CHARACTERIZATION OF MULTIFUNCTIONAL COMPOSITES OBTAINED FROM CARBON FIBER/EPOXY PREPREGS CONTAINING GRAPHENE RELATED MATERIALS

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Abstract
This paper presents the results of the physic-chemical and mechanical tests performed to multiscale materials consisting of a epoxy matrix modified with three different types of graphene related materials (GRM) and standard modulus carbon fiber. These composite materials were obtained from unidirectional carbon fiber/epoxy prepregs containing a fixed amount of GRMs. The use of prepregs avoids the filtration problems related to the infusion and injection technologies for the manufacturing of composite laminates. In the mechanical properties evaluated in this paper (tensile and flexural tests), it was found that the presence of the GRMs does not have a significant influence. The calorimetric and rheological study of the uncured prepregs suggest a catalytic effect of the graphite nanoplatelets in the cure reaction of the epoxy matrix.

1. Introduction

There is an actual demand from the aerospace and automotive industry for a next generation of advanced materials which are required to reduce weight, thus cost, and provide multifuntionality. Graphene related materials (GRM) have been focus of study since its discovery due to the broadly known outstanding properties of graphene, from mechanical to barrier, thermal and electrical properties, including its large surface area ratio and light weight. The addition of these GRMs to epoxy resins has been proved to be effective and can enhance some properties of the matrix [1-4]. In addition to that, several authors have revealed that the incorporation of GRM to fiber reinforced polymer composites improve its performance [5]. This incorporation can be found to be done mainly by dispersion of the GRM in the epoxy matrix and then manufacturing the composites by hand lay-up [6] or resin infusion [7], or by deposition of the GRM on the carbon fiber [5]. However, these process are not industrially scalable and show problems related to homogeneous dispersion and distribution of the GRMs through the composite.

Taking all of this into account, in this study, modified CF/epoxy laminates were manufactured by prepreg hand lay-up and cured in autoclave, following industrial methods currently applied in the aeronautical sector. Three GRMs were selected for modifying the epoxy matrix: graphite oxide,

reduced graphene oxide and graphite nanoplatelets. These particles were dispersed in the epoxy resin in a concentration equal to 2 wt.% by high shear mixing in order to get homogeneization and distribution of the nanoparticles. Then, unidirectional carbon fiber tapes with standard modulus fiber were impregnated with the charged resin by hot melt filming process. This study is included in a complete mechanical and physic-chemical characterization of the three modified carbon fiber/epoxy composites and the reference which has been manufactured in the same way without alteration of the resin with GRMs. In order to evaluate the multifunctional behavior, the electrical conductivy was also evaluated, the results will be reported elsewhere. In this paper, a selection of the tests performed is reported.

2. Experimental procedure

2.1. Materials

A tri-functional epoxy resin formulated by Delta-Tech was used as the matrix. The fiber selected was standard modulus carbon fiber T700G-12k aerospace grade in the form of unidirectional tape, with 200 gsm FAW, supplied by Toray.

The GRMs selected are: graphite oxide exfoliated in-situ in the resin (A0227) and reduced graphene oxide (A0228) produced by Avanzare, and graphite nanoplatelets (G2Nan) produced by Nanesa. Table 1 collects some properties of the GRMs provided by the suppliers.

Table 1. Data of the GRMs and panel identification.

GRM	Lateral size (μm)	BET (m^2/g)	Oxygen content (%)	Prepreg identification
-	-	-	-	REF
A0227	43	562	31	A1
A0228	39	780	12	A2
G2Nan	30	> 30	< 3	NAN

2.2. Manufacturing of the GRM-doped laminates

First, the GRMs were dispersed in the base resin using the mixer Dispermat with a cowless helix, in a concentration of 2 wt.%. Additionally, the graphite oxide (A0227) was exfoliated in-situ in the resin by dip ultrasonication, and for the graphite nanoplatelets (G2Nan) a second stage of homogeneisation and distribution was performed by high shear mixing.

Then, the resin formulation was completed and combined with the carbon fibre tape by hot melt impregnation. The resin content of the prepregs obtained is 34 wt.% and the GRM content is 0.61 wt.%.

Composite panels were made by hand lay-up of the prepreg with vacuum compaction. The stacking sequence was $[0^o]_{10}$. The laminates were cured in autoclave at 180 ºC for 120 min. The heating and cooling rates were 1 and 2 ºC/min, respectively, and a pressure of 6-7 bar was applied. Four panels were obtained (three with GRMs and the reference), identified as indicated in Table 1. Additionally, panels with different stacking sequence were also manufactured for mechanical tests that will be reported elsewhere. Specimens from these panels were also used for microscopic studies.

