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Multiscale Analysis of the Mechanical Performance improvement of composites CFRP laminates, and composites with short glass Fibers, through the addition of Nanoplatlets of Graphene.

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Key words: Nanocomposites, Graphene, Improvement Strength, Automotive applications, Interlaminar Stress, Fracture Toughness.

Summary: *In this work we described the analisys of the behavior of polymeric composites reinforced with short glass fibers and unidirectional carbon fibers when the matrix is functionalized with Graphene Nanoplatlets (GNP). The graphene Nanoplatlets dispersed in a matrix (thermoplastic or thermoset), can be able to improve in general the strength of materials and their resistance to crack propagation (Fracture Toughness). In particular, for the CFRP laminates, Graphene Nanoplatlets could improve the resistance to delamination (Interlaminar Shear Strength). In fact , between two adjacent plies of the laminate there is only the matrix and so the delamination resistance depends only by the dispersed Graphene that can improve the matrix fracture toughness and strength. This study was conducted through the use of Analisys Micromechanics tools and typical software for the structural simulation of the component at macro scale. Some experimental results were used for the validation of the simulations.*

1 INTRODUCTION [1]

The environmental sustainability represents one of the major driving forces for the innovation considering European Commission's regulation for CO2 emissions which sets stringent values for fuel economy depending on the average vehicles weight. In 2020 EU fixed the target in 95g CO2/km and in 2025 75g CO2/km. Apart from powertrain changes, the most promising way to reduce the CO2 emissions of the vehicle (that are proportional to fuel consumption) is the use of lighter structural and semi-structural materials including polymer-based materials as glass fibers and carbon fibers reinforced plastic (GFRP, CFRP). Material selection depends on the performance requirements, on automotive parts' location and functional role in the car. The use of advanced materials to lighten, however, must guarantee the fundamental performance of vehicles, among which for example the crashworthiness. This guarantee often needs technical design specifications and engineering of innovative solutions. One of the strategies that can be applied is multifunctional design with the combination of light structures and nanostructured materials realized with additive nano fillers such as carbon nanotubes or graphene particles (fig. 1).

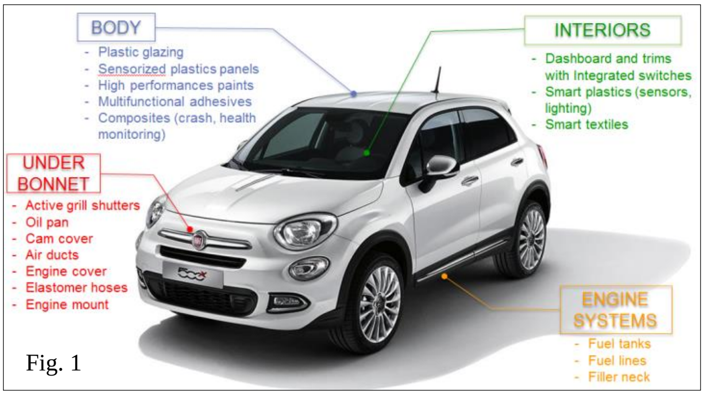


Fig. 1

In particular, Graphene Nanoplatelets (GNP) is a new class of carbon nanoparticles has shown an excellent capacity as barrier to liquid and gases, and an a good capacity as electrical and thermal conductors. In this work we focused on the potential capacity of the Graphene to improve the mechanical properties of the short glass fibers thermoplastic composites and carbon fibers thermoset composites (CFRP). The automotive sector is interesting to investigate as the graphene may be able to improve composites' crashworthiness.

2 OVERVIEW

Based on several studies found in literature [2], mechanical behavior of Nanocomposites, in terms of stiffness and strength, is fundamentally different from the behavior of short fiber composites as well as continuous fibers. For stiffness, you see how to size below a certain threshold, there is a shape effect that generates a significant dependence on volume fraction. Above this threshold the effect is not present and we find a lower slope of the curve (Fig. 2).

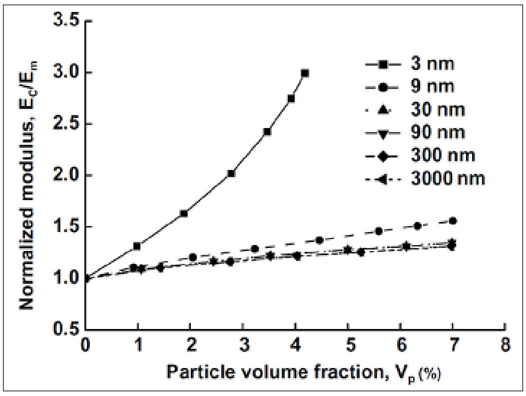


Fig. 2 – Elastic Modulus in dependence of the Volume Fraction

In other words, to the same volume fraction of nanoparticles, elastic modulus increases with decreasing particle size. For Nanocomposites you can also see a behavior that changes significantly depending on the type of interface that is established between the matrix and nanofillers. While in the case of micrometer size stiffness does not change the characteristics of the interface (Fig. 3), for nanometer dimensions the type of interface becomes relevant (Fig. 4).

