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Mechanical properties and adhesive behavior of epoxy-graphene nanocomposites

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Abstract

The influence of the type and content of graphene nanoplatelets (GNP) on the thermo-mechanical and adhesive properties of epoxy-graphene nanocomposites was investigated. Two types of graphene have been used: un-functionalized and functionalized graphene. The functionalized graphene (GNP_{NH2}) contains amine groups that react with the epoxy prepolymer. Two types of un-functionalized graphene with different nanoplatelet dimensions were used. A universal testing machine was used to determine the Young´s modulus, deformation at break, mechanical strength and toughness at 22ºC. Dynamic Mechanical Thermal Analysis experiments were performed to compare the glass transition temperature and the storage modulus in the glassy and rubber states. Epoxy-graphene nanocomposites were used as adhesives on aluminum substrates in single lap geometry, and the shear strengths were determined. All nanocomposites presented higher modulus than the neat epoxy thermoset. The increase in the storage modulus was higher in the in the rubbery state than in the glassy state. Nanocomposites showed lower tensile strength and were more fragile than the neat epoxy thermoset, which was attributed to the aggregation of graphene nanoplatelets. Epoxy/GNP_{NH2} nanocomposites presented a lower decrease of tensile strength and less fragile behavior. Epoxy/graphene adhesives

presented lower lap shear strength than neat epoxy adhesive. Increasing GNP content caused the lap shear strength to decrease.

Keywords

Epoxy/graphene nanocomposites, mechanical properties, adhesive properties

1. Introduction

Graphene has become popular as a reinforcement for advanced nanocomposites. Graphene nanoplatelets, GNP, can increase the mechanical properties and thermal stability of polymers. Moreover they are available at low prices [1]. Graphene nanoplatelets are often difficult to disperse in polymer matrices; GNP/polymer nanocomposites with weak interfaces and GNP aggregation yield poor mechanical properties [2,3].

The improvement in mechanical properties is determined by high interfacial adhesion and good stress transfer across the interface, which can be achieved by introducing covalent bonds between the matrix and the nanoplatelets. Carbon nanomaterials have been functionalized to achieve chemical interactions with the polymer matrix. Epoxy nanocomposites reinforced with modified graphene nanoplatelets have been investigated recently [4-8]. The results revealed that the inclusion of unmodified GNP, oxidized and amine functionalized GNP enhanced the elastic modulus of the epoxy matrix. However there is an undoubted conclusion in relation to the ultimate strength, in general best results have been reported for low graphene concentrations (<3%) [2-5,8].

Recently, several studies have used GNP as a reinforcement for epoxy adhesives [9-15]. It has been reported that higher concentrations of GNP lead to poor dispersion of the nanoplataletes, causing a decrease in joint strength.

A study of the effect of graphene content and the type of graphene on the mechanical and adhesive properties of epoxy thermosets would be useful. Therefore, in this work, epoxy/GNP nanocomposites were prepared using three different graphenes: two un-functionalized graphenes (GNP_n and GNP_{M25}) having different lateral sizes and an amine functionalized graphene (GNP_{NH2}) of similar dimensions to GNP_n. The aim was to

investigate the effect of the different graphenes on the mechanical and adhesive properties of an epoxy resin.

2. Materials and methods

2.1 Materials

An aeronautical grade epoxy prepolymer based on a basic DGEBA, *Araldite LY556*, cured with an aromatic amine, *Araldite XB3473* was used as matrix. Both products were purchased from *Huntsma*n.

The study of the epoxy-graphene systems was carried out using two types of graphene: un-functionalized and functionalized graphene. The functionalized graphene containing amine groups (0.5 %) average thickness < 4 nm and an average lateral size of 1-2 μm (GNP_{NH2}) was purchased from *Cheap-Tubes* (GNP_S grade 4).

Two un-functionalized graphenes with different nanoplatelet dimensions: graphene nanoplatelets with an average thickness of 6-8 nm and an average lateral size of 25 μm provided by *XGScience* (GNP_{M25}), and graphene nanoplatelets with an average thickness < 4 nm and an average lateral size of 1-2μm (GNP_n) provided by *Cheap-Tubes* with similar geometric characteristics than GNP_{NH2}, were selected.

Frekote from Loctite was employed as mold release product.

2.2 Methods

2.2.1 Preparation of nanocomposites

Dispersions of graphene nanoplatelets on LY556 were obtained through mechanical stirring at 700 rpm for 10 min. at 70 ºC, followed by sonication for 60 min with a horn and a UP400S Hielscher sonicator: 0.5 s cycles with a power of 400 W and amplitude of 50%. The temperature did not exceed 40 ºC. Once the dispersions were obtained, the appropriate amount of curing agent (XB3473) for a stoichiometric ratio (weight fraction prepolymer/ hardener = 100/23) was added and mixed for 5 min, and then the samples were degassed under vacuum (40 mbar) at 80 °C for 15 minutes

These dispersions were used to prepare lap shear joints, specimens for tensile tests, and samples for DMTA experiments. The dispersions were poured into aluminum molds, previously treated with mold release product, and were cured at 140 °C for 8 h under atmospheric pressure [10].

Nanocomposites having 2, 4, 6, 8 10, 12 wt% of GNP_{NH2}, 2, 4 and 6 wt% of GNP_n and 6 wt% of GNP_{M25} together with the neat epoxy thermoset (LY556+XB3473) were prepared. These GNP proportions were selected based on a previously published study [13,15].

