GRAPHENE-BASED HYBRID MICROSTRUCTURES FOR INTERLAMINAR REINFORCEMENT OF FIBER-REINFORCED POLYMERS

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Abstract
An attractive solution to tackle the challenge of increasing both the mechanical and the electrical properties of fibre-reinforced polymers is to strategically position micro- or nano-structures in composite materials. In the present work, hybrid graphene-based microstructures have been synthesized and added to the interlaminar region of laminate composites to modify their interlaminar failure behaviour. For comparison purposes, laminates with graphite nanoplates have also been produced. It has been obtained that the modification of the interlaminar region with hybrid microparticles can results in laminates with improved fracture toughness. Thus, this approach has to be further analysed.

1. Introduction

From a mechanical aspect, aerospace composites are made of carbon fibre "plies" held together by a polymer. This polymer can easily crack, which results in the delamination of the plies and the failure of the structures if not detected on time. In order to render these materials more resistant to failure, micrometre diameter stitches [1], Z-pinning [2] or fibre weaves [3] can be used to join the plies together. Failure of aerospace structures can also result from common environmental damage, such as lightning strikes, electromagnetic interferences, electrostatic discharge, etc. Various methods are currently used to address these concerns, such as the use of metallic meshes. However, these meshes are difficult to produce and repair, and significantly increase the overall weight of an aircraft.

An attractive solution to tackle the challenge of increasing both the mechanical and the electrical properties of composite materials is to strategically position nano-structures in composite materials. However, up to now, strategies aimed at adding conductivity to the interlaminar regions of composites have not been accompanied by observations regarding mechanical reinforcement. Companies have recently been researching strategies to enhance the through-the-thickness electrical conductivity, but the reinforcing effect on the mechanical properties is negligible as compared to thermoplastic interleaves. A relatively new approach is to use carbon nanotube (CNT)-based nano-architectures placed strategically in the material interface to mechanically reinforce and to improve the electrical conductivity of the composite materials [4,5].

Here, we propose to use carbon-based micro- and nano-materials, that, when inserted into interlaminar regions of composites will enhance the mechanical properties of the composite by mechanical interlocking [6]. Concurrently, the electrical properties of the composite in the through-thickness direction are also enhanced. Graphite nanoplates (GNPs) and graphene-based hybrid microstructures

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have been added to the interlaminar region of laminate composites to improve their toughness and electrical conductivity.

2. Experimental

2.1. Graphene-based nanostructures

Graphite nanoplates were purchased from Avanzare (Logroño, Spain) and used with no further treatment. The particle size-analysis has been carried out in [7].

Graphene-based hybrid microparticles (HMPs) were synthesized by means of a chemical vapour deposition (CVD) process. A ceramic boat supporting the as-received micron-diameter metallic particles was placed in the middle of a horizontal quartz tube (25 mm in diameter), heated by a tube furnace at high temperature (above 500 °C). During the CVD process, a mixture of gasses was passed through the tube [8,9]. After the synthesis process, the furnace quartz tube was rapidly cooled down to room temperature.

The as-synthesized micron-diameter particles were analysed by Raman spectroscopy, X-ray diffraction, transmission (TEM) and scanning electron microscopy (SEM).

2.2. Filler distribution on the prepreg surface

In order to produce laminates, with different amounts of filler placed at the interlaminar region, the desired amount of HMPs and GNPs were first dispersed in ethanol. This solution was sonicated and carefully sprayed on a clean teflon film to uniform distribute the mixture. Once the solvent is evaporated, a ply of prepreg (unidirectional carbon/epoxy AS4/8552 prepreg, Hexcel) was placed over the teflon film and pressure was applied on the teflon film to transfer the filler to the tacky prepreg. Pressure was varied until full transfer of the nanostructures was achieved [10,11]. An example of a prepreg ply with filler on its surface can be observed in Figure 1a.

