

# Carbon black/graphite nanoplatelet/rubbery epoxy hybrid composites for thermal interface applications

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**Abstract** Hybrid composites were developed by dispersing carbon black (CB) nanoparticles and graphite nanoplatelets (GNPs) at 4–6 and 12–14 wt%, respectively, into rubbery epoxy resin. SEM analysis showed that CB particles improved the dispersion of GNPs in the hybrid composite. The thermal conductivity of 4 wt% CB/14 wt% GNP-15/rubbery epoxy hybrid composite, 0.81 W/m K, is ca. four times higher than that of rubbery epoxy. When silane-functionalised, the fillers reduced the viscosity of the hybrid dispersion and made the hybrid composite highly electrically insulating. Nevertheless, filler functionalisation decreased the composite's thermal conductivity by only 16.6%. Compression testing showed that the hybrid fillers increased the compressive modulus and strength of rubbery epoxy by nearly two and three times, respectively. Overall, the hybrid composites with their thermal paste-type morphology, low viscosity, high compliance, improved thermal conductivity and, when fillers are functionalised, low electrical conductivity makes them promising materials as thermal interface adhesives.

## Introduction

Thermal management is critical and demanding in microelectronics applications as it ensures the reliability and enables further miniaturisation. Thermal management in electronics packaging involves the use of materials which

can help to attain efficient heat dissipation from microchips etc. These materials are used in heat sinks, thermal interface materials (TIMs), devices (fans, heat pipes, etc.) and packaging. TIMs hold a key position; in electronic packaging, TIMs are inserted between the chip (silicon die) and heat spreader and between the heat spreader and heat sink. TIMs reduce or eliminate air gaps at the interface by conforming to the rough and uneven mating surfaces and in this way overcome the thermal contact resistance at the interfaces. Although high thermal conductivity is a very important requirement for TIMs, this alone does not ensure good performance. Besides having a high thermal conductivity, TIMs should also provide an efficient contact between the mating surfaces (i.e. low thermal contact resistance), by forming a thin bond line with a good spreadability and conformability and with a coefficient of thermal expansion close to that of the mating surfaces [1–4]. Surface roughness is also very important as it influences wetting and adhesion behaviour [5]. It is important that TIMs should have low cost so as to be economically viable for the electronics industry.

Various TIMs are commercially available, including thermal pastes, solders, phase change materials, resilient thermal conductors and polymer composites. Thermal pastes are by far the most widely used TIMs. They are produced by dispersing thermally conductive fillers such as silver, boron nitride, aluminium nitride, alumina, silica or carbon black (CB) into silicone or hydrocarbon oils [1, 6]. Pastes can provide a good contact between mating surfaces as they have the ability to fill the gaps and valleys of the proximate surfaces which in most of the cases are micron-to nanometre-sized [7–9]. The pastes can be applied as a thin bond line and need very low mounting pressure to provide good contact. However, they exhibit problems of “pump-out”, phase separation and degradation of

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performance over relatively short periods of time [10]. Polymer composites, which can be used as gels or adhesives, thermal pads or tapes, can offer an alternative to the thermal pastes. These are developed by dispersing thermally conductive fillers into curable polymers like silicone or epoxy [10]. They can be applied as thin layers, like pastes, before curing and can fill the cavities in the surfaces [11]. After curing, they do not need high mounting pressure as they bond the two surfaces together and thus provide mechanical integrity to the package.

Carbon nanomaterials such as carbon nanotubes, graphite nanoplatelets (GNPs) or carbon nanofibers have been exploited as fillers for the development of TIMs due to their high thermal conductivity [12–15]. Of all the carbon nanomaterials, GNPs have perhaps shown the most potential for developing thermally conductive polymer composites. GNPs are composed of one or more layers of graphene with a thickness of 0.3 to 100 nm and are produced by the exfoliation of graphite intercalated compounds at temperatures >600 °C. They have high aspect ratio and large surface area. Single-layered graphene has in-plane thermal conductivity of 5,300 W/m K (estimated, cf. single wall carbon nanotube, 2,900 W/m K) and through-plane thermal conductivity of 3–6 W/m K [16–20]. Furthermore, GNPs have lower cost than carbon nanotubes [21] and commercial fillers used in TIMs (see Table 1). GNP-based TIMs can thus offer significant cost savings as they offer thermal conductivities comparable to those of existing TIMs but at 40–60 wt% lower loadings of filler [13, 22].

The excellent in-plane properties of GNPs and the production of thinner GNPs could lead to GNP/polymer nanocomposites with superior thermal, electrical and mechanical properties at very low loadings of GNPs [23]. Indeed, GNP/epoxy composites have recently been proposed as TIMs [13, 24] for use as adhesives or pads. These composites display very high thermal conductivity in the range of ~4–6 W/m K at a GNPs loading of 20 wt%

[13, 24, 25]. Recently, Lin and Chung [26] have published their work on CB and GNP-based pastes in which they compare the performance of these pastes as TIMs by measuring the thermal contact resistance of these pastes between rough and smooth surfaces. They found that the optimum filler volume fraction, for achieving the lowest thermal contact resistance, decreased as the roughness of the surface decreased from 15 to 0.009  $\mu\text{m}$ . The authors reported that the GNP-based pastes offered lower thermal contact resistance between the rough surfaces whilst CB-based pastes had lower thermal contact resistance between the smooth surfaces. They explained that, in case of smooth surfaces, the lower contact resistance offered by CB-based pastes was due to the ability of CB (having particle size less than 100 nm) to fill the valleys in the surface topography of proximate surfaces which can be as small as 1 nm in size. The authors ascribed the poorer performance of GNP-based pastes, compared to CB-based pastes, to the large size of the GNP particles (3–8  $\mu\text{m}$ ) and their ability to orient themselves parallel to the interfacial plane. It was also reported that the effectiveness of GNP-based paste dropped significantly above the optimum volume fraction of GNPs due to decreases in conformability and spreadability of the paste. Another factor, which makes CB-based pastes superior to GNP-based pastes, is their ability to be applied as thin bond lines. The thermal conductivity of GNP-based pastes was reported to be 0.47 W/m K at 5.28 wt% (2.4 vol.%) of filler, compared to 0.14 W/m K for CB-based pastes at equivalent filler loading. However, the authors reported that both pastes have significantly higher thermal contact conductance than the highest value of  $8 \times 10^3 \text{ W/m}^2 \text{ K}$  that had been previously reported for aligned multiwalled carbon nanotube (0.4 vol.%) arrays. This study clearly demonstrates the potential of GNPs and CB for developing high performance TIMs but it also highlights the limitation of GNPs when used with smooth surfaces.

