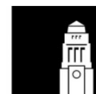

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Comparison of carbon nanofiller-based polymer composite adhesives and pastes for thermal interface applications

Mohsin Ali Raza*[1], Aidan Westwood[2], Chris Stirling[3]

[1]College of Engineering and Emerging Technologies, University of the Punjab, Lahore, Pakistan

[2]Institute for Materials Research, SPEME, University of Leeds, LS2 9JT, UK

[3]Morgan Advanced Materials, Swansea, SA6 8PP, UK (current address: Haydale Ltd., Ammanford, SA18 3BL, UK)

*Corresponding author email: mohsinengr@yahoo.com

Abstract

Graphite nanoplatelets (GNP), carbon black (CB) and carbon nanotubes are extensively researched to produce thermal interface materials (TIMs). This work reports comparison of interfacial thermal conductance (ITC) of carbon nanofiller-based polymer composite adhesives and pastes. The results show that total thermal contact resistance (TTCR) of GNP/rubbery epoxy composite was the same as that of an equivalent glassy epoxy composite. Although CB-based rubbery epoxy and silicone composites can be applied as thin bondlines, their TTCRs were significantly higher than GNP/rubbery epoxy. GNPs incorporation into CB/rubbery epoxy composite improves the ITC of the CB/rubbery epoxy composites but the performance of CB/GNP/rubbery epoxy was inferior to GNP/rubbery epoxy. The thermal paste of GNP/polyetheramine had TTCR of 4.8×10^{-6} m^2.K/W which is comparable to commercial TIM-paste. The paste produced with silicone had relatively poor ITC versus that prepared with polyetheramine. The paste having smaller particle sized GNPs offers lower TTCR than that prepared with large sized GNPs. The GNP/rubbery epoxy adhesives produced from precursor pastes gave the lowest TTCRs in comparison with the other adhesives. This study suggests that GNPs offer potential for enhancing ITC of TIMs and that ITC of adhesives depends on fillers' thermal conductivity and their interfacial contact with substrates.

Key words: Graphite nanoplatelets; carbon black; thermal interface materials; thermal contact resistance; epoxy; silicone

Corresponding author: Mohsin Ali Raza, email address: mohsin.ceet@pu.edu.pk, mohsinengr@yahoo.com

1. Introduction

Thermal management is a key aspect in electronic devices and has become even more challenging due to miniaturization. As a result, large amounts of heat are generated in ever smaller volumes. Only efficient heat dissipation from microchips can ensure their fast and reliable operation. Continued growth of the microelectronic industry at today's pace will thus be dependent upon improving electronic thermal management. Therefore, there is a strong demand for the electronic industry to devise and explore new thermal management systems that can overcome the challenges of heat dissipation from present and future microelectronic devices [1-3].

Thermal interface materials (TIMs) are a vital component of modern electronic packaging. In electronic packaging, TIMs are inserted between the chip (silicon die) and the heat spreader and between the heat spreader and the heat sink. TIMs reduce or eliminate the air gaps at the interface by conforming to the relatively rough and uneven mating surfaces. In this way, they overcome the thermal contact resistances at the interfaces [4] and thus facilitate heat removal from the chips. Current TIMs include thermal greases/pastes, solders, phase change materials and filled polymer matrices (polymer composites) in the form of thermal pads, adhesives or gels. With the exception of solders, all other TIMs essentially contain thermally conducting fillers such as alumina, silica, boron nitride (BN) or aluminium nitride. These fillers are loaded into an organic matrix such as silicone oil or polyol ester oil to form thermal pastes or into polymers such as silicone, acrylic, or epoxy to form thermally conductive adhesives or gels [5-7]. Fillers are typically loaded into the polymer matrix at 50-70 vol. % to achieve thermal conductivities in the range of 1-5 W/m.K [8]. Consequently, composites produced with such high filler loadings are highly stiff and cannot be applied as thin coatings between the interfaces. Furthermore,

commercial fillers have low thermal conductivity, resulting in TIMs with very low thermal conductivity. Therefore, there is a compelling need to investigate new fillers for TIMs.

Thermal interface adhesives are polymer-based composites which improve contacts between the mating surfaces, offer good thermal conductivity and also bind mating surfaces to improve mechanical integrity of the electronic packaging [9]. High thermal conductivity and low thermal contact resistance are desirable characteristics of TIMs [10]. Carbon nanofillers such as graphite nanoplatelets (GNP), graphene, carbon nanotubes and carbon nanofibres are being extensively researched as fillers for polymer composites due to their very high thermal conductivity [8, 11]. On the other hand, carbon black (CB)-based thermal pastes have been reported to offer very low thermal contact resistances despite their low thermal conductivity [12]. Researchers have reported the potential of carbon nanofiller-based polymer composites for thermal interface applications due to their high thermal conductivity [8, 13]. However, high thermal conductivity alone cannot guarantee good TIM performance. The performance of TIMs mainly depends on wt.%, size, shape and orientation of the fillers and on the adhesion, wettability and spreadability of the resulting polymer composite dispersions, which improves thermal contacts between the mating surfaces [6]. The effectiveness of TIMs cannot be judged solely on the thermal conductivity data. This also requires the investigation of thermal contact resistance under conditions similar to those which prevail in electronic packaging.

The present work reports comparison of thermal contact resistance of carbon nanofiller-based polymer composite adhesives and pastes, measured according to an ASTM standard, D5470, that mimics the conditions prevailing in electronic packaging. The effects of incorporating GNP, hybrid combinations of CB and GNP, types of polymer matrix and CB on the thermal contact resistance of the composites (as adhesives) was studied and is reported here. The effect of

applied pressure, temperature and surface roughness of the substrate on the thermal contact resistance of these composites is also reported. In addition to this, two different types of GNPs were mixed in resins to produce dispersions/pastes and their thermal contact resistances as pastes and adhesives were also investigated and compared with that of commercial adhesives and TIMs.

2. Experimental

2.1 Materials and Method

GNPs obtained from XG Sciences, Ltd are labelled as GNP-5 and GNP-15 and those obtained from Asbury graphite mills are labelled as GNP-As. The average particle size and thickness of these GNPs are presented in Table 1 and their scanning electron microscopy (SEM) images are presented in Fig. 1. Nanosized CB particles were obtained from Evonik Degussa, Ltd with average particle size less than 30 nm. Two types of CB were used to produce composites: CBP and CBU. The morphology and particle size of these CB are discussed elsewhere [14]. Two types of epoxy were used as matrices to produce composite adhesives; one is called rubbery epoxy (RE) due to its compliant nature and other is called glass epoxy (GE) due to its brittle nature. Silicone elastomer was also used as matrix to produce pastes and adhesives. The details of the fabrication and properties of these composites can be found elsewhere [15, 16]. Briefly, appropriate amount of GNPs were mixed in rubbery epoxy resin or glassy epoxy resin by using conventional mechanical mixer with a high speed motor and a propeller attached to a shaft which was rotated at 2500 rpm for 20 min to make composite dispersions. For preparation of pastes, the GNPs were mechanically mixed in polyetheramine (J2000, which is main constituent of rubbery epoxy, Ex Huntsman) or in silicone matrix (Sylgard 184 part A, Ex Dow Corning Corp) for 100 h. The composite adhesives and pastes studied in this work are listed in Table 2. The effect of mixing time on the thermal contact resistance was also investigated. These composites were

tested as adhesives, with cured matrix, according to ASTM standard D5470 on a thermal contact resistance measurement rig. The details of the rig and the testing procedure have been demonstrated previously [17]. In short, the rig consists of two copper cylinders between them an adhesive or paste (the material whose thermal contact resistance was measured) was sandwiched. Each cylinder had two holes at precise locations for the insertion of resistance temperature detector (RTD) probes (1/10 DIN PT 100 Probe, Omega Engineering Ltd) for temperature measurement. The copper cylinders having TIM (adhesive or paste) were placed between the heating and cooling stages. The hot stage had two embedded barrel heaters controlled by temperature controller. The cooling stage had channels through which a coolant was circulated by a low temperature-circulator. Once the steady states were obtained, temperatures were recorded which were used to calculate thermal contact resistances according to equations reported in [17]. The total thermal contact resistance (TTCR) of coating is proportional to bondline thickness which was measured by using the values of temperatures recorded under steady state conditions. The geometrical interfacial thermal resistances were obtained from extrapolation of thermal resistance vs thickness curves. The composite pastes (uncured) were sandwiched between copper substrates and cured at 125 ºC for 3 h and then placed in the rig for the measurement of TTCR. For studying the composite dispersions as an uncured paste, these were applied on copper substrate having average roughness 0.03 µm and sandwiched under a pressure of 0.06 MPa to form a thin layer of the paste. The excessive dispersion was wiped from the sides of the copper blocks. The copper blocks with sandwiched paste were placed in the rig for the measurement of TTCR. The TTCR of the paste was measured at a pressure of 0.3-0.6 MPa. Prior to measurement of TTCR of paste or composites, the TTCR of the copper block without TIM was also measured for comparison.