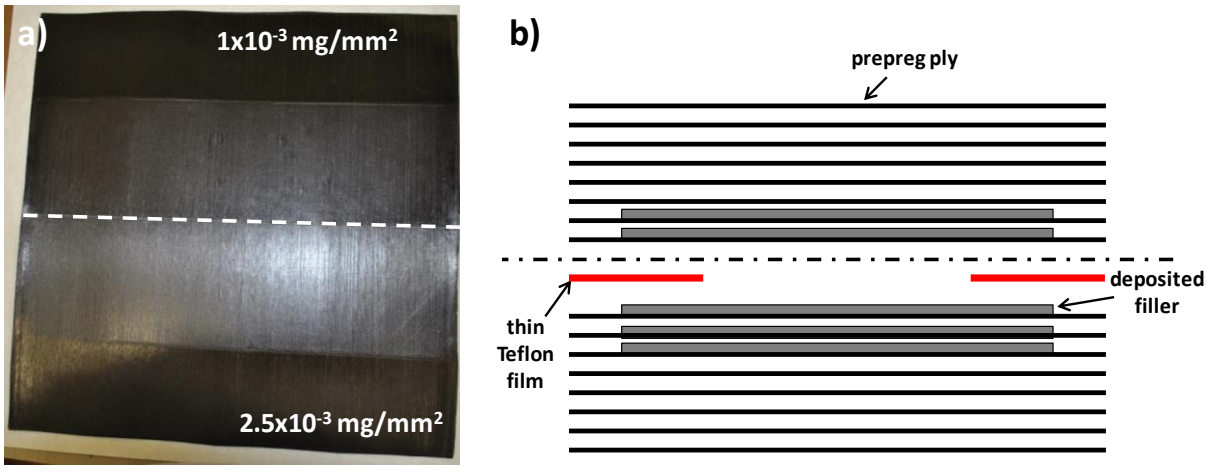

Figure 1. a) prepreg ply with 1 and 2.5 x 10^{-3} mg/mm^2 of graphite nanoplates transferred to its surface and b) schematic of laminate assembly.

2.3. Composite manufacturing and characterization

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Once the HMPs and the GNPs were transferred to the prepreg ply, laminates with the stacking sequence $[0]_{16}$ were fabricated. A schematic of the laminate assembly is shown in Figure 1b. First, 300 x 300 mm prepreg plies were cut and laid up by hand to create a 5-layer laminate. Three layers of the filler-modified prepreg were then added to the top of the lay-up, with the nanostructure side of the prepreg facing upward. This 8-layer laminate made up half of the laminate composite [11]. A thin film of teflon was placed at the midplane to form an initiation site for the interlaminar crack [12]. Then two layers of filler-modified prepreg, followed by 6 layers of prepreg were stacked together. Debulking was performed every 3 plies during the lay-up process of the laminates with hybrid microparticles.

In this configuration, the five central interfaces of the composites were interleaved with graphite nanoplates and graphene-based hybrid microparticles. The specimens were cured by hot pressing (Fontijne Grotnes LabPro400). After curing, the specimens for the opening mode I test were trimmed and white paint was applied to the edges to allow the visual tracking of the crack. Hinges were then attached to the end of each specimen using epoxy adhesive Figure 2.

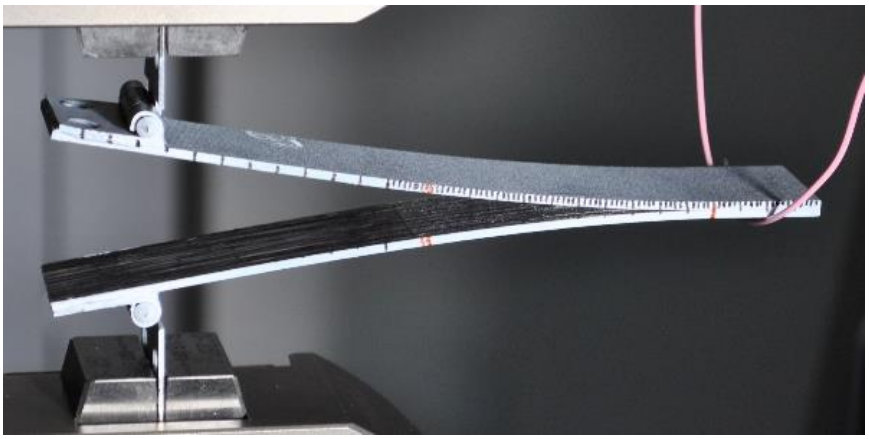

Figure 2. Specimen during a mode I interlaminar fracture test. It can be observed the bonded hinges and the marks for the recording of the delamination length.

