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Advantages and disadvantages of the addition of graphene nanoplatelets to epoxy resins

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A B S T R A C T

Graphene nanoplatelets (GNPs), in different contents, are added to epoxy resin. This work mainly consists of a deep characterization of the composites in order to evaluate their behavior regarding neat epoxy resin. In fact, their main properties, such as their morphological features, their thermo-mechanical and mechanical properties, their electrical conductivity and thermal diffusivity, their hydrophobic behavior and their barrier properties have been studied. It is confirmed that the GNP addition induces an important stiffing of thermosetting resin. However, the rest of mechanical properties, strength and elongation, are diminished due to a weak interface formed between the epoxy matrix and non-functionalized GNPs. The electrical conductivity and thermal diffusivity show an important increase. Electrical conductivity increases several orders of magnitude from a minimum value of percolation while the thermal diffusivity increases proportionally to GNP content. Other advantage of the GNP addition is the increase of the hydrophobic behavior of the composites, determined by measurements of contact angle of water drops. Finally, GNP/epoxy composites present higher barrier properties in humid environments. The addition of GNP decreases the maximum water content absorbed and the diffusion coefficient. However, this enhancement is not too large due to the weak interface and therefore the presence of hollows in the GNP/epoxy composites.

1. Introduction

Polymer composites reinforced with carbon nanofillers have been widely studied during the last decade [1–3]. The addition of carbon nanotubes or nanofibers into thermosetting resins can improve the mechanical and thermal properties, together with an increase of the electrical conductivity. The industrial application of these materials is mainly limited by two factors: the poor dispersion of nanofillers, which implies the need of complex procedures of dispersion, and the high cost of carbon nanotubes. Both aspects cause an excessive price increase, which does not compensate the enhancement of properties on numerous occasions. Recently, the use of graphene nanoplatelets (GNP) as nanofiller is being studied. The main advantage is their low cost regarding to that one of carbon nanotubes. This is due to a lower manufacturing cost.

Their stiffness, two-dimensional geometry and low thermal interface resistance make graphene a successful filler to manufacture composite materials with improved thermal conductivity [4–6]. In addition, their planar geometry should induce a substantial improvement of the barrier properties and hydrothermal resistance of the composites. Their effect on the mechanical and electrical properties is not clear yet. For this reason, this work constitutes a deep study of the properties and behavior of epoxy composites reinforced with GNPs in order to clarify their main advantages and disadvantages.

Graphene nanoplatelets can present very different geometric features as a function of the size and number of atomic layers. These characteristics significantly modify

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their aspect ratio and specific surface area [7]. As it is known, a higher specific surface area should induce a higher properties enhancement with a lower amount of nanofiller if a good dispersion is achieved. Large surfaces result in large van der Waals forces and strong π–π interactions, which usually induces problems in the dispersion stage [8]. Very thin nanoplatelets with low amount of graphitic sheets usually are more expensive and tend to self-roll. In this work, the authors have selected GNP with an intermediate geometry. Their thickness is 6 nm, corresponding to 18 graphitic sheets, and its lateral size is 25 μm, generating a relative low specific surface, 120–150 m^2/g. This reduces possible dispersion problems and avoids large increases of the viscosity of non-cured nanoreinforced resins. Thinner and larger GNPs could cause higher enhancement of some properties of composites but also they would induce more problems during manufacturing process.

In this work, we investigate the influence of the amount of graphene nanoplatelets on numerous aspects of the materials behavior, such as their mechanical properties, maximum service temperature and electrical and thermal conductivities. The hydrophobicity is also determined and chemical resistance in aggressive humid environmental. The main objectives are to confirm which are the main advantages of adding graphene into epoxy resins, and additionally, to determine which are the optimum GNPs contents as a function of the expected enhancement. It is worthy to note that the conclusions obtained in this work will be useful for similar systems while a significant modification of the geometry of the nanoplatelets could affect to the final properties of the composite.

2. Experimental

2.1. Materials

Graphene nanoplatelets (GNPs) were supplied by XGScience, with the commercial name of M25. Their purity was higher than 99.5% w/w. The average flake thickness was 6 nm and the average lateral particle size was 25 μm. The epoxy resin is based on Diglycidyl Ether of Bisphenol A cured with an aromatic amine. It was manufactured by Araldite with the commercial name of Araldite LY556 (epoxy monomer) and XB3473 (amine hardener).

