IN-PLANE SHEAR PROPERTIES OF MULTISCALE HYBRID F-MWCNTS / LONG CARBON FIBRES / EPOXY LAMINATES

Gustavo Vargas[1*], José Ángel Ramos[2], Iñaki Mondragon[2], Faustino Mujika[1]

[1] *'Materials + Technologies' Group, Department of Mechanical Engineering*
[2] *'Materials + Technologies' Group, Department of Chemical & Environmental Engineering*
Polytechnic School, Universidad País Vasco/Euskal Herriko Unibertsitatea, Plaza Europa 1, 20018. Donostia-San Sebastián, Spain
** Corresponding author: gustavo.vargas@ehu.es*

Keywords: In-plane shear behaviour, Nano-structures, Mechanical properties, Multiscale hybrid composites.

Abstract

The effect of Multi-Wall Carbon Nanotubes (MWCNTs) inclusion on both in-plane shear modulus and strength of multiscale hybrid composites (MHCs) is presented on this study. Multiscale hybrid composites are based on epoxy matrix reinforced with long carbon fibre and containing functionalized MWCNTs. In-plane shear properties have been theoretically predicted according to micromechanical models. Experimental characterization 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). 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.

1 Introduction

On the last decade there have been numerous studies regarding the development of polymer composites reinforced with carbon-nanotubes. 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 [1]. On that sense, the replacement of fibre-reinforced polymer composites by polymer nanocomposites is considered not viable [2], 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 another [3]. 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 properties [4]. 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.

The aim of this work is to study the influence of functionalized carbon-nanotubes (f-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 predicted from a theoretical point of view considering micromechanical models, and those results have been compared with experimental shear tests values. The characterization 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.

2 Micromechanics models for in-plane shear stiffness

In order to study the elastic behaviour of unidirectional MHCs subjected to in-plane shear loads, it is possible to use micromechanical methods based on material and geometric properties of constituents. Under in-plane shear loading, the response of unidirectional laminate composites is dominated by both the matrix properties and the local stress distributions. This in-plane shear response can be investigated according to several mechanical approaches, in order to determine the in-plane shear modulus of the multiscale hybrid composite, G_{12} [4,5].

Strength of materials approach

$$G_{12} = \frac{G_{12f}\, G_m}{V_f\, G_m + (1-V_f)\, G_{12f}} \tag{1}$$

Halpin-Tsai approach

$$G_{12} = G_m \frac{1+\xi\,\eta\,V_f}{1-\eta\,V_f} \tag{2}$$

$$\eta = \frac{(G_{12f}/G_m)-1}{(G_{12f}/G_m)+\xi} \tag{3}$$

$$\xi = 1 + 40\,V_f^{10} \tag{4}$$

Elasticity approach

$$G_{12} = G_m \frac{(1+V_f)\, G_{12f} + (1-V_f)\, G_m}{(1-V_f)\, G_{12f} + (1+V_f)\, G_m} \tag{5}$$

Chamis approach

$$G_{12} = \frac{G_m}{1-\sqrt{V_f}\left(1-\dfrac{G_m}{G_{12f}}\right)} \tag{6}$$

Spencer approach

$$\frac{G_{12}}{G_m} = \frac{\Gamma-1}{\Gamma} + \frac{1}{k}\left[\frac{\pi}{2} + \frac{2\Gamma}{\sqrt{\Gamma^2-k^2}}\,Tan^{-1}\sqrt{\frac{\Gamma+k}{\Gamma-k}}\right] \tag{7}$$

$$k = 1 - \frac{G_m}{G_{12f}} \tag{8}$$

$$\frac{1}{\Gamma} = \sqrt{\left(1.1\,V_f^2 - 2.1\,V_f + 2.2\right)V_f} \tag{9}$$

where G_{12f} and G_m are the in-plane shear moduli of the fibre and matrix, and V_f is the fibre volume fraction.

