

THERMAL CONDUCTIVITY OF GNP/EPOXY NANOCOMPOSITES AND THEIR APPLICATION AS THERMAL INTERFACE MATERIALS

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Abstract

Graphene is known to have a high thermal conductivity around 5000 W/mK and its combination with an epoxy matrix results in a potential material applicable in heat dissipation due to the adherence provided by the polymer.

Thermal properties of different GNP nanocomposites are evaluated as well as wettability. By adding just a 1 wt% to the polymer matrix, thermal diffusivity is amplified a 23.42% reaching near a 210% of enhancement with an 8 wt%. Additionally, wettability of different employed substrates considerable increases with the GNP incorporation.

1. Introduction

Continuous advances in microelectronic and high performance devices require new high thermal conductive materials to assure enough heat dissipation. Microprocessors constitute an example of this continuous evolution. Thermal interface materials (TIMs) are used in order to create a thermally conductive path between the chip and the heat spreader and also between the heat spreader and the sink. Another important field is photovoltaic solar cells where the generated heat can degrade the performance and cause damage to the cell. Some studies identify an efficiency lost of a 0.5% per each 1°C of temperature increase [1]. Commercially TIMs have a thermal resistance on the order of 0.5 cm²K/W [2].

Contact thermal resistance is a critical factor that can induce heat concentration in the component blocking the heat transfer. The contact thermal resistance between two solid surfaces is usually high due to the high surface roughness, i.e. the contact thermal resistance between silicon and copper varied in the range of 120-200 mm²K/W [3]. For that reason TIMs need to assure conformability to a solid surface. An option to enhance this conformability is to increase the wettability of the TIM on the surface of the joined components achieving a better thermal contact.

Graphene is a 2D material of sp²-hybridized C atoms forming a monoatomic layer with a hexagonal honeycomb structure. This structure is responsible of the peculiar physical properties presented. Graphene is known to have a high thermal conductivity, of around 5000 W/mK, and its combination with an epoxy matrix results in a potential material applicable in heat dissipation due to the adherence provided by the polymer.

Graphene nanoplatelets (GNPs) consist on a limited number of graphene layers bonded by van der Waals forces with a thickness minor to a 100 nm [4]. Those are an alternative to the expensive graphene monolayer and present the advantage of the capability to be produce in relative large scale so it can be implemented in mass production.

2. Materials and methods

2.1. Materials

Precursor of the epoxy resin was a basic DGBEA monomer (*Araldite LY556*) cured with an aromatic amine (*Araldite XB3473*), both purchased to *Uneco*. GNPs of different morphology, provided by *XGScience*, were used in the study: grade M25, with an average thickness of 6 nm and an average lateral size of 25 μm .

Aluminum 2024 and copper substrates were purchased to *Fundiciones Gomez S.A.*

2.2. Methods

Different GNPs contents were dispersed into the resin by a two step method. First, nanoplatelets were dispersed using sonication probe for 45 minutes by applying a cycle of 0.5 s and a 50% of intensity. The second step was three-cycles of calendaring what provokes an extension of the platelets that tends to wrinkle.

Once the GNPs were dispersed through the monomer, a degassing process under vacuum was applied at 80°C for 15 minutes to assure the elimination of possible dissolved gasses. After the degassing process was completed hardened was added in stoichiometric ratios, i.e. a weight ratio of 100:23 (monomer: hardener).

The mixture was cured into a plate of 35 x 12 x 1.5 mm³ and the machined to obtain desired samples for the analysis. The rest of the mixture was used as adhesive for copper and aluminum substrates as they are common in the industry where TIMs are employed. Samples were cured at 140°C for 8 hours. Obtained contents are 1, 2, 3, 5 and 8 wt% for M25 based nanocomposites.

Microstructural analysis was carried by optical microscopy with a *Leica/DMR* microscope in order to evaluate the dispersion of particles. In addition, scanning electron microscopy (SEM) images were obtained in order to evaluate the lateral thickness and as-received GNPs in a *Hitachi S-2400N*.