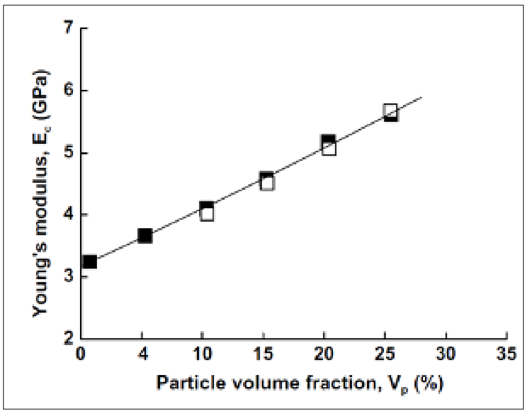


Fig. 3 – PS with Glass particle composite with excellent (□) and poor (■) surface adhesion

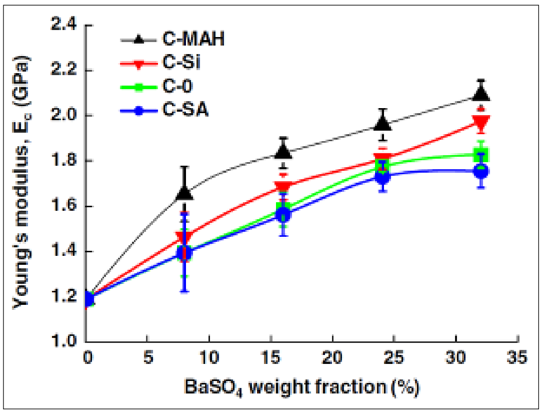


Fig. 4 – PP-BaSO4 composite with different surface treatment: BaSO4 without treatment (C-0); BaSO4 treated with 1% stearic (C-SA); BaSO4 treated with 1% silan AMPTES (C-Si).

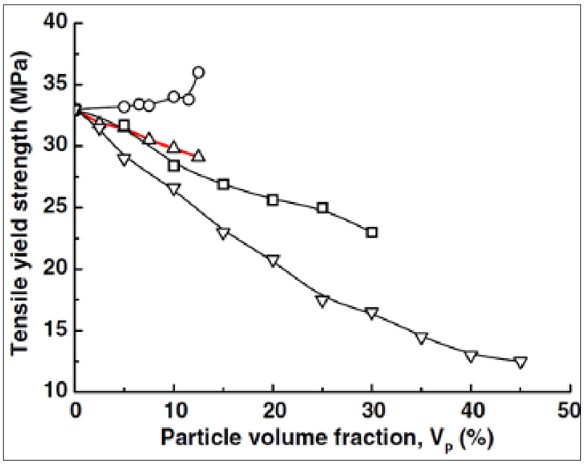


Fig. 5 – Dimensional effect of the sferic particle on the Yield strength of the PP–CaCO3 composites. Particles Diameter : (O) 10 nm, (Δ) 80 nm, (O) 1.3 μm e (▽) 58 μm.

In the fracture of polymer Nanocomposites we can see a growing trend of resistance depending on the quality of the interface between matrix and nanoparticles and decreasing size of diameter of nanofillers (Fig. 5). The dependence of resistance from volume fraction has a double trend: for nanoparticles, an increase of filler increases the performance of the composite. Micrometric particles filler increase lowers the resistance. In fact in general, the effect of filler it worsens the behavior of the composite matrix due to the concentration of stress which leads, but at the same time it has the effect a barrier for the development of matrix cracks.

This is the case of Nanocomposites consisting of polymer matrix with Graphene Nanoplatelets (GNP) in which you can see how the beginning of the damage is determined primarily by the debonding between platelets and matrix.

For this typology of Nanocomposite, the type of interface between Nanoplatlets GNP and polymer matrix has a fundamental importance. The quality of the interface depends on the uniform dispersion of the nanoparticles into the matrix.
For graphene Nanoplatelets (GNP), we can see a capacity of interlocking with the polymer chain that generates extensive and strong interface zone. The problem of the particles clustering is important, especially in the industrial processes for mass production in which it’s difficult to apply advanced techniques of dispersion as in a lab environment.

3 INITIAL DATA AND ASSUMPTIONS

This paper describes the Micromechanics analysis of behavior of polymeric composites reinforced with short glass fibers and UD carbon fibers when the matrix is functionalized with GNP. The materials considered, are the following.

TAB. 1 – MATERIALS CHARACTERISTICS

	Thermoplastic with Short Glass Fibers		
Characteristics	Matrix: PA6-B3K		Fibers: Short Glass
ρ	1.13 g/cm3		2.49 g/cm3
ν	0.39		0.22
E	2000 Mpa		89 Gpa
Tensile Strength			4750 Mpa
Tensile Strain at yield	3.5 %		4500 Mpa
Compressive Strength			
Yield Stress	60.5 Mpa		
Hardening Modulus	63 Mpa		
Hardening Model	Power law		
Hardening exponent	0.4		
Aspect Ratio			23.5
Characteristics	Epoxy with Carbon Unidirectional (UD)		
	Matrix: EM120		UD T300 - Toray
ρ	1.2 g/cm3		1.76 g/cm3
ν	0.34		
E	3407Mpa		230 Gpa
Tensile Strength	85 Mpa		3530 Mpa
Tensile Strain			1.5%
Compressive Strength			
Yield Stress			
Hardening Modulus			
Hardening Model			
Hardening exponent			
Filament Diameter			7 μm
	Nanofillers for functionalized Matrix		
		Vf%	
Characteristics	GNP	PA6-B3K / Short Glass	FibersEM120 / UD Carbon
ρ	2.2 g/cm3	1%	2%
ν	0.22		
E	1000 Gpa		
Tensile Strength	5 Gpa		
Thickness	10 nm		
Ave lateral size	10-60 μm		
D90	60 μm		

Micromechanics analysis were performed using the software Digimat 6.0.1, of the e-xstream (www.e-xstream.com).