2.2. Sample preparation

GNP dispersion on non-cured resin was carried out through a combination of different dispersion techniques [9]. First, an ultrasonication process was applied for 45 min with a sonicator probe UP400S from Hielscher company. The cycle was 0.5 s, the sonication power was 400 W and the amplitude was 50%. Then, the mixture was treated in a three-roll miller (Exakt 80E GmbH) [4,5,10]. The rolling speed was 250 rpm and the gap size between each pair of rolls was 5 μm. The calendering process was applied four consecutive times. The time of each mill-rolling cycle was approximately 5 min. Afterwards, the dispersed GNP/epoxy mixture was degassed in vacuum at 80 °C for 15 min. Then, the hardener was added in a 100:23 (LY556:XB3473) stoichiometric ratio at 80 °C. The curing treatment consisted of heating at 140 °C for 8 h. The cured samples were cooled slowly to room temperature inside the oven. The studied contents of GNPs added were 1.5; 2.0; 3.0; 5.0 and 8.0 wt%.

2.3. Measurements

The characterization of composites consisted of the analysis of their main morphological features, the determination of their thermal and mechanical properties, the measurement of the electrical and thermal conductivities, the study of their hydrophobicity and also the determination of their behavior during hydrothermal ageing.

The morphology of isolated GNPs was observed by High Resolution Transmission Electron Microscopy (TEM, Philips CM200) while the morphology of composites was determined by Scanning Electron Microscopy (Hitachi 2400-N). The samples of composite were cut by cryo-ultramicrotomy (Leica) and coated with a thin Pt layer (~2 nm).

Thermomechanical behavior was studied by Dynamic Mechanical Thermal Analysis (DMTA, Q800 V7.1 from TA Instruments) in a single cantilever bending mode. The experiments were carried at 1 Hz frequency, scanning from 20 to 250 °C using a heating rate of 2 °C/min. The dimensions of samples were $35 \times 12 \times 1.5$ mm^3. The maximum of $\tan\delta$ vs. temperature plots was used to identify the α-relaxation associated to the glass transition.

The mechanical properties were determined by flexural test in a universal machine (Instron 4465), following the ASTM D-790 at a crosshead speed of 0.8 mm/min. The fracture surfaces were also covered with Au (Pd) and observed by SEM in order to study the fracture mechanisms. In order to confirm the mechanical properties of composites, some materials were also tested by tensile test. The tensile tests were carried out, following the ASTM D638 standard, to measure the tensile strength, the Young's modulus, and the deformation at break in the epoxy resin and several composites reinforced with different GNPs contents. Type I specimens with $13 \times 3 \times 57$ mm^3 in the narrow section were tested on an electromechanical testing machine (MTS Alliance RF/100), under displacement control at a crosshead speed of 1 mm/min. The strain was measured during the tests with an extensometer attached to the sample (model MTS 654-12F).

The electrical conductivity was measured following the standard ASTM D257. A Source-Meter Unit instrument (KEITHLEY 2410, Keithley Instruments) connected through an interface GPIB to a PC was used. The electrical resistance was determined by calculating the slope of the current–voltage characteristic curve, from which can be determined the electrical conductivity taking into account the geometry of specimens ($10 \times 10 \times 1$ mm^3).

The thermal diffusivity was measured with Laserflash LFA 457 MicroFlash equipment, applying a temperature scan from 20 to 200 °C.

The hydrophobicity of composites was determined by measurements of the contact angle of water. The contact angle was measured with a goniometer equipped with a camera and video monitor (Ramé-Hart 200 mod. p/n 200-F1). Water drops of 0.3 ml were carefully placed on the substrate with a microlitre syringe. The obtained contact angle was the average value of ten measurements, at left and right sides, of two drops for each liquid.

Finally, the hydrothermal resistance was measured by immersion in water at 80 °C. Prior to ageing, the weight of each sample was determined. During the period of ageing study, gravimetric measurements were performed on balance (Mettler Toledo AX205) with a measurement precision of 10^{-5} g. At selected times, different samples were removed from the chamber, dried superficially and cooling to ambient temperature prior to their characterization. Two specimens were measured per composition, confirming that the maximum error of the measurement was lower than 0.08%.

3. Results and discussion

The GNPs morphology was determined by TEM. The geometry of as received nanoplatelets was observed. In addition, in order to evaluate the influence of dispersion procedure in the geometry or morphology of the nanofiller, GNP/epoxy mixtures were subjected to repetitive washing cycles with acetone to remove the epoxy monomer. The main objective of this study is to analyze the appearance of structural defects on the sheets or the exfoliation phenomena due to the dispersion procedure applied. Also, the spatial distribution of the sheets is evaluated, to study different phenomena, such as stacking, rolling or curling. Fig. 1 shows some selected TEM images. Fig. 1a confirms that the GNPs thickness is several nanometers, in accordance with the data supplied by the manufacturer. The comparison of micrographs 1a, 1c and 1e allows confirming that the exfoliation phenomenon does not occur, since the nanoplatelets present similar thickness after the dispersion by sonication and calendering. However, it is possible to affirm that the sonication seems to induce the self-twining of the sheets (Fig. 1d). This effect tends to disappear during the calendering because the nanoplatelets are again stretched (Fig. 1e). The two dispersion techniques, calendering and sonication, are commonly used in the dispersion of carbon nanotubes. In this work, it is confirmed that both allow obtaining good dispersion of GNPs in epoxy composites but there are not exfoliation phenomena. More aggressive conditions and longer times of sonication could induce exfoliation.

