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Raza, MA, Westwood, AVK, Stirling, C et al. (1 more author) (2015) Effect of boron nitride addition on properties of vapour grown carbon nanofiber/rubbery epoxy composites for thermal interface applications. Composites Science and Technology, 120. 9 - 16. ISSN 0266-3538

https://doi.org/10.1016/j.compscitech.2015.10.013

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Effect of boron nitride addition on properties of vapour grown carbon nanofiber/rubbery epoxy composites for thermal interface applications

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Submitted to Composites Science and Technology

June 2015

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Abstract

This work is focused on developing an epoxy-based hybrid composite using BN and VGCNF, with the main motivation of producing thermally conducting but electrically insulating composite thermal interface materials (TIMs). Various compositions of BN/VGCNF/rubbery epoxy hybrid composites were developed by 3-roll milling. The thermal conductivity of hybrid composites increases with increasing VGCNF content and electrical conductivity decreases with increasing BN content. SEM showed that BN inclusion inhibits VGCNF contacts resulting in more electrically insulating composites. Compression testing showed that BN inclusion produced stiffer composites than those produced with VGCNFs at equivalent loading. The thermal contact resistance of 6 wt.% BN/8 wt.% VGCNF/rubbery epoxy composite was 3.36×10^{-5} m^2.K/W at a bond line thickness of 18 μm. Thermal contact resistance measurements showed that hybrid composites can offer better interfacial thermal transport at thick bond lines and this improves with increasing VGCNF content due to increased thermal conductivity imparted by VGCNF.

Keywords: A. Hybrid Composites; B. Electrical properties; B. Mechanical properties; D. Scanning electron microscopy

1. Introduction

Thermal interface materials (TIMs) are vital for microelectronics packaging as they are responsible for improving interfacial thermal contacts between components, such as microprocessors, and heat sinks, thus ensuring sufficient heat removal from these components [1]. Conventional TIMs are made by dispersing inorganic fillers such as boron nitride (BN), aluminium nitride or silicon carbide in polymer matrices. These are primarily marketed as thermal pastes. Thermal pastes offer superior thermal interfacial contacts but they have issues of pump-out or dry out from interfaces when exposed to thermal and power cycle resulting in increase in thermal contact resistance which threatens microelectronic devices long term reliability [2]. Polymer composites are commonly used as adhesive TIMs since, as well as offering good thermal conductivity, their compliant nature suits gap-filling applications thereby improving contacts between the mating surfaces and also binding the surfaces to improve mechanical stability [3]. High thermal conductivity and low thermal contact resistance are the most desirable characteristics of TIMs [4].

Recently, carbon nanofillers such as graphene, graphite nanoplatelets, carbon nanotubes and carbon nanofibres have been widely researched as fillers to produce heat dissipating polymer-based composites [5-8] and thermal pastes [4, 9, 10] that offer great potential for thermal interface applications due to their high thermal conductivity and low thermal contact resistance, respectively. However, high thermal conductivity alone cannot ensure good interfacial thermal conductance. The performance of TIMs depends on many factors such as concentration and morphology of filler and on the wettability, spreadability and adhesion of the resulting polymer composite dispersions on substrates/components, which improve thermal contacts between the mating surfaces [11]. Also, the potentially high electrical conductivity of carbon nanofiller-based polymer composites is considered a drawback in microelectronic packaging. For carbon black thermal pastes, Lin et al. [12] addressed this problem by incorporation of exfoliated clay and fumed alumina into to carbon black-based thermal pastes.

Production of hybrid composites seems an easy solution for further improving conducting and mechanical properties of carbon nanofiller-based composites. By dispersing different types of carbon nanofillers or combining carbon nanofillers with inorganic fillers in a polymer matrix, a composite with multifunctional properties can be developed. There are several reports in which researchers have reported that hybrid combination of fillers can produce synergetic effects on the thermal, electrical and mechanical properties of composites [13-16].

BN is the most popular filler material for TIMs mainly due to its high electrical resistivity, which is important for avoidance of short-circuiting in certain systems, and high thermal conductivity (280 W/m.K). Like carbon nanomaterials, BN can also have several nanostructures which make it an interesting filler material for polymer composites [17]. Few research articles report thermal conductivity of hybrid composites produced with BN and carbon nanomaterials. Teng et al. [18] produced hybrid filler composites by dispersing functionalized multiwalled carbon nanotubes (MWCNTs) and BN in epoxy resin. They reported that thermal conductivity of 1 vol.% MWCNT/epoxy composite increased with increasing vol.% of BN. A composite containing 30 vol.% BN and 1 vol.% MWCNT had thermal conductivity of 1.9 W/m.K which was ca. 8x higher than for neat epoxy. This increased thermal conductivity was attributed to better conductive networks formed by the hybrid fillers. Pak et al. [19] reported polyphenyl sulphide-based composites produced by dispersing a mixture of BN and MWCNT fillers. A maximum thermal conductivity of 1.74 W/m.K was obtained for a composite consisting of 1 wt.% MWCNT and 50 wt.% BN compared to 1.0 W/m.K for a composite having 50 wt.% BN particles only. The synergetic effect on thermal conductivity of composites was attributed to the formation of three-dimensional thermal transfer pathways between BN and MWCNTs. Ng et al. [20] reported that employing mixed BN and carbon fibre fillers in polybutylene terephthalate (PBT) composites did not enhance thermal conductivity and this was attributed to the low aspect ratio of the carbon fibres which could not help in formation of conducting networks. However, the authors found that incorporation of carbon fibres improved tensile properties and processability of BN/PBT composites.

