Graphene and related materials in hierarchical fiber composites: production techniques and key industrial benefits

Filippo Valorosi,[1] Enea De Meo,[2,3] Tamara Blanco-Varela,[4] Brunetto Martorana,[2] Antonino Veca,[2] Nicola Pugno,[5] Ian A Kinloch,[6] George Anagnostopoulos,[7] Costas Galiotis,[7] Francesco Bertocchi,[8] Julio Gomez,[9] Emanuele Treossi,[1*] Robert J Young,[6*] Vincenzo Palermo[1,9*]

[1] *Istituto per la Sintesi Organica e la Fotoreattività, CNR, via Gobetti 101, 40129 Bologna, Italy.*

[2] *CRF, Centro Ricerche FIAT, Strada Torino 50, 10043 Orbassano, (Torino), Italy.*

[3] *Department of Chemistry and NIS Centre, University of Turin, Via P. Giuria 7, Torino 10125, Italy*

[4] *Airbus Operations, S.L., Getafe, 28906, Spain.*

[5] *Laboratory of Bio-inspired and Graphene Nanomechanics, Department of Civil, Environmental and Mechanical Engineering, University of Trento, via Mesiano, 77, I-38123 Trento, Italy; Ket-lab, E. Amaldi Foundation, Via del Politecnico, 00133 Rome, Italy. School of Engineering and Materials Science, Queen Mary University, Mile End Road, London E1 4NS, United Kingdom,*

[6] *National Graphene Institute and School of Materials, Oxford Road, The University of Manchester, Manchester, M13 9PL, United Kingdom.*

[7] *Institute of Chemical Engineering Sciences, Foundation for Research and Technology – Hellas (FORTH/ ICE-HT) and Department of Chemical Engineering, University of Patras, Patras 265 04, Greece.*

[8] *Nanesa S.r.l. Via del Gavardello 52c 52100 Arezzo.*[9] *AVANZARE INNOVACION TECNOLOGICA S.L. Avenida Lentiscares 4-6, 26370 Navarrete, La Rioja Spain.*

[10] *Industrial and Materials Science, Chalmers University of Technology, Hörsalvägen 7, 41258 Göteborg, Sweden.*

[*]*Contacts: treossi@isof.cnr.it; robert.young@manchester.ac.uk; palermo@chalmers.se*

Abstract

Fiber-reinforced composites (FRC) are nowadays one of the most widely used high-tech materials. In particular, sporting goods, cars and the wings and fuselages of airplanes are made of carbon fiber reinforced composites (CFRC). CFRC are mature commercial products, but are still challenging materials. Their mechanical and electrical properties are very good along the fiber axis, but can be very poor perpendicular to it; interfacial interaction have to be tailored for specific applications to avoid crack propagation– and delamination; fiber production includes high-temperature treatments of adverse environmental impact, leading to high costs. Recent research work shows that the performance of CFRC can be improved by addition of graphene or related 2-dimensional materials (GRM). Graphene is a promising additive for CFRC because: 1) Its all-carbon aromatic structure is similar to the one of CF. 2) Its 2-dimensional shape, high aspect ratio, high flexibility and mechanical strength allow it to be used as a coating on the surface of fiber, or as a mechanical/electrical connection between different fiber layers. 3) Its tunable surface chemistry allows its interaction to be enhanced with either the fiber or the polymer matrix used in the composite and 4) in contrast to carbon fibers or nanotubes, it is easily produced on a large scale at room temperature, without metal catalysts. Here, we summarize the key strategic advantages that could be obtained in this way, and some of the recent results that have been obtained in this field within the Graphene Flagship project and worldwide.

1   Introduction

Fiber-reinforced composites (FRC) are increasingly used in sport cars, airplanes, boats, sporting tools, building components… a large number of high-tech fashionable products need to have at least some part made of FRC, in particular made of carbon fiber reinforced composites (CFRC). These fibers composed mainly of carbon have already replaced the state-of-the-art metal alloys in many parts of commercial airplanes and in most of the structural parts of high-level sport cars. The current trend to electrification of mainstream cars will also push for lower weight and thus wider use of CFRC in mass-produced vehicles.

Historically it was Thomas Alva Edison who produced the first carbon fibers during the development of the incandescent electric bulb, in year 1879. In his search for a filament able to withstand electric current, Edison treated cotton threads or bamboo slivers at high temperature, in absence of oxygen, obtaining a carbonized filament that could glow for hours in vacuum inside a glass bulb. Carbon was soon replaced in the lamps by tungsten wires; though, ca. 80 years afterward, researchers from Union Carbide discovered how to exploit the outstanding mechanical properties of carbon fibers obtained by high-temperature treatments of textiles or other carbon-based precursors [1]. Such microscopic fibers could be added to thermoplastic or thermosets polymers to obtain materials as stiff and strong as metals, but much lighter.

Today CFRC are mature commercial products, but still present a number of technical challenges that limit their use to high-cost/high performance applications. In particular, they exhibit high anisotropy between axial and radial directions and they have to be oxidised in order to be fully wetted and bonded to polymer matrices. The strength of that interaction has also to be tailored to specific applications as strong interfacial bonding leads to brittle behavior whereas weak bonding leads to delamination and poor off-axis properties. Finally, conventional carbon fiber production processes involve toxic solvents and high temperatures and that adds to high production costs and adverse environmental impact. In recent years, results obtained in the scientific community indicate that the performance of CFRC can be improved by addition of graphene or related 2-dimensional materials (GRM).

In the following sections, we summarize the main technological challenges of FRC use and recent, state-of-the-art examples of how GRM can help to solve such challenges. In section 1, we will introduce briefly how and why CF and GRM are useful in composites. Section 2 will discuss the best ways to process GRM into composites, and the beneficial effect that GRM can have to improve the performance of the composite at nanoscopic and mesoscopic scale. In section 3 we will describe

what are the major issues limiting wider use of CF for applications in key industrial sectors, and how GRM can help to solve such issues. Finally, section 4 will briefly describe FRC-GRM composites that are already available commercially.

1.1 Use of carbon and glass fibers for mechanical reinforcement at the mesoscale

Both glass fibers (GF) and carbon fibers (CF) are widely used at the commercial level, with the former being cheaper but heavier, and the latter being stronger, lighter but more brittle and expensive. The mechanical properties of carbon fibers are strongly dependent upon processing conditions that control fiber microstructure [2-4]. Although there are many types of carbon fibers available, those used in engineering applications fall into two broad categories: *high strength* fibers with relative low or intermediate level of Young's modulus and *high modulus* fibers that exhibit a relative low or intermediate tensile strength. Carbon fibers are inert and have good electrical and thermal conductivities depending on modulus and degree of crystallinity. As mentioned below, however, the fibers exhibit a turbostratic structure and anisotropic physical properties with a much lower Young's modulus and worse general properties transverse to the fiber axis [3].

The main method now employed in the manufacture of carbon fibers is through the pyrolysis of the polymer polyacrylonitrile (PAN). The PAN is spun into fibers in which the molecules are aligned along the fiber axis. The fibers are then heated and the PAN becomes converted into a ladder polymer. Increasing the temperature and heating the fibers under tension in an oxygen-containing atmosphere causes further reaction in which the ladder molecules form crosslinks with each other. The material is then reduced and heated at high temperatures to give a 'turbostratic' graphitic structure [5]. This is an allotropic form of carbon, in which the graphene basal planes are not packed regularly as in a graphite single crystal. The basal planes are, however, aligned approximately parallel to each other along the fiber axis, leading to fibers with high levels of axial stiffness and strength.

A different type of CF is obtained by spinning of pitch, a viscoelastic material coming from distillation of crude oil, coal or plants. Pitch fibers are often more rigid than PAN fibers (higher tensile modulus), while PAN fibers have higher strength and lower density than pitch fibers.

Glass fibers have been for long time the most commonly-used type of fiber, employed in a range of –applications due to their low cost and good mechanical properties. They are inorganic fibers based upon silica mixed with other oxides and a number of different types of glass fibers are used. The most common kind of fiber is E-glass and other types of silica-based fibers with somewhat different

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compositions are employed; the more expensive S-glass for higher modulus and strength, and C-glass for better corrosion resistance in acids and water [5].

Impressive levels of reinforcement in polymer composites are obtained through the use of high-performance fibers. This reinforcement is controlled by the geometry of fiber packing, the mechanical properties of the fibers and matrix polymer, along with the properties of the fiber/matrix interface [6]. One of the advantages of using fiber-reinforced composites is that it is possible to tailor different fiber arrangements to take advantage of the anisotropic properties of the fiber reinforcement [5, 6]. It is also possible to stack layers of continuous fibers in unidirectional (stacked parallel), angle-ply (stacked at angles) and cross-ply (stacked at 90°) arrangements. Fiber-reinforced composites (FRC) with the highest axial stiffness and strength are obtained with unidirectional fibers in all plies whereas angle-ply or cross-ply configurations yield quasi-isotropic composites that exhibit, however, lower mechanical property values than unidirectional composites in the fiber direction.

Other arrangements of continuous fibers include knitted or woven structures that can be draped into complex shapes and then impregnated with a thermosetting resin. The off-axis fibers tend to reduce the reinforcement efficiency and reduce the composite modulus compared with composites containing straight fibers. As mentioned also above, such composites tend to have more uniform properties and the interlacing of the fibers leads to composites with better impact and penetration resistance [5]. Table 1 shows an indicative comparison of the properties of typical fibers used in FRC and typical GRM.

Table 1 Mechanical properties of mesoscopic fibers vs. typical GRM. All data are indicative and should be considered as order-of-magnitude estimations, varying greatly with the preparation technique and producer.

		Density (g cm^{-3})	Tensile Strength (GPa)	Young's modulus (GPa)
Mesoscopic additives	Carbon fiber (PAN Std. Mod.)	1.8	4.9	230
	Glass fiber	2.5	4.8	87
Nanoscopic additives	Graphene	n.d.[1]	130	1 050
	Graphene oxide	n.d.[1]	30	200

[1] Not defined. Density of nano-materials is not defined univocally, depends on packing and exfoliation grade. Perfectly packed graphene sheets (graphite) have a macroscopic density of 2.2 g cm^{-3}. For a list of measured density of commercial graphene-based materials, see ref. [7].

