INTERFACE INVESTIGATION OF HYBRID POLYMER COMPOSITES WITH GRAPHENE-MODIFIED MATRIX

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Abstract

Over the years, it has been proved that fibre-matrix interface quality has a critical role on the performance of carbon fibre reinforced composite. In this work, we aim to study the interfacial quality of carbon fibre reinforced composites after the modification of the host epoxy matrix with graphene nanoplatelets. This method directly introduces graphene nano-platelets (GNPs) dispersed in the host epoxy system and exhibits an interface enhancement in the range of 50% provided an addition of 3 wt% in nano-fillers. For this single-filament interface evaluation technique, Raman spectroscopy has been adopted along with the basic principles of the shear lag theory. The calculated shear lag parameter (β-parameter) was used as a criterion to determine and quantify the enhancement of the interfacial properties. In addition, mechanical tests, such as tensile loading of epoxy/graphene nanocomposite films and interlaminar shear stress tests on hybrid composites, were performed in order to evaluate the contribution of GNPs inclusions to the macro mechanical properties.

Introduction

During the past few decades carbon fibre reinforced composites have replaced metal counterparts in a wide range of high performance automotive and aerospace structural applications, as they exhibit –among other benefits- high strength and stiffness to weight ratios [1]. The role of interface-interphase has been traditionally one of the most important subjects of study in the field of advanced polymeric composites. It is well established that the level of interfacial adhesion between the host material and the inclusions dominates the transfer mechanism of stresses from the 'weak' matrix to the 'strong' reinforcing phase. Also, it is widely accepted that a composite with good mechanical properties and environmental stability requires an optimum interface [2].

Graphene nanoplatelets (GNPs) are short stacks of individual (or very few) layers of graphite. GNPs are recently developed, and their production requirements nowadays does not classify them any more as high cost material. Inclusion of graphene nano-platelets (GNPs) in epoxy has been shown to improve mechanical and electrical properties with respect to the un-reinforced epoxy, thus triggering the research on using epoxy/GNP systems as a host matrix in several composite applications. The resulting hybrid composite can potentially exhibit enhanced mechanical properties in respect to traditional carbon fibre composites [3-4].

This modification route is based onto altering the properties of the host matrix instead of those of the reinforced fibres by controlled dispersing of graphene flakes into epoxy resin. In this work, commercially available carbon fibres were embedded into epoxy films containing graphene flakes in different volume fractions varying from 0.2 to 3 wt%. The preparation of the modified epoxy matrix follows a rather simple but effective path of mixing graphene nanoparticles in a two step procedure. Initially, GNPs are dispersed into the 'hardener' agent of the two-component epoxy

system by discrete steps of magnetic steering and bath sonication for suitable timings. Following the above the GNP/hardener compound is mixed with the required quantity of epoxy resin under magnetic steering of the solution. The modified epoxy system is then used to fabricate the single filament model coupons as described subsequently. Raman spectroscopy has been successfully adopted to study the stress-transfer characteristics in carbon fibre/epoxy systems, since the Raman lines of the reinforcing carbon fibres exhibit distinct and reproducible shifts when subjected to axial load in the fibre direction [5]. As stated in our early works [6] the strain transfer profiles obtained by Raman spectroscopy can be converted into interfacial shear stress profiles along the length of the reinforcement by means of a straightforward balance of forces argument. This indeed captures the very essence of reinforcement in polymer composites that incorporate stiff inclusions (e.g., fibre, graphene flakes, etc.) since the principal mechanism is shear at the interface, which is converted into normal stress at the inclusion.

Experimental

Materials

In the first part of this study high modulus PAN based Toray M40 fibres, with a diameter of 7 microns, were used. Host medium consisted of a two-part 'water clear' (base agent: R2820 / hardener: H8390, ratio: 2:1) epoxy system provided by Fibermax. The resin system is mixed and cured at Room Temperature (RT) and an additional post-curing at 40-80^{o} C is implemented for achieving the final mechanical properties. Graphene powder consisted of 5 to 7 layer and 5 μm diameter flakes, provided by Thomas Swain.

Low modulus CF cloth supplied by Fibermax and the already mentioned epoxy system, been used for the hybrid CFRP fabrication. It is a unidirectional weave fabric with 50% consisted of 12K T300 carbon fibres.

