be simply modeled by thermal resistances in series. Thus,

$$R = \frac{h}{kA} + R_1 + R_2, \quad (9)$$

where  $h$  is the bond-line thickness,  $A$  is the area of the thermal contact,  $k$  is the thermal conductivity of the thermal interface material,  $R$  is the total thermal resistance of the sandwich, and  $R_1$  and  $R_2$  are the contact resistances of the interface between the thermal interface material and the two surfaces that sandwich the interface material. Eq. (9) means that a higher bond-line thickness will give a higher thermal resistance, which means a lower thermal conductance.

Eq. (8) shows that a higher DBP value ( $D$ ) will lead to a higher bond-line thickness ( $h$ ) when the pressure is fixed. As a consequence of the notion in Eq. (9), a higher DBP value leads to a lower conductance, as indeed shown in Fig. 3.

Combining the information from optical microscopy, DBP value (Table 1), bond-line thickness and thermal contact conductance, we conclude that a highly structured carbon black, which has relatively large agglomerates and a relatively high DBP value, tends to give a higher bond-line thickness and thus results in a lower thermal contact conductance. The factors that affect the bond-line thickness also include the particle size and degree of dispersion of the carbon black. The DBP value is not the only factor, but it is

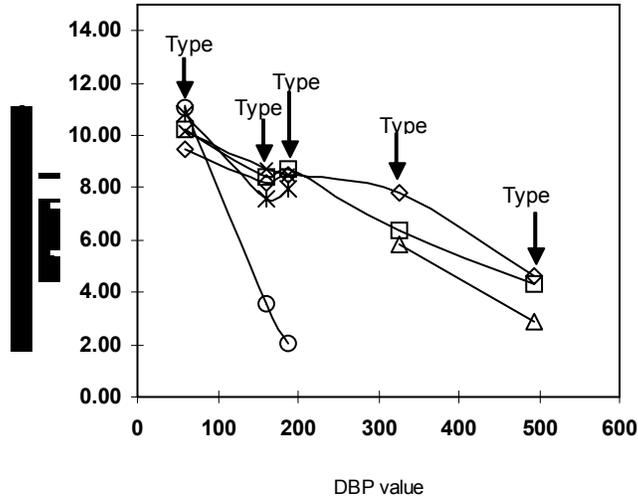


Fig. 3 Dependence of the thermal contact conductance on the carbon black DBP value. ◇: 1.2 vol. %, □: 2.4 vol. %, △: 3.6 vol. %, ×: 4.8 vol. %, \*: 8 vol. %, ○: 12 vol. %.

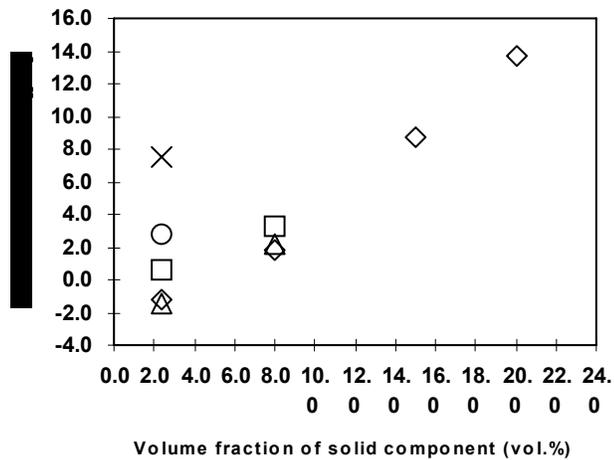


Fig. 4 Dependence of the bond-line thickness on the carbon black volume fraction. ◇: Type I; □: Type II; △: Type III, ○: Type IV; ×: Type V.

probably one of the most important factors. The viscosity, which relates to the DBP value, may also affect the thermal contact conductance and is discussed in the next section.

*Viscosity* In a dispersion comprising particles and a vehicle and subjected to a shear stress (as provided by a viscometer), the interaction between particles and that between particles and the vehicle govern the viscosity of the dispersion. In general, the viscosity of a dispersion of carbon black is higher for a more structured carbon black, i.e., one with a higher DBP value. The viscosity of selected pastes and the unfilled vehicle is shown in Fig. 5 for various shear rates. The presence of carbon black, whichever type, increases the viscosity. Type III has more than twice the DBP value and specific surface area than Type I (Table 1), and consequently a much higher viscosity. At the same filler content of 2.4 vol.%, the highly structured Type IV gives much higher viscosity than the moderately structured Type III. The viscosity of Type V, with even higher structure than Type IV (as shown by the DBP values in Table 1), is too high to be measured by the viscometer used in this work.

