HYDROTHERMAL AGEING OF GRAPHENE/CARBON NANOTUBES/EPOXY HYBRID NANOCOMPOSITES

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ABSTRACT

The hydrothermal ageing of hybrid nanocomposites formed by carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) incorporated into an epoxy matrix was studied. In order to avoid the weak interface, amine functionalized GNPs were used which are reactive with the epoxy matrix. The content of CNTs was 0.1 wt% and the GNPs content ranged from 5 to 12 wt%. The isothermal water absorption was measured until very long times (almost two years). Reduction of water absorption with the addition of either carbon nanotubes or graphene nanoplatelets has been found independently of the ageing time. The results can be described by a two-stage diffusion model with the first and second stages being diffusion and matrix relaxation controlled respectively. The obtained diffusion coefficient for the neat epoxy thermoset is higher than those of nanocomposites, which decreases with the increase of GNPs content. The effect of water absorbed on the dynamic-mechanical properties and on the electrical conductivity of the nanocomposites was analyzed. Whatever the temperature the storage modulus shows a continuous increase with the increase of the nanoparticles content, the effect of hydrothermal ageing is to decrease the modulus only in the glassy state ($T < T_g$). Water aged specimens show broadening of the $\tan\delta$ peak related to the plasticization of the matrix. T_g of aged specimens coincides with the one of the unaged matrix, indicating that hydrothermal ageing does not produce noticeable matrix damage even after two years. Water aged specimens show similar electrical conductivity than unaged ones, which is another indication of no degradation of samples by water.

Key words: epoxy, graphene, carbon nanotubes, water ageing, diffusion coefficient, two stage diffusion, thermo-mechanical and electrical properties.

1. Introduction

Nanocomposites formed by polymer matrices with graphitic nanofillers are a new class of materials with interesting properties. Carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) are one and two dimensional nanofillers that are used in polymer nanocomposites to improve mechanical properties, thermal and electrical conductivity among other properties [1-4]. Graphene nanoplatelets also provide low permeability, being available at relatively low cost compared to CNTs. On the other hand, carbon nanotubes dispersed in polymer matrices achieve electrical conductivity percolation threshold at very low concentrations.

Few works have been carried out to investigate the effects of combining CNTs and GNPs as fillers of epoxy matrices, although the combination of GNPs and CNTs in a polymer matrix to form hybrid nanocomposites offers the opportunity to obtain new materials. Making hybrid nanocomposites is aimed to reach synergistic effects between GNPs and CNTs. Most of the research published works on epoxy hybrid nanocomposites refer increment of mechanical properties [1, 4-9] and some of them show a synergic increase by the joint addition of CNTs and GNPs [1, 6-8]. The improvement of properties is attributed to the formation of an interconnected network in which the carbon nanotubes create bridges between the graphene nanosheets [1,5]. Electrical properties of CNTs and GNPs hybrid epoxy nanocomposites are scarcely reported [4,6,10-13]. The changes in electrical conductivity by the simultaneously addition of CNTs and GNPs, is related to the CNTs bridging between adjacent GNPs which results in a more efficient conductive network [4,11,13]. Moreover thermal conductivity also gives a synergistic behavior, but electrical properties seem to remain unaffected or even decrease [6].

Chemical modification of carbon nanofillers has been done to achieve a strong adhesion at the nanofiller/polymer interface [14-16]. Weak interfaces with the matrix are more critical for GNPs than for CNTs, causing a higher decrease of the mechanical properties of composites [17,18]. However chemical modification undesirably affects the conductivity of the nanocomposites [6,19,20].

When materials are exposed to environmental agents, such as temperature and moisture, modification in their properties can occur. The ageing processes are related to physical and chemical changes, that need to be studied to evaluate the material durability, that is the time up to which the properties changes are acceptable. Moreover it is interesting to

know if these changes are reversible. Epoxy thermosets are widely used in the industry due to their superior characteristics such as good mechanical properties. However, it is known that hydrothermal ageing of epoxy thermosets may cause modification of glass transition temperature (plasticization), changes in cross-linking, and even chemical degradation [21-27]. Epoxy composites are exposed to a humid environment in many applications. The water uptake of polymers can be reduced by incorporating graphene nanoplatelets [17, 28-30]. The diffusion of water in epoxy graphene nanocomposites decreases in relation to neat epoxy that is explained by the more tortuous pathways that water molecules have to take to penetrate in the nanocomposite. However, it should be considered that the exposure to water under long periods can affect the thermo-mechanical properties of the nanocomposites. In relation to water absorption the combined effect of the addition of CNTs and GNPs into epoxy resins, has scarcely been studied [8]

