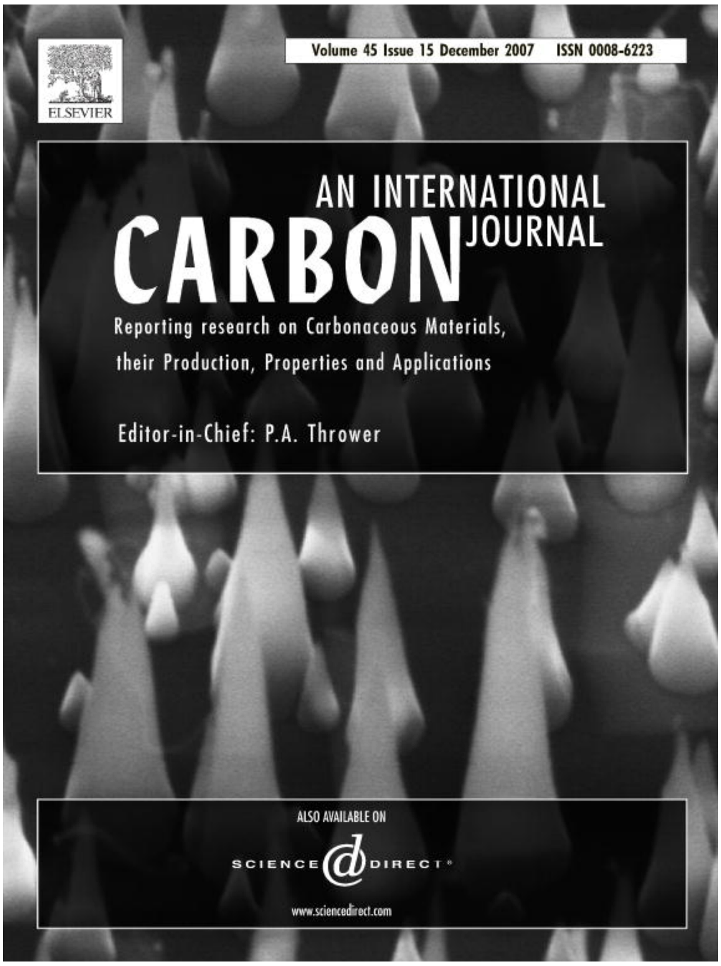

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Effect of carbon black structure on the effectiveness of carbon black thermal interface pastes

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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 μm. This is because a carbon black with a lower structure gives a smaller bond-line thickness, which is preferably less than 3 μm. 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. For the same type of carbon black, this optimum is higher when the paste is tested between rougher surfaces. 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.

1. Introduction

Thermal interface pastes are commonly applied at the interface between a heat source (such as the microprocessor of a computer) and a heat sink in order to improve the thermal contact, thereby promoting the heat flow from the heat source to the heat sink [1–3]. Due to the importance of microelectronic cooling [4,5], thermal pastes are critically needed by the electronic industry. Heat dissipation limits the further miniaturization, power and reliability of microelectronics.

The performance of a thermal paste depends on the conformability, spreadability and thermal conductivity of the paste. 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 (a thermal insulator) from the interface [4,5]. 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

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pastes, as shown for one particular type of carbon black [6–10], which outperforms silver [6], boron nitride [6] and carbon nanotube [11–13] as the thermally conductive component of a thermal paste. In addition, the carbon black paste outperforms solder [7] and carbon nanotube arrays [14–18] as thermal interface materials.

There are numerous types of carbon black that differ in structure and in their interaction with various materials [19–21]. 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 [22]. 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.

2. Experimental methods

2.1. Materials

Except for the choice of carbon black, the formulation, ingredients and preparation method of the thermal pastes of this work are identical to those in prior work on carbon black thermal paste with a polyol ester vehicle [8].

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 [6–10], the carbon black is Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. Besides this type of carbon black (Vulcan XC72R, 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). Two other types of carbon black included in this study 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 Φ (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 commonly 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 illustrated in Fig. 1, which shows aggregates that decrease in size from Fig. 1a, b and c.

