Vargas G, Ramos JÁ, De Gracia J, Ibarretxe J, Mujika F. In-plane shear behaviour of multiscale hybrid composites based on multiwall carbon nanotubes and long carbon fibres. Journal of Reinforced Plastics and Composites. 2015;34(23):1926-1936. Copyright © 2015 The Author(s), published by Sage . <u>https://doi.org/10.1177/0731684415603491</u>

In-plane shear behaviour of multiscale hybrid composites based on MWCNTs and long carbon fibres

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ABSTRACT

Both in-plane shear modulus and in-plane shear strength of multiscale hybrid composites (MHCs) have been studied. Carbon fibre-based laminates have been fabricated including functionalized Multi-Wall Carbon Nanotubes (f-MWCNTs) by means of solvent spraying method and hot compression process. Mechanical in-plane shear characterisation has been carried out by using off-axis three-point flexure test. Fibre volume fraction of MHCs has been determined through thermogravimetric analysis (TGA) and fracture surfaces after testing have been imaged by scanning electron microscopy (SEM). Results reveal that the inclusion of f-MWCNTs on laminates has a small influence on in-plane shear modulus, although it increases up to 15% the in-plane shear strength. MWCNT functionalization improves shear stress transmission between matrix and carbon nanotubes, which represents a reinforcement effect responsible for the increase on in-plane shear strength. SEM micrographs have confirmed in-plane shear tests results.

Keywords

Polymer-matrix composites (PMCs), Nano-structures, Mechanical properties, Mechanical testing

INTRODUCTION

On the last decade there have been numerous studies regarding the development of polymer composites reinforced with carbon-nanotubes^{1- 11}. Compared with traditional fibre-reinforced polymer composites (FRPs) those nanocomposites have represented small enhancements in mechanical properties. Furthermore, in spite of great expectation, the use of polymer composites reinforced with carbon-nanotubes for structural applications has been unsatisfactory^{12,13}. On that sense, the replacement of fibre-reinforced polymer composites by polymer nanocomposites is considered not viable^{14,15}, due to the high level of development, the good positioning, and the excellent combination of properties of FRPs.

Recent interest has been generated with the use of nanoreinforcement in fibre-reinforced polymers, a new opportunity for nanotubes in composites. In those multiscale hybrid composites the main reinforcing phase could be continuous fibres (meso-scale) and a secondary reinforcing phase could be carbon-nanotubes (micro- and nano-scale). The motivation for adding CNTs to fibre-reinforced polymer composites is to extend the concept of tailoring properties to compensate the disadvantages of one component by the addition of another¹⁶⁻¹⁹. Some mechanical drawbacks are associated with the polymeric matrix. Matrix dominated mechanical properties, as in-plane and interlaminar shear properties, fracture toughness and compressive strength, are lower than fibre dominated properties²⁰. As a result, several studies have been carried out in order to enhance matrix dominated properties of FRPs by means of the inclusion of carbon-based nanoreinforcements.

Several works have been focused on the enhancement of matrix dominated properties of fibre reinforced polymer composites with carbon-based nanoreinforcements: fracture toughness^{13,14,21-25}, interlaminar shear properties^{14,21,26-30}, compressive strength³¹⁻³⁵ and transverse tensile properties³³. There are also studies related to improve adhesives for joining FRPs^{36,37}. Those matrix dominated mechanical behaviour of FRPs depends on both the properties of the constituent materials and the quality of the interfacial bond between those constituents. This interfacial bond is responsible of the mechanism of load transfer, also called the fibre/matrix interface³⁸. In order to study the influence of carbon-based nanoreinforcements on this interfacial bond between fibre and matrix, several works have been carried out by means of single fibre tests³⁸⁻⁴¹.

In long fibre-reinforced composites, the matrix transfers the load to the reinforcement through shear stresses. If the interfacial strength is deficient, less shear stress is transferred to the reinforcement, producing a less efficient composite. For improving the interfacial strength, several methods have been developed, being the most common the enhancement of the chemical adhesion of the reinforcement with the matrix or creating an interphase region by means of sizing treatments⁴¹. This can be also obtained through the use of carbon-based nanoreinforcements. In this line, some works have dealt with in-plane shear properties of continuous fibre-reinforced composites modified with carbon-based nanoreinforcements: Kim et al. have studied satin weave fabric carbon fibre reinforced epoxy matrix composites modified with XD-grade carbon nanotubes⁴², and Cho et al. have modified carbon fibre/epoxy composites with graphite nanoplatelets in both unidirectional⁴³ and satin weave reinforcement arrangements⁴⁴.