2.2.2 Experimental

Tensile mechanical properties of the nanocomposites were measured using a QTest 2L model MTS machine fitted with a MTS extensometer (model 63411F-54) with 2 kN load cell capability. The experiments were conducted at room temperature (22 ºC). The rectangular specimens (140x10x1.8 mm^3) were loaded at a constant rate of 1 mm min^{-1} until fracture. Stress–strain curves were recorded for six or more specimens of each composition to obtain the average value of the mechanical properties. Tensile modulus, tensile strength, strain at break were obtained and toughness was determined by integrating the area under the curve of the engineering stress versus engineering strain.

Dynamic mechanical thermal analysis (DMTA) of cured samples was performed in dual cantilever bending mode using a DMTA V Rheometric Scientific instrument. Measurements were done at 1, 2, 5, 10 and 50 Hz, with temperature increasing from 20 °C to 220 °C at a heating rate of 1 °C min^{-1}. Specimen dimensions were: 35x10x1.8 mm^3. The elastic or storage modulus ($E´$), loss modulus ($E´´$), and loss tangent ($tan\ \delta$) isochrones as a function of temperature were recorded.

Joint strength was determined by single lap shear test following the ASTM D1002-01 standard. After surface treatment, aluminum pieces (100x25x2 mm^3) were assembled into single-lap shear joints with 12.5 mm of overlap length. At least five samples were tested for each adhesive composition. The adhesive thickness was controlled to 0.22±0.02 mm and the dimensions of the overlapped joints were 25x12.5 mm^2.

Two surface treatments for the aluminum substrates were performed: Treatment 1 (T1) involved abrasive blasting, rinsing in tap water, degreasing with methyl ethyl ketone (MEK) at room temperature, rinsing in tap water, etching with 100 g/ L NaOH solution at 60 ºC for 1 min, rinsing in tap water; Treatment (T2) included all steps of T1 with a final step of oxidation by immersion in an aqueous solution of 127 g/L $Fe_2(SO_4)_3$-$7H_2O$ and

185 mL/L H_2SO_4. Treatment T2 is usually named as P2 etch. Finally, all the specimens were rinsed with distilled water and dried in the open air.

3. Results and discussion

3.1 Tensile properties of epoxy/GNP nanocomposites

To investigate the effect of graphene content on epoxy/GNP nanocomposites as well as the influence of different graphene nanoplatelets on the mechanical properties of the epoxy matrix, tensile testing was carried out. The most representative stress-strain curves of pure epoxy thermoset and epoxy/GNP_{NH2} nanocomposites are shown in **Figure 1**. **Figure 2** shows the comparison of the stress-strain representative curves of the neat epoxy and the nanocomposites prepared with 6% of the three types of graphene nanoplatelets used, GNP_{NH2}, GNP_n and GNP_{M25}.

The variation of the tensile properties (Young´s modulus, tensile strength, strain at break and toughness) of epoxy/GNP_{NH2} nanocomposites with graphene content is shown in **Figure 3**. It can be observed that the nanocomposites showed higher modulus than the pure epoxy matrix, which increased as the GNP_{NH2} content increased. However, in general, the nanocomposites showed lower strength, deformation at break and toughness than neat epoxy thermoset. Epoxy/GNP_n nanocomposites presented a similar mechanical behavior to epoxy/GNP_{NH2} nanocomposites (see **Figure 4**).

Table 1 shows the comparison of the neat epoxy and the nanocomposites prepared with 6% of the three types of graphene nanoplatelets, GNP_{NH2}, GNP_n and GNP_{M25}. In all the cases, the nanocomposites showed an increase in stiffening with respect to the neat epoxy. The improvement in modulus can be attributed to the high Young´s modulus of graphene nanoplatelets. Yasmin et al [8] found an analogous variation of the elastic modulus of epoxy/un-functionalized graphene nanocomposites using a graphene similar to GNP_n. The nanocomposite reinforced with 6% GNP_n showed about 40% increase in elastic modulus, a similar increase was reached for epoxy/GNP_{NH2} nanocomposites only when GNP_{NH2} content was 12%. The stoichiometric imbalance originated by the reaction of the amine groups of GNP_{NH2} and epoxy would give rise to networks with lower cross-linking density, thus GNP_{NH2} nanocomposites have a lower modulus than GNP_n nanocomposites.

Epoxy/graphene nanocomposites prepared with 6% GNP_{M25} graphene had a slightly lower Young´s modulus than the epoxy nanocomposites prepared with 6% GNP_n. This could be a consequence of the different platelet dimensions of these graphenes. Larger nanoplatelets tend to bend; indeed it has been shown that GNP_{M25} nanoplatelets adopt wavy or wrinkled structures, which may effectively reduce the modulus [13]. On the other hand, from measurements of flexural modulus, Chatterjee et al. [14] concluded that the reinforcing capability of 25 μm GNP was higher than that of 5 μm GNP for epoxy nanocomposites at low GNP concentrations 1-2%. This is evidence of different behavior of nanocomposites, with low and high GNP concentrations.