Fig. 2 shows DMTA results, confirming that the stiffness of the epoxy resin increases by the addition of GNPs [11,12] when the GNPs content added is higher than 2 wt%. Considering the error bars, the addition of low GNPs contents does not seem to affect the storage modulus of epoxy resin. Even, the addition of 2 wt% GNPs could induce a slight decrease of this property. This could be explained by the low amount of nanoreinforcement added, their relative low specific surface area (in comparison with other nanoreinforcements, i.e. carbon nanotubes) and the weak interface between the GNPs and matrix due to the fact the GNPs are not functionalized. The tendency changes at relative high GNPs content. An increase of GNPs content from 2 to 3, 5 and 8 wt% induces a proportional increase of the storage modulus. The increase of the modulus reaches 38% regarding the one of neat epoxy resin for the composite doped with 8% GNPs. Higher GNPs contents are not studied in this work because of the difficulty to manufacture suitable composites due to the increase of viscosity. The glass transition temperature remains constant. The graphene nanoplatelets have not any significant effect on the glass transition of the matrix.

The mechanical properties were determined by flexural test and they are shown in Fig. 3. The flexural modulus of composites are similar to the modulus of the neat epoxy resin (E = 2.7–2.9 GPa). However, the obtained values for mechanical strength and maximum deformation are significantly lower than those supplied by the manufacturer for the neat epoxy resin (σ = 110–120 MPa; ε = 5.5–6.5%). In order to confirm these results, the neat epoxy resin and composites reinforced with 2 and 3 wt% were also analyzed by tensile test. The tensile modulus remains constant or slightly increases, from 2.28 ± 0.09 GPa for pure resin to 2.54 ± 0.07 for composite reinforced with 3 wt% GNPs. However, the tensile strength and elongation at break decrease from 75 ± 5 MPa and 4.7 ± 0.8% for neat epoxy resin to 58 ± 2 MPa and 3.7 ± 0.3 for GNP/epoxy composite.

This means that the addition of GNPs induces a deterioration of the mechanical behavior of the thermosetting resin, being the main disadvantage found for these materials. The main reason is the low interaction between the graphitic sheets and the matrix, generating a very weak interface [13]. This weak interface prevents the load transfer from matrix to nanofiller. For this reason, the nanofillers act as stress concentrators, causing the significant decrease of the mechanical properties of the GNP/epoxy composites. In order to avoid this effect, it is necessary to enhance the interaction between the graphene nanoplatelets and the matrix [13–15]. This can be reached by the functionalization of the nanofiller. Raza et al. [13] found the same behavior for GNP/silicone composites manufactured by three roll mill, observing an increase of the modulus but an important decrease of mechanical strength and strain by compression test. Their justification is the lack of continuous matrix enabling sliding between overlapping GNPs and the subsequent crack initiation at the interface between the GNPs and the matrix. In order to confirm this limitation, the fracture surfaces of tested specimens were observed by SEM. Fig. 4a and b shows micrographs at relative high magnifications, where the lack of adhesion between the epoxy matrix and the nanofiller is marked with red narrows. In addition, although most of nanoplatelets are stretched (Fig. 3a), some nanoplatelets can be found bent, which decreases their effectiveness as mechanical reinforcement. The main approach to solve this GNPs limitation as mechanical reinforcement is their functionalization or the use of graphene oxide. Tang et al. [14] proposed epoxy composites reinforced with grafted epoxy chains into oxide graphene. In this case, the interface was stronger and the mechanical properties of composites widely increased regarding to the neat resin. T. Wang [15] used graphene oxide as nanofiller. They confirmed the strong interfacial interaction between the graphene oxide and the matrix, obtaining an important increase in mechanical properties of composites. In fact, the