This study of Lin and Chung [26] raised a question mark over the prospects of GNP/epoxy composites for TIMs. It can be envisaged that, despite having high thermal conductivity, GNP/epoxy composites (as adhesives) may not provide efficient contact between surfaces due to (i) the large particle size of the GNP which cannot fill the nano-sized topography of the surface, (ii) the propensity of GNP to orient itself parallel to the interfacial plane and (iii) the thick bond lines which would be unavoidable at higher volume fraction of filler. To alleviate these problems, it would be possible to use a small particle-sized GNPs but this will drastically reduce the thermal conductivity of the composite and increase the cost of the GNPs due to the grinding required for size reduction.

Another drawback of GNP/epoxy composites is their stiffness and non-conformable matrix [26]. All of the published study on GNP/epoxy composites uses “glassy

**Table 1** Cost comparison of commercial TIMs’ fillers with GNPs

Material	Source	Price ~ (GBP/g)
GNPs (average size 15 $\mu\text{m}$ )	XG Sciences	0.18
Multi wall carbon nanotubes	Sigma-Aldrich (SA)	15
Double wall carbon nanotubes	SA	625
Boron nitride (size ~ 1 $\mu\text{m}$ )	SA	1.15
Aluminium nitride (size ~ 10 $\mu\text{m}$ )	SA	0.48
Silver flakes (~10 $\mu\text{m}$ )	SA	3
Diamond powder (~1 $\mu\text{m}$ )	SA	23–60

epoxy” ( $T_g > 80\text{ }^\circ\text{C}$ ) which is highly stiff [27]. Such glassy epoxies are not conformable materials, meaning that they would be unable to dissipate internal stresses as adhesives and this could lead to delamination. On the other hand, their use in thermal pads is impossible due to their non-compliant nature; they would require higher applied pressure to develop contact with the mating surfaces than is possible in electronic packaging. However, it has been observed from Lin and Chung’s study that the thermal conductivity of CB-based pastes is very low and this may be unacceptable in certain applications. On the other hand, whilst GNP/epoxy has high thermal conductivity these composites are electrically conducting which, again, may be unacceptable in certain other applications.

This article is an effort to solve the issues related to the GNP/epoxy composites for TIM applications. Two approaches have been used. First, replacement of the glassy epoxy matrix with a rubbery epoxy (RE) which has low modulus and is conformable. The RE is not a true elastomer but its behaviour is somewhat elastomeric and it has a low glass transition temperature around  $-35\text{ }^\circ\text{C}$  [27, 28]. Second, development of a hybrid composite of GNPs, CB particles and RE. It is anticipated that the dispersion of nanosized CB particles into the RE matrix would produce a matrix similar to that in CB-based pastes, which may help to develop good contact between the surfaces and which could also discourage the preferred orientation of GNPs, whilst inclusion of GNPs may significantly enhance the thermal conductivity of the composite. Suppression of the electrical conductivity of these composites, which is also a requirement for some thermal interface applications, is achieved by silane functionalisation of the fillers. To date, there has been just one other report of a CB/GNP/epoxy hybrid composite [29] but this used rather lower levels of the fillers and was solely aimed at modification of the electrical transport properties of epoxy resin.

This article presents the characterisation of CB/GNP/RE hybrid composites produced by conventional mechanical mixing (MM) and via dual asymmetric centrifuge mixing by speed mixer (SM). The effects of mixing technique, wt% loading of GNPs and silane functionalisation of the fillers on the thermal conductivity, electrical conductivity and compression properties of the hybrid composites have been investigated.

## Experimental

### Materials

GNPs were purchased from XG Sciences Ltd. These GNPs have platelet morphology with reported thickness in the range of 5–10 nm. Platelets with average widths of 5  $\mu\text{m}$

(GNP-5) and 15  $\mu\text{m}$  (GNP-15) were used in this study. CB, Printex XE2, was supplied by Evonik Degussa GmbH. This CB has a primary particle size of 30 nm with a reported surface area of 600  $\text{m}^2/\text{g}$  (CTAB surface area, ASTM D 3765). Epoxy resin EPIKOTE™ EP862 (Hexion Speciality Chemicals) and curing agent Jeffamine D2000 (Huntsman Corp.) were used in this study. RE was produced by mixing EP862 and Jeffamine D2000 at a weight ratio of 25:75 and curing this mixture. The CB and GNP particles were chemically functionalised with 3-aminopropyltriethoxysilane (APS) (Fisher Scientific Ltd.) according to the reported method [24] and are abbreviated hereafter as FCB and FGNP, respectively.

### Fabrication of the composites

#### Mixing by SM

GNPs and CB particles were mixed in the RE resin under dual asymmetric centrifuge action using a DAC 150 FVZ-K SpeedMixer™. This action is achieved by the spinning of a high speed mixing arm in one direction whilst a basket or cup containing the particles and resin rotates in the opposite direction. The combination of forces in different planes enables good mixing.

Composites were produced by first mixing CB into RE at 3,540 rpm for 5 min followed by addition of GNP particles. The CB/GNP/RE dispersion was further mixed for 5 min at 3,540 rpm. After mixing, the dispersion was degassed, poured into a mould, degassed again and cured. All of the composites produced by SM have a final CB content of 4 wt%. This was selected because in trials it was observed that CB at 6 wt% would not allow the addition of GNP-15 particles at loadings of 12 and 14 wt% due to the high viscosity of the 6 wt% CB/RE dispersion. Both GNP-5 and GNP-15 particles were used to prepare hybrid composites at 12 and 14 wt% loading. A sample of 4 wt% CB/RE was also produced for comparison.

#### MM

The CB and GNPs were mixed in appropriate proportions with RE using a conventional mechanical mixer with a high-speed motor and a propeller attached to a shaft. Both CB and GNPs were dried in an oven at 80  $^\circ\text{C}$  for a prolonged period to remove any moisture adsorbed on their surfaces. CB was first dispersed into the RE resin by mixing at 2,500 rpm for 10 min. Then GNPs were mixed into this CB/RE dispersion for 10 min at a mixing speed of 2,500 rpm. After mixing, the batch was degassed under vacuum to remove trapped air and was poured into a custom-made aluminium mould. The filled mould was again degassed for half an hour to completely remove any

trapped air. Two hybrid composite samples were produced by MM, one containing 6 wt% CB and 12 wt% GNP-5 particles and the other having 6 wt% silane-functionalised CB (FCB) and 12 wt% silane-functionalised GNP-5 (FGNP-5). A sample of 6 wt% CB/RE was also produced for comparison.

### Characterisation

The viscosities of the selected composite dispersions and pure RE before curing were measured using a rheometer (AR100 TA instruments). Flow tests were performed using a parallel plate geometry with a diameter of 25 mm and a 500  $\mu\text{m}$  gap between the plates. Stress was applied from 5 to 2,000 Pa, and shear rates up to  $1\text{--}1,000\text{ s}^{-1}$  were achieved. The data are reported as viscosity versus shear rate.