Thermal diffusivity was measured in a *Laserflash LFA 457 Microflash* equipment, in a temperature range of 20-200°C. Samples with a diameter of 12 mm and a thickness of 2.5 mm were analyzed.

DMTA was performed as the standard *D5418-01* indicates, in a dual cantilever bending mode. Measurements were carried by using a *DMTA Q800 V7.1* from *TA Instruments*. All the experiments were carried at 1 Hz of frequency from 20 to 250°C with a heating rate of 2°C/min. The samples dimensions were 35 x 12 x 1.5 mm³. In order to evaluate the glass transition temperature, the maximum of $\tan \delta$ vs. temperature was examined.

3. Results

Due to the importance of the GNPs dispersion through the polymer matrix, it is necessary to assure that a good dispersion is achieved without the appearance of agglomerates that could cause a detriment of the properties.

The disposition of the GNPs once the nanocomposite is cured, is important as the waviness of the sheets has a strongly influence on thermal properties as the mechanism is based on phonons through the sp^2 atomic plane. Previous studies have demonstrated that the optimized two-step method permits to obtain unwrinkled GNPs achieving that way enhanced thermal properties [5].

Figure 1a shows a representative optical micrograph showing the dispersion of the GNPs through the nanocomposites. It can be seen that no agglomerates are formed and particles are homogenously distributed along the matrix. It is important to note that the manufacturing method used do not apparently change the lateral size of the particles either the thickness. The fact has been corroborated by the SEM study of as-received GNPs and dispersed ones. Figure 1b presents a SEM image of as-received GNPs before being dispersed into the resin.

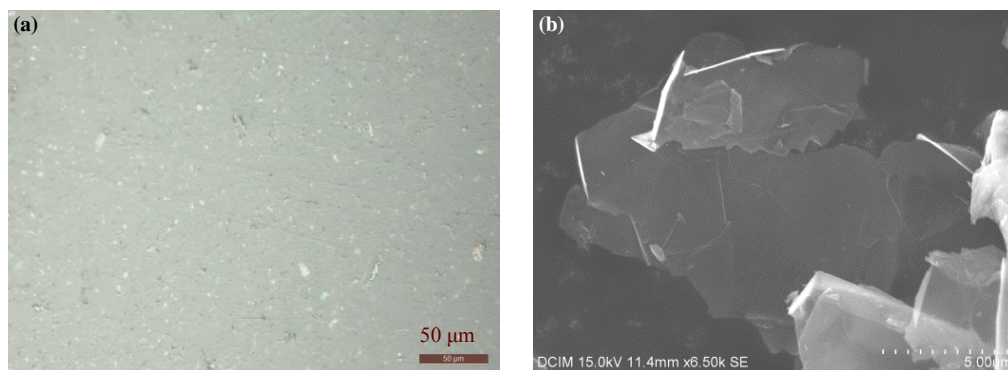


Figure 1. Optical micrograph of a 3 wt% GNPs nanocomposite and SEM image of as-received GNPs.

The first point to analyze for a TIM is the thermal diffusivity as a high value is needed. Obtained values, at 28°C and 138°C, are plotted in Figure 2. Neat epoxy has a thermal diffusivity of $0.111 \pm 0.005 \text{ mm}^2/\text{s}$ at 28°C. By adding a 1 wt% GNPs, an augment of more than a 30% is achieved. For higher contents, the reached enhancement can be increased to a 208% when an 8 wt% GNPs is added. The thermal diffusivity at 138 °C diminishes a maximum of a 24.5% when an 8 wt% GNPs is used and is minor for a 3 wt% (20.1%). Those contents are considerably minor to that used by R. J. Warzoha *et al.* (54 wt%) employing the same GNPs [6].

Those diffusivity values mean thermal conductivities of around 0.7 W/mK for nanocomposites reinforced with an 8 wt% GNPs. Some of the TIMs used in the automotive electronic control unit adhesives doped with aluminum particles, fiber glass and polyamides present values of thermal conductivity in the range of 0.4-2 w/mK [7].