The aim of this work is to study the water uptake of hybrid epoxy nanocomposites doped with CNTs and GNPs reaching long absorption times (almost 2 years). Moreover it is investigated how the hydrothermal ageing at long times influences the mechanical and electrical properties of the nanocomposites. Amine functionalized graphene nanoplatelets were selected in order to enhance the interface between the nanofiller and matrix. The studied epoxy hybrid nanocomposites contained 0.1 wt% of CNTs which gives percolation referred to electrical conductivity and different amounts of GNPs (5-12 wt%). In a previous work we have reported that these nanocomposites present a synergic effect on the stiffness [6]. The results here obtained will be helpful in understanding the effects of hydrothermal ageing on the long term durability of epoxy hybrid nanocomposites.

2. Experimental

2.1. Materials

The epoxy resin Araldite LY556 (diglycidyl ether of bisphenol A type (DGEBA)) was cured with Araldite XB3473 (aromatic diamine, mainly diethyltoluenediamine) both were purchased from Huntsman. Functionalized graphene nanoplatelets, with a thickness lower than 4 nm, and 5 μm of lateral size, were supplied by Cheaptubes. They were amino-functionalized (0.5 wt%) and their specific area was 750 m^2/g . Carbon

nanotubes NC7000 were purchased from Nanocyl, with length lower than 1.5 μm and average diameter 9.5 nm and their specific area was 250-300 m^2/g .

2.2. Sample preparation

The mixtures LY+XB were prepared in stoichiometric ratio (LY556:XB3473 = 100:23 w/w). **Table 1** collects the composition of the studied samples. The percentages of nanofiller were selected considering the electrical percolation threshold [5]: the electrical percolation with CNTs (NC7000) is close to 0.1 wt %, while the threshold with amino-functionalized GNPs is higher than 5 wt%. Appropriate amounts of CNTs and GNPs were loaded into the epoxy resin to obtain hybrid samples. The dispersion of GNPs and CNTs into epoxy resin (LY) was carried out by mini-calendering (three-roll miller Exakt 80E GmbH). The rolling speed was 250 rpm and the gap size between adjacent rolls was 5 μm . The calendering process was applied four consecutive times. Afterwards, the dispersions were degassed under vacuum at 80 $^{\circ}\text{C}$ for 15 min. Then, the hardener was added at 80 $^{\circ}\text{C}$. These dispersions were cast onto aluminum open molds that were treated with a mold release product. The curing consisted of heating at 140 $^{\circ}\text{C}$ for 8 h. The cured samples were slowly cooled to room temperature.

2.3. Measurements

Hydrothermal aging of the specimens has been carried out by immersion in distilled water at 40 $^{\circ}\text{C}$ controlled to better than ± 0.1 $^{\circ}\text{C}$. Two specimens have been tested for each composition. The specimens have dimensions of 45x10x1.9 mm^3 . The specimens were periodically removed from water, carefully wiped to remove excess of water and weighted with accuracy of ± 0.01 mg. The change in weight of the specimens was monitored as a function of the immersion time, t . The total period for which the sample was out of water was less than 1 minute. The water sorption, that is, the water uptake at time t , was calculated as:

$$M_t = (\Delta W / W_0) \quad (1)$$

being W_0 the initial weight of the dry sample and $\Delta W = W_t - W_0$, where W_t is the weight of the hydrothermally aged specimen at each time.

Dynamic mechanical thermal analysis (DMTA) was performed in dual cantilever bending mode using a DMTA V Rheometric Scientific instrument. Measurements were done at 1Hz, with temperature increasing from 30 $^{\circ}\text{C}$ to 220 $^{\circ}\text{C}$ at a heating rate of 2

$^{\circ}\text{C}\cdot\text{min}^{-1}$. Specimen dimensions were: $45\times10\times1.9\text{ mm}^3$. Two samples were measured per each composition. The elastic or storage modulus (E'), the loss modulus (E'') and loss tangent ($\tan\delta$) were recorded for each frequency as a function of temperature. The maxima in $\tan\delta$ -temperature curves were determined to identify the α -relaxations associated to the glass transitions.