Sample preparation

The fabrication of CF reinforced resin "model" composites was carried out by pouring a small quantity (in order to form a thin layer) of resin over the CFs, which were placed and aligned on a flat polished surface. The flat substrate was covered by stretched release film to ensure proper removal without damaging the cured coupon. In this way, fibres were embedded close to the outer surface of the matrix in order to be optically accessible to Raman Microscope. Films were cured for 48 h at RT and then for 24 h at 40^{o} C. The aforementioned procedure resulted to the fabrication of single fibre reinforced coupons with dimensions 6cm x 5mm x 0.1 mm. The single filament coupon fabrication method was kept constant for both examined cases herein.

For the hybrid composite preparation epoxy resin was modified by incorporating different wt% of GNPs and desired size of CF fabric was impregnated to get the prepreg. The prepregs stored at -18^{o} C for 10 days. For the CFRP lamination hand lay-up technique was used, followed by vacuum bagging process, to remove trapped air. The composite cured in Aeroform autoclave for 3 h at 85^{o} C under 2.5 bar applied pressure. The fabricated samples measured for ILSS tests had dimensions of 4cm x 12mm x 5mm.

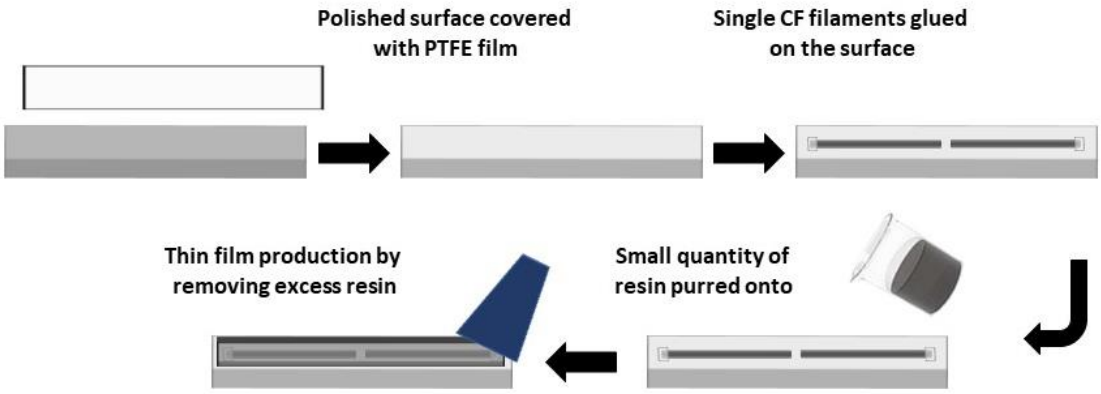

Figure 1. *Model composite fabrication*

Results and discussion

Mechanical characterization of modified matrix films

In order to evaluate the effect of adding graphitic nano-inclusions into epoxy resin, tensile test performed at neat matrix and at modified nanocomposites films for different volume fraction of GNPs varying from 0.2 to 3 wt%. As clearly presented in figure 2, the modulus of elasticity increases with the addition of graphene nanoplatelets, while there is no effect of the maximum stress of the nanocomposite films. As expected, the addition of a randomly dispersed and oriented filler with high stiffness into the epoxy matrix causes an increasing trend in the values of the Young modulus while the effect on the elongation to fracture has a negative impact, revealing that the material becomes more brittle as the GNP content increases.