The aim of this work is to study the influence of functionalized MWCNTs incorporation on in-plane shear properties of epoxy-based hybrid composites reinforced with long carbon fibres. Both in-plane shear modulus and strength have been experimentally characterised. The characterisation of these shear properties has been carried out by means of the off-axis three-point flexure test method. In addition, hybrid composite fracture behaviour have been analysed by scanning electron microscopy, imaging specimen fracture surfaces after in-plane shear tests.

EXPERIMENTAL WORK

Constituent materials

The multiscale composite was formed by an epoxy resin reinforced with long carbon fibres, and modified with f-MWCNTs. Carbon fibre (T300) - epoxy resin (F-593) prepregs provided by Hexcel Composites were used to fabricate the laminates. Mechanical properties of the fibre and the matrix are shown in Table $1^{45,20}$, and the reference mechanical properties of the laminates are listed in Table 2^{46} . MWCNTs were provided by ARKEMA (diameter of 10 - 15 nm, length of 1 - 10 µm) and they were used after a functionalization treatment (see below).

Functionalization of MWCNTs

MWCNTs were mainly functionalized with carboxylic and alcohol groups by means of an oxidation treatment in a solution composed of nitric and sulphuric acid, according to the method presented by Goyanes et al.⁴⁷ and Fernandez d'Arlas et al.⁴⁸. Afterwards, functionalized carbon nanotubes were dispersed in ethanol in a horn-sonicator working at 750 W, 20 kHz and 20% of amplitude for 30 minutes, prior to be included onto the laminates. In order to study the influence of functionalized carbon nanotubes on in-plane shear properties of MHCs, four values of f-MWCNTs mass fraction were considered: 0%, 0.05%, 0.10% and 0.20%, named as MHC0, MHC0.05, MHC0.1, and MHC0.2 respectively. This carbon nanotubes mass fraction is determined with respect to the mass of the matrix in the laminate.

Processing of modified laminates

Unidirectional laminates [0]₄ modified with the different values of carbon nanotubes mass fraction were prepared and analyzed. The modification of the laminates was done by spraying the f-MWCNTs/solvent dispersion over the material, as employed by several authors^{25,49-5152}. Mujika et al.⁵² have sprayed f-MWCNTs only between the two central layers of the laminate, i.e. at the central interlaminar plane; instead, in this work, the carbon nanotubes were applied over all the prepreg layers of the laminate. The spraying was performed using an airbrush (0.2 mm exit diameter) working with compressed air at 7 bar. All laminates were manufactured by hot compression⁵³.

Fibre volume fraction

One of the most important properties considered in micromechanics models is the fibre volume fraction of the laminates. It has been determined through thermogravimetric analysis (TGA). The

determination of fibre volume requires the measurement of the composite density, which was measured in accordance with ASTM D 792⁵⁴. Based on both laminate fibre volume fractions and laminate densities, the void content of the laminates has also been calculated. TGA was performed on a TGA/SDTA 851e Mettler Toledo thermogravimetric analyzer, following the recommendations of Polis and Sovinski⁵⁵. Each specimen was heated from room temperature to 800°C at a heating rate of 5°C/min using a nitrogen purge in order to avoid carbon fibre degradation. Specimen weight was monitored in-situ throughout the test. Approximately 10 mg of specimen was used for each TGA measurement.

In-plane shear tests

For determining the in-plane shear properties the off-axis three-point flexure test method, proposed by Mujika et al.⁵⁶, has been considered. This method has been studied for two loading contact conditions, depending on either lift-off between specimen and fixture supports takes place. The proposed method considers the condition of small displacements and that lift-off between the specimen and the fixture supports occurs at the supports. The off-axis three-point flexure test specimen configuration is presented in Figure 1.

