

Article

# Influence of Thickness and Lateral Size of Graphene Nanoplatelets on Water Uptake in Epoxy/Graphene Nanocomposites

Silvia G. Prolongo \*, Alberto Jiménez-Suárez, Rocío Moriche and Alejandro Ureña

Materials Science and Engineering Area, Universidad Rey Juan Carlos, Calle Tulipan, s/n, 28933 Móstoles, Spain; alberto.jimenez.suarez@urjc.es (A.J.-S.); rocio.moriche@urjc.es (R.M.); alejandro.urena@urjc.es (A.U.)

\* Correspondence: silvia.gonzalez@urjc.es; Tel.: +34-914-888-292

Received: 25 July 2018; Accepted: 30 August 2018; Published: 4 September 2018



**Abstract:** In this study, the hydrothermal resistance of an epoxy resin (aircraft quality) reinforced with graphene is analyzed. Different geometries and aspect ratios (thickness and lateral dimensions) of graphene nanoplatelets were studied. The addition of these graphene nanoplatelets induces important advantages, such as an increase of the glass transition temperature and stiffness and an enhancement of barrier properties of the epoxy matrix, in spite of the excellent behavior of pristine resin. The effectiveness of graphene nanoplatelets increases with their specific surface area while their dispersion degree is suitable. Thinner nanoplatelets tend to wrinkle, decreasing their efficiency as nanofillers. Graphene used as reinforcement not only reduces the absorbed moisture content but also decreases its effect on the thermal and mechanical properties related to the matrix.

**Keywords:** graphene nanoplatelet; epoxy composite; water absorption

## 1. Introduction

Carbon-based nanofillers, such as carbon nanotubes (CNTs), graphene nanosheets (G) or/and graphene nanoplatelets (GNPs) are being widely investigated as reinforcements of epoxy resins [1–4]. Their excellent electrical, thermal and mechanical properties induce interesting expectations of improving the behavior of these thermosetting resins. Among other advantages, the high aspect ratio of these nanofillers together with their hydrophobic character allow them to act as efficient barriers against water transport through the resin. Some authors [5–7] have reported that the reduction of water permeability is associated with both the reduction of the free volume and the restriction of the molecular dynamics of the polymer chain surrounding the nanofiller. Several works [5–10] have been published related to the reduction of the maximum water absorbed caused by the addition of CNTs or GNPs. This effect can be enhanced by the increase of the nanofiller content added into the matrix and its dispersion degree.

On the other hand, it is well known that the absorption of water into thermosetting resins causes a plasticization effect [11,12]. This is due to the fact that water increases the chain segments mobility, which implies a decrease of the glass transition temperature and even the reduction of modulus and mechanical strength. It is expected that the nanofillers addition acts in two different ways: Reducing the rate and/or the maximum content of water uptake and improving the mechanical properties of non-aged composites.

Recently, O. Starkova et al. [5,6] studied the moisture uptake and its effect on the thermo-mechanical properties in composites reinforced with CNTs and reduced graphene oxide. They concluded that the CNTs addition decreases the diffusivity rate but the maximum water

absorption remains unchanged. However, the addition of graphene oxide nanoparticles reduces the water absorption capability of the epoxy resin. This means that the geometry of graphitic nanofiller is significant as the GNPs seems to be more efficient. CNTs usually have a higher specific surface area than GNPs. Theoretically, the high specific area of the nanofiller should increase the barrier properties but the higher aspect of CNTs decreases this phenomenon. In addition, graphene nanoparticles tend to a self-orientation, showing a preferential orientation through the in-plane direction, which enhances barrier properties.

In this paper, the influence of GNPs geometry on the moisture uptake of epoxy/GNPs nanocomposites is analyzed. In addition, we analyze the plasticization effect caused by water in the neat epoxy resin and nanocomposites in order to evaluate the influence of the GNPs addition.

## 2. Materials and Methods

The epoxy matrix was based on a monomer denominated Araldite LY556, cured with an aromatic amine Araldite XB3473. Both components were provided by Antala Group, Cataluña, Spain. The curing was carried out at 140 °C for 8 h, reaching a glass transition temperature ( $T_g$ ) of 162–165 °C, measured by dynamic mechanical thermal analysis (DMTA).

In this work, different graphene nanoplatelets have been used as nanofiller, the commercial denominations are AO1, AO2, AO3 and AO4, named in this work as GNP1, GNP2, GNP3 and GNP4, respectively. All of them were supplied by Graphene Laboratories Inc, Calverton, NY, USA with a purity close to 99%. Their main geometric characteristics are collected in Table 1. Dimensions were supplied by the manufacturer and corroborated by transmission electron microscopy (TEM).