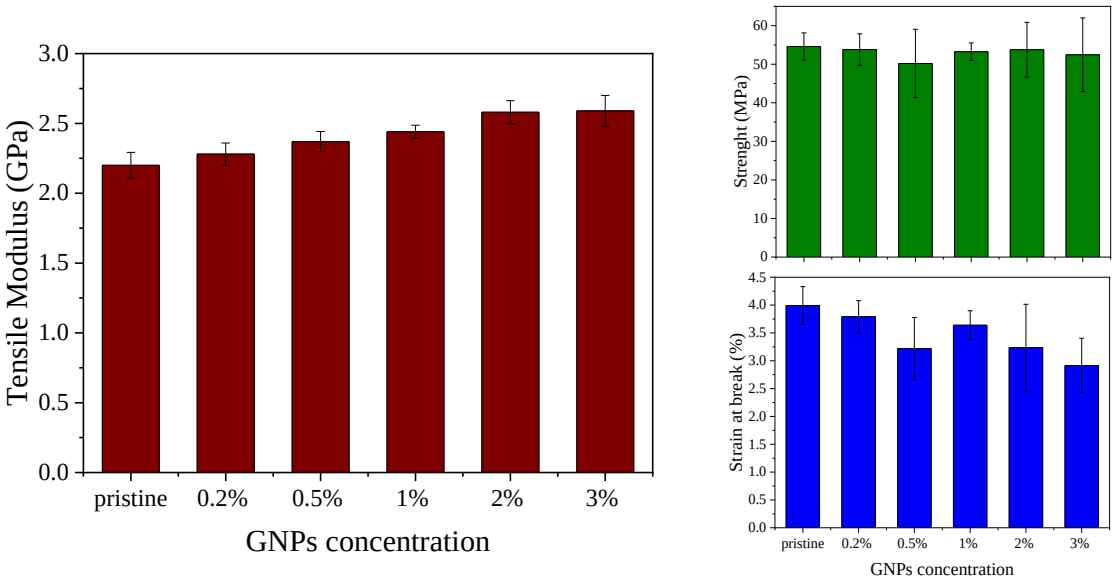

Figure 2. *Tensile properties of pristine and different concentrations GNP/epoxy nanocomposites films.*

Table 1. *Tensile properties of neat and different concentrations GNP/epoxy nanocomposites*

GNPs Concentration	Tensile Modulus (GPa)	Strenght (MPa)	Strain at break (%)
Pristine	2.19±0.063	55.37	3.99
0.2%	2.28±0.08	53.80	3.79
0.5%	2.35±0.072	48.20	3.22
1.0%	2.44±0.017	53.24	3.64
2.0%	2.52±0.083	53.77	3.23
3.0%	2.54±0.11	52.46	2.92

Interface investigation for GNP-modified epoxy matrix via Raman

As mentioned above, Raman spectroscopy has been adopted for the interface investigation. More detailed, point by point Raman spectra of the embedded single fibre filaments under axial tension were acquired, starting from the edges, until a total fibre length of approximately 1 mm was covered. Raman shift was converted to strain and then subsequently to axial stress, as derived from the calibration and mechanical testing data. In the present work the effect of the matrix modification on the interface properties was studied by measuring the corresponding interfacial shear stress (ISS) at the interface region certain levels of applied strain using a balance-of-forces approach [6]. The ISS distribution is obtained by the following equation:

$$\tau_{rx} = -\frac{r\beta\sigma_{f,\infty}}{2} e^{-\beta x} \quad (1)$$

Where, r is the radius of CF, $\sigma_{f,\infty}$ is the far field stress and β is a fitting parameter, which equals to the inverse transfer length value. The shear-lag parameter, β, [6] can effectively serve as a stress-transfer efficiency index. In Figure 3 the normalized axial stress for different GNPs loading (0 to 3%) is presented. It is apparent that the axial stress build-up rate is increasing with the wt% of GNPs exhibiting a peak for concentration of 2 wt% and decreasing again at 3 wt%. We can safely assume that additional quantities of graphene inclusions cannot further enhance the interfacial properties. This behaviour probably is due to the interaction between the graphene nanoplatelets with the CFs, as the GNPs attached onto the fibre's rough surface, thus increasing the mechanical interlocking with the matrix.