Table 1. Size and thickness of as-received GNPs and CB particles.

Type of GNPs	Particle size	Thickness by XRD (nm)	Thickness by TEM (nm)
GNP-5[18]	5 ± 4 μm	30 ± 10	18-32
GNP-As (determined for present study)	5 ± 2 μm	118 ± 10	40-60
GNP-15[16]	15 ± 5 μm	62 ± 10	10-40
CBP[14]	29 ± 5 nm	-	-
CBU[14]	40 ± 7 nm	-	-

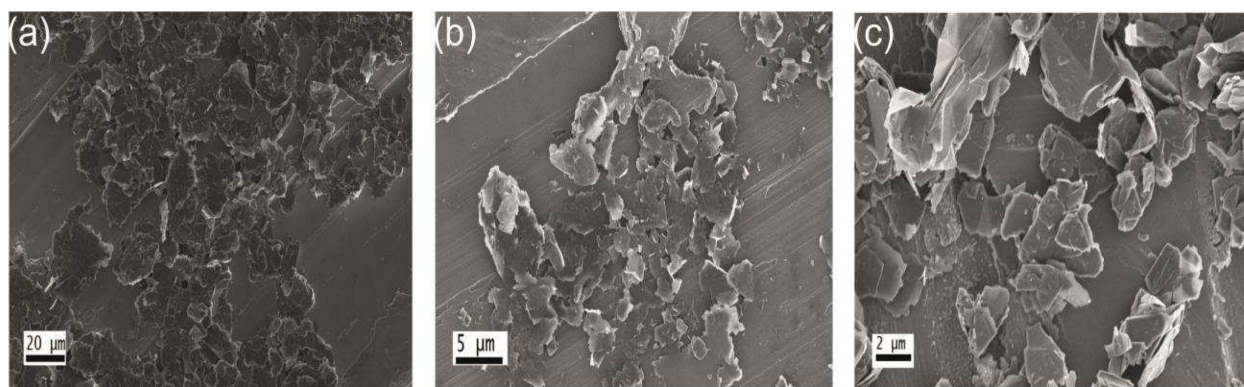

Fig. 1. SEM images of (a) GNP-15 (b) GNP-5 (c) GNP-As

Table 2. List of composites tested in TTCR measurement rig.

Composite	Tested as adhesive or paste	Thermal conductivity measured by hot disk thermal constant analyser (W/m.K)
25 wt.% GNP-5/rubbery epoxy (RE) composite [15]	Adhesive	1.12
25 wt.% GNP-5/glassy epoxy (GE) composite	Adhesive	1.23
6 wt.% CBP/RE [14]	Adhesive and paste	0.227
8 wt.% CBU/silicone [14]	Adhesive and paste	0.199
6 wt.% CBP/12 wt.% GNP-5/RE [19]	Adhesive and paste	0.58
25 wt.% GNP-As/J2000 dispersion	Paste	-
25 wt.% GNP-As/RE	Adhesive	1.13
25 wt.% GNP-As/Silicone dispersion	Paste	-
18 wt.% GNP-15/J2000 dispersion	Paste	-
Composite when cured between the copper substrate is adhesive as it binds the two copper blocks.		

3. Results and discussion

3.1. Thermal contact resistance of GNP-5/RE composite adhesives

3.1.1. Effect of surface roughness

The TTCR of 25 wt. % GNP-5/RE composite measured on smooth and rough surfaces as a function of coating thickness (BLT) is presented in Fig. 2.

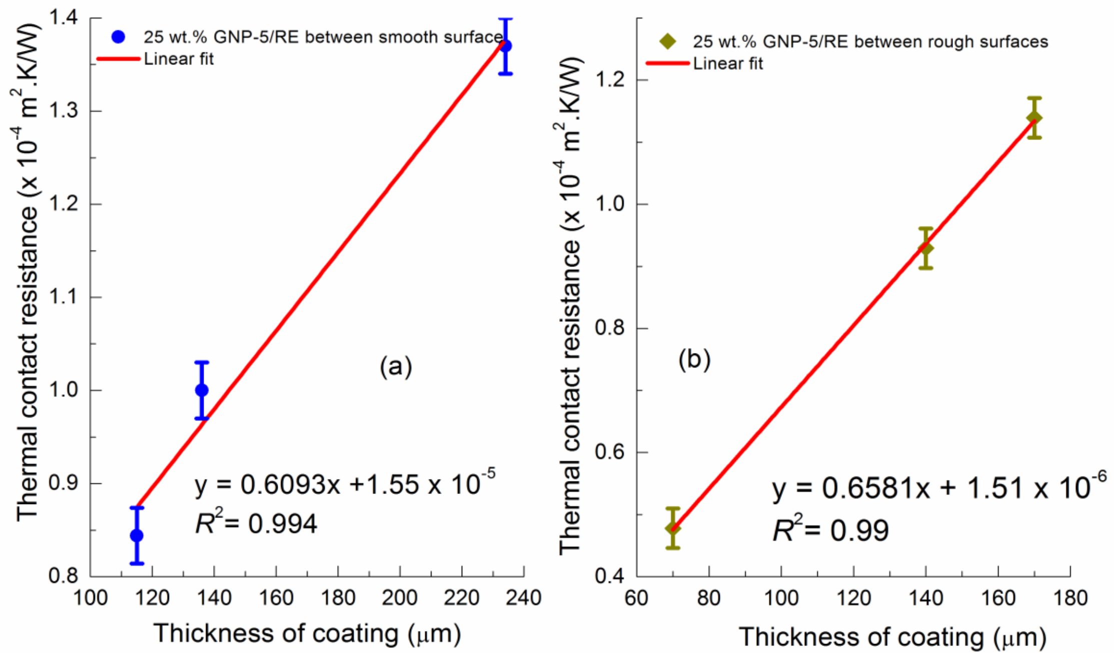

Fig. 2. TTCR of 25 wt.% GNP-5/rubbery epoxy (RE) composite (cured between copper substrates) as a function of coating thickness measured between (a) smooth surfaces (Ra=0.03 μm) (b) rough surfaces (Ra= 0.45 μm) at 25 ºC and under a pressure of 0.032 MPa (data was average of data points recorded for 20 min under steady state condition). Error bars are deliberately stretched than the originally obtained to include errors such as errors due measurements on multiple samples of the same composition.

The 25 wt.% GNP-5/RE composite was produced at maximum possible loading of the GNP-5 and the bulk composite had thermal conductivity of 1.12 W/m.K, measured by hot disk thermal constant analyser [15]. The minimum thickness of this composite on smooth substrate achieved without application of additional load was ca. 110 μm. At this thickness, it had a TTCR of 0.85 x 10^{-4} m^2.K/W. The TTCR of copper cylinders with no interface material between them was measured prior to the measurements of the composites and found to be 2.1 × 10^{-4} m^2.K/W. Thus, the incorporation of composite TIM reduced the TTCR at the interfaces. By deliberately achieving a bondline thickness of 20 μm or less, the TTCR can be significantly reduced by using GNP/RE composite as can be seen from TTCR value extrapolated from equation of linear fit (Table 3).

