Nano-toughened carbon fibers composite materials by SAATI Group (SEAL S.p.A.), a partner of Nanoledge.

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Introduction

In the last few years words such as *nanotechnologies* and *nanometric materials* have taken place in common discussions in many different areas of science, technology and industry.

Composite materials trade has only recently turned its attention, but with growing interest, towards these innovations: properties of materials can change radically when zooming from common dimension to microscopic dimension. This behavior is still enigmatic and addresses to some topics that are not easy to translate in intuitive concepts; however they often turn into extraordinary features that can be exploited to create brand new materials, with novel attributes, or modifying and enhancing already know materials.

Carbon fibers composite materials industry, which works in a discipline where the research of high performance is at a very high level, looks with interest in the direction of newborn products that the market of nanomaterials makes available, in order to offer solutions in a process of continuous research and development.

SEAL is a company that operates in the area of advanced composite materials and personal protection systems, that's why has focused its efforts in the research and

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development of carbon fibers composite materials with high toughness: fracture mechanics of carbon composite materials are usually quite complex because of the anisotropy and disomogeneity of the material and they include both intralaminar damage (rupture of the fiber) and interlaminar fracture (delamination). These materials are particularly fragile to delamination fracture (due to the lack of reinforcement trough the thickness), that is the separation of contiguous layers of a laminate consequent of an interlaminar propagation of a flaw present in the material.

One of the technological process available to improve this particular feature consists of the modification of the matrix through the use of fillers that can influence the dynamic of the fracture process with the purpose of reducing the intrinsic fragility of composite materials.

Materials and methods

SEAL has come across 2 class of product which can play a role of tougheners when employed inside an epoxy matrix, that, along with the fiber, forms a prepreg: carbon nanotubes are the first kind of fillers identified as useful of the purpose, the second are kind are nanometric elastomers.

Matrix

The starting mix for the development of these composite materials is based on an epoxy resin system with stechiometric additions of hardeners.

Carbon NanoTubes

Carbon NanoTubes (CNT) are structures of nanometric dimension (1,2) built up entirely by atoms of carbon and they have a ratio of length-to-diameter up to 10’000:1. The carbon-carbon atomic bond is one of the strongest existing in nature and this leads to outstanding mechanical performances: very high specific strength and elastic modulus, high thermal and electrical conductivity, low density, high superficial area, almost free-defect structure (see table 1) and the opportunity to be functionalized with reactive chemical units that can form bonds with system in which they are dispersed.

	Carbon NanoTubes	Steel	Aluminum
Density (g/cm^3)	1,3-2,0	7,8	2,7
Elastic Modulus (GPa)	1000	200	70
Tensile strength (GPa)	10-60	0,3-0,5	0,22-0,25
Thermal conductivity (W/m·K)	3000	10-100	100-250

Table 1 – Properties of carbon nanotubes confronted to steel and an aluminum alloy.

In front of these features it comes immediately to mind the desire of exploiting carbon nanotubes as fillers inside and epoxy matrix.

Elastomeric tougheners

This family of products includes a large number of polymers for which the main characteristic must be the compatibility with the matrix in which they are dispersed and they must withstand a big quantity of energy during the fracture of the composite material.

SEAL has chosen in this category 2 different products, based on different chemical formulations and different dimensions: the first one has micrometric size; the second kind has nanometric length.

Beside these formulations, SEAL has studied a multi-component system: in an epoxy resin matrix are dispersed both carbon nanotubes and nanometric elastomeric tougheners.

Procedures and testing devices

All formulations have been tested in SEAL laboratories with thermo-chemical (DSC Q100 - *TAInstrument*) and thermo-mechanical (PyrisDiamond DMA - *PekinElmer*) devices, with the aim of verifying that the epoxy systems would respect the required specifics. Then SEAL has analyzed the rheological behavior with a Rheometer (AR500 Rheometer – *TAInstrument*) in order to validate the compatibility with the manufacturing process; afterward SEAL has performed a micrographic analysis with a scanning electron microscope (SEM) to evaluate the degree of dispersion of the nanometric fillers.

Once the prepreg has been produced, some laminates have been produced following an identical polymerization process in autoclave, so that SEAL has obtained specimens for tensile test[I], bending test[II], short beam strength test[III] and Mode I interlaminar fracture toughness[IV], performed on a SUN10 device (Galdabini).

This last test gives interesting results: following the standard ASTM5528, it is necessary to realize prismatic specimens from a plane plate of composite material; next a pre-crack, of known length, is created and then the opening of the specimen is imposed while load and crack opening are recorded. With this procedure it is possible to measure the intensity of the toughness resistance to the interlaminar fracture Mode I of the material and it expressed in J/m^2. The knowledge of the fracture toughness resistance is useful for the development of a product and for the correct selection of the material, especially for advanced composite materials for high performance. Furthermore, a measure of the interlaminar fracture toughness is helpful to determine the sustainable loads during the projection phase and the analysis of the damage tolerance of a composite structure made of these materials.