DC volume electrical conductivity of nanocomposites was measured according to ASTM D257 using a Source Meter Unit instrument (KEITHLEY 2410). The applied voltage was within the range of 0-15 V. Two samples were measured per each composition. Specimen dimensions were: $10\times10\times1\text{ mm}^3$. Silver paint was used to minimize the electrical contact resistance between the samples and the copper electrodes used as contacts. Aged samples were taken out of the water immediately before their measurement: they were gently wiped out with a tissue and afterward the silver paint was applied and they were measured immediately. The applied voltage was within the range of 0-15 V in 5 steps. The electrical conductivity was then calculated from the characteristic I-V curve by using the Ohm's Law. Two samples were measured per each composition. Specimen dimensions were: $10\times10\times1\text{ mm}^3$.

Nanocomposites morphology was analyzed by Field Emission Gun Electron Scanning Microscopy (FEG-SEM, Nova NanoSEM Fei. Houston. USA). The samples were coated with a thin layer ($\sim 2\text{ nm}$) of Pt.

3. Results and discussion

3.1. Morphological characterization

The SEM micrographs of fracture surfaces of unaged and water aged 8G-0.1C nanocomposite are shown in **Fig. 1**. The morphological characterization of similar samples was investigated in a previous work [6]. It can be summarized that there were not detected aggregates of CNTs or GNPs in the samples. On hybrid samples CNTs tend to selectively locate between GNPs forming bridges between nanoplatelets. Micrographs of unaged samples are shown in **Fig. 1**: at low magnification 1A and at high magnifications 1B and 1C. The micrograph 1B shows mainly a graphene nanoplatelet and its interface with the matrix while micrograph 1C shows a region with high concentration of CNTs. After hydrothermal ageing: micrographs 2A at low magnification and 2B and 2C at high magnifications are also shown in **Fig. 1**. The fractography of the samples can be observed in micrographs at lower magnification (1A

and 2A). It seems that the fracture, after the immersion in water (2A), is rougher with different fracture planes while the surface of the unaged sample (1A) seems to be smoother. This is explained because the aged sample is plasticized by absorbed water, showing higher plastic deformation and therefore higher toughness. At high magnification, the details of the interface between the graphene nanoplatelet and the epoxy matrix can be observed in the micrographs 1B and 2B. It seems that the interface of the non-aged sample is strong and continuous, without showing loss of adherence (marked with white rectangles in micrograph 1B). However, after the hydrothermal ageing, some spaces are detected at the interfaces between the graphene and the matrix (marked with white rectangles in micrograph 2B). As it is well known, this lack of adherence could be associated with the absorption of water that weakens the interfaces in spite of the chemical bounding between amine modified GNPs and the epoxy matrix. Finally, the micrographs 1C and 2C show the dispersed nanotubes in the matrix. The length of the pulled out nanotubes is slightly lower in the unaged sample (1C) regard to the water aged sample (2C). Again, this implies that the CNT-epoxy interface was slightly stronger before water absorption. Even though water seems to weaken the interface the micrographs after water ageing do not show the development of microvoids, indicating that almost no damage has been produced in the hybrid epoxy nanocomposites.

3.2. Water absorption of epoxy nanocomposites

The water absorption curves (M_t versus $t^{1/2} \cdot h^{-1}$, being h the specimen thickness), for Epoxy, 0.1C, and 12G-0.1C samples are plotted in **Fig. 2**. Two specimens were tested for each composition and both followed the same pattern. The other compositions (12G, 5G-0.1C, 8G-0.1C and 10G-0.1C) present similar **behaviour. The curves** are linear in the early stage of absorption, which is one of the characteristics of fickian diffusion [31]. After the initial rapid water uptake, a continuing absorption of water takes place at very slow rate. It can be seen that even after long times of immersion (~ 16000 h which correspond to $\sim 4000 \text{ s}^{1/2} \cdot \text{mm}^{-1}$) equilibrium has not been reached and the samples continued absorbing water at very low **rate. Diamine** cured epoxy thermosets absorb water due to the presence of polar groups, mainly hydroxyl groups generated by the epoxy-amine reaction. It is worth to note that the water absorbed by this epoxy thermoset is small compared to other epoxy systems like DGEBA cured with diamine