The following assumptions are made:

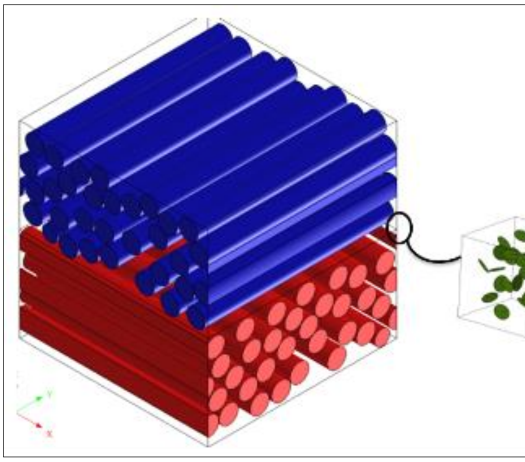


Fig. 6

1. The Graphene platelets dispersed in a matrix (thermoplastic or thermoset) can improve in general the strength of material and in particular, for the CFRP laminates, their resistance to delamination (Fracture Toughness). In fact, between two adjacent plies of the laminate there is only the matrix and so the delamination resistance depend only by it (Fig. 6). The dispersed Graphene can improve matrix fracture toughness and strength. For verification of this concept it's necessary to determine the curve until breakage of the Matrix with Graphene dispersed and its fracture toughness. In fact we assume that he beginning of the damage is basically determined by debonding between platelets and matrix. This assumption is even truer when there are many GNP dispersed. In other words the cracks evolve primarily due to the debonding between nanoparticles and matrix. Therefore we assume that the energy for the debonding of nanoparticles is equal to matrix fracture toughness (Fig. 7), and the debonding curve is equal to the curve until break. The maximum value of the load is similar to the value of the material's Yield Stress.

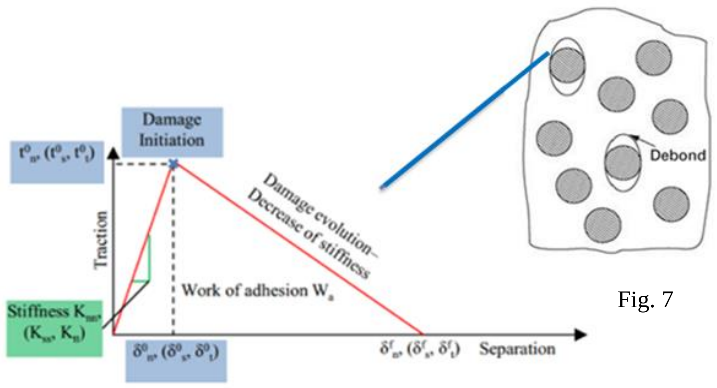


Fig. 7

2. For GNP/PA6 Debonding Modeling, Abaqus and Marc use a Cohesive Zone Model described through a traction-separation law, where the values of max tension before the damage initiation, the stiffness of the interface and the damage evolution law until the complete separation are necessary. The area under the curve of evolution of the damage is the separation energy between particles and matrix. Using data from literature [3] [4], we have chosen values (tab. 2) corresponding to an interface that has average strength (Media interface), taking into account the difficulty to evenly disperse the nanoparticles. An interface with average strength also considers that the surface of the Nanoplatelets is not treated in a perfect way in an industrial process.

TAB. 2 – VALUES OF THE STRENGTH OF THE GNP/MATRIX INTERFACE

	Strong interface	Media interface	Weak Interface
Shear mode	110 Mpa	96 Mpa	30 Mpa
Normal mode	170 Mpa	150 Mpa	40 Mpa

Micromechanical analysis was made with a sensitivity of the principal parameters of the behavior of the nanocomposite consisting in GNP and polymer matrix. In particular we have considered the following parameters:

a. Young Modulus of Graphene;

b. Volume Fraction of GNP;

c. Aspect Ratio of GNP;

d. Interface typology between GNP and Matrix;

For each parameter we made comparisons with the matrix polymer without GNP.

4. MICROMECHANICAL ANALYSIS OF PA6 MATRICES WITH GRAPHENE NANOPLATLETS

Set an initial size of GNP given by an Aspect Ratio = 0.054 a first sensitivity analysis on Young's modulus of Graphene was made, considering the following values: EGNP1 = 1000 GPa, EGNP2 = 700 GPa e EGNP3 = 400 GPa, considering an interface GNP/PA6 Perfectly Bonded. The results of the homogenization process with Digimat are:

TAB 3 - PA6-B3K WITH GNP – SENSITIVITY ON YOUNG’S MODULUS OF GRAPHENE

GNP - E (GPa)	1000	700	400
Vf GNP = 1%			
E_1 (MPa)	2277	2284	2279
G_{12} (MPa)	786	775	773
ν	0.38	0.38	0.38
ρ	1.14	1.14	1.14
Vf GNP = 2%			
E_1 (MPa)	2476	2435	2446
G_{12} (MPa)	844	846	842
ν	0.38	0.38	0.38
ρ	1.14	1.14	1.14
Vf GNP = 5%			
E_1 (MPa)	3169	3135	3072
G_{12} (MPa)	1044	1034	1014
ν	0.38	0.38	0.38
ρ	1.14	1.14	1.14

The variation of stiffness depending on the Vf of the GNP for the same Aspect Ratio = 0,054 and perfectly bonded interface is shown in the following chart (Fig. 8):