The tensile strength of the epoxy/GNP_{NH2} nanocomposites at low GNP_{NH2} contents (2-4%) was similar to that of the neat epoxy thermoset, while higher GNP_{NH2} content induced a decrease of tensile strength (see **Figure 3b**). This behavior has been observed for nanocomposites [8,13,15] and is associated with poor nanoplatelet dispersion. Higher nanoparticle content favors their aggregation, and the aggregates may cause a high stress concentration and premature failure. The nanocomposites obtained with the other graphene nanoplatelets, GNP_n and GNP_{M25}, exhibited lower strength than the neat epoxy thermoset, as can be observed in **Figure 2** and **Table 1.** The interfacial strength usually controls the ultimate mechanical properties. Thus the aggregation of nanoplatelets and weak interfacial adhesion between them and the epoxy matrix, can explain the reduction of strength. Epoxy/6% GNP_{M25} nanocomposites showed a lower strength in comparison to epoxy/6%GNP_n nanocomposites; this could be a consequence of the different dimensions of the graphenes. Larger GNP nanoplatelets tend to bend favoring the presence of defects, and lower strength. The lower decrease in tensile strength found for epoxy/GNP_{NH2} nanocomposites (see **Table 1**) is related to the bonds formed between GNP_{NH2} nanoplatelets and the epoxy matrix.

It can be observed that the strain at break decreased as the GNP content increased for all the nanocomposites. Nevertheless, the differences in the strain at break of the three types of nanocomposites were close to experimental error (see **Table 1**).

As can be seen in **Figures 3d, 4d** and **Table 1**, all nanocomposites presented lower toughness than the neat epoxy thermoset, that is, the nanocomposites were more fragile. As expected, GNP_{NH2} led to less fragile nanocomposites, because strain at break and

toughness are related to the interactions between phases, and GNP_{NH2} nanoplatelets are bonded to epoxy matrix by chemical bonds. The chemical reaction between the amine-functionalized nanoparticles and the epoxy matrix has been confirmed by different techniques in a previous study [16].

3.2 DMTA of epoxy/GNP nanocomposites

The storage modulus ($E´$), the loss modulus ($E´´$), and loss tangent ($tan\ \delta$) isochrones as a function of temperature were recorded for neat epoxy thermoset and epoxy/GNP nanocomposites. The variation in the storage modulus of epoxy thermoset and epoxy/GNP_{NH2} nanocomposites as a function of temperature at 1Hz is shown in **Figure 5**. As the temperature increased, there was a gradual decrease in storage modulus, followed by a sudden decrease at the glass transition temperature (T_g). The incorporation of graphene nanoplatelets resulted in an increase of the storage modulus over the whole temperature range. Indeed, all the nanocomposites showed a higher storage modulus than the neat epoxy thermoset, both in the glassy ($T< T_g$) and rubbery states ($T > T_g$). The behavior of the storage modulus for epoxy/$GNP_{n.}$ was similar to that observed for epoxy/GNP_{NH2} nanocomposites. **Figure 6** shows the comparison of neat epoxy with nanocomposites having 6% of the three types of graphene nanoplatelets used, GNP_{NH2}, GNP_n and GNP_{M25}. As usual, the storage modulus values were lower than Young´s modulus determined by tensile tests.

Tables 2 and Table 3 collect the values of the relative storage modulus: $E_r´$ = E'(sample)/ E'(neat epoxy thermoset) at T=80 ºC (glassy state) and at T =200 ºC (rubbery state). The variation of $E´$ with the composition was in accordance with the variation of Young´s modulus. The nanocomposites with 2-6% of graphene presented an increased storage modulus with regard to neat epoxy thermoset, in the glassy state being ~10-20% higher for GNP_{NH2}, ~20-30% higher for GNP_n and 50% higher for GNP_{M25}. In the rubbery state, the graphene nanoplatelets gave rise to major increases of $E´$, being ~40-70% higher for GNP_{NH2}, ~100-150% higher for GNP_n and 110% higher for $GNP_{M25.}$ The storage modulus in the rubbery state is related to the cross-linking density; the stoichiometric unbalance caused by the presence of amine groups in the GNP_{NH2} gives rise to less cross-linked networks. Therefore, in the rubbery state, the GNP_{NH2}

nanocomposites showed lower storage modulus than GNP_n and GNP_{M25} nanocomposites. Consequently the relative storage modulus (see Tables 2 and 3) behaves similar. It is worth noting that the sample having 12% GNP_{NH2} presented an E_r' value similar to those of the samples containing 6% GNP_{M25} or 6% GNP_n.

In order to evaluate the effect of the graphene nanoplatelets on the glass transition of the epoxy thermoset, **Table 2** shows the temperature at which the loss modulus presented a maximum together with the temperature of the maximum in tan δ; these maximums are a consequence of α-relaxation related to the glass transition temperature, T_g of the epoxy network. The presence of graphene led to higher T_g values than for neat epoxy thermoset. However, there was no correlation with the content of graphene, that is, higher graphene content did not lead to higher T_g. Furthermore, higher increases appeared at lower GNP content (2-4%). This is in accordance with results previously reported for very low graphene content (thermally reduced graphite oxide < 0.2%) [17]. It was concluded that at lower GNP content, the well-dispersed nanoplatelets were much more effective in improving the T_g.