**Table 1.** Main geometric characterizes of graphene nanoplatelets.

Graphene Type	Purity (%)	Specific Surface Area ( $m^2/g$ )	Average Flake Thickness (nm)	Average Particle Lateral Dimension ( $\mu m$ )
AO1 (GNP1)	98.0	510	1.6 (less than 3 layers)	~10
AO2 (GNP2)	99.9	100	8 (20–30 layers)	0.55 (0.15–3)
AO3 (GNP3)	99.2	80	12 (30–50 layers)	4.5 (1.5–10)
AO4 (GNP4)	98.5	<15	60 (~180 layers)	3–7

The manufacture of GNP/epoxy composites has been optimized in previous works [13,14]. The procedure consists in GNPs dispersion, in all the proposed cases in a weight content of 0.5%, into the neat epoxy monomer using a high-speed mixer (Dispermat; Lumaquin, S.A, Barcelona, Spain) at 6000 rpm for 15 min to obtain the optimum doughnut effect. In order to remove the trapped air, once dispersion was completed, the mixture was degassed under vacuum at 80 °C for 15 min. Then, the stoichiometric ratio of the amine curing agent was added at 80 °C and the curing treatment was applied in an oven.

The morphological study of pristine graphene nanoparticles and epoxy composites reinforced with different GNPs was carried out by Transmission Electron Microscopy (TEM, Phillips Tecnai 20 of 200 kV, FEI Company, Hillsboro, OR, USA) and Field-Emission Gun Scanning Electron Microscopy (FEG-SEM, Nova NanoSEM FEI 230, FEI Company). For electron microscopy (TEM and FEG-SEM), epoxy samples were cut by cryomicrotomy. In addition, the film was coated with a thin layer (5–10 nm) of Au for FEG-SEM observation. The experimental conditions of the sputtering were 30 mA for 120 s (Bal-tec, SCD-005 sputter).

Bar-shape samples were cut with different dimensions:  $35 \times 12 \times 1.5 \text{ mm}^3$  for DMTA (dynamic thermomechanical analysis) measurements and  $60 \times 12.5 \times 2 \text{ mm}^3$  for flexural test. In order to carry out the study, samples were introduced in a hydrothermal chamber with a relative humidity of

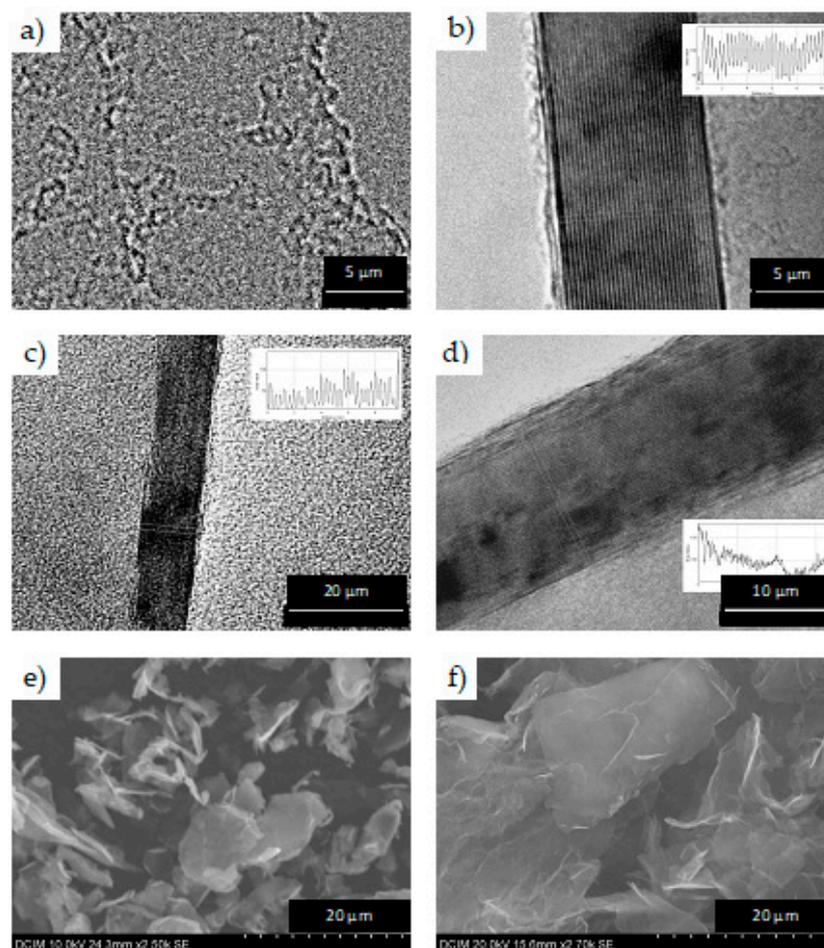
85% and a temperature of 40 °C. The moisture absorption was determined by gravimetric method. The samples were periodically removed and weighted with an accuracy of 0.01 mg. At selected times, some samples were tested by DMTA and flexural test.