1.2   Use of graphene nanosheets for mechanical reinforcement at the nanoscale

Carbon fibers have typical sizes at the micron range (typically 5-10 μm in diameter), thus only reinforce the structure of the composite at a mesoscopic scale. One of the most spectacular developments in Materials Science over the past 40 years has been the identification and exploitation of new nano-sized allotropes of carbon in the form of different nanocarbons, starting with the discovery of C60 in the 1980s [8]. This was followed by the discovery of carbon nanotubes (CNT) (first multi-walled [9], then single-walled [10] and double-walled) in the 1990s. Carbon nanotubes were soon found to have interesting and exciting physical properties, in particular high levels of stiffness and strength [11, 12]. Soon after these nanocarbon allotropes were first identified, researchers started to investigate the properties of nanocomposites produced by processing them in polymer matrices. It was anticipated that the high inherent values of stiffness and strength of the CNTs might be realised when reinforcing nanocomposites. Poor levels of reinforcement were obtained with C60 nanospheres [13] but it was soon demonstrated that CNTs could in certain cases provide good reinforcement of polymer matrices [14-20] .
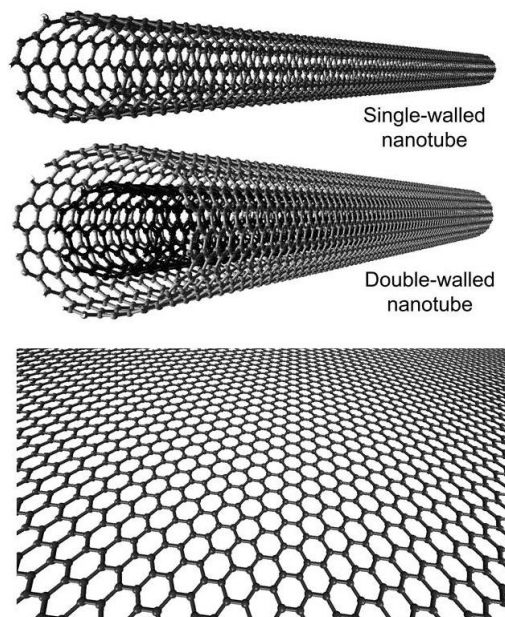
Figure 1. Carbon nanotubes and graphene (Courtesy of Professor Feng Ding).

The isolation and identification of graphene (Figure 1) was first reported in 2004 [21] and over recent years a number of different forms of graphene have been identified [22]. The material of initial interest was mechanically-exfoliated by 'scotch-tape'. A number of other different forms of graphene are now recognised [23], including mechanically-exfoliated (mono- and few-layer) graphene, CVD graphene, graphene nanoplatelets, graphene oxide (GO) and reduced graphene oxide (rGO), that are usually termed graphene-related materials (GRM). The literature is full of

papers that have used different terminologies to describe their materials and attempts now have been made to standardise the terminology of this range of different materials as can be seen in a number of publications [24, 25]. The different forms of GRM have different physical properties with monolayer having perhaps the most spectacular mechanical properties of a Young's modulus up to 1050 GPa and strength values of up to 130 GPa [26]. Such mechanical properties have led to a high level of interest in both the academic and industrial communities, accompanied the rapid development of nanocomposites based upon GRM. Initial studies employed GO or reduced GO (rGO), the preparation of which can be readily upscaled to produce large enough quantities to make specimens that can be deformed on conventional mechanical testing machines. Differently from other nano-additives (e.g. fullerenes or CNT), graphene can be prepared at low temperature, with no need of metal catalysts, by exfoliation of bulk graphite using ultrasonic methods,[27] high-speed mixing,[28] or water-jet milling.[29]

The current situation after nearly two decades of research upon nanocomposites reinforced with carbon nanotubes and graphene has recently been reviewed by Kinloch and co-workers [30]. They pointed out questions which still remain about the practical impact of such materials and suggested that this uncertainly stems from factors that include poor load transfer, interfacial engineering, dispersion, and viscosity-related issues that lead to challenges with processing the nanocomposites. One major issue is that CNTs form bundles and individual GRMs can agglomerate such that their ability to reinforce nanocomposites is compromised. Such factors make the effective aspect ratio of the nanofillers smaller which reduces the efficiency of load transfer, similar to the behaviour of short fiber composites [6]. Secondly, the surfaces of both CNT and graphene are devoid of any dangling bonds or defects that make strong matrix-filler bonds difficult to achieve. It is possible to remedy the situation to a certain extent for CNTs and graphene or graphene nanoplatelets (GNP) through chemical functionalization, although care must be taken to avoid compromising their intrinsic properties [31]. Moreover, such surface treatments may also help to reduce problems with agglomeration or restacking. The situation is somewhat different with GO and rGO, whose surface functionality can be easily tuned to improve the interfacial strength in nanocomposites [32].

2 Preparation and characterization of FRC-GRM composites

2.1 Production techniques

While both CF and GRM have exceptional properties, they also share difficulties in processing, being complicated or even impossible to simply process in a solvent. Combining them in a hierarchical composite with the appropriate structure is thus a major challenge.

In standard GRM-polymer composites, the objective is to disperse GRM as uniformly as possible. In FRC, conversely, different approaches are possible, being often preferable to include the nanosheets in the polymer matrix or on the fiber surface, in the pre-peg, in between different FRC layers. Figure 2 shows a cartoon depicting all possible approaches which illustrates the challenges encountered for the efficient decoration of FRC with GRM.
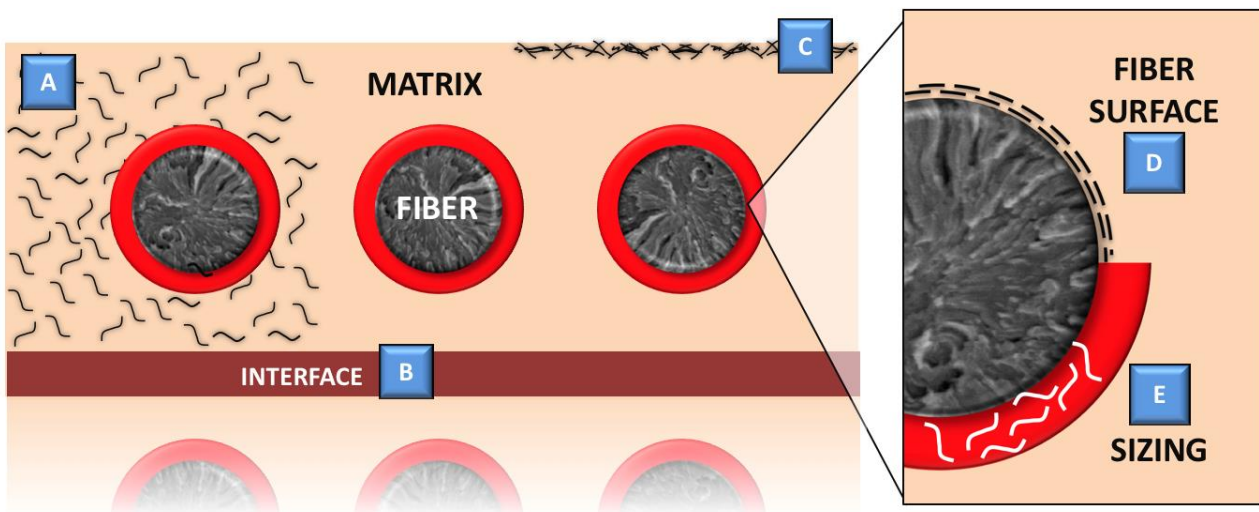

Figure 2. Schematic representation of the different ways to include GRM into FRC: A) dispersion in the polymer matrix; [33] [34] B) at the interface between different laminate layers; [35] C) on the surface, as gas and moisture barrier; [36] D) on the bare fiber surface; [37] [38-40] [41] E) in the sizing (pre-peg) layer. [42]

There are, in general, two main approaches to fabricate FRC containing GRM. One method involves simply adding the GRM to the matrix and processing the nanocomposite in a conventional way. The other approach ensures that the GRM are positioned at the interface between the fibers and matrix in order to optimize the stress transfer efficiency at the interface.

One important issue to highlight is that the inter-fiber separation in FRC is relatively small even at low volume fractions of fibers. For example, it is easy to show [5] that this separation is less than one fiber diameter at a volume fraction as low as about 0.3. This means that for most FRC there is very little space between the fibers and so the matrix may be constrained by the presence of fibers. As carbon fibers, for example are typically less than 10 μm diameter, the space matrix occupies

between the fibers has dimensions of microns, so that any matrix modifiers will need to be of sub-micron dimensions, such as in the case of GRM.

During composites processing methods such as resin infusion, the matrix resin needs to flow through the narrow gaps between the fibres. One of the main issues that then arises upon adding GRM to the matrix of a nanocomposite before resin impregnation is that the GRM may be filtered out by the fiber assembly during impregnation and therefore not be correctly positioned between the fibers in the final nanocomposite [43]. A number ways for overcoming this "filtering" effect have been developed, as detailed below.

Filtering can be avoided by using graphene-based particles with submicrometric size, as demonstrated by the Antolin group in collaboration with Airbus and Aernnova.[33] They used highly graphitic helical ribbon carbon nanofibres (CNFs, Figure 3) as additives in CF-epoxy composites for aeronautic applications, and observed no increase of viscosity during RTM and no filtering effect, ensuring that the production process could be implemented without major changes in the manufacturing process. A similar technology based on such CNF is likely also implemented in commercial sport tools. [44]
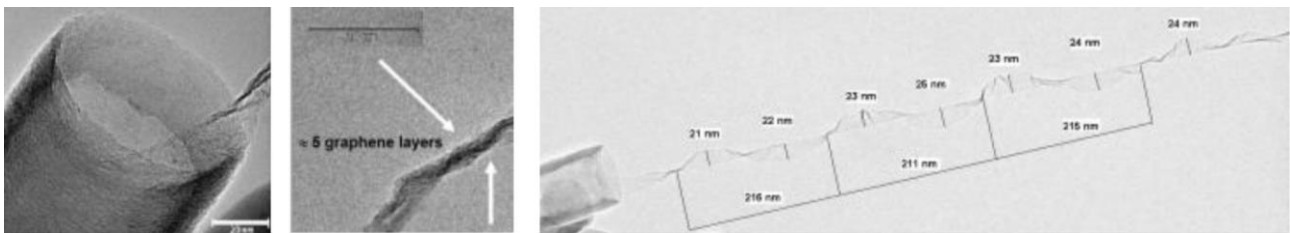

Figure 3 Helical ribbon carbon NanoFibre (GANF) used as graphitic precursor for obtaining graphene related materials with small size, able to infiltrate into CF fabric. From ref. [33].