Every panel was subjected to ultrasonic non-destructive inspection (NDI) prior to machining for obtaining the test specimens. The C-scans obtained revealed the absence of porosity and delaminations.

2.3. Experimental techniques

The uncured prepreg was tested with a rheometer AR-G2 from TA Instruments in order to study the gelation during the cure cycle. The tests were performed is oscillation mode keeping constant normal force, and the criterium used for the determination of the gel point was the onset in the drop of the normal force. Differential scanning calorimetry (DSC) tests were performed in a DSC Q2000 from TA Instruments with a heating rate of 10 ºC/min for the evaluation of the cure degree. The reference enthalpy corresponding to 100% cure has been obtained for every material in the same conditions. The glass transition temperature was obtained by dynamic mechanical analysis (DMA) with a heating rate of 5 ºC/min, amplitude 15 μm and frequency 1 Hz, determined as the peak of the tanδ curve.

The fiber, resin and void content were calculated following the acid digestion method (standard EN 2564 method B). A precision scale Mettler Toledo XP205DR was used for the weight and density measurements.

For the mechanical characterization, tensile and flexural tests were carried out. Tensile test were performed according to ISO 527 standard using a universal test machine MTS Landmark 370.10 System with a load cell of 100 kN. For the flexural tests according to EN2562 standard, a universal test machine Zwick AllroundLine Z01OTH with a load cell of 10 kN was used. Five specimens of each material were used for each mechanical test.

3. Results

3.1. Characterization of uncured prepregs

The tests performed to the uncured prepregs reveal a not-significant influence of the different GRMs in the cure reaction of the epoxy matrix. In the DSC thermograms (Fig. 1), it can be observed a slight shift to lower temperatures in the cure reaction for the configurations A1 and NAN, which agrees with a reduction of the gel temperature (T_{gel}) determined in the rheology tests (Table 2). It was reported that the addition of different graphene related materials, such as graphene oxide, graphite oxide or graphene nanoplatelets can have a catalytic effect in the cure reaction of epoxy resins [8-10]. In this case, the variations observed in the peak temperature of the cure reaction and the gelation temperature could be due to a catalytic effect in the prepreg with graphite nanoplatelets (NAN) and a slight retardant effect with reduced graphene oxide (A2).

3.2. Characterization of the cured laminates

First of all, the fiber, resin and void contents were determined. It was checked that the average resin content is 34.7 wt.%, which agrees with the nominal value, and the void content is lower than 0.5 % for each panel.

The results of the DSC tests of the laminates reveal a cure degree (α) higher than 97 %, meaning that they are all completely cured, as it can be observed in Table 2. The glass transition temperature (T_g), obtained in DMA tests (Fig. 2), is the same for the four material configurations, indicating that none of the GRMs selected, in the concentration of 2 wt.% in the matrix, have an influence on its T_g. Prolongo et al. observed the same behavior with graphene nanoplatelets [4], while other authors have reported an increase of the glass transition temperature due to the presence of different types of GRMs. These

nanoparticles can limit the movement of molecular chains, shifting the glass transition to higher temperatures, or have a chemical cross-link with the matrix, decreasing its T_g value [11, 12].

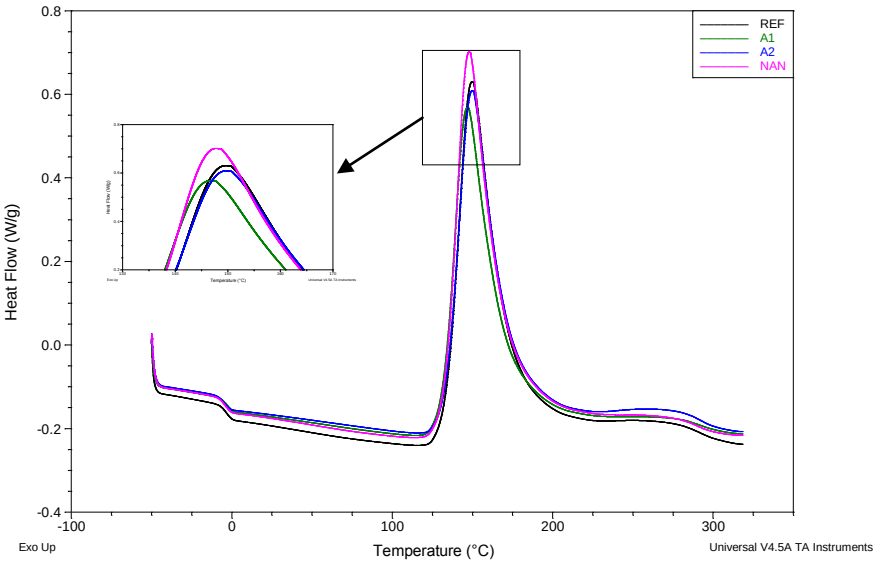

Figure 1. Thermograms of the DSC tests of the uncured prepregs.