The mechanical characterization of composites was carried out by flexural test (ZwickLine Z2.5, Zwick-Roell, Ulm, Germany), following the ASTM D-790 (procedure A and B). DMTA was performed following the standard D5418-01, using the single cantilever bending mode in a DMTA Q800 V7.1 from TA Instruments, New Castle, DE, USA. All the experiments were carried out at 1 Hz frequency, by bending deformation, and scanning from 20 to 250 °C with a heating rate of 2 °C/min.

### 3. Results

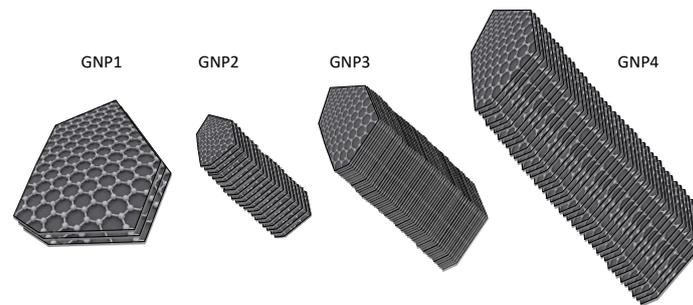
#### 3.1. Morphology

Figure 1 shows high resolution micrographs of the different types of the graphene nanoplatelets used in this work. It can be clearly seen that the thickest platelets are GNP4 and the thinnest ones are GNP1, according to the datasheets of the manufacturer (Table 1). Despite not showing a cross-section of GNP1, the fact that the thickness of GNP1 is the lowest of the four types is attributed to the lack of different contrast between the nanoplatelet and the background shown in Figure 1a, elucidating the low number of layers. The average lateral dimension is difficult to determine, but it is possible to observe that GNP2 nanoplatelets are smaller, while the largest ones are GNP4. Figure 2 shows the schematic morphology of each type of graphene nanoplatelet used in the study.



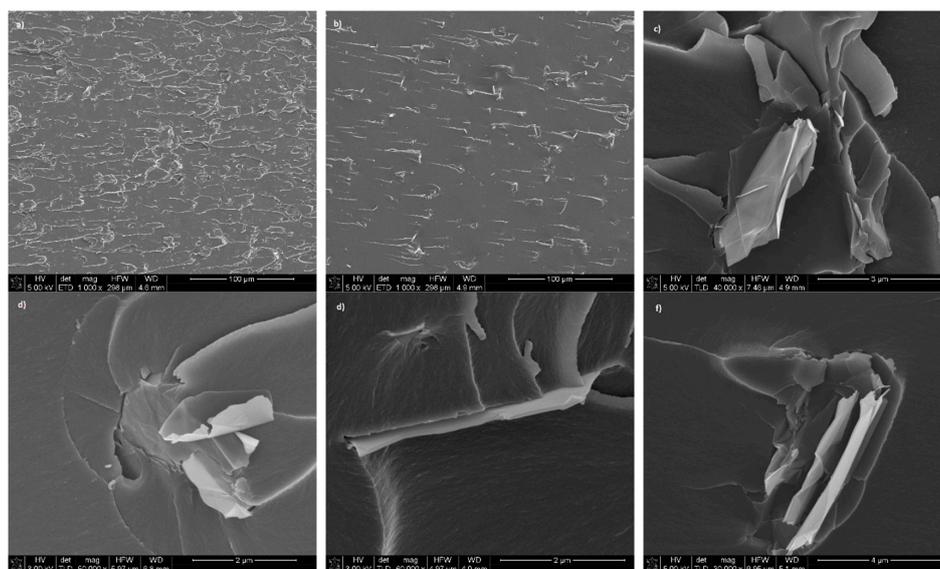
**Figure 1.** TEM micrographs of (a) GNP1; (b) GNP2; (c) GNP3; (d) GNP4 and SEM micrographs of (e) GNP2 and (f) GNP4.

The aspect ratio of the GNPs, as well as dispersion and morphology, has a strong influence on resulting properties of nanocomposites. For that reason, it is necessary to analyze the morphology of the composites in order to determine the dispersion degree, which is the relative position of the GNPs through the epoxy matrix, in addition to the spatial distribution, referring to the possible exfoliation of graphite nanosheets or the appearance of wrinkling or stretching phenomena [15]. In a previous study carried out by X-Ray diffraction [13], it was confirmed that the exfoliation phenomenon does not occur with the applied dispersion technique.