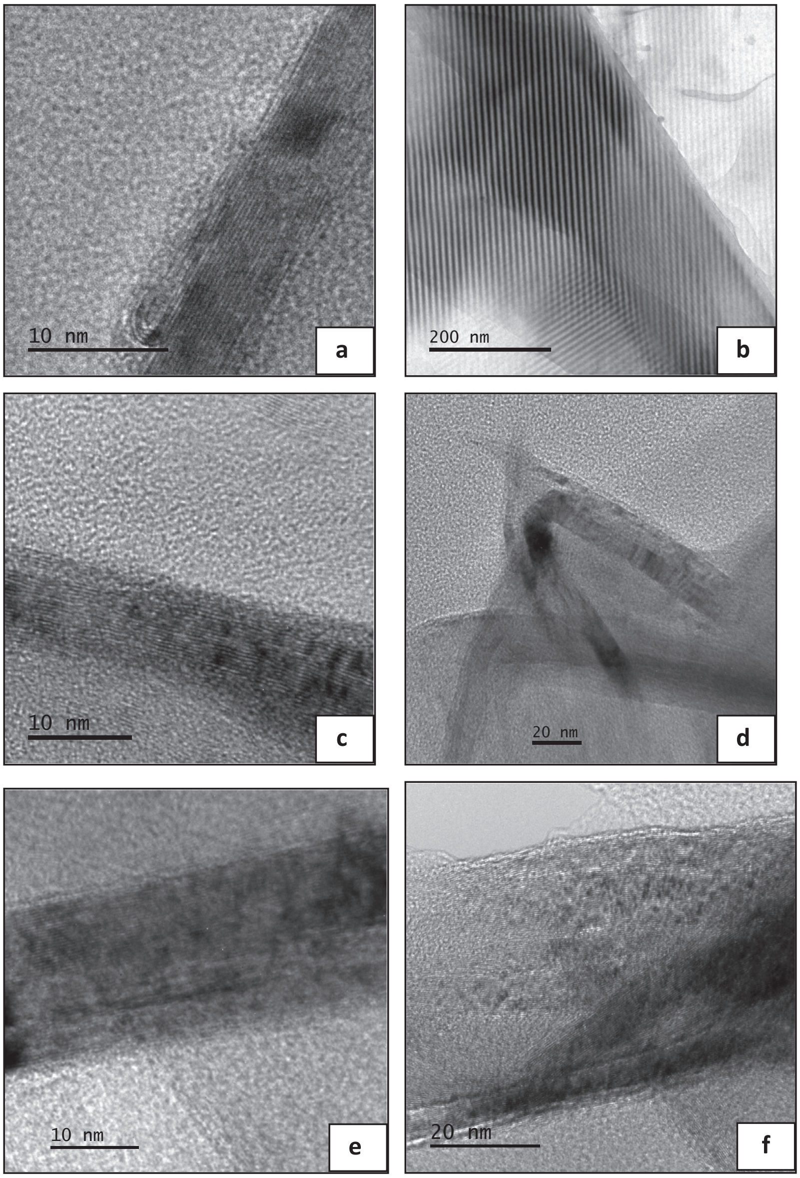

Fig. 1. TEM images of graphene nanoplatelets: (a and b) as received ones; (c and d) after sonication and (e and f) after sonication and calendering process.

observation of the fracture surfaces showed that the main fracture mechanism implied was interfacial debonding of graphene oxide. Young [16] studied the role of functional groups on the surface of graphene oxide upon its ability to reinforce an epoxy resin. The best levels of reinforcement were found with the addition of low loadings of graphene oxide with high concentration of functional groups due to the good interfacial stress transfer in the nanocomposites. However, both approaches present important limitations for the electrical behavior of the composites. On one hand, graphene oxide is electrically insulator. On the other hand, the formation of a strong interface between the functionalized electrically conductive nanofiller and the polymer matrix usually induces a decrease of the electrical conductivity of the final composite due to the insulating polymer coating around the nanofiller. Also, the functionalization of graphene nanofillers usually induces structural defects decreasing the intrinsic electrical conductivity of nanofiller.

With the exception of neat epoxy resin, the mechanical properties of composites present a clear tendency as a function of the GNPs content. As it was already mentioned above, the stiffness of composites increases with the increase of GNPs content. In contrast, the deformation ability slightly decreases with the GNPs percentage added. This stiffening is associated to the large modulus of the graphene. The mechanical strength of composites increases with the GNPs content up to 3 wt%, while higher percentages of GNPs induces a slight decrease. This behavior is common on the composites reinforced with

