



Free-standing graphene films embedded in epoxy resin with enhanced thermal properties

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Abstract

The poor thermal conductivity of polymer composites has long been a deterrent to their increased use in high-end aerospace or defence applications. This study describes a new approach for the incorporation of graphene in an epoxy resin, through the addition of graphene as free-standing film in the polymeric matrix. The electrical and thermal conductivity of composites embedding two different free-standing graphene films was compared to composites with embedded carbon nanotube buckypapers (CNT-BP). Considerably higher thermal conductivity values than those achieved with conventional dispersing methods of graphene or CNTs in epoxy resins were obtained. The characterisation was complemented with a study of the structure at the microscale by cross-sectional scanning electron microscopy (SEM) images and a thermogravimetric analysis (TGA). The films are preconditioned in order to incorporate them into the composites, and the complete manufacturing process proposed allows the production and processing of these materials in large batches. The high thermal conductivity obtained for the composites opens the way for their use in demanding thermal management applications, such as electronic enclosures or platforms facing critical temperature loads.

Keywords Functional composites · Nanocomposites · Polymer-matrix composites (PMCs) · Thermal properties · Scanning electron microscopy (SEM)

1 Introduction

Thermal management of aerospace structures is extremely important for many applications including space or defence platforms, re-entry vehicles, propulsion systems, electronics or high energy systems. Next-generation aerospace structures could potentially use more thermally conductive materials to direct heat flow in satellites, thermal protection systems, near-propulsion structures, electronic boxes or radiators. The inherent poor thermal conductivity of polymer composites, which are the most widely used materials in aerospace structures due to their high strength-to-weight ratio, is a significant drawback in such kind of applications.

The use of graphene as a thermal filler to increase the thermal conductivity of composites has been extensively studied due to its superior thermal properties. High in-plane thermal conductivity, great flexibility, and low density are the main properties that make graphene-related materials a good candidate for creating advanced functional materials [1].

Reduced graphene oxide (rGO) and graphene nanoplatelets (GNPs) are generally selected from among the variety of graphene-based materials for their potential use in polymer composites for thermal conductivity enhancement. In the last years, several research groups have reported enhanced thermal conductivity values for dispersed graphene/epoxy resins through blending methods [2, 3]. These methods include conventional mixing methods such as three roll milling or calendaring and high shear mixing processes. The analysis of these results shows that thermal conductivity of polymer-based composites is enhanced with the increased loading of fillers. However, the incorporation of high concentrations of graphene is difficult and hard to perform, due to the increase in the polymer viscosity.

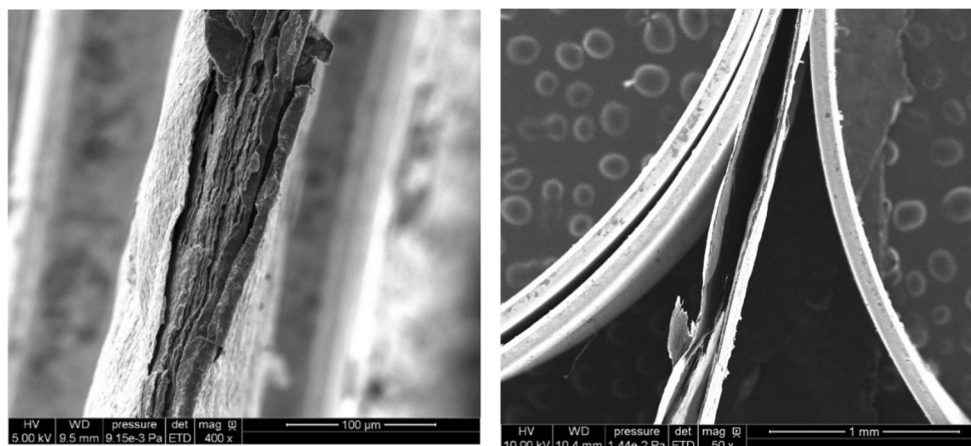
Changqing Liu et al. [4] achieved thermal conductivity values of 1.26 W/mK of graphene epoxy composites with

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Fig. 1 SEM images of rGO free-standing film (annealed at 200 °C)