diphenyl methane-DDM [32] reaching ~ 1.74 wt% and ~ 3 wt% respectively for $2000 \text{ s}^{1/2} \cdot \text{mm}^{-1}$ under similar conditions. The more compact polymer structure, the smaller its free volume is [33-34] and there is less space available for water absorption therefore this epoxy thermoset (LY-XB) behaves as a tighter network than DGEBA-DDM.

As shown in **Fig. 2**, the amount of absorbed water is reduced by the addition of carbon nanofillers. In order to compare the effect of the different carbon nanofillers **Fig. 3** shows the variation of M_t corresponding to $2500 \text{ s}^{1/2} \cdot \text{mm}^{-1}$ with the content of GNPs. As expected M_t of the hybrid nanocomposites, decreases with increasing GNPs content, and the dependence with the GNPs content is almost linear. Obviously, the matrix is the nanocomposite's component accountable of the water sorption since graphene nanoplatelets and carbon nanotubes hardly absorb water. Therefore, the water uptake referred to the epoxy mass in the specimen, M_t^{ep} , would be more adequate in order to compare the capability of water absorption of the matrix in the nanocomposites. The values of M_t^{ep} (calculated taking W_0 in Eq. (1) as the mass of epoxy matrix in the specimen) are also plotted in **Fig.3**. As expected for the 0.1C nanocomposite, M_t^{ep} is similar to M_t due to the low content of CNTs, while for nanocomposites containing graphene nanoplatelets M_t^{ep} is higher than M_t . It can be observed that M_t of neat epoxy thermoset is slightly higher than M_t^{ep} of nanocomposites this could be justified by the increase of hydrophobicity of the samples containing GNPs or CNTs [17]. The addition of CNTs lowers the water absorption of neat epoxy and hybrid nanocomposite, being this effect higher for the neat epoxy because the hydrophobicity change is higher respect to the sample that contains GNPs.

Reduction of water absorption with the addition of carbon nanofillers has been explained in terms of hindered intermolecular movements of the epoxy due to the fillers [28]. Indeed, in similar samples to the ones here studied [6] it was found that the presence of the nanofillers leads to increase the T_g . Consequently, the nanocomposites have lower free volume than neat epoxy and the lower is the level of absorbed water compared to the neat epoxy.

In **Fig 3** it can be seen that M_t^{ep} slightly increases as the graphene content increases this can be explained taking into account that amine groups of GNPs can modify the stoichiometry of the epoxy matrix lowering its crosslinking degree, thus increasing free volume, this effect would be proportional to the GNPs content. Therefore there are contrary effects, on one hand the water absorption decreases due to the carbon nanofillers hydrophobicity and to the epoxy restricted mobility around them, on the

other hand water sorption increases due to the lower crosslinking degree induced by stoichiometry unbalances.

Additionally, it has been reported that the degradation of the graphene-epoxy interface, can originate voids where the water can be trapped [17]. However, as it was above discussed, in the systems here studied no voids or damage were detected, it was only observed weakening of interfaces that facilitates to pull out the fillers.

3.3. Diffusion coefficients

Fickian behavior assumes that the water concentration gradient is the driving force for diffusion. Therefore, the absorption curves are linear at the initial stage and they asymptotically approach the equilibrium water absorption, M_∞ , and the diffusion coefficients can be calculated according to Fick's second law [32]:

$$M_t = \left(1 - \exp \left[-7.3 \left(\frac{Dt}{h^2} \right)^{0.75} \right] \right) M_\infty \quad (2)$$

where D is the diffusion coefficient, h is the thickness of the specimen, and M_∞ is the equilibrium value of the water uptake.