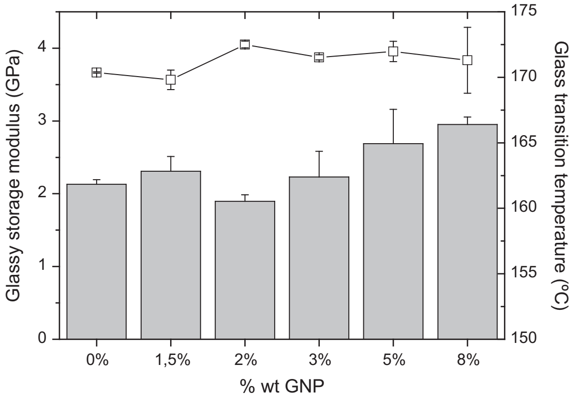

Fig. 2. DMTA results of GNP/epoxy composites: storage modulus in glassy stage (bars graph) and glass transition temperature (graph of symbols and line).

nanofillers and it is associated to dispersion problems. At high contents of nanofiller, the dispersion degree of composites decreases, appearing agglomerations. These aggregations act as stress concentrators, decreasing the mechanical properties of the composites.

Fig. 4 shows SEM micrographs of fracture surfaces of tested specimens with different GNPs content. In contrast with the fracture surfaces of neat epoxy resin, the surfaces of composites are rough, indicating toughening. As it is well known, thermosetting resins are brittle and the addition of stiff and resistant nanoreinforcements induces the appearance of the fracture mechanism of crack deviation. This generates numerous fracture rivers which grow in different planes. The graphene nanoplatelets effectively disturbed and deflected the crack propagation due to its two dimensional structure [11]. Unfortunately, this fracture mechanism does not induce a toughening of composites due to the weak interface. In fact, some hollows or regions with poor adhesion can be observed in the micrographs of the composites. As it is expected, greater number of smaller fracture flakes appears as a function of GNPs content. Although the fractography is similar for all studied composites, it is possible to observe that the roughness of the fracture surfaces increases with the GNPs content of the composite. This implies that the nanoplatelets acts hindering the crack propagation and inducing crack deviation.

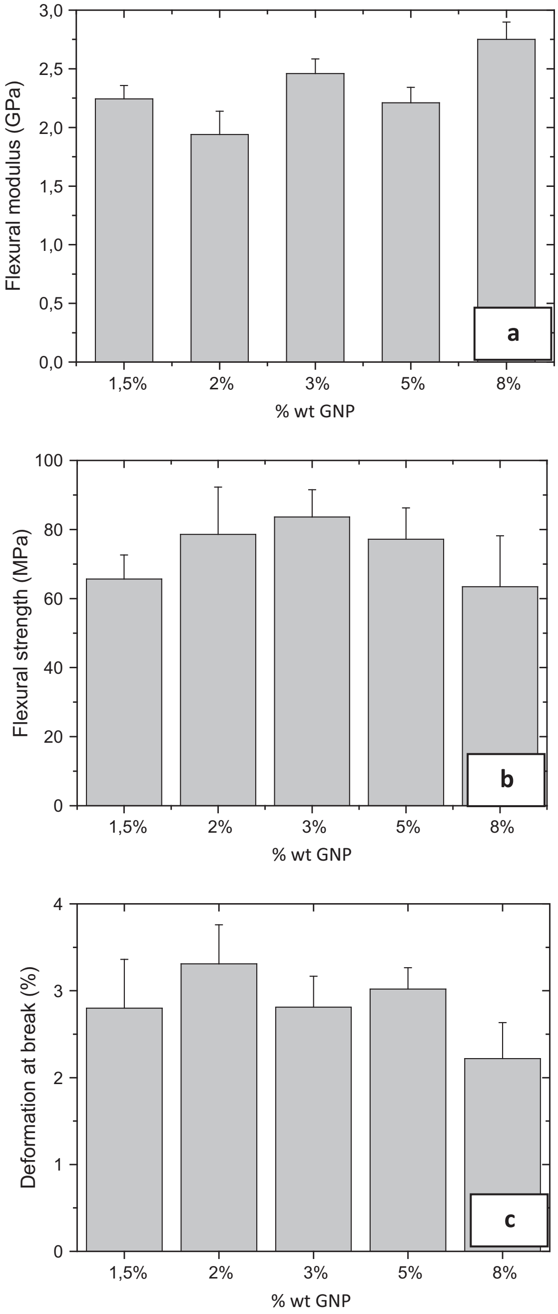

Fig. 3. Mechanical properties of GNP/epoxy composites: (a) flexural modulus; (b) flexural strength; (c) deformation at break.