Vapour grown carbon nanofibers (VGCNF) are very similar to MWCNT in morphology but have larger diameters than MWCNTs. Their low cost and ease of dispersion in polymers compared to carbon nanotubes make them suitable filler for producing heat dissipating polymer composites (TIMs). A large number of publications on VGCNF/polymer composites have appeared in the last decade. Review articles [21, 22] give a good overview of fabrication, properties and applications of VGCNF/polymer composites. In our prior work [23], we reported that VGCNF/rubbery epoxy composites gave thermal conductivity of 1.31 W/m.K and 1.8 W/m.K at 15 and 26 vol. % of VGCNF, corresponding to 7-fold and 10-fold increases, respectively, over neat rubbery epoxy. We also reported that these composites, even at a high loading of 26 vol.% of fibres, are very compliant (having low compressive modulus), have good ease of processing, low viscosity before curing and good spreadability as coating or adhesive, which makes them suitable candidates for thermal interface applications. However, these composites have high electrical conductivity which undermines their usefulness in thermal interface applications. The incorporation of inorganic fillers such as BN can decrease the electrical conductivity of VGCNF/rubbery epoxy composites and at the same time can produce synergetic improvements in the thermal conductivity of these composites by developing efficient conducting networks as reported by others [18, 19].

The present work reports novel hybrid rubbery epoxy composites produced by co-dispersing an inorganic filler, BN, and a carbon nanofiller, vapour grown carbon nanofibres (VGCNF), in the polymer matrix with the aim of producing TIMs with much better properties than conventional TIMs by exploiting the ability of BN as a co-filler to decrease electrical conductivity and enhance thermal conductivity. BN/VGCNF/rubbery epoxy composites were produced by 3-roll milling at various loadings of BN and VGCNF. The morphology, thermal conductivity, electrical conductivity and mechanical compression properties of the resulting composites were studied. To evaluate the performance of these composite adhesives as heat dissipating materials i.e., TIMs, selected hybrid composite coatings were studied as thermal interface adhesives according to ASTM D5470.

2. Materials and Methods

Hexagonal BN particles with average particle size of 5-10 μm and VGCNF (Applied Sciences, Inc) with diameters of 70-200 nm and lengths from 10-50 μm were used as composite fillers in this study (Fig. 1 (a-c)). Further details on VGCNF can be seen in [5]. Both BN and VGCNF were used as-received. Rubbery epoxy resin (RE) was used as a matrix, details of which can be seen in [24]. Briefly, rubbery epoxy is formed by mixing polyetheramine, a difunctional primary amine with repeating oxypropylene units in the backbone and a molecular weight of about 2000 (Jeffamine D2000, ex Huntsman corporation) with epoxy resin (Epikote 828 ex Hexion Chemicals) at a ratio of 75/25. Jeffamine D2000 is an amine curing agent, however, it should be noted that in rubbery epoxy the Epikote 828 epoxy resin effectively crosslinks the Jeffamine D2000 because Jeffamine D2000 is present in 3× higher quantity than the Epikote 828. The resulting material could therefore be logically termed “crosslinked polyether” but it is commonly known as “rubbery epoxy” because it has a glass transition temperature below normal ambient temperature [25] and significantly lower modulus than highly crosslinked glassy epoxy [24].

The composites were produced using a 3-roll mill by dispersing BN and VGCNF in RE according to procedures described in our previous publication [26]. Briefly, a weighed amount of resin, BN and VGCNF was first mixed with mechanical stirrer at 1000 rpm for 5 min. The resulting dispersion was mixed in the roll mill according to the procedure described in [26]. Composites were produced with BN content fixed at 6 wt.% while VGCNF content was varied from 8 to 12 wt.%. These total filler contents from 14 to 18 wt.% were selected to produce hybrid composites because dispersions with higher loadings could not be easily coated as thin bond lines between substrates. A composite was also produced with 2 wt.% BN and 12 wt.% VGCNF. Finally, since commercial TIMs are comprised of BN fillers with a loading greater than 40 wt.%, a BN/RE composite was developed as a reference material with a loading of 45 wt.% using the roll mill.

The morphology of the freeze-fractured samples, sputter coated with thin layer of Pd/Pt alloy, was studied in secondary electron imaging mode using a LEO 1530 field emission gun scanning electron microscope operated at 3 kV. The thermal conductivity was measured by hot disk thermal constant analyser (Hot Disk® AB) with a sensor (radius 3.180 mm) which was placed between the two halves of each sample, having thickness of 8-10 mm and cross section of 20 × 20 mm^2. The electrical conductivity was measured by placing cuboidal composite samples (~5 × 5 × 2 mm^3) between two copper electrodes which were connected to a multimeter (Agilent 34401A) for the measurement of resistance. Compression testing of samples was carried out on cuboidal samples using an Instron Universal testing machine (Model No. 3382, load cell 100 kN) at a strain rate of 0.5 mm min^{-1} [26, 27]. These composites were also tested, with cured matrix, as adhesives according to ASTM standard D5470 on a thermal contact resistance measurement rig to quantify their performance as TIMs. The details of the rig and the testing procedure have been described in our previous publication [28]. Briefly, the rig uses two copper cylinders between which an adhesive was sandwiched, whose thermal contact resistance is to be measured. Firstly, 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 thermal contact resistance.

There were two holes at precise locations in each cylinder for the insertion of probes (RTD, 1/10 DIN PT 100 Probe, Omega Engineering Ltd) for temperature measurement. The copper cylinders assembly (sandwiching the TIM composite adhesive) was placed between the heating and cooling stages. After achieving steady state conditions, temperatures were noted which were used to calculate thermal contact resistances according to equations reported in [17]. The total thermal contact resistance of the coating is proportional to its bond line thickness. The sandwiched paste after curing has a certain thickness, defined as the “bond line thickness”, which was measured using a profilometer after thermal contact resistance measurement and subsequent separation of the copper cylinders.

3. Results and Discussion

3.1 Morphology

SEM images of freeze-fractured surfaces of BN/VGCNF/RE hybrid composites produced by 3-roll milling are shown in Fig. 1 (d-f). It can be observed from these SEM images that both VGCNFs and BN are uniformly dispersed in the RE matrix. No significant agglomerates of the fibres or BN were observed. VGCNFs are interconnected to form conducting networks within the matrix whereas the BN particles do not form interconnects with one another and are separated by the matrix and VGCNFs. The effect of hybrid combination can be seen from the fact that BN inclusion in VGCNF/RE composite improved dispersion of VGCNF in the matrix. Analogously, VGCNF reduced the number of interconnects between BN.