The morphology of the composites was observed using a Carl Zeiss LEO 60 mm 1530 field emission gun scanning electron microscope (FEG-SEM). The images were obtained using secondary electrons at 3 kV with a working distance of about 3 mm. The samples for SEM analysis were prepared by immersing strips of the composite, cut from the centre of moulded material, in liquid nitrogen for 10 min and then brittle-fracturing them in a vice. The fractured surface of the sample was sputter coated with a thin 5 nm layer of Pt/Pd alloy before the SEM analysis. All of the samples studied by SEM were sectioned in such a manner that one of the surfaces parallel to the direction of gravity during curing of the composite in the mould was exposed for analysis.

Thermal conductivity of the RE and synthesised composites was measured by a Hot Disk [30] thermal constant analyzer (Hot Disk AB). For measurements, the sensor (C3891, radius 3.0 mm) was sandwiched between the two halves of the sample having flat surfaces each with thickness of about 8–10 mm and minimum other dimensions of  $30 \times 30\text{ mm}$ . The thermal conductivity of the samples was measured in the direction parallel to the direction of gravity that applied whilst the samples were left to settle/cure. The Hot Disk method measures thermal conductivity with a reproducibility of  $\pm 2\%$ . This level of reproducibility takes into account the variability between different section of the same sample, sample surface preparation and contacts of sample faces with the sensor etc.

For electrical conductivity measurement, cuboidal samples of the materials ( $\sim 4 \times 4 \times 1\text{ mm}$ ) were placed between two copper electrodes having dimensions slightly greater than those of the sample. The electrodes were connected to an Agilent multimeter that measured the resistance of the sample according to the two probe method, which was deemed to be suitable owing to the relatively low electrical conductivity of the samples. To ensure the good contact between the sample and the copper electrode, samples were

slightly compressed between the electrodes. To observe the effect of orientation of the GNPs in the composites, the electrical conductivity of the samples was measured both through the samples, i.e. in the direction parallel to the direction of gravity, designated as  $\sigma_c$ , and perpendicular to the force of gravity during curing in the mould, designated  $\sigma_{ab}$  (measurements were always made in the short direction of the sample, with sample cuboids cut accordingly).

Compression testing of the RE and composites was carried out on an Instron universal testing system (Model no. 3382 with a 100 kN load cell). Cuboidal samples ( $\sim 8 \times 8 \times 10\text{ mm}$ ) were compressed at a strain rate of 0.5 mm/min. The compression tests were performed on the samples so that compression occurred parallel to the direction of gravity that applied in the original curing moulds.

## Results and discussion

### Viscosity

The plots of viscosity versus shear rate for pure RE and CB/GNP/RE dispersions measured at  $25\text{ }^\circ\text{C}$  are presented in Fig. 1. It can be seen from Fig. 1 that, at the start of the test, the viscosities of all dispersions were very high. However, with a small increase of shear rate of about  $10\text{--}15\text{ s}^{-1}$ , the viscosities dropped rapidly and then leveled off. The viscosity of pure RE resin is about 643 cP at shear rate of  $15\text{ s}^{-1}$ . The addition of CB particles at 4 wt% loading does not increase the viscosity of the RE and this shows that the 4 wt% CB/RE dispersion is potentially a good host for GNP filler. The viscosity of 14 wt% GNP-5/RE dispersion is 1.5 times higher than pure RE and 1.36 times higher than 4 wt% CB/RE at the shear rate of  $15\text{ s}^{-1}$ . However, the viscosity of dispersion containing both 4 wt% CB and 14 wt% GNP-5 particles is 3,234 cP, which is five times higher than RE and three times higher than the dispersion containing 14 wt% GNP-5 particles. On the other hand, the viscosity of the 4 wt% CB/14 wt% FGNP-5/RE dispersion is two times lower than that of the 4 wt% CB/14 wt% GNP-5/RE. Thus, silane functionalisation reduced the viscosity of the hybrid dispersion—probably by reducing the interaction between the GNPs and the epoxy/CB. The viscosity of 4 wt% CB/14 wt% GNP-15/RE is about the same as that of 4 wt% CB/14 wt% GNP-5/RE at the beginning of the flow test but decreased at a rapid rate with the increase of shear rate. It has the viscosity 2,060 cP at the shear rate of  $15\text{ s}^{-1}$ . The rapid drop in the viscosity might have occurred due to the aligning of GNPs parallel to the rheometer's surface geometry which enables the GNPs to glide over one another. Ganguli et al. [24] reported the viscosity of a 16 wt% exfoliated graphite/

epoxy dispersion produced by SM as  $\sim 200,000$  cP and the CB/GNP/RE hybrid dispersions produced in this study thus have viscosities almost 100 times lower at 18 wt% of the total filler loading.

The hybrid compositions were prepared at their maximum possible loading, beyond which the composition becomes too viscous to allow efficient mixing. These compositions at maximum possible loading are workable and can be coated or applied onto other surfaces. It was observed that the 4 wt% CB/RE dispersion has good spreadability and can coat easily offering the potential for a thin bond line at maximum coverage. This behaviour is attributed to the spherical CB particles that increase the conformability of GNP/RE. The advantage of functionalised GNPs is that, by decreasing the viscosity of the dispersion, it makes dispersions more workable and also allows more addition of filler.

### Morphology

The representative SEM images of 14 wt% GNP-5/RE, 4 wt% CB/14 wt% GNP-5/RE and 4 wt% CB/14 wt% GNP-15/RE hybrid composites produced by SM are shown in Fig. 2a–f. It can be observed from the SEM images of the hybrid composites that CB particles are well distributed throughout the matrix at nanoscale and have formed a catenated network within the matrix. GNPs are dispersed in the matrix uniformly with few agglomerates. Most of the GNPs seem to be oriented at acute angles as their edges appear bright in the images. Some of the GNPs form contacts with one another to produce a potentially conducting network within the matrix. The addition of CB particles helps to improve the dispersion of GNPs and

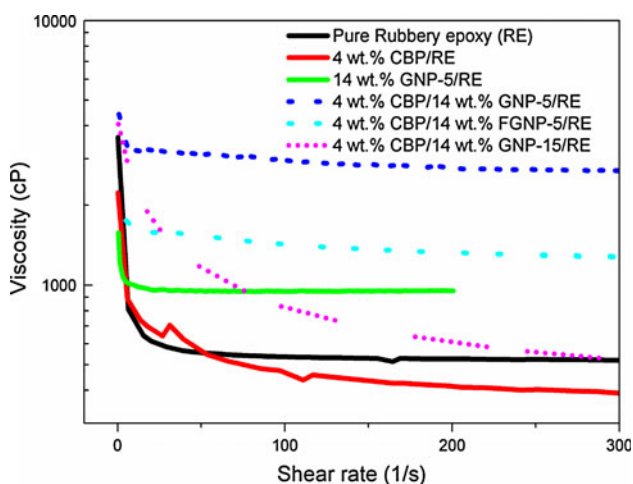
prevent the settling of GNPs in the RE matrix. The presence of a GNP concentration gradient in a 10-mm thick sample of 14 wt% GNP-5/RE composite (cured in a mould) is clearly visible in the SEM image (Fig. 2a), which shows that a  $\sim 5$ -mm thick layer from the top surface of the sample is virtually free from GNPs. However, no such concentration gradient was observed in the SEM image of 4 wt% CB/14 wt% GNP-5/RE composite (Fig. 2b).