3 Micromechanics models for in-plane shear strength

The ultimate in-plane shear strength, X_{12}, of the unidirectional MHC can also be estimated through different micromechanical models [4,5].

Strength of materials approach
$$X_{12} = G_{12} \frac{X_{sm}}{G_m} \left[\frac{d}{s} \frac{G_m}{G_{12f}} + \left(1 - \frac{d}{s}\right) \right] \quad (10)$$

$$\left.\frac{d}{s}\right|_{Squ} = \sqrt{\frac{4\,V_f}{\pi}}, \qquad \left.\frac{d}{s}\right|_{Hex} = \sqrt{\frac{2\sqrt{3}\,V_f}{\pi}} \quad (11)$$

Matrix shear failure approach
$$X_{12} = X_{sm} \left[\frac{1 - \frac{d}{s}\left(1 - \frac{G_m}{G_{12f}}\right)}{1 - V_f\left(1 - \frac{G_m}{G_{12f}}\right)} \right] \quad (12)$$

Fibre/matrix interface approach
$$X_{12} = \frac{X_{sm}}{\left(1 + V_f\right)^2} \quad (13)$$

Chamis approach
$$X_{12} = X_{sm} \left[1 - \left(\sqrt{V_f} - V_f\right)\left(1 - \frac{G_m}{G_{12f}}\right) \right] \quad (14)$$

where X_{sm} is the ultimate shear strength of the matrix, s is the fibre spacing and d is the fibre diameter. The ratio d/s varies with geometrical package. For circular fibres with square and hexagonal array packing such ratio is determined according to Eqs. (11).

4 Experimental work

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 constituents are shown in Table 1 [6], and mechanical properties of reference laminate are listed in Table 2 [7]. MWCNTs were provided by ARKEMA (diameter of 10 - 15 nm, length of 1 - 10 μm) and they were used after a functionalization treatment. MWCNTs were 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 Fernandez d'Arlas et al. [8]. 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.

Fibre		Matrix	
E_f (GPa)	230	E_m (GPa)	2.96
G_{12f} (GPa)	27	ν_m (-)	0.35
ν_{12f} (-)	0.20	ρ_m (kg/m^3)	1220
ρ_f (kg/m^3)	1760	X_m (MPa)	60.4
X_{1tf} (MPa)	3100		

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

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. As micromechanical models require the precise determination of the fibre volume fraction, it was determined through thermogravimetric analysis (TGA). Experimental characterization of multiscale hybrid laminates was performed by off-axis three-point flexure test [9]. Fracture behaviour of MHCs has been also studied by scanning electron microscopy (SEM), imaging specimen fracture surfaces after testing.

E_1 (GPa)	117 - 136	X_{1t} (MPa)	1370
E_2 (GPa)	8.0 - 8.5	X_{2t} (MPa)	55
G_{12} (GPa)	3.5 - 4.5	X_{12} (MPa)	98
ν_{12} (-)	0.3	V_f (%)	50 - 55

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

5 Results and discussion

5.1 In-plane shear modulus

In-plane shear modulus values of MHCs with 0, 0.05, 0.1 and 0.2%w of f-MWCNTs, with respect to the resin mass, are presented in Fig. 1. Shear stiffness results are compared with reference range: $G_{12\text{-}R}$ = 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 G_{12} of almost 5% compared with the laminate without MWCNTs, MHC0.