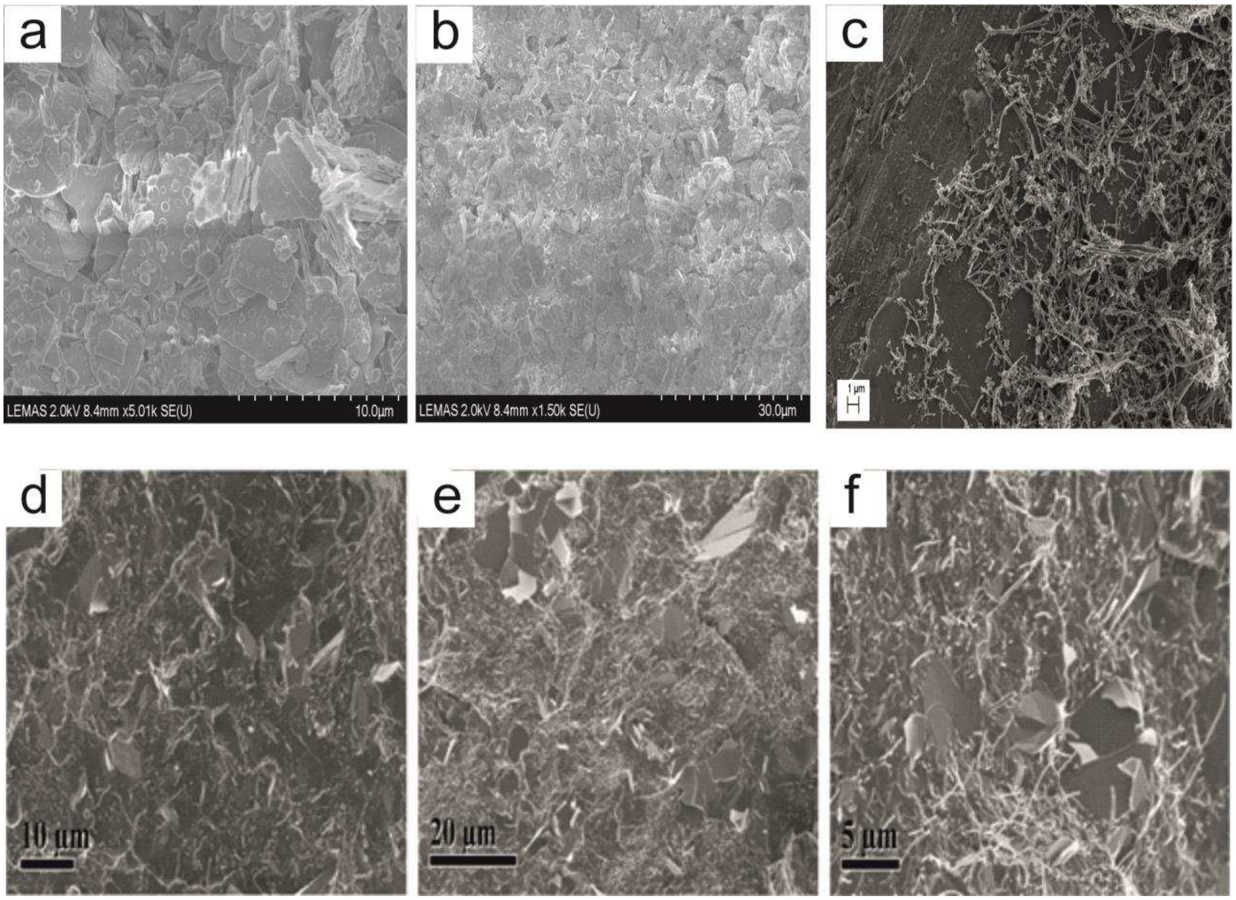

Fig. 1. SEM images of (a & b) BN (c) VGCNF (d) 6 wt.% BN/8 wt.% VGCNF/RE (e & f) 6 wt.% BN/12 wt.% VGCNF/RE composites produced by roll milling.

The SEM images of the 45 wt.% BN/RE composite are presented in Fig. 2. It can be observed that BN particles are well dispersed and distributed in the matrix. The particles’ interconnects can be clearly seen from these images. In contrast, particle interconnects are lessened in hybrid composites (Fig. 1). It is important to mention here that further higher loading of BN was found to be difficult using the roll mill as the resulting dispersion had very high viscosity which cannot be poured in a mould or coated on any substrate.

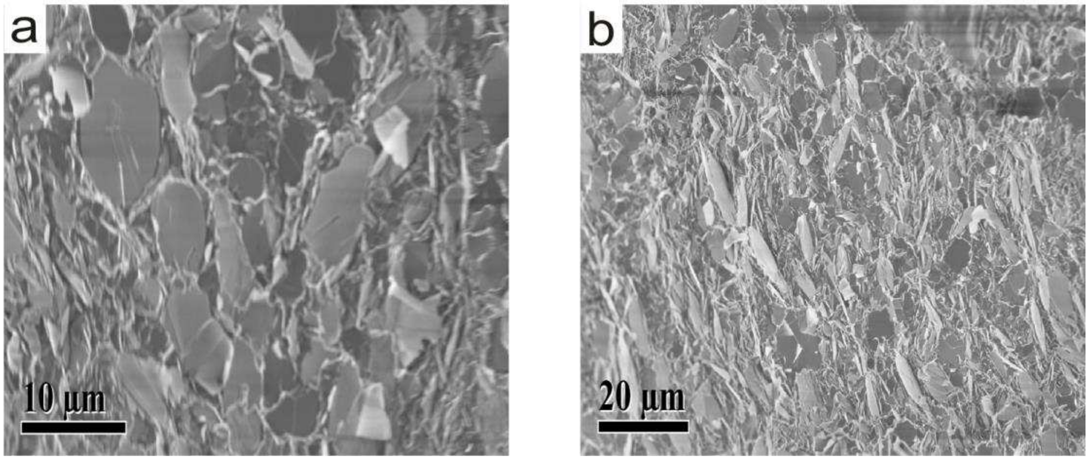

Fig. 2. SEM images of 45 wt.% BN/RE composite produced by 3-roll mill.

3.2 Thermal conductivity

The thermal conductivities of BN/VGCNF/RE hybrid composites (bulk samples) are presented in Fig. 3. For comparison thermal conductivity of VGCNF/RE composites at equivalent loadings of filler are also presented in Fig. 3.