The main advantages of the off-axis three-point bending method are: the simplicity of flexure test configuration, the absence of end-constraint effects on the specimen, there is no need of strain gages to determine G_{12} , it considers the deformation of the whole specimen, and the failure can be supposed to start at a precise point. Furthermore, Vargas and Mujika⁵⁷ have carried out an experimental comparison for determining the in-plane shear strength of unidirectional composite materials by means of two off-axis tests: three-point flexure and tensile. Some of the conclusions of this work are that in-plane shear strength values obtained by off-axis flexure are greater than in the case of off-axis tensile because the failure zone is located at an interior point of the specimen instead of being located at the edge where machining could have a detrimental effect.

Following the recommendations of Vargas and Mujika⁵⁷, in-plane shear tests have been performed considering an off-axis fibre orientation angle of 20°, in order to obtain high τ_{12}/σ_2 ratio, and to promote a linear behaviour of the specimen. More enlightenment about the stress state in the off-axis bending specimens can be examined on both Ref.⁵⁶ and Ref.⁵⁷.

All specimens had the same nominal cross-section: width b = 12.5 mm and thickness h = 0.8 mm, and the same nominal length L' = 60 mm, as depicted in Figure 1. For each configuration, five specimens were tested. Once the tests were carried out, fibre orientation angles were measured taking as reference the specimen edge and the failure edge. Deviations up to $\pm 1^{\circ}$ with respect to off-axis angle nominal values were found.

A universal testing machine MTS–Insight 10 with a load cell of 250 N and standard bending test fixtures were used to perform the flexure tests, at a nominal strain rate of 1%/min, according to UNE-EN ISO 14125⁵⁸. In order to increase the shear stresses at the failure critical point the span-to-width ratio must be as high as possible, bearing in mind the small displacement condition, ensuring that the maximum deflection during the test do not exceed the 10% of the span. The critical values of the span-to-width ratio for lifting-off to occur c_{LO}^{56} considered in this study are between 3.0 and 3.3. For all tests the span-to-width ratio must be higher than c_{LO} in order to asses lifting-off during the test, which originates a statically determinate

configuration, making suitable the use of the mentioned method. On that sense, the nominal span considered in all tests was L = 50 mm, obtaining a nominal span-to-width ratio c = 4.0.

Scanning Electron Microscopy (SEM)

In order to study the fracture behaviour of the MHCs after in-plane shear tests, specimen edgewise fracture surface were imaged, as represented in Figure 2. Images have been taken at 500X, 2500X, and 20000X with a Schottky-type field emission scanning electron microscope JEOL JSM-7000F, with both secondary and retroscattered electrons. Secondary electrons are more sensitive to topography, and retroscattered electrons to variations of atomic number, where pure carbon zones (fibres and nanotubes) appear lighter. The specimen surfaces were coated with a 20 nm carbon layer to make them conductive.

RESULTS AND DISCUSSION

Laminate quality

The quality of fabricated multiscale hybrid composites has been evaluated by means of some physical properties. Fibre volume fraction results of the four studied multiscale hybrid composites are presented in Table 3. Those results are compared with nominal fibre volume fraction, reported by the prepreg manufacturer: $V_f = 50 - 55$ %. Thermogravimetric analysis results of fibre volume fraction are slightly higher than nominal range values. Laminate densities and laminate void contents are also stated in Table 3. As noticed, the void content is within regular limits for carbon fibre reinforced plastics and is higher for the MHC0.2 laminate, the highest carbon nanotube content, due to the formation of agglomerates. Furthermore, the appearance of laminates can be seen in Figure 3: failed specimens with straight failure surfaces.

In-plane shear modulus

In-plane shear modulus values of MHCs with 0, 0.05, 0.1 and 0.2%wt of f-MWCNTs, with respect to the resin mass, are presented in Figure 4. Shear stiffness results are compared with reference range: $G_{12-R} = 3500 - 4500$ MPa. For all composites, in-plane shear modulus values are within the reference range, near to the lower bound. Those results reveal that laminate modification with MWCNTs does not affect the in-plane shear modulus. In other words, during the shear tests in the load range where G_{12} is determined, i.e. applied strain from 0.05% to 0.25%, the inclusion of MWCNTs does not play a shear stiffness reinforcing role. However, for the highest content of carbon nanotubes, that is MHC0.2, there is a reduction in the mean value of G_{12} of almost 5% compared with the laminate without MWCNTs, MHC0. This decrease on in-plane shear modulus of the multiscale hybrid composite can be explained by the diminution on shear modulus of the matrix, caused by the presence of MWCNTs agglomerates.