The interfacial thermal conductance of 25 wt.% GNP-5/RE composite is 13.5 % higher between smooth surface than rough surfaces at bondlines thickness of 100 µm. In our previously published study [17], we found that GNPs with average lateral width of 15 µm reduced interfacial thermal conductance much more between rough surfaces than smooth surfaces. In the present study, the small difference in TTCRs between smooth and rough surfaced substrate is a result of the smaller lateral sizes of the GNP-5 platelets and their consequent reduced alignment with the planes of the composite/block interfaces, independent of the surface roughness.

3.1.2. Effect of Matrix

The interfacial thermal conductance of composite produced by dispersing GNP-5 in glassy epoxy (GE) matrix at 25 wt.% loading was also studied as adhesive between the smooth surfaced copper blocks. The TTCR of this composite as a function of coating thickness is presented in Fig. 3. The bulk thermal conductivity, measured by hot disk thermal constant analyzer, of 25 wt.% GNP-5/GE composite is almost the same as that of 25 wt.% GNP-5/RE composite and is not affected by the nature of matrix (Table 2). The TTCR of 25 wt.% GNP-5/GE composite was found to be 9.85 x 10^{-5} m^2.K/W at 150 µm bondline thickness, which is 10 % lower than the TTCR of corresponding RE composite. The slightly better interfacial thermal conductance of the GNP-5/GE composite is associated with its observed stronger adhesion with the copper substrates. It was found however that the 25 wt.% GNP-5/GE dispersion had much higher viscosity than the corresponding RE composite and consequently it was not possible to achieve a thin bondline at the interface.

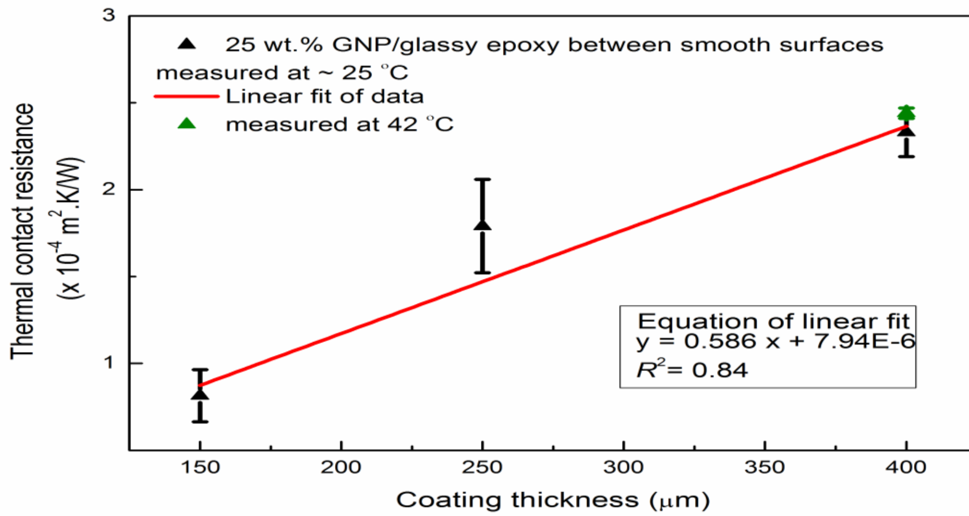

Fig. 3. TTCR of 25 wt.% GNP-5/glassy epoxy (GE) composite (cured between copper substrates) as a function of coating thickness measured between smooth surfaces (Ra= 0.03 μm) at 25 ºC and under a pressure of 0.032 MPa. Errors are estimated from at least 20 data points recorded under steady state conditions for 20-40 min. Error bars are deliberately stretched than the originally obtained to include errors such as errors due to measurements on multiple samples of the same composition.

In our previous study, the TTCR of 25 wt.% GNP-5/silicone composite was found to be 6×10^{-5} m^2.K/W at a bondline thickness 35 μm between rough surfaces. At the same bondline thickness, the TTCR of 25 wt.% GNP-5 based epoxy composites would be 3.63×10^{-5} m^2.K/W (obtained from equation of linear fit). This projection suggests that epoxy based composite adhesive can perform better than silicone based adhesives. The more adhesive nature of epoxy based adhesives due to their polar nature [20] than silicone based adhesive [21] is mainly responsible for the improved interfacial thermal conductance.

The TTCR of GNP-5/GE epoxy composite adhesive was also measured at 42 °C and was found to be almost same as that obtained at 25 °C (Fig. 3). It was also observed that GE-based composite joined the two copper blocks much more strongly compared to RE composite, which suggests that GE-based adhesive should give substantial improvement in the interfacial thermal conductance since better adhesion at interfaces promotes a lower TTCR, by analogy with the

comparison of TTCR of silicone-based and rubbery epoxy-based composite adhesives. Therefore, one possible explanation for the inferior performance of GE-based adhesive is that voids in the GE coating formed during curing [15] might have reduced its performance as TIM adhesive.

The TTCR was also measured for commercial epoxy adhesive (H70E, www.EPOTEK.com), which has thermal conductivity of 1 W/m.K (reported by manufacturer) close to that determined for our 25 wt.% GNP-5 composites. The TTCR of H70E was measured as both uncured paste and adhesive, which were sandwiched between smooth copper blocks under high pressure (~0.1 MPa) to achieve a bondline thickness of ca. 20 µm. This commercial adhesive gave a TTCR of 7.7×10^{-5} m^2.K/W which is significantly higher than that of GNP-5/epoxy composite adhesive produced in this study (Table 3). The GNP-5/epoxy adhesive also has better interfacial thermal conductance performance than a commercial (65 wt%) BN-filled silicone adhesive, ex Nusil (www.nusil.com). The TTCR of 25 wt.% GNP-5/RE composite is 1.5× lower than that of this silicone-based adhesive at equivalent thickness. These comparisons suggest that GNP-5-based epoxy is better thermal interface adhesive material than the commercial adhesives. The 2-dimensional nature of GNPs can help in lateral heat flow at the interfaces and their nanometer thickness forms bridges between the asperities of mating surfaces resulting in faster heat transport across the interface.

It can also be observed from Table 3 that 25 wt. % GNP-5/RE has higher TTCR as paste (uncured) than the cured form. This result suggests that curing is beneficial in reducing TTCR of rubbery epoxy-based coatings. On the other hand, H70E has slightly lower TTCR as paste (uncured) than the cured form. The curing of H70E coating at 120 °C might have resulted in some voids or delamination at the interface, which lowered interfacial thermal conductance as

adhesive cf. paste.

Table. 3. Comparison of TTCR of GNP/rubbery epoxy composite with that of commercial epoxy adhesive

Material	Bond line thickness (μm)	Total thermal contact resistance (m^2.K/W)	Standard deviation
25 wt.% GNP-5/rubbery epoxy (cured adhesive)	18	2.7×10^{-5} (extrapolated from equation of linear fit)	-
25 wt.% GNP-5/rubbery epoxy (paste)	~20	5.82×10^{-5}	4.31×10^{-6}
H70 E Commercial epoxy (cured adhesive)	~20	7.69×10^{-5}	1.089×10^{-5}
H70 E Commercial epoxy (paste)	~20	5.3×10^{-5}	3.36×10^{-6}

3.2. Thermal contact resistance of CB-based composites

The main motivation for studying the TTCR of CB/polymer composites as thermal interface adhesive was the work of Lin et al [22]. They reported that CB-pastes can be applied as very thin bondlines and that, despite very low thermal conductivities they offer very low TTCRs (high thermal conductance) due to the ability of nanosized CB particles to enter the cavities of the surface [10]. It was also reported by Lin et al. [22] that low structure CB could offer better performance than high structure CB in thermal pastes. Therefore, two composites one with high structure CB (6 wt.% CBP/rubbery epoxy) and other with low structure CB (8 wt.% CBU/silicone) were selected for study of their TTCR as thermal interface adhesives. The former also has slightly higher thermal conductivity (0.227 W/m.K) than the latter (0.199 W/m.K) as measured by hot disk method.