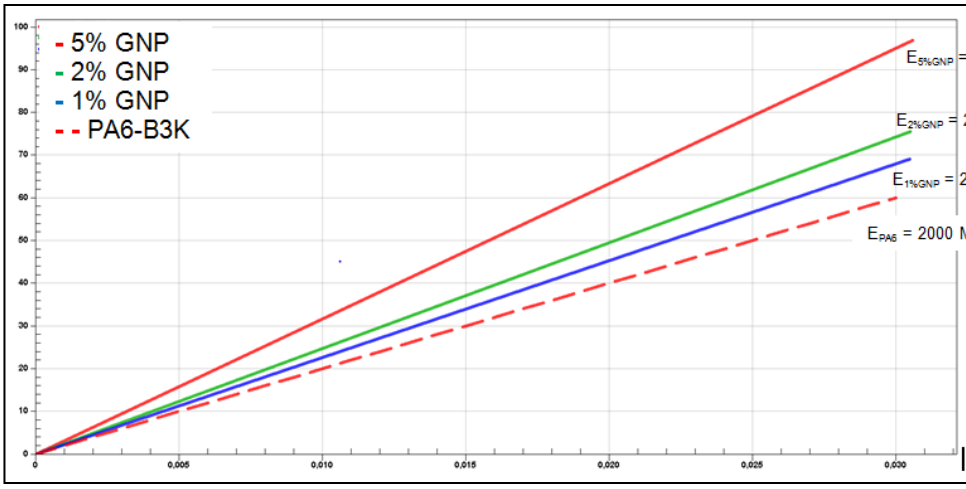


Fig. 8

It must be highlighted that the introduction in the matrix of the 1% of the GNP gives an improvement of about 13 % of the stiffness of the matrix PA6-B3K. In Figure 9 you can see the different density of GNP for each Vf.

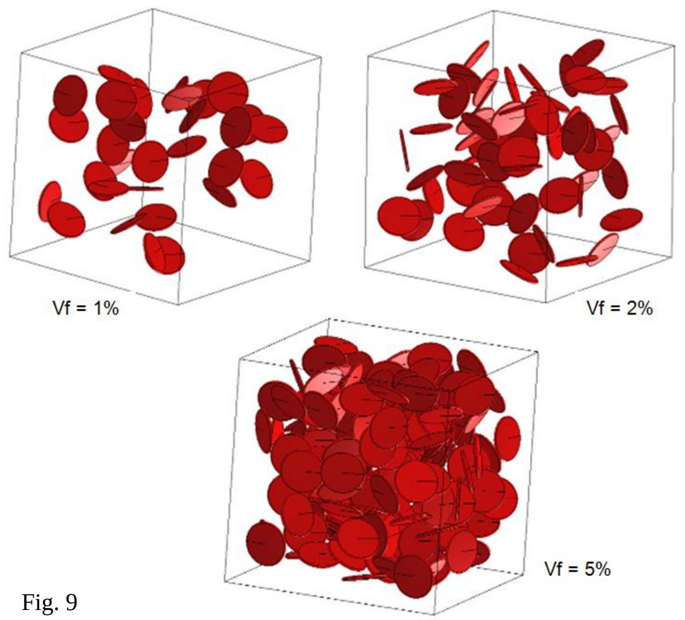


Fig. 9

Set the percentage of GNP dispersed in PA6-B3K equal to 1%, a sensitivity analysis was made on the Aspect Ratio of the GNP, taking the following values:

AR= 0.054, 0.015, 0.008, 0.004, 0.002, 0.00125, 0.001, 0.00042, 0.00022, 0.00015.

Considering a GNP/PA6 interface Perfectly Bonded. The results of the homogenization process with Digimat are:

TAB 4 - PA6-B3K WITH 1% GNP - SENSITIVITY ON ASPECT RATIO OF GNP

Aspect Ratio (AR)	E_1 (Mpa)
0.054	2277
0.015	2357
0.008	2322
0.004	2286
0.002	2504
0.00125	2678
0.001	2163
0.00042	2136
0.00022	2140
0.00015	2122

The effect of the GNP dimensions is evident. The Young modulus improved until value of AR=0.00125. The nanocomposite actually is constituted by a combination of the GNP with different Aspect Ratio as you see in the following table:

%	5	5	20	20	20	10	10	5	5
AR	0.002	0.00125	0.001	0.00042	0.00033	0.000222	0.0001695	0.0001428	0.00125

We can consider a weighted average of the values of the stiffness calculated: E1 = 2213 MPa. This value is equal to about 11 % of the improvement of the stiffness, with respect to PA6-B3K without GNP, value in line with the experimental data provided by Basf and visible following:

In Figure 10 are you can see the different dimensions of the GNP with different Aspect Ratio.

The value of the stiffness equal to 2213 MPa it's a value near to what obtained with AR=0.001. We take this value as reference for the evaluation of the debonding of the nanocomposite.

Using the maximum values of the debonding stresses between PA6-B3k and GNP by table 2, the debonding curve of the nanocomposite was determined for a different Volume Fraction of the GNP (Fig. 11). Considering the assumptions of the section II, from this curve we also obtained the maximum value of the load supported by the material.