In-plane shear strength

In-plane shear strength results are present in Figure 5 for the four studied laminates in order to analyse the influence of MWCNTs on unidirectional long carbon fibre / epoxy composites. Those results are compared with reference in-plane shear strength: $X_{12-R} = 98$ MPa. In general terms, in-plane shear strength values obtained by off-axis three-point flexure test are greater than X_{12-R} because the failure zone is located at an interior point of the specimen instead of being located at the edge where machining and material defect could have a higher detrimental effect, as in the case of [±45] tensile test and 10° off-axis tensile test^{56,57}. This fact can also be attributing to strength scale effect, similar to the normal strength obtained by flexure tests⁵⁹.

Such results point out that multiscale hybrid MWCNTs/epoxy/carbon fibre composites exhibit higher shear strength than conventional epoxy/carbon fibre composites. On that sense, by including 0.05%wt of functionalized carbon nanotubes in the composite, X_{12} increased 5%, and by including 0.1%wt increased 15%. Nevertheless, the inclusion of f-MWCNTs above a given amount (e.g. 0.2%wt) affects the in-plane shear strength: by including 0.2%wt, X_{12} decreased 12%. Therefore, the addition of functionalized carbon nanotubes up to 0.1%wt has a reinforcing effect on the studied composite.

Theoretically, on unidirectional composites subjected to shear stresses there is a stress concentration in the matrix around the fibres that affects the strength response of the material. On this study a linear behaviour to failure has been assumed, since 20° off-axis flexure specimen behaves linearly, which is consistent with the theoretical testing approach, because used equations to determine in-plane shear properties are based on a linear model⁵⁷. Furthermore, regarding off-axis flexure test, shear nonlinearity decreases when fibre orientation angle increases and when span-to-width ratio decreases⁵⁶.

Another way of analyzing the shear reinforcement effect of MWCNTs on studied composites is through the calculation of the shear stress concentration factor K_s . According to Gibson⁶⁰, K_s can be determined based on the strength of materials micromechanical approach⁶¹, considering a linear response of the multiscale hybrid composite and assuming that the fibre is perfectly bonded to the matrix, as:

$$K_{s} = \frac{G_{12}}{X_{12}} \frac{X_{sm}}{G_{m}}$$
(1)

where $X_{\rm sm}$ is the ultimate shear strength of the matrix, and $G_{\rm m}$ is the in-plane shear moduli of the matrix.

In Figure 6 the variation of shear stress concentration factor with the carbon nanotube mass content is shown. Those results indicate that there is a decreasing tendency of K_s as the MWCNT content increases, as mentioned by Cho et al.^{43,44} for carbon fibre/epoxy/graphite nanoplatelet hybrid composites. Afterwards, the increase of the in-plane shear strength of the multiscale hybrid composite with the modification of functionalized carbon nanotubes can be explained, from a mechanical viewpoint, by a decrease on the shear stress concentration factor. Such tendency is not achieved for the MHC0.2 laminate because a higher content of MWCNTs bring about the formation of agglomerates that represent microflaws within the material, acting as stress concentration points, and then leading to a decrease of X_{12} .

In this manner, the increasing of in-plane shear strength depends on an adequate transmission of shear stresses between the matrix phase and the reinforcement phase. Thus, the inclusion on laminates of sprayed f-MWCNTs improves their dispersion, avoiding the formation of agglomerates, as stated by several authors for mechanical performance of MHCs fabricated by the solvent spraying method^{25,49-51}. Mujika et al.⁵² have used the solvent spraying method for studying the potential improvement on interlaminar toughness of carbon fiber reinforced epoxy composite by means of carbon nanotube integration. In addition, functionalization

treatment promotes higher adhesion between matrix and carbon nanotubes, as extensively mentioned by other researchers working with multiscale hybrid carbon-based composites^{18,21,25,26,28,62}.