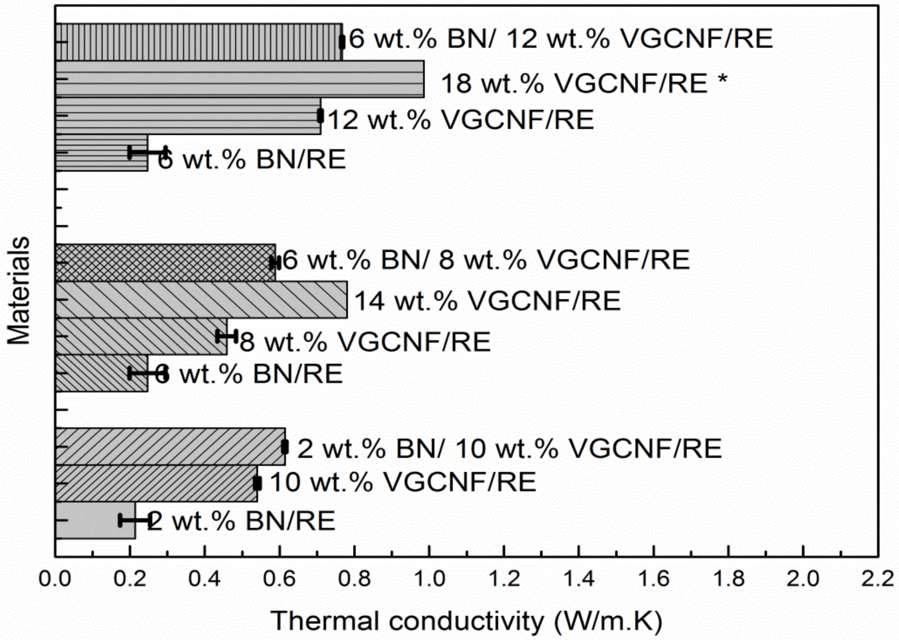

Fig. 3. Comparison of thermal conductivities of BN/VGCNF/RE hybrid composites with VGCNF/RE and BN/RE composites produced by roll milling. *Interpolated from thermal conductivity vs. wt.% VGCNF plot in [23].

The addition of BN in hybrid combination with VGCNF did not increase the thermal conductivity of the composites very much. The thermal conductivity of 6 wt.% BN/8 wt.% VGCNF/RE composite (0.588 W/m.K) is 2.38× and 1.28× higher than that of the non-hybrid composites of 6 wt.% BN/RE and 8 wt.% VGCNF/RE, respectively. However, the thermal conductivity of 12 wt.% VGCNF/RE composite is still 1.2× higher than 6 wt.% BN/8 wt.% VGCNF/RE even though the latter's total filler loading is higher. Similarly, the thermal conductivities of non-hybrid 12 wt.% VGCNF/RE, 14 wt.% VGCNF/RE and 18 wt.% VGCNF/RE composites are 1.15×, 1.3× and 1.28× higher than those of 2 wt.% BN/10 wt.% VGCNF, 6 wt.% BN/8 wt. VGCNF and 6 wt.% BN/12 wt.% VGCNF hybrid composites, respectively. These results suggest that the hybrid combination of BN and VGCNF does not enhance the thermal conductivity of the composites at these total loadings. It was observed in SEM images of VGCNF/RE composites that VGCNFs form continuous conducting networks within the matrix [23]. The BN inclusions in VGCNF/RE may destroy VGCNFs' conducting networks in the matrix. Owing to their 5-10 µm size, BN plates occupy a large space between the networks of VGCNFs. In such a matrix, point contacts between VGCNFs and BN are formed as observed by SEM (Fig. 1) and also the BN plates are not connected with each other. It appears that the high thermal contact resistance between VGCNF and BN plates due to the decrease in contact area (formation of more interfaces) reduces the efficiency of the VGCNF conducting networks and this might account for the lower thermal conductivity of the hybrid composites compared with the non-hybrid ones at equivalent total loadings.

The thermal conductivity of 45 wt.% BN/RE composite measured by hot disk thermal constant analyser is 1.33 W/m.K at room temperature. In our previous publication [23], we reported that a VGCNF/RE composite also offered similar thermal conductivity (1.31 W/m.K) to that of 45 wt. % BN/RE composite, but at 20 wt.% less loading of VGCNFs. The comparison clearly confirms the common notion that nanofillers offer improved properties at significantly lower loadings.

The thermal conductivity of BN/RE composite at 45 wt.% (30 vol.%) BN is comparable to that reported for such composites in the literature. Lee et al. [29] reported a ~4-fold increase in thermal conductivity for BN/epoxy composite (particle size 1 µm) at 18 vol.% BN over pure epoxy. The same group also reported thermal conductivity of BN/epoxy composite to be 3.66 W/m.K at 50 vol.% BN [30]. Hill et al. [31] reported the thermal conductivity of BN/RE composite (particle size 27 µm) to be 1 W/m.K at 27 vol.% of BN corresponding to ~8-fold increase over pure epoxy. In the present work, the increase in thermal conductivity of 30 vol.% BN/RE composite, with ~5× smaller BN particles compared to those used by Hill et al. [31], is ~7.5-fold over pure RE. The 5× smaller BN particles would be expected to yield lower thermal conductivity composites if it weren't for the superior BN dispersion achieved by roll milling. Perhaps, thermal conductivity of BN-based composites can be further enhanced by surface treatment of BN with silane as the work of Xu et al. [32] suggests. They have reported that BN/epoxy composites produced with 55 vol. % of silane-treated BN gave thermal conductivity of 10 W/m.K. More recent work on BN/epoxy composites by Wang et al. [33] reports that silane treated- boron nitride nanoplatelets at ~50 vol.% improved thermal conductivity of epoxy up to 5.24 W/m.K, corresponding to 16-fold increase over pristine epoxy.

3.3 Electrical conductivity

The electrical conductivities of BN/VGCNF/RE hybrid composites are presented in Table 1. For comparison electrical conductivities of VGCNF/RE composite at equivalent loadings of filler are also presented in Table 1.