Li and coworkers [34] exfoliated and dispersed natural graphite in an epoxy resin using a three-roll mill which then enabled the direct vacuum-assisted infusion of the doped resin into carbon fiber fabrics in a steel mould, without problems with particle filtering. They also pointed out that this method is industrially scalable and environmentally friendly and does not require the use of solvents.

Dip-coating is a widely used method whereby a suspension of GRMs is dispersed in the resin matrix using techniques such as sonication or mechanical stirring, usually with the aid of a solvent [42, 45, 46]. The fiber tows can then be dipped into the GNP-modified resin as shown in Figure 4. This ensures that a good dispersion of GRMs is obtained in the matrix between the fibers when the tows are finally pressed together to produce the nanocomposite.
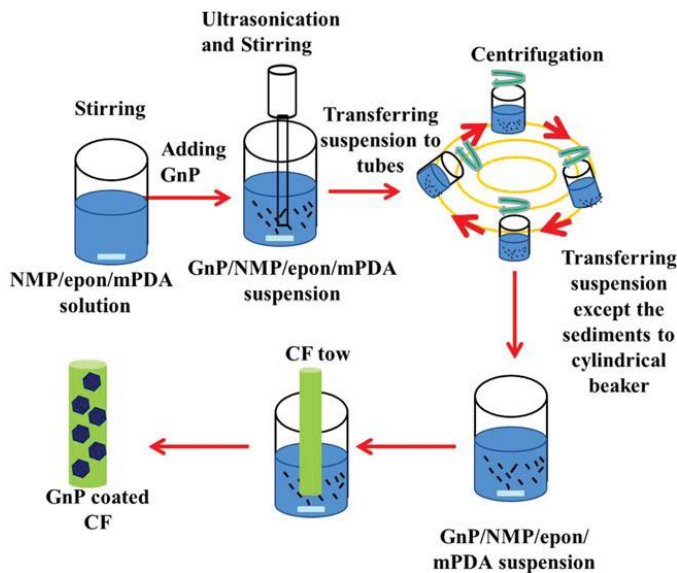
Figure 4. Schematic of a dip-coating method of dispersing GRM in a matrix resin and then coating a fiber tow (from ref. [42]).

Using another technique, Du and co-workers [35] prepared partially-cured GRM/epoxy nanocomposites and used them as interleaves between sheets of carbon fiber fabric that were then cured in a hot press inside a vacuum bag as shown in Figure 5. This method ensures that the GRMs are dispersed correctly in the nanocomposites although it should be pointed out that a solvent needs to be employed in the manufacture of the interleaves.

Besides dispersing GRM in the whole matrix, placing them selectively on the surface of the fibers is also an interesting approach, because it would allow to use minimal amounts of GRM and reinforce selectively the most critical part of FRC, i.e. the fiber-polymer interface.

The surface modification of carbon fibers using GRM has recently been reviewed by Hung and coworkers [37] who gave a detailed account of the methods that can be employed to coat the fibers with GRM for the manufacture of GRM-modified FRC. Hence only a brief summary will be given here. There are essentially two main methods used, electrophoretic deposition and chemical grafting.
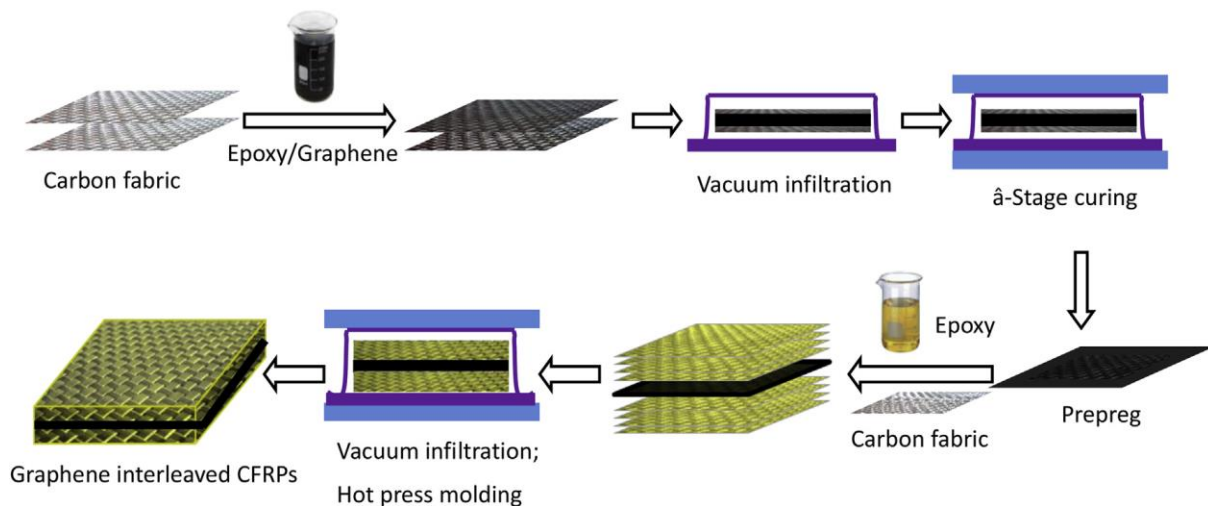
Figure 5. Schematic diagram of the fabrication of GRM interleaved FRCs. (After [35])

Strong interaction between nanofillers and fiber surfaces can be achieved when the two are bonded together chemically. The surfaces of carbon fibers generally contain few functional groups and so normally need to be oxidised to produce reactive functional groups on their surfaces [37]. Because it contains functional groups, GO is favoured for chemical grafting with surface-modified carbon fibers [38-40]. Oxidising carbon fibers can potentially lead to a deterioration in their mechanical properties through the creation of defects on their surfaces but chemical modification through carboxyl functionalization has recently been shown to maintain fiber strength by avoiding the creation of surface defects [47].

An effective chemical functionalization to attack GO nanosheets on mesoscopic objects is by formation of amide bonds. The fibers' surface is first functionalized to create NH_2 groups, for example using (3-Aminopropyl)triethoxysilane (APTES). This results in uniform coating (Figure 6), and improves inter-laminar shear strength (ILSS). [41] The opposite approach is also possible, functionalizing first the GO with NH_2 groups, and then attaching them to CF functionalized with acyl chloride groups (-COCl) [38].

More complex coatings, stacked multilayers of GO and polymers, can be fabricated on the fibers using layer-by-layer deposition [48] [49] [50]. This is a powerful technique based on successive dipping the fibers in a solution of positively charged polymer and negatively charged GO. Each step deposits a well-defined bilayer, with nanometric thickness, self-limited due to electrostatic interactions; the number of layers deposited can be tuned by the number of dipping steps, and works even on complex geometrical shapes, allowing to obtain composite GRM multilayers for packaging[49] or energy storage applications [50]. Deposition of up to 15 GO-PEI bilayers on carbon

fibers led to improvements in interfacial shear strength (IFSS), tensile strength storage modulus and elongation at break in PP/CF–GO hierarchical composites.
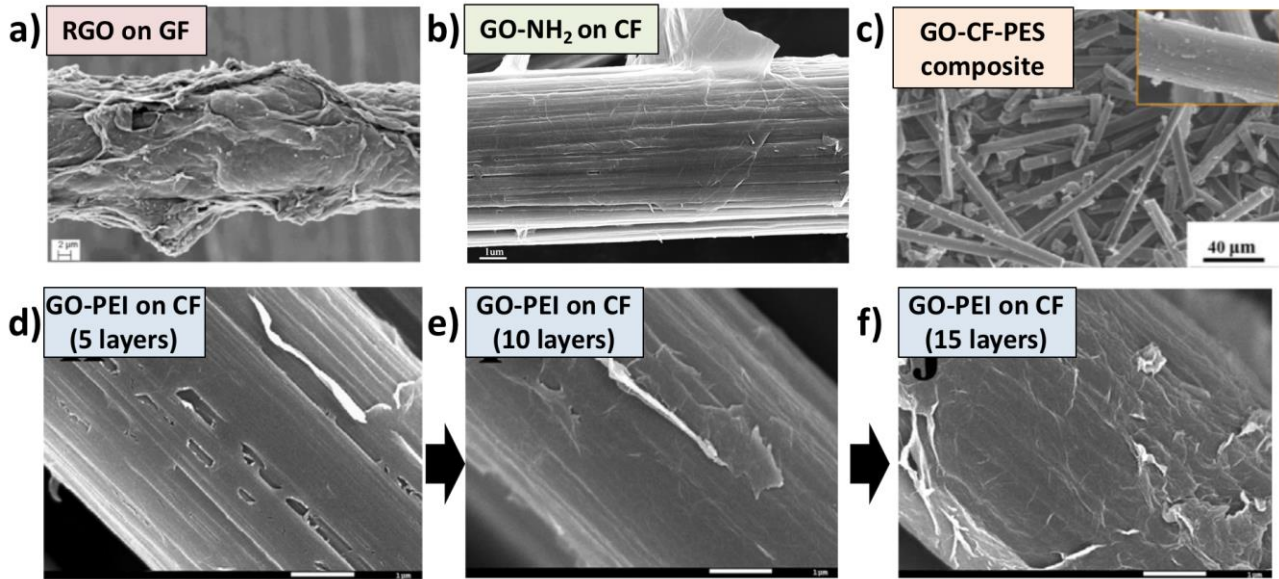

Figure 6 Examples of fibers coated with GO, from literature. See text for more details. a) GF electrophoretically coated with GO deposited at 7.5 V/cm and subsequently reduced to rGO.[51] b) GO-NH$_2$ directly grafted onto CF.[38] c) 0.5 wt% GO-coated SCF/PES composite, image taken after removing PES matrix by thermal ablation in N$_2$ atmosphere.[52] d-f) CF coated with an increasing number of GO-polymer layers using LbL technique. Scale bar in d-f is 1 μm.[48]

Electrophoretic deposition can be used to produce a homogenous high surface area coating of electrically-conductive nanofiller on fibers [37]. This has been demonstrated for both carbon [53, 54] and glass [51] fibers. This process is, however, only really applicable to GO which is negatively charged in solution and has hydrophilic functional groups. The negatively-charged GO migrates to a positively-charged fiber and gives it a uniform coating. Pristine graphene, on the other hand, is not suitable for this process since it is hydrophobic and so will not disperse uniformly in aqueous solvents. In this case other methods have to be employed such as by spray coating GNP on to fiber fabrics before resin infusion [55].

