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Carbon nanotubes-modified carbon fibre reinforced polymer (CFRP) composites with tailored interfaces

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June 4-6, 2018
Arcachon, France

Avantage Aquitaine

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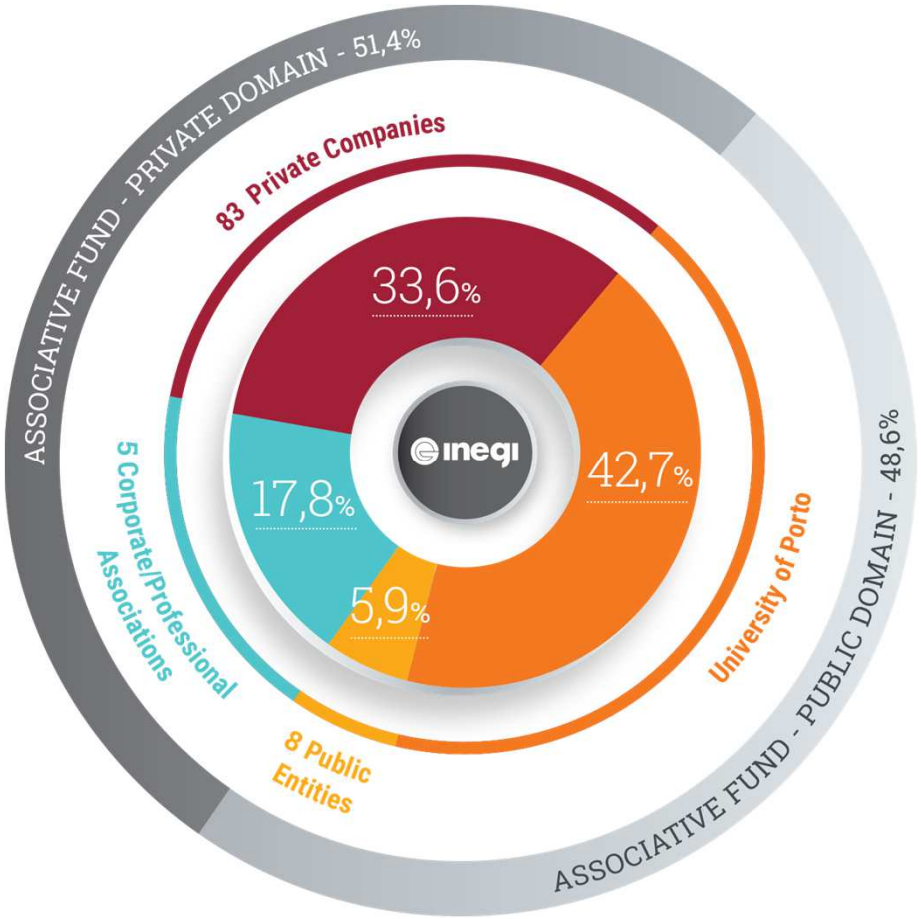
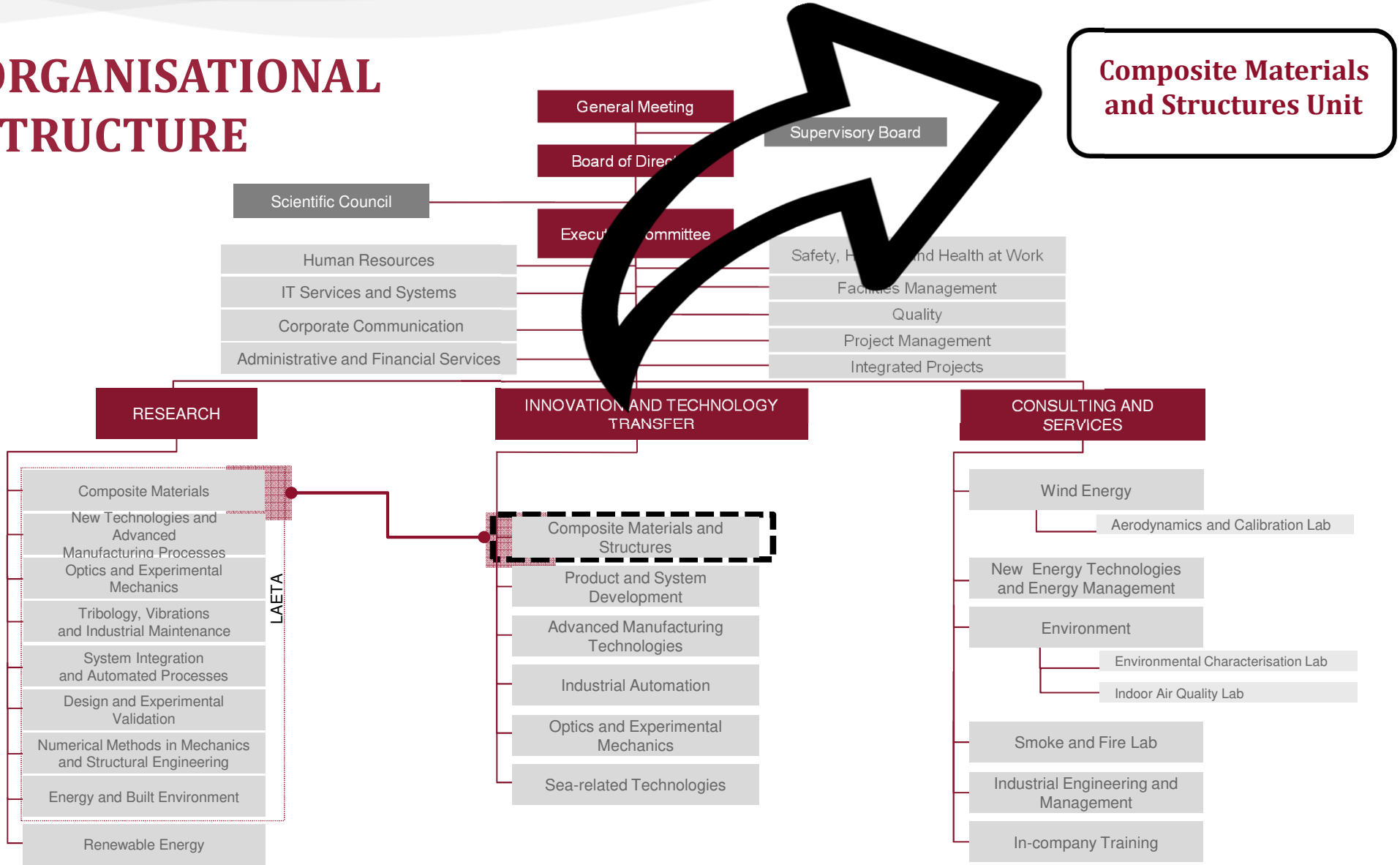
ASSOCIATES



- Research Institute founded in 1986 in Porto as an interface between the U. Porto and industry.
- Non-profit RTO.
- Private (biggest shareholder is U. Porto).
- Results from the merging of two Institutes of the U. Porto and is the largest Mechanical Engineering Institute in Portugal.