The water absorption curves shown in **Fig. 2**, reveals diffusion behavior in two steps. The absorption at the early times associated to Fickian diffusion and after that, a continuous increase of absorption. This behavior has been observed in other systems [23, 32, 35-39]. In such cases, a two-stage diffusion model can be used to fit the data: the first stage is controlled by a concentration gradient, according to Fick's law and the second one takes into account the steady increment of the absorption:

$$M_t = (1 + k\sqrt{t}) \left(1 - \exp \left[-7.3 \left(\frac{D \cdot t}{h^2} \right)^{0.75} \right] \right) M_{\infty 0} \quad (3)$$

where $M_{\infty 0}$ is the quasi-equilibrium uptake of the diffusion-dominated first stage and D is the diffusion coefficient. The term $(1 + k t^{1/2})$ characterizes the second stage, k is a constant that represents the rate of absorption of the second stage and it has been proposed to be related to the rate of relaxation of the polymeric matrix [35]. The structural relaxation is assumed to be much slower than the diffusion process. This is particularly true in the systems studied here, in which the aging temperature (40°C) is much lower than the T_g of the systems (around 170°C).

The experimental data M_t versus $t^{1/2} \cdot h^{-1}$ were fitted using Eq. (3). In all the cases a good agreement between the experimental data and fitted results was obtained as it is illustrated in **Fig. 2**. The obtained values for $M_{\infty 0}$, D and k are listed in **Table 2**. As all specimens have similar dimensions, the “edge effect” correction [32] on D is similar in all them. The values of $M_{\infty 0}$ are lower than the values of M_t corresponding to $2500 \text{ s}^{1/2} \cdot \text{mm}^{-1}$ though the variation with nanofiller content follow the same trend. The addition of any of the nanofiller produces a reduction on the diffusion coefficient. The reduction of D by the addition of GNPs seems to be proportional to the GNPs content as it is illustrated in **Fig. 4**. The graphene nanoplatelets force water to follow a tortuous pathway leading to the decrease of D . The addition of 0.1% CNTs to neat epoxy thermoset and to 12G nanocomposite has a similar effect lowering D .

Regarding the second stage of absorption the k values of 0.1C nanocomposite and Epoxy are similar while for GNPs nanocomposites k values are lower (see **Table 2**). This effect can be related to the anchorage of the amino functionalized GNPs to the epoxy matrix that constrains the segmental motions of the epoxy matrix and makes slower the epoxy relaxation. Therefore the amino functionalized GNPs which react with the matrix originate strong interfaces being water diffusivity and the level of water uptake lower than neat epoxy thermoset. The behavior of the nanocomposites is in accordance with their morphology, that is, agglomerates and voids that would increase diffusivity [40] were not detected.

The T_g values (see **Table 3**) are much higher than the hydrothermal ageing temperature (40°C) so the epoxy relaxations should occur very slowly, accordingly a constant value for M_t was not reached even after 16000 hours of hydrothermal ageing. In less tightly crosslinked epoxies having lower T_g (around 100°C) [23] the two stage absorption curves disappears at water aging temperature (70°C) near the T_g of the network, where the relaxation takes place at shorter times.

3.4. Effect of hydrothermal ageing on the thermo-mechanical properties

To evaluate the effects of hydrothermal ageing on the thermo-mechanical properties DMTA tests were performed for: “as-produced” and “water-aged” specimens (after 1 and almost 2 years of immersion in water at 40°C). **Fig. 5** shows $\tan\delta$ -temperature curves for non-aged and water aged specimens. The $\tan\delta$ curve of the non-hydrothermally aged samples shows one relaxation peak at high temperature, located

around 170°C, with narrow distribution indicating that the epoxy network behaves as homogeneous. The water uptake influences the height and shape of $\tan\delta$ curves, and water aged specimens show widening of the $\tan\delta$ peaks. Aged neat epoxy and 0.1 CNT nanocomposite show an asymmetric broadening of the $\tan\delta$ peak. While for the samples containing GNPS a shoulder is observed at lower temperatures. The peak is located around 170°C and the shoulder around 145°C. It is worth to note that as the peak broadens the height of the peak lowers. The breadth (area) of the $\tan\delta$ peak is related to the damping behavior and the peak width represents the temperature range over which the glass transition takes place. Thus, a broad $\tan\delta$ peak can be attributed to a more heterogeneous network containing different relaxations regions.