The TTCR of 6 wt.% CBP/rubbery epoxy composite adhesive versus coating thickness measured between smooth (Ra = 0.03 μm) and rough surfaced (Ra=0.45 μm) copper substrates, at ~28 °C

and 0.032 MPa (compressive stress), is presented in Fig. 4. Compared to GNP/rubbery epoxy composite coatings, the 6 wt.% CBP/rubbery epoxy composite can be easily applied as a very thin coating. A very thin bond line of ~15 µm was easily obtained without the application of additional pressure on the copper samples. This coating also had very good spreadability. The 6 wt.% CBP/rubbery epoxy coating offered a TTCR of $\sim 1.1 \times 10^{-4}$ m^2.K/W at a bondline thickness of 36 µm on smooth and rough surfaces (Fig. 4). The similar TTCR values might indicate that CB readily distributes itself throughout the bondline and hence creates a more isotropic effect. The thermal conductivity of 6 wt.% CBP/rubbery epoxy coating is 0.38 W/m.K calculated according to the steady state method (Fig. 4). This is ~2× higher than that measured by hot disk method for the bulk composite. A TTCR of $\sim 5.49 \times 10^{-5}$ m^2.K/W would be obtained at a bond line thickness of 15 µm on smooth surface (estimated from the equation of linear fit presented in Fig. 4). The TTCR of pure rubbery epoxy between smooth copper surfaces at ~15 µm bond line thickness was 9.4×10^{-5} m^2.K/W. This is 1.7× higher than for the 6 wt.% CBP/rubbery epoxy composite coating, showing that CBP addition into rubbery epoxy improves its interfacial thermal conductance.

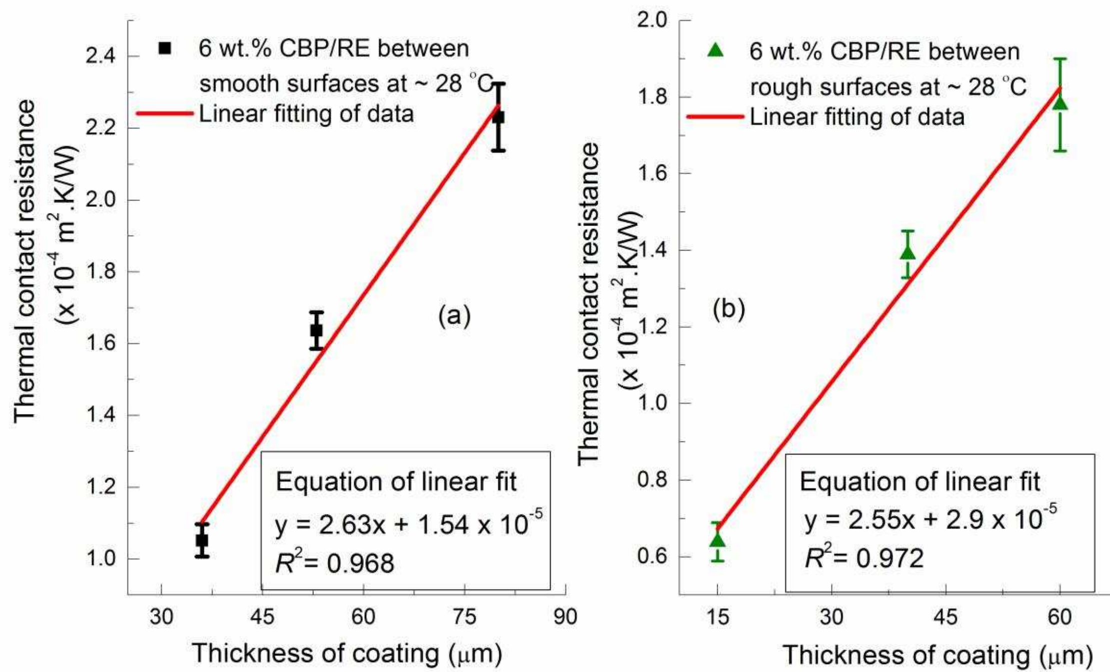

Fig. 4. TTCR versus coating thickness of 6 wt.% CBP/rubbery epoxy (RE) composite (produced by mechanical mixing) measured between smooth copper surfaces (Ra= 0.03 μm) and rough surfaces (Ra= 0.45 μm) at ~28 °C and 0.032 MPa (compressive stress). Linear fit of data and equations of linear fit are also presented. Coating thicknesses have accuracies of ± 2 μm. Errors are estimated from at least 20 data points recorded under steady state conditions for 20-40 min. Error bars are deliberately stretched than the originally obtained to include errors such as errors due to measurements on multiple samples of the same composition.

The effect of temperature on the TTCR of 6 wt.% CBP/rubbery epoxy coating is presented in Fig. 5. It can be seen from Fig. 5 that the TTCR of CBP/rubbery epoxy coating increases very little with increase of temperature from 28-50 °C.

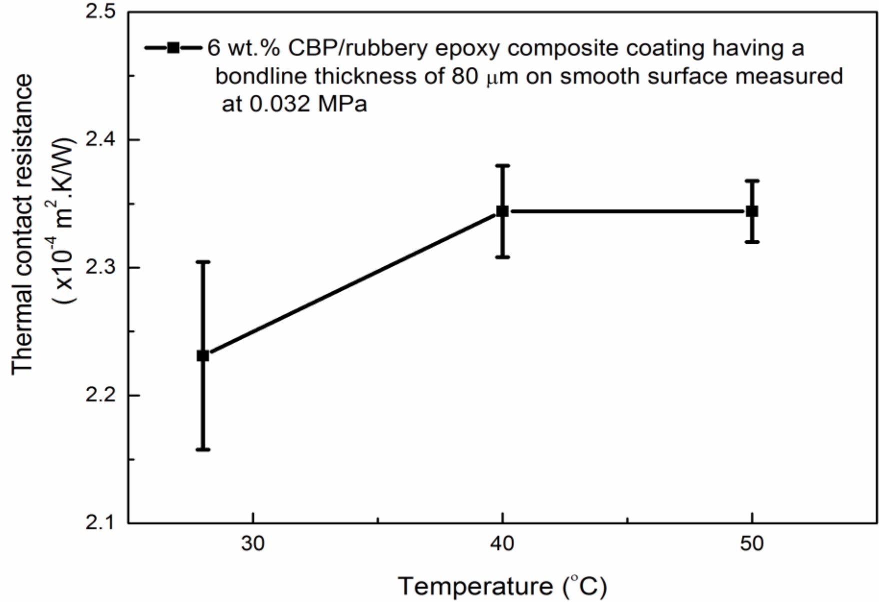

Fig. 5. Plot of TTCR of 6 wt.% CBP/rubbery epoxy coating vs. temperature at a bond line thickness of 80 μm applied between smooth surfaces measured at compressive stress of 0.032 MPa. Errors are estimated from at least 20 data points recorded under steady state conditions for 20-40 min.

The TTCR of 8 wt.% CBU/silicone coating versus coating thickness applied between smooth copper surfaces and measured at a temperature of ~28 °C and under compressive stress of 0.032 MPa is presented in Fig. 6. It can be observed from Fig. 6 that 8 wt.% CBU/silicone coatings have much thinner bondlines compared to 6 wt.% CBP/rubbery epoxy coating. These much thinner bond lines are achieved by deliberately increasing the pressure on the coated copper cylinders before in-situ curing.