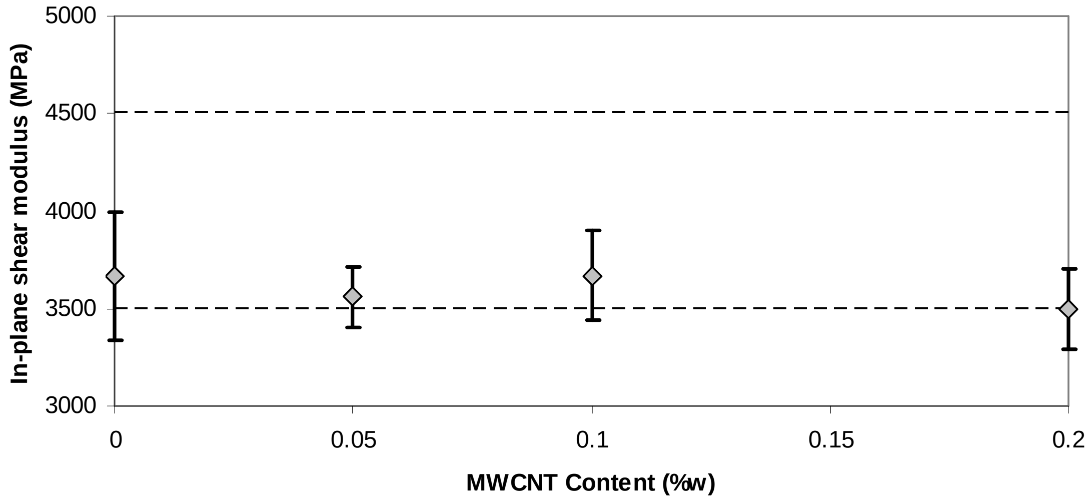

Figure 1. In-plane shear modulus of multiscale hybrid composites with 0, 0.05, 0.1 and 0.2wt% of functionalized MWCNTs compared with reference range values.

In Fig. 2 micromechanical models for determining in-plane shear modulus are presented. Such models are compared with experimental results in order to study their suitability for the prediction of shear stiffness of studied multiscale hybrid composites. Results disclose that the model of Spencer -Eq. (7)- overestimates the in-plane shear stiffness, and that strength of materials approach -Eq. (1)- underestimates it. Nevertheless, there is a good agreement between the elasticity approach -Eq. (5)- and the Halpin-Tsai approach -Eq. (2)-, when the stiffness reinforcing factor ξ takes values around 1.25. Regarding the model of Halpin-Tsai, results for the calculation of ξ according to the formula of Hewitt and De Malherbe -Eq. (4)- are not displayed in Fig. 2, because the value of reinforcing factor remains between 1.12 and 1.42, which almost coincides with presented cases. Results presented in Fig. 2 also indicate that G_{12} is not affected by the inclusion of carbon nanotubes on the laminates, although the addition of a certain amount of MWCNTs over 0.2%w has a detrimental effect on shear stiffness: a reduction of the stiffness reinforcing factor from the MHC0 laminate ($\xi = 1.25$) to the MHC0.2 laminate ($\xi = 0.50$).