The values of temperature for the maximum in $\tan\delta$ curves ($T_{\tan\delta_{max}}$) for unaged and aged samples (1 and 2 years of hydrothermal ageing) are reported in **Table 3**. It can be seen that for unaged samples, the T_g of nanocomposites is higher than the T_g of neat epoxy. The presence of CNTs and amino functionalized GNPs in the epoxy matrix induces a noticeable increase in T_g associated to the hindrance of polymer chain-segments movements [6]. The values reported in **Table 3** show that the $\tan\delta$ peak appears at similar temperatures in aged and unaged specimens, which evidences that no chemical degradation took place after two years of water immersion. On the other hand, the DMTA scans after one and two years of hydrothermal ageing are similar indicating that the absorption of water during the second year does not affect the matrix, which is in accordance with the small amount of absorbed water during the second ageing year. Therefore the absorbed water did not produce noticeable matrix damage even during large periods of ageing.

It has been frequently reported splitting of $\tan\delta$ peaks for hydrothermally aged polymers and attributed either to drying effect during DMTA tests or to the heterogeneous plasticization of epoxy matrix by the absorbed water [32,39,41-43]. Whatever the origin, the shoulder observed at lower temperatures (**Fig.5**) could be related to the T_g of the plasticized matrix and the peak at higher temperatures should correspond to the T_g of the dried matrix. The Fox relationship is commonly used to describe the plasticizing effect:

$$\frac{1}{T_{gP}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (9)$$

being T_{g1} , T_{g2} and T_{gp} the T_g of water, dry epoxy and plasticized epoxy respectively, and $w_1=1-w_2$ the water weight fraction. From the T_g of water $T_{g1}=100-150\text{K}$ [32] T_{g2} of the unaged epoxy given on **Table 3**, and the mass of absorbed water corresponding to two years of immersion (see **Fig 2**) $w_1 \sim 0.019-0.018$, values of $T_g \sim 412-423\text{K}$ (139-150°C) are predicted for hydrothermally aged epoxy, which are in accordance with the position of the shoulder in $\tan\delta$ peak, located 20-26 °C lower than $\tan\delta$ peak.

It is well known that the addition of rigid nano-fillers increases the modulus of nanocomposites, as we have reported for samples similar to those studied here [6]. **Fig. 6** shows the variation of E' with the temperature for one year hydrothermally aged samples, it can be seen that the E' -temperature curves of the nanocomposites are above those corresponding to the neat epoxy thermoset, evidencing that fillers increase E' in both rubbery ($T > T_g$) and glassy region ($T < T_g$). **Fig. 7** compares the E' modulus of aged and unaged samples in the glassy region (at $60^\circ\text{C} < T_g$) for neat epoxy and nanocomposites. GNPs and CNTs cause an increase of E' in the glassy region (E'_G) and this effect appears both in the unaged and water aged samples. Namely 16% increment of E'_G is observed for 0.1C nanocomposite, and 25%, 33%, 37% and 48% for 5G-0.1C, 8G-0.1C, 10G-0.1C and 12G-0.1C hybrid nanocomposites respectively. Hydrothermal ageing provokes a noticeable reduction in the glassy modulus this decrease could be attributed to water plasticization of the matrix and to degradation of the polymer-filler interface. As the E'_G decrease is about 15% regardless of whether it is referred to neat epoxy or nanocomposites, the dominant factor should be the water plasticization of the matrix.

On the other hand, as can be seen in **Fig. 6** in the rubbery region the increments of E'_R due to the addition of 0.1CNTs is almost unnoticeable (6%), however the addition of GNPs provokes significant increments of E'_R , that is, 75%, 100%, 130% and 130% for 5G-0.1C, 8G-0.1C, 10G-0.1C and 12G-0.1C hybrid nanocomposites respectively. There was not detected any decrease of modulus, E'_R , after hydrothermal ageing as it is show in **Fig. 8** that compares E'_R of unaged and water aged samples at $T= 200^\circ\text{C} > T_g$ for neat epoxy and nanocomposites. The rubbery modulus of neat epoxy is correlated with its crosslink degree, thus the similar values of E'_R obtained for aged and unaged epoxy samples indicate that there is no degradation of the epoxy thermoset. Moreover, for nanocomposites both unaged and water aged samples behave similar in the elastomeric zone, this is the consequence of drying the samples during the DMTA measurement, thus at 200°C the absorbed water has been eliminated. Therefore there is no evidence of

irreversible degradation caused by water absorption, which agrees with the morphological study.