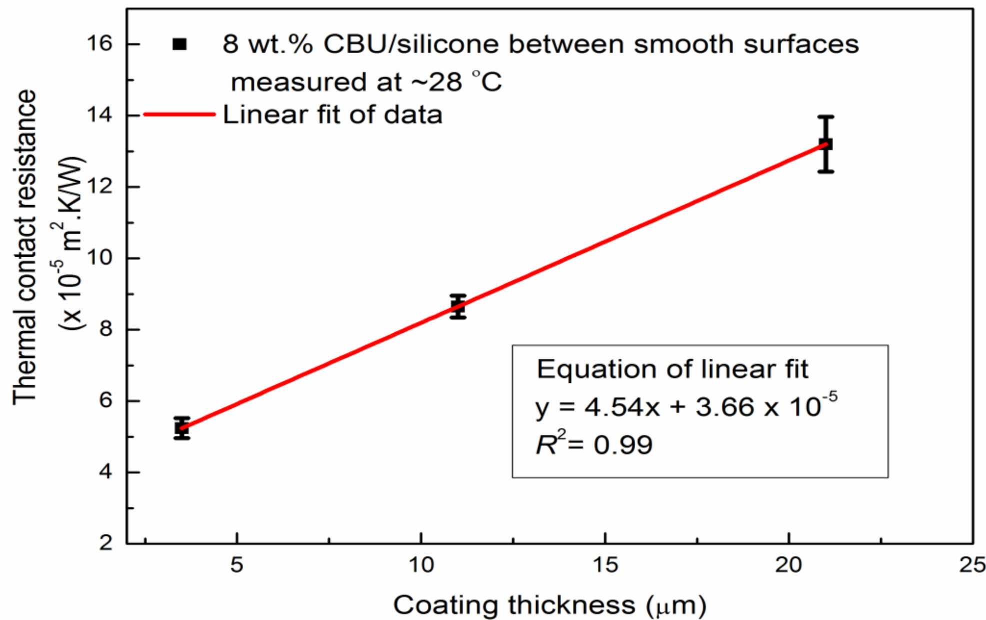

Fig. 6. TTCR versus coating thickness of 8 wt.% CBU/silicone composite (produced by mechanical mixing) measured between smooth copper surfaces (Ra= 0.03 μm) at ~28 °C and 0.032 MPa (compressive stress). Linear fit of data and the equation of linear fit are also presented. Coating thicknesses have accuracy of ± 2 μm. Errors are estimated from at least 20 data points recorded under steady state conditions for 20-40 min.

It can be observed from Fig. 6 that the TTCR of 8 wt.% CBU/silicone coating at a bond line thickness of ~4 μm is 5.24×10^{-5} m^2.K/W. The TTCR of pure silicone at ~4 μm bond line thickness was ~5.29×10^{-5} m^2.K/W. This shows that the addition of 8 wt.%, low structure, carbon black in silicone has essentially not contributed in reducing TTCR. The thermal conductivity of 8 wt.% CBU/silicone coating is 0.22 W/m.K which is ~10% higher than that measured by hot disk method for the bulk composite (inverse of slope in Fig. 6).

The interfacial thermal conductance of 8 wt.% CBU/silicone coating was also measured in the uncured state as a paste. The TTCR of the uncured paste was ~5.47×10^{-5} m^2.K/W at 0.032 MPa (bond line thickness was not determined, however coating was compressed prior to measurement at pressure of ~0.1 MPa to obtain a very thin bond line). This is almost the same as that obtained

for the cured composite coating at ~4 μm bond line thickness. This result indicates that, in this case, the curing has not affected the performance of the CBU/silicone coatings. It can also be seen from the equation of linear fit (Fig. 6) that the 8 wt.% CBU/silicone coating (3.66×10^{-5} m^2.K/W) has higher geometric thermal interfacial resistance than 6 wt.% CBP/rubbery epoxy coating (1.54×10^{-5} m^2.K/W). Although silicone is a more conformable material than rubbery epoxy this demonstrates that silicone cannot develop such a good interfacial contact with the mating surfaces. This might be due to the weakly adhesive nature of silicone with copper surfaces compared to rubbery epoxy.

Previously, Lin et al. [22] reported that thermal pastes developed with low structure CB can give much lower TTCRs and significantly lower bondline thickness than the pastes developed with high structure CB. In the present work, although 8 wt.% CBU/silicone composite prepared with low structure CB can be applied as thin bond lines, it has ~10× higher TTCR in both cured and uncured state than the low structure CB-thermal pastes reported by Lin et al [22] (at a bondline thickness of ~1 μm). The findings of the present work show that low structure CB is not effective in reducing TTCR at the interfaces. Although the matrix does affect the TTCR of the adhesives, the present work nevertheless suggests that a high structure CB/rubbery epoxy adhesive has much better interfacial thermal conductance than a low structure CB/silicone adhesive.

3.3. Thermal contact resistance of CB/GNP/rubbery epoxy hybrid composite

The TTCR of 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy hybrid composite adhesive versus coating thickness measured between smooth surfaces (Ra = 0.03 μm) and rough surface (Ra=0.45 μm) at ~30 °C and 0.032 MPa (compressive stress) is plotted in Fig. 7.

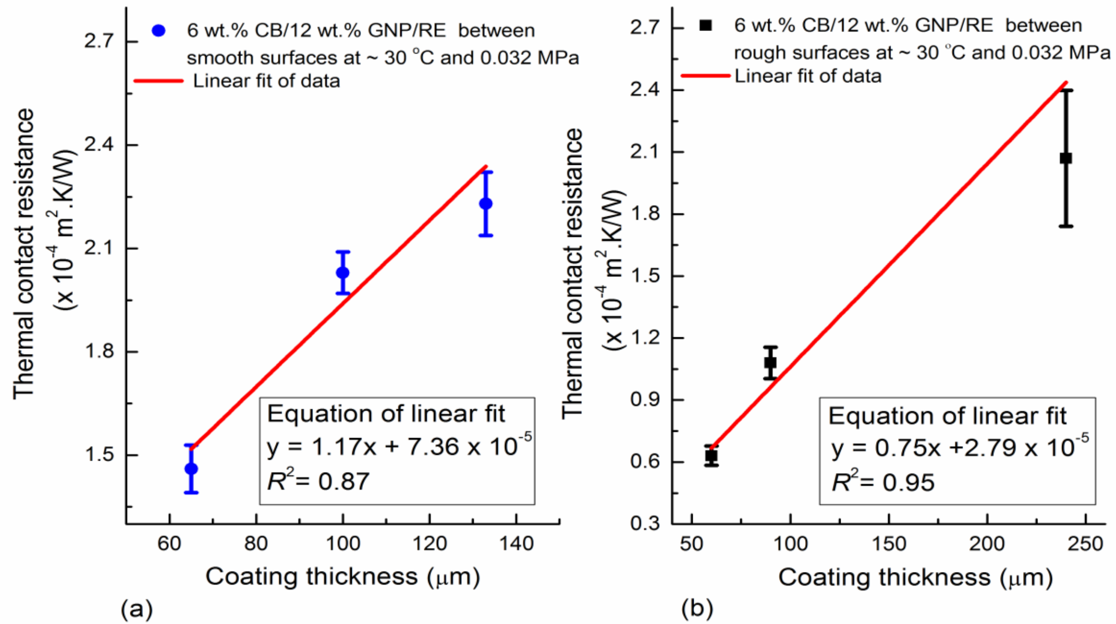

Fig. 7 TTCR versus coating thickness of 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy hybrid composite (produced by mechanical mixing) measured between (a) smooth (Ra= 0.03 μm) & (b) rough copper surfaces (Ra= 0.45 μm) at ~30 °C and 0.032 MPa compressive stress. Linear fit of data and the equation of linear fit are also presented. Errors are estimated from at least 20 data points recorded under steady state conditions of 20-40 mins. Error bars are deliberately stretched than the originally obtained to include errors such as errors due to measurements on multiple samples of the same composition.

The 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy hybrid composite coating cannot be applied as thinly as 6 wt.% CBP/rubbery epoxy composite coatings due to the significantly increased viscosity of the hybrid coating [19]. However, bondline thicknesses of ~60 μm were easily achieved and the potential exists to decrease this thickness further by increasing the pressure between the interfaces.