10 vol% while Yunfei Sun et al. [5] achieved a thermal conductivity of 6.1 W/mK, with a maximum loading of 20 wt% rGO to the epoxy resin. On the other hand, the influence of GNPs on the thermal properties of epoxy composites has also been widely published [6]. Yuan-Xiang Fu et al. [7] reported that graphene nanoplatelets can effectively enhance the k of epoxy matrices, 4.01 W/mK for a maximum filler loading of 10 wt%, which is more than 22 times the thermal conductivity of the pure epoxy resin. Yi Wang [8] outlined that the thermal conductivity of the epoxy composites with 8 wt% GNPs was 1.18 W/mK. However, Haddon and his co-authors [9] reached a thermal conductivity of 6.44 W/mK increasing the load of graphite nanoplatelets up to 34%. Therefore, the improvement of thermal conductivity in polymer composites is strongly influenced by the filler loading and also by the filler dispersion in the matrix [10]. It is known that the thermal transport in graphite, graphene and their derivatives is dominated by acoustic phonons [11], meaning that the process used for its embedding and the resulting interfaces are crucial for the thermal transport. In this context, the use of free-standing

graphene films can overcome the problem of high loadings and can be handled in a reproducible way. A free-standing graphene film consists of a highly dense network structure of graphene usually manufactured by vacuum filtration or the direct evaporation method [12, 13]. In general, these processes require further thermal treatment that can reduce oxygen content and restore C sp² bonds. Other post-treatment methods such as high-pressure compression are conducted in order to remove air pores from graphene films. The different fabrication and post-treatment methods lead to different thermal behaviour. It was found that free-standing graphene films can exhibit thermal conductivities in a wide range of 30–3300 W/mK [14]. The highest value of 3300 W/mK was reported by Gee et al. [15]. It corresponds to graphene films prepared through an electrochemical and filtration process.

Besides, huge attention has been paid to the effect of the graphene content on the electrical conductivity of epoxy nanocomposites. The typical percolation threshold values that were reported in literature vary from 1 to 15 wt% for GNP composites obtaining conductivity values from 10^{-3} to $\sim 10^{-1}$ S/m

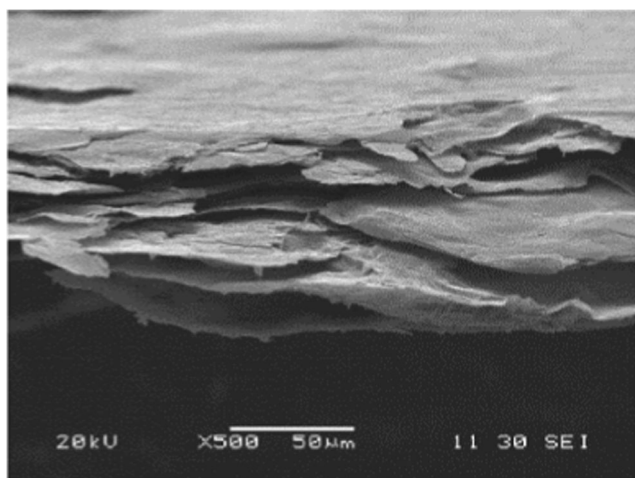


Fig. 2 SEM image of GNP film from Nanografi

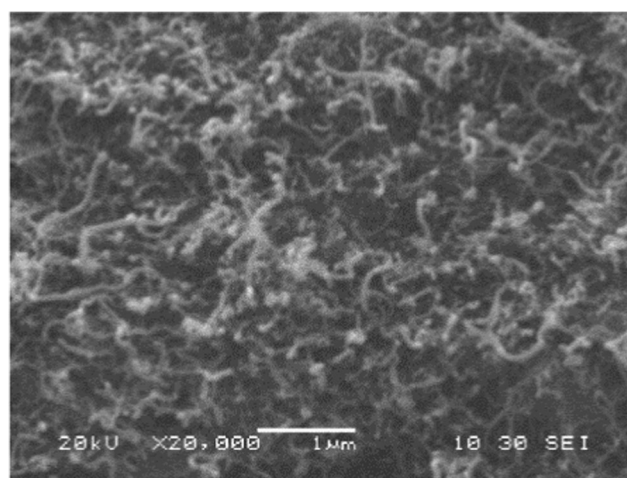


Fig. 3 SEM image of as-prepared CNT Buckypaper by Tecnalia

Table 1 Properties of free-standing graphene films and CNT BP used

Free-standing graphene film	Size mm	Thickness μm	Electrical conductivity S/m	Thermal conductivity (W/mK)	Density (g/cm^3)
GNP (Nanografi)	290 × 290	35	3.75×10^5	580	1.82
rGO ($T=200\text{ }^\circ\text{C}$) (Graphenea)	140 × 90	20	5.1×10^2	10	1.87
CNT-BP (Tecnalia)	45 × 45	52	5.0×10^3	8	0.9

[16, 17]. Such large variations of percolation threshold values show that the graphene content, aspect ratio, dimensions and geometrical arrangement, and also composite processing conditions are important.