ORGANISATIONAL STRUCTURE



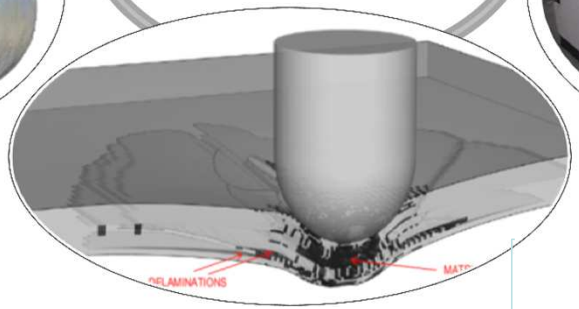
The Composite Materials and Structures Unit, 2018

SCOPE OF ACTIVITIES

MATERIAL DEVELOPMENT

STRUCTURES

MANUFACTURING



MODELLING

PROTOTYPING AND TESTING

3. Carbon nanotubes-modified carbon fibre reinforced polymer (CFRP) composites with tailored interfaces

- Background & Objectives
- Performed activities
- Results and discussion
- Conclusions

MODCOMP Project

Background

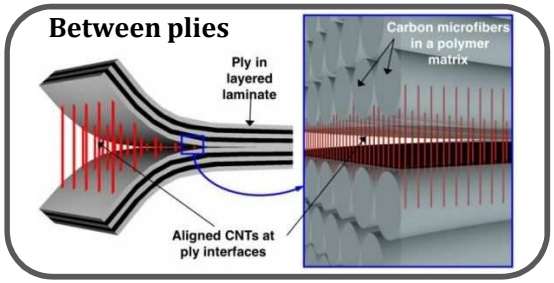
DRAWBACK…!

Out-of-plane properties of composite laminates ➡ **Mechanical failure** through the initiation and propagation of microcracks, interfacial debonding, low impact damage resistance, weak interface, presence of voids, among others.

- **Carbon nanostructures** ➡ with special focus on multiwall carbon nanotubes (MWCNTs), are promising multifunctional fillers. Development of **high-performance polymeric matrices** and composites, as well as **health monitoring** and **damage sensing**.

MWCNTs have been incorporated into CFRP composites using different **strategies**:

and/or



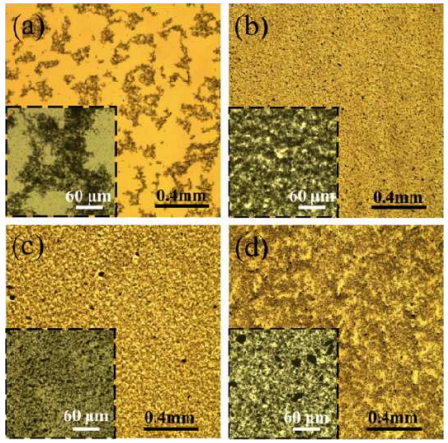
Garcia *et al.*, Composites: Part A 39 (2008) 1065 – 1070.

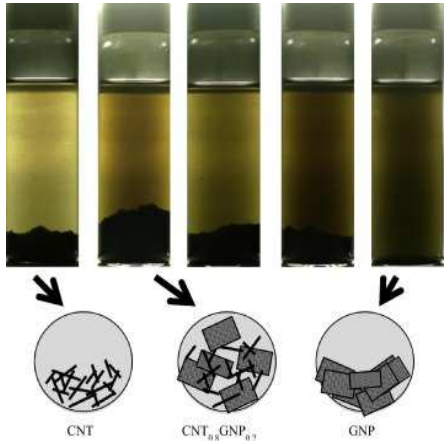
Background

CHALLENGES ON DISPERSION…!

- Huge increase of the resin viscosity ➡ Processing problems.
- Van der Walls interactions ➡ Hinders homogeneous dispersion and particle size distribution.
- Lack of chemical functionalities at the MWCNTs surface ➡ Hinders the formation of strong interfacial bonding with most of polymers.

Dispersion and re-agglomeration prevention is challenging!





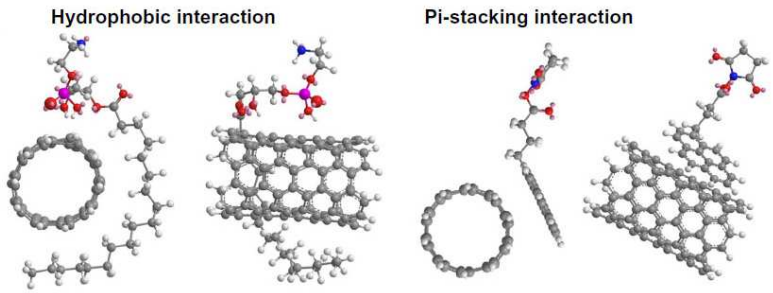
L. Yue *et al.* Carbon (2014).

Background

Ensuring dispersion and interfacial bonding

Non-covalent functionalization:

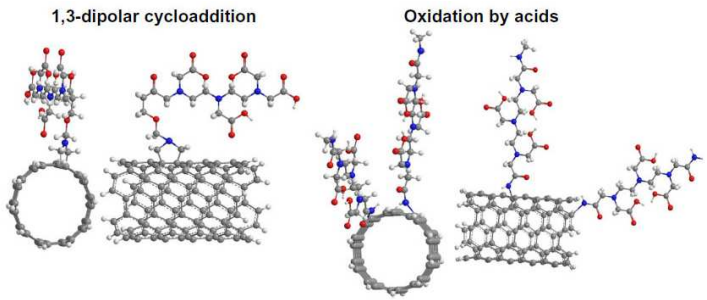
Electrostatic interactions
Van der Walls interactions
Hydrogen bonding
π-π stacking interactions



No structural damage of the graphitic lattice

Covalent functionalization:

Covalent bonding of chemical groups to the carbon atoms



Stronger interfaces

Disruption of the sp^2 hybridization

Objectives

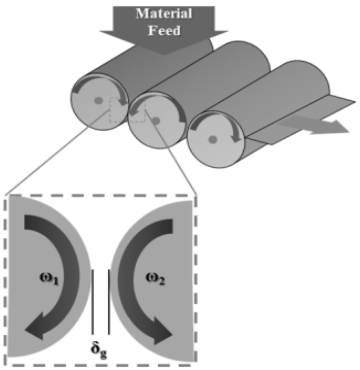
- Development of epoxy-based nanocomposites, containing different types and loadings of MWCNTs, with low percolation threshold and enhanced mechanical performance.
- Study the efficiency of the functionalization route.
- Development of modified CFRP composites having multifunctionality and tailored interfaces.