In terms of minimising thermal resistance, the performance of 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy composite was better on the rough surface than on the smooth surface. It has a TTCR of 7.6×10^{-5} m^2.K/W at a bond line thickness of 65 μm between rough surfaces which is ~2× lower than the TTCR at equivalent coating thickness measured between smooth surfaces. The equations of linear fit (Fig. 7) show that the geometric interfacial thermal resistance of 6

wt.% CB/12 wt.% GNP-5/rubbery epoxy hybrid composite coating is significantly lower on rough surface (2.79×10^{-5} m^2.K/W) than on smooth surface (7.36×10^{-5} m^2.K/W), forming a better interface with the rough copper substrate and providing better interfacial thermal conductance on the rough surface.

It was observed that carbon black/rubbery epoxy coating had poor performance as a thermal interface adhesive, probably due to its very low thermal conductivity (Section 3.2). It can be seen from the CB/GNP/rubbery epoxy hybrid composite results that addition of GNP into 6 wt.% CB/rubbery epoxy improves its interfacial thermal conductance. The TTCR of 6 wt.% CBP/rubbery epoxy composite was 1.56×10^{-4} m^2.K/W at a bond line thickness of 50 μm between rough surfaces. This is 2.4× higher than for the 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy hybrid composite coating at equivalent thickness (on rough surfaces). The geometric thermal interfacial resistance of 6 wt.% CBP/rubbery epoxy composite (Fig. 4) is almost the same as that of 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy hybrid composite (Fig. 7), therefore it is believed that the improved interfacial thermal conductance of hybrid composite coating is due to its ~2× higher thermal conductivity compared to 6 wt.% CB/rubbery epoxy coating. On the other hand, the TTCR of 6 wt.% CBP/rubbery epoxy coating is only 1.1× higher than the hybrid composite coating at bondline thickness of 50 μm on smooth surface. The geometric thermal interfacial resistance of 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy hybrid coating is significantly higher on smooth surface than on rough surface (Equations in Fig. 7), and it is also significantly higher than that of the 6 wt.% CBP/rubbery epoxy coating on smooth surfaces (Fig. 4(a)). This indicates that the hybrid coating does not develop good contact with the smooth copper surface and thus, despite its ~2× higher thermal conductivity vs. the 6 wt.% CBP/rubbery epoxy composite, the hybrid coating was unable to perform much better. It can also be observed

from Fig. 7 that the 6 wt.% CBP/12 wt.% GNP-5/rubbery epoxy hybrid composite coating has higher thermal conductivity when measured between rough surface (1.33 W/m.K, according to steady state method) than smooth surface (0.83 W/m.K). It is possible that on rough surfaces GNPs are less oriented parallel to interface (i.e., more GNPs are standing perpendicular to the interfacial surfaces) than on the smooth surface and this might result in the higher thermal conductivity of hybrid coating between rough surface. Thus, a combination of improved thermal conductivity and good interfacial contacts result in improved interfacial thermal conductance for the hybrid coating on the rough surface. The synergy between CB and GNP also improves the conductance at interfaces - perhaps with more particle-to-particle contacts involving platelet edges.

A comparison of the interfacial thermal conductance of 6 wt.% CB/12 wt.% GNP-5/rubbery epoxy composite coating with commercial pastes and other nanocarbon-filled adhesives measured under similar conditions is presented in Table 4.

Table. 4. Comparison of TTCR of 6 wt.% CBP/12 wt.% GNP-5/rubbery epoxy adhesives with the commercial TIMs and other nanocarbon-filled adhesives measured on smooth surfaces under similar conditions.

Material	Bond line thickness (μm)	TTCR (m^2.K/W)
*6 wt.% CBP/12 wt.% GNP-5/rubbery epoxy (cured adhesive)	18	9.46×10^{-5}
6 wt.% CBP/12 wt.% GNP-5/rubbery epoxy (paste)	~18	1.1×10^{-4}
Matrix II (commercial paste)	~18	4.77×10^{-6}
6 wt.% CBP/rubbery epoxy	18	6.2×10^{-5}
8 wt.% CBU/silicone	18	1.18×10^{-4}
*6 wt.% CBP/12 wt.% GNP-5/rubbery epoxy	95	1.84×10^{-4}
*25 wt.% GNP-5/rubbery epoxy (produced by mechanical mixing)	95	7.33×10^{-5}
65 wt.% BN/silicone (EPM 2490, a commercial TIM adhesive)	95	1.01×10^{-4}
*interpolated from equation of linear fit		

It can be observed from Table 4 that the TTCR of 6 wt.% CBP/12 wt.% GNP-5/rubbery epoxy is 23× higher than the Matrix II thermal paste at equivalent thickness of 18 μm. Similarly, the 6 wt.% CBP/rubbery epoxy and 8 wt.% CBU/silicone composite adhesive had significantly higher TTCRs than Matrix II paste. This clearly shows the poor interfacial thermal conductance of the hybrid composite coating and CB-based coatings as thermal interface adhesive compared to a commercial BN-based thermal paste. Furthermore, it can also be observed from Table 4 that the TTCR of the hybrid coating is 1.8× higher than the commercial TIM (EPM 2490). Similarly, the

TTCR of the hybrid coating is 2.5× higher than the 25 wt.% GNP-5/rubbery epoxy composite coating at equivalent thickness of 95 µm (when produced by mechanical mixing these have approximately the same viscosity and thermal conductivity). These comparisons suggest that the combination of CB and GNP in hybrid composite coatings, as thermal interface adhesives, is not advantageous. However, as mentioned earlier, when considering adhesives, the 25 wt.% GNP-5/epoxy adhesive has better interfacial thermal conductance than the commercial (65 wt%) BN-filled silicone.

3.4. Thermal contact resistance of pastes

GNP-As was dispersed in polyetheramine (J2000) and silicone resin to form pastes. These pastes were prepared after long-duration mechanical mixing and tested immediately after applying between the copper blocks and also after 66 h of application during which the paste remained under a pressure of 0.03 MPa, which might have substantially further reduced the thickness of the coating.

3.4.1 Effect of pressure

The TTCRs of 30 wt. % GNP-As/J2000 paste as a function of applied pressure (measured immediately after sandwiching between copper substrates and after 66 h under pressure in the rig) are presented in Fig. 8.

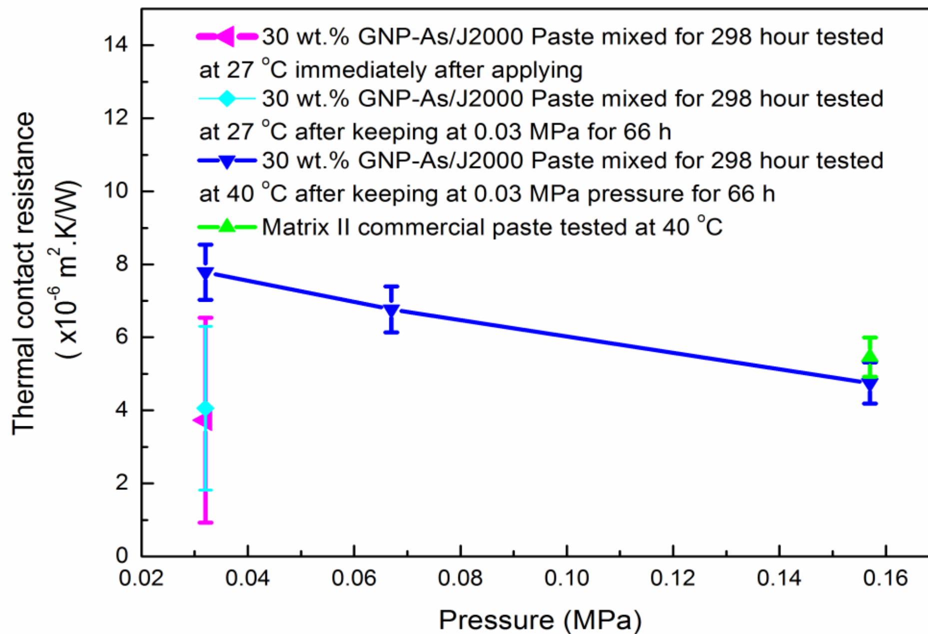

Fig. 8 Effect of applied pressure on TTCR of 30 wt.% GNP-As/J2000 paste produced after 298 h of mixing. TTCR of commercial thermal paste is also presented.