Hao Hou [18] managed to prepare an epoxy composite embedded with a quasi-isotropic graphene film by a simple two-step process: vacuum filtration of small graphene sheets to obtain the film followed by the infiltration of epoxy resin. At a low graphene loading of 5.5 wt%, graphene/epoxy in- and through-plane thermal conductivities of 10.0 and 5.4 W/mK, respectively, were reported. The An F. group [19] described a thermal conductivity of 35.5 W/mK through-thickness while in-plane is 17.2 W/mK at 19 vol% for epoxy containing a densely packed and vertically aligned graphene film. Solutions based on vertically aligned graphene are reporting high through-thickness thermal conductivity of epoxy composites; Zhang et al. present values up to 384.9 W/mK in through-thickness and 0.18 W/mK in-plane at 44 vol% graphene [20]. Unfortunately, the processes proposed are not easily scaled up.

So far, there are very few reports on graphene films embedded in epoxy composites for thermal management applications [21]. In this work, three free-standing films based on carbon nanostructures—commercial graphene film made by Nanografi, carbon nanotube buckypapers (CNT-BP) manufactured at Tecnalia and thermally-reduced graphene oxide (GO) film produced by Graphenea Nanomaterials S.A.—were embedded in a commercial liquid epoxy-based resin (Resoltech 1800/1805) to enhance their thermal conductivity. The composites were prepared by manual impregnation of the carbon films with the uncured liquid epoxy resin.

This paper is organised as follows: characterisation of the carbon-based films and fabrication of the nanocomposite followed by the comparison of the electrical and thermal conductivity values of the different composites fabricated with the carbon-based films.

Table 2 Porosity values of free-standing graphene films

Free-standing graphene	Thickness (μm)	Porosity (%)	Mean pore diameter
GNP (Nanografi)	35	13	0.1 μm
Thermal treatment of rGO film at 200 $^\circ\text{C}$ (Graphenea)	20	21	6.7 μm
CNT-BP (Tecnalia)	50	65	30 nm

2 Materials and methods

2.1 Carbon-based films

Free-standing films obtained from graphene or graphene oxide (GO) have attracted interest due to their high thermal conductivity, superior electrical conductivity and excellent mechanical properties. Two free-standing graphene films—graphene film made by Nanografi (with a density of 1.82 g/cm^3 and 35 μm thick) and graphene oxide (GO) film with a thermal treatment at 200 $^\circ\text{C}$ for 18 h made by Graphenea (with a density of 1.87 g/cm^3 and 20 μm thick)—were compared to carbon nanotube buckypaper (CNT-BP) manufactured by Tecnalia (with a density of 0.9 g/cm^3 and 52 μm thick).

The graphene films fabricated using different initial graphene solutions exhibited different macroscale properties: morphology, colour and flexibility.

Graphenea-reduced GO film is obtained by the reduction of the GO result of the pre-production of GO from natural graphite via Hummers method followed by chemical or thermal post-processes. Several rGO films post-processed at different temperatures (from 200 $^\circ\text{C}$ to 1000 $^\circ\text{C}$) were analysed. Figure 1 shows the SEM images of the products.

Graphenea has reported thermal conductivity values of the rGO films post-processed at different temperatures (from 200 to 1000 $^\circ\text{C}$) [22]. The room temperature in-plane thermal conductivity increases from 2.9 W/mK for the reference GO film to 61 W/mK for the rGO film annealed at 1000 $^\circ\text{C}$. Reduced GO films become more conductive but also more brittle as the post-processing temperature increases and, as a consequence, the mechanical strength is significantly reduced. For that reason, rGO film thermally treated at a moderately low temperature of 200 $^\circ\text{C}$ was selected for further integration into the composites.

Free-standing graphene films from Nanografi were also analysed and fully characterised. Figure 2 shows a SEM