Performed activities

Development of epoxy-based nanocomposites

≠ gap
≠ rolls speed

≠ residence time
≠ shear rates and hydrodynamic stresses



Setup:
the mixer consists of a sequence of three rolls having different gaps (ω_1, ω_2, ω_3)
$\omega_3 = 3\ \omega_2 = 9\ \omega_1$

1st cycle: nominal shear rate = 28.000 s^{-1}
2nd cycle: nominal shear rate = 37.000 s^{-1}
3rd cycle: nominal shear rate = 56.000 s^{-1}
4th cycle: nominal shear rate = 110.000 s^{-1}
5th cycle: nominal shear rate = 220.000 s^{-1}

$$\dot{\gamma} = \frac{V}{2H_0} + \frac{V_1 - V_2}{2H_0}$$

O. Cohu and A. Magnin. Journal of Rheology 39 (4), 767 – 785, 1995.

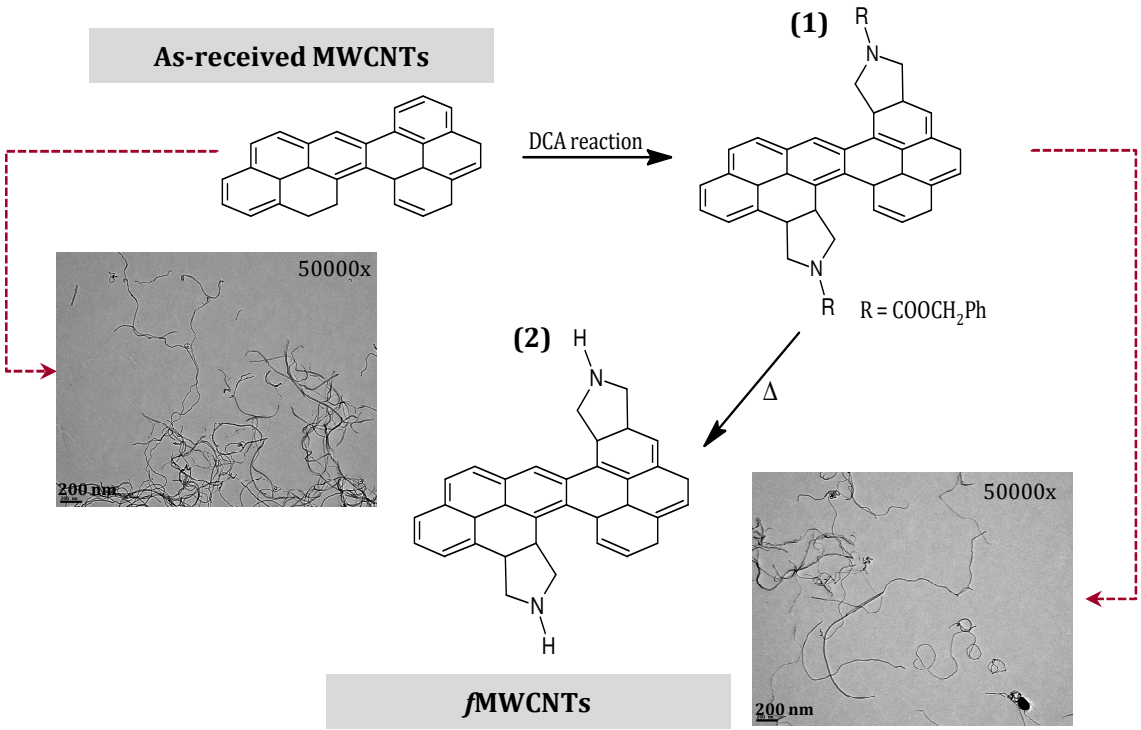
Formulations development using a three-roll mill.

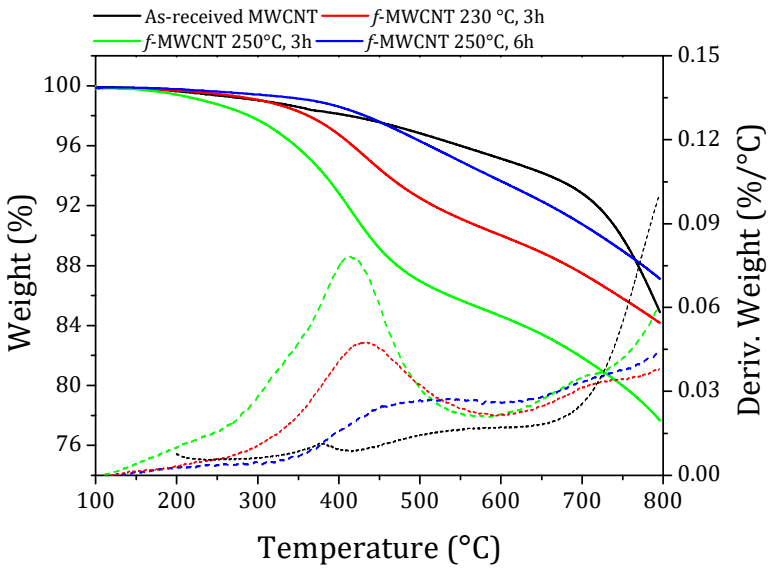
Samples code	NC7000 (wt. %)	Graphistrength C100 (wt. %)
LY 556	---	---
LY 556/MWCNTs	0.011	---
	0.021	0.021
	0.043	0.043
	0.089	0.089
	0.179	0.179
	0.357	0.357
	0.536	0.536
	0.714	0.714
LY 556/fMWCNTs	0.043	---
	0.089	---
	0.179	---
	0.269	---
	0.536	---