Fig. 8 shows that the TTCR of GNP-As/J2000 paste remained almost the same when tested immediately after applying and after keeping paste between copper blocks at a pressure of 0.03 MPa for 66 h, which indicates that the paste did not flow under applied pressure. The TTCR of paste slightly increased with increase of temperature from 27 to 40 °C. At 40°C and ca. 0.16 MPa, the TTCR of 30 wt.% GNP-As/J2000 paste was found to be 4.8×10^{-6} m^2.K/W, which is almost the same as that of the best performing commercial thermal paste (Matrix II) measured under similar conditions as that of GNP-As/J2000 paste. The GNP-As/J2000 paste developed in this study is therefore a close competitor to Matrix II paste. The GNP-based paste is also electrically conducting which could be beneficial for electronic packaging in special circumstances.

3.4.2. Effect of Matrix

A comparison of the TTCRs of 30 wt.% GNP-As/J2000 paste and 30 wt.% GNP-As/silicone paste mixed at 2000 rpm for 130 h is presented in Table 5.

Table 5. TTCR of GNP-As/J2000 and GNP-As/silicone paste measured by sandwiching between smooth copper surfaces (Ra= 0.06 μm) at 27 °C and 0.03MPa.

Paste name	TTCR $m^2.K/W$	Standard deviation $m^2.K/W$
30 wt.% GNP-As/J2000	5.7×10^{-6}	2.43×10^{-6}
30 wt.% GNP-As/silicone	1.56×10^{-5}	2.71×10^{-6}
Matrix II paste	4.6×10^{-6}	1.79×10^{-6}

It can be observed from Table 5 that the silicone based paste has 2.7× higher TTCR than polyetheramine (J2000)-based paste. The comparison clearly demonstrates that the matrix characteristics such as wettability or surface tension play an important role in decreasing the TTCR of the paste. Polyetheramine, due to its polar nature, may form better contact with the copper compared to silicone resulting in substantially higher interfacial thermal conductance for the J2000 (polyetheramine)-based paste.

3.4.3. Effect of mixing time on interfacial thermal conductance of the pastes

The GNPs were dispersed in J2000 for several hours using a mechanical mixing technique. The effect of mixing time on TTCRs of 35 wt.% GNP-As/J2000 and 18 wt.% GNP-15/J2000 is presented in Fig. 9. Both pastes were prepared at their maximum possible loading, and exhibited similar viscosities.

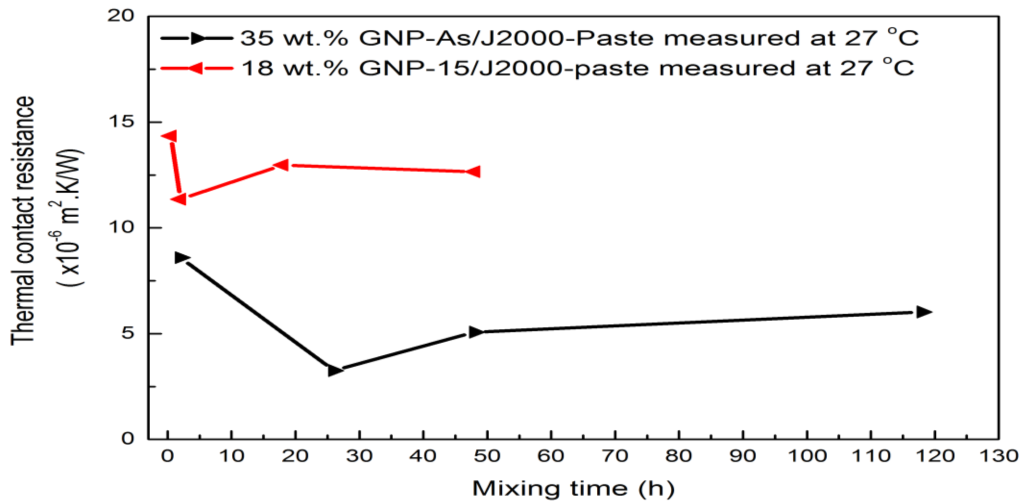

Fig. 9. Effect of mixing time on TTCRs of pastes measured by sandwiching between smooth copper surfaces at 0.03 MPa and 27 °C.

It can be seen from Fig. 9 that TTCR of both pastes initially decreased with increase of mixing time. In the case of 35 wt.% GNP-As/J2000, the TTCR decreased from 8.76×10^{-6} to 3×10^{-6} m^2.K/W with increase of mixing time from 2 to 26 hour. After the initial reduction in TTCR upon further mixing, and certainly beyond about 24 hours of mixing, there was no evidence of further reduction in the TTCR for either paste. The performance of this paste is comparable to the best commercially available paste (Matrix II, Table 4). The 18 wt.% GNP-15/J2000 paste had higher TTCR than 35 wt.% GNP-As/J2000 paste. The better interfacial thermal conductance of the latter is attributed to the smaller particle size of GNP-As than GNP-15 (Table 1) which can form better asperity contacts as mentioned in Section 3.1. It might also be possible that increased mixing time further reduced the particle size and this contributed to the improved interfacial thermal conductance of the pastes.

3.4.4. TTCR of adhesives produced from 30 wt.% GNP-As/J2000 paste

The 30 wt.% GNP-As/J2000 paste was diluted by the addition of epoxy resin, which was mixed manually, to cure the paste. The resulting composite dispersion had ~25 wt.% GNP-As. Two adhesives obtained from GNP-As/J2000 paste were studied, one mixed for 130 h and another mixed for 298 h. These adhesives (25 wt.% GNP-As/rubbery epoxy composite) were applied as interface adhesive layer between smooth copper surfaces under conditions similar to those used for application of thermal paste so that minimum bondline thickness was achieved. The samples were cured at 80 °C for 12 h. After the TTCR measurement, the bondline thickness was measured by profilometer on debonded samples. An average bond line thickness of ~10 µm was obtained. This decrease in bondline thickness might be due to some reduction in viscosity of rubbery epoxy resin at 80 °C before curing. On the basis of profilometer measurement, it can be implied that the pastes whose studies are described above also had bondline thicknesses of approximately 5-10 µm.

The TTCRs of 25 wt.% GNP-As/rubbery epoxy composite produced from pastes which were mixed for 130 and 298 h are presented in Fig. 10.

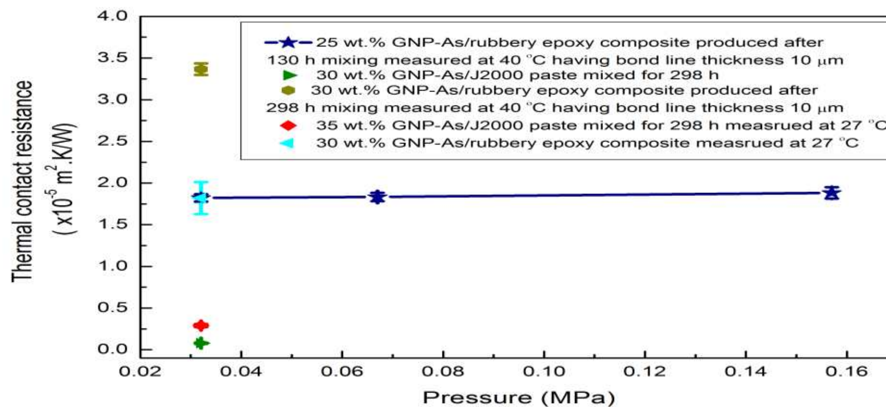

Fig. 10. TTCR of the composite adhesives produced from GNP-As/J2000 pastes applied under conditions similar to those used to apply pastes. Comparison of TTCRs of composites with corresponding GNP-As/J2000 pastes has also been presented.