It can be observed from Table 1 that, due to its high electrical resistivity, the incorporation of BN decreases the electrical conductivities of hybrid composites significantly compared with the corresponding VGCNF-only composite. In the case of 2 wt.% BN/10 wt.% VGCNF/RE composite, electrical conductivity decreased by ~2.5× compared to 10 wt.% VGCNF/RE. Furthermore, the electrical conductivity of 6 wt.% BN/8 wt.% VGCNF/RE composite is 6.6× lower than that of 8 wt.% VGCNF/RE and 28× lower than the non-hybrid composite consisting of approximately equivalent loading of VGCNF (14 wt.% VGCNF/RE). The electrical conductivity of 6 wt.% BN/12 wt.% VGCNF/RE hybrid composite at total filler loading of 18 wt.% is also ~6× lower than the 18 wt.% VGCNF/RE composite. Thus, the electrical conductivity data suggests that additions or substitutions of BN in the conducting networks of VGCNFs add significant resistance to the electron transport and reduce the efficiency of the conducting networks. The results also highlight the fact that addition of electrically insulating filler into carbon nanofiller/polymer composites could be a way of producing composites with low electrical conductivities for thermal interface applications.

Table 1. Electrical conductivities and Compressive properties of BN/VGCNF hybrid RE and VGCNF/RE composites.

Composite	***σ*** **(S.m^{-1})**	**Compressive modulus (at 20 % strain) MPa**	**Compressive strength at failure MPa**	**Compressive strain at failure (%)**
Pure RE (RE)	Insulating	7.91 ± 0.0095	2.26 ± 0.21	26.15 ± 1.74
2 wt.% (1.1 vol.%) BN/RE	Insulating	8.84 ± 0.07	4.85 ± 0.43	40.03 ± 2.07
6 wt.% (2.89 vol.%) BN/RE	Insulating	12.67 ± 0.75	6.04 ± 0.52	38.26 ± 0.61
8 wt.% (4.69 vol.%)VGCNF/RE	0.04 ± 0.001	10.93 ± 0.76	6.54 ± 0.09	42.21 ± 0.95
10 wt.% (5.92 vol.%)VGCNF/RE	0.078 ± 0.0005	11.59 ± 0.49	6.67 ± 1.71	40.74 ± 3.03
12 wt.% (7.22 vol.%)VGCNF/RE	0.147 ± 0.056	-	-	-
***14 wt.% (8.5 vol.%)VGCNF/RE**	0.17	-	-	-
***18 wt.% (11.1 vol.%)VGCNF/RE**	0.35	-	-	-
15 wt.% (9.15 vol.%) VGCNF/RE [23]	0.186 ± 0.04	14.47 ± 1.09	9.27 ± 2.01	44.72 ± 3.10
2 wt.% (1.1 vol. %) BN / 10 wt.% (5.2 vol.%) VGCNF/RE	0.031 ± 0.02	12.67 ± 0.82	6.05 ± 0.51	38.03 ± 0.65
6 wt.% (3.3 vol. %) BN / 8 wt.% (4.2 vol. %) VGCNF /RE	0.006 ± 0.001	13.24 ± 1.61	6.53 ± 2.14	38.84 ± 5.04
6 wt.% (3.4 vol. %) BN /12 wt.% (6.5 vol. %) VGCNF /RE	0.06 ± 0.002	15.13 ± 0.75	7.52 ± 0.59	39.48 ± 1.94
45 wt.% (30 vol. %) BN/RE	-	31.96 ± 1.32	18.29 ± 4.63	48.58 ± 7.27
Data represent an average of measurements on at least 3 specimens of each sample *Interpolated from an electrical conductivity vs. wt.% VGCNF plot in [23].				

3.4 Compression testing

The compression properties of BN/VGCNF/RE hybrid composites and of VGCNF/RE composites produced by roll milling are presented in Table 1 and Fig. 4.

It can be seen from Table 1 that inclusion of BN alone at 6 wt.% increases the compressive modulus, strength and strain to failure of RE composite by ~1.6×, 2.7× and 1.5×, respectively. Compared to 6 wt.% BN/RE composite, the modulus of 8 wt.% VGCNF/RE composite at 2 wt.% higher loading of VGCNFs decreased while the compressive strength and strain to failure increased slightly. This shows that BN can produce stiffer composites than VGCNFs at equivalent filler loading. The BN used in this study consists of micron sized particles, whereas VGCNF are nanosized fibres. Thus the interfacial area of BN with rubbery epoxy is lower than that of the VGCNF with rubbery epoxy. The lower interfacial contact area for the former means that BN particles can also develop some interconnects which could be much more extensive than those between VGCNFs due to their platelet morphology, as can be seen from Fig. 2. Thus, there would be less resin present between BN particles, thereby allowing more interaction between BN particles under compression. This increases the modulus of BN-based composites resulting in less compliance. On the other hand, the higher interfacial area between the fibres and resins, and greater dispersion of VGCNF on sub-microscopic level, allows fewer interconnects between the fibres. This allows deformation of rubbery epoxy before the stress transfers to the fibres, leading to lower modulus and more compliant composites. It can also be seen from Table 1 that addition of 6 wt.% BN into 8 wt.% VGCNF/RE composite increased the modulus by ~1.2× with no significant change in the compressive strength of the composite. The modulus of this hybrid composite is almost the same as that of 15 wt.% VGCNF/RE composite. In the case of 6 wt.% BN/12 wt.% VGCNF/RE composite, the compressive modulus is also similar to that of 15 wt.% VGCNF/RE composite. The data suggest that the combination of BN and VGCNF (at the loadings studied in this work) neither improves the mechanical properties of the hybrid composites nor deteriorates them.

The compression properties of 45 wt.% BN/RE composite are also presented in Table 1. It can be observed from Table 1 that 45 wt.% BN/RE composite has ~4.5× higher compressive modulus compared to the pure RE. On the other hand, VGCNF at 40 wt.% loading also produced a composite with only ~2.8× higher modulus than pure RE [23]. This comparison suggests that VGCNFs not only produce composites with comparable thermal conductivity to that of BN based composites at significantly lower loadings of filler but also produce more compliant composites than BN. It should also be noted that BN increases the compressive strength of RE by ~7× at maximum possible loading (45 wt.%) which is attributed to better dispersion of BN in RE by roll milling.