The increase in T_g is associated with a restriction in molecular motions, a reduction in free volume or a higher degree of cross-linking. The T_g of 6% GNP_{NH2} was higher than the T_g of 6% GNP_n. This result means that the motion restriction caused by the GNP_{NH2}-epoxy bond outweighs the lower degree of cross-linking due to the stoichiometric unbalance. When the content of GNP_{NH2} increased up to 12%, T_g reached a value similar to that of neat epoxy thermoset. This would mean that in this sample, the stoichiometric unbalance caused by GNP_{NH2} produced a decrease in T_g that offset the increases in T_g due to restriction in molecular motions by the GNP nanoplatelets. The comparison of the glass transitions of nanocomposites with un-functionalized graphenes (GNP_n and GNP_{M25}) containing 6% GNP (see **Table 3**) provides evidence for a higher restriction of the molecular motion caused by the largest nanoplatelets.

The T_gs (determined as the temperature of tan δ_{max}) increased as a function of frequency (ν). The Arrhenius equation was used to evaluate the apparent value of the activation energy of the glass transition relaxation (E_{aGT}), which is the energy barrier that must be overcome by the molecular motions causing the transition. E_{aGT} was calculated, from the slope of the plots of ln (ν) vs. T_g^{-1}, giving similar values for neat epoxy thermoset

(500±30 kJ·mol^{-1}) and the nanocomposites 6%GNP$_{NH2}$ (450±30 kJ·mol^{-1}), 6% GNP$_n$, (450±40 kJ·mol^{-1}), E_{aGT} being slightly higher (560±30 kJ·mol^{-1}) for the 6% GNP$_{M25}$ nanocomposites.

3.3 Lap shear strength of epoxy/GNP adhesives

Lap shear strength of epoxy adhesives was determined according to the ASTM D1002-01 at 22 ºC with aluminum substrates in single lap shear configuration. The surface treatments were specified in the experimental section. The experiments were performed on freshly prepared joints and the results obtained are shown in **Table 4.** The shear strength of neat epoxy adhesive (LY+XB) depends on the surface treatment, becoming 10% higher when the complete treatment T2 was applied. Nevertheless, the surface treatment had no effect on epoxy/graphene adhesives.

The largest strength value was found with the neat epoxy adhesive, where the shear strength for all epoxy/graphene adhesives was lower, independently of the type of graphene. This behavior can be attributed to the lower tensile strength and toughness of the epoxy/GNP nanocomposites (see **Figures 3, 4** and **Table 1**). The failure surfaces of joints are shown in **Figure 7**. It can be seen for epoxy/graphene adhesives that the greater amount of adhesive is located on one of the surfaces, with bits of graphene remaining adhered on the other surface, confirming cohesive failure. For the LY+XB adhesive, the fracture may appear as an adhesive fracture with the naked eye, however there remains a thin epoxy layer adhered to one of the surfaces together with a thick layer on the opposite surface. Therefore, the adhesive joints also failed cohesively in the adhesive but close to the interface.

The lap shear strength for 1% GNP nanocomposites was higher than for 6% GNP; these results are in agreement with those reported in the literature [8-11]. Specifically, it was found that for low GNP content (0.5%) joint strength was improved, but when the GNP content was increased, the strength of the joints decreased. This behavior has been attributed to the formation of agglomerates when the GNP content is increased.

Adhesive containing 6% GNP$_{NH2}$ presented similar joint strength to that containing 6% GNP$_n$ (see **Table 4**). Thus the formation of chemical bonds between GNP$_{NH2}$ and the epoxy matrix did not significantly influence joint strength.

4. Conclusions

This work investigated the influence of three types of graphene nanoplatelets on the mechanical and adhesive properties of an epoxy resin. Two un-functionalized graphenes (GNP_n and epoxy GNP_{M25}) having different lateral size and an amine functionalized graphene (GNP_{NH2}) with similar dimensions to GNP_n were used.

It was found that all nanocomposites presented higher Young´s modulus than the neat epoxy thermoset and Young´s modulus increased as the GNP content increased.

The tensile strength of the epoxy/GNP nanocomposites was lower than that of neat epoxy thermoset, except for nanocomposites having low GNP_{NH2} content (2-4%) which showed similar strength to the neat epoxy thermoset. The decrease in the tensile strength is attributed to the aggregation of graphene nanoplatelets. The lower decrease in tensile strength of epoxy/GNP_{NH2} nanocomposites could be the consequence of the bonds formed between GNP_{NH2} nanoplatelets and the epoxy matrix.

For all the nanocomposites, the strain at break and the toughness decreased as the GNP content increased, that is, the epoxy/GNP nanocomposites were more fragile than the neat epoxy thermoset. GNP_{NH2} nanocomposites were the least fragile.

In the rubbery state, graphene nanoplatelets resulted in higher increases in the storage modulus, determined by DMTA, than in the glassy state. Epoxy/GNP_{NH2} nanocomposites presented lower rubber modulus than epoxy/unmodified GNP nanocomposites, which is related to less cross-linked networks.

Epoxy/graphene adhesives had lower lap shear strength than neat epoxy adhesive independently of the type of graphene. This is a consequence of their lower tensile strength and toughness.

The lap shear strength for 1% GNP nanocomposites was higher than for 6% GNP, which is a consequence of agglomerates when the GNP content is increased. The formation of chemical bonds between GNP_{NH2} and the epoxy matrix had no significant influence on the joint strength.