An original approach to produce innovative FRC-GRM is based on continuous CNT fiber fabric preform in a polymer matrix with chemically-modified CNT or GRM as matrix modifiers such as that shown in Figure 7. [30] In this case, the same nano-additives would be present both in the fibers part and in the matrix region of the FRC, thus enhancing the interaction and the strength of the FRC.
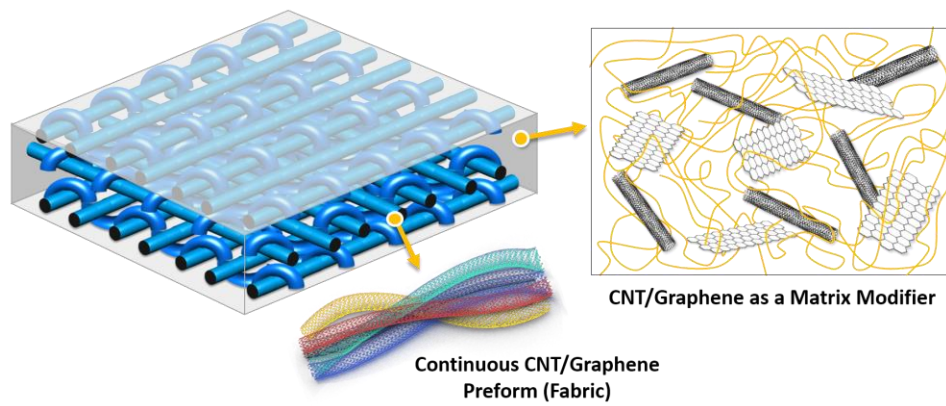
Figure 7. A schematic illustration of a futuristic CNT/graphene polymer composite that consists of continuous CNT fiber preform (fabric) in a polymer matrix and chemically-modified CNT/graphene as matrix modifiers [30].

2.2   Nanoscale interfacial interactions of GRM with the polymer matrix of FRC

GRM, thanks to their nanometric size, high flexibility and ultimate strength can be an ideal additive to both toughen the matrix and improve adhesion between mesoscopic fibers and polymers in a composite. The study and the control of such interaction is, however, challenging in a material having a complex hierarchical structure going from the nano- to the macro-scale. Here we summarize recent results obtained to better understand and enhance the benefits of GRM in FRC, in particular for structural reinforcement, while benefits on the electrical or thermal properties have been discussed in previous publications [56, 57].

The mechanical integrity of FRC depends primarily on the strength of the interface between the polymer, the GRM and the fibers. A detailed study of the micromechanics of the deformation of individual graphene monolayer flakes has shown that continuum mechanics is still applicable at the nano-level [58], enabling a full understanding of the deformation of graphene in bulk nanocomposites to be obtained [23].

A number of different micromechanical test methods have been devised to determine the strength of the interface [59] involving single-fiber model composites. One method that has been employed is the micro-bond test whereby the force needed to pull a single fibre out of a resin droplet is measured from which the strength of the interface (IFSS) can be determined. This has been done both for specimens where the GRM is introduced into the sizing of carbon fibres [60] and others for which the GRM has been added to the resin used for the droplet [61]. In both cases a significant increase is found in the interfacial shear strength with the presence of the GRM. The behaviour is shown clearly in Table 2 where it can be seen that the IFSS increases with the addition of pristine graphene to the epoxy resin in the droplet [61], in particular when the graphene is chemically functionalized.

Table 2. Measured values of IFSS for a series of carbon fiber microbond specimens with epoxy resin droplets containing different loading of graphene, both pristine and functionalized [61].

Graphene Content (wt%)	Interfacial shear strength (MPa)		
	Pristine graphene	COOH graphene	COOH+NH$_2$ graphene
0	62.4 ± 5.7	62.4 ± 5.7	62.4 ± 5.7
0.1	72.7 ± 7.3	73.9 ± 4.0	73.9 ± 4.8
0.3	76.3 ± 5.4	75.8 ± 4.4	77.2 ± 4.8
0.5	79.0 ± 6.1	80.2 ± 5.6	82.4 ± 6.1

Lee and coworkers [61] examined the surfaces of their fibers after a droplet of polymer matrix was detached and concluded that the interfacial failure mechanism was not affected by the presence of the graphene in the epoxy resin matrix. They explained the increase in IFSS with the presence of the GRM in the resin as being due to the graphene leading to a more complicated path through resin adjacent to the carbon fiber as shown in Figure 8.
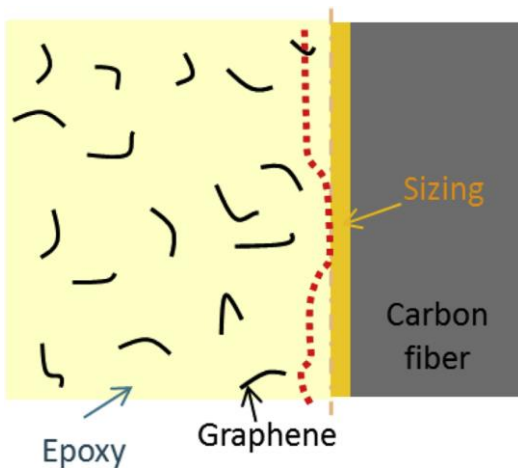
Figure 8. Schematic diagram of the path of crack propagation through a GRM-modified epoxy matrix near the surface of an embedded carbon fiber. (After [61])

It is also possible to evaluate the strength of the interface between fiber laminates (ILSS) for a GRM-modified FRC, rather than for single-fiber model composites, using techniques such as the short-beam shear test upon unidirectional composites. Zhang and co-workers [60] introduced GO into the sizing of carbon fibres and correlated its effect upon both the single-fiber IFSS measurements and ILSS values for unidirectional composites. They found an increase in both parameters upon the addition of the GRM to the sizing. Research upon the effect of the modification of FRC with GRM

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upon the values of IFSS and ILSS has recently been reviewed by Hung and coworkers [37]. Overall it is found that both parameters increase with the addition of the GRM, with the IFSS values typically increasing by 30-90% whereas the increase in ILSS is smaller, generally by no more than 40%.

We have undertaken extensive studies of stress transfer at composites interfaces at the nanoscale using Raman spectroscopy [32, 58, 62] [63-65]. A strong interaction allows to have a shorter "critical length" of the flakes actively reinforcing the composite [32, 66]. We recently demonstrated that such interaction can be enhanced by the generation of atomic defects [67] and investigated it by means of AFM nano-mechanical mapping and Raman microscopy [68]. In addition, we demonstrated that the graphene/polymer interface can exhibit a mechanical recovery after cycling loading conditions under the influence of moderate thermal stimulus [69]. Controlling the interfacial adhesion between the graphene and the polymer substrate can be achieved by modulating the surface conditions such as its roughness. In this way the fracture mechanism of graphene can be altered [70].

GRM can thus act as structural linkers between the matrix and the fibers in hierarchical composites. To this aim, the simplest system that has been studied is a single CF filament-epoxy matrix model composite. Single fibers were subjected to quasi-static tension and simultaneous Raman spectra acquisition, to measure the shear stress on the fibre outer surface [71] . GRM gave a 50% enhancement of the fibre-matrix interface (using the shear stress value as the criterion) compared to the non-doped epoxy matrix materials, confirming the finding of the earlier studies using the micro-bond test described above [61]. Overall, GRM can work as hierarchical fillers (with high surface area and capillary wetting by the surrounding polymer) to improve the interfacial interactions of the FRC; the mechanisms of such improvement are still under investigation, being probably due to increased mechanical locking (friction), the local enhancement of the shear modulus of the matrix caused by the GRM sheets and a more tortuous path of crack propagation [71].

2.3   Mesoscopic mechanisms of structural reinforcement of GRM in FRC

The addition of GRM to FRC can lead to a significant improvement in mechanical properties of the FRC also at the meso/macro-scale. Recent research in this field has recently been reviewed by Hung and coworkers [37]. In general it is found that that the increases are obtained in Young's modulus [52, 72-74] and tensile strength [52, 53, 72-74] upon the addition of the GRM to an FRC.