In case of 6 wt% CB/12 wt% GNP-5/RE hybrid composite produced by MM, shown in Fig. 2g, h), the SEM images are not much different to those of the composites produced by SM. However, the SEM images of the composite produced with both functionalised fillers (6 wt% FCB/12 wt% FGNP-5/RE) are different. These SEM images (Fig. 2i, j) show that the FGNPs are dispersed uniformly in the matrix but are also significantly apart from one another with fewer contacts between them. It can also be observed from Fig. 2j that the FCB particles are more isolated and lack the catenated structure in the RE matrix, compared to the unfunctionalised CB (Fig. 2h). This shows that the functionalisation of the filler improves the dispersion quality but that such dispersion impairs the formation of the conducting networks required for thermal and electrical transport.

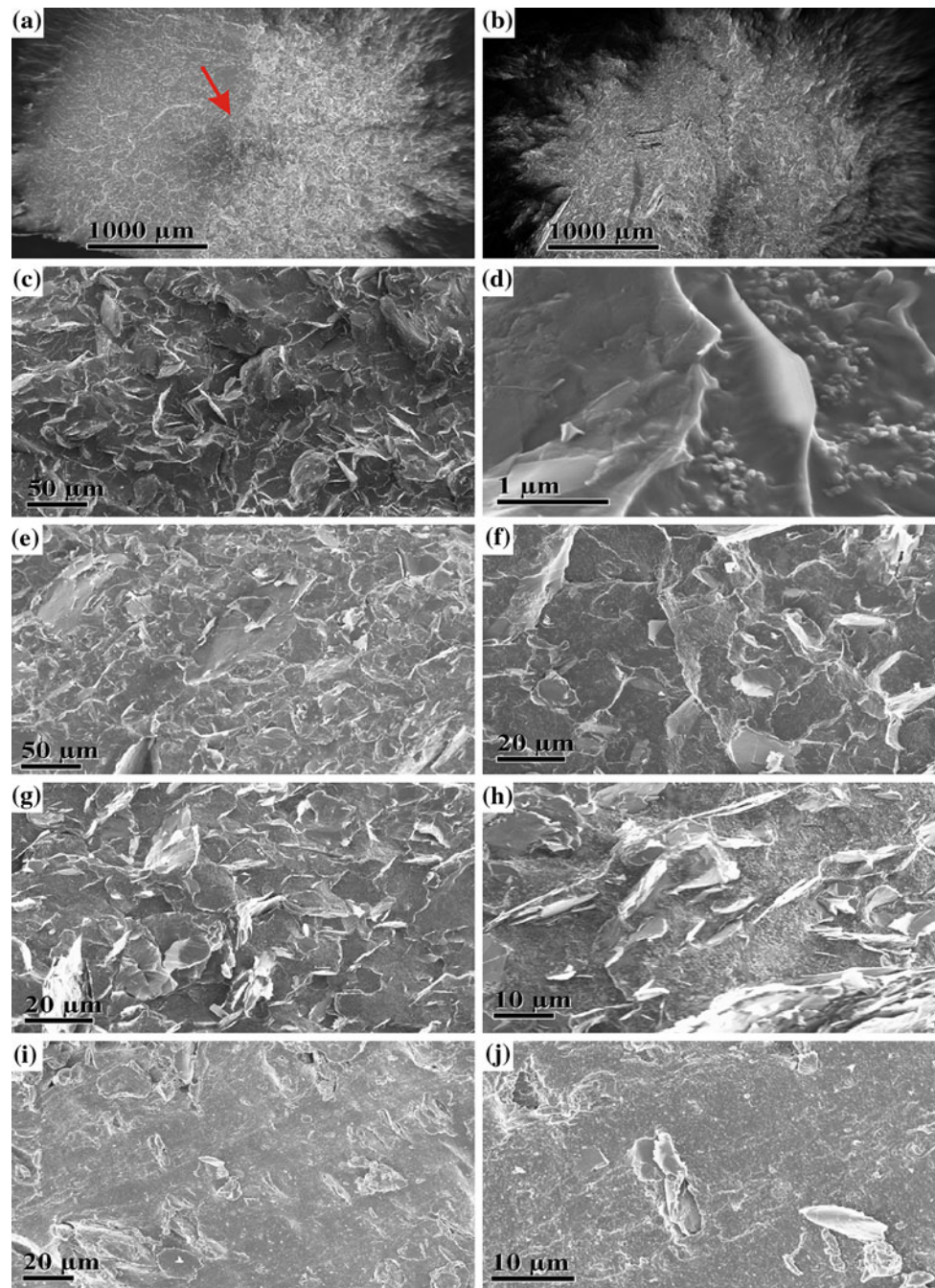
As mentioned in the introduction, despite their high thermal conductivity, the GNP/epoxy composites cannot be used as efficient TIMs, particularly in the form of gels or adhesives on smooth surfaces, due to the propensity of GNPs to orient preferentially in the plane of the thermal interface [26]. However, this study suggests that the use of CB in a hybrid composite would prevent the settling and orientation of GNPs in the matrix. At the same time, it will also produce a matrix similar to those in thermal pastes, as the CB is dispersed at nanoscale in the RE and has a diameter less than 60 nm, which can easily fill nanosized valleys in a thermal interface and could improve the contact between the proximate surfaces.