Fracture surfaces

With the aim of evaluate the interphase behaviour and to understand the in-plane shear properties enhancement mechanism for MWCNTs-modified laminates, the fracture surfaces of tested specimens were observed by SEM with secondary electrons. Under off-axis bending loading the failure mode of unidirectional laminates is inter-fibre failure, due to interfacial shear stresses τ_{12} and transverse normal stresses σ_2 . The test conditions considered for off-axis bending characterisations carried out promotes a shear dominant failure, confirmed by a high τ_{12}/σ_2 ratio⁵⁷.

Fracture surfaces reveal differences between fracture behaviour of specimens including different MWCNTs mass content. Figure 7a and b are from MHC0 laminate; Figure 7c and d, from MHC0.05 laminate; Figure 7e and f, from MHC0.1 laminate, and Figure 7g and h, from MHC0.2 laminate. SEM micrographs of laminates without carbon nanotubes MHC0, Figure 7a and b, show poor fibre-matrix bonding, characterised by smooth zones and clear fibre surfaces. In contrast, laminates modified with MWCNTs disclose a stronger interfacial bonding between carbon fibres and epoxy matrix, which can be observed in Figure 7c, d, e and f. These fracture surfaces are rougher and present plastic dimples on the matrix. Comparing MHC0.05 and MHC0.1 micrographs, it can be seen that laminate with 0.1%wt of carbon nanotubes have more hackle features in the matrix than laminate with 0.05%wt, indicating a better adhesion between fibres and matrix. Finally, Figure 7g exposes a zone of smooth river line structure, which is distinctive when the matrix is completely removed from the fibre as a result of a weak adhesion among them. This weak bonding between fibres and matrix is probably due to MWCNTs agglomerates, which have a size of about 1 µm.

SEM results agree with in-plane shear experimental results. In the case of the laminate without MWCNTs, a weak fibre-matrix bonding goes along with a low value of X_{12} . The incorporation of carbon nanotubes cause the enhancement of in-plane shear properties, specially for a 0.1%wt of MWCNTs mass content, which correspond to rougher fracture surfaces. The addition of 0.2%wt of carbon nanotubes causes both reduction of in-plane shear strength and smooth fracture surfaces zones.

In order to confirm the hypothesis of MWCNTs agglomerates in MHC0.2 laminate, that reduce considerably the in-plane shear properties and is displayed by a smooth river line structure, SEM micrographs with retroscattered electrons were captured. As retroscattered electrons are sensitive to variations of atomic number, pure carbon zones, i.e. MWCNT-rich regions, appear lighter. In SEM micrographs of Figure 8 carbon-rich spots are highlighted with dotted circles. Figure 8c, corresponding to the laminate with 0.2%wt of carbon nanotubes, confirms the presence of more MWCNTs agglomerates than in the rest of the laminates, which has a detrimental effect on in-plane shear strength.

SUMMARY AND CONCLUSIONS

This study examined the effect of Multi-Wall Carbon Nanotubes (MWCNTs) inclusion on both inplane shear modulus and strength of multiscale hybrid composites (MHCs). Those multiscale hybrid composites are based on epoxy matrix reinforced with long carbon fibre and containing f-MWCNTs. Four values of carbon nanotube weight ratio, determined with respect to the matrix mass, were used: 0%, 0.05%, 0.10% and 0.20%. Unidirectional MHCs were fabricated spraying f-MWCNTs dispersed on solvent over carbon fibre/epoxy matrix prepregs, followed by a hot compression procedure. Furthermore, the fibre volume fraction was determined through thermogravimetric analysis (TGA). Experimental characterisation of multiscale hybrid laminates was performed by off-axis three-point flexure test. Fracture behaviour of MHCs has been also studied by scanning electron microscopy (SEM), imaging specimen fracture surfaces after testing.

Results reveal that in-plane shear modulus is faintly affected by the incorporation of f-MWCNTs on laminates. On the contrary, the inclusion of functionalized carbon nanotubes on laminates exhibit a beneficial effect on in-plane shear strength, with increases up to 15% with respect to the laminate without MWCNTs. But the addition of carbon nanotubes above 0.2%wt affects harmfully the in-plane shear strength of the MHC. Functionalization of MWCNTs improves their dispersion, avoiding the formation of agglomerates, and promotes greater adhesion between matrix and carbon nanotubes, which is reflected in mentioned improvements on in-plane shear strength. On that sense, functionalized carbon nanotubes enhance the transmission of shear stresses between matrix and nanoreinforcement phase. Finally, observed fracture surfaces coincide with in-plane shear experimental evidence: weaker fibre-matrix bonding is associated with lower in-plane shear properties and smoother fracture surfaces; stronger adhesion between fibre and matrix, characterised by dimpled fracture surfaces, corresponds to higher shear strength of MHCs.