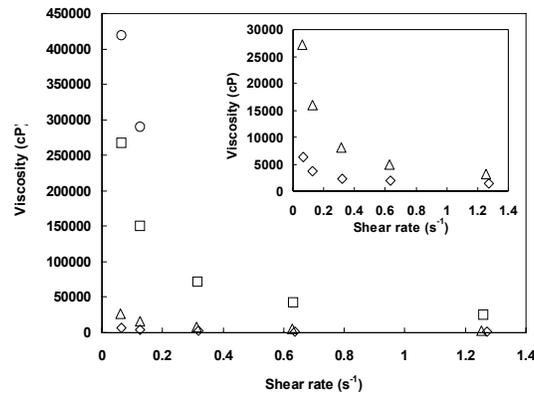


Fig. 5 Viscosity of selected carbon black pastes and its variation with the shear rate. The inset shows a magnified view of the part of the graph up to a viscosity of 30,000 cP. ◇: Pure vehicle; △: Type I; □: Type III; ○: Type IV.

All the carbon black pastes exhibit shear thinning behavior (i.e., decrease of viscosity with increasing shear rate), as shown in Fig. 5. This behavior can be attributed to the particles becoming more aligned and hence less entangled and less resistant to deformation as the shear rate is increased.

Besides the effect of the carbon black structure on the bond-line thickness and thus on the thermal contact conductance, the high viscosity of a thermal paste may also decrease the thermal contact conductance. A higher viscosity will make the paste harder to spread and flow into the valleys in the surface topography, thus decreasing the conformability of the dispersion. Due to the air in the valleys, the limited filling of the valleys will increase the thermal resistance.

The effectiveness of a carbon black thermal paste is maximum at an intermediate carbon black content, such that the optimum carbon black content (Table 2) essentially decreases as the DBP value increases. This effect is attributed to the increase of viscosity with increasing carbon black content and with increasing carbon black structure (i.e., with increasing DBP), and the detrimental effect of high viscosity to the conductance. A highly structured carbon black causes the viscosity to increase significantly with increasing carbon black content, thus resulting in a low value of the optimum carbon black content.

#### 4. Conclusion

The DBP value is an important parameter that governs the effectiveness of a carbon black for use in a thermal paste. A carbon black with a lower DBP value (i.e., a lower structure) is more effective, as shown by a higher value of the thermal contact conductance. This is because a carbon black with a lower structure gives a smaller bond-line thickness. In addition, this is because a lower structure gives a lower viscosity for the paste, thereby promoting conformability of the paste. Furthermore, a lower structure results in a higher value of the optimum carbon black volume fraction. By using Type I carbon black (with a DBP value of 60 ml/g), a thermal paste that is more effective than the previously reported paste with Type III carbon black (with a DBP value of 188 ml/g) has been attained.

#### References

- Bishai, A.M., Ghoneim, A.M., Ward, A. and Younan, A.F. 2003. Electrical conductivity of styrene-butadiene rubber/polyester short-fiber reinforced with different types of carbon black. *Polymer-Plastics Technology and Engineering* 42(4):701-710.
- Choi, S-S. 2004. Effect of bound rubber on characteristics of highly filled styrene-butadiene rubber compounds with different types of carbon black. *J. Appl. Chem.* 93(3):1001-1006.
- Chuang, H. F., Cooper, S. M., Meyyappan, M. and Cruden, B. A. 2004. Improvement of thermal contact resistance by carbon nanotubes and nanofibers. *Journal of Nanoscience and Nanotechnology* 4(8): 964-967.
- Chung, D. D. L. 2006. Advances in thermal interface materials. *Advancing Microelectronics* 33(4):8-11.
- Chung, D. D. L. 2001. Materials for thermal conduction. *Applied Thermal Engineering* 21(ER16):1593-1605.