**Figure 2.** Scheme of graphene nanoplatelets: GNP1, GNP2, GNP3 and GNP4. These schemes are only comparatives. The thickness of nanoplatelets ( $\sim$ nm) is much lower than the lateral dimensions ( $\sim$  $\mu$ m).

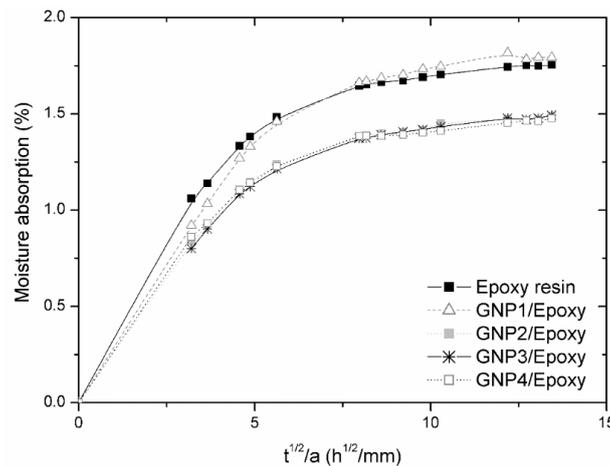
Figure 3 shows micrographs of the studied composites captured by FEG-SEM. These micrographs confirm a suitable dispersion degree for all the studied samples (Figure 3a,b) but also that high shear stirring could induce a wrinkling effect of the nanosheets [13]. This phenomenon seems to be more noticeable for composites reinforced with lower thickness GNPs (Figure 3c,d), while GNPs with higher thickness remain mostly stretched (Figure 3e,f). It is worthy to note that the percentage of GNPs added was the same one for all the samples. However, making a comparison between the micrographs (Figure 3a,b), it is possible to observe that the concentration of nanoplatelets, determined as the number of GNPs per observed area, is highest in the epoxy resin reinforced with GNP1. This concentration seems to decrease as the size of the nanoplatelets does. This is due to the different aspect ratios of the GNPs. GNP1 GNPs have the highest specific surface area and lowest thickness whereas GNP4 GNPs have specific surface area several orders of magnitude lower than GNP1 ones and higher thickness.



**Figure 3.** FEG-SEM micrographs of epoxy composites reinforced with GNP1 (a,c); GNP 2 (d), GNP3 (e) and GNP4 (b,f).

### 3.2. Moisture Absorption

Figure 4 shows the moisture absorption curves obtained for neat epoxy resin and composites reinforced with the different types of graphene nanoparticles. Firstly, it is worth pointing out that the pristine epoxy resin studied in this work is aircraft quality and, therefore, its hydrothermal resistance is initially very high, absorbing only 1.75% *w/w* of water. For this reason, the enhancement reached by graphene addition is less pronounced than other published works with epoxy resins of different nature, with a curing process at room temperature [5,6]. The crosslinking degree of these resins is lower and thus, their water uptake was higher, close to 6% *w/w*.



**Figure 4.** Moisture absorption of neat epoxy resin and epoxy composites reinforced with different types of graphene, commercially named GNP1, GNP2, GNP3 and GNP4, where  $t$  is time, and  $a$  is area.

At the first stage, the water uptake curves present a tendency that can be approximated to linear growth. After this first region, the tendency changes and the curves asymptotically approach the equilibrium. From these results, the diffusion coefficient can be calculated by knowing the water absorption rate, according to the Fick's model from the initial slope of the absorption curves [16]. The other characteristic parameter is the maximum absorbed water content when the saturation is reached. These parameters are summarized in Table 2 for all the studied samples. It is worthy to note that the incorporation of graphene nanoplatelets into the epoxy matrix causes different effects on the water uptake of the resin as a function of the GNPs geometry.

**Table 2.** Water diffusion coefficients ( $D$ ) calculated by Fick model and weight fraction of water at the saturation equilibrium ( $W_{\infty}$ ).

Sample	$D \times 10^9$ ( $\text{cm}^2 \cdot \text{s}^{-1}$ )	$W_{\infty}$ (%)
Epoxy resin	10.8	1.75
GNP1/epoxy	7.99	1.79
GNP2/epoxy	7.97	1.78
GNP3/epoxy	6.56	1.46
GNP4/epoxy	7.53	1.45

