

GRAPHENE AND ITS APPLICATION IN POLYMER COMPOSITES

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Abstract

This paper looks at the development of graphene/polymer nanocomposites to be used as adhesives for Thermal Interface Materials (TIMs) and lightweight high performance CFRP composite laminates with conductive properties. The addition of graphene, even at a very low concentration level (usually less than 5%), into a polymeric matrix can significantly improve its thermal conductivity. The achievement of a good dispersion of graphene and the interfacial bonding of graphene and the polymer matrix is a key aspect. Different qualities of graphene material have been characterised and tested to obtain good dispersion in the polymer matrixes tested. High improvements in the thermal conductivity for both applications under study have been achieved.

1. Introduction

Polymers have usually a very limited thermal conductivity. There are many reasons to increase thermal conductivity of polymer based materials in various industrial applications including lightweight aerospace structures, electronic packaging and thermal interface materials (TIMs).

Graphene is emerging as a promising nanomaterial for polymer composites applications because of its unique combination of very high strength and stiffness, and excellent electrical and thermal conductivities. Graphene is an extraordinary good heat conductor, measurements revealed that graphene's near room temperature thermal conductivity is in the range from 3500-5300 W/mK [1]. Polymer matrices reinforced with graphene platelets present higher thermal conductivities at lower loading when comparing with currently used conventional thermally filler materials [2]. High filler loading alters the polymer mechanical behavior and density for these reasons obtaining good thermal conductive polymers and usual polymer processability is very challenging at present.

This study has been focused on the improvement of the thermal conductivity of polymer systems by the addition of graphene in different resins. The preparation, characterization and properties of graphene based nanocomposites are discussed in this article.

This paper presents the work carried out to integrate graphene in epoxy and cyanate resins to obtain composite laminates with enhanced mechanical and thermal performance in structures for space applications and thermally conductive adhesives for applications as TIM (Thermal

Interphase Materials). For the first application, micro and nano Boron Nitride has also been selected for comparison.

2. Experimental

2.1. Materials

Graphite nanoplates (references GR122, SG8 and GR13) were obtained from Avanzare (Spain); Graphene oxide (GO) and reduced graphene oxide (rGO) were obtained from Graphenea (Spain); nanoBN (BN nanopowder) was obtained from Plasmachem (Germany) and microBN (S12) from ES K Ceramics (Germany). YS80 pitch based carbon fibers were obtained from Nippon Graphite Fiber Corp. (Japan). LTM123R which is part of LTM123 cyanate ester resin was obtained from Cytec (UK). Eccobond 55-catalyst 11 (Henkel) was used as the reference epoxy adhesive system. All other reagents and solvents were purchased from commercial suppliers and used as received.

	nanoBN (Plasmachem)	microBN (S12- ESK)	Graphite nanoplates Avanzare
Particle morphology	Nanopowder cubic	Hexagonal Boron Nitride	Plates
Particle size	165±15nm (Average)	3-36µm	2 x5 µm less than 10nm in thickness
Thermal conductivity	>300 W/mK	>300 W/mK	>400 W/mK
Density	2.2 g/cm ³	2.2 g/cm ³	1.7-1.9 g/cm ³

Table 1. Characteristics of the different fillers used in the cyanate ester resin

2.2. Dispersion of graphene in the resins

2.2.1 Dispersion in cyanate based prepreg resin

LTM123R part of LTM123 cyanate ester resin was selected as the base material to be modified. The dispersion of nanofillers was carried out by a high shear mixer, (Dispermat CA 60 VMA-Dispermat). The selected fillers were added gradually to a fixed amount of cyanate ester resin up to its maximum acceptable load. The agitation was maintained during 20 minutes at the appropriate rate (10.000-15.000 m/s). Several doped preblends were prepared with graphene percentages ranging 7-18%wt, microBN and nanoBN.

The doped preblends were mixed with other ingredients to form fully formulated resin systems- LTM123+filler. Neat resin plaques were manufactured for thermal conductivity measurements. All the samples present a minimum size of 60 x 60mm and a minimum thickness of 2mm.

2.2.2 Epoxy based adhesive nanocomposites

Firstly, the study of the dispersion and the stability of GO and rGO in different solvents and in the epoxy part of the adhesive Eccobond 55, was carried out. For that purpose, 1 mg/ml of GO and rGO were sonicated for 15 minutes in the following solvents: N,N-

dimethylformamide (DMF), acetone, tetrahydrofuran (THF) and distilled water. For both graphene qualities, the most stable dispersions were obtained in acetone and DMF.

Finally, acetone was selected for preparing the epoxy-based nanocomposites as it was also compatible with the epoxy part of the adhesive Eccobond 55. Different percentages of GO or rGO powder were dispersed in acetone and then sonicated for 40 min in an ice bath to form a uniform suspension. Then, the epoxy part was added and the mixture was sonicated for another 40 min. The acetone solvent was evaporated afterwards by heating the mixture for 15h at 50°C. Then the curing agent, catalyst 11 was added and the resulting mixture was placed under vacuum for another 15 min. Finally, the mixture was cast into a metal mould and cured at 80°C for 16 h.