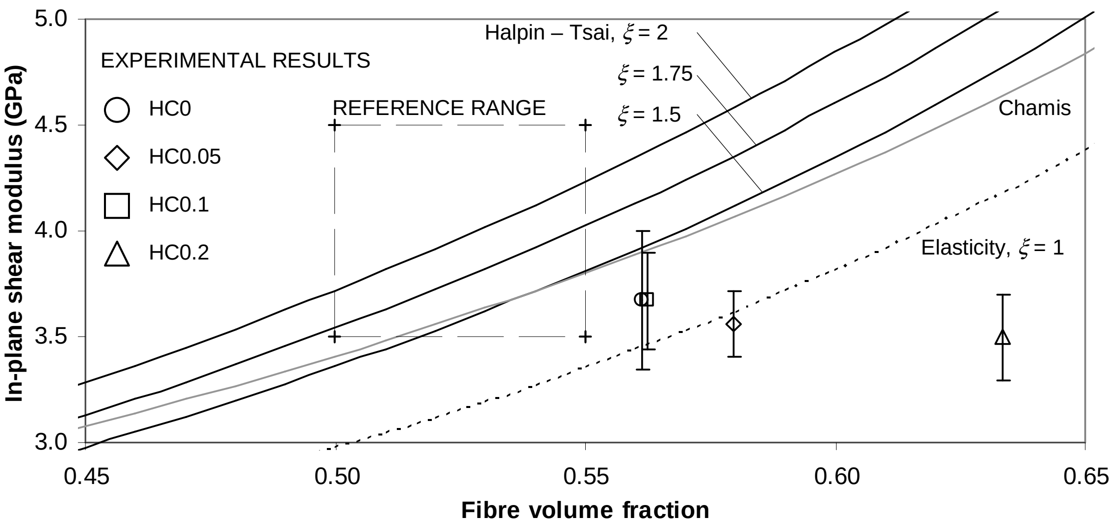

Figure 2. Results of tensile tests on neat and nanomodified epoxy resin. (Times New Roman 10 pt, centered text alignment. Leave 6 pt space before the caption and a blank single line after it)

5.2 In-plane shear strength

In-plane shear strength results are present in Fig. 3 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: $X_{12\text{-}R}$ = 98 MPa. In general terms, in-plane shear strength values obtained by off-axis three-point flexure test are greater than $X_{12\text{-}R}$ because the failure zone is located at an interior point of the specimen instead of being located at the edge where machining and material defects could have a higher detrimental effect, as in the case of [±45] tensile test and 10º off-axis tensile test. This can be attributed to a strength scale effect, similar to the normal strength obtained by flexure tests.

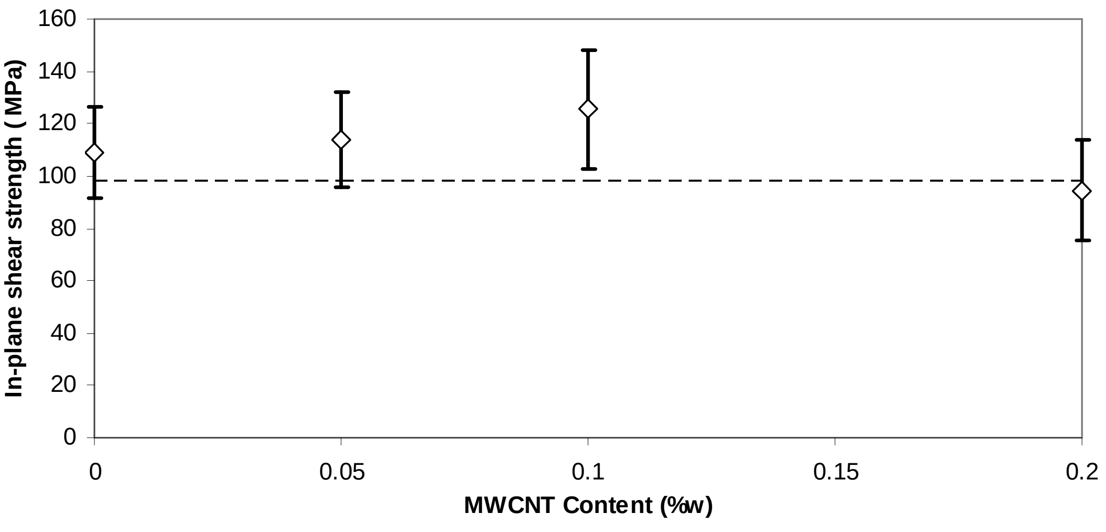

Figure 3. Results of tensile tests on neat and nanomodified epoxy resin. (Times New Roman 10 pt, centered text alignment. Leave 6 pt space before the caption and a blank single line after it)

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%w of functionalized carbon nanotubes in the composite, X_{12} increased 5%, and by including 0.1%w increased 15%. Nevertheless, the inclusion of f-MWCNTs above a given amount (e.g. 0.2%w) affects the in-plane shear strength: by including 0.2%w, X_{12} decreased 12%. Therefore, the addition of functionalized carbon nanotubes up to 0.1%w has a reinforcing effect on the studied composite.