ACKNOWLEDGMENTS

The authors wish to thank the Local Government of Guipúzcoa for its financial support on the research project N° DG 09/05. Technical and human support provided by SGIker (UPV/EHU, MICINN, GV/EJ, ESF) is also gratefully acknowledged. This paper is dedicated *In memoriam* to Prof. Iñaki Mondragon.

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FIGURE CAPTIONS

Figure 1. Configuration of the off-axis three-point flexure test.

Figure 2. Specimen zone along the edgewise fracture surface analysed by SEM.

Figure 3. Straight edgewise fracture surfaces of failed specimens.

Figure 4. In-plane shear modulus of MHC with 0, 0.05, 0.1 and 0.2wt% of functionalized MWCNTs compared with reference range values.

Figure 5. In-plane shear strength of multiscale hybrid composites with 0, 0.05, 0.1 and 0.2wt% of functionalized MWCNTs compared with the reference value.

Figure 6. Shear stress concentration factor versus carbon nanotube mass content in multiscale hybrid composites: (•) experimental results.

Figure 7. Fracture surface SEM micrographs with secondary electrons of tested specimens including different MWCNTs mass content. (a), (b) MHC0, (c), (d) MHC0.05, (e), (f) MHC0.1, and (g), (h) MHC0.2. (a), (c), (e), (g) micrographs at x500 magnification, and (b), (d), (f), (h) micrographs at x2500 magnification.

Figure 8. Fracture surface SEM micrographs at x2500 magnification with retroscattered electrons of tested specimens including different carbon nanotubes mass content, indicating MWCNTs agglomerates (highlighted). (a) MHC0.05, (b) MHC0.1, and (c) MHC0.2.



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(a)



(b)



(c)

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TABLE CAPTIONS

 Table 1. Mechanical properties of carbon fibre T300 and epoxy matrix F593.

Table 2. Mechanical properties of T300/F593 unidirectional composite.

Table 3. Results of fibre volume fraction, density and void content, determined by TGA.

Property	Value
Fibre	
Elastic modulus, $E_{\rm f}$ (GPa)	230
In-plane shear modulus, G_{12f} (GPa)	27
Poisson's ratio, $v_{12f}(-)$	0.20
Density, $\rho_{\rm f}$ (kg/m ³)	1760
Longitudinal tensile strength, X_{1tf} (MPa)	3100
Matrix	
Elastic modulus, $E_{\rm m}$ (GPa)	2.96
Poisson's ratio, $v_{\rm m}$ (-)	0.35
Density, $\rho_{\rm m} ({\rm kg/m^3})$	1220
Tensile strength, $X_{\rm m}$ (MPa)	60.4

Table 1. Mechanical properties of carbon fibre T300 and epoxy matrix F593.

Property	Value
Longitudinal modulus, E_1 (GPa)	117 - 136
Transverse modulus, E_2 (GPa)	8.0 - 8.5
In-plane shear modulus, G_{12} (GPa)	3.5 - 4.5
Poisson's ratio, v_{12} (-)	0.3
Longitudinal tensile strength, X_{1t} (MPa)	1370
Transverse tensile strength, X_{2t} (MPa)	55
In-plane shear strength, X_{12} (MPa)	98
Fiber volume fraction, $V_{\rm f}$ (%)	50 - 55

Table 2. Mechanical properties of T300/F593 unidirectional composite.

Multiscale hybrid composite	Fiber volume fraction,	Composite density,	Void content,
	<i>V</i> _f (%)	$ ho_{\rm c} ({ m g/cm^3})$	V _v (%)
MHC0	55,55	1,499	2,01
MHC0.05	57,69	1,501	2,63
MHC0.1	56,23	1,504	1,85
MHC0.2	63,34	1,528	3,26

Table 3. Results of fibre volume fraction, density and void content, determined by TGA.