Table 2. Results of the physic-chemical tests.

Specimen Type	T_{gel} (ºC)	α (%)	T_g (ºC)
REF	118.6 ± 2.2	98.5 ± 0.5	201.4 ± 0.9
A1	116.6 ± 2.2	98.8 ± 0.0	200.9 ± 0.8
A2	120.1 ± 1.7	97.0 ± 0.1	201.1 ± 0.7
NAN	114.5 ± 0.5	98.4 ± 0.4	200.1 ± 0.3

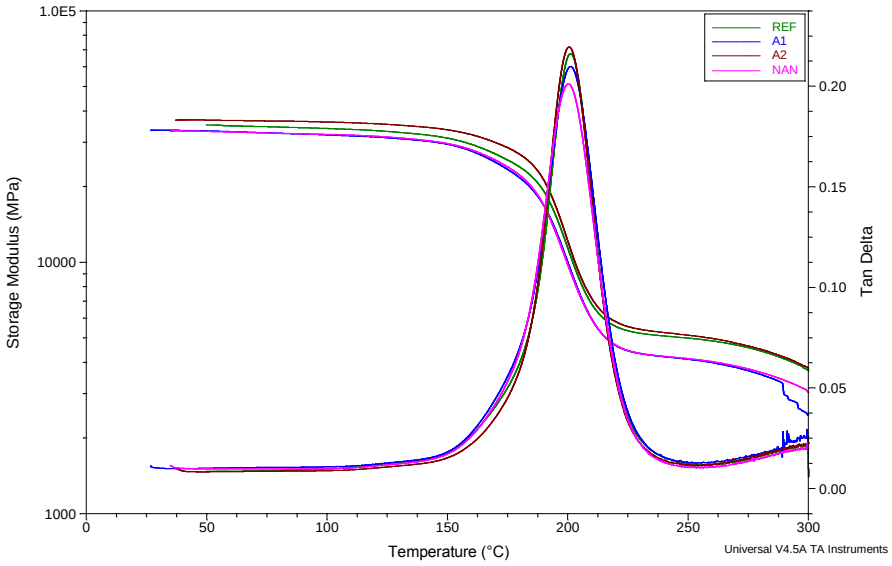

Figure 2. Thermograms of the DMA tests.

Typical stress-strain curves of each material obtained in the tensile and flexural tests are shown in Fig. 3. A light decrase in the Young modulus and tensile strength was obtained in the GRM-doped composites, compared to the reference (Table 3). It is not significant taking into account the dispersion of the results, except for the modulus in the A1 configuration, with a drop of 5 % in this property. The properties obtained in this test depend on the fibre, with an almost negligible influence of the matrix modification, and thus no improvements were expected with the addition of the nanofillers. Anyway, this test was selected because it was important to check that the properties were maintained. Other authors have reported an improvement in the mechanical properties of graphene oxide/carbon fiber/epoxy composites, for example Ashori et al. [6], but they used laminates with a different lay-up, [0/90/0]. The presence of plies at 90º makes easier to detect the beneficial effect, if any, of the GRM in the composite.

In the flexural tests, the configuration A1 shows the lowest properties, but the decrease in the strength and modulus is not high. The values obtained for A2 and NAN are almost the same than for the reference.