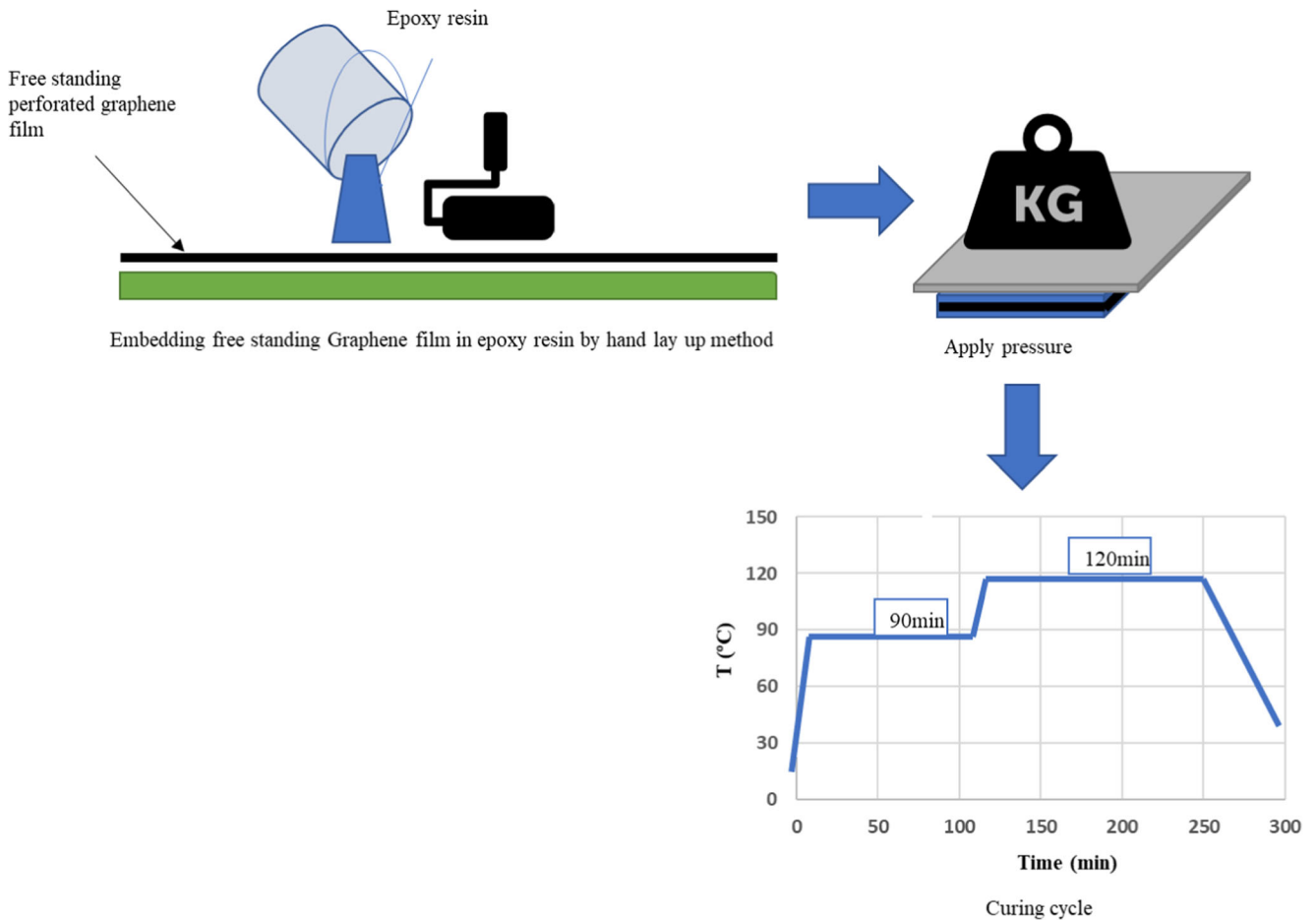


Fig. 4 Fabrication process of nanocomposites

image of the Nanografi graphene film. The multiple sheets strongly compacted can be observed.

Figure 3 shows a SEM image of CNT-Buckypapers (CNT-BP) as prepared where the morphology of the BP can be clearly appreciated: it consists of randomly entangled carbon nanotubes (CNTs) forming a network structure [23, 24]. The CNT-BP is manufactured using a pilot line that enables a continuous filtration process. This method consists of several steps: in the first one, CNTs are received in liquid masterbatch form and then dispersed and stabilised via ultrasonication using a surfactant in distilled water. In a second step, the suspension is filtrated

through a polyvinylidene fluoride (PVDF) filter with the aid of vacuum. Next, distilled water is filtrated to wash out the surfactant and finally the buckypaper is dried [25].

The three materials were characterised in terms of electrical resistivity, thermal conductivity and porosity:

- (a) Electrical resistivity. The electrical resistivity of these materials was measured by the Van der Pauw method using 4-probe measurement. A Keithley 2410 was used as a source of DC current
- (b) Thermal conductivity was measured by Hot disk sensors TPS 2500 S

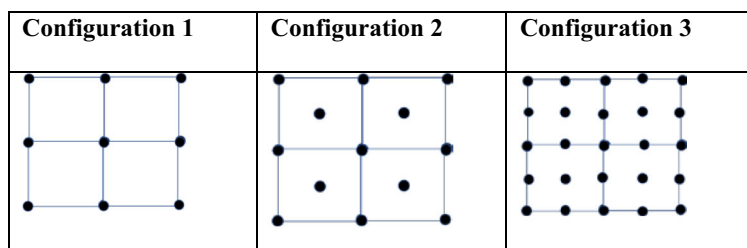
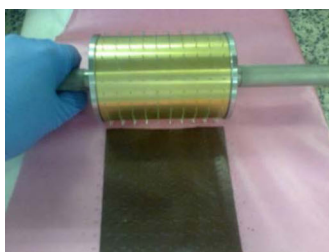


Fig. 5 Pinned roller used to perforate graphene films and configurations implemented