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Figures:

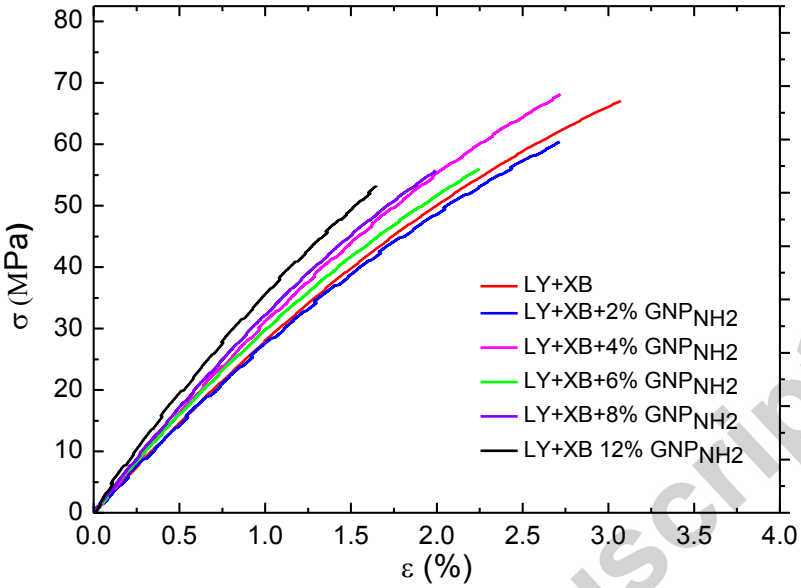

Fig. 1. Stress-strain curves for epoxy thermoset and epoxy/GNP$_{NH2}$ nanocomposites at 22 ºC.

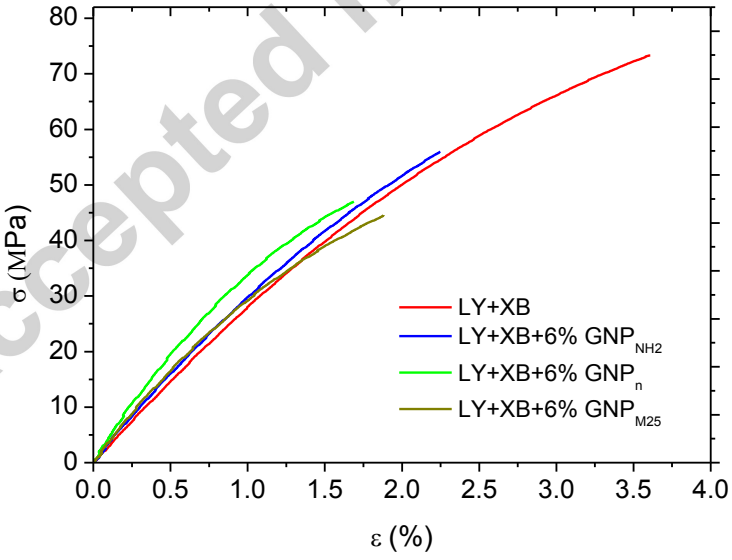

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Fig. 2. Stress-strain curves for epoxy thermoset, epoxy/GNP nanocomposites containing 6% GNP$_n$ at 22 ºC.