### Thermal conductivity

The thermal conductivity of neat RE is 0.17 W/m K and that of 4 wt% CB/RE composite is only 0.20 W/m K. The addition of CB at 4 wt% loading thus increased the thermal conductivity of RE by only  $\sim 17\%$ . This shows that the CB, due to its amorphous nature, is not an effective filler for enhancing polymer thermal conductivity. The thermal conductivity of GNP-5/RE composite produced by SM containing only GNP-5 at 14 wt% is 0.55 W/m K, with a standard deviation of 0.40. The large standard deviation is due to the presence of concentration gradients of GNPs, as observed in Fig. 2a, in the 10-mm thick samples used for the measurement of the thermal conductivity by the hot disk method. At 14 wt% GNPs, the concentration gradient



**Fig. 1** The viscosity profiles of RE, 4 wt% CB/rubbery epoxy, 14 wt% GNP-5/rubbery epoxy and CB/GNP/rubbery epoxy dispersions produced by SM



**Fig. 2** SEM images of **a** 14 wt% GNP-5/rubbery epoxy composite; the *arrow* points towards the interface between regions of high GNP concentration (*right*) and low GNP concentration (*left*); **b–d** 4 wt% CB/14 wt% GNP-5/rubbery epoxy; no concentration gradient observed; **e** and **f** 4 wt% CB/14 wt% GNP-15/rubbery epoxy hybrid composites produced by SM; **g** and **h**) 6 wt% CB/12 wt% GNP-5/

rubbery epoxy produced by MM; CB particles are uniformly dispersed on the nanoscale in the matrix and GNPs form interconnects with one another; **i** and **j** 6 wt% FCB/12 wt% FGNP-5/rubbery epoxy hybrid composites produced by MM; fewer interconnects can be seen due to the wide spacing of the GNPs

developed due to settling of the rather more dense GNPs into the initially low viscosity RE resin. Lower thermal conductivities were, therefore, measured when the sensor was sandwiched between upper cross sections of the as cast sample than when the sensor was sandwiched between lower cross sections. The results show that it is very difficult

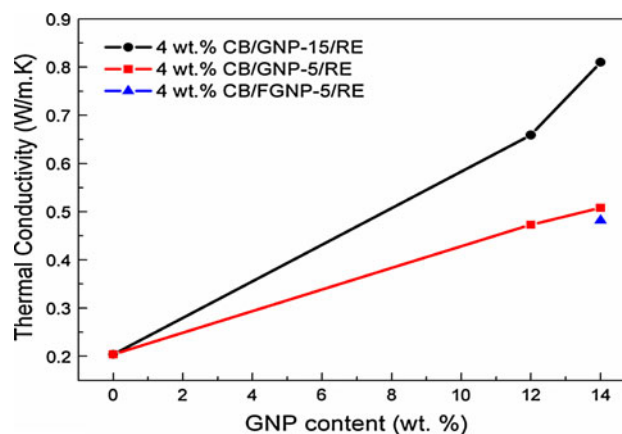
to produce a 14 wt% GNP-5/RE composite with homogeneous thermal conductivity throughout the material.

The thermal conductivity of 4 wt% CB/GNP/RE composites produced by SM, as a function of wt% of GNPs, is presented in Fig. 3. The standard deviations in thermal conductivity of all of these hybrid composites were

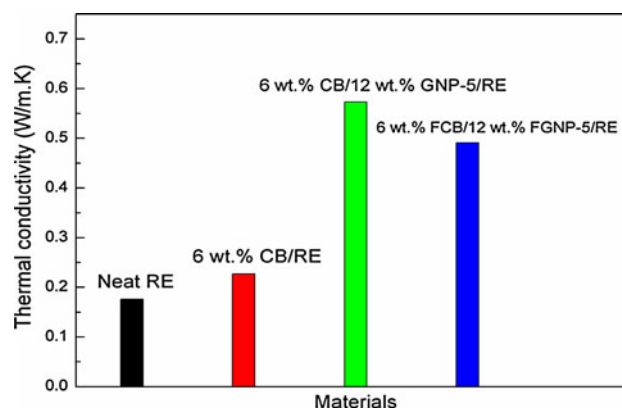
negligible which indicates these composites show no concentration gradient due to settling of GNPs. It can be observed from Fig. 3 that the thermal conductivity of the hybrid composites increases with the increase of both wt% and the particle size of GNPs. Compared to RE alone, the thermal conductivity of 4 wt% CB/RE at 14 wt% GNP-15 increases  $\sim 4.4$ -fold to 0.81 W/m K, whereas at 14 wt% GNP-5 the increase is 2.5-fold to 0.51 W/m K. Thus, the particle size of GNPs plays a vital role in the thermal transport behaviour of the resulting composites. It is clear from the thermal conductivity data that at equivalent wt% loadings, the thermal transport in hybrid composites with large particles is more effective than in those with small particles. The high aspect ratio of GNP-15 particles appears to increase the density of the conducting networks [25], involving fewer particles in the formation of the conducting networks and hence reducing thermal resistance between the particles. The thermal conductivity of hybrid composition containing FGNP-5 particles is 5.5% lower than the composition containing unFGNP-5 since functionalisation of the GNP particles slightly increases the thermal resistance between them.

The thermal conductivities of the composites produced by MM are presented in Fig. 4. The thermal conductivity of RE at 6 wt% of CB is 0.23 W/m K. This increases 2.5-fold to 0.57 W/m K with the incorporation of 12 wt% GNP-5. The thermal conductivity of 6 wt% CB/RE composite produced by MM is similar to that of 4 wt% CB/RE composite produced by SM. Owing to this similarity, it is reasonable to compare the thermal conductivities of hybrid composites containing 12 wt% GNP-5 produced by MM and SM, despite the higher wt% of CB in the composite produced by MM. It can be observed that the thermal conductivity of 6 wt% CB/12 wt% GNP-5/RE hybrid composite produced by MM is 20% higher than that of the 4 wt% CB/12 wt% GNP-5/RE hybrid composite produced by SM. The higher thermal conductivity of the former is attributed to better dispersion of GNPs achieved by MM, which might have resulted in thinner GNP particles and fewer agglomerates. The thermal conductivity of 6 wt% FCB/12 wt% FGNP-5/RE hybrid composite, containing both functionalised fillers, is 16% lower than the equivalent hybrid composite with unfunctionalised fillers.

It was previously observed, in the case of composites produced by SM, that the use of functionalised GNPs, but with unfunctionalised CB, resulted in thermal conductivity of 4 wt% CB/14 wt% FGNP-5/RE hybrid composite which was 5.5% lower than that of the equivalent hybrid composite containing unfunctionalised GNPs. However, it can be observed from the thermal conductivity of the hybrid composite produced by MM containing both functionalised fillers that the combination of functionalised fillers resulted in 16% total drop in thermal conductivity compared with



**Fig. 3** Thermal conductivity versus wt% of GNP of 4 wt% CB/GNP/rubbery epoxy hybrid composites produced by SM



**Fig. 4** Comparison of thermal conductivities of rubbery epoxy, 6 wt% CB/rubbery epoxy, 6 wt% CB/12 wt% GNP-5/rubbery epoxy and 6 wt% FCB/12 wt% FGNP-5/rubbery epoxy composites produced by MM

the use of unfunctionalised fillers in otherwise equivalent composites. As observed by SEM, functionalisation breaks down the catenated structure of CB particles, resulting in fewer contacts between CB particles and it has also been observed this reduces the viscosity of the dispersion. This may facilitate the further dispersion of FGNP-5, thereby reducing thermal conductivity by breaking down the thermally conductive GNP networks, as can be seen from comparison of Fig. 2f and h.