Xiaojuan Tian *et al.* has published thermal conductivities of graphite nanoplatelet-based composites for their application as TIMs showing values in the range of 0.5–0.9 W/mK for GNPs loading between 11 and 14 wt% [8]. Those conductivities are inferior to that obtained in the present work employing less GNPs reinforcement loads.

Zhou *et al.* has published a thermal conductivity of 0.6 W/mK for a 10 wt% GNPs reinforced nanocomposite [9], what means that the obtained value presents a conductivity near a 11.5% higher by adding less quantity of GNPs. This is possibly due to facts like the lateral size of the particles as it is going to define the sp^2 domain size and how nanoplatelets are located into the cured epoxy modifying the waviness into the sp^2 plane, as it has been mentioned before.

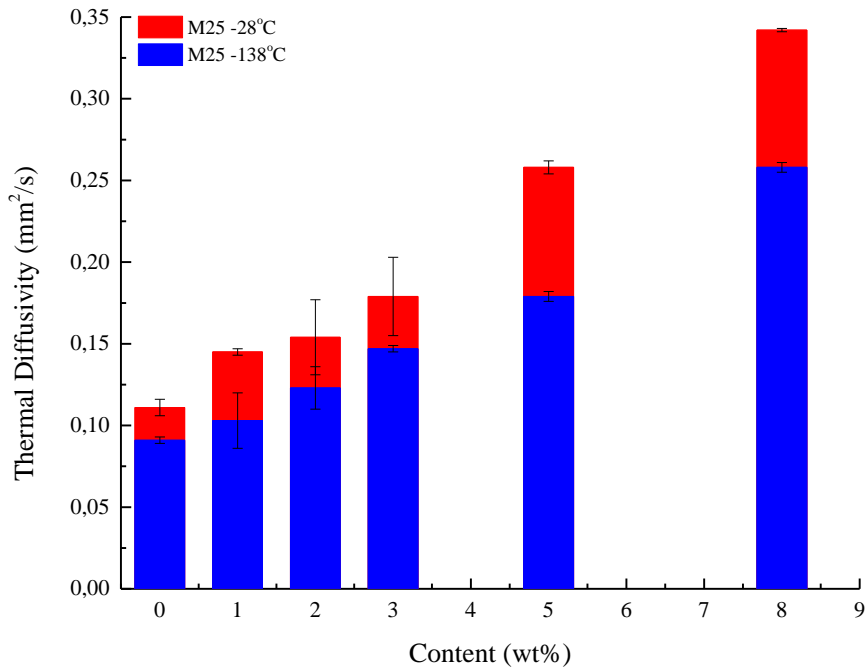


Figure 2. Thermal diffusivity of neat epoxy and GNPs reinforced nanocomposites.

Materials for TIMs are thought to work at high temperature, for this reason it is important to determine the maximum service temperature that assures the correct performance of the adhesive. For this purpose, glass transition temperature is calculated from DMTA test by the maximum at the $\tan \delta$ curve. Those values are presented in Table 1. As it can be extracted, the glass transition temperature is around 170 °C in all cases. That means that above 170 °C a loss in rigidity is produced so it could damage the device performance, constituting the maximum temperature at which those GNPs/epoxy nanocomposites can work.

Specimen	Tg [°C]
Neat epoxy	170.37
1 wt% GNPs	169,8
2 wt% GNPs	172,5
3 wt% GNPs	171,5
5 wt% GNPs	171.8
8 wt% GNPs	171,3

Table 1. Glass transition temperature GNP/epoxy nanocomposites.

Contact angles on the aluminum and copper surfaces of the GNP-monomer mixture were measured, as wettability is another important factor that is going to determine the device behavior. TIMs needs to wet the surface in order to achieve a good interface and consequently the less thermal contact resistance [10]. A diminution in the contact angle on aluminum alloys is not achieved ($\sim 42^\circ$). An increment is experimented when using a nanocomposite reinforced with an 8 wt% due to an augment in the viscosity. This could be avoided by heating the mixture before the application. When copper substrates are used an average of $\sim 40^\circ$ is obtained and it is independent on the GNPs content used. This fact could be due to the low surface energy of pristine graphene (46.7 mJ/m^2 at room temperature) [11].