The structure of carbon black is conventionally analyzed by using a method based on measuring the amount of dibutyl phthalate (an oil, abbreviated as DBP) absorbed by the carbon black. The result is expressed in terms of the volume of DBP absorbed by 100 g 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 (Φ) in random media according to the relation [23]

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

where ρ is the density of the carbon black and D is the DBP value. The density of 1.80 g/cm^3 was used for all types of carbon black in this study, in accordance with manufacturers' product specifications. A higher DBP value gives a higher value of Φ. The value of Φ is related to the yield stress of the carbon black suspension [24]. The yield stress is relevant to explaining the thermal paste performance. The values of Φ, as calculated by using Eq. (1), are listed in Table 1.

All the pastes in this work, 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 vacuum chamber (which involves a mechanical vacuum pump) 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. The uniformity of the dispersion is indicated by the consistency of the test data obtained from various specimens from the same batch of paste.

2.2. Testing

2.2.1. Thermal contact conductance measurement

The testing method (guarded hot plate method, which is a steady-state method of heat flux measurement, i.e., ASTM Method D5470) is the same as that in prior work [10], 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 × 1 in. (25 × 25 mm) surfaces of two copper blocks (both 1 × 1 in. surfaces of each block having a controlled degree of roughness). Each copper block has a height of 35 mm.

Table 1
Characteristics of the five types of carbon black used in this comparative study

	DBP (ml/100 g)	pH	Specific surface area (m^2/g)	Particle size (nm)	Φ
I: Tokaiblack #3800	60	–	27	70	0.481
II: Tokaiblack #3845	161	–	57	40	0.257
III: Vulcan XC72R	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

Φ relates to DBP, as defined in Eq. (1).

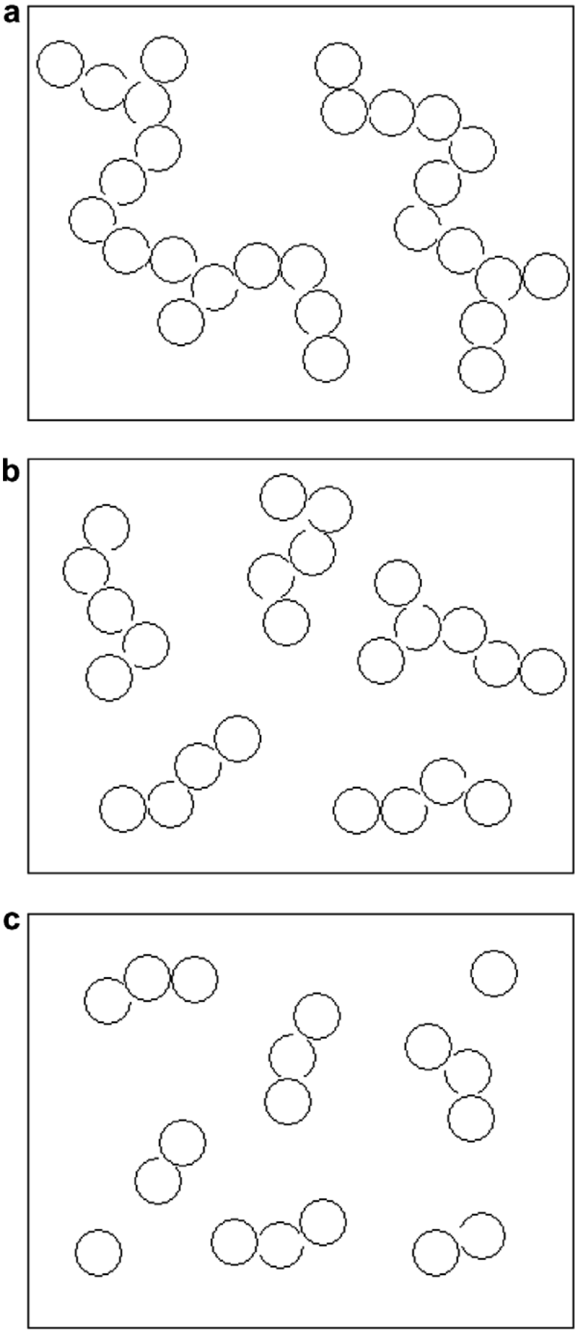

Fig. 1. Schematic illustration of carbon black structures. (a) High structure; (b) medium structure; (c) low-structure.