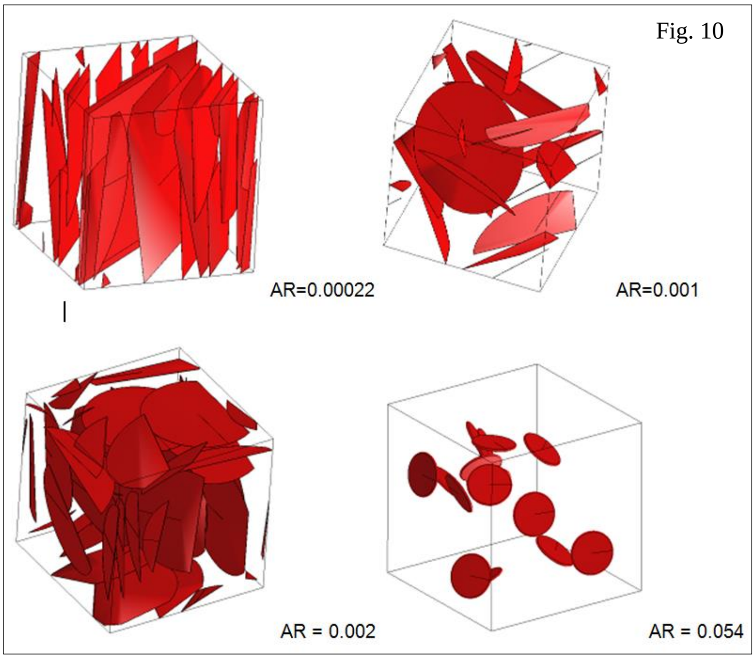


Fig. 10

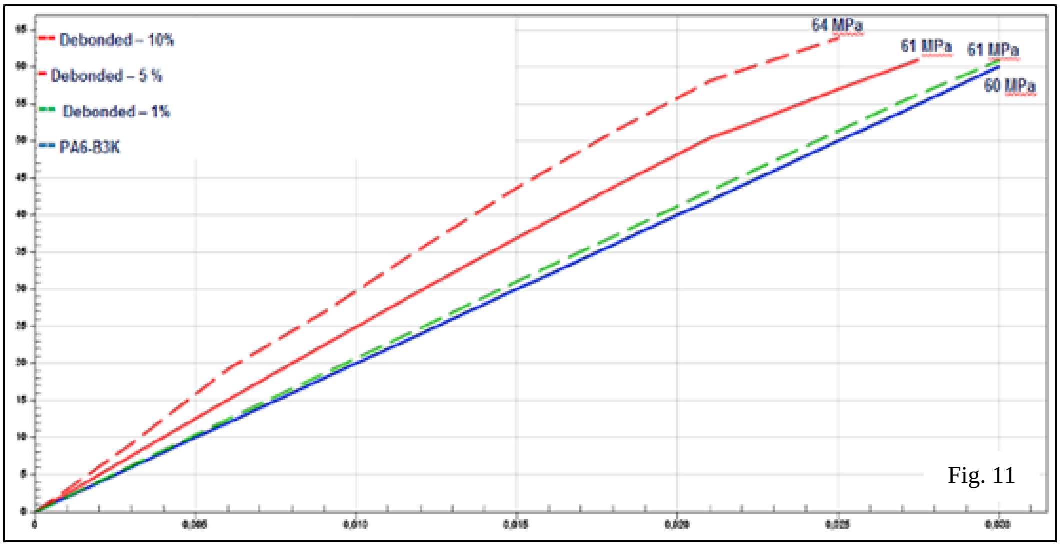


Fig. 11

	Debond 5%	Debond 10%	Debond 1%	PA6
Smax (MPa)	61	64	61	60

The debonding curve will be used in the final phase for the virtual characterization of the composite with short glass fibers. In Figure 12 you can see the debonding phenomena between GNP and matrix.

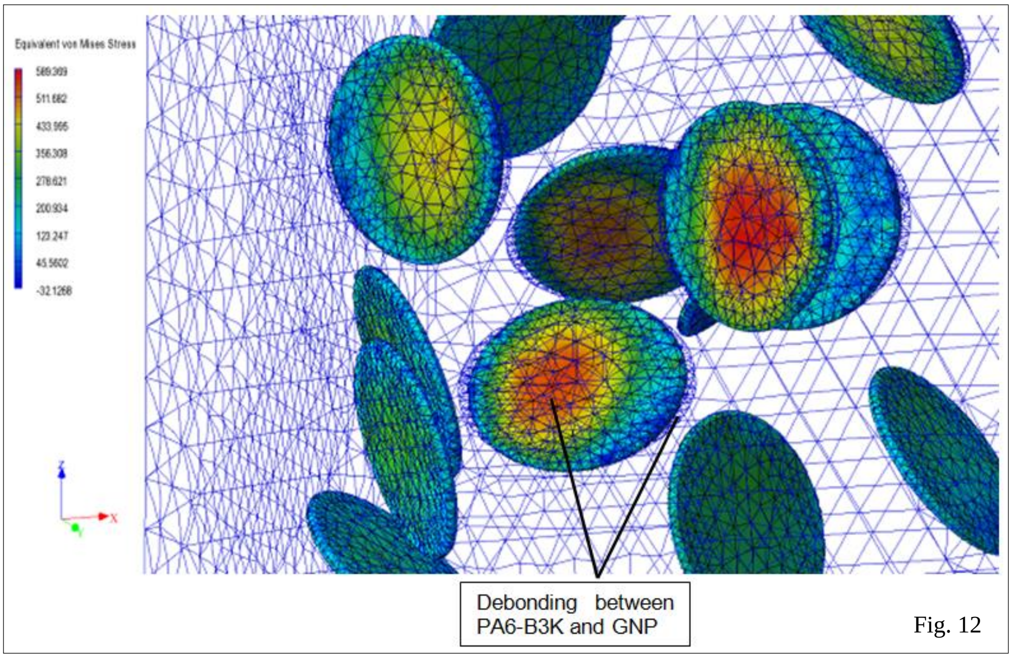


Fig. 12

You can see how passing from Perfectly Bonded at Debonding we get a decrease of the Young modulus of the material (Fig. 13).