Results

The rheological and thermo-chemical analysis have shown a good processability of the filler employed and a good level of dispersions have been reached, verified with an electron microscopic analysis: this last aspect is remarkable, because a good level of homogeneity of the fillers in the matrix guarantee uniformity of properties in the composite material and moreover the full exploitation of the features of the nano-fillers inside the different systems (3,4).

In table 2 the results of the mechanical test for different laminates of composite materials are compared: they are manufactured with all the formulations mentioned, following the methodologies explained before.

Composite's Matrix	Elastic Modulus E [GPa]	Tensile Strength σ_R [GPa]	Interlaminar Shear Strength [MPa]
Standard	61	0.80	65
+ carbon nanotubes	75	0.90	69
+ micrometric elastomeric tougheners	62	0.75	61
+ nanometric elastomeric tougheners	53	0.70	60
+ carbon nanotubes and nanometric elastomeric tougheners	70	0.77	70

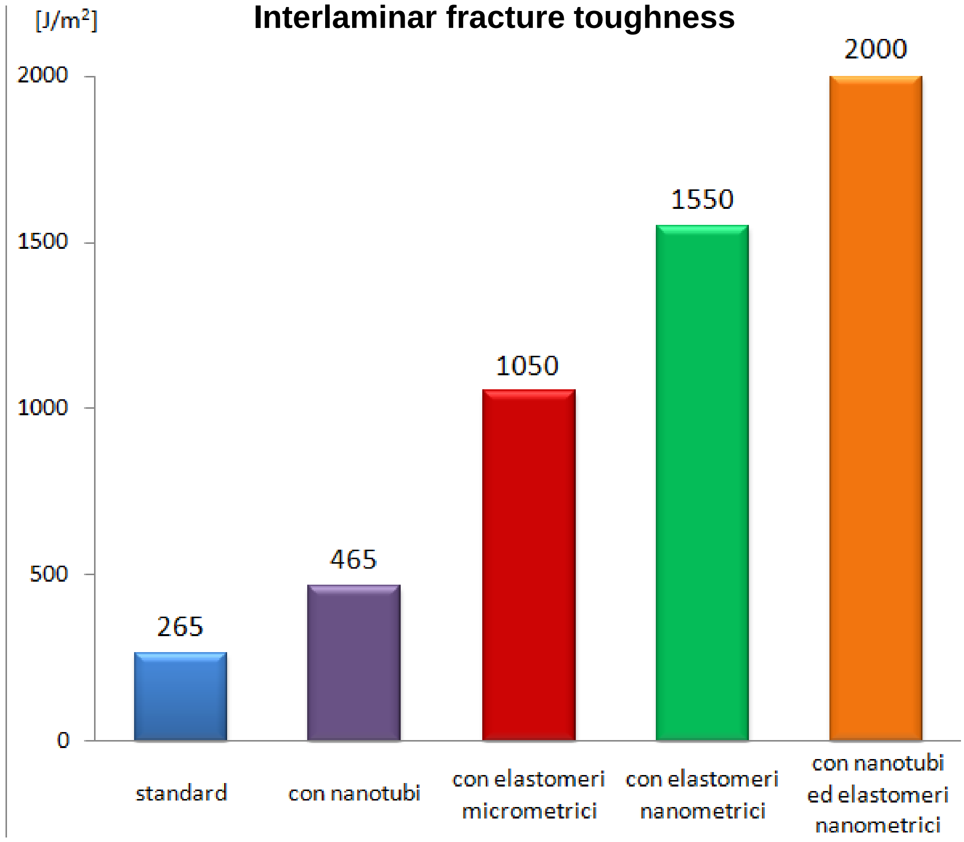
Table 2 – Comparison of the mechanical performance of a composite material manufactured with the same process, using different formulation of the resin matrix system.

The addition of carbon nanotubes raises the values of the elastic modulus and of the tensile strength of 22% and 35% versus a standard product, while the shear strength grows up to 6%.

The use of elastomers alone diminishes the structural properties of the composite: this decrease is higher for nanometric fillers than for micrometric: the diminution of the elastic modulus and the tensile strength are 13% and 6%, while ILSS drops to 7%.

The resin system the take advantage of carbon nanotubes and nanometric elastomers in the meantime has an elastic modulus and tensile strength similar to a standard product, whilst the interlaminar shear strength is 7% higher.

The results the SEAL has got with the Mode I interlaminar fracture test, are shown in graphic 1.



Graphic 1 – Interlaminar fracture toughness for carbon composite materials manufacture with the resin system studied.

It is obvious that the addition of the carbon nanotubes alone raises the fracture toughness versus a standard system of 75%. The benefit from the use of elastomeric tougheners grants a superior increment than CNT: micrometric elastomers improve performance up to 300% whilst nanometric elastomers over 400%.