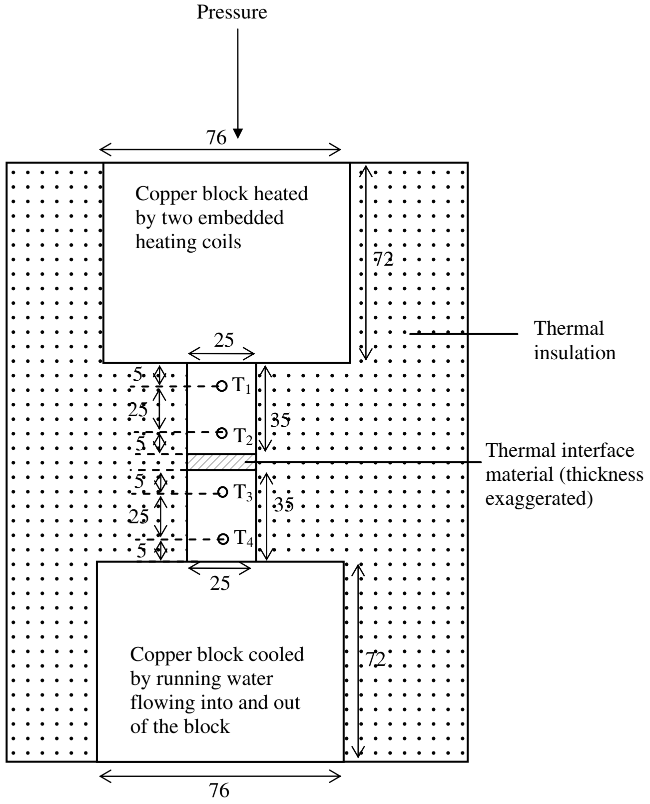

Fig. 2. Experimental set-up of the guarded hot plate method of thermal contact conductance measurement. T_1, T_2, T_3 and T_4 are holes of diameter 2.4 mm. A thermocouple (Type *T*) is inserted in each hole. All dimensions are in mm.

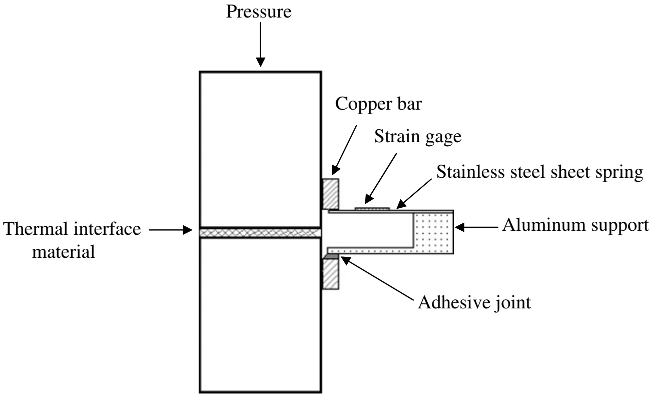

Fig. 3. Schematic illustration of the bond-line thickness testing method.