Performed activities

Functionalization route: 1.3 dipolar cycloaddition of azomethine ylides

M. C. Paiva *et al.*, ACS Nano 12 (2010) 7379-7386.

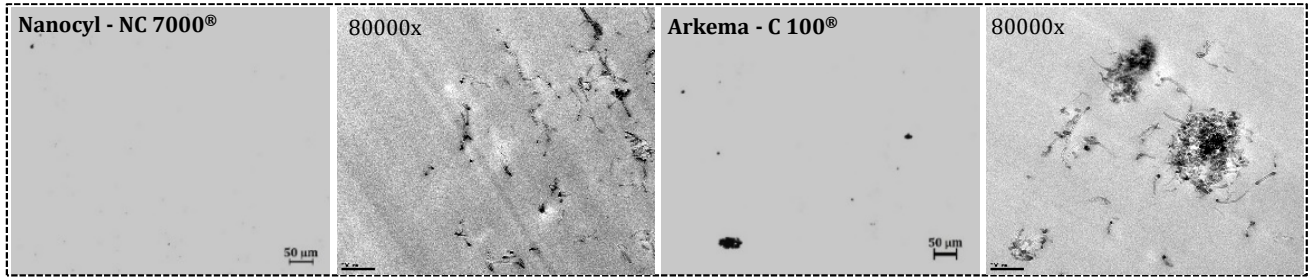




- The relative concentration of cyclic benzyl carbamate (1) and pyrrolidine (2) varied with reaction time and temperature.
- The solvent-free reaction was performed at 250 °C for 3 hours, owing to the high amount of **covalently bonding organic groups** formed.
- The **morphology** of MWCNTs is apparently **maintained** after DCA reaction.

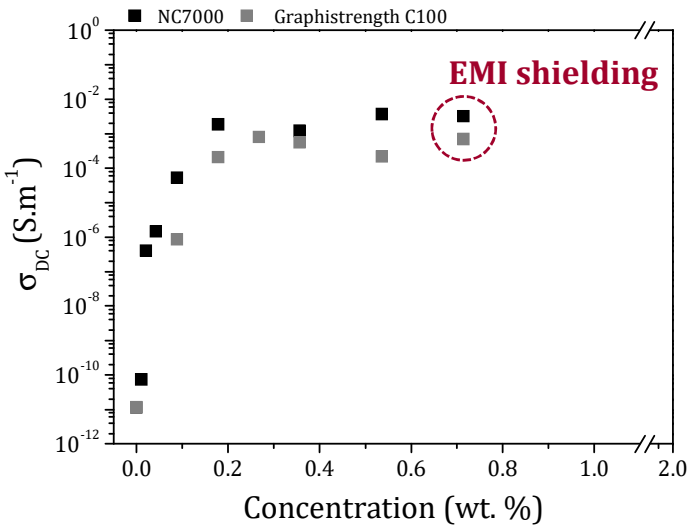
Results and discussion

Development of epoxy-based nanocomposites



$A_r = 0.048 \pm 0.010$ %
$N = 37 \pm 14$ mm^{-2}

$A_r = 0.21 \pm 0.08$ %
$N = 45 \pm 20$ mm^{-2}



$$Fa = \frac{\dot{\gamma}.\eta}{\sigma_M}$$

Where, $\dot{\gamma}$ is the shear rate, η is the flow viscosity and σ_M is the agglomerate cohesive strength.

$$\sigma_M = \frac{Z.f.F_H}{O_p}$$

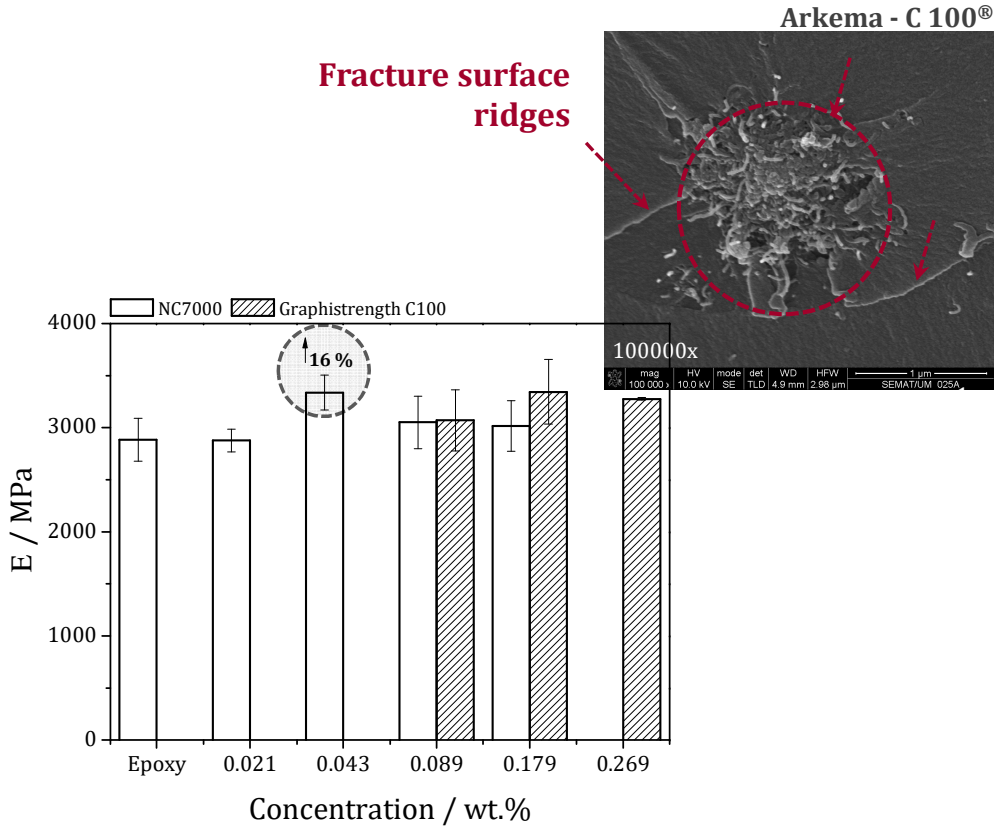
Where, Z is the coordination number of primary particles, f is the **packing density,** F_H is the adhesive force and O_p is the **particle surface area**.