The comparison between micromechanical models to predict X_{12} and experimental values is expounded in Fig. 4. This comparison indicates that all micromechanical approaches underestimate the in-plane shear strength of MHCs: experimental values of X_{12} are between 8.8 and 3.2 times predictions. In Fig. 4 can also be appreciated that to enhance in-plane shear strength the most efficient MWCNTs mass fraction is 0.1%w, and that 0.2%w MWCNTs represents an unfavourable consequence on X_{12}.

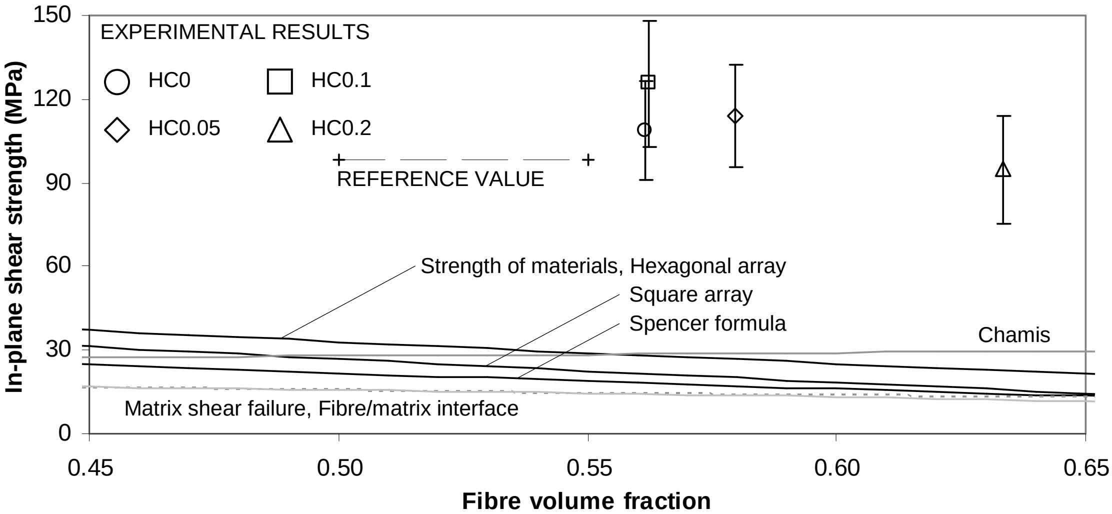

Figure 4. Results of tensile tests on neat and nanomodified epoxy resin. (Times New Roman 10 pt, centered text alignment. Leave 6 pt space before the caption and a blank single line after it)

5.3 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-fiber failure, due to interfacial shear stresses τ_{12} and transverse normal stresses σ_2. The considered off-axis bending test conditions promote a shear dominant failure, confirmed by a high τ_{12}/σ_2 ratio [10].

Fracture surfaces reveal differences between fracture behaviour of specimens including different MWCNTs mass content. Fig. 5a and b are from MHC0 laminate; Fig. 5c and d, from MHC0.05 laminate; Fig. 5e and f, from MHC0.1 laminate, and Fig. 5g and h, from MHC0.2 laminate. SEM micrographs of laminates without carbon nanotubes MHC0, Fig. 5a and b, show poor fibre-matrix bonding, characterized 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 Fig. 5c, 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%w of carbon nanotubes have more hackle features in the matrix than laminate with 0.05%w, indicating a better adhesion between fibres and matrix. Finally, Fig. 5g 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 is weak bonding between fibres and matrix is probably due to MWCNTs agglomerates.

SEM results coincide 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%w of MWCNTs mass content, which correspond to rougher fracture surfaces. The addition of 0.2%w 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 considerably reduce the in-plane shear properties and that lead to 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 (e.g. MWCNT-rich regions) appear lighter. In SEM micrographs of Fig. 6 carbon-rich spots are highlighted with dotted circles. Fig. 6c, corresponding to the laminate with 0.2%w 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.