Mode I fracture testing and data reduction have been carried out following the ASTM D-5528 standard [12]. During the test, crack propagation began at the end of the Teflon insert and the delamination length was recorded at every mm up to a total delamination length of 50 mm. Load, delamination length and load point deflection as a function of time were recorded. The results of these measurements are used to determine the mode I strain energy release rate (G_I) using the Compliance Calibration reduction method, described in [12]. As a parameter for the fracture characterization of the composites, we present the steady-state strain energy release rate of the composites (G_I), which is directly determined from the full R-curve. A total of five samples were tested for each type of laminated composite specimen

3. Results and Discussion

The morphology of the as-received GNPs and the hybrid microparticles obtained by CVD has been analysed by means of SEM (Figure 3). The individual GNPs have a particle size of 2 x 5 μm and a thickness lower than 10 nm. However, it has been observed that the as received material was in an agglomerated state (Figure 3a). The agglomerate size distribution can be found in [7].

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The graphene-based hybrid microparticles that were synthesized are composed of a central micron-diameter particle and 2 to 7 "branches" grown on surface of this particle (Figure 3b). These "branches" are mainly composed of graphite crystals and carbon.

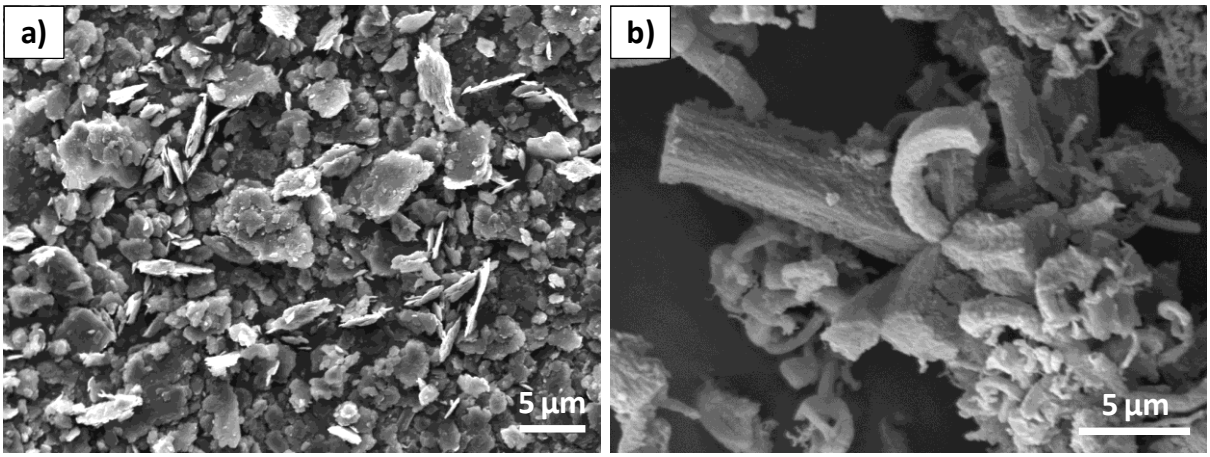

Figure 3. SEM images of the a) as-received graphite nanoplates and b) graphene-based hybrid microparticles obtained after the CVD process.

Figure 4 shows the mode I interlaminar fracture toughness of laminates with the interlaminar region modified with graphite nanoplates and hybrid microparticles. For the laminates with the GNPs, the amounts transferred to the interlaminar region were 0.5, 1 and 2.5x10^{-3} mg/mm^2. In the case of the laminates with graphene-based hybrid microparticles, the amounts transferred were 5, 10 and 20 x10^{-3} mg/mm^2. A rough estimation of the filler volume fraction has been performed for comparison purposes. Thus, the GNP-modified laminates have filler volume fractions of 0.04, 0.07 and 0.20. In the case of the composites with hybrid microparticles, the values of the volume content are 0.20, 0.45 and 0.9 vol.%. It can be observed that the placement of GNPs in the interlaminar region of the composites results in laminates with lower fracture toughness compared to the unmodified laminate. For the hybrid microparticles-modified laminates, the interlaminar fracture toughness increased up to ca. 10% for a 0.9 vol.% of filler.