Following the full characterization of GNP/epoxy composites, the electrical conductivity and thermal diffusivity were also measured. The results are shown in Fig. 5. The thermal diffusivity was measured at two different temperatures, 28 and 137 °C. As it is expected, the addition of low amounts of graphene nanoplatelets scarcely implies variations on the electrical conductivity of composites. In fact, the percolation threshold is close to 5 wt% GNPs. This is the value at which the electrical conductivity of composite increases several orders of magnitude. This threshold value is higher than the reported ones for epoxy composites reinforced with carbon nanotubes, whose threshold is in the range of 0.05–0.1 wt% [17,18]. This is due to the higher specific surface of carbon nanotubes and their higher aspect ratio. Both characteristics allow getting the percolation at lower contents of nanofiller. The thermal diffusivity also increases by the addition of graphene nanoplatelets but the tendency is different. In the case of thermal diffusivity, there is not a minimal value of percolation. This parameter increases proportionally to the GNPs percentage added [4,19,20]. The increase of electrical conductivity of composites, close to 5 wt% GNPs, is less clear in the case of the thermal diffusivity. This is because thermal diffusivity does not require the formation of a GNPs network. In addition,

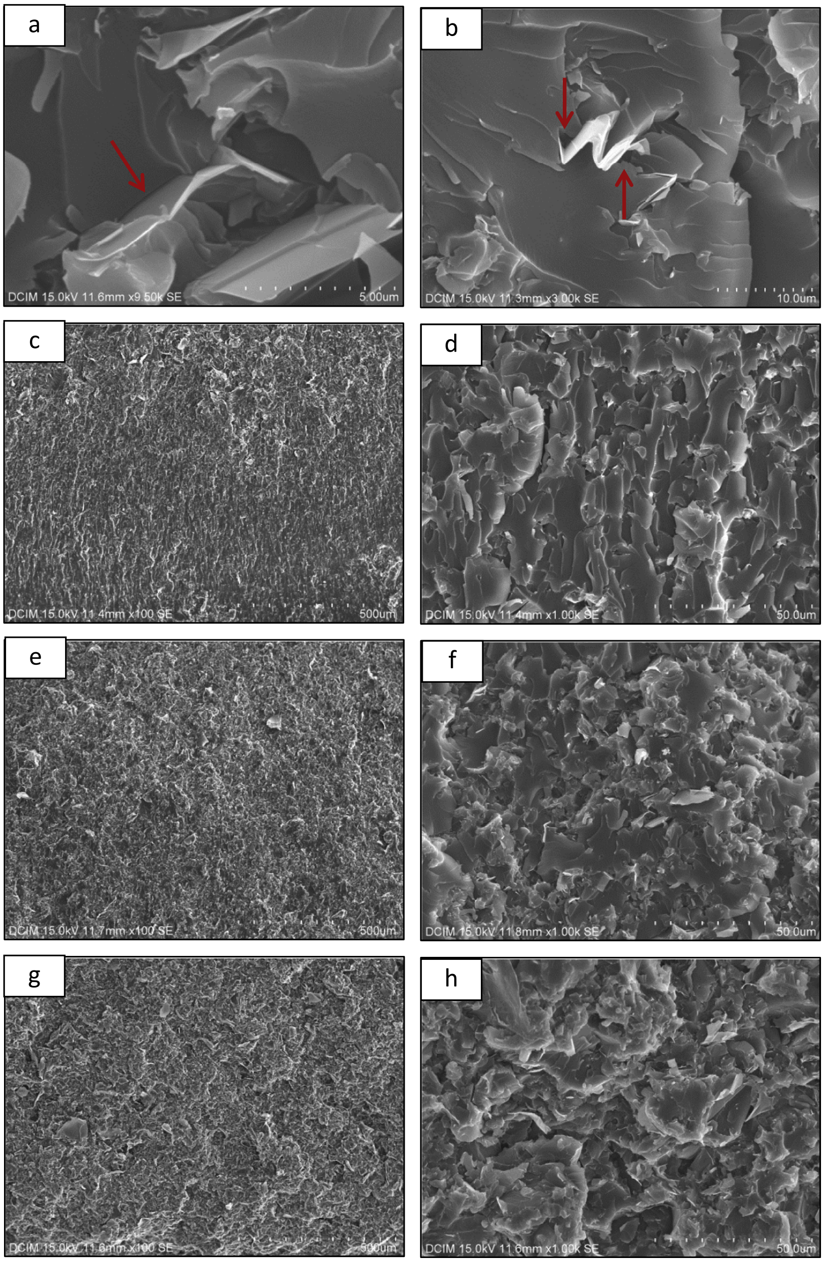

Fig. 4. SEM micrographs of fracture surfaces of GNP/epoxy composites at high resolution (a and b) and different GNP content: 1.5 wt% (c and d); 3.0 wt% (e and f) and 8 wt% (g and h).

the thermal diffusivity increases several times regarding to neat epoxy resin. In fact, this increase is close to 210% for the composite reinforced with 8 wt% GNPs. This is one of the main advantages of the addition of graphene compared to other graphitic nanoreinforcement, such as carbon nanotubes or nanofibers. This is due to the excellent thermal conductivity of graphene. Thermal diffusivity was measured at two different temperatures, confirming that the enhancement of thermal diffusivity by GNPs addition occurs at room temperature and higher temperatures. As it is expected, the thermal diffusion is lower at higher temperature. However, the tendency is similar. The thermal diffusivity increases proportionally to the GNPs content. This means that there is not any change in the thermal transport mechanism. This is due to the fact that the highest temperature is 137 °C, which is lower than the glass transition temperature of the epoxy matrix (close to 172 °C, Fig. 2). The obtained results also allow confirming that the increase of thermal diffusivity of composites due to the GNPs addition is more effective at room temperature.