- Desai, A., Mahajan, S., Subbarayan, G., Jones, W., Geer, J. and Sammakia, B. 2004. An analytical study of transport in a thermal interface material enhanced with carbon nanotubes. *9<sup>th</sup> Intersociety Conf. on Thermal and Thermomechanical Phenomena in Elec. Sys.*, IEEE, Piscataway, NJ, 1: 403-409.
- Howe, T. A., Leong C-K. and Chung, D. D. L. 2006. Comparative evaluation of thermal interface materials for improving the thermal contact between an operating computer microprocessor and its heat sink. *J. Electron. Mater.* 2006;35(8):1628-1635.
- Hu, X., Jiang, L. and Goodson, K. E. 2004. Thermal conductance enhancement of particle-filled thermal interface materials using carbon nanotube inclusions. *Proc. 9<sup>th</sup> Intersociety Conf. on Thermal and Thermomechanical Phenomena in Elec. Sys.*, IEEE, Piscataway, NJ; 1: 63-69.
- Khizhnyak, P. E., Chechetkin, A.V. and Glybin, A. P. 1979. Thermal conductivity of carbon black. *Inzhenerno-Fizicheskii Zhurnal* 37(3):475-8.
- Lee, T., Chio, u K., Tseng, F. and Huang, C. 2005. High thermal efficiency carbon nanotube- resin matrix for thermal interface materials. *Proc. 55<sup>th</sup> Electronic Components and Tech. Conf.*, IEEE, Piscataway, NJ, 1:55-59.
- Leong, C-K. and Chung, D. D. L. 2003. Carbon black dispersions as thermal pastes that surpass solder in providing high thermal contact conductance. *Carbon* 41(13):2459-2469.
- Leong, C-K. and Chung, D. D. L. 2004. Carbon black dispersions and carbon-silver combinations as thermal pastes that surpass commercial silver and ceramic pastes in providing high thermal contact conductance, *Carbon* 42(11):2323-2327.
- Leong, C-K. Aoyagi, Y. and Chung, D. D. L. 2005. Carbon-black thixotropic thermal pastes for improving thermal contacts. *J. Electron. Mater.* 34(10):1336-1341..
- Leong, C-K. Aoyagi, Y. and Chung, D. D. L. 2006. Carbon black pastes as coatings for improving thermal gap-filling materials. *Carbon* 44(3):435-440.
- Mallete, J. G., Quej, L. M., Marquez, A. and Manero, O. 2001. Carbon black-filled PET/HDPE blends: effect of CB structure on rheological and electric properties. *J Appl Polym Sci* 81(3):562-9
- Nasr, G. M., Badawy, M.M., Gwaily, S. E., Shash, N. M. and Hassan, H. H. 1995. Thermophysical properties of butyl rubber loaded with different types of carbon black. *Polymer Degradation and Stability* 48(2):237-241.
- Ngo, Q., Cruden, B. A., Cassell, A. M., Sims, G., Meyyappan, M., Li, J. and Yang, C.Y. 2004. Thermal interface properties of Cu-filled vertically aligned carbon nanofiber arrays. *Nano Letters* 4(13): 2403-2407.
- Prasher, R., Shipley, J., Prstic, S., Koning, P. and Wang, J. 2001. Thermal resistance of particle laden polymeric thermal interface materials. *J. Heat Transfer* 123(5): 969-75.
- Sample, J. L., Rebello, K. J., Saffarian, H. and Osiander, R. 2004. Carbon nanotube coatings for thermal control. *9<sup>th</sup> Intersociety Conf. on Thermal and Thermomechanical Phenomena in Elec. Sys.*, IEEE, Piscataway, NJ, 1:297-301.
- Shenoy, A.V. 1999. *Rheology of Filled Polymer Systems*. Norwell: Kluwer Academic Publishers, p. 248.
- Wu, Y., Liu, C. H., Huang, H. and Fan, S. S. 2005. Effects of surface metal layer on the thermal contact resistance of carbon nanotube arrays. *Applied Physics Letters* 87: 213108-1-213108-3.
- Xu, Y., Luo, X. and Chung, D. D. L. 2002. Lithium doped polyethylene-glycol-based thermal interface pastes for high thermal contact conductance. *J Electron Packaging* 124(3):188-191.
- Xu, Y., Luo, X. and Chung, D. D. L. 2000. Sodium silicate based thermal pastes for high thermal contact conductance. *J. Electron. Packaging* 122(2):128-131.
- Xu, Y., Leong, C.-K. and Chung, D. D. L. Carbon nanotube dispersions as thermal pastes. *J. Electron. Mater.*, in press.