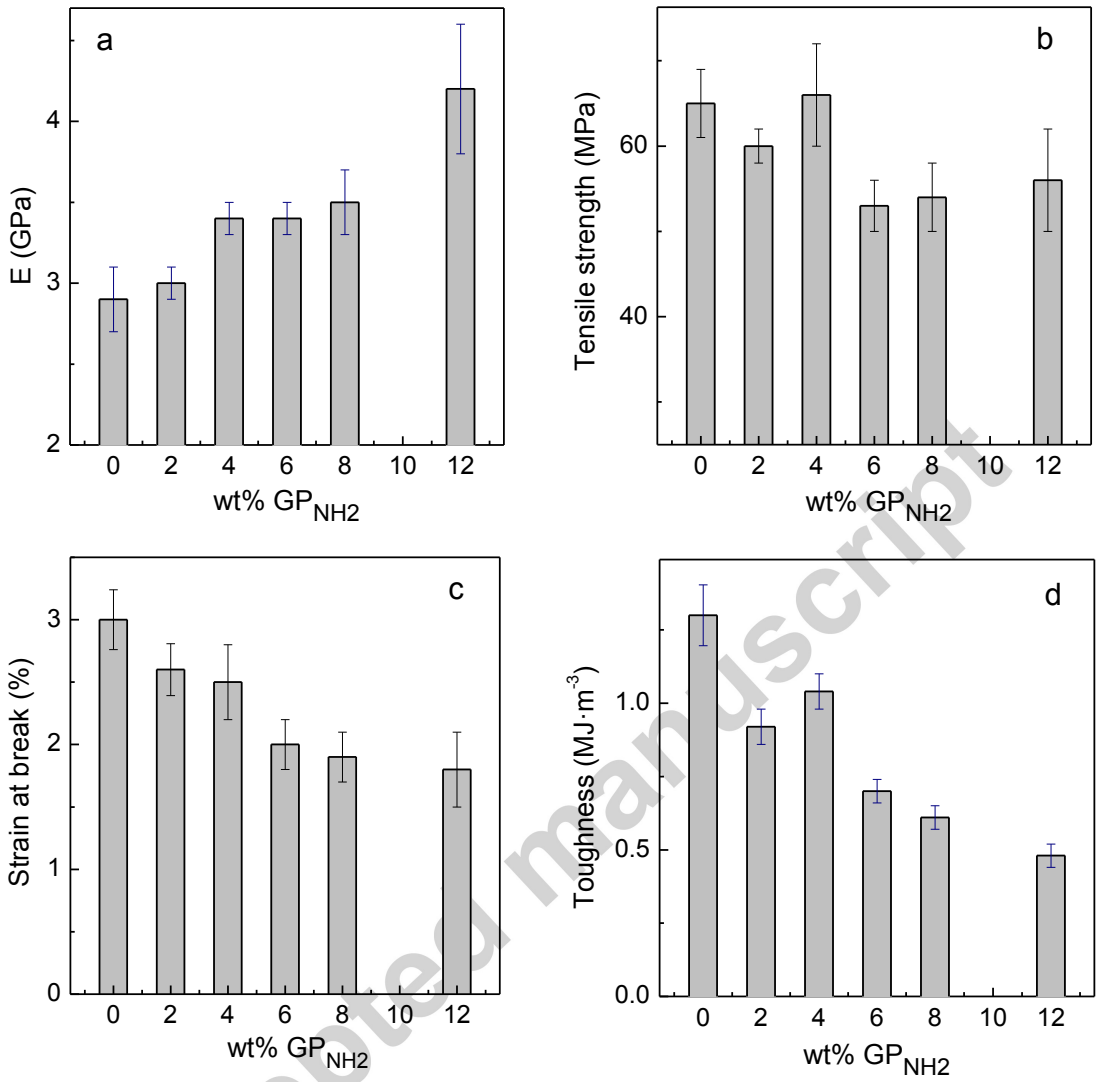

Fig. 3. Tensile properties of epoxy thermoset and epoxy/GNP$_{NH2}$ nanocomposites at 22 ºC.

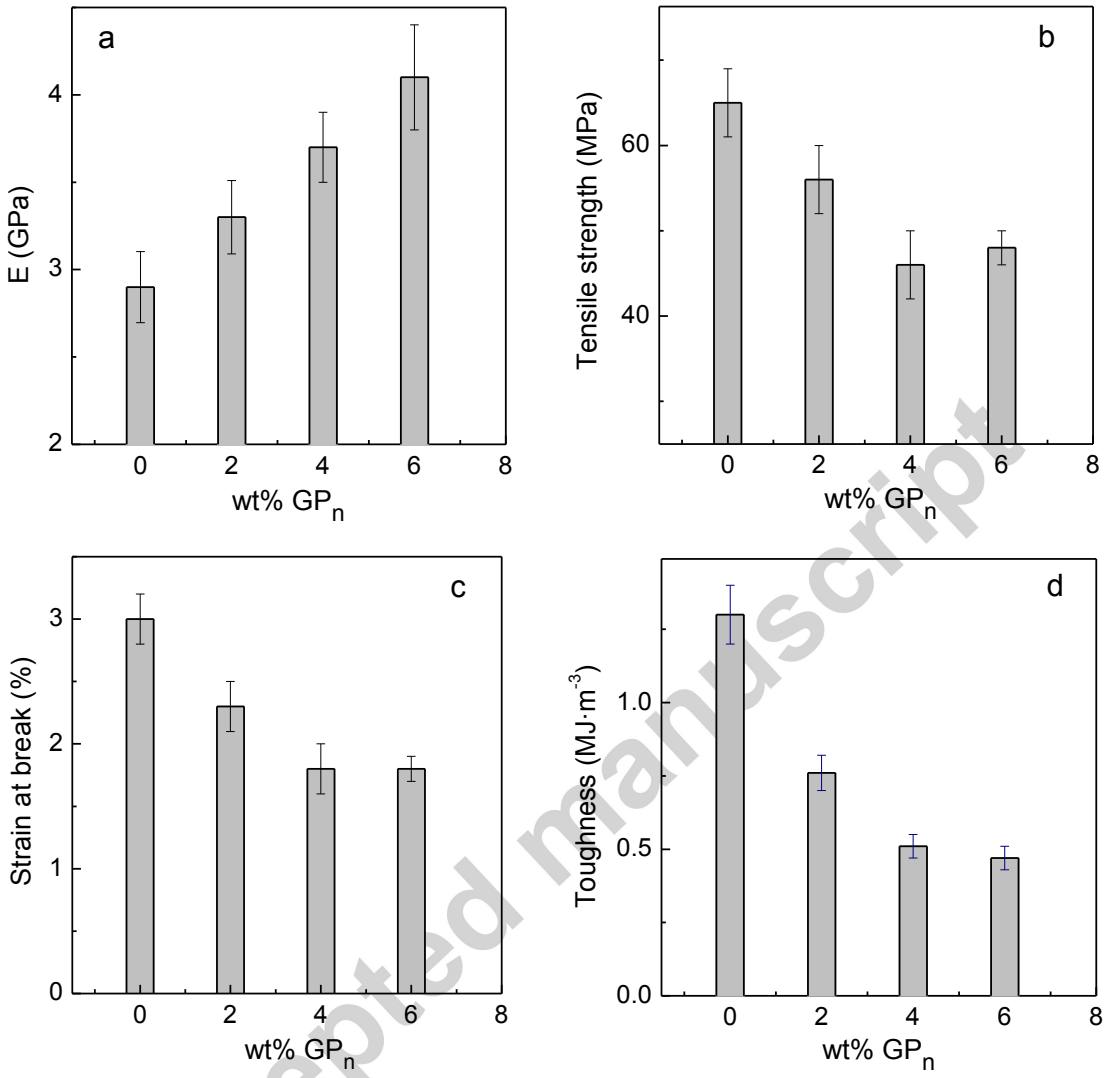

Fig. 4. Tensile properties of epoxy thermoset and epoxy/GNP_n nanocomposites at 22 ºC.