An interesting characteristic of graphene is its high hydrophobicity [21]. In order to analyze the hydrophobicity

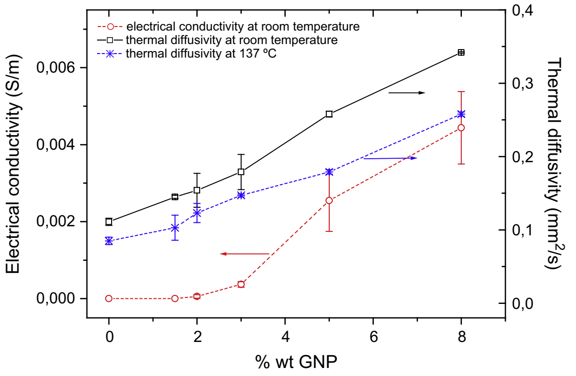

Fig. 5. Electrical conductivity and thermal diffusivity of GNP/epoxy composites.

of composites, the contact angle of the water drop is measured over the surface of GNP/epoxy composites. The obtained values are collected in Fig. 6. As it is clearly appreciated, the GNPs addition induces an important increase of the hydrophobicity of composites. In fact, the common classification of materials as a function of their hydrophilicity and hydrophobicity is: (1) superhydrophilic material, when the contact angle of water is close to 0° and lowers than 30°; (2) hydrophilic material, when the range of water contact angle is from 30° to 90°; (3) hydrophobic materials, when the water contact angle is higher than 90° and (4) superhydrophobic materials, when the water contact angle is higher than 150°. In our case, the neat epoxy resin is a hydrophilic material because the contact angle of water over their surface is 70° while the addition of GNPs induces hydrophobicity. The contact angle of water over GNP/epoxy composites is in the range of 92–104°.

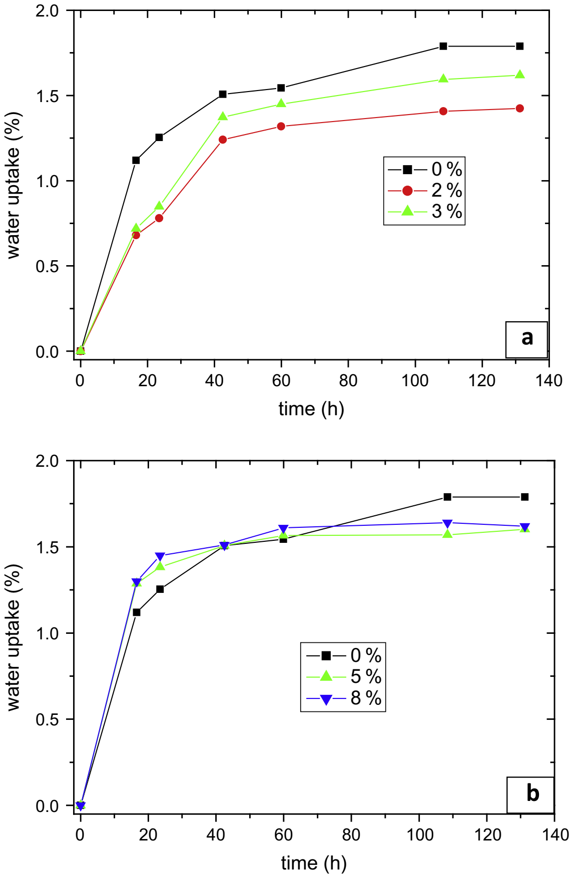

Fig. 7. Curves of water uptake in water immersion at 80 °C for neat epoxy resin and composites with relative low GNP content (a) and high GNP content (b).