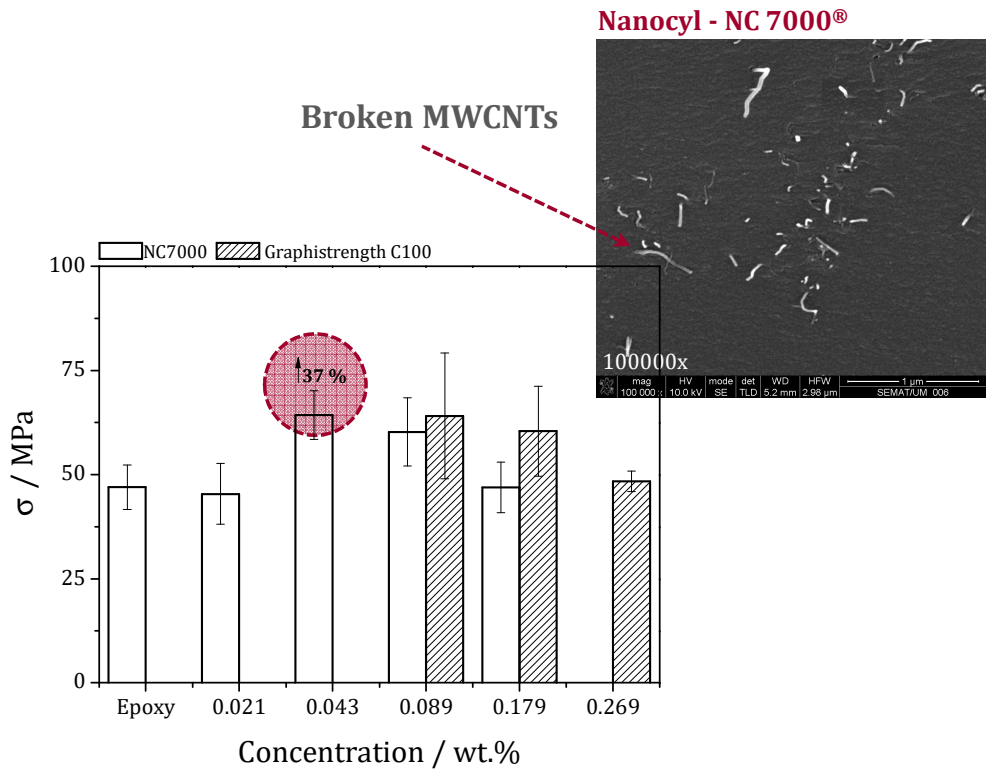
I. Alig *et al.* Polymer (2012).
A. Scurati *et al.* Chem. Eng. Sci., (2005).

- After incorporation of only **0.043 wt. %** of NC7000®, the electrical conductivity of epoxy resin increases **6 orders** of magnitude.
- The **twice amount** of Graphistrength C100® is required to achieve similar electrical conductivity.

Results and discussion

Development of epoxy-based nanocomposites

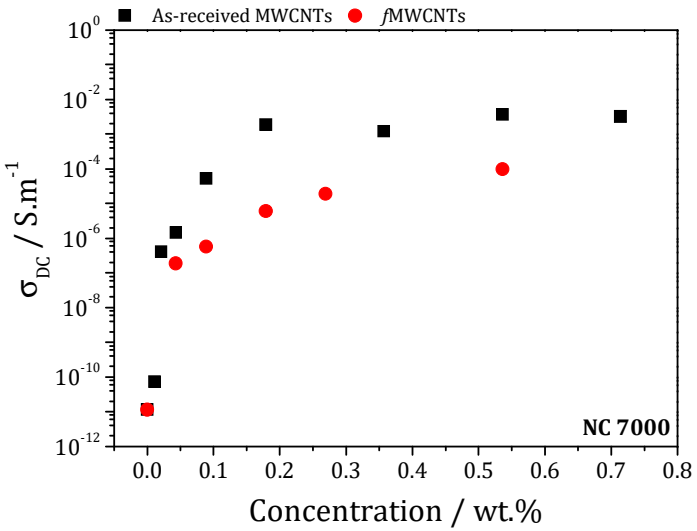


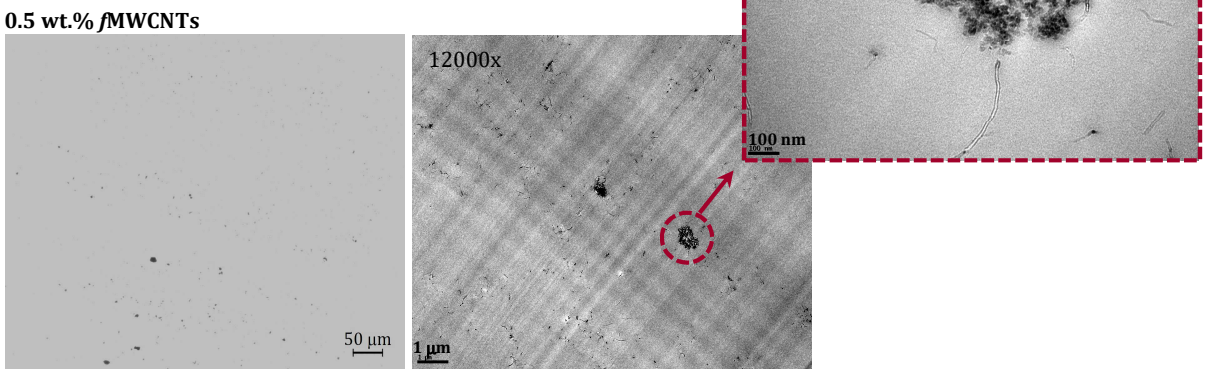


- The incorporation of 0.043 wt. % of NC7000® increases the elastic modulus (~16%) and tensile strength (~37%) of the epoxy resin.
- SEM images show that nanocomposites containing **C100®** present a surface having **several ridges**, which results in the **poor absorption of energy** during mechanical solicitation.

Results and discussion

Development of epoxy-based nanocomposites





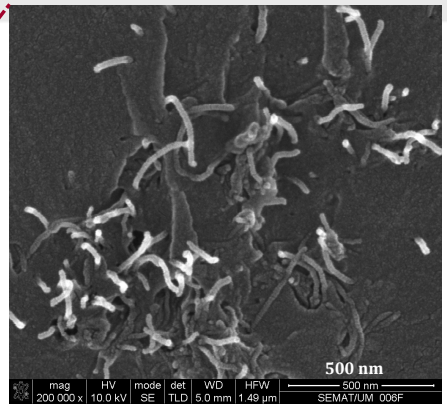
$A_r = 0.42 \pm 0.14$ %
$N = 759 \pm 264$ mm^{-2}

- Even when extensive damage of MWCNTs is avoided, the covalent functionalization leads to a disruption of the π conjugation combined with the **conversion of *sp²* carbons to *sp³***. Thus, as expected, it was found a significant **drop** of the **electrical conductivity** with incorporation of *f*MWNCTs.
- Moreover, the dispersion assessement shows that the **size** and **number** of agglomerates per unit area, *N*, is typically **larger** for the nanocomposite comprising *f*MWNCTs.