Figure 9 shows a typical improvement observed for GO-coated short carbon fibers in a polyethersulphone (PES) matrix [52]. It can be seen that the optimal loading is around 0.5 wt% of GO. Above this loading level the modulus still increases slightly but the strength starts to decrease.
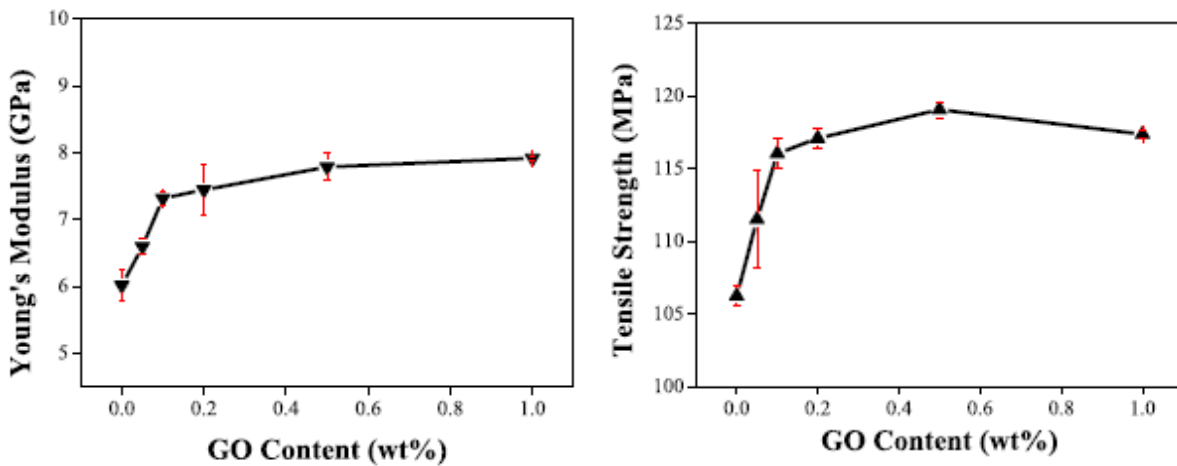

Figure 9. Effect of GO content upon (a) Young's modulus and (b) Tensile strength for short CF/PES composites. (After [52]).

We have recently undertaken a detailed study of the effect of the addition of graphene to the matrix of a unidirectionally-reinforced carbon fiber epoxy composite. It was found that that the addition of around 2% by weight of graphene can lead to a significant enhancement in mechanical properties [75]. In particular, it was found that the axial stiffness of the composites could be increased by the order of 10 GPa accompanied by an increase in axial strength of 200 MPa. X-ray computed tomographic imaging and polarized Raman spectroscopy demonstrated that the graphene was highly aligned parallel to the axes of the carbon fibers. Moreover stress-induced Raman band shifts showed that the self-aligned graphene is subjected to high levels of stress during axial deformation of the composite [75]. The graphene was found to have an effective Young's modulus in the composite of around 880 GPa, approaching its theoretical value of 1.05 TPa. This behaviour was modelled using the rule of mixtures and shear-lag analysis and it was demonstrated that highly-aligned graphene in a constrained environment between high-modulus fibers can give significantly better mechanical reinforcement than graphene in conventional polymer-based nanocomposites [75].

Figure 10a-c shows different characterization of a typical FRC-GRM composite made with a specific graphene nanoplatelets (GNP) with average lateral dimensions of ~5-10 μm (Figure 10a). The position of the symmetric 2D band at 2660 cm^{-1} in the Raman spectrum from the GNP (Figure 10b) shows that it is few-layer graphene (~5 layers) [76]. The Raman spectra of the neat epoxy and T700 carbon fiber are also shown in Figure 10b. The spectrum of the carbon fiber has very broad D and G

bands, in accordance to the turbostratic structure in PAN-based carbon fibers [2]. The presence of the GNP in the enhanced carbon-fiber composite was confirmed by examination of the polished transverse section shown in Figure 10c. Also for such systems, a positive improvement of ILSS (+45%) is observed by addition of GRM up to 0.5%, with a degradation of the properties for higher loadings (figure 10d). [77]
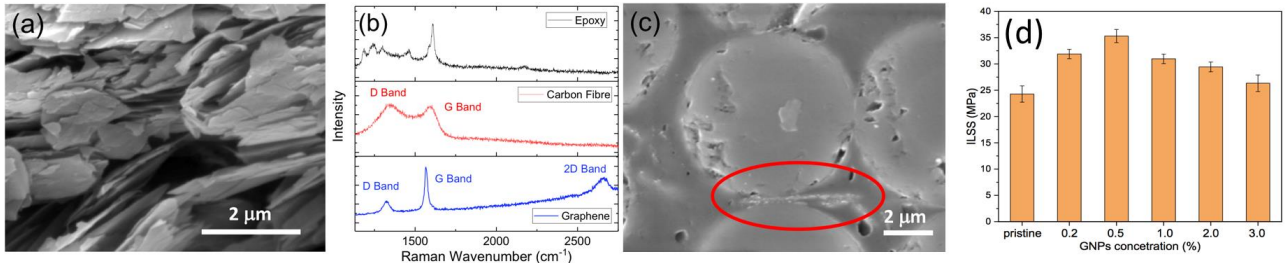

Figure 10. Characterization of the different materials of a FRC-GRM composite. (a) SEM micrograph of the graphene flakes. (b) Raman spectra of the epoxy resin, T700 carbon fiber and graphene flakes. (c) SEM micrograph of a polished section of the graphene-enhanced composite showing a graphene flake (highlighted) confined between the carbon fibers. (After [75]). D) Interlaminar Shear Stress values of GRM-doped CFRP for graphene loading of 0.5 wt%, (After [77]).

The dispersion of the graphene can be quantified by determining the ratio of the intensity of the graphene Raman 2D band (I_{2D}) to the resin intensity at the wavenumber of 1900 cm^{-1} (I_{1900}) (Figure 11a) [75]. The dispersion of graphene was also analysed by using X-ray CT scans that revealed the spatial arrangement of both the graphene and fibers (Figure 11d). The majority of the graphene flakes are within ±20° parallel to the fibers with their normals at right angles to the direction of the fiber axis. This suggests that the graphene flakes are aligned and flattened when the graphene/epoxy mixture passed through the gaps between the fibers (Figure 11c).
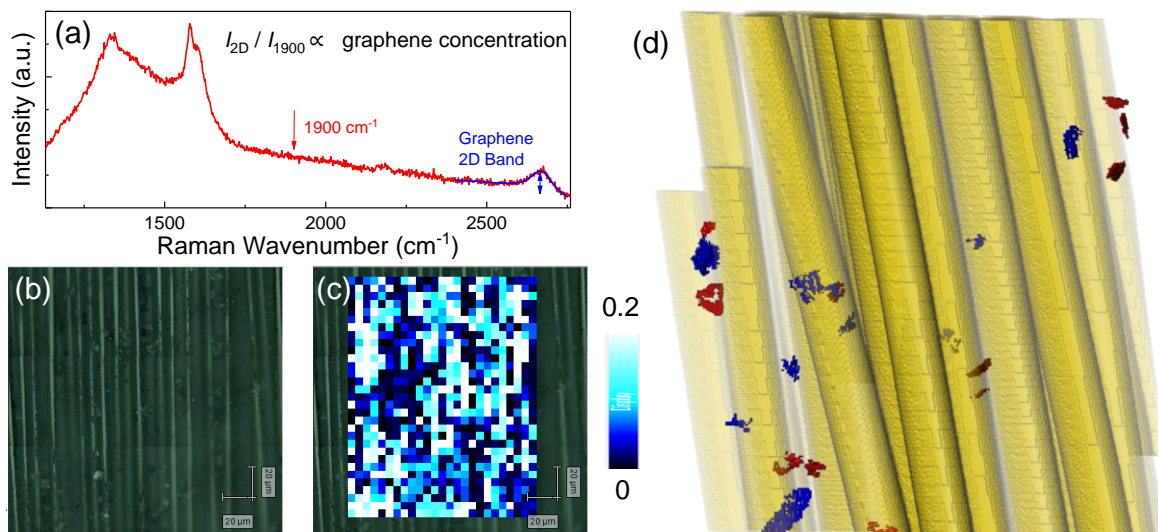

Figure 11. Graphene-enhanced carbon-fiber composite. (a) Raman spectrum showing the method of determining the Raman band intensities for the graphene and epoxy resin. (b) Optical micrograph. (c) Raman map of the variation of I2D/I1900 in (b) showing the distribution of graphene. (d) CT scan showing the spatial arrangement of the carbon fibers and graphene. (After [75])

Delamination in FRC is a major issue [6] and poor delamination resistance limits the use of FRC in a number of applications. Srivastava and coworkers [78] compared the effect of the addition of GNP, CNT or carbon black to the matrix of a woven carbon fabric reinforced polymer composite upon the mode I and mode II fracture toughness. They showed that both the GRM and CNT led to an increase in toughness whereas the addition of carbon black actually reduced toughness. Overall the CNT gave better properties than the GRM.

GRM/epoxy interleaves in carbon fiber/epoxy composite laminates can show significantly improved delamination toughening fiber-matrix adhesion, interlaminar properties (interlaminar shear strength), off-axis properties (90° flexural strength and modulus), and even the 0° flexural and compressive strengths of CF-epoxy unidirectional composites.[35, 45] Figure 12 shows that the highest level of toughening is found for a graphene loading of 1.0 wt%. even in this case, the properties deteriorate above this loading as a result of agglomeration of the GRM in the resin.

SEM images of fracture surfaces (figure 13) are also often used to confirm an improvement in interfacial adhesion, with a switch from a purely interfacial failure mode with non-coated fibers to a cohesive failure mode between fibers with GRM.
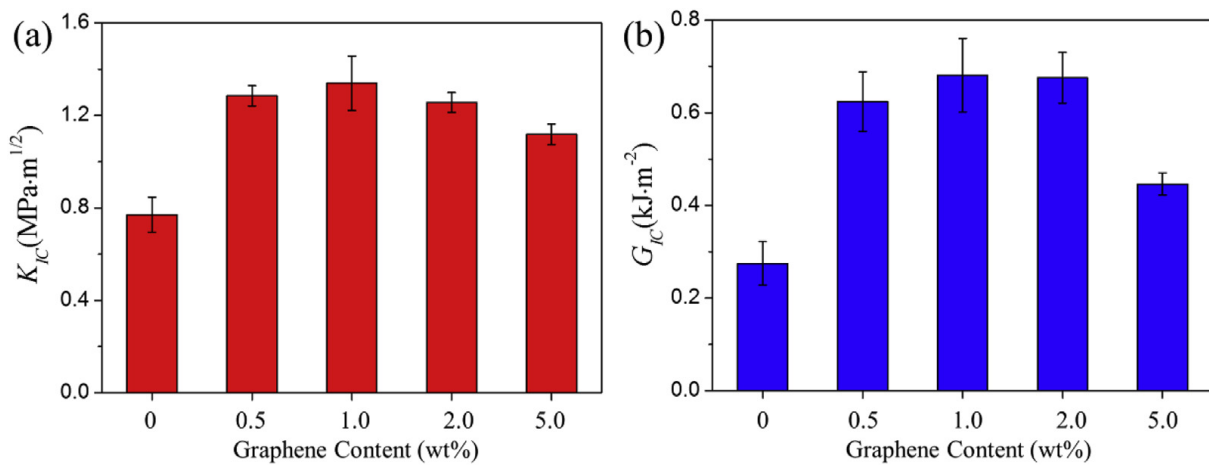