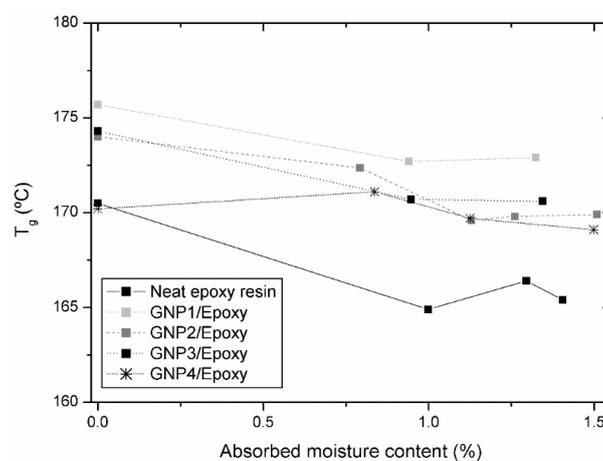
In fact, it is striking that the addition of GNPs induces a reduction of the maximum absorbed moisture content in most cases except for GNP1/epoxy composites. However, this is the nanofiller with the highest specific area and aspect ratio, therefore, it would be expected that this composite presents the highest barrier properties. These controversial results can be explained by the morphology of the composites. As it is shown in Figure 3d, GNP1 suffers an important phenomenon of weaving. This implies two different effects: A decrease of its effective area and a weak interphase with the matrix,

that results in areas with low wettability. Despite GNPs difficult water absorption, the final amount of absorbed water is higher due to this weaker interface, which allows water to go in between. In contrast, the addition of only a 0.5 wt % of GNP2, GNP3 and GNP4 causes an important reduction of water absorption. It confirms that, when the graphite nanosheets are stretched, they act as effective barriers. This affirmation is corroborated by the diffusion coefficient. The water absorption rate decreases by the GNPs addition. This parameter is lower for epoxy/graphene composites with regards to neat epoxy resin, but this remains practically constant for all the studied composites. This decrease of diffusion coefficient by graphitic nanofiller addition has been already observed by other authors.

As it is indicated by O. Starkova et al. [5,6], water absorption is a complex phenomenon, influenced by many factors, including free volume, crosslinking degree of the matrix, morphology, hydrophobicity, etc. [17]. They explain the increase of water resistance in epoxy composites, reinforced with nanofillers, by two effects. In the first place, nanofillers act as efficient barriers against water absorption due to the increased tortuosity for water molecules diffusing through the epoxy matrix. The second reason is that nano-sized particles restrict intermolecular movements of the surrounding epoxy thus, retarding the relaxation of polymer chain segments. This would explain the results in the present work. Graphene addition induces a decrease of the absorbed water content and diffusion coefficient. A higher specific surface area enhances the barrier properties when graphene nanoplatelets are well dispersed and stretched. Nevertheless, the thinnest nanosheets (GNP1) can suffer wrinkling during the dispersion stage, thus the molecular mobility restriction is less effective, increasing the maximum absorbed water content.

### 3.3. Thermal Effect

The effect of the water absorption in the epoxy resin and composites was studied by DMTA. DMTA specimens were introduced in the climatic chamber and removed at selected periodic times. In all cases, the curves of loss of tangent ( $\tan \delta$ ) presented only one peak. A shoulder at low temperature was not observed in any case, this behavior has also been observed by other authors [5,6]. The reason is the low moisture content absorbed by the studied system. Differences in  $T_g$  due to duplicate samples did not exceed 1–2 °C, while the standard deviation obtained in the storage modulus in the glassy state was higher, close to 10%. For this reason, the effect of moisture uptake on the mechanical properties was studied by flexural test. In spite of the good reproducibility of  $T_g$  measurements, the  $T_g$  decreases due to the fact that the plasticization effect was small, in account of the low water absorption content. For this reason, the  $T_g$  was measured at different aging times in order to obtain the tendency, which is shown in Figure 5.



**Figure 5.** Decrease of glass transition temperature due to the water absorption.

As produced, the glass transition temperature increases by the GNPs addition in a range of 4 or 5 °C, except for the composites reinforced with GNP4, whose  $T_g$  remains constant. Again, it is worthy to note that the initial  $T_g$  value of pristine resin is very high due to its high crosslinking degree, associated to its high curing temperature (140 °C). This could be associated to the rheological percolation [5,17]. Nanofiller loads close to percolation hinder the mobility of polymer chain segments. The percolation threshold decreases with the increase of the specific surface area of nanofillers. GNP4 has lower specific surface area and higher thickness (Table 1), which implies that individual nanoparticles, due to their higher volume, are not as close as they are when using GNP1, GNP2 or GNP3 (see Figure 3c), limiting its influence on the polymer chain mobility and making glass transition temperature remain constant.