The thermal contact conductance between two 1 × 1 in. (25 × 25 mm) copper blocks with a thermal paste between them is measured. The heat is provided by a 3 × 3 in. (76 × 76 mm) copper block that has two embedded heating coils (top block in Fig. 2). 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 × 1 in. copper blocks that sandwich the thermal interface material. The cooling is provided by a second 3 × 3 in. copper block, which is cooled by running water that flows into and out of the block (bottom block in Fig. 2). This block is in contact with the other one of the two 1 × 1 in. copper blocks that sandwich the thermal paste. The two mating surfaces of the two 1 × 1 in. copper blocks are either "rough" (15 µm roughness, as attained by mechanical polishing) or "smooth" (0.009 µm roughness and 0.040–0.116 µm flatness, as attained by diamond turning). An RTD probe (connected to Digi-Sense ThermoLogR RTD Thermometer from Fisher Scientific Co., with accuracy ±0.03 °C) is inserted in four holes. (T_1, T_2, T_3 and T_4 in Fig. 2, each hole of diameter 3.3 mm) one after the other. Two of the four holes are in each of the 1 × 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 ±0.01 °C in a period of 15 min. At equilibrium, the temperature of the hot block is in the range 60–80 °C, that of the cold block is in the range 30–50 °C, while that of the thermal paste is in the range 50–60 °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, 0.69 and 0.92 MPa. The system is thermally insulated by wrapping laterally all the copper blocks with glass fiber cloth.

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

$$Q = \frac{\lambda A}{d_A}\Delta T \tag{2}$$

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

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

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

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

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 θ, which is the thermal resistance multiplied by the area, is given by