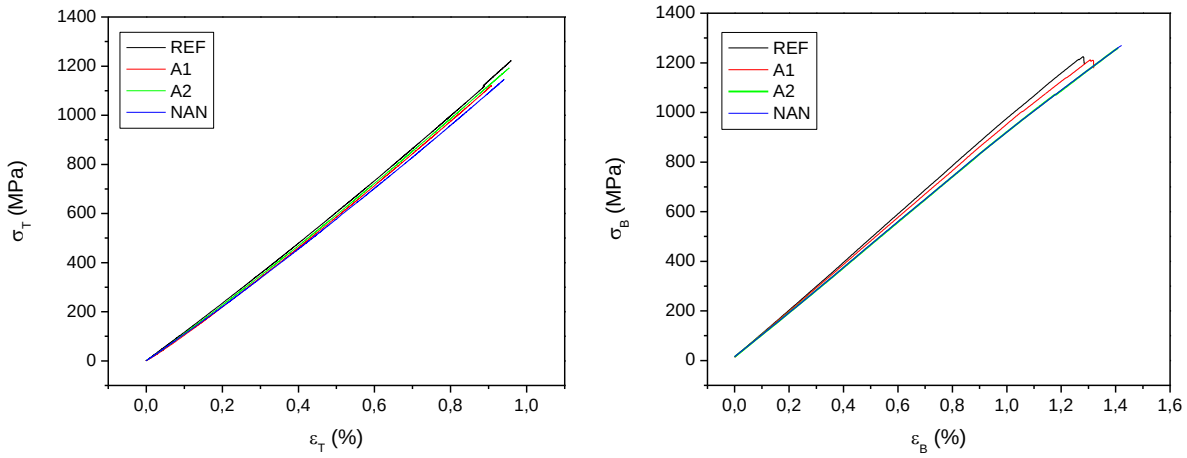

Figure 3. Stress-strain curves of the tensile (left) and flexural (right) tests.

Table 3. Results of the mechanical tests.

Specimen Type	Tensile properties		Bending properties	
	E_t (GPa)	σ_t (MPa)	E_b (GPa)	σ_b (MPa)
REF	117 ± 2	1225 ± 63	96 ± 1	1287 ± 61
A1	112 ± 4	1186 ± 57	93 ± 1	1219 ± 48
A2	114 ± 5	1192 ± 51	94 ± 3	1268 ± 57
NAN	116 ± 3	1089 ± 227	96 ± 11	1299 ± 53

Fracture surfaces from specimens with stacking sequence $[+45/-45]_{4s}$, tested for the determination of the in-plane shear strength, were observed in the scanning electron microscope (SEM) (Fig. 4). Agglomerates of the graphite nanoplatelets were easily observed in the fracture surface of the specimen with configuration NAN (marked with a circle in the micrograph 4d). The GRMs A0227 and A0228 (configurations A1 and A2 respectively) are better dispersed and also it seems that they present a better interaction with the polymer matrix, probably due to the higher oxygen content compared to G2Nan (Table 1). In the three GRM-doped composites, the fracture surface exhibits more roughness than the reference, suggesting the activation of new mechanisms of energy consumption that could improve other mechanical properties that were not tested in this work (they will be included in the continuation of this research).