The moisture absorption induces a  $T_g$  decrease. This is the best-known consequence of the water plasticization. As was expected, the  $T_g$  decrease is more noticeable at the beginning of the aging treatment and, after that,  $T_g$  remains nearly constant. This could be related to a catalytic effect. Absorbed water molecules can form hydrogen bonds (named Type II or bonded water) with some remaining oxirane groups, enhancing a postcuring reaction. In fact, this phenomenon could explain the dispersion of glassy storage modulus values. On the other hand, the plasticization effect of water should decrease the rigidity of the matrix, enhancing the chain mobility, but the resultant postcuring reaction would increase the crosslinking degree. Each of them provokes contrary effects on the storage modulus.

The  $T_g$  of neat epoxy resin decreases 3.6 °C per each 1% in weight of moisture absorbed while this effect decreases in composites up to 2.5 °C. This means that the addition of graphene nanoplatelets shows numerous advantages related to the hydrothermal resistance: Decreasing the absorbed water content and the consequences of its plasticization.

### 3.4. Mechanical Effect

Finally, as mentioned above, the modification of mechanical properties due to hydrothermal aging was also studied by DMTA. Table 3 collects the results obtained for epoxy resin and composites reinforced with different types of graphene at different aging states. The specimens were aged during 1 and 17 days, respectively.

**Table 3.** Mechanical properties of neat epoxy resin and composites at different aging states.

	Moisture Absorption (%)	E (GPa)	$\sigma$ (MPa)	$\epsilon$ (%)
Epoxy resin	0	2.24 ± 0.24	146 ± 20	5.7 ± 1.3
	0.86	2.32 ± 0.02	137 ± 7	4.5 ± 0.2
	1.55	3.61 ± 0.44	166 ± 29	3.5 ± 0.3
GNP1/epoxy	0	4.20 ± 0.37	140 ± 10	1.9 ± 0.5
	0.92	3.94 ± 0.02	120 ± 2	2.1 ± 0.1
	1.79	3.87 ± 0.23	95 ± 3	1.9 ± 0.1
GNP2/epoxy	0	4.30 ± 0.80	111 ± 4	2.6 ± 0.4
	0.84	3.41 ± 0.05	133 ± 12	3.2 ± 0.4
	1.49	3.39 ± 0.09	127 ± 20	2.9 ± 0.3
GNP3/epoxy	0	3.52 ± 0.53	97 ± 17	2.0 ± 0.1
	0.80	3.48 ± 0.03	113 ± 2	2.4 ± 0.1
	1.49	3.42 ± 0.51	101 ± 1	2.3 ± 0.4
GNP4/epoxy	0	3.33 ± 0.0	136 ± 5	2.7 ± 0.1
	0.85	3.09 ± 0.05	93 ± 4	2.9 ± 0.2
	1.47	3.18 ± 0.16	137 ± 18	3.3 ± 0.3

The water uptake on pristine resin induces an important increase of stiffness, a slight increase of mechanical strength and a decrease of elongation. These phenomena confirm that the postcuring reaction is catalyzed by the absorbed water, increasing the crosslinking degree. However, this effect

is scarcely observed in composites. The stiffness and mechanical properties remain constant or suffer slight decreases by the moisture absorption. The decrease of mechanical properties could be associated to two different causes. Firstly, the water induces plasticization and also promotes the weak GNP-matrix interphase. Secondly, the slight increase of elongation on graphene/epoxy composite is clearly explained by the plasticization effect of the matrix.

Initially, the mechanical behavior of non-aged samples is analyzed. The graphene addition induces an important increase of stiffness in spite of the high elastic modulus of the pristine resin. The addition of 0.5% GNPs induces an increase of the elastic modulus from 2.24 GPa to 3.94 GPa (76%) for GNP1/epoxy composites. The modulus increase of the composites seems to be proportional to the specific surface area of the graphene nanoplatelets, being the highest for GNP1 (76%) and the lowest for GNP3 and GNP4 (41%). In contrast, the mechanical strength and elongation at break markedly decrease with the graphene addition. This is mainly associated with the weak interphase, which makes necessary the incorporation of functional groups in the nanofiller in order to enhance a chemical interphase with the epoxy matrix [17,18].

In contrast to the thermomechanical properties, the influence of moisture in mechanical properties of the neat epoxy resin and nanocomposites differ. In order to analyze it in depth, Figure 6 shows the variation of each flexural property as a function of the amount of absorbed moisture for neat epoxy resin and graphene/epoxy composites. In general, at the same moisture content, the mechanical properties of epoxy resin are significantly influenced by the presence of water in the network while the ones of composites are slightly influenced. Similar behavior was observed in the water uptake effect on the glass transition temperature. As mentioned above, the addition of graphene nanofillers induces a molecular mobility restriction, reducing the water uptake. This hindering of intermolecular movements could also cause the water effect to be lower in the composites. One issue to take into account is that, due to the presence of microcavities between nanoplatelets and the epoxy matrix, water molecules can diffuse and locate at the interphase of the nanoplatelets. This preferential location induces a lower effectiveness in the load transfer [19], which is the reason for the differences observed.