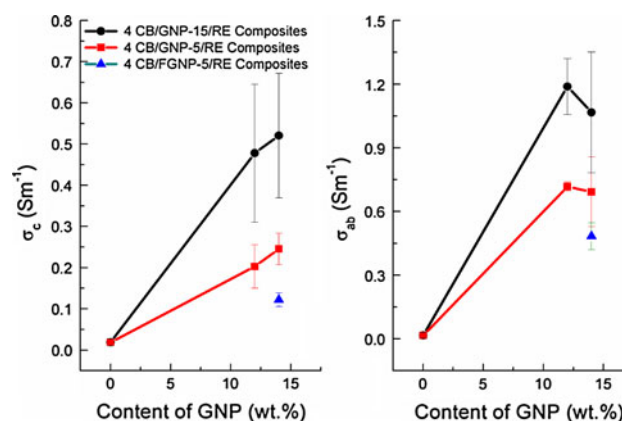
The decrease in thermal conductivity of hybrid composites by functionalisation of GNPs in this study is in disagreement with the study of Ganguli et al. [24] who reported that the silane functionalisation of GNPs resulted in GNP/epoxy composites with  $\sim 38\%$  higher thermal conductivity. They attributed this increase to the formation of more strongly bonded interfaces between FGNPs and the epoxy which helped to minimise phonon scattering. In contrast to their study, Gojny et al. [31] reported that the

thermal conductivity of carbon nanotubes/epoxy composites decreased when the amino-functionalised carbon nanotubes were used. These authors suggest that the functionalised carbon nanotubes form more strongly bonded interfaces with the epoxy matrix and that such a change could increase the phonon damping behaviour at the filler/matrix interfaces. More strongly bonded interfaces could, in particular, result in increased damping of phonons when the matrix is a poor conductor, leading to a composite with poor thermal transport. Since the present findings are in good agreement with Gojny et al.'s study, it is believed that the formation of these stronger interfaces upon filler functionalisation after curing could have caused the observed decrease in thermal conductivity of the hybrid composites. Another factor might be the improved dispersion of FGPs in the RE, which breaks the contacts between the GNPs as observed by SEM (Fig. 2f and h) and thus produces inefficient conducting networks within the matrix. Another possibility might be that the silane coating on the functionalised fillers might have acted as barrier in the transport of phonons between filler particles.

Although hybrid composites produced in this study have lower thermal conductivities than the GNP/epoxy composites produced by others [13, 24, 25], they still have similar or higher thermal conductivities compared with the GNP- and CB-based pastes developed by Lin and Chung [26]. Therefore, the hybrid composites presented in this study, having thermal conductivities and morphologies similar to those of CB pastes could be promising TIMs adhesive materials. Furthermore, it was observed that GNP/RE composite cannot be produced with uniform thermal conductivity at GNP loading levels less than 15 wt%, due to the effects of GNPs settling but use of GNP and CB hybrid composites can overcome this settling problem and make it possible to produce GNP/RE composites at low loading levels of GNPs. The addition of small amounts of CB might also have helped to increase the overall thermal conductivity of the composites by bridging the gaps between the GNP particles or by improving the thermal conductivity of the matrix.

### Electrical conductivity

The electrical conductivities of 4 wt% CB/GNP/RE hybrid composites produced by SM as a function of wt% of GNPs are presented in Fig. 5. The electrical conductivity of a hybrid composite incorporating FGNP-5 particles is also shown in Fig. 5. The electrical conductivities presented in Fig. 5 are measured both in the direction parallel to gravity during curing,  $\sigma_c$ , and perpendicular to this,  $\sigma_{ab}$ , to study the effect of GNP orientation in the hybrid composites.



**Fig. 5** Electrical conductivity of hybrid composites produced by SM as a function of wt% of GNPs

The electrical conductivity of 4 wt% CB/RE composite is 0.0187 S/m. The electrical resistivity of pure RE in the cured state is very high and its exact value was not determined due to a limitation of the instrument, which has detectable range only up to 100 M $\Omega$ . This significant increase in the electrical conductivity of RE with the addition of CB is attributed to the nanoscale dispersion of the CB in the RE matrix. The CB particles develop aggregates or catenate (forming chain-like structures) in the matrix leading to formation of conducting networks in the matrix as can be seen from the SEM images (Fig. 2). Apart from this, the gaps between the CB particles are of a few nanometres in size which can allow electrons to tunnel from one particle to another [32, 33] and hence contribute to the increased electrical conductivity of the composite.

The hybrid composites showed slightly higher  $\sigma_{ab}$  than  $\sigma_c$ , suggesting the presence of anisotropy in these composites. The  $\sigma_c$  of 4 wt% CB/GNP/RE composites increases with the increase of GNPs content up to 14 wt% whilst the  $\sigma_{ab}$  increases at 12 wt% and decreases at 14 wt% loading of GNPs. Although the large standard deviations make interpretation uncertain, this behaviour is in line with the idea that anisotropic alignment of GNP particles by settlement under (and with their basal planes perpendicular to) the direction of gravity diminishes at higher contents of GNPs. This could be due to the fact that at high loading levels, there is not enough free volume available for GNPs to orient themselves under gravity in the curing mould. The  $\sigma_c$  of 4 wt% CB/14 wt% GNP-15/RE composite (0.5206 S/m) is an order of magnitude higher than the 4 wt% CB/RE composites (0.0187 S/m) and  $\sim$ two times higher than the corresponding hybrid composites using GNP-5 particles (0.2545 S/m). The high electrical conductivity of hybrid composites with large size GNP-15 particles is attributed to the formation of a conductive network with fewer interfaces between particles [25].

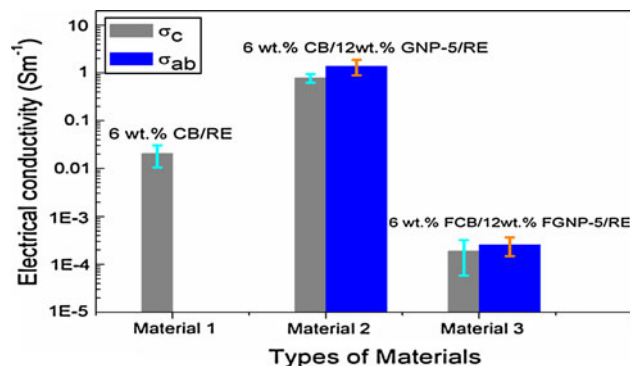


When FGNP-5 particles were used, the electrical conductivity of the hybrid composite decreased, like its thermal conductivity, but more significantly. It can be seen that the  $\sigma_c$  of hybrid composites consisting of 4 wt% CB and 14 wt% FGNP-5 (0.1221 S/m) is two times lower than for the corresponding composite having unfunctionalised GNP-5 (although it is still six times higher than for the 4 wt% CB/RE composite).