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

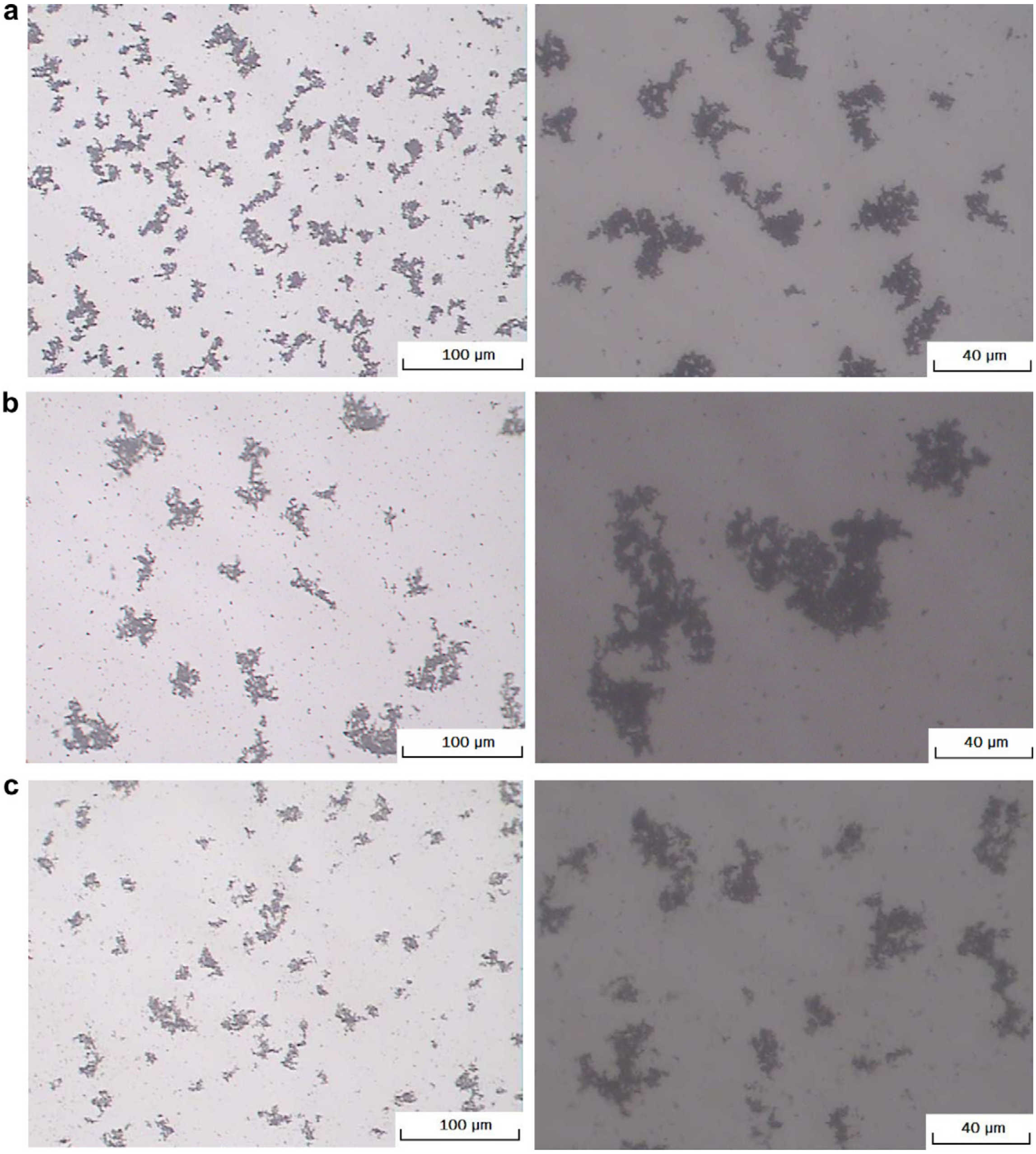

Fig. 4. Optical microscope images of dispersion containing 0.1 vol.% carbon black. (a) Type I; (b) Type II; (c) Type III; (d) Type IV; (e) Type V.