An important issue, that also influences the performance of TIMs, is the water absorbance as it can cause short-circuit when TIMs are used in electronic devices. The water absorbance can be reduced by achieving more hydrophobic surfaces.

Figure 3 shows obtained water drops on the nanocomposites surfaces. The contact angle on the neat epoxy is 69.81° . By adding only a 1 wt% GNPs the contact angle is increased to 103.5° , what means an increment of a 33.69%. Xingcheng Xiao *et al.* attribute this hydrophobic behavior to the topography of the sample producing a similar effect to that of the lotus surface [12]. Surfaces with distributed microparticles induced hydrophobicity to the surface [13]. In obtained nanocomposites the surface is constitute of GNPs dispersed through the matrix changing the topography. Additionally, as it has been mentioned before, the low surface energy of graphene brings hydrophobic properties to the surface. Other authors has corroborated this effect in graphene-based nanocomposites reaching contact angles as high as 162° when graphene oxide is used as reinforcement [14].

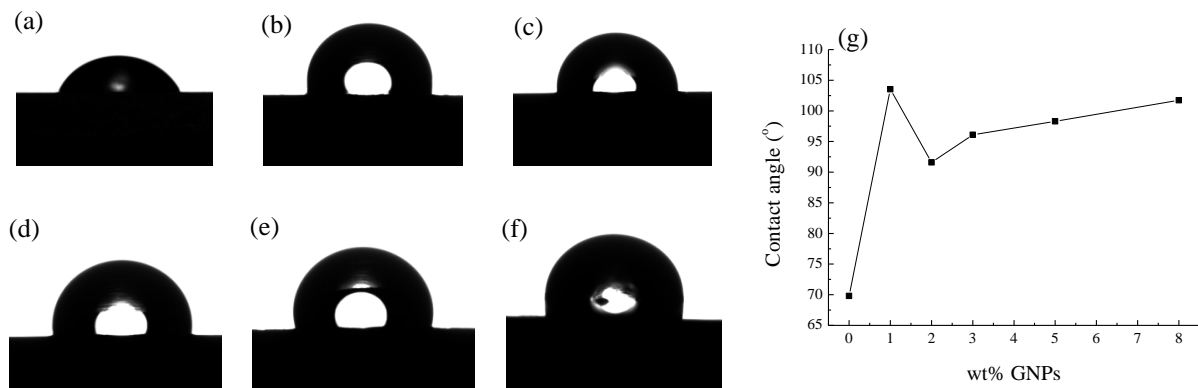


Figure 3. Drops from water-nanocomposite wettability study of (a) neat epoxy, (b) 1, (c) 2, (d) 3, (e) 5 and (f) 8 wt% GNPs; and (g) contact angle variation as a function of the GNPs content.

4. Conclusions

Discussed results make possible to conclude that GNP/epoxy nanocomposites are potential to be used as TIM in numerous applications. For higher contents, the reached enhancement in thermal diffusivity can be increased up to a 208% when an 8 wt% GNPs is added. GNPs/epoxy nanocomposites present thermal conductivities even higher than the implemented ones, presenting the advantage of having less density if comparing with reinforcements used in the industry as silver and carbides. That means that the weight of the

system is slightly incremented and those can be used in applications where weight restrictions are strict.

Additionally, reinforcement loads (< 8 wt% GNPs) are considerably minor compared to that of other TIMs (~20-50 wt%). This permits to achieve better wettability on the surfaces of the devices where they need to be applied assuring, that way, a better thermal contact between components and so a better heat transfer.

Finally, obtained nanocomposites have shown to present a high water contact angle (103.5°) making the surface hydrophobic. A hydrophobic surface can prevent fails in the device as short-circuits can be induced. This effect is due to a lotus surface phenomena where the distribution of GNPs through the surface plays a fundamental role combined with the low surface energy inherent to graphene.

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