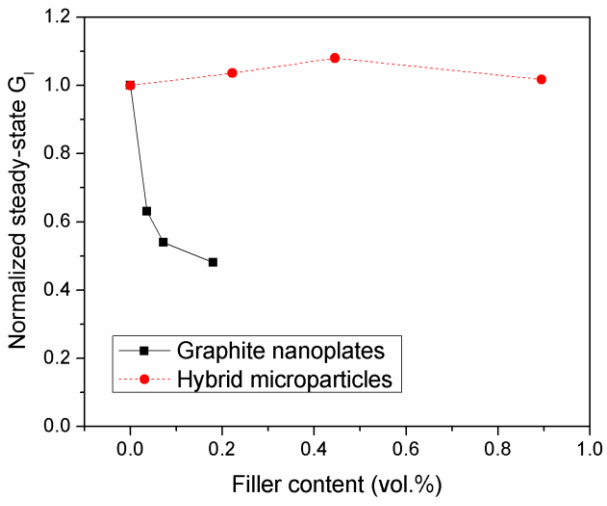

Figure 4. Normalized steady-state strain energy release rate, with the interlaminar region modified with graphite nanoplates and hybrid microparticles, as a function of the filler content (vol.%).

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Electron microscopy analyses (Figure 5) have shown that both fillers have not been homogeneously distributed in the interlaminar space. Large size fillers agglomerates clusters (up to 200 μm) have been observed on the prepreg surface. On the other hand, for the GNP-modified laminates, air voids are formed at the ply interfaces. Therefore, a deep analysis of the different processing parameters and the reinforcing mechanism must be performed.

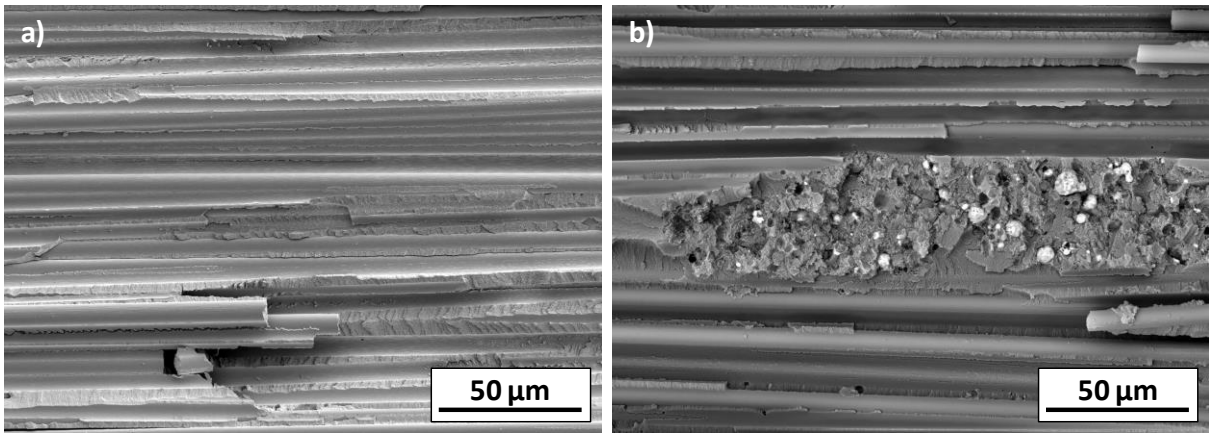

Figure 5. SEM image of the interlaminar fracture surface of a) the unmodified laminate composite and b) the composite with 0.45 vol.% of hybrid microparticles.

4. Conclusions

Graphite nanoplates and graphene-based hybrid microparticles have been added to the interlaminar region of laminate composites to modify their interlaminar fracture toughness. Graphene-based microstructures have enhanced the mode I toughness of AS4/8552 prepreg laminates. However, graphite nanoplates-modified laminates have lower mode I fracture toughness, probably due to the high porosity produced during the fabrication process. The different reinforcement mechanism and process parameters must be analysed.

Acknowledgments

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