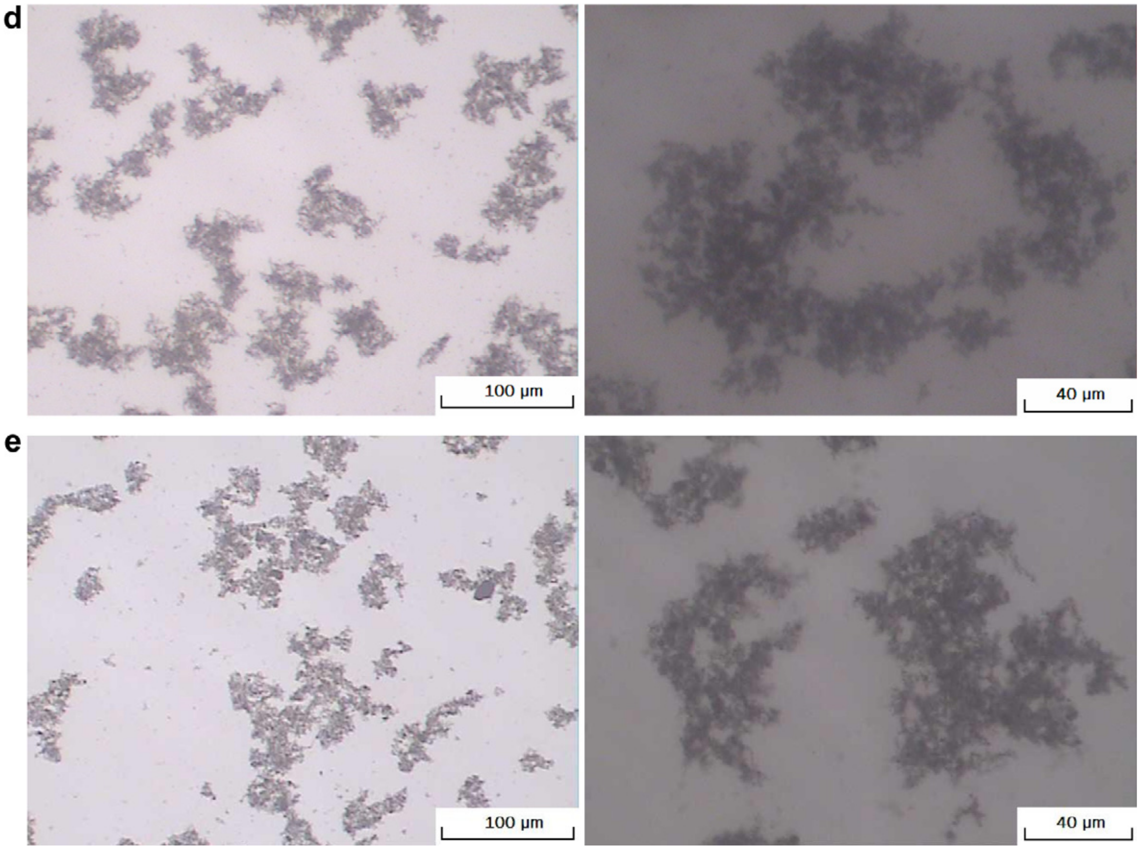

Fig. 4 (*continued*)

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

2.2.2. Bond-line thickness measurement

The bond-line thickness refers to the thickness of the thermal interface material between the 1 × 1 in. copper blocks under the condition of the thermal contact conductance measurement. It is measured 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 (Section 2.2.1). A strain gage is mounted on a stainless steel spring which is fastened to an aluminum support (Fig. 3). 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 μm and 25 μm. This copper foil test shows an error of 15% in the thickness measurement. The bond-line thickness measurement is conducted at room temperature to avoid experimental error associated with the thermal expansion of the copper blocks and of the strain gage.

2.2.3. Optical microscopy

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

2.2.4. Viscosity measurement

The viscosity describes the resistance to shear deformation. It is a common attribute for describing the behavior of 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).

3. Results and discussion

3.1. Optical microscopy

Optical microscopy is used in this work to observe the structure of carbon blacks. Fig. 4 shows the typical distributions and agglomerates of carbon black in dispersions with 0.1 vol.% carbon black. Images at the same two magnifications are shown for each type of carbon black. Carbon blacks of 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

Table 2
Thermal contact conductance (for rough and smooth surfaces) and bond-line thickness (for rough surfaces only) of carbon black pastes, as measured at various pressures applied perpendicular to the plane of the thermal contact

Carbon black		Thermal conductance (10^4 W/m^2 °C)					Bond-line thickness (μm)
		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	30.41 ± 0.47	32.75 ± 0.19	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	17.48 ± 0.17	22.33 ± 0.29	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	–	–	–

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.

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).

3.2. Thermal contact conductance

Table 2 and Fig. 5 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, as reported in Section 3.3). A high viscosity degrades the conformability. Type I carbon black reaches a conductance of (11.27 ± 0.34) × 10^4 W/m^2 °C at 15 vol.%; Type II reaches a conductance of (8.68 ± 0.07) × 10^4 W/m^2 °C at 4.8 vol.%; Type III reaches a conductance of (8.72 ± 0.07) × 10^4 W/m^2 °C at 2.4 vol.%; Type IV reaches a conductance of (7.83 ± 0.12) × 10^4 W/m^2 °C at 1.2 vol.%. For Type V, the conductance monotonically decreases with increasing carbon black content, so that the highest conductance (6.24 ± 0.05) × 10^4 W/m^2 °C) is attained at the lowest carbon black content of 0.3 vol.%. That the optimum carbon black content is 2.4 vol.% for Type III is consistent with prior work [7].

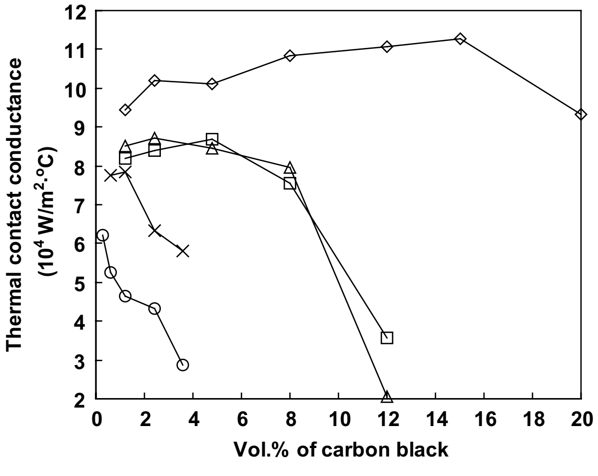

Fig. 5. Dependence of the thermal contact conductance on the carbon black volume fraction for the case of rough surfaces. ◇: Type I, □: Type II, △: Type III, ×: Type IV, ○: Type V.