Figure 12. Values of (a) fracture toughness, KIC and (b) fracture energy GIC of carbon fiber/epoxy composite laminates containing GRM/epoxy nanocomposites interleaves with the indicated graphene contents. (After [35])
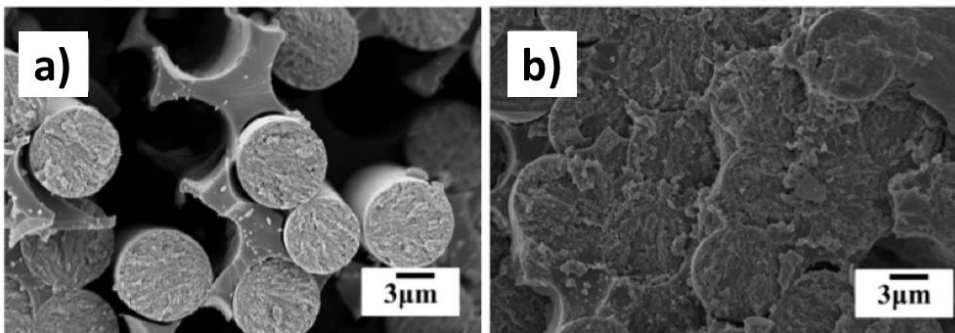

Figure 13 SEM micrographs of CF composites fracture samples after flexural 0° test : (a) non-coated CFs, (b) GRM coated CF. From [45].

2.4 Modelling of hierarchical composites

Understanding the macroscopic reinforcement effect of GRM in hierarchical structures is challenging, due to the very different length scales involved. That is why modelling and computational approaches are even more important here than in the study of uniform, conventional composites. Various multiscale numerical models capable of simulating fracture propagation in heterogeneous/hierarchical/multiscale materials have been developed, to capture the mechanisms involved in the optimization of the global material mechanical properties and aid in preparing experimental solutions [79],

In a typical multiscale approach, interaction of graphene layers and an epoxy matrix could be first modelled with atomic resolution using Molecular Dynamics (MD), see Figure 14a. The properties calculated in the MD unit cell are then used as input for mesoscopic analysis in a system that contains additional sub- cells of pure epoxy to arrive at the desired GNP volume fraction, using the generalized method of cells (GMC) micromechanics theory, Figure 14b. Finally, the data obtained for the GNP epoxy matrix are implemented into a GNP/Carbon fiber/Epoxy composite, Figure 14c.[80]

The so-called Fiber Bundle Model [81] is also particularly appropriate for the simulation of fibrous materials common in FRC. Hierarchical implementations [82, 83] have shown that specific combinations of hierarchy and material heterogeneity can lead to increased damage resistance [84]. The Hierarchical Fiber Bundle Model has already been used to estimate the strength and stiffness of hierarchical carbon nanotube fibers, also including the effect of defects at the nanoscale [83].

Further examples of modelling approaches are the Lattice Spring [85] or Random Fuse models [86], which both provide a continuum description of the media through a network of discrete elements (springs or "resistors"), and which have been used to simulate plasticity, damage propagation and avalanche statistics in heterogeneous materials and extended for treating hierarchy. Other computational approaches that could also be used in a multilevel scheme are 3D meshless models (based on the element-free Galerkin method) to simulate complex 3-D heterogeneous media with non-local effects [87] or more standard Finite Element Modelling (FEM strategies) [88].
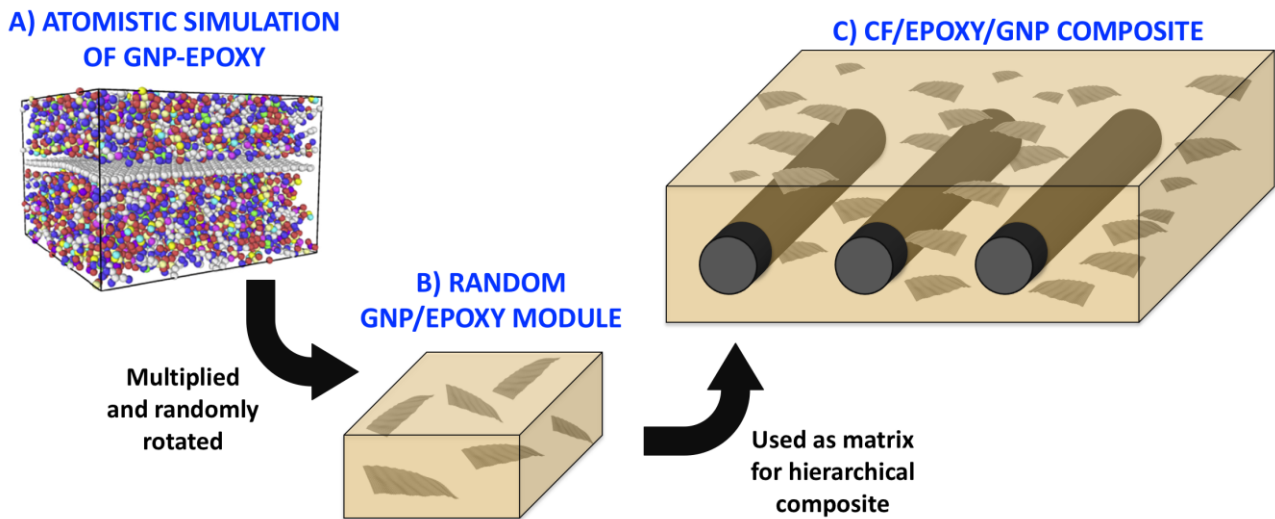
Figure 14 Multiscale modeling technique. Adapted from ref. [80].

Fracture nucleation and propagation is challenging to model by FEM, especially in the dynamic regime. Generally, this limit is overcome with the use of erosion algorithms that on the other hand show a strong dependence on the mesh size, and are not feasible with complex geometries at the mesoscale. An exception to this is a periodic structure, e.g. a honeycomb structure, whereby the whole structure can be characterized by simply modelling the basic cell [89]. Mesh-adaptive refinement on the go can represent a solution, even if it is computationally expensive. When fracture is expected in preferential regions, such as at materials interfaces (e.g., see [90]), the Cohesive Zone Model (CZM)-based elements can be used to describe the cohesive forces that occur under tensile fracture [91]. Extended FEM (XFEM) approaches need to be used instead for damage propagation within the continuum, implementing enriched shape functions that allow the treatment of discontinuous field functions with singularities without need of mesh refinement. Both are more expensive computationally than standard FEM, so that their use within a model should be carefully assessed.

Silling proposed a non-local and integral reformulation of the standard continuum theory of solid mechanics, called *peridynamics* [92]. Unlike partial differential equations, peridynamics equations are applicable even when cracks and other singularities appear in the deformation field. Thus, continuous and discontinuous media can be modelled with a single set of equations. This theory naturally yields a meshless method the non-local response of which represents an ideal bridge between atomistic (MD) and continuum methods (FEM).

Improvements in specific extreme properties, e.g. impact toughness, may also be obtained with the aid of numerical design, by the adoption of GRM-based nanocomposites [93, 94]. Modelling has been shown to provide new insights into controlling failure initiation in interphase regions between

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fiber/graphene/matrix, a process complex to understand due to the nonlinear response and intrinsic multiscale feature of the damage in this region [95].

3   Possible benefits of FRC-GRM in industrial applications

3.1   Challenges for the use of FRC in the aerospace industry

There has been increasing use of fiber reinforced composites (FRC) materials by the aerospace industry over recent years as can be seen from Figure 15a. A remarkable example is the Airbus A350 XWB, which has its entire fuselage, wing covers and tails made of CFRC – more than half of the structural weight; its production now requires >9,000 tons of FRC per year. This can be contrasted with the A300 Airbus produced in the 1970s that contained less than 5% by weight of FRC. The reason for this is that FRC are lighter, stronger and more corrosion resistant than traditional metallic components and provide a higher strength-to-weight ratio. They also require 50% fewer structural maintenance tasks, and the threshold for airframe checks is at 12 years compared to 8 years for the A380.
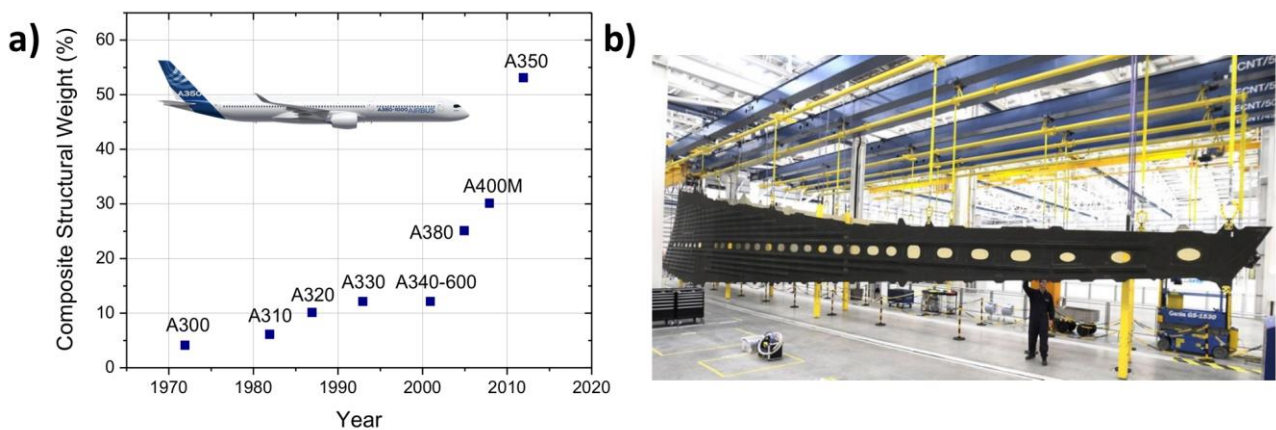
Figure 15. a) The percentage by weight of FRC materials in airplanes manufactured by Airbus over the past 50 years . b) The lower CFRC wing cover for a A350 XWB aircraft.[96].