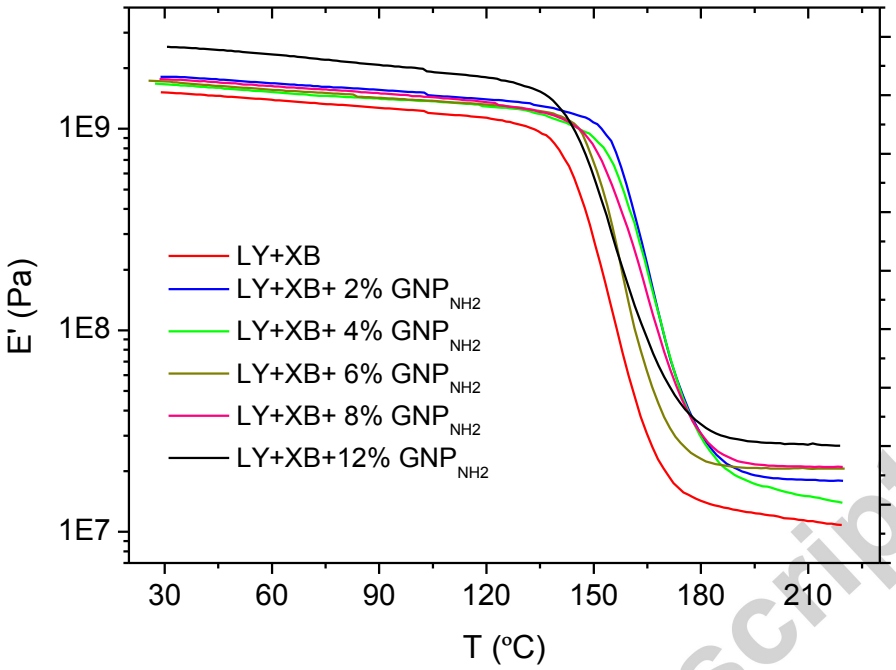

Fig. 5. *E´* vs. temperature for epoxy thermoset and epoxy/GNP_{NH2} nanocomposites at 1Hz.

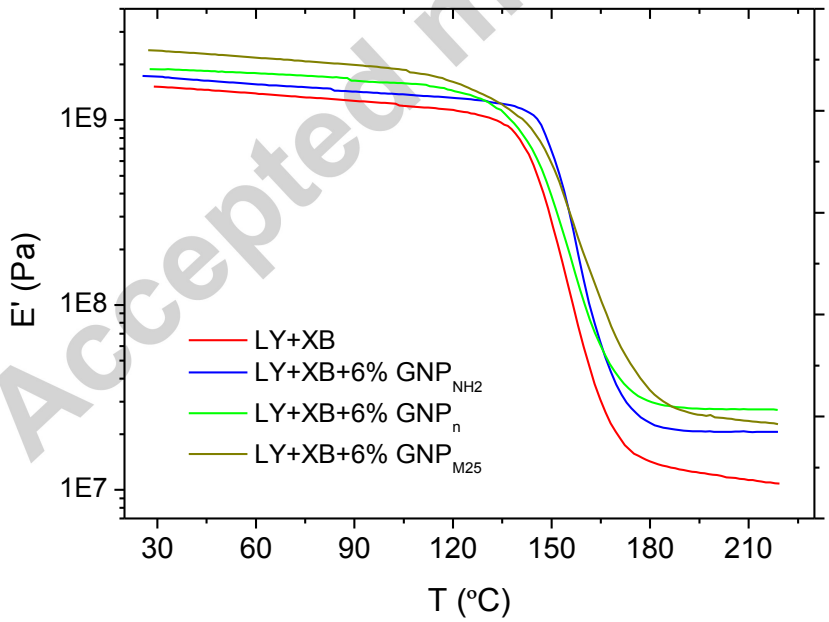

Fig. 6. *E´* vs. Temperature for epoxy thermoset and epoxy/6% GNP nanocomposites at 1Hz.

