GRAPHITE NANOPLATELET/SILICONE COMPOSITES FOR THERMAL INTERFACE APPLICATIONS

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I. Introduction

Thermal interface materials (TIMs) play a key role in dissipating the heat generated in microprocessors and electronics. Current TIMs include thermal greases/pastes, solders, phase change materials and filled polymer matrices (polymer composites) [1, 2].

Graphite nanoplatelets (GNP) are an emerging class of nanomaterials which are becoming attractive for use in TIMs due to their high thermal conductivity. GNP are composed of one or more layers of graphene with a platelet thickness in the range of 0.3-100 nm and a very high aspect ratio [3]. The in-plane thermal conductivity of a single layer graphene sheet has been estimated to be up to 5300 W/m.K, as compared to 2900 W/m.K for single wall carbon nanotubes [3-5].

This paper presents the results of a study on composite materials that have been developed by dispersing GNPs into a silicone (polydimethysiloxane) matrix for TIM applications. The properties of GNP/silicone composites are also compared with a commercial silicone based adhesive TIM, EPM 2490 (Nusil Silicone Technology), filled with 65 wt.% BN particles.

II. Experimental – Composite Fabrication

GNP (XG Sciences Ltd.) with an average particle size of 5 μm (GNP-5) or 15 μm (GNP-15) and thickness of 20-200 nm were used in this study. Sylgard 184 silicone elastomer (Dow Corning) was employed as the silicone matrix material. GNP/silicone composites were prepared with 2-25 wt.% loading of GNP using a Speed Mixer (SM) (model DAC 150 FVZ-K), mixing via dual asymmetric centrifuge action at 3540 rpm for 10 min. The GNP/silicone mixture was degassed under vacuum, poured into a custom-made aluminum mould and further degassed for 15 min. The neat silicone and GNP/silicone dispersions were cured at 100°C for 1 hr.

III. Experimental – Characterisation

The composites were characterised for their curing behaviour (Perkin Elmer DSC7), morphology (FEG-SEM), thermal conductivity (Hot Disk® thermal constant analyser), electrical conductivity (2-probe method), compression (Hounsfield tensometer) and hardness properties (Shore hardness tester using scale A, Zwick).

IV. Results and Discussion

The DSC scans of neat silicone and GNP-5/silicone containing 20 wt.% of GNP are presented in Fig. 1. The DSC results showed that GNP addition into silicone increased the curing temperature of silicone from 92°C to 116°C. The higher exotherm temperature and the lower heat of curing upon reaction suggest that the GNP retarded the silicone curing reaction. This may be due to hindering of polymer chain mobility by GNP [6].

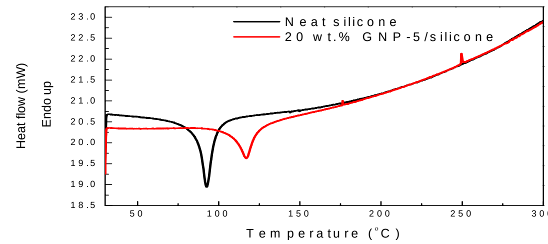
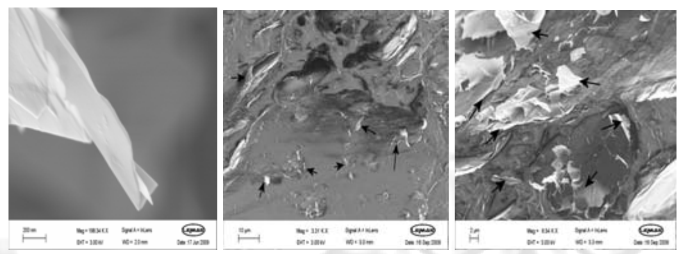


Fig. 1. DSC scans of neat silicone and GNP/silicone dispersion

SEM micrographs of 20 wt.% GNP-5/silicone and 20 wt.% GNP-15/silicone composites are shown in Fig. 2. The thickness of GNP is between 40-200 nm. It can also be seen



(a) (b) (c)

Fig. 2. SEM images of (a) GNP, (b) 20 wt.% GNP-5/silicone and (c) 20 wt.% GNP-15/silicone composites produced by SM (arrows pointing towards some of the GNP in the silicone matrix)

from Fig. 2 that the GNPs are randomly oriented in the silicone at 20 wt.% loading to form an isotropic composite. In the case of GNP-15/silicone composite (Fig. 2c), it appears that, whilst uniform dispersion of the GNP in the silicone has been achieved, an extensive network of interconnects has formed, due to the larger size of the GNP-15 particles, as is required for the formation of effective conduction networks.

The thermal conductivities of neat silicone and GNP/silicone composites as a function of GNP loading measured at 20°C are presented in Fig. 3. It can be observed from Fig. 3 that the thermal conductivity of the GNP/silicone composites increases with the increase of both the wt.% of GNP and the particle size of GNP. Thermal conductivity increases to a maximum of 1.417 W/m.K for GNP-15/silicone composite at 20 wt.% filler concentration. This represents a 7-fold increase compared to neat silicone. The higher thermal conductivity of 20 wt.% GNP-15/silicone composite compared to the 20 wt.% GNP-5/silicone composite is attributed to the effect of the increased GNP particle size which results in efficient conducting networks. The thermal conductivity of EPM 2490 is 1.46 W/m.K (quoted by the manufacturer as determined according to ASTM C177). Thus, the GNP/silicone composite achieved this comparable thermal conductivity at 45% lower loading of filler than in the EPM 2490.