Considerable investment has taken place in companies such as Airbus and Boeing in the development of CFRC manufacturing to meet the demanding requirements in modern aviation. Figure 15b shows the 32 m by 6 m lower wing cover for an A350 XWB Airbus. This is the largest single composite part currently being produced in commercial aviation.

In spite of this impressive change in materials selection, some of the main challenges that still need to be solved to increase the use of FRC in aerospace further are reported below:

- Electrical conductivity. While CFRC can replace metals for structural applications, their electrical conductivity is very low, in particular in the direction perpendicular to the CFRC panel plane. Thus,

FRC-based airplanes need to be coated with metallic nets, to act as a Faraday cage against lightning strike. The integration of the electrical functionality within the aircraft composite structure through the application of graphene could yield a significant weight saving. CFRC with electrical conductivities in the order of 10^5 S/m would be required to remove the metallic nets.

- **Fracture toughness** is critical for CFRC, that can crack after impact with birds or with flying debris. Typical CFRC used for this task have a compression after impact strength (CAI) of 275 MPa. A 20% improvement on such values would be significant.

- **Thermal conductivity** is often an issue in CFRC. The inhomogeneous structure of the composites gives poor and uneven heat transport across the CF and the polymer matrix. Increasing thermal conductivity could benefit key aeronautical applications such as the development of anti- and de-icing of structures, and enabling composite curing and welding through resistive heating[57].

- **Gas barrier properties.** Moisture adsorption due to the airplane changes of altitude and pressure is a critical process in CRFC, because water degrades the mechanical properties of the polymer resins currently used and weakens the resin/fiber interface. Barriers able to slow down or block these processes are highly desirable. Here, key targets would be to reduce diffusion coefficient of water in the material by ≥ 50%, reduce maximum absorbed water (at equilibrium) also by ≥ 20%, to achieve a maximum water uptake by CF epoxy composite ≤ 1.5% wt.

- **Multi-functionality.** One of the key areas where more effort is being made is the addition of non-inherent functionalities to aeronautic materials such as *piezo-resistivity*, to allow deformation and damage sensing in case of impacts, strain and dynamic loads. Also, adding an *energy storage* functionality to structural CFRC is high desirable, due to the ever increasing need of distributed electrical power in all parts of modern airplanes [97]. Another key challenge would be to improve the flame resistance and flame retardant performance of all materials used in aerospace.

3.2 Benefits of using GRM in the aerospace Industry

GRM are perceived as potential enablers to overcome many of the above-mentioned drawbacks of using composites in aerospace sector. Within the wide scenario of potential applications of GRM to improve aerospace composites, Airbus has defined priorities to focus on, based on added value versus development and industrialization efforts.

On the basis of the earlier work [35] , as discussed in section 2–, GRM can improve the mechanical properties of the composite by hindering or deflecting crack propagation, thus reducing the weight penalty linked to low fracture toughness and/or poor damage tolerance behavior of aeronautical composites. GRM can be a suitable additive to the carbon fiber/epoxy resin prepreg widely used in

commercial aircraft such as the A350, where it represents more than 95% of composite structural weight (> 100 tons per Aircraft, 13 Aircraft per month), although this material share will likely change for future Long Range and/or Single Aisle aircraft models. GRM can also improve the properties of A350 parts made by RTM (Resin transfer Molding), i.e. the HTP leading edge, the design of which is driven by developing resistance to bird impact [33].

GRM have also been used to decrease the moisture absorption of epoxy resin which leads to significant decrease of properties after Hot / Wet ageing, by applying the graphene in bulk and /or on the material surface. Significant improvement in water diffusion coefficient and water uptake was observed in aeronautical composites in this way [36].

Multifunctionality properties enabled by GRM have also been demonstrated with the use of flexible graphene papers and serpentines as electro-thermal systems for de- / anti-icing, which can be integrated industrially in composite parts affected by ice accretion during operation [98]. These innovative approaches will be able to guarantee lightweight, high integration in CFRC and homogeneous thermal behavior in a selected area. This approach can also be used to develop multifunctional applications, for example different thermoelectric systems to be applied always in CFRC as connectors with high electrical conductivity [99] or in moulds for out-of-autoclave curing, which is always an time consuming step in the production of FRC [57].

Another possible application that has been studied is the use of GRM to improve composite lighting strike protection. There have been a number of recent publications on this topic [98, 100-102]. Wang and co-workers [100] fabricated a carbon fiber epoxy composite in which rGO had been added to the matrix resin and found that the surface conductivity of the FRC increased from 16 S/cm without the GRM to 440 S/cm on including the GRM. They showed that this led to an improvement in the lightning damage resistance compared with the unmodified CFRP. They pointed out, however, that further improvements in properties would be needed to match the performance of metal protection. The numbers mentioned above are still very far from the one of copper, which has a conductivity of around 6×10^5 S/cm, but also the disadvantage of undergoing corrosion and increasing the airplane weight. It is clear that the results obtained up to now indicate that use of GRM for such lightning strike protection in FRC are challenging, due to the high level of electrical conductivity required, but offer great potential if this issue can be resolved.

Table 3 summarizes the possible impact of GRM in the different industrial sectors discussed. An estimate of quantitative improvement required is also reported, for reference.

Table 3 Summary of possible impact of GRM in different sectors using FRC[1].

	Aerospace	Automotive	Wind turbines	Pipes	Indicative Target[2]
Structural reinforcement (tensile strength, Young modulus)	**	**	**	*	Depending on application
Fracture toughness (Compression After Impact strength)	****	**	***	*	CAI >330 MPa
Electrical conductivity (lightning strike)	****	*	****	*	$\sigma > 10^5$ S/m
Electrical conductivity (antistatic-dissipative)	*	*	*	***	$R_s < 10^9$ Ω/□
Thermal conductivity	***	***	*	*	Depending on application
Gas barrier	***	*	*	*	Water uptake ≤ 1.5% wt.
Multi-functionality	***	****	*	*	Electrical conductivity, Energy storage, damage sensing etc.
Flame resistance	***	***	**	**	FAR/CS 25.853[3] & ABD 0031 test passed ISO 3795/FMVSS 302[5] test passed UL94[6]: V0
Better/faster production (e.g. curing time)	****	***	**	**	Ideally, no autoclave required.

[1] Potential impact goes from *=incremental benefit up to ****=potential breakthrough.
[2] Requirements depend strongly on the target final applications. Most requirements refer to the most demanding application (aerospace).
[3] FAR: Federal Aviation Regulations; Certification Specifications and Acceptable Means of Compliance for Large Aeroplanes by the European Aviation Safety Agency: CS.
[4] Fire Test to Aircraft Material - Airbus Standard
[5] Federal Motor Vehicle Safety Standard No. 302
[6] Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances

3.3   Challenges for the use of FRC in the automotive industry

A remarkable growth of the presence of FRC in cars is expected in future years, driven principally by the need for a reduction of CO_2 emissions through reduction of weight. A timeline for the amounts of glass and carbon fibers used in the automotive sector over the past 70 years is reported in Figure 16, including some of the milestones of composites in automotive applications. It can be seen that the use of FRC in automotive dates back to the 1950s with the GFRC being employed in the bodies

of kit cars whereas CFRC have only started to be used in recent years, mainly in high-performance vehicles.
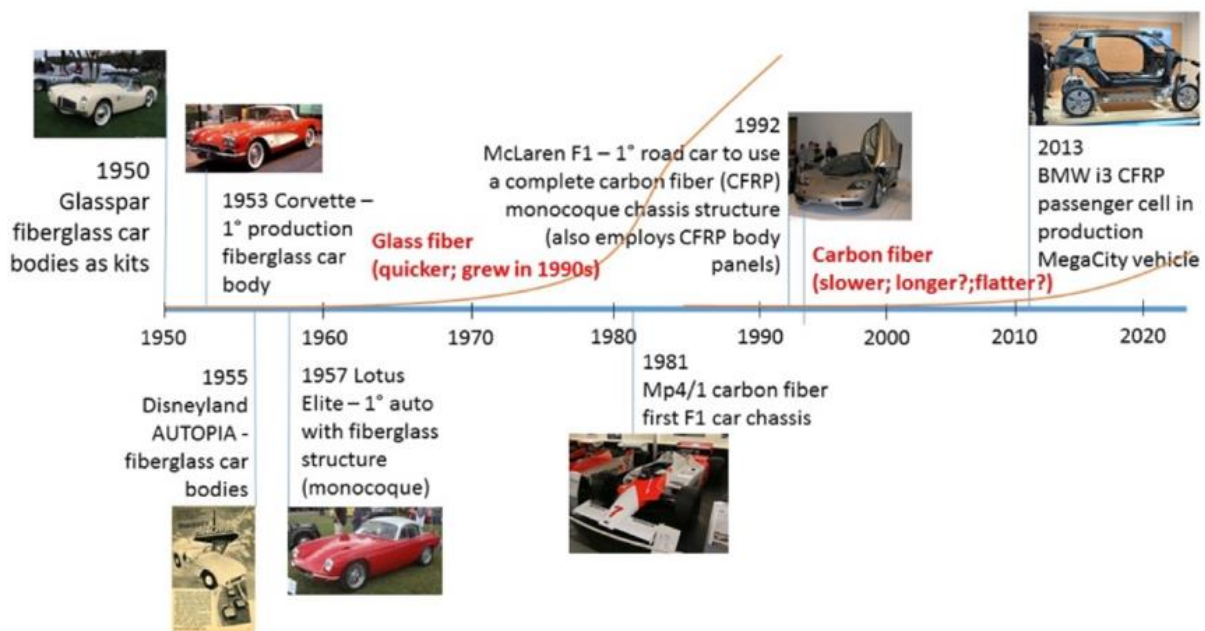

Figure 16. Evolution of glass fiber and carbon fiber use in the automotive sector and the main automotive applications [103].