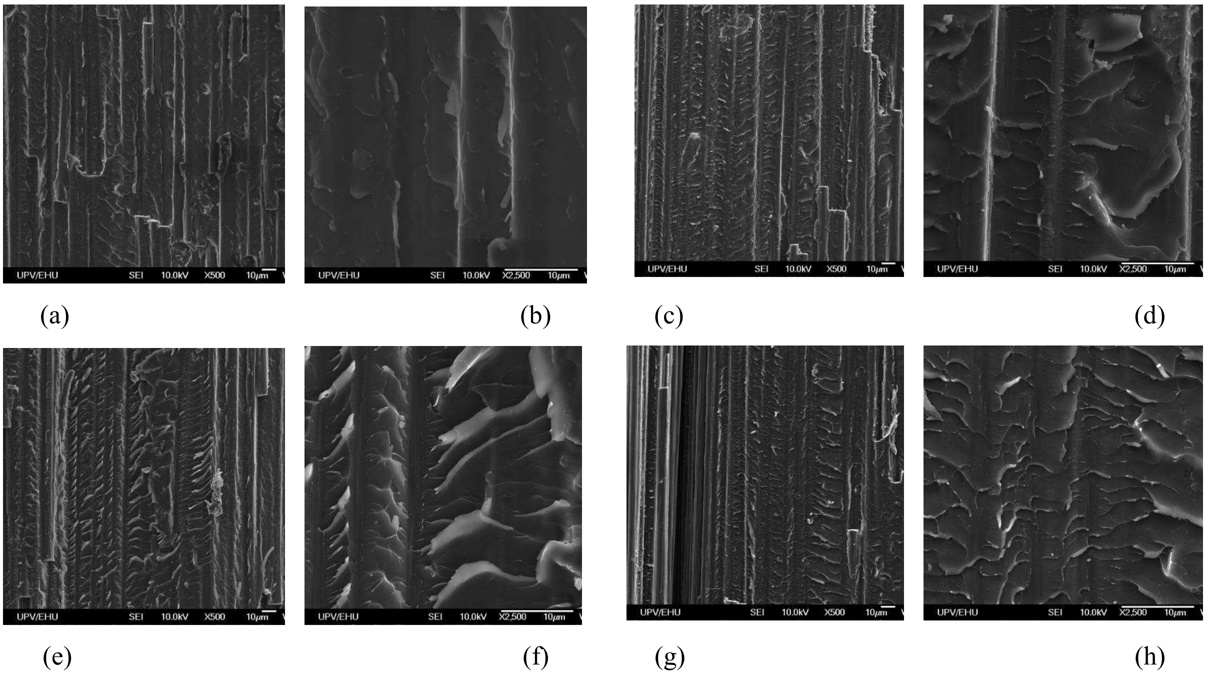

Figure 5. Fracture surface SEM micrographs with secondary electrons of tested specimens including different MWCNTs mass content. (a), (b) MHC0, (c), (d) MHC0.05, (e), (f) MHC0.1, and (g), (h) MHC0.2. (a), (c), (e), (g) micrographs at x500 magnification, and (b), (d), (f), (h) micrographs at x2500 magnification.