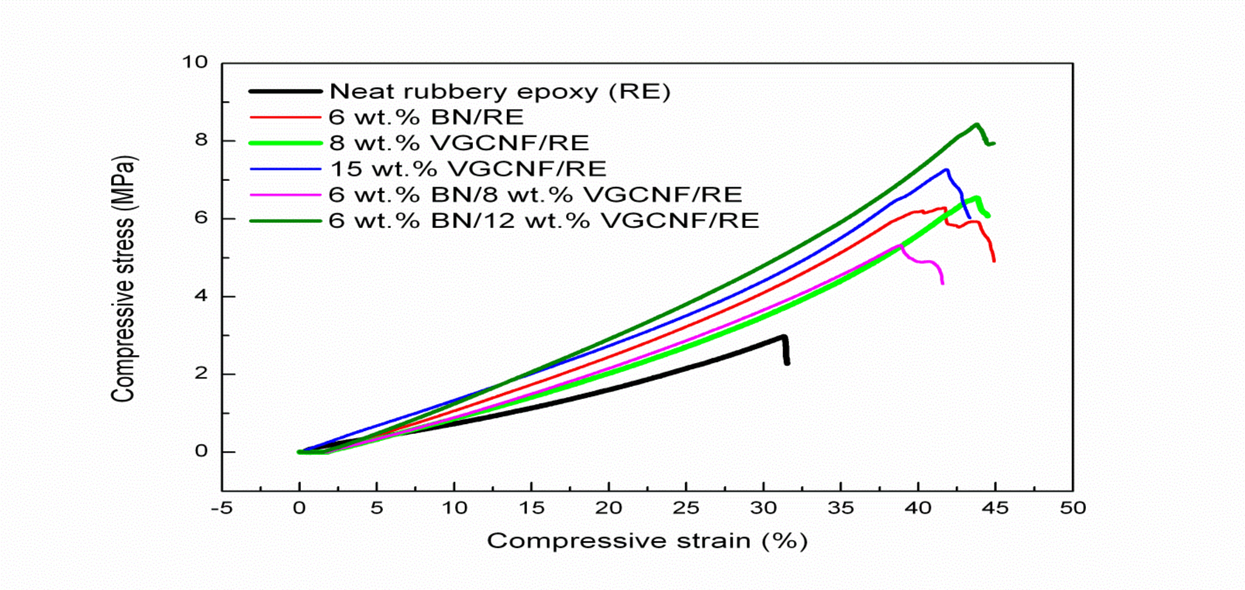

Fig. 4. Compression stress-strain curves of BN/rubbery epoxy, VGCNF/rubbery epoxy and their hybrid composites.

3.5 Thermal contact resistance

The total thermal contact resistance of hybrid composite (6 wt.% BN/8 wt.% VGCNF/RE) adhesive versus bond line thickness measured between smooth surfaces (Ra = 0.06 µm) at ~25 °C and 0.032 MPa compressive stress is presented in Fig. 5. The thermal contact resistance of 6 wt.% BN/12 wt.% VGCNF/RE composite ~~coating~~ at a bond line thickness of 22 µm measured is also presented in Fig. 5.

A very thin bond line of ~15 µm could be obtained with 6 wt.% BN/8 wt.% VGCNF/RE composite. The minimum bond line thickness increased to 22 µm with increase of VGCNF content from 8 to 12 wt.% when applied under the same conditions. The thermal conductivity of 6 wt.% BN/8 wt.% VGCNF/RE composite is 0.72 W/m.K according to the steady state method (Equation of linear fit, Fig. 5). This is 22 % higher than that measured by the hot disk method for the bulk composite.

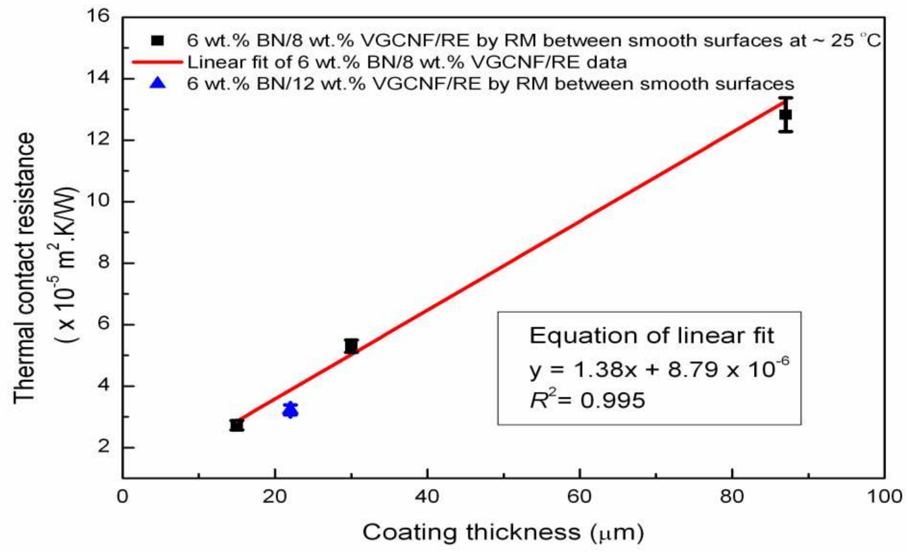

Fig. 5. Total thermal contact resistance vs. bond line thickness of 6 wt.% BN/ 8 wt.% VGCNF/RE (RE) and 6 wt.% BN/12 wt.% VGCNF/RE composite (produced by roll milling) measured between smooth copper surfaces (Ra= 0.06 µm) at 25 °C and 0.032 MPa compressive stress. Data and errors were obtained from at least 20 data points recorded under steady state conditions over 20-40 min.

In the case of 6 wt.% BN/8 wt.% VGCNF, the lowest thermal contact resistance of 2.72×10^{-5} m^2.K/W is obtained at 15 µm bond line thickness. The thermal contact resistance of 6 wt.% BN/12 wt.% VGCNF/RE composite is 3.22×10^{-5} m^2.K/W at a bond line thickness of 22 µm. This is estimated to be 1.2× lower than that of the 6 wt.% BN/8 wt.% VGCNF/RE composite at equivalent thickness (based on the equation of linear fit, Fig. 5). This suggests that the thermal contact resistance of a hybrid composite decreases with increase of VGCNF loading. Increasing the amount of VGCNF increases the thermal conductivity of the hybrid composite (Fig. 3) and so it appears that the higher thermal conductivity of 6 wt.% BN/12 wt.% VGCNF/RE hybrid composite contributes to reducing the thermal contact resistance of this composite cf. 6 wt.% BN/8 wt.% VGCNF/RE.