In the near future, the European regulation on the CO_2 emissions will become more demanding, forcing car manufacturers to reduce the amount of materials used by reducing the thickness and modifying the shape of structural parts, whilst maintaining the same mechanical properties. The main efforts in this direction have been to replace metal structural parts with FRC materials. For example, the vehicle bumper beam and the anti-intrusion bar are two structural parts that could be replaced with FRC. Simulations have shown that such elements could be replaced without affecting impact energy absorption [104]. Moreover, glass or carbon fibers do not affect the recyclability of the final automotive components, as shown in recent work [105].

What hinders the use of FRC in the automotive sector being as widespread as in the aerospace sector is cost. The benefits of introducing FRC in the automotive sector are normally not sufficiently profitable and competitive with respect to the conventional materials. While it is challenging to reduce further the cost of CFRC, more properties and functionalities need to be added to existing FRC to increase their added value in the automotive sector. In particular, future vehicles will be equipped with an increasing number of sensors and devices that will be an integral part of complex features designed to satisfy demanding customer (especially in the Premium brands markets). *Piezo-resistivity* could be a key property that might represent the breakthrough point for CFRC. Moreover, piezo-resistivity will be a fundamental feature for allowing the structural health monitoring of FRC

which will increase the reliability of FRC components. Piezoresistivity could also be used to develop a new generation of Human interface devices (e.g. door handles, dashboard controls etc.).

3.4   Benefits of using GRM in the automotive Industry

The key properties of GRM currently more interesting for the Automotive sector are related to the electrical conductivity of hierarchic composites filled with graphene and related materials. The GRM are planned to be used with the objective of developing new smart automotive components based on polymeric materials with electrically conductive graphenes in order to integrate wirings and switches making them lighter and more environmental friendly (reduction of copper cabling and electronics). The introduction of smart devices (integrated wirings, sensors, switches) in the automotive sectors is expected to enhance the fuel saving and consequently the CO_2 emission at different levels; the number of electronic devices installed in car is continuously growing (more than 60 actuators and 80 sensors are today installed in some cars) and the energy request in the next years on board will increase exponentially (today the average request for power is 3 kW with 4-5 km of wires and 60 kg of weight) with related needs for integrated systems helping the weight reduction and environmental friendly systems.

The main focus is on vehicle interiors applications. Polymer and composite applications in the cars increased in the last decade to up to 13% the total weight of the car. Recently, a major car producer has announced large-scale application of GRM (non hierarchic) composites in car interiors to reduce noise inside its vehicles and increase performance under the hood[106].

Besides classical composites, panels and trims functionality can be improved by substituting metal electrical wirings, handles, knobs and touch pads with electrically conductive paths of GRM integrated directly into the polymer bulk materials. GRM have already been used to make innovative pressure sensors [107, 108] and highly conductive and flexible conductors, which can be embedded in polymers or textiles for electronics or internet-of-things applications.[99]

The possible advantages of using GRM the industrial process are:

1) Add new functionalities, as example piezoresistive properties in GFRC for sensing.

2) Improve recyclability of dashboard and internal components, through the elimination of electrical wires with CFRP, i.e. rear dashboard connections and switches [109].

3) Decrease costs of electronics by realizing conductive tracks, without adding any extra material to the component [110], hence decrease component weight by producing all-plastic components.

4) Tune mechanical properties of GFRC and CFRP, which can be settled according to the structural application, i.e. front-end complete system (which is made on GFRC).

5) Ensure compatibility with mass production lines.

6) Replacing metal wires as heating elements in the steering wheel heating system.

GRM can give advantages in structures for multifunctional and semi-structural components for: i) system weight reduction (up to 20%), ii) integration capabilities with reduced assembling costs (up to 15%), iii) expected decrease of cost staying within 2-3 €/kg saved and iv) compatibility with existing production processes lines.

Advanced racing vehicle technology (as example in Formula 1) is expected to be the spearhead for the GRM-doped FRCs to penetrate the automotive industry at the commercial product level, by introducing mass production multifunctional polymer-based parts with better thermal, impact, weight and flame resistance properties.

3.5   Use of FRC in other sectors: wind turbines, pipes and tanks

Wind turbines are one of the largest markets for FRC with a market penetration of 20%, used in blades and in nacelles [111]. FRC (either with glass or carbon fibers) are used to improve the mechanical properties in the most demanding region of the blade spar cap and edges of panels to achieve the fatigue, deflection and buckling specifications. To achieve this goal, an improvement in mechanical performance - particularly the fracture energy G_{Ic}, ultimate strength and fatigue response - is needed.

Fire represents the second major cause of accidents in wind turbines following lightning strike or blade failure. The combustion of wind turbines can trigger forest fires in many areas, leading to several tens of millions of euros of losses [112, 113]. Thus, flame retardancy is a key issue in this field (Table 3).

Market penetration of composites in pipes and tanks is smaller than in wind turbines, and represents only 3% of the global materials market for this sector. Pipes and tanks manufactured using the centrifugal casting and filament winding processes are primarily used in the oil/gas and chemical industries. There is also here a significant advantage in using FRC especially in buried pipes for water and waste water projects due to their better chemical resistance compared with metals. Improving FRC electrical conductivity (e.g. for antistatics) and flame resistance would, however, be needed to expand their potential applications and increase market penetration [114, 115].

Also in these applications GRM can give significant benefits. For example, we recently demonstrated how amine-functionalized graphene oxide (GO) using aminopropylsilane with low lateral size (D50 = 5 μm) is able to improve the mechanical performance of unsaturated polyester resin (UPR) E-glass fiber composites for wind turbines at low loadings (0.5 wt%) [116].

It has also been demonstrated that GRM can also improve the fire resistance of FRC [117]. Doping a CFRC with 0.5 wt% of graphene materials is able to reduce the peak of the Heat Release Rate (PHHR) by 30%. A 1 wt% loading is able to give rise to reduction of 45% in PHHR in a cone calorimeter test. [118, 119]

4   Examples of FRC-GRM in commercial products

Composite materials represent one of the most mature applications for GRM, with several products already commercially available. Nowadays it is possible to find numerous products for the sports and leisure market that contain GRM, for example: tennis rackets, skis, fishing rods, watches, shoes, hockey sticks, etc. (Figure 17). Here we give some representative, non-exhaustive examples of commercial products with FRC and GRM.

| SKIS | TENNIS RACKETS | PADEL RACKETS | BIKE WHEELS | FISHING RODS |
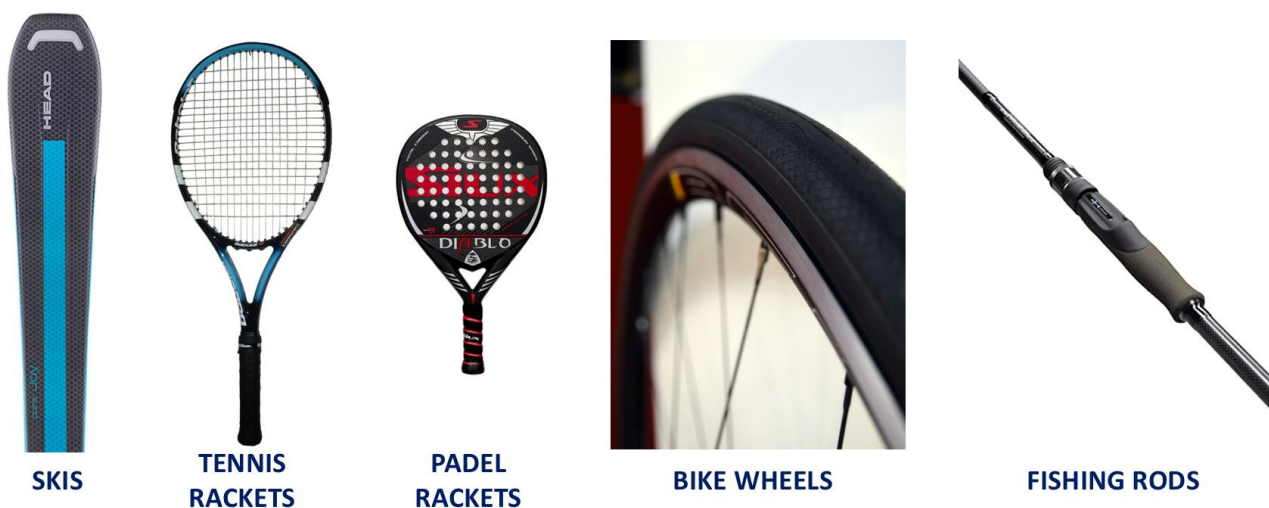
Figure 17. Some examples of commercial products using GRM in hierarchic composites.

Innovative materials are often introduced on the market as sporting goods before reaching strategic sectors such as aeronautical and automotive. The first commercial widespread application of GRM was in 2013, when HEAD launched a new tennis racquet series with GRM, which allow the weight redistribution in the racquet (up to 20% lighter) providing better manoeuvrability and increased swing weight. Thanks to the success obtained, in the following years Head commercialized new series of racquets, skis and snowboards reinforced with GRM,[120, 121] Padel rackets are also currently commercialized, with GRM claimed to provide more rigidity to the racket, better control over the ball, and resistance. [44, 122]

Vittoria Industries has developed a new class of cycling tyres and CFRC wheels with GRM. They claimed that GRM-enhanced composites show around 10~30% improvement in material properties.

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The addition of GRM into the cycle wheels has a great positive impact, reinforcing the brake track for increased safety and durability.[123] Also Dassi released the first cycle with a frame reinforced with GRM giving both a strength and weight benefit [124]. G-Rods International introduced the first GRM-based fishing rods on the market. Their patented graphene technology gives an enhancement of the fishing rods by generating 25% more strength, while reducing weight by 25% [125]. Ashland composites reported in 2016 the first industrial tanks of glass FRC with graphene, developed in collaboration with Avanzare [126, 127].

5   Conclusions

The use of nano-additives such as GRM in FRC is more