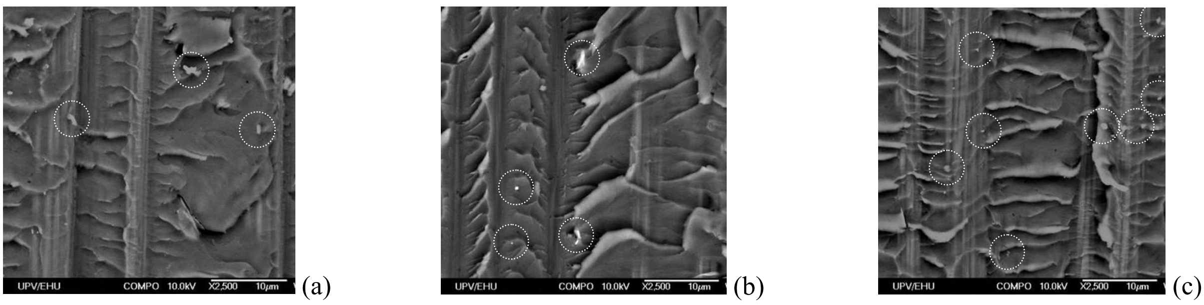

Figure 6. Fracture surface SEM micrographs at x2500 magnification with retroscattered electrons of tested specimens including different carbon nanotubes mass content, indicating MWCNTs agglomerates (highlighted). (a) MHC0.05, (b) MHC0.1, and (c) MHC0.2.

Conclusions

This study examined the effect of Multi-Wall Carbon Nanotubes (MWCNTs) inclusion on both in-plane shear modulus and strength of multiscale hybrid composites (MHCs). 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. On the contrary, the addition of carbon nanotubes above 0.2%w affects harmfully the in-plane shear strength of the MHC. The comparison of micromechanical analysis with experimental results reveals that, in the case of shear stiffness, both the elasticity model and the Halpin-Tsai model predict suitably in-plane shear modulus of the studied multiscale hybrid composites. In the case of shear strength, all considered micromechanical approaches underestimate the in-plane shear strength of MHCs. Functionalization of MWCNTs improves their dispersion, avoiding the formation of agglomerates, and promotes higher 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, characterized by dimpled fracture surfaces, corresponds to higher shear strength of MHCs.

Acknowledgments

The authors wish to thank the Local Government of Gipuzkoa for its financial support on the research project Nº 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* of Dr. Iñaki Mondragon Egaña.

References

[1] Veedu V.P., Cao A., Li X., Ma K., Soldano C., Kar S., Ajayan P.M., Ghasemi-Nejhad M.N. Multifunctional composites using reinforced laminae with carbon-nanotube forests. *Nature Materials*, **5**(6), pp. 457-62 (2006).

[2] Gojny F.H., Wichmann M.H.G., Fiedler B., Bauhofer W., Schulte K. Influence of nanomodification on the mechanical and electrical properties of conventional fibre-reinforced composites. *Composites Part A*, **36**(11), pp. 1525-35 (2005)

[3] Godara A., Mezzo L., Luizi F., Warrier A., Lomov S.V., van Vuure A.W., Gorbatikh L., Moldenaers P., Verpoest I. Influence of carbon nanotube reinforcement on the processing and the mechanical behaviour of carbon fibre/epoxy composites. *Carbon,* **47**(12), pp. 2914-23 (2009).

[4] Daniel I.M., Ishai O. *Engineering mechanics of composite materials*. 2nd Ed. Oxford University Press, New York (2006).

[5] Kaw A.K. *Mechanics of composite materials*. 2nd Ed. CRC Press, Boca Raton (2006).

[6] HexPly F593. *Resin Systems for Advanced Composites Product Data*. Hexcel Corporation, Stamford (2011).

[7] T6T-190-12-F593-8. *Identification Data*. Hexcel Corporation, Livermore.

[8] Fernandez d'Arlas B., Goyanes S., Rubiolo G.H., Mondragon I., Corcuera M.A., Eceiza A. Surface modification of multiwalled carbon nanotubes via esterification using a biodegradable polyol. *Journal of Nanoscience and Nanotechnology*, **9**(1), pp. 6064-71 (2009).

[9] Mujika F, Valea A, Gañán P, Mondragon I. Off-axis Flexure Test: A New Method for Obtaining In-plane Shear Properties. *Journal of Composite Materials*, **39**(11), pp. 953-80 (2005).

[10] Vargas G., Mujika F. Determination of in-plane shear strength of unidirectional composite materials using the off-axis three-point flexure and off-axis tensile tests. *Journal of Composite Materials*, **44**(21), pp. 2487-507 (2010).