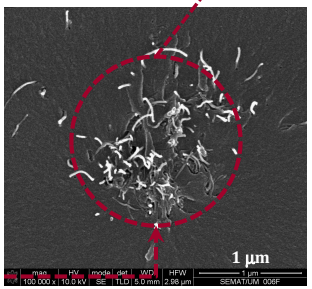
Results and discussion

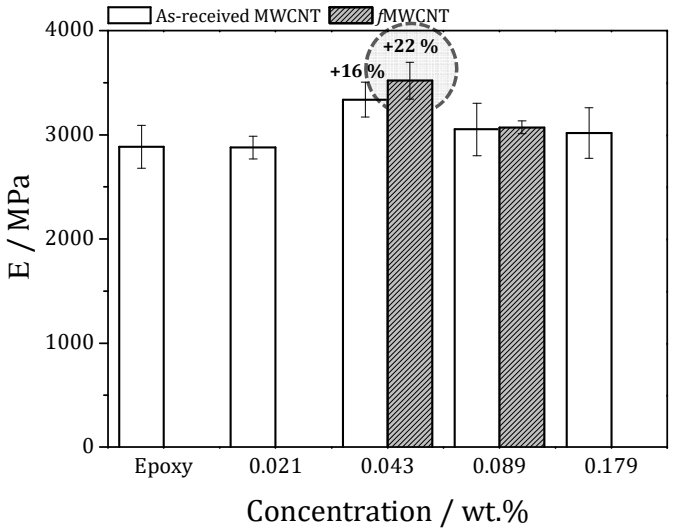
Development of epoxy-based nanocomposites

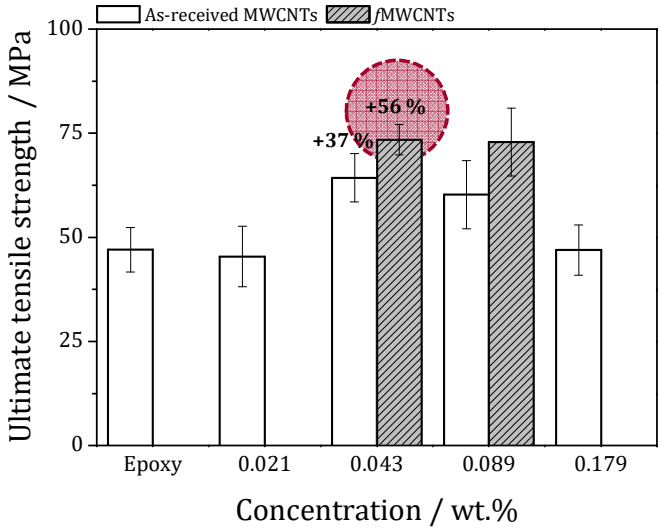
*f*MWCNTs (NC 7000®)



*f*MWCNTs are broken and some of them are slightly pulled-out.





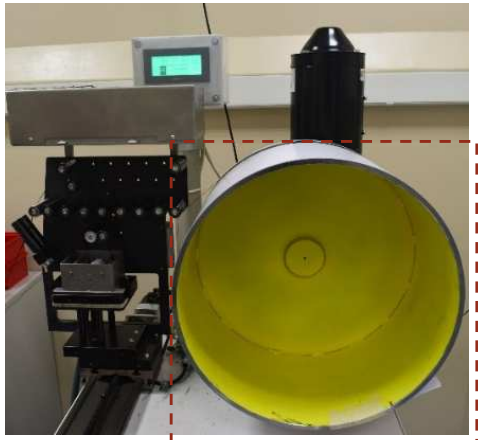


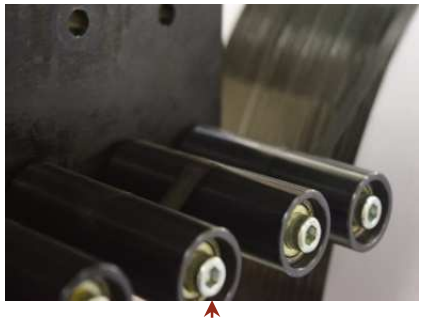
- An increase in tensile modulus (22%) and ultimate tensile strength (56%) is found with the addition of *f*MWCNTs, without ductility loss ($\varepsilon_b \sim 5$ %).
- The results evidence that an **effective interface was achieved**, suggesting that 1.3 dipolar cycloaddition is a promising route to produce high-performance nanocomposites.

Perfomed activities

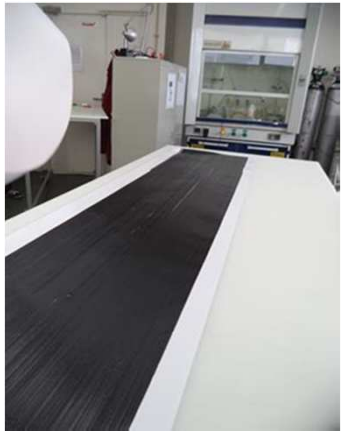
Manufacturing of unmodified and modified prepreg

Impregnation setup



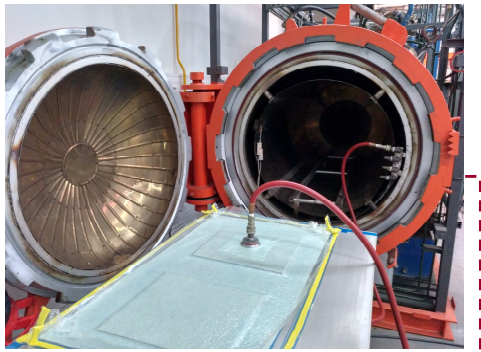


Produced prepreg



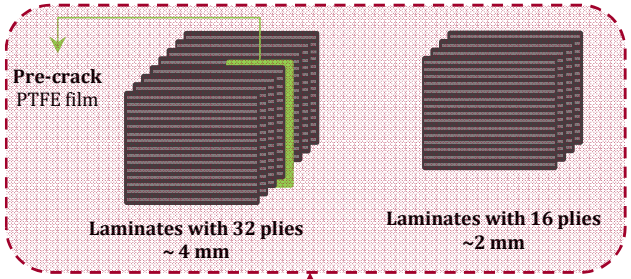
1 prepreg = 4 plies

Autoclave



Prepreg processing conditions:
Fibre pre-tension: 4 N
Pitch: 0.39 cm
Rotation speed: 2 rpm (0.048 m.s^{-1})
Room temperature