The thermal contact resistance of 6 wt.% BN/8 wt.% VGCNF/RE composite is 1.74× higher than that of the 15 wt.% VGCNF/RE composite at equivalent bond line thickness of 18 µm. This is attributed both to the former's lower thermal conductivity (0.72 W/m.K, cf. 1 W/m.K for the latter, according to the steady state method) and to its lower conformability. Even with its increased VGCNF content, the thermal contact resistance of 6 wt.% BN/12 wt.% VGCNF/RE composite is still 1.4× higher than that of the 15 wt.% VGCNF/RE composite. This again suggests that inclusion of BN in VGCNF-based composites deteriorates their performance as thermal interface adhesives and that the VGCNF-only composites can perform much better than hybrid composites. BN particles due to their large size (5-10 μm) have decreased conformability of VGCNF/RE composites resulting in increased thermal contact resistance of hybrid composite. The thermal contact resistance of 6 wt.% BN/8 wt.% VGCNF/RE composite does not change as a function of applied pressure as shown in Fig. 6 and this confirms that adhesives do not pump-out from interface like thermal pastes.

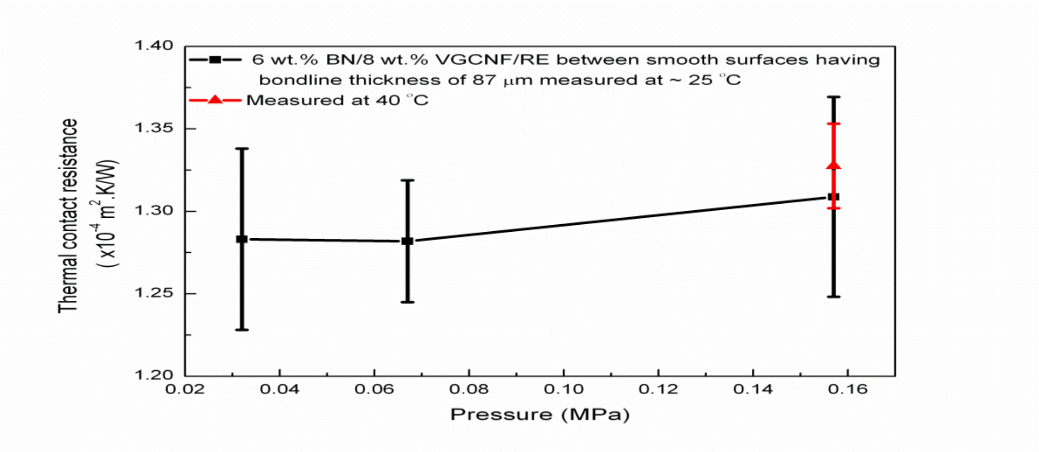

Fig. 6. Total thermal contact resistance of 6 wt.% BN/8wt.% VGCNF/RE measured between smooth surfaces as function of pressure.

The thermal contact resistance of 45 wt.% BN/RE composite as a thermal interface adhesive was studied between smooth copper surfaces. A bond line thickness of 20 µm was easily achieved by increasing the pressure on the coating before curing. The total thermal contact resistance of 45 wt.% BN/RE composite adhesive versus bond line thickness measured between the smooth surfaces (Ra = 0.06 µm) at ~25 °C and 0.032 MPa compressive stress is presented in Fig. 7.

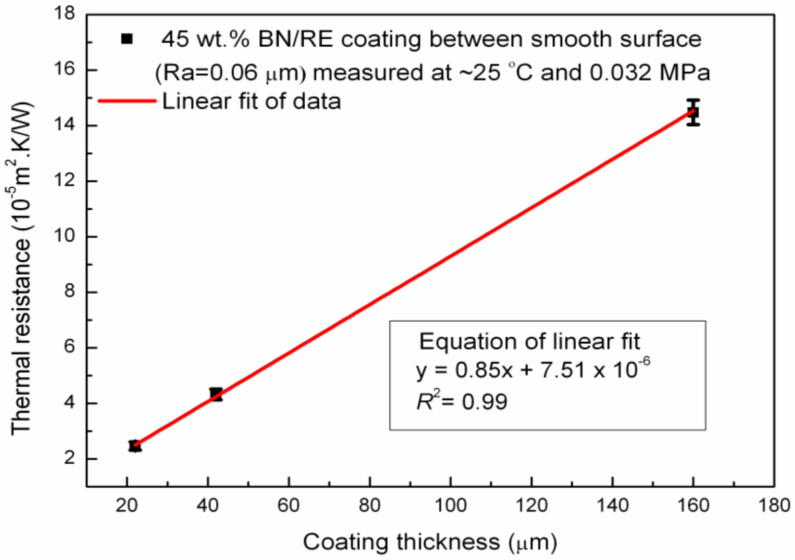

Fig. 7. Total thermal contact resistance versus bond line thickness of 45 wt.% BN/RE measured between smooth copper surfaces (Ra= 0.06 µm) at ~25 °C and 0.032 MPa compressive stress. Linear fit of data and equation of linear fit are also presented. Data and errors were obtained from at least 20 data points recorded under steady state conditions over 20-40 min.

The total thermal contact resistance of 45 wt.% BN/RE composite is 2.46×10^{-5} m^2.K/W at a ~22 µm bond line thickness between smooth surfaces. The thermal conductivity of 45 wt.% BN/RE according to the steady state method is 1.17 W/m.K, which is ~13 % lower than that measured by hot disk method. This drop in thermal conductivity as an adhesive might have occurred due to preferential orientation of BN particles parallel to the interfacial plane during curing between copper cylinders.

The comparison of the thermal contact resistance of 45 wt.% BN/RE composite with those of VGCNF/RE composites, thermal pastes and commercial TIMs is presented in Table 2.