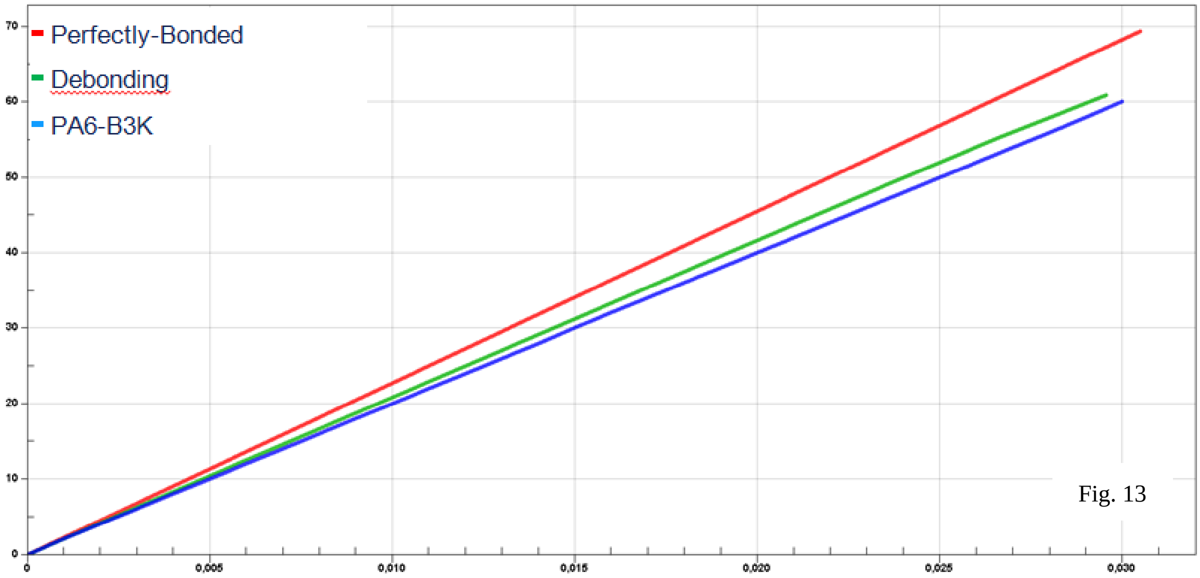


Fig. 13

We pass from a E1 equal about 2200 MPa at a Young modulus equal to about 2080 MPa. The nanocomposite, however, should have another behavior, more rigid in the initial phase in line with the perfectly bonded data, and after it should deviate from linear behaviour and assume a non-linear behavior of the debonding.

To obtain the same stiffness of the 2200 MPa in the debonding curve it is necessary to start from higher initial values of the AR with higher stiffness, i.e. values near AR = 0,002 and a stiffness of 2504 MPa. This way we get the final curve of the material (Fig. 14).

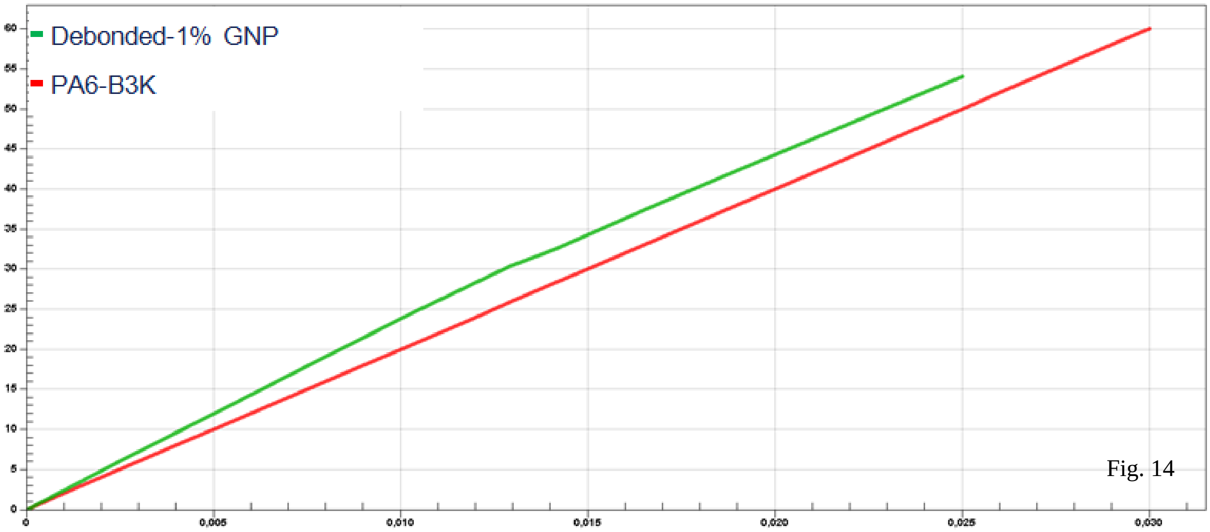
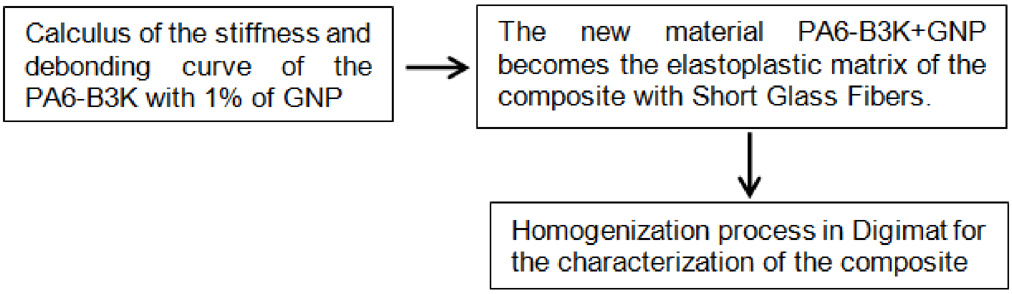


Fig. 14

	Debond 1%GNP	PA6	Δ%
Smax (MPa)	54	60	-11

5. VIRTUAL CHARACTERIZATION OF COMPOSITE WITH SHORT GLASS FIBERS

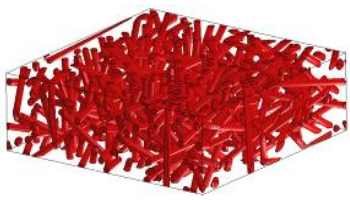
The methodology used to determine the characteristics of the final composite composed by PA6-B3K with GNP and Short Glass Fibers is the following:



The calculations were also made on the matrix PA6-B3K without Graphene. The final results are shown in the following table:

Tab 5 - PA6-B3K-GNP with short glass fibers - results of the mechanical characteristics comparison with PA6-B3K with short glass fibers without GNP

	PA6-B3K without GNP Short Glass Fibers	PA6-B3K – with GNP Short Glass Fibers	Δ%
E_1 [Mpa]	13370	14000	4.7
G_{12} [Mpa]	5129	5416	5.6
ν	0.30	0.30	
ρ [g/cm^3]	1.94	1.95	
S_r [Mpa]	184	179	-2.7
ε%	1.4%	1.4%	



6. MICROMECHANICAL ANALYSIS OF EM120 MATRICES WITH GRAPHENE NANOPLATLETS

Set the percentage of GNP dispersed in epoxy matrix EM120 equal to 2%, a sensitivity analysis was made on the Aspect Ratio of the GNP, taking the following values:

AR= 0.054, 0.015, 0.008, 0.004, 0.002, 0.00125, 0.001, 0.00042, 0.00022, 0.00015.

considering a GNP/EM120 interface Perfectly Bonded. The results of the homogenization process with Digimat are:

Tab 6 – EM120 WITH 2% GNP Sensitivity on AR of GNP

Aspect Ratio (AR)	E_1 (MPa)
0.054	3969
0.015	4221
0.008	3947
0.004	4000
0.002	3587
0.00125	3529
0.001	3862
0.00042	3700
0.00022	3430
0.00015	3450

The nanocomposite actually is constituted by a combination of the GNP with different Aspect Ratio as you see in the following table:

%	5	5	20	20	20	10	10	5	5
AR	0.002	0.00125	0.001	0.00042	0.00033	0.000222	0.0001695	0.0001428	0.00125

We can consider a weighted average of the values of the calculated stiffness: $E_1 =$ 3670 MPa

This value represents about 8 % of the improvement of the stiffness of the EM120 without GNP and it's an intermediate value between those obtained with AR=0.001 and AR=0.00042. We take these values as reference for the evaluation of the debonding of the nanocomposite (Fig. 15)

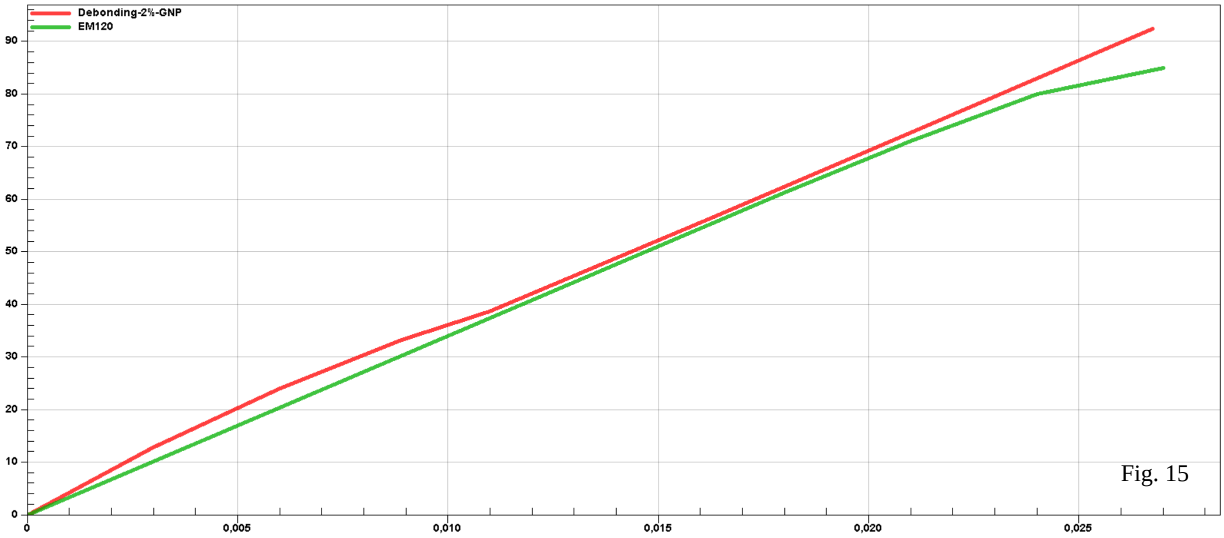


Fig. 15

	Debond 2%GNP	EM120	Δ%
Smax (MPa)	93	85	9

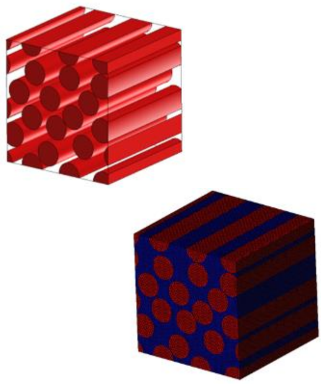
7. VIRTUAL CHARACTERIZATION OF COMPOSITE WITH UNIDIRECTIONAL CARBON FIBERS

The methodology used to determine the characteristics of the final composite made of EM120 with GNP and UD Carbon Fibers is the same used for the thermoplastic matrix with short glass fibers.