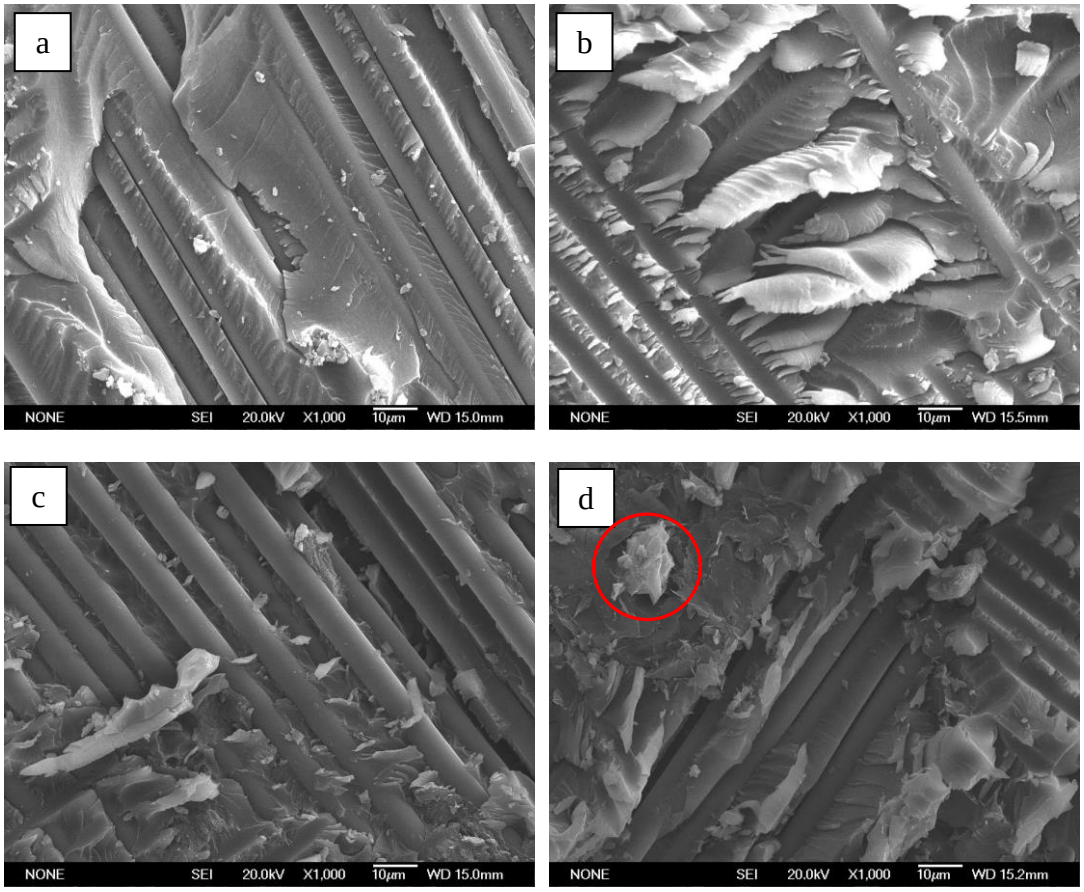

Figure 4. SEM micrographs of fracture surfaces: a) REF, b) A1, c) A2, d) NAN.

4. Conclusions

Multiscale composite laminates were successfully manufactured, with no porosity and good quality according to the non-destructive inspection. The results of the characterization performed indicate that the presence of the selected GRMs does not have a significant influence in the tensile and flexural strength and modulus of specimens with unidirectional lay-up. However, the differences found in the microscopic analysis of the fracture surfaces of the multiscale composites with regard to the reference could be attributed to the activation of new mechanisms of energy consumption associated to the presence of the GRMs. Additional mechanical tests and a detailed fractographic analysis will be performed.

The DSC and rheology tests carried out on uncured prepregs suggest a catalytic effect of the graphite nanoplatelets (configuration NAN) in the cure reaction of the epoxy matrix. No variations were measured in the cure degree and glass transition temperature of the cured specimens.

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References

[1] F. Wang, L.T. Drzal, Y. Qin and Z. Huang. Effects of functionalized graphene nanoplatelets on the morphology and properties of epoxy resins. *High Performance Polymers*, 28:525-536, 2016.

[2] B. Ahmadi-Moghadam, M. Sharafimasooleh, S. Shadlou and F. Taheri. Effect of functionalization of graphene nanoplatelets on the mechanical response of graphene/epoxy composites. *Materials and Design*, 66:142-149, 2015.

[3] R.J. Young, I.A. Kinloch, L. Gong and K.S. Novoselov. The mechanics of graphene nanocomposites: A review. *Composites Science and Technology*, 72:1459-1476, 2012.

[4] S.G. Prolongo, R. Moriche, A. Jimenez-Suarez, M. Sanchez, A. Ureña. Advantages and disadvantages of the addition of graphene nanoplatelets to epoxy resins. *European Polymer Journal*, 61:206-214, 2014.

[5] P. He, B. Huang, L. Liu, Q. Huang and T. Chen. Preparation of multiscale graphene oxide-carbon fabric and its effect on mechanical properties of hierarchical epoxy resin composite. *Polymer Composites*, 37:1515-1522, 2016.

[6] A. Ashori, H. Rahmani and R. Bahrami. Preparation and characterization of functionalized graphene oxide/carbon fiber/epoxy nanocomposites. *Polymer Testing*, 48:82-88, 2015.

[7] H. Zhang, Y. Liu, S. Huo, J. Briscoe, W. Tu, O.T. Picot, A. Rezai, E. Bilotti and T. Peijs. Filtration effects of graphene nanoplatelets in resin infusion processes: Problems and possible solutions. *Composites Science and Technology*, 139:138-145, 2017.

[8] D.R. Bortz, E.G. Heras and I. Martin-Gullon. Impressive fatigue life and fracture toughness improvements in graphene oxide/epoxy composites. *Macromolecules*, 45:238-245, 2012.

[9] M. Mauro, M.R. Acocella, C.E. Corcione, A. Maffezzoli and G. Guerra. Catalytic activity of graphite-based nanofillers on cure reaction of epoxy resins. *Polymer*, 55:5612-5615, 2014.

[10] M.G. Prolongo, C. Salom, C. Arribas, M. Sánchez-Cabezudo, R.M. Masegosa and S.G. Prolongo. Influence of graphene nanoplatelets on curing and mechanical properties of graphene/epoxy nanocomposites. *Journal of Thermal Analysis and Calorimetry*, 125:629-636, 2016.

[11] J. Gu, X. Yang, Z. Lv, N. Li, C. Liang and Q. Zhang. Functionalized graphite nanoplatelets/epoxy resin nanocomposites with high thermal conductivity. *International Journal of Heat and Mass Transfer*, 92:15-22, 2016.

[12] Z. Li, R.J. Young, R. Wang, F. Yang, L. Hao, W. Jiao and W. Liu. The role of functional groups on graphene oxide in epoxy nanocomposites. *Polymer*, 54:5821-5829, 2013.