3.5. Effect of hydrothermal ageing on the electrical conductivity of nanocomposites

The effect of hydrothermal ageing on electrical conductivity was measured at room temperature (24°C) using samples that were previously aged in water at 40°C. The water absorbed for these samples corresponds to $2500 \text{ s}^{1/2} \cdot \text{mm}^{-1}$ in **Fig. 2**. The electrical conductivity for unaged and hydrothermally aged specimens is shown in **Fig. 9**. It is well known that graphitic fillers give an increment of the electrical conductivity of the epoxy resin. As we have reported in a previous study [6], the addition of 0.1 %CNT induces an important increase of electrical conductivity, since the CNT load is higher than the percolation threshold. However, the addition of amino functionalized GNPs up to 12% renders a very low value of the electrical conductivity, this is because of the functionalization of GNPs that induces reduction of the intrinsic electrical conductivity of the graphene nanoplatelets, moreover the reaction of amine groups of GNPs with the epoxy groups of the matrix hinders the electrical contact between graphene nanoplatelets lowering the electrical conductivity.

Few published results deal with electrical properties of epoxy hybrid nanocomposites by combining CNTs and GNPs. Lee et al. [10] have reported the same surface conductivity for CNTs and CNT-GNPs nanocomposites. Yue et al. [11] have found that the CNT-GNP combination reduces the percolation threshold. Li et al. [12] have reported synergy in the electrical conductivity of a CNT-GNP nanocomposite. Safdari et al. [13] have reported both, high decrease in the electrical percolation threshold and synergy effect for the electrical conductivity for nanocomposites. As it is shown in **Fig.9** the addition of 0.1% CNT to GNPs-based nanocomposites increases their electrical conductivity 3 orders of magnitude, but no synergistic effect is observed as neither of the hybrid compositions overcomes the 0.1C nanocomposite conductivity. This would be a consequence of the reduced conductivity of functionalized GNPs, that don't add efficient conductive pathways in the hybrid nanocomposite. Regarding to the effect of hydrothermal ageing, it is remarkable that water aged specimens do not show any deterioration of electrical conductivity, as it is shown in Fig. 9 aged and unaged nanocomposites have similar electrical conductivity, this is another indication of no degradation of the epoxy matrix neither of the electrical network by water.

4. Conclusions

The water absorption and its effect on the thermo-mechanical properties of hybrid CNT/ GNP/epoxy nanocomposites were studied. The content of CNTs was 0.1 wt% which gives percolation referred to electrical conductivity. The GNPs used were amino functionalized in order to enhance the interface nanofiller-epoxy matrix. The GNPs content ranged from 5 to 12 wt%. These nanocomposites were selected because they exhibit a synergetic effect on the stiffness.

The isothermal water absorption was measured until very long times (almost two years). Nano-fillers in the epoxy matrix led to a significant reduction of the water absorption. The water absorption curves were fitted to a two-step diffusion model, the first step is diffusion controlled and the second one is associated with relaxation of the epoxy matrix. The diffusion coefficients are lower in the nanocomposites than in neat epoxy thermoset, due to the tortuous paths created by the addition of the nano-fillers.

T_g of nanocomposites is higher than the T_g of neat epoxy and is similar in aged and unaged samples, evidencing that no chemical degradation took place. CNTs and GNPs improve the rigidity of the nanocomposites both before and after water ageing.

Whatever the temperature the storage modulus shows a continuous increase with the increase of the nanoparticles content, the effect of hydrothermal ageing is to decrease the modulus only in the glassy state ($T < T_g$).

The addition of 0.1% CNTs to amine functionalized GNPs-based nanocomposites increases their electrical conductivity 3 orders of magnitude. Water aged specimens show similar electrical conductivity than unaged ones, which is another indication of no degradation of the samples by water. These results together with the morphology observed by FEG-SEM allow to affirm that no significant degradation takes place over two years of immersion in water at 40 °C in the epoxy thermoset neither in the hybrid nanocomposites.