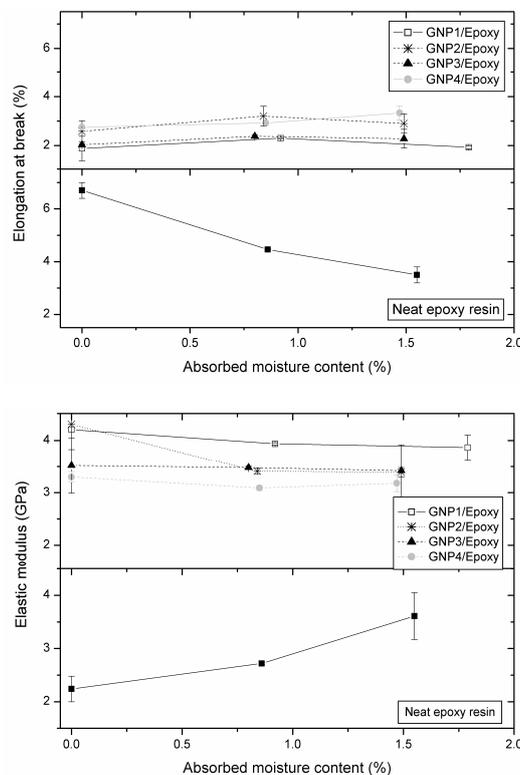
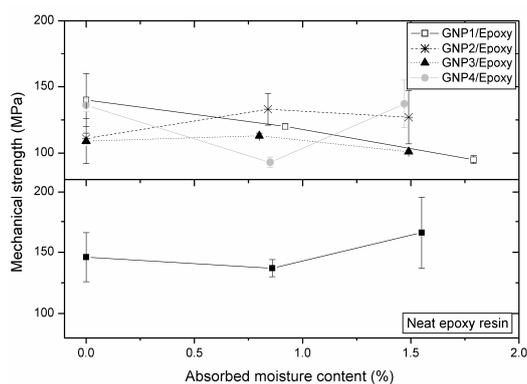


Figure 6. Cont.



**Figure 6.** Variation of mechanical properties due to the water absorption.

#### 4. Conclusions

The barrier properties of graphene nanoplatelets, used as nanoreinforcement into epoxy composites, strongly depend on their geometry: Their thickness and lateral dimensions. In general, an increase of the specific surface area induces an increase of hydrothermal resistance of the composite when the nanofiller dispersion is suitable. Thinner nanoplatelets usually are not totally stretched and thus, remaining partially wrinkled, decreasing their efficiency as water barrier elements. The addition of GNPs into epoxy resins has several advantages against moisture absorption: A decrease of the maximum water content, the diffusion coefficient and even the mentioned catalytic effect of absorbed water in which hydrogen bonds are formed. In fact, mechanical and thermal properties suffer variation of less significance by the water entrance in the epoxy network than those of pristine resin.

The addition of GNPs to the epoxy resin reduces the common phenomenon observed in pristine epoxy resin, mainly the plasticization and catalyst effect of postcuring reaction due to the formation of hydrogen bonds between water molecules and residual oxirane rings. This effect has been attributed to mobility restriction of molecular chain segments due to the presence of the nanofillers.

**Author Contributions:** S.G.P. contributed to article writing, funding support, design of experiments and analysis of results. A.J.-S. contributed to article reviewing, design of experiments, test performing and analysis of results. R.M. contributed to article reviewing, design of experiments, test performing and analysis of results. A.U. contributed to funding support for this research and research supervision.

**Funding:** This research was funded by Ministerio de Economía y Competitividad of Spain Government (Project MAT2016-78825-C2-1-R) and Comunidad de Madrid (Project P2013/MIT-2862).

**Acknowledgments:** The authors wish to thank the Ministerio de Economía y Competitividad of Spain Government (Project MAT2016-78825-C2-1-R) and Comunidad de Madrid (Project P2013/MIT-2862).