An outstanding result is reached when CNT and nanometric elastomers are combined together: they enhance the fracture toughness beyond 650% versus a standard product.

In picture 2 it is possible to look one of the mechanism through which carbon nanotubes display their toughening effect in the matrix and consequently in the composite material: they build up “bridges” that keep the fracture surfaces stuck while they are being created during the fracture process (5).

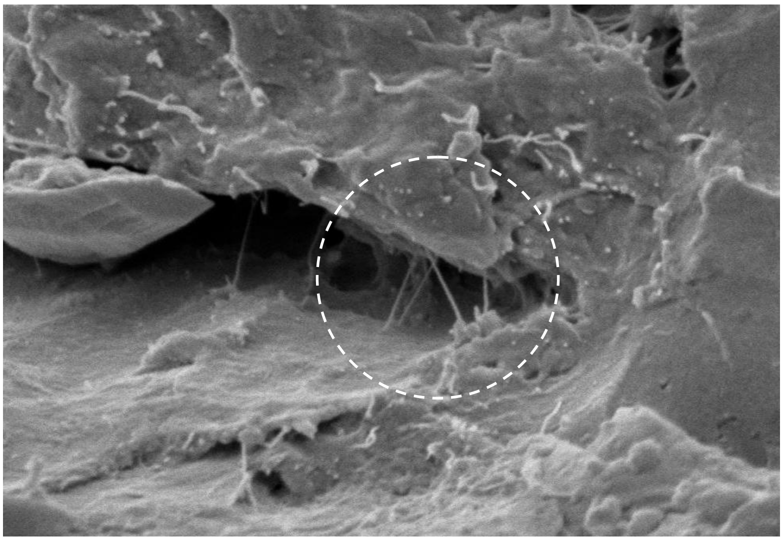


Figure 2 – Carbon nanotubes in an epoxy matrix – SEM 10000 magnification

The fracture morphology in figure 3 is completely different: nanometric elastomers, during the growing of the fracture through the composite, withstand the major part of the fracture energy process (6,7).

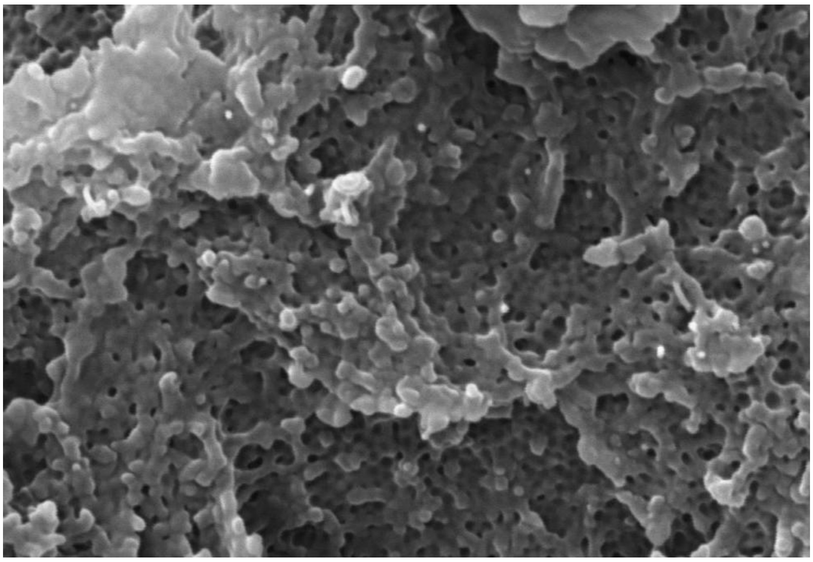


Figure 3 – Fracture surface of a composite material realized with an epoxy matrix toughened with nanometric elastomers – SEM 20000 magnifications

Conclusions

SEAL has shown in this work that it is possible to exploit different nanotechnologies, using them contemporaneously inside the same resin system employed in a carbon fiber prepreg, such as a correct formulation of the constituents' leads to full utilization of the potentiality which they offer.

The formulations studied are employed both on unidirectional and fabrics made of carbon, glass, aramid and hybrid prepregs. Material composites that have been manufactured with these products with nano-echnological fillers show very good mechanical and outstanding performances, which go even over 10 times a standard carbon composite material.

They are ideal for applications in which high performance are required, such as in automotive of marine structures, sport goods or industrial devices.

List of Standards

I ASTM D3039 – *Standard test method for tensile properties of polymer matrix composite materials*

II ASTM D790 – *Standard test method for flexural properties of unreinforced end reinforced plastics and electrical insulating materials.*

III ASTM D2344 – *Standard test method for short beam strength of polymer matrix composite materials and their laminates*

IV ASTM D5528 – *Standard test method for Mode I interlaminar fracture toughness of unidirectional fiber-reinforced polymer matrix composites*

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