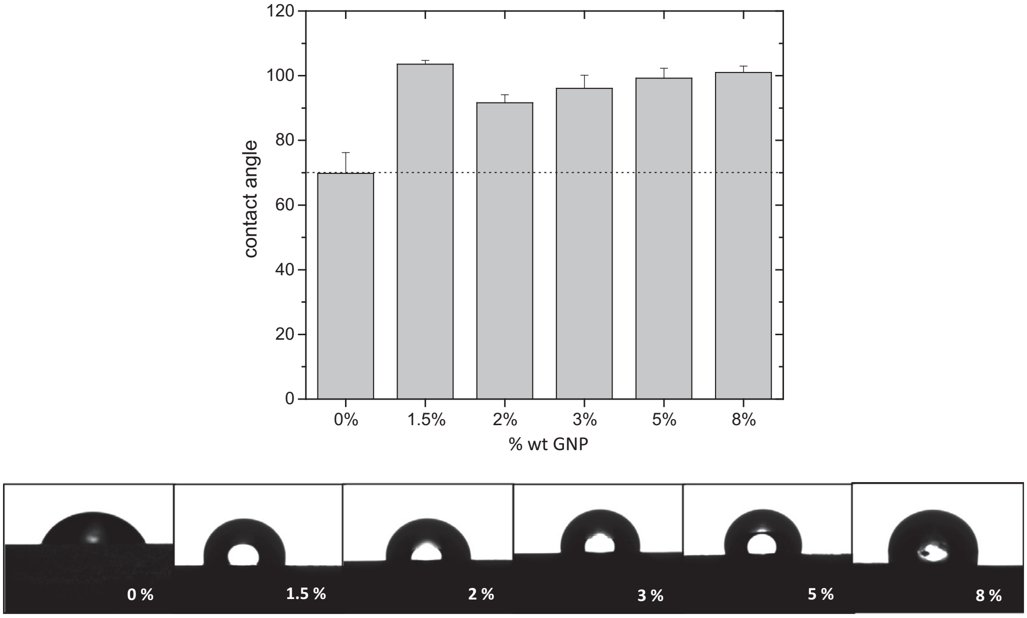

Fig. 6. Contact angle of water drops over GNP/epoxy composites as a function of GNP percentage.

The higher hydrophobic behavior of GNP/epoxy composites can imply a higher chemical strength in humid environmental [22]. For this reason, in order to complete the characterization of GNP/epoxy composites, the samples were suggested to hydrothermal ageing. The main objective is to analyze the barrier properties, since the planar geometry of graphene nanoplatelets should enhance this property. The water uptake curves are shown in Fig. 7. The maximum water content absorbed decreases for GNP/epoxy composites regarding the neat thermosetting resin. This is justified by the increase of their hydrophobicity. However, the behavior is not proportional to the GNPs content. At low GNP contents added, the maximum water percentage absorbed varies from 1.78% for neat resin to 1.42% for composite reinforced with 2 wt% GNPs. This is associated to the presence of barriers of graphene since the diffusion coefficient, measured as the initial slope of the curve, also decreases. However, the maximum water absorbed increases up to 1.60–1.62%, for the rest of studied composites. In fact, at higher GNPs content, the diffusion coefficient of the composites is similar to the one of neat resin. This behavior is associated to the weak interface between the polymer matrix and the nanofiller, generating holes, where the water can be trapped. This means that the addition of graphene nanoplatelets has two contrary effects for the water uptake: decreasing it due to the barrier properties and the hydrophobicity and increasing it due to the presence of holes.

4. Conclusions

This work consists in a deep characterization of GNP/epoxy composites. The main goal is to confirm the main advantages and disadvantages of adding graphene nanoplatelets into thermosetting resins. It is worthy to note that the manufactured composites studied contain well dispersed non-exfoliated graphene nanoparticles. The conclusions are summarized as a function of the effects of GNPs addition on the main properties of composites:

(1) The glass transition temperature remains constant by the GNPs addition.
(2) The storage modulus in glassy state is significantly increased by the addition of relative high GNPs content. In fact, the increase of GNPs content induces higher stiffening of composites.
(3) The mechanical strength and deformation at break of composites is much lower than the ones of neat epoxy resin due to the poor interface between the nanofiller and matrix.
(4) The electrical conductivity presents an important increase of several orders of magnitude when the GNP content added reaches the percolation threshold. The percolation concentration is close to 5 wt%, much higher than the published ones for carbon nanotubes. This is due to the lower specific surface area and different aspect ratio.
(5) The thermal diffusivity of GNP/epoxy composites is much higher than the one of the neat resin. Additionally, this value increases proportionally to the GNPs content. There is not a critical percolation threshold because the formation of network is not required.
(6) GNP/epoxy composites are hydrophobic materials, in contrast to the neat epoxy resin which presents hydrophilic behavior. For this reason, the water uptake is lower for composites regarding the neat thermosetting polymer. However, the decrease of water absorption is limited due to the poor graphene–epoxy interface, which generates the presence of voids.

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