It can be observed from Fig. 10 that TTCRs of the composites produced from the GNP-As/J2000 paste are significantly higher than those of the thermal pastes. The TTCR of the 25 wt.% GNP-As/rubbery epoxy composite produced after 130 h mixing is 18× higher than the precursor paste (30 wt.% GNP-As/J2000) from which this composite was developed. For the adhesives, the lowest TTCR was obtained for 25 wt.% GNP-As/rubbery epoxy composite and for 30 wt.% GNP-As/rubbery epoxy composite produced from precursor pastes which were mixed for 130 h and 298 h, respectively. The TTCRs for these composites are approximately 1.8×10^{-5} m^2.K/W at a bond line thickness of ~10 μm. The data suggest that curing increases the TTCR of pastes, which is contrary to our previous observations. The addition of epoxy resin in J2000 for curing might have deteriorated the wettability of the J2000 which resulted in increased TTCR of composite. It seems that matrix plays an important role in controlling the interfacial thermal conductance of the pastes as it was also observed that silicone-based paste had significantly higher TTCR than polyetheramine-based paste (Table 5). The effect of curing temperature and time cannot be neglected as this could also affect the surface nature of the copper substrate. The formation of oxide film on copper during curing at 120 °C, for instance, can add to the TTCR for thermal transport. In order to gain further understanding of the role of curing on TTCR, the curing of adhesives should be carried in vacuo.

In order to understand the effects of curing and matrix on TTCR, we have studied the TTCR of 25 wt.% GNP-As/rubbery epoxy composite (i.e. paste diluted with epoxy resin) as uncured paste, which was applied under similar conditions to those of the paste and tested at 27 °C (Fig. 11). The uncured composite, applied as paste, has 2× higher TTCR than the precursor amine-based (J2000) paste but halfway to that measured for cured composite (Fig. 10). Thus, the addition of epoxy resin in Jeffamine (J2000) paste affects the interfacial thermal conductance. It might be

possible that the process of manual mixing of epoxy resin promotes some agglomeration of the fillers, dilutes the concentration of the filler and, by decreasing the viscosity, increases the gaps between the fillers resulting in fewer filler-filler contacts. All of these factors could be playing a role in reducing the interfacial thermal conductance during conversion of pastes to composites. It can be concluded from this study that curing at high temperature does not appreciably affect the TTCR of the composite.

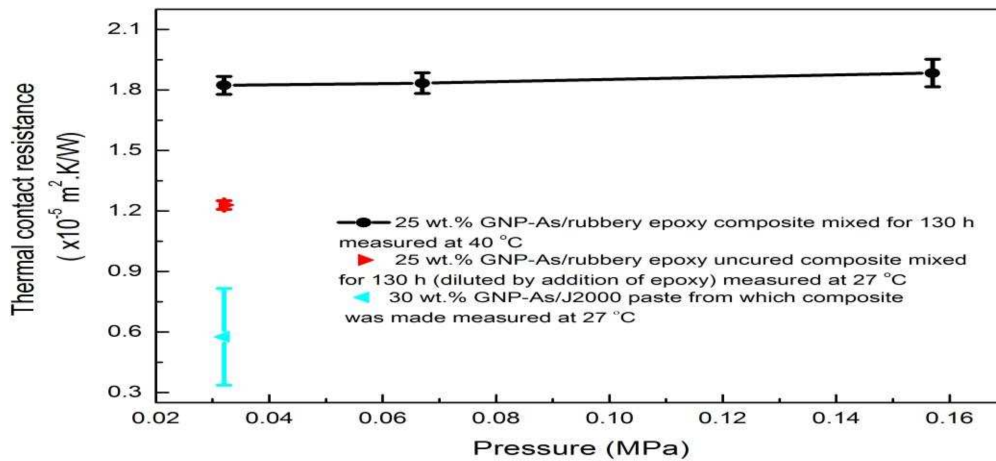

Fig. 11. Comparison of TTCR of 30 wt.% As-EG/J2000 paste with the 25 wt.% As-EG/rubbery epoxy uncured paste (produced from the former paste by manual addition of epoxy resin).

4. Conclusions

The following conclusions can be drawn from this study:

(i) GNP/rubbery epoxy adhesive (having average GNP particle size of 5 μm) offers better interfacial thermal conductance (better heat transfer at interfaces) than commercial epoxy- and silicone-based adhesives. This is attributed to the 2D-shape of GNPs which can allow better lateral heat transport at the interface and to the nanometer thickness of GNPs which can allow formation of better contacts at the interfaces by forming bridging contacts with the asperities of the substrate surface.

(ii) GNP/rubbery epoxy and GNP/glass epoxy adhesives have similar interfacial thermal conductance. GNP/glass epoxy, despite stronger bonding/adhesiveness, was unable to outperform GNP/rubbery epoxy adhesive, possibly due to the formation of voids in the coating during curing.

(iii) GNP-based adhesives have lower TTCRs than CB-based adhesives. Although carbon black-based adhesives had comparable geometric thermal interfacial resistances to those of carbon black-pastes reported in literature (i.e, adhesives conform to the surface similarly to the CB-pastes), they did not perform well as thermal interface adhesives. This is believed to be due to very low thermal conductivity of the carbon black-based adhesives. Thus, a combination of higher thermal conductivity and good interfacial contacts with the substrates are essential for producing high performance TIMs.

(iv) High structure carbon black (CBP)-based rubbery epoxy adhesives performed better than the low structure (CBU) CB-based silicone adhesives. Although matrix affects TTCR, the comparison nevertheless suggests that low structure CB is less effective in reducing TTCR compared to high structure CB.

(v) The interfacial thermal conductance of hybrid composite (CB/GNP/rubbery epoxy) was also lower than that of the non-hybrid GNP composites. It was observed that addition of GNP in CBP/rubbery epoxy composites increases its thermal conductivity which resulted in lower TTCR compared to CB-based composites, but still the TTCR was higher than for non-hybrid GNP composites. The result suggests that good interfacial contact alone cannot improve the interfacial thermal conductance, a good thermal conductivity of TIM also is vital for better interfacial thermal conductance.

(vi) The best interfacial thermal conductance was displayed by the thermal paste which was developed by dispersing GNP-As in J2000. The TTCR of this paste was found to be 4.8×10^{-6} m^2.K/W which was comparable to the best commercial paste, Matrix II. The smaller particle size and narrow size distribution of GNP-As which enabled better filling of surface asperities than GNP-15 is mainly responsible for improved interfacial thermal conductance of the paste developed by GNP-As. GNP-As/J2000 paste had better spreadability on copper surfaces than GNP-5 or GNP-15/J2000 paste, which could be due to the more hydrophilic nature of GNP-As cf. that of GNP-5 resulting in better interaction with J2000 paste.

(vii) The TTCR of GNP-As/J2000 paste decreased with increase of pressure due to flow of the paste.

(viii) GNP-As/silicone paste had 2.7× higher TTCR than the corresponding GNP-As/J2000 paste. The result clearly suggests that the nature of the matrix has crucial role in controlling TTCR.

(ix) Adhesive produced from GNP-As/J2000 (precursor) paste offered TTCR of 1.8×10^{-5} m^2.K/W. This is the lowest value of TTCR obtained for an adhesive in this study. However, this value is significantly higher than that of the precursor paste.

(x) The study suggested that curing does not appreciably affect TTCR, instead dilution of J2000 paste with epoxy resin affected TTCR, perhaps by disturbing filler concentration and distribution or by changing the wetting characteristics of J2000 paste.

(xi) The TTCR of composite adhesives was not affected by varying low applied pressures (0.03-0.16 MPa), which shows that the adhesives do not flow or “pump out” because

they are well bonded with the substrate. In this way, adhesives can overcome the "pump out" or leakage issues of thermal pastes and can offer longer-term performance than thermal pastes.

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