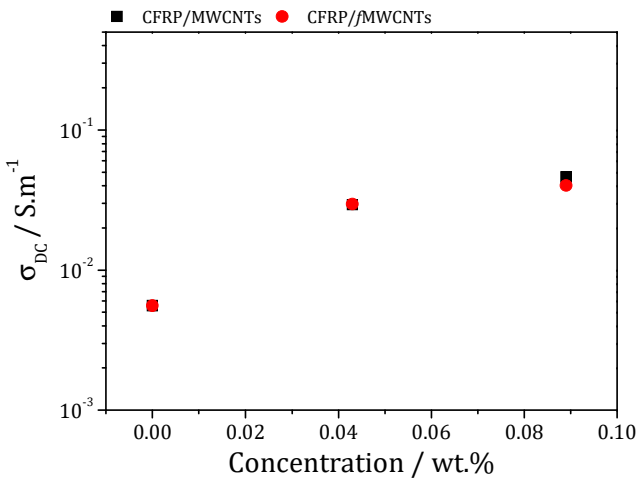
Formulations studied:
Unmodified CFRP
Modified CFRP with 0.043 wt.% of as-received and *f*MWCNTs
Modified CFRP with 0.089 wt.% of as-received and *f*MWCNTs



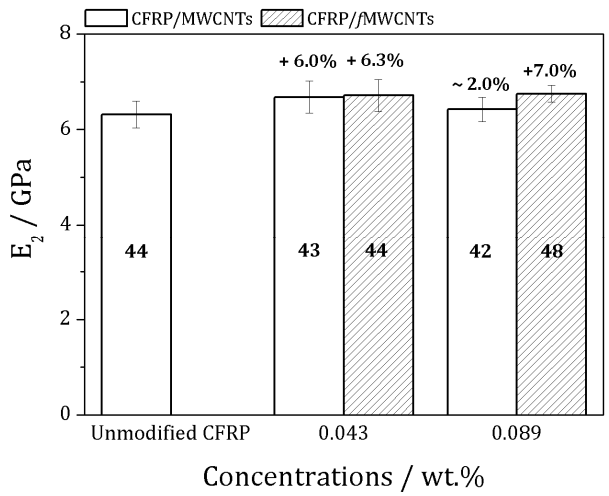
Results and discussion

Manufacturing and characterization of CFRP composites

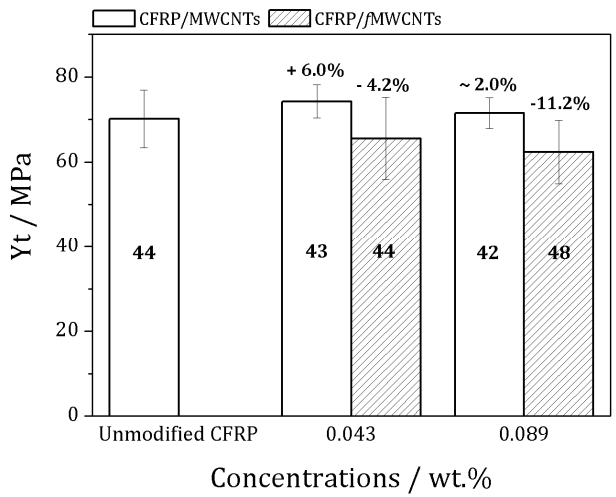
Electrical conductivity



Elastic modulus at 90°



Tensile strength at 90°

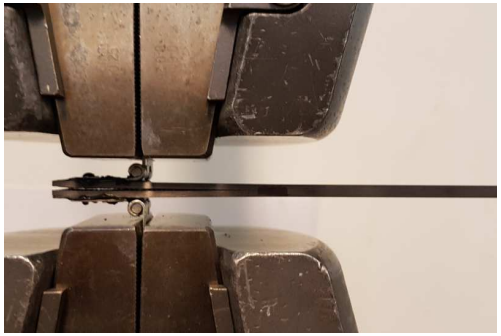


Note: The values are not normalized to fibre volume fraction of 60 %.

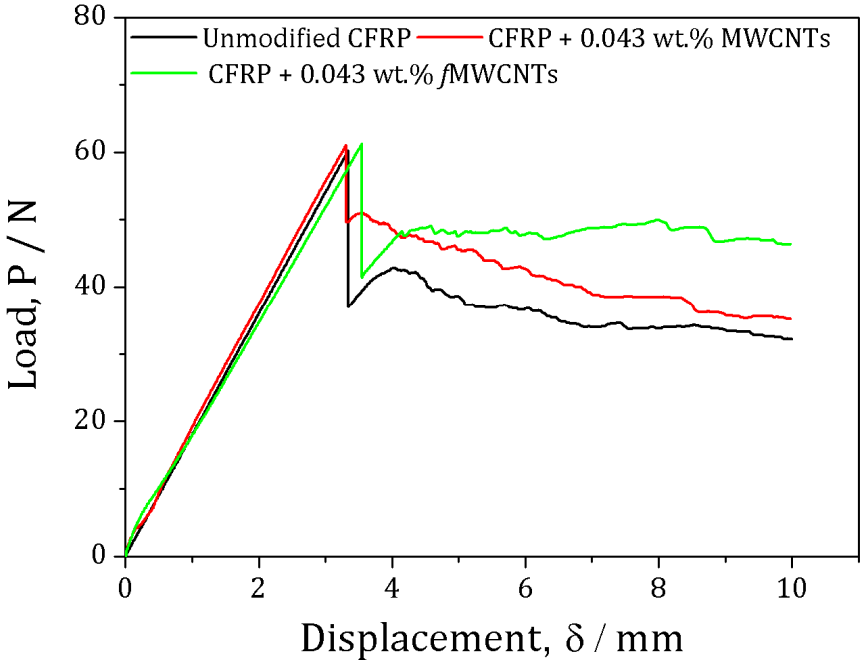
- The **electrical conductivity of CFRP** composites **is slightly enhanced** through incorporation of as-received or *f*MWCNTs, at low concentrations.
- MWCNTs do not seem to be effective to enhance the tensile properties of UD-laminates at 90°, because only slightly improvements were found (~6%).
- These findings point out that **it is not straightforward** to transfer the remarkable intrisic properties of MWCNTs to the composite level.