Although the GNPs themselves are highly electrically conducting fillers, the GNP-15/silicone and GNP-5/silicone composites produced by SM are electrically insulating up to loading of 15 and 20 wt.%, respectively.

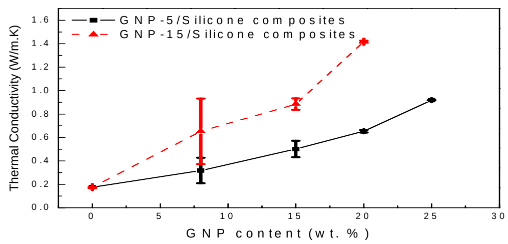


Fig. 3. Thermal conductivity of GNP/silicone composites produced by SM as a function of wt.% of GNP

The electrical conductivities of GNP-15/silicone at 20 wt.% and GNP-5/silicone composites at 25 wt.% loadings are 1.7 x 10^{-4} $S.m^{-1}$ and 5.1 x 10^{-4} $S.m^{-1}$ respectively. However, it was observed that under very low applied pressure (~ 0.6 MPa) these composites also become highly electrically insulating. Thus the low electrical conductivity of silicone (8.3 x 10^{-15} $S.cm^{-1}$) plays a key role in making these composites electrically insulating. As the GNP/silicone composite samples did not become electrically conducting upon compression, this suggests that the GNP particles are enveloped with a layer of silicone that prevents the particles from touching each other to form electrically conducting networks, even under compression.

The compression stress-strain curves of neat silicone, GNP/silicone composites and EPM 2490 are presented in Fig. 4 for two replicates (samples 1 and 2) of each material. It can be observed from Fig. 4 that the portions of the GNP/silicone composite stress-strain curves below 50% strain are almost identical to that of the neat silicone.

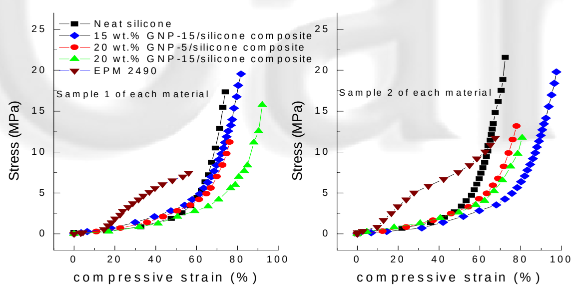


Fig. 4. Two replicate compressive stress-strain curve sets for neat silicone, EPM2490, GNP-5/silicone and GNP-15/silicone composites

This indicates that GNP addition into the silicone does not significantly detract from its elastomeric nature. These materials have very low stiffness. The compressive modulus of neat silicone and the GNP/silicone composites (at a compressive strain of 40 %) was found to be just 4-5 MPa in each case. This unexpected compression behavior of GNP/silicone composite is attributed to the extremely homogenous dispersion of GNP into the silicone matrix, which resulted in the wrapping of GNP particles with silicone, as shown in Fig. 2. On the other hand, after initially similar behaviour up to ca. 10% strain, the EPM 2490 has significantly higher compressive modulus (up to 40-60 % strain) than the GNP/silicone composites. High conformability, as observed for the GNP/silicone composites, is an important requirement for thermal interface materials used in gap filling applications. The Shore hardness of neat silicone and GNP/silicone composites is presented in table 1.

Table 1. Shore Hardness of neat silicone and GNP/silicone composites

Material	Shore Hardness (Scale A)	Standard deviation
Neat silicone	53.06	1.0237
20 wt.% GNP-5/silicone	49.8	1.2909
15 wt.% GNP-15/silicone	57.02	1.4328
20 wt.% GNP-15/silicone	54.6	1.160
EPM 2490	81.2	2.1447

In the case of the GNP-5/silicone composite, the hardness decreased by 6 % compared with neat silicone while in case of GNP-15/silicone it increased by 3-7 %, although no clearly explicable trends emerged. However, compared with the most highly thermally conducting GNP composite, i.e. 20 wt.% GNP-15/silicone, the Shore hardness of the EPM 2490 benchmark material is, undesirably in the context of TIMs, ~ 49 % higher.

V. Conclusions

The thermal conductivity of GNP/silicone increases with increase of GNP wt.% and particle size. The room temperature thermal conductivities of the 20 wt.% GNP-5/silicone and 20 wt.% GNP-15 silicone composites are 0.653 W/m.K and 1.412 W/m.K, respectively, compared to 0.175 W/m.K for neat silicone. GNP retards the curing of silicone, possibly by acting as a physical hindrance to the free movement of the silicone chains. The GNP/silicone composites are highly electrically insulating. It appears that the nature of the matrix contributes significantly to electrical transport. Compression and hardness testing of GNP/silicone composites showed that GNP addition neither increased the compressive strength nor reduced the compliance, cf. silicone. The GNP/silicone composites, with their high thermal conductivity, high electrical resistivity and high conformability, are promising candidates for thermal interface materials in the form of either TIM adhesives or thermal pads.

Acknowledgements

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