Table. 2. Comparison of thermal contact resistance of 6 wt.% BN/8 wt.% VGCNF/RE hybrid composite and 45 wt.% BN/RE adhesive an with other VGCNF/RE and commercial TIMs measured on smooth surfaces under similar conditions (* data estimated from equations of linear fit).

Material	**Bond line thickness (µm)**	**Thermal contact resistance (m^2.K/W)**
Matrix II paste (Commercial TIM)	18	4.2×10^{-6}
*5 wt.% (2.4 vol.%) GNP-based paste [4]	18	4.4×10^{-5}
*5 wt.% (2.4 vol.%) GNP-based paste [4]	95	2.05×10^{-4}
*5 wt.% (2.4 vol.%) CB-based paste [4]	18	1.3×10^{-4}
*5 wt.% (2.4 vol.%) CB-based paste [4]	95	6.9×10^{-4}
6 wt.% BN/8 wt.% VGCNF/RE	18	3.36×10^{-5}
*15 wt.% VGCNF/RE	18	1.93×10^{-5}
*45 wt.% BN/RE composite	18	2.28×10^{-5}
*45 wt.% BN/RE composite	95	8.82×10^{-5}
6 wt.% BN/8 wt.% VGCNF/RE	95	1.40×10^{-4}
65 wt.% BN/silicone (EPM 2490)	95	1.36×10^{-4}

The 45 wt.% BN/RE composite has 1.18× higher thermal contact resistance than 15 wt.% VGCNF/RE composite (for thin bond lines) suggesting better interfacial thermal conductance for the latter. These results clearly demonstrate that VGCNF are real competitors to the commercial BN filler and are potential candidates for producing higher performance TIMs.

The performance of BN/RE composites was also compared with that of commercial thermal paste, Matrix II (also known as Quantum), which is marketed by TIM consultants. This paste consists of a silicone matrix in which three fillers: aluminium, aluminium oxide and zinc oxide are dispersed. BN/RE composites are unable to outperform the commercial thermal paste, Matrix II. The thermal contact resistance of BN/RE composite is ~5.4× higher than that of Matrix II paste at equivalent bond line thickness (Table 2). However, BN/RE's performance is better than the commercial BN/silicone adhesive, EPM 2490, because the latter has 5.96× higher thermal contact resistance at an equivalent bond line thickness of 95 µm (Table 2). This improved interfacial thermal conductance of BN/RE composite compared to BN/silicone composite, despite their similar fillers, is attributed to the stronger bonding of the RE composite to the copper cf. the silicone based composite. This shows that the bonding ability (adhesiveness) of the matrix also plays an important role in improving the thermal performance of thermal interface adhesives. The thermal contact resistance of 6 wt.% BN/8 wt.% VGCNF/RE composite as adhesive for bond line thicknesses of 18 and 95 μm is also presented in Table 2 for comparison. Like VGCNF/RE composites and BN/RE composites, this hybrid composite adhesive does not outperform Matrix II paste but, with the benefits of an adhesive, it has comparable thermal contact resistance to that of commercial silicone adhesive (EPM 2490) at only just over one fifth of the filler loading of the latter. This demonstrates that hybrid combination of fillers can be beneficial in improving thermal interfacial contact with substrates.

The thermal contact resistances of graphite nanoplatelet (GNP)-based and carbon black (CB)-based pastes reported by Lin et al. [4] are also presented in Table 2. These authors reported very low thermal contact resistance for these pastes on both smooth and rough surfaces. For example, the thermal contact resistance of 5 wt.% GNP-based paste measured under a pressure of 0.46 MPa between smooth surfaces was ~ 4×10^{-6} m^2.K/W but was obtained at bond line thickness of 0.2 μm. However, thermal contact resistances of these pastes for thick bond lines under no loading condition are much higher as shown in Table 2. The thermal contact resistance of our hybrid 6 wt.% BN/8 wt.% VGCNF/RE composite adhesives is 23 % and 31 % lower than that of 5 wt.% GNP-based paste at bond line thicknesses of 18 and 95 μm, respectively. Similarly, CB-paste had much higher thermal contact resistances than our hybrid composites for thick bond lines. The results show that hybrid composites produced in this study can perform better for thick bond lines since these require high thermal conductivity from the TIM and, with the additional benefit of bonding the mating surfaces, can give longer-term performance.

4. Conclusions

Hybrid composites of BN/VGCNF/RE were developed by 3-roll milling. SEM analysis showed that both BN and VGCNF were uniformly dispersed in the matrix. The combined usage of two fillers promoted better dispersion of one another in the matrix. BN/VGCNF/RE hybrid composites have lower thermal conductivity than the non-hybrid VGCNF/RE at the equivalent total filler loading. The BN inclusions act as resistance in the conducting networks of VGCNFs and reduce the efficiency of the conducting networks as inferred from SEM analysis. Such disruption in the conducting networks reduced the electrical conductivity of the hybrid composites significantly and this could be advantageous for thermal interface applications. The thermal conductivity of the hybrid composites increased with increasing VGCNF content whereas electrical conductivity decreased with increasing BN content. Compression testing of the composites showed that BN produced stiffer composites than those produced with VGCNFs at equivalent loading. The interfacial thermal conductance of BN/VGCNF/RE composites as thermal interface adhesives improved with increase of VGCNF content. However, the addition of BN into RE reduced the conformability of the hybrid composite as adhesive. The thermal contact resistance measurements showed that addition of micron-sized BN is not beneficial for improving the interfacial thermal conductance of VGCNF/RE composites. Nevertheless, the BN/VGCNF/RE hybrid composites offered similar thermal contact resistance as that of commercial TIM adhesive at equivalent bond line thickness and lower thermal contact resistance than GNP-based thermal pastes at thick bond lines suggesting their suitability for thick gap filling applications and with additional advantage of bonding the mating surface can overcome pump-out issues of thermal pastes ensuring mechanical integrity of electronic package.

Acknowledgements

The authors would like to thank EPSRC and Morgan Advanced Materials for sponsoring M.A.Raza's PhD studies. Thanks are also due to Mr. Robert Simpson and Dr. Richard Foster for their help with microscopy and XRD, respectively.

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