Table 3 Electrical sheet resistance of free-standing graphene perforated films

Material	Perforated (Y/N)	Thickness (μm)	Electrical sheet resistance (ohm/sq)	
GNP films	N	32.5	6.50 E-2	
Nanografi	N	35	6.32 E-2	
45 mm \times 45 mm	N	34	5.99 E-2	
	Y (config 1) sample1	32.5	6.46 E-2	
	Y (config 1) sample2	31	7.44 E-2	
	Y (config 1) sample3	28	6.88 E-2	
	Y (config 2) sample1	32.5	6.58 E-2	
	Y (config 2) sample2	31	6.88 E-2	
	Y (config 2) sample3	29	7.23 E-2	
	Y (config 3) sample1	32.5	6.72 E-2	
	Y (config 3) sample2	26	7.46 E-2	
	Y (config 3) sample3	31	6.56 E-2	
	CNT BP	N	62	2.22
	Tecnalía	N	46	2.75
45 mm \times 45 mm	N	46	2.69	
	Y (config. 1)	50	2.62	
	Y (config. 1)	37	3.15	
	Y (config. 1)	55	2.30	
Thermal treatment of rGO films at 200 °C 18 h	N	18.2	116	
	N	17.7	91.1	
Graphenea 140 \times 90 mm	N	21.6	87.0	
	Y (config 1)		123	
	Y (config 1)		94.9	
	Y (config 1)		93.0	
	Y (config 3)		163	
	Y (config 3)		110	
	Y (config 3)		Broken sample	

(c) Porosity. The porosity was characterised by mercury intrusion porosimetry, using an Autopore IV Micromeritics Hg Porosimeter.

Technical data of thermal and electrical conductivities is compiled in Table 1 together with the sizes and densities of the carbon-based films used in this study.

Both the electrical and thermal conductivity of the GNP film are significantly higher than the CNT-BP and the rGO film values.

The porosity of these free-standing graphene films is important for anticipating the infiltration behaviour in epoxy resins. Table 2 shows the large difference of the CNT-BP porosity and mean pore diameter compared to the two graphene-based film values. The porosity percentage and

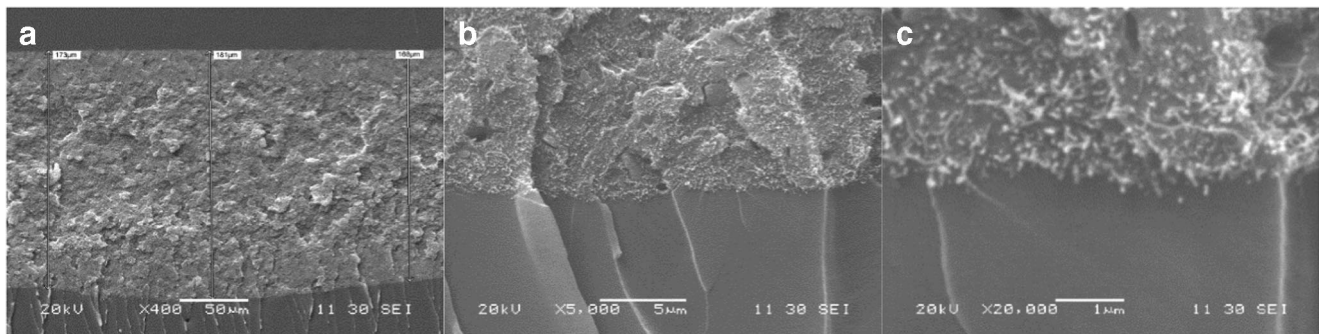
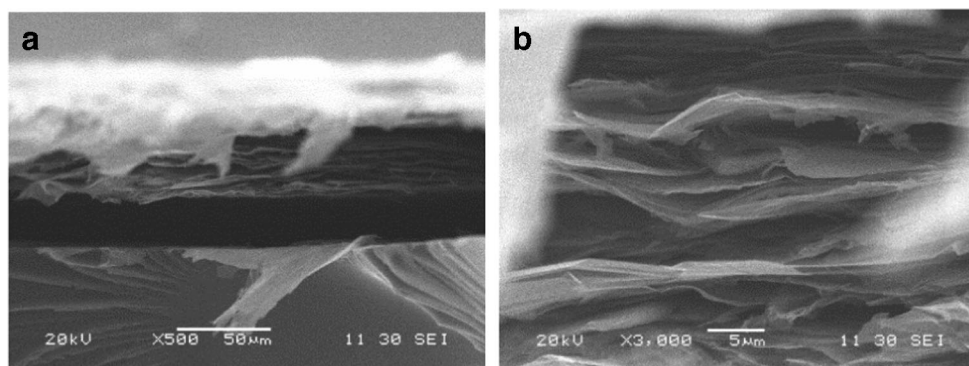


Fig. 6 Cross-sectional SEM images of CNT BP integrated in 1800/1805 epoxy resin at different magnifications: **a** 50 μm , **b** 5 μm and **c** 1 μm

Fig. 7 GNP film with 1800/1805 epoxy resin at two magnifications **a** 50 μm and **b** 5 μm



mean pore diameter of GNP films are significantly lower than rGO films. CNT-BP shows the highest porosity with the lowest mean pore diameter.