The electrical conductivities of hybrid composites produced by MM with unfunctionalised and functionalised CB and GNP-5 are presented in Fig. 6. The  $\sigma_c$  and  $\sigma_{ab}$  of 6 wt% CB/12 wt% GNP-5/RE composite are only slightly different from one another, suggesting little or no GNPs anisotropy in this composite. The electrical conductivity of this composite increased by an order of magnitude with the addition of 12 wt% GNP-5 compared to the 6 wt% CB/RE composite. On the other hand, the electrical conductivity of the corresponding composite incorporating both functionalised fillers decreased by  $\sim 4$  orders of magnitude, again with little difference between  $\sigma_c$  and  $\sigma_{ab}$ . It can be seen that incorporation of both functionalised fillers in the hybrid composite render the composite highly electrically insulating. This large reduction in the electrical conductivity of the hybrid composite is mainly attributed to the FCB. This is because it has already been observed in the hybrid composite produced by SM (4 wt% CB/14 wt% FGNP-5/RE), containing functionalised GNPs and unfunctionalised CB particles, that the electrical conductivity was only halved compared with the corresponding composite containing both unfunctionalised fillers.

The mechanism of electrical conduction in hybrid composites depends on the contacts between the particles and the electron tunnelling between the particles or through the nanometre-thin insulating layer of the matrix as the electrical conductivities of these composites are well above that defined by their percolation threshold [34]. It seems the CB particles are mainly responsible for the electrical transport and this may be due to their catenated structure in the matrix, whilst GNPs helped to strengthen the conducting networks. The silane functionalisation of the CB particles appears to have broken these catenated structures into more isolated CB particle aggregates as observed by SEM (Fig. 2i and j) and thus rendered the matrix electrically insulating. Furthermore, silane functionalisation breaks the contacts between the GNP-5 particles thereby adding irregularity to the conducting networks.

The decrease in hybrid composite electrical conductivity due to functionalisation agrees with the study of Gojny et al. [31], who reported that the amino-functionalised carbon nanotubes/epoxy have lower electrical conductivity than the unfunctionalised carbon nanotube/epoxy composites. On the other hand, Ganguli et al. [24] reported that functionalised exfoliated graphite/epoxy composites have



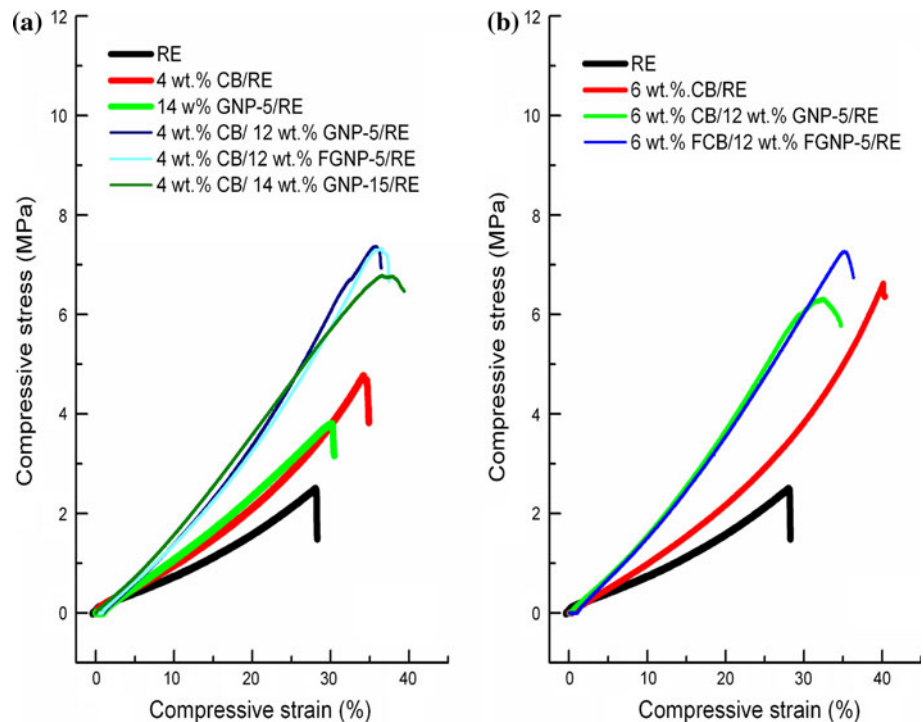
**Fig. 6** Electrical conductivity of 6 wt% CB/rubbery epoxy and hybrid composites produced by MM

higher resistivity at low loading levels of exfoliated graphite but that at loading levels higher than 12 wt%, and they found that both functionalised and unfunctionalised exfoliated graphite/epoxy composites have the same quite low electrical resistivity. Contrary to their study, hybrid composites reported in this study at 18 wt% total loading of fillers, at least 12 wt% of which is GNPs, are highly electrically insulating. It is important to note that although the electrical conductivity of 6 wt% CB/12 wt% GNP-5/RE hybrid composite produced by MM reduced by 4 orders of magnitude when functionalised fillers were used, the thermal conductivity decreased by only 16.6%, compared to the corresponding composites consisting of unfunctionalised fillers. Such electrically insulating and thermally conducting composites are of major interest for thermal interface applications. This study thus shows that functionalisation can be a useful way of producing electrically insulating composites without significantly compromising the thermal conductivity.