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Table 1. Composition of the studied samples.

Sample	Name	GNP (wt%)	CNT (wt%)	Total nanofiller (wt%)
Neat epoxy	Epoxy	0	0	0
CNT/epoxy	0.1C	0	0.1	0.1
GNP/epoxy	12G	12	0	12.0
Hybrid GNP/CNT/epoxy	5G-0.1C	5	0.1	5.1
	8G-0.1C	8	0.1	8.1
	10G-0.1C	10	0.1	10.1
	12G-0.1C	12	0.1	12.1

Table 2. Quasi-equilibrium water uptake values ($M_{\infty 0}$) diffusion coefficients (D) and values of the parameter of the second stage (k), according to Eq. (3).

Material	$M_{\infty 0}$ (%)	$D \cdot 10^7$ ($\text{mm}^2 \cdot \text{s}^{-1}$)	$k \cdot 10^5$ $\text{s}^{-1/2}$
Epoxy	1.50 ± 0.01	6.45 ± 0.06	5.2 ± 0.2
0.1C	1.40 ± 0.01	6.28 ± 0.04	4.9 ± 0.1
12G	1.30 ± 0.01	5.34 ± 0.10	4.1 ± 0.3
5G-0.1C	1.36 ± 0.01	5.95 ± 0.01	4.5 ± 0.3
8G-0.1C	1.36 ± 0.01	5.87 ± 0.10	4.1 ± 0.3
10G-0.1C	1.34 ± 0.01	5.29 ± 0.06	4.0 ± 0.3
12G-0.1C	1.33 ± 0.01	5.19 ± 0.02	4.0 ± 0.2

Table 3. Temperature values of $\tan \delta_{\max}$ (T_g from DMTA) for unaged and hydrothermally aged specimens at 40°C after 1 year and after almost 2 years (values in brackets)

Material	T_g (°C)	
	Unaged	Hydrothermally aged
Epoxy	165	167(168)
0.1C	169	169 (168)
12G	171	169 (169)
5G-0.1C	170	171 (169)
8G-0.1C	171	172 (172)
10G-0.1C	171	170 (171)
12G-0.1C	174	174 (174)

Fig. 1. FEG-SEM micrographs of 8G-0.1C nanocomposite: unaged samples (1A, 1B and 1C) and water aged (1 year 40°C) samples (2A, 2B and 2C) at different magnifications

Fig. 2. Water absorption curves for neat epoxy (■) and nanocomposites: 0.1C (●) and 12G-0.1C (▲), lines represent the theoretical fitting (Eq.3).

Fig. 3. Water absorption at $2500 \text{ s}^{1/2} \cdot \text{mm}^{-1}$ as a function of GNP content: referred to the total mass of the specimen (open symbols) and referred to the epoxy mass (filled symbols) for neat epoxy: (■), 12G nanocomposite (▲,△) and hybrid graphene-0.1%CNT nanocomposites (●○). When the error bars are smaller than the size of the symbol they are not shown.

Fig.4. Diffusion coefficients for: neat epoxy (■), 12G nanocomposite (▲) and hybrid graphene-0.1%CNT nanocomposites (●). When the error bars are smaller than the size of the symbol they are not shown.

Fig. 5. DMTA $\tan \delta$ - temperature curves for samples: unaged (—), one year aged (···) and two year aged (---).

Fig. 6. DMTA E' -temperature curves for one year aged specimens.

Fig. 7. E' in the glassy state (60°C) for neat epoxy (♦) and hybrid graphene-0.1%CNT nanocomposites (●). Filled symbols stand for unaged samples and open symbols for aged samples.

Fig. 8. E' in the rubbery state (200°C) for neat epoxy (♦) and hybrid graphene-0.1%CNT nanocomposites (●). Filled symbols stand for unaged samples and open symbols for aged samples. When the error bars are smaller than the size of the symbol they are not shown.

Fig. 9. Electrical conductivity for the nanocomposites: 0.1 C, 12G and hybrid graphene-CNT nanocomposites: 5G-0.1C, 8G-0.1C 10G-0.1C and 12G-0.1C.