Results and discussion

Manufacturing and characterization of CFRP composites



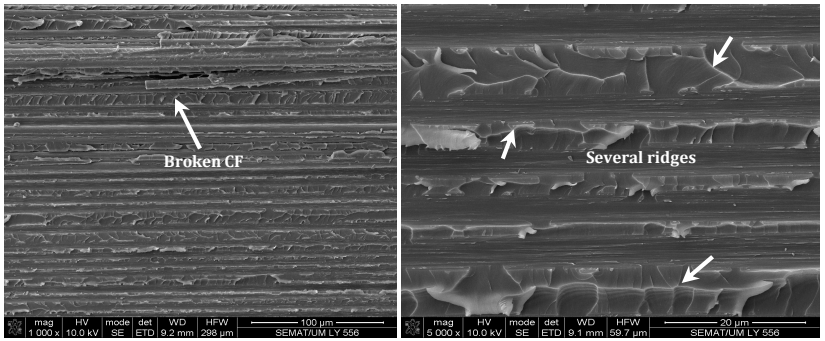
- An increase of load at the post peak region is observed after incorporation of MWCNTs when comparing the load-displacement curves (P *vs* d).



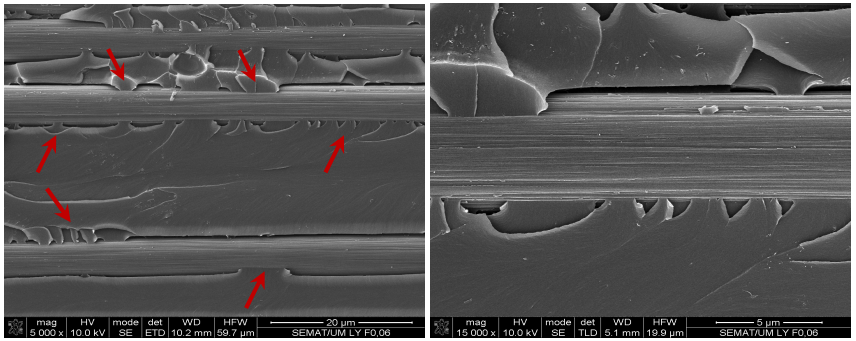
- The **interlaminar fracture toughness** (G_{IC}) was determined at the propagation crack plateau of the R-curves, until a steady-state value is reached.

Results and discussion

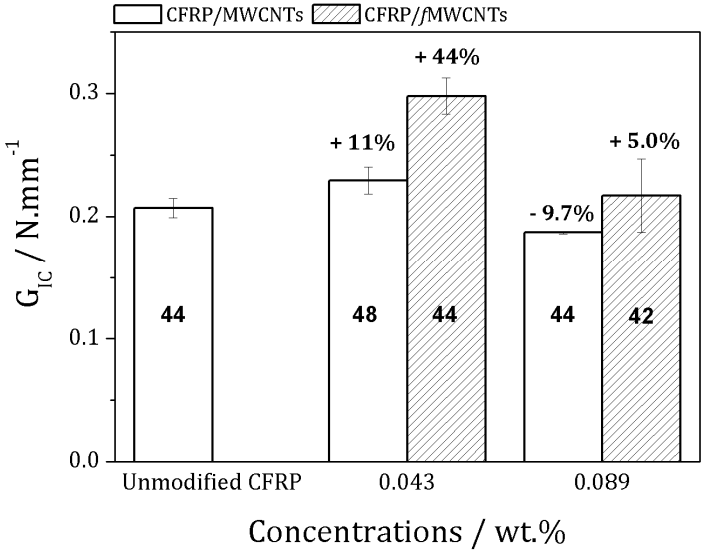
Manufacturing and characterization of CFRP composites

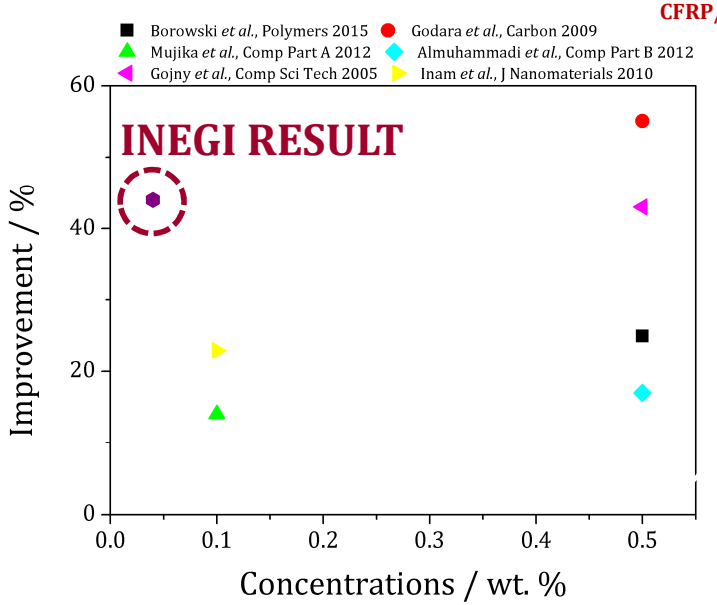


Unmodified CFRP



CFRP/*f*MWCNTs





- The G_{IC} increases in modified CFRP composites at 11 and 44 % for as-received and *f*MWCNTs, respectively.
- These results point out that MWCNTs can be used as efficient reinforcements in the midplane of CFRP composites.

Concluding remarks

- Modified epoxy resins with MWCNTs were sucessfully prepared using a three-roll mill (good dispersion) to be applied in pre-impregnation processes of CFRP composites.

- The dispersion assessement at different length scales showed that NC7000® presents lower agglomerate cohesion (lower bulk densities), resulting in better performance than nanocomposites containing Graphistrength C100®.

- At the nanocomposite level, noticiable enhancements of the mechanical and electrical performance was found with the incorporation of MWCNTs.

- *f*MWCNTs *via* 1.3 dipolar cycloaddition showed higher tendency to agglomerate (higher cohesive strength), being more difficult to disperse.

- The tensile properties of unidirectional CFRP laminates are less sensible to the incorporation of as-received or *f*MWCNTs.

- The results obtained by DCB show an improvement of 40 % for CFRP composites containing 0.043 wt.% *f*MWCNTs in terms of mode I interlaminar fracture toughness.

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MODCOMP

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR Portugal

ModComp – Modified cost effective fibre based structures with improved multifunctionality and performance (Project ID: 685844), financed and supported by European Union under "H2020-EU.2.1.3. - INDUSTRIAL LEADERSHIP - Leadership in enabling and industrial technologies - Advanced materials.

Nano-MFC – High performance multifunctional composite materials based on self-assembly approaches (with reference PTDC/CTM-POL/4607/2014)

Thank you for your attention!