2.2 Fabrication of nanocomposites

The integration of the conductive films was performed in the following way: a layer of liquid epoxy resin was applied, coating the CNT-Buckypapers, GNP films and rGO films. An extra resin layer was applied to the films to be soaked by the resin. The samples were then cured in an oven on a flat mould using a caul plate to press the sample to obtain a full impregnation and to remove excess resin under pressure. The curing cycle consisted of 90 min at 90 °C + 120 min at 120 °C (Fig. 4).

The techniques and parameters used for the introduction of nanomaterials into resins have a substantial impact on the performance of the final composite. In this work, the free-standing films were perforated using a pinned roller to facilitate resin impregnation. CNT-Buckypapers and GNP films are easy to handle, and the perforation step was performed without difficulty. In the case of rGO films, as they present a fragile behaviour, the perforation step damaged them in different areas (Fig. 5).

Different perforation configurations were studied in order to select the highest perforation level to ensure a good impregnation by the resin without modifying the electrical and thermal conductivity of the films. The electrical sheet resistance

was measured using the Van der Pauw method with a 4-probe measurement and the results are summarised in Table 3.

It can be observed that the perforation vaguely modified the electrical resistance of the films. Assuming that the thermal behaviour will not be affected by the perforations either, configuration 3 was chosen for both GNP and rGO films. Configuration 1 was selected for CNT BP according to previous results from TECNALIA in terms of good impregnation and integration in the composite [26].

For the CNT BP integrated in 1800/1805 epoxy resin, a good impregnation is observed in the section of the sample as it can be observed on Fig. 6. After comparing these images with those corresponding to the bare BP, it can be concluded that, in general, the BP is completely impregnated by the epoxy resin. The spaces between CNTs observed in the bare BP were filled by the resin.

On Fig. 7, GNP film not fully impregnated by the resin can be observed at two different magnifications:

The compacted structure of the sample avoided the resin infiltration through it (Fig. 7b).

For the perforated rGO film embedded in 1800/1805 epoxy resin, the film was not impregnated by the resin either. As it can be observed on Fig. 8 at two magnifications, the resin vaguely infiltrated between the graphene layers:

The infiltration of the resin is of utmost importance for the optimisation of electrical properties. A continuous electrical network is mandatory to reach electrical percolation threshold,

Fig. 8 rGO film integrated in 1800/1805 epoxy resin at two magnifications **a** 100 μm and **b** 2 μm

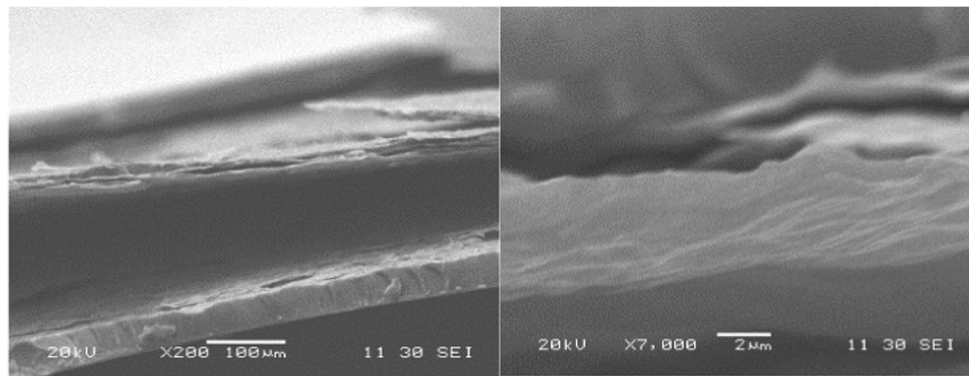


Table 4 Sheet resistance values of graphene films before and after impregnating in the 1800 resin

Graphene film	Thickness	Sheet resistance of the bare films (Ohm/sq)	Sheet resistance of film 1800 resin composites (Ohm/sq)
GNP film from Nanografi	35 μm	0.06	>MOhm
rGO film from Graphenea	18 μm	98	>MOhm
CNT BP (Tecnalia)	52 μm	2.6	8.87

whereas to improve the thermal conductivity, other mechanisms occur like phonon scattering which can result in thermal conductance through electrically insulating films.

3 Results

Electrical and thermal conductivity of the prepared composites (with GNP, rGO and CNT-BP films) was measured and comparatively analysed. Based on those results, GNP-based composites have been further analysed in terms of thermal stability.