3. Characterization of nanocomposites

3.1. Characterization of nanofillers: Graphene Microstructural analysis

Scanning Electron Microscopy (SEM) experiments were carried out in a SEM JEOL JSM-5910-LV.

Figure 1 shows the morphology of graphene grades GR122 (a) and GR13 (b).

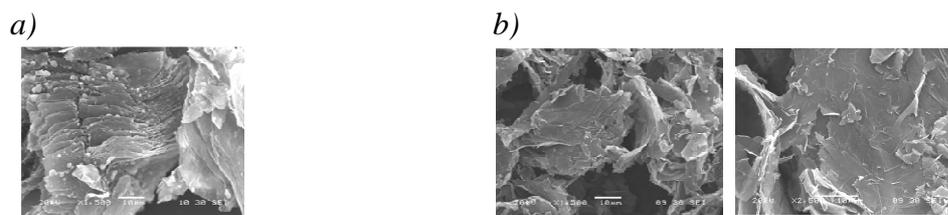


Figure 1. SEM images of graphite nanoplatelets as received from Avanzare a) GR122 and b) GR13.

Figure 2 corresponds to the SEM images of the morphology of graphene oxide (GO) and reduced graphene oxide (rGO).

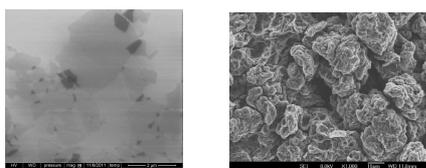


Figure 2. SEM images of Left: Graphene Oxide GO and right: reduced graphene oxide rGO, right.(courtesy of Graphenea)

3.2. Characterization of polymer composites

3.2.1 Cyanate based nanocomposites

3.2.1.1 Rheology analysis

Rheology measurements were performed using a Bohlin CVO50 NF Rheometer. Dynamic viscosity profiles were obtained in the temperature range 25 °C-200 °C at a heating rate of 2 °C/min for selected formulations.

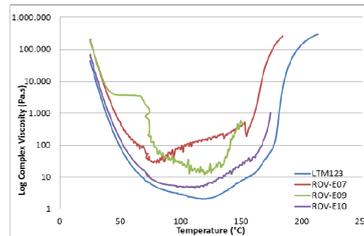


Figure 3. Dynamic viscosity profile for doped preblends (blue: neat resin; red: graphene 122; red: nanoBN; purple: microBN)

It can be seen from figure that all of the filled resin system investigated had higher viscosities than the baseline LTM123. It can also be seen that the fillers had an impact on the reliability of the viscosity curves, introducing significant noise in the traces, this could be related to shear thinning or shear thickening effects resulting from the fillers.

The results showed that the minimum viscosity was increased with the addition of the fillers. In some cases, noisy viscosity profiles were obtained due to the existence of some large particles; this indicates that improvements can still be made in dispersing the fillers into the resin matrix.

3.2.1.2 Thermal Conductivity

This property was determined by Hot Disk Thermal Constants Analyser TPS 2500 S.

Reference	Filler load (%wt)	Thermal Conductivity (W/Km)	Improvement (%)
LTM123	0	0.2	
LTM 123R + nanoBN	26.2	0.4	100
LTM 123R + microBN	12.6	0.5	150
LTM 123R+SG8	14	0.4	100
LTM 123R + GR122	5.5	0.5	150
LTM 123R + GR122	14	1	400

Table 2. Thermal conductivity values for different fillers reinforced cyanate ester resin.

From table 2, graphene doped dispersions show similar values of conductivity to nano and microceramic doped dispersions with half the percentage in weight. The particle size and the morphology may be the reason for this tendency.

The best results have been achieved with a 14%wt of GR122 graphene. The thermal conductivity of the resulting nanocomposite increased by 400% while that for SG8, with the same percentage, only increased by 100%.

3.2.1.3 Microstructural analysis

Figure 4 shows the aspect and quality of the fully formulated cyanate based systems prepared dispersions with SG8 and GR122 graphite nanoplatelets.

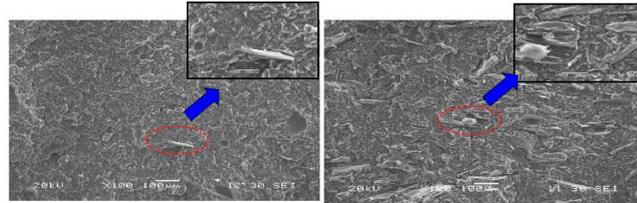


Figure 4. SEM image of fully formulated LTM123resin+filler. 14% wt of GR122 (left) and SG8 (right) in cyanate ester

As can be appreciated in figure 4, GR122 leads to more homogeneous dispersions. Also, GR122 processability and dispersability is better than in SG8.

3.2.2 Epoxy adhesive nanocomposites: Thermal conductivity

The results in thermal conductivity, measured by the Hot disk method, for the graphene doped epoxy adhesives are shown in table 3.