Calculations were also made on the matrix EM120 without Graphene. Final results are shown in the following table:

Tab 7 – EM120-GNP with UD Carbon fibers - results of the mechanical characteristics comparison with EM120 with UD Carbon fibers without GNP

	EM120 without GNP UD Carbon T300 Toray	EM120 with GNP UD Carbon T300 Toray	Δ%
E_1 [MPa]	130000	130500	0.4
E2 [MPa]	10890	12000	10
G_{12} [MPa]	3743	4160	11
ν_{12}	0.45	0.45	
ρ [g/cm^3]	1.5	1.52	
Xt [MPa]	2000	2005	0.25
Yt [MPa]	100	116	16
S_{12} [MPa	124	129	4
ε% (Xt)	1.5%	1.5%	



8. FAILURE ANALYSIS OF THE MULTI AXIAL UD LAMINATE

Consider a laminate cross ply [0/90/0] (fig. 16) with thickness t=0.15 mm for each ply. For this laminate we calculate, with Digimat, the in-situ transverse tensile strength for the first ply at 0° and second ply at 90°.

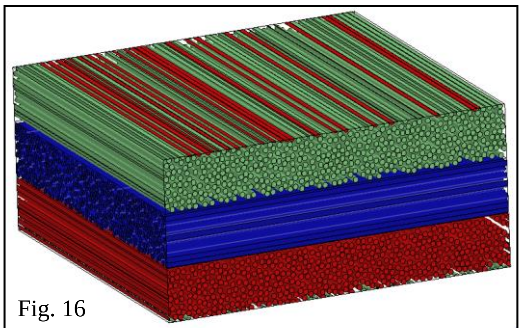


Fig. 16

We obtained for UD with and without GNP the following values:

Tab 8 – In-Situ transverse tensile strength for cross ply laminate.

	With GNP [Mpa]	Without GNP [MPa]
$Y^{is}_{t\,[0]}$	479	470
$Y^{is}_{t\,[90]}$	783	780

Consider now the following analytical formulation, available in literature [5], for the calculation of in-situ transverse tensile strength for UD laminate:

$$Y_t^{is} = \sqrt{\frac{8\cdot G_{Ic}(L)}{\pi t \Delta_{22}^{0}}}$$

In this formula $G_{Ic}(L)$ is Intralaminar longitudinal fracture toughness (fig. 17)

that maybe determined, in a first approximation , with an experimental test ASTM D5528 “Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites”.

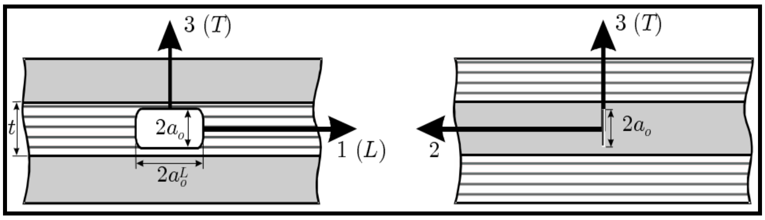


Fig. 17

Using this formula, knowing the in-situ transverse tensile strength from Digimat, it's possible to obtain, with an approximate calculation, the interlaminar fracture toughness for UD Material with and without GNP. The values are following:

Tab 8 – Calculate Fracture Toughness in mode I.		
	With GNP [mm*MPa]	Without GNP [mm*MPa]
G_{Ic}^*	6.02	6.58

These values are in accordance with the experimental data determined with ASTM D5528 test (fig. 18) and reported in the following table:

Tab 9 – Experimental Fracture Toughness in mode I		
	With GNP [mm* MPa]	Without GNP [mm*MPa]
G_{Ic}	5.26	5.39
	UD150-UTS50(F13) EM121-GNAN.78%-36%	UD150-UTS50(F13)-EM121 Neat-36%

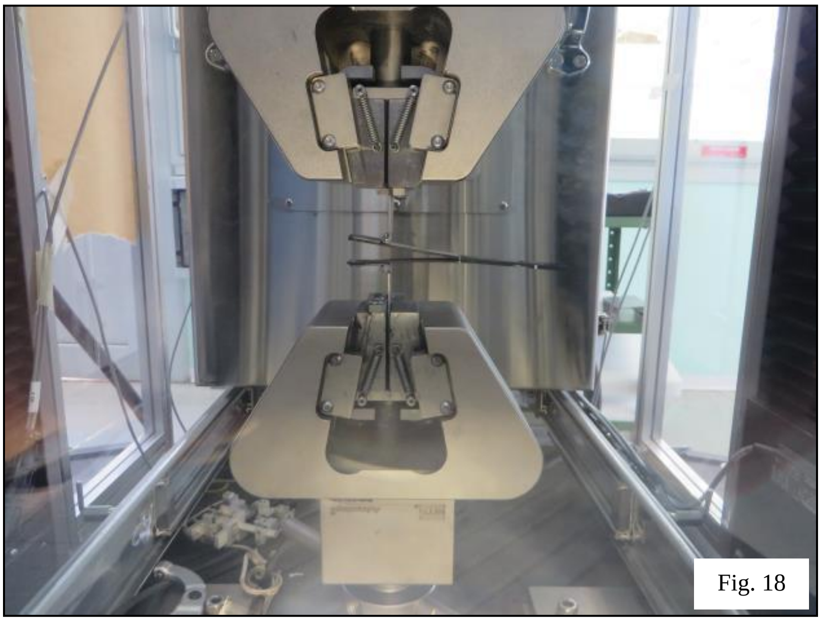


Fig. 18

9. CONCLUSIONS

Micromechanics analysis conducted in this work highlight the potential for improvement of mechanical performance of polymers by adding Graphene NanoPlatelets even in small quantities. These results are in line with available experimental data and with the scientific literature. Significant improvements can be obtained with higher percentages of GNP. With small amount of GNP, the improvement is not evident on high performance composites such as UD Carbon and Glass fibers.

The problem is of the technological nature, that is the improvement the capacity of the uniform dispersion of the Graphene NanoPlatelets in the Polymeric matrix. It's necessary to realize the dispersion of the quantities of the Graphene over of the 2% of the achievable today, while simultaneously ensuring the absence of clustering and a strong interface between GNP and matrix.

Acknowledgments

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