3.1 Electrical conductivity

Electrical conductivity measurements were performed following Van der Pauw method (VDP, 4 probe method). The sheet resistance values for those films before and after their introduction in the matrix are gathered in Table 4.

The composites based on GNP film, not well impregnated by the resin, presented a very high electrical resistance, as well as the composites based on reduced graphene oxide films. The pictures show that a continuous electrical path has not been obtained in neither of the two graphene film composites. However, the impregnated buckypaper composite presented an electrical sheet resistance of 8.87 Ohm/sq. The good integration of CNT-BP material in the resin allowing a continuous network is behind these results.

Table 5 Thermal conductivity of free-standing films embedded in epoxy resin

Material	Thermal conductivity (W/mK)	Graphene/CNT content in the resin (wt%)
Neat resin Resoltech (1800/1805)	0.227 ± 0.002	–
GNP film Nanografi	450 ± 50	100
GNP film in epoxy resin Resoltech 1800/1805	9 ± 1	9.5
GNP film in epoxy resin Resoltech 1800/1805	15 ± 2	19
GNP film in epoxy resin Resoltech 1800/1805	20 ± 3	30
rGO film Graphenea	10 ± 1	100
rGO film in epoxy resin Resoltech 1800/1805	< 0.5	8
CNT- BP Tecnalia	8 ± 1	100
CNT- BP in epoxy resin Resoltech 1800/1805	1 ± 0.5	5

3.2 Thermal conductivity

The effect of resin thickness and the total graphene loading was analysed in relation to thermal conductivity. The reference value of the neat resin is 0.23 W/mK. The thermal conductivity of the free-standing films embedded in epoxy resin samples after the curing process was measured in a TPS 2500 S Hot Disk Analyser. Several thicknesses of the composites result in different graphene concentrations that were analysed to understand the influence of the content of carbon nanostructures in the composite. The graphene contents were calculated by the weight change before and after impregnation.

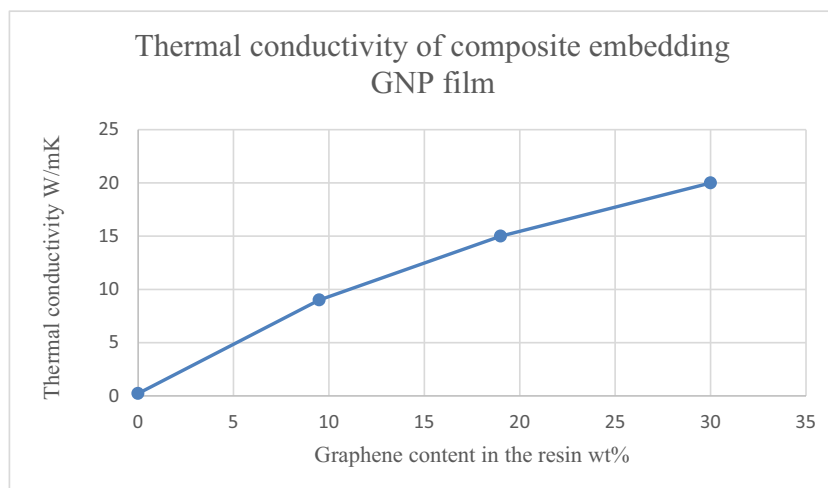
The thermal conductivity results are summarised in Table 5.

The thermal conductivity value of the GNP film dramatically decreased (from 450 ± 50 to 9 ± 1 Wm/K) when it was combined with the polymer. The rGO film presented the same trend (from 10 to 0.5 W/mK) whereas CNT BP showed a lower decrease (8 ± 1 to 1 Wm/K).

The composite based on the rGO film presented a very low improvement in thermal conductivity, from 0.23 of the neat resin up to 0.5 W/mK with an rGO content of 8 wt%. In the case of CNT-BPs, the increase was more notable, 1 Wm/k was obtained for a 5 wt% CNT content incorporated in the resin.

The thermal conductivity increased significantly from 0.23 W/mK of the polymer reference to 20 W/mK of the composite with GNP film embedded in the resin at a concentration of 30% wt. The trend of this increase can be observed in Fig. 9.