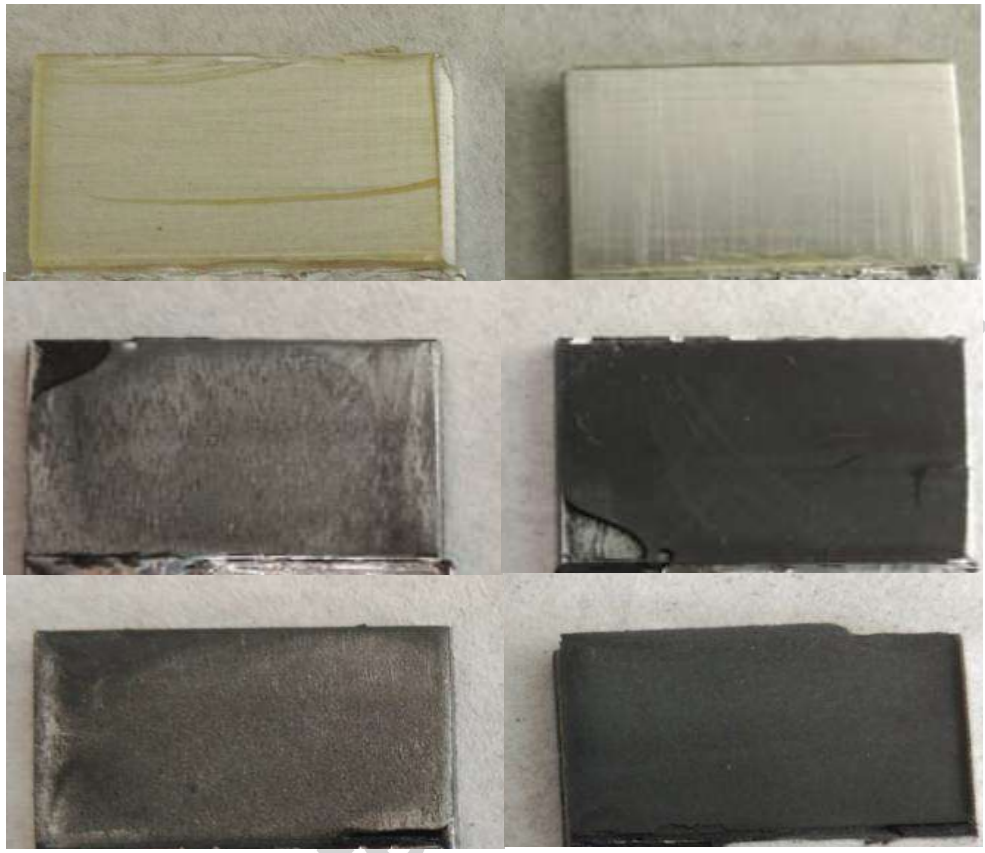

Fig. 7. Faillure surfaces of epoxy adhesives on aluminum joints: a) and a´) neat LY+XB, b) and b´) LY+XB+6%GNP_{NH2} c) and c´) LY+XB+6%GNP_n.

Table 1 Tensile properties of epoxy thermoset and epoxy/GNP nanocomposites containing 6% GNP at 22 ºC.

	Young´s modulus (GPa)	**Tensile strength (MPa)**	**Strain at break (%)**	**Toughness* ($MJ \cdot m^{-3}$)**
LY+XB	2.9±0.2	65±4	3.0±0.2	1.30±0.1
LY+XB+ 6%GNP_{NH2}	3.4±0.1	53±3	2.0±0.2	0.70±0.06
LY+XB+ 6%GNPn	4.0±0.3	48±1	1.8±0.1	0.47±0.04
LY+XB+ 6%GNP_{M25}	3.6±0.2	44±2	1.7±0.1	0.49±0.04

*Area under the stress-strain curve.

Table 2 Relative storage modulus ($E_r' = E'$(sample)/E'(neat epoxy thermoset)) in the glassy (80 ºC) and rubbery (200 ºC) states, E''_{max} and $tan\ \delta_{max}$ temperatures of neat epoxy thermoset and epoxy/GNP_{NH2} nanocomposites at 1Hz.

	E_r' 80ºC	E_r' 200ºC	E''_{max} (ºC)	$tan\ \delta_{max}$ (ºC)
LY+XB	1	1	143	160
LY+XB+ 2%GNP_{NH2}	1.2	1.5	158	172
LY+XB+ 4%GNP_{NH2}	1.1	1.4	156	172
LY+XB+ 6%GNP_{NH2}	1.1	1.7	150	163
LY+XB+ 8%GNP_{NH2}	1.2	1.8	154	171
LY+XB+ 12%GNP_{NH2}	1.7	2.3	146	160

Table 3 Relative storage modulus ($E_r' = E'$(sample)/E'(neat epoxy thermoset)) in the glassy (80 ºC) and rubbery (200 ºC) states, E''_{max} and $tan\ \delta_{max}$ temperatures of neat epoxy thermoset, epoxy/GNP_n and epoxy/GNP_{M25} nanocomposites at 1Hz.

	E_r' 80ºC	E_r' 200ºC	E''_{max} (ºC)	$tan\ \delta_{max}$ (ºC)
LY+XB	1	1	143	160
LY+XB+ 2%GNP_n	1.2	2.0	157	169
LY+XB+ 4%GNP_n	1.3	2.5	152	167
LY+XB+ 6%GNP_n	1.3	2.3	143	159
LY+XB+ 6%GNP_{M25}	1.5	2.1	147	165

Table 4 Lap shear strength of epoxy and epoxy/GNP adhesives at 22 ºC. Surface treatments: T1: Alkaline Bath (100 g/L) and T2: Alkaline bath + oxidation with $Fe_2(SO_4)_3$.

Adhesive	**Shear Strength** (MPa)	**Surface treatment**
LY+XB	9.3±0.8	T1
LY+XB	11.2±0.4	T2
LY+XB+6%GNP_{NH2}	8.5±0.6	T1
LY+XB+6%GNP_{NH2}	8.9±0.6	T2
LY+XB+6%GNP_n	9.1±0.6	T1
LY+XB+6%GNP_n	9.1±0.3	T2
LY+XB+ 1%GNP_{NH2}	9.8±0.7	T2
LY+XB+1%GNP_n	9.6±0.6	T2