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Saravanan, N.; Rajasekar, R.; Mahalakshmi, S.; Sathishkumar, T.P.; Sasikumar, K.S.K.; Sahoo, S. Graphene and modified graphene-based polymer nanocomposites—A review. *J. Reinf. Plast. Compos.* **2014**, *33*, 1158–1170. [[CrossRef](#)]
2. Mohd Zulfli, N.H.; Abu Bakar, A.; Chow, W.S. Mechanical and water absorption behaviors of carbon nanotube reinforced epoxy/glass fiber laminates. *J. Reinf. Plast. Compos.* **2013**, *32*, 1715–1721. [[CrossRef](#)]
3. Kingston, C.; Zepp, R.; Andrady, R.; Boverhof, D.; Fehir, R.; Hawkins, D.; Roberts, J.; Sayre, P.; Shelton, B.; Sultan, Y.; et al. Release characteristics of selected carbon nanotube polymer composites. *Carbon* **2014**, *68*, 33–57. [[CrossRef](#)]
4. Guadagno, L.; De Vivo, B.; Di Bartolomeo, A.; Lamberti, P.; Sorrentino, A.; Tucci, V.; Vertuccio, L.; Vittoria, V. Effect of functionalization on the thermo-mechanical and electrical behavior of multi-wall carbon nanotube/epoxy composites. *Carbon* **2011**, *49*, 1919–1930. [[CrossRef](#)]

5. Satarkova, O.; Chandrasekaran, S.; Prado, L.A.S.A.; Tölle, F.; Mülhaupt, R.; Schulte, K. Hydrothermally resistant thermally reduced graphene oxide and multi-wall carbon nanotube based epoxy nanocomposites. *Polym. Degrad. Stab.* **2013**, *98*, 519–526. [[CrossRef](#)]
6. Satarkova, O.; Buschhorn, S.T.; Mannov, E.; Schulte, K.; Aniskevich, A. Water transport in epoxy/MWCNT composites. *Eur. Polym. J.* **2013**, *49*, 2138–2148. [[CrossRef](#)]
7. Liu, W.; Hoa, S.V.; Pugh, M. Water uptake of epoxy–clay nanocomposites: Model development. *Compos. Sci. Technol.* **2008**, *68*, 156–163. [[CrossRef](#)]
8. Guadagno, L.; Vertuccio, L.; Sorretino, A.; Raimondo, M.; Naddeo, C.; Vitoria, V. Mechanical and barrier properties of epoxy resin filled with multiwalled carbon nanotubes. *Carbon* **2009**, *47*, 2419–2430. [[CrossRef](#)]
9. Prolongo, S.G.; Gude, M.R.; Ureña, A. Water uptake of epoxy composites reinforced with carbon nanofillers. *Compos. Part A* **2012**, *43*, 2169–2175. [[CrossRef](#)]
10. Alamri, H.; Low, I.M. Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites. *Mater. Des.* **2012**, *42*, 214–222. [[CrossRef](#)]
11. Perrin, F.X.; Nguyen, M.H.; Vernet, J.L. Water transport in epoxy–aliphatic amine networks – Influence of curing cycles. *Eur. Polym. J.* **2009**, *45*, 1524–1534. [[CrossRef](#)]
12. DeNève, B.; Shanahan, M.E.R. Water absorption by an epoxy resin and its effect on the mechanical properties and infra-red spectra. *Polymer* **1993**, *34*, 5099–5105. [[CrossRef](#)]
13. Moriche, R.; Prolongo, S.G.; Sánchez, M.; Jiménez-Suárez, A.; Sayagués, M.J.; Ureña, A. Morphological changes on graphene nanoplatelets induced during dispersion into an epoxy resin by different methods. *Compos. Part B* **2015**, *72*, 199–205. [[CrossRef](#)]
14. Prolongo, S.G.; Jiménez-Suárez, A.; Moriche, R.; Ureña, A. Graphene nanoplatelets thickness and lateral size influence on the morphology and behavior of epoxy composites. *Eur. Polym. J.* **2014**, *53*, 292–301. [[CrossRef](#)]
15. Liu, S.; Yan, H.; Fang, Z.; Wang, H. Effect of graphene nanosheets on morphology, thermal stability and flame retardancy of epoxy resin. *Compos. Sci. Technol.* **2014**, *90*, 40–47. [[CrossRef](#)]
16. Crank, J. *The Mathematic of Diffusion*; Clarendon Press: Oxford, UK, 1956.
17. Choudalakis, G.; Gotsis, A.D. Free volume and mass transport in polymer nanocomposites. *Curr. Opin. Colloid Interface Sci.* **2012**, *17*, 132–140. [[CrossRef](#)]
18. Ahmadi-Moghadam, B.; Sharafimasooleh, M.; Shadlou, S.; Taheri, F. Effect of functionalization of graphene nanoplatelets on the mechanical response of graphene/epoxy composites. *Mater. Des.* **2015**, *66*, 142–149. [[CrossRef](#)]
19. Tam, L.; Wu, C. Molecular Mechanics of the Moisture Effect on Epoxy/Carbon Nanotube Nanocomposites. *Nanomaterials (Basel)* **2017**, *7*, 324. [[CrossRef](#)] [[PubMed](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).