Fig. 9 Thermal conductivity vs graphene content in GNP film-based composites

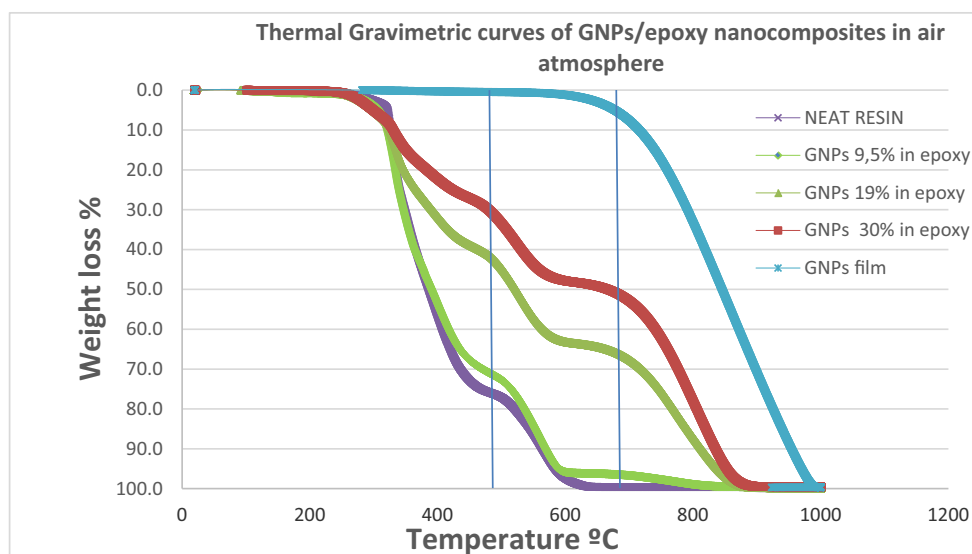


Overall, the results obtained are very promising, 20 W/mK is high if compared with the thermal conductivities of plastics in general (<0.5 W/mK). These can also be compared with nanocomposites obtained by adding graphene in powder directly in the matrix (not as a film), where maximum values of 6.4 W/mK are reported in the prior art. Novel solutions based on vertically aligned graphene nanoplatelets report thermal conductivities as high as 35.5 W/mK through-thickness and 17.2 W/mK in-plane [19]. However, these solutions require difficult to scale-up processes.

3.3 Thermal stability of GNP film composites

The thermal stability in air atmosphere of neat epoxy resin (Resoltech 1800/1805), free-standing GNP-film and composites with different contents of this GNP-film are presented in Fig. 10. Figure 10 shows the weight change as a function of the increasing temperature (TG curves).

Fig. 10 Thermal gravimetric curves of GNPs/epoxy nanocomposites in air atmosphere



The neat resin curve displays a gradual weight loss starting at 290 °C up to 620 °C at which the resin is totally decomposed. The high stability of the free-standing GNP film is verified; there is no weight loss up to 600 °C. Clear differences are observed as a function of the content of GNPs in the epoxy resin. The TG curve at low content of GNPs (9.5 wt%) shows decomposition temperatures similar to the epoxy resin, reaching the 96% of weight loss at 595 °C. The TG curves are shifted to higher temperatures for GNP contents of 19 wt% and 30 wt%. The enhancement of the thermal stability in the resins embedded with graphene nanoplatelets has been already reported by other authors [27]. An increase of GNP content implies an increase in the thermal stability, as it is observed in Table 6.

Therefore, the thermogravimetric analysis of the studied GNPs/epoxy composites has shown that the presence of graphene films embedded in the resin induces an increase in thermal stability of the nanocomposite. It has also been shown that the mechanisms that rule the thermal behaviour are

Table 6 Weight loss of GNP/epoxy nanocomposite at 480 and 680 °C

Temperature °C	Weight loss of GNP/epoxy nanocomposite (wt%)				
	Neat resin	GNPs 9.5% in resin	GNPs 19% in resin	GNPs 30% in resin	GNPs 100%
480	76	70	40	30	0
680	100	96	66	51	5,2

different to the electrical conductivity mechanisms in a composite. The phonon scattering can happen through insulating polymer layers; however, an electrical network is necessary for electron conduction [11].

This work gives a novel and simple approach for the fabrication of graphene-filled polymer composites increasing the graphene loading to obtain a high thermal conductivity. The fabrication method can be easily scaled up to allow the production and processing of these materials in large batches.

4 Conclusions

Graphene composites obtained by integrating graphene free-standing films show a significant improvement in thermal conductivity values when compared to conventional methods of integrating graphene in epoxy resins. The methodology developed introduces clear benefits compared to competing technologies in terms of performance as a result of the incorporation of high graphene contents into a composite without the high viscosity issues encountered using liquid technologies, as well as in the up-scaling of the manufacturing process.

The results obtained are very promising. It has been demonstrated that the thermal conductivity of the polymer increases by two orders of magnitude (from 0.2 to 20 W/mK) with the introduction of a graphene loading of 30 wt% as graphene-film, improving also the thermal stability of the composite.

The high thermal conductivity of graphene/epoxy resins enables them to be used in thermal management applications as efficient heat-dissipating structural materials in future structures and systems where temperature loads are critical. Military applications requiring multifunctional structures where thermal management is needed will benefit from the use of free-standing graphene films embedded in polymer matrixes.

Compliance with ethical standards

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