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. 5. 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 investigated, the thermal contact conductance increases with increasing pressure (Table 2). This trend is consistent with prior work [6] and is possibly due to one or more of the following: (i) the pressure helping the filling of the valleys by the thermal 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 [7]. The higher conductance for the smooth case compared to the rough case is due to the smaller depth of the valleys in the surface topography 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.

In the case of Type I carbon black, the thermal contact conductance is highest at 8 vol.% when the paste is tested between smooth surfaces and at 15 vol.% when the paste is tested between rough surfaces, as shown in Table 2, Figs. 5 and 6. This is because a rough surface has deeper valleys than a smooth surface, thus resulting in the need for heat to go through a relatively long distance within the paste. As a consequence, the thermal conductivity within the paste is more important for rough surfaces than smooth surfaces. Thus, a higher carbon black volume fraction is preferred for rough surfaces than smooth surfaces.

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 exhibits 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. 7, which shows that the thermal conductance decreases with increasing DBP value for each volume fraction of carbon black.

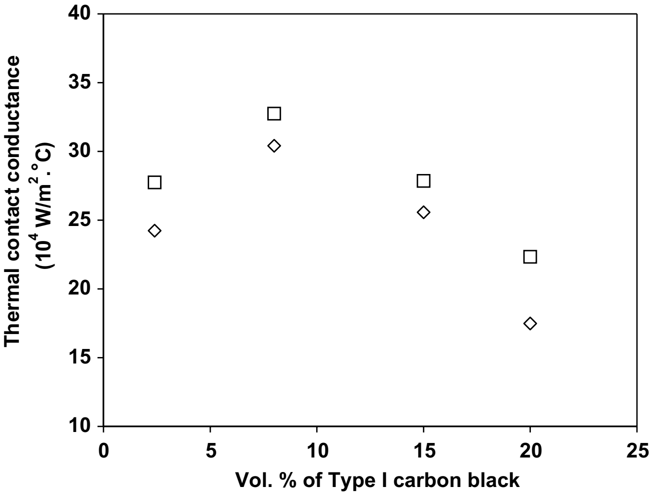

Fig. 6. Dependence of the thermal contact conductance on the Type I carbon black volume fraction for the case of smooth surfaces. ◇: 0.46 MPa, □: 0.69 MPa.

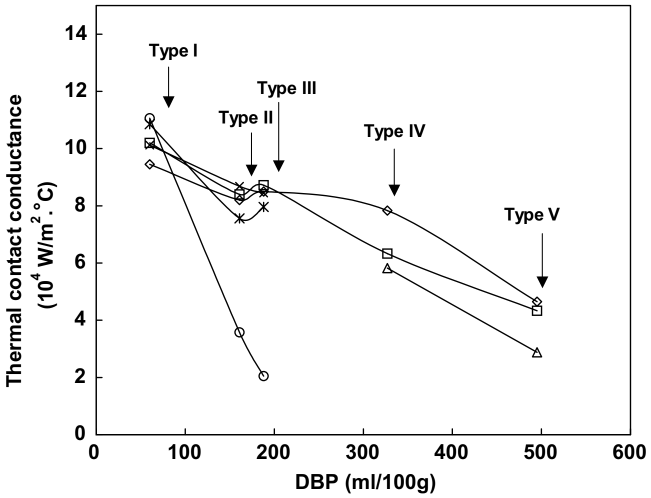

Fig. 7. Dependence of the thermal contact conductance on the carbon black DBP value. ◇: 1.2 vol.%, □: 2.4 vol.%, △: 3.6 vol.%, ×: 4.8 vol.%, *: 8 vol.%, ○: 12 vol.%.