#### Compression testing

TIMs, either in the form of adhesives or thermal pads, are mainly used under compression although the maximum pressure in microprocessor applications does not exceed 0.116 MPa (16.8 psi) [6]. Therefore, it is of interest to study hybrid composites under compression to determine whether they possess sufficient compliance to be used effectively under low pressures. The compression stress–strain curves and properties of RE and its composites produced by SM and MM are presented in Fig. 7 and Table 2. It can be observed from Fig. 7 that the pure RE has very low stiffness and low compressive strength. Its compressive modulus is comparable to a silicone elastomer [22], which shows its highly compliant nature. The compressive modulus of RE increased by 1.2 $\times$  and 1.4 $\times$  with the addition of CB at 4 wt% (composite produced by SM) and 6 wt% loading (composite produced by MM),

**Fig. 7** Compression stress–strain curve of composites produced by **a** SM and **b** MM



**Table 2** Compression testing data for rubbery epoxy and hybrid composites produced by SM and MM

Material	Fabrication method	Compressive modulus (at 10% strain) MPa	Compressive strength on appearance of crack MPa	Compressive strain at appearance of crack (%)
Neat rubbery epoxy (RE)	MM	$7.39 \pm 0.10$	$2.26 \pm 0.2$	$26.15 \pm 1.74$
4 wt% CB/RE	SM	$8.81 \pm 0.63$	$4.75 \pm 1.25$	$35.61 \pm 3.66$
14 wt% GNP-5/RE	SM	$11.32 \pm 0.56$	$4.08 \pm 0.26$	$31.53 \pm 2.02$
4 wt% CB/14 wt% GNP-5/RE	SM	$16.39 \pm 1.34$	$7.3 \pm 0.87$	$32.39 \pm 1.28$
4 wt% CB/14 wt% FGNP-5/RE	SM	$15.66 \pm 0.74$	$7.26 \pm 0.21$	$33.66 \pm 0.3$
4 wt% CB/14 wt% GNP-15/RE	SM	$17.63 \pm 1.9$	$6.29 \pm 0.42$	$33 \pm 3.03$
6 wt% CB/RE	MM	$10.22 \pm 0.01$	$7.25 \pm 0.54$	$41.61 \pm 1.57$
6 wt% CB/12 wt% GNP-5/RE	MM	$16.68 \pm 1.24$	$5.65 \pm 0.3$	$29.32 \pm 0.35$
6 wt% FCB/12 wt% FGNP-5/RE	MM	$17.55 \pm 0.7$	$8.54 \pm 1.81$	$35.54 \pm 2.02$

respectively. This small increase in RE modulus, therefore, suggests that the CB-filled RE represents a suitable matrix for the development of compliant hybrid composites. On the other hand, inclusion of CB increased the compressive strength of RE by  $\sim 2$ – $3$  times and thus made it a slightly more attractive material in terms of robustness.

The compressive modulus of the hybrid composites produced by SM increased by  $\sim 2\times$  with the addition of GNPs at 14 wt% loading compared to the 4 wt% CB/RE composite. The increased stiffness of the hybrid composites is due to close interactions between GNPs and CB particles and the inherent high modulus of GNPs. The compressive strength of the hybrid composites also increased (by  $1.5\times$ ) as expected. Overall, the hybrid

combination of fillers incorporated by SM increased the modulus and strength of RE by  $\sim 2\times$  and  $\sim 3\times$ , respectively.

However, although hybrid composites produced by MM showed similar increases in compressive modulus, the compressive strength and compressive strain of the 6 wt% CB/RE composite decreased with the inclusion of 12 wt% GNP-5 particles. On the other hand, the hybrid composite incorporating both functionalised fillers has increased compressive strength and strain compared to the composite produced with unfunctionalised fillers. This behaviour is attributed to the increased dispersion of both fillers, as observed by SEM, and to their increased bonding with the matrix due to their silane functionalisation.

Overall, the compression testing results showed that the combination of GNPs and CB particles slightly increased the modulus of the RE, but nevertheless suggests that the hybrid composites are highly compliant materials, which is an important requirement for TIMs.

## Conclusions

Hybrid composites were prepared by dispersing GNP and CB particles into RE by MM and by SM. The composites produced by SM had a CB content fixed at 4 wt%, whilst the GNPs (GNP-5 or GNP-15) content was varied between 12 and 14 wt%. In case of the composites produced by MM, the CB and GNPs (having particle size 5  $\mu\text{m}$ ) were fixed at 6 and 12 wt%, respectively. Although these composites were prepared at their maximum possible loading, their viscosities are still low enough for them to be workable and they can be coated or applied on other surfaces as a thin bond line. SEM analysis showed that the use of CB in the hybrid composites improved the dispersion of GNPs and prevented the settling of GNPs. It also produced a matrix similar to that in thermal pastes as the CB particles were dispersed on the nanoscale in the RE and have diameters less than 60 nm, which can easily fill nanosized valleys in proximate surfaces and could improve the contact between them.

The thermal conductivity of the hybrid composites produced by SM increased with increase of the wt% and the GNP particle size. The thermal conductivity of hybrid composites containing 4 wt% CB particles and 14 wt% GNP-15 particles (0.81 W/m K) represented a  $\sim 5$  fold increase over that of pure RE (0.17 W/m K). There is also evidence that the better dispersion of GNPs achieved using MM, cf. speed mixing, leads to hybrid composites with higher thermal conductivity. Although hybrid composites have slightly lower thermal conductivity than commercial TIMs, their thermal conductivity is still comparable to that of thermal pastes.

Electrical conductivity measurements showed that the anisotropic behaviour of the hybrid composites diminished with increase of GNP-15 content from 12 to 14 wt%. The electrical conductivity ( $\sigma_c$ ) of 4 wt% CB/14 wt% GNP-15/RE hybrid composites (0.5206 S/m) is nearly an order of magnitude higher than that of the 4 wt% CB/RE composites (0.0187 S/m). Nevertheless, there is evidence to suggest that the CB particles are mainly responsible for the electrical transport due to their catenated structure in the matrix, whilst GNP particles help to strengthen the conducting networks. The hybrid composite incorporating both FCB and GNP-5 fillers is effectively electrically insulating; it has electrical conductivity 4 orders of magnitude lower than that of the corresponding hybrid composite containing

unfunctionalised fillers. The CB functionalisation reduces the electrical conductivity of the hybrid composites more strongly than that of GNP-5 alone, perhaps by breaking the catenated structure of CB in the matrix and by improving the dispersion of GNPs in the matrix, thereby breaking the conducting networks between them.

The functionalised fillers decreased the thermal conductivity of the hybrid composite by 16.6%. It is possible that the silane coating on the fillers strengthened their bonding with the matrix and acted as a barrier (by adding additional resistance) to phonon transport between the particles, thereby breaking the contacts between GNPs and CB particles. Silane functionalisation of the fillers is thus an effective way of making electrically insulating but thermally conducting TIMs.

The compression testing showed that, at their maximum wt% loading, the hybrid combination of the fillers increased the compressive modulus and strength of RE by  $\sim 2\times$  and  $\sim 3\times$ , respectively. Despite this increase in the modulus, all of these hybrid composites retain high compliance. For example, the 4 wt% CB/14 wt% GNP-15/RE hybrid composite has a modulus of 18 MPa, which is comparable to silicone-based commercial TIMs [22].

Overall, the hybrid composites with their morphology typical of thermal pastes, low viscosity before curing, high compliance, improved thermal conductivity (with the additional benefit of electrical insulation when fillers are functionalised) are promising materials for use as thermal interface adhesives.

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