Reference	Graphene type	Filler load (%wt)	Thermal Conductivity (W/Km)	Improvement (%)
Eccobond 55		0	0.22	
Cod 24	rGO	0.15	0.25	14
Cod 29	rGO	2.0	0.30	36
Cod 30	GO+rGO	2.8	0.40	82

Table 3. Thermal conductivity values for different fillers load in epoxy adhesive resin.

4. Mechanical and thermal characterization of Graphene based composite laminates

4.1 Preparation of doped resin based composites

From previous results, Graphene GR122 was selected as the nanofillers in composite laminate manufacturing as it displayed a higher improvement in thermal conductivity. During the preparation of the dispersions, some difficulties associated with dispersion of entangled graphene sheets that could lead to poor interfacial interaction between graphene and polymer matrix were detected and corroborated by SEM images. Ultrasonication was a pre-step selected to enhance the graphene dispersion. Acetone was used as the solvent and the time for sonication was determined to be 45min. The acetone was then removed before graphene was dispersed into the resin. The resulting dispersions after the removal of the acetone displayed good graphene dispersion (Figure 5).

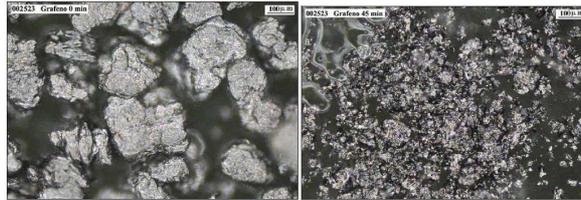


Figure 5. Optical microscopy picture of graphene GR122 left: as supplied; right: after 45 min ultrasonication

Having as reference the thermal properties of a prepreg based on cyanate ester resin /K13D2U fibre, a new prepreg has been developed using other range of pitch fibre (YS80of NGF) with somewhat lower properties but more cost- effectiveness, and graphene as thermally conductive nanofiller with the aim to improve the through the thickness thermal conductivity and in plane conductivity of a carbon fibre composite laminate without the need of expensive and difficult handling graphitized carbon fibres (Type K).

Unidirectional and Quasiotropic laminates were manufactured to assess the mechanical and thermal properties: $[0^\circ]_{12}$ laminates for Tensile strength and modulus at 0° and 90° ; $[0^\circ]_{140}$ – laminates for thermal conductivity at 90° and through thickness and $[0^\circ, 90^\circ, +45^\circ, -45^\circ]_4$ laminates for Tensile strength and modulus and Interlaminar Shear Strength (ILSS).

4.2 Mechanical characterization

Next table summarizes the obtained mechanical results of laminate composite.

Laminate Reference	Tensile strength (MPa)	Tensile modulus (GPa)	ILSS Strength (MPa)	Shear modulus (GPa)	Shear strength (MPa)
LTM123/YS80 (0°)	1369	431	44.7		
LTM123/graphene/YS80 (0°)	1242	4.6	41.1		
LTM123/YS80 (90°)	10.4	5.9			
LTM123/graphene/YS80 (90°)	10.7	6.6			
$[0,90]$ LTM123/YS80				4.14	58
$[0,90]$ LTM123/graphene/YS80				5.97	59
LTM123/YS80 (QI)	364	164.4	29		
LTM123/YS80 (QI)	471	142	21.1		

Table 4. Mechanical properties of doped cyanate ester composite laminate

4.3 Thermal characterization

These tests were performed according to three methods

- Based on thermal resistivity measurements. (Through thickness thermal conductivity)
- Based on thermal diffusivity. This property was determined by a Laser Flash Apparatus NETZSCH model 457 “MicroFlashTM”. (Through thickness thermal conductivity). The thermal diffusivity is calculated by the “Parker expression”:
- C-THERM. (Through thickness and in plane thermal conductivities).

Next table summarizes the obtained results. A comparison in properties with a high thermally conductive fiber (K13D2U) but stiffer is made.

Laminate Reference	Thermal conductivity (W/mK)			
	Through the thickness		In plane	
K13D2U/EX1515 (0°)	1.19		420	
	Thermal Resistivity	Laser Flash	C-THERM	
LTM123/YS80 (0°)	1.88	0,625	2.23	132
LTM123/graphene/YS80 (0°)	3.62	1.31	4.94	163
% Improvement	93	110	122	23

Table 5. Thermal conductivity results of doped cyanate resin composite laminate

5. Conclusions

- Ultrasonication allows to obtain stable graphene dispersion in cyanate esters and epoxy based polymer systems
- In composite laminates, improvements in thermal conductivity have been obtained doping the resin with graphene, especially in through the thickness direction (around 100 %). The use of graphene really improves the thermal conductivity of the CFRP laminates, although it is clear that absolute values depend on the method used. Based on the C-THERM measurement method, the in plane thermal conductivity is increased around 23%.
- In two component epoxy adhesive, the thermal conductivity increases by the addition of graphene. However, the study is in progress at the time this paper was written. Further developments will allow to bring the thermal conductivity values to higher values

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