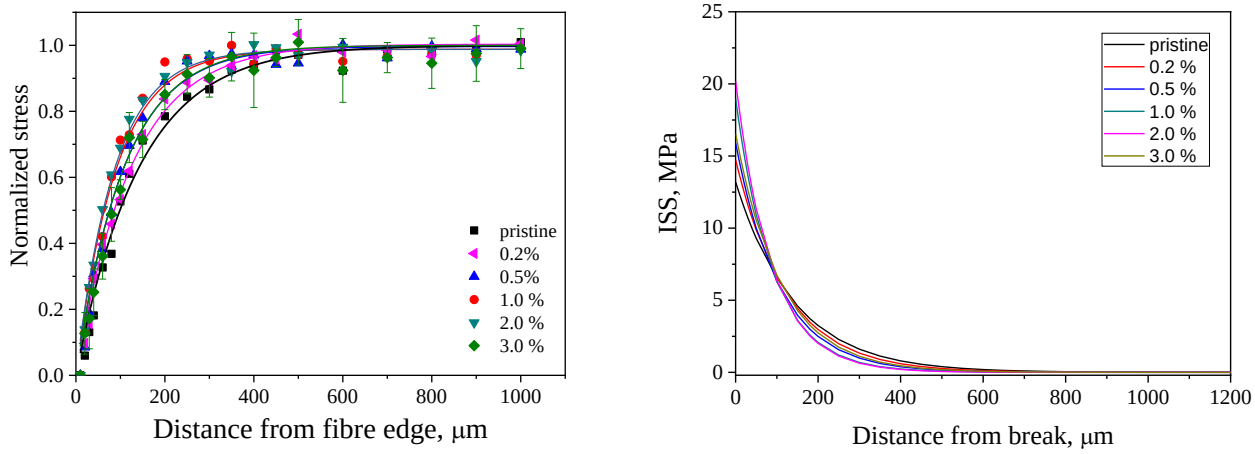

Figure 3. *Normalized axial stress (left) & ISS (right) versus the distance from the discontinuity of CF embedded in the epoxy resin for different GNP concentrations.*

In Figure 3 the calculated ISS values for each case are presented. Again, it is obvious that higher graphene inclusion concentrations lead to higher observed initial ISS values at the edge of the fibre, while the shear stress reduction rate is also increased. The shear lag parameter, β, as well as the initial ISS values for each case are calculated and presented in Table 2.

The interfacial evaluation results in case of GNP-modified epoxy matrix show a noticeable improvement compared to the pristine unmodified system, since the axial stress build-up rate is increased along with the initial ISS values, in accordance with the concentration of the graphene inclusions. The first experimental approach gives strong evidence of a concentration threshold above which no further enhancement is achieved. Using the β-parameter as a criterion, a maximum improvement of the interfacial quality in the range of 64% was observed.

Table 2. *Maximum ISS and the shear-lag parameter, β, values for different GNPs concentrations.*

GNPs Concentration (%)	β (μm^{-1})	ISS (MPa)
0	0.00702	13.20
0.2	0.00802	14.74
0.5	0.00927	15.89
1.0	0.01106	18.97
2.0	0.01154	20.20
3.0	0.00908	16.54

ILSS measurements of hybrid CFRP

Modified short beam shear (ASTM 2344) test was used to measure the interlaminar shear strength (ILSS) of hybrid GNPs/CFRP composites. The ILSS cuves and values are reported in Figure 4. A clear increase was obtained with the adding of 0.2 to 1 wt% of GnP in the interphase region (+ 45% in comparison to pristine sample). The adding of GnP increases the shear modulus of the matrix in the interphase region and coupled with the mechanical interlocking between fibre and matrix, reduces the inter-laminar stress concentrations at a given load.

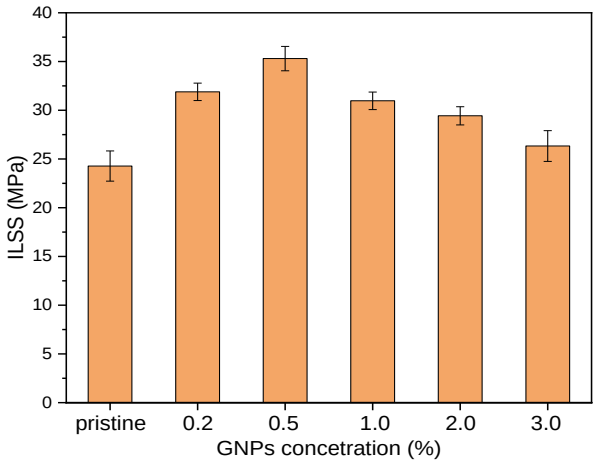

Figure 4. *Interlamine shear strength values of pristine and different concentrations GNP/epoxy nanocomposites films.*

Table 3. *Maximum interfacial shear strength values for different GNPs concentrations.*

GNPs Concentration (%)	ILSS (MPa)	Improvement (%)
0	24.28±1.52	-
0.2	31.89±0.89	31.32
0.5	35.30±1.25	45.35
1.0	30.97±0.90	27.55
2.0	29.43±0.94	21.19
3.0	26.33±1.58	8.44

Conclusion

In the present work authors demonstrate the effect of the matrix modification by adding of GNPs in the interfacial behavior of single filament model composites using the shear lag parameter –as derived from combined mechanical/spectroscopic experimental procedure- as a criterion. The presented method aims to modify the host matrix by dispersing graphene nano-inclusions in certain concentrations. The improvement of the interfacial parameter is noticeable and seem capable of producing composite materials with enhanced mechanical properties, while the corresponding improvement in the case of matrix modification with graphene reached 65%. Also large scale hybrid composite samples, of modified CFs / epoxy resin, present a significant interlaminar shear strength improvement of 45%.

Acknowledgments

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