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 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 [9,10].

Based on the data in Table 2, the relation between bond-line thickness and carbon black volume fraction is obtained and shown in Fig. 8. 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 τ may be expressed as [24]

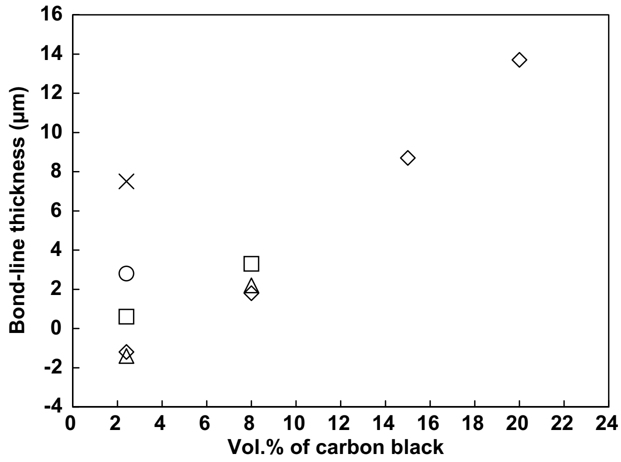

Fig. 8. Dependence of the bond-line thickness on the carbon black volume fraction. ◇: Type I; □: Type II; △: Type III, ○: Type IV; ×: Type V.

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

where B is a positive constant that depends on the particle size, Φ is the maximum filler volume fraction and ϕ is the filler volume fraction.

According to Prasher [25], the bond-line thickness h of a thermal interface material can be expressed as

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

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

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

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

Eq. (8) also shows that the bond-line thickness (h) increases with increasing filler volume fraction (ϕ), as indeed shown in Fig. 7 for Types I, II and III.

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,

$$R = h/kA + R_1 + R_2, \tag{9}$$

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. 7.

Combining the information from optical microscopy (Section 3.1), DBP value (Table 1), bond-line thickness (Section 3.2) and thermal contact conductance (Section 3.2), 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 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 Section 3.3.

3.3. 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. 9 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.

All the carbon black pastes exhibit shear thinning behavior (i.e., decrease of viscosity with increasing shear rate), as shown in Fig. 9. 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.

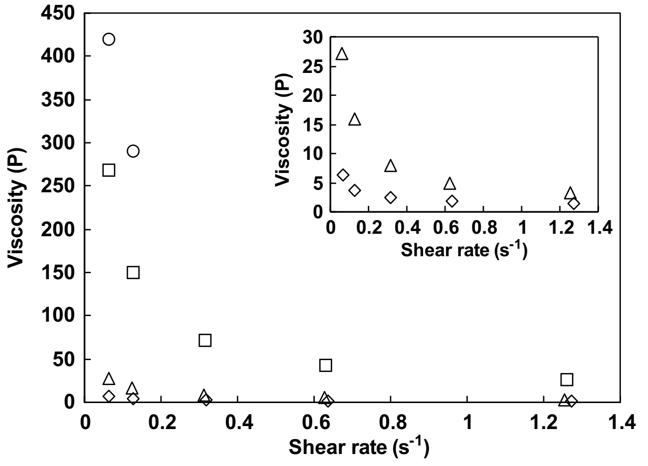

Fig. 9. Viscosity of selected carbon black pastes at 2.4 vol.% and its variation with the shear rate. The inset shows a magnified view of the part of the graph up to a viscosity of 30 P. ◇: Pure vehicle; △: Type I; □: Type III; ○: Type IV.

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. For the same type of carbon black, this optimum is higher when the paste is tested between rougher surfaces. By using Type I carbon black (with a DBP value of 60 ml/100 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/100 g) has been attained; a thermal contact conductance value of 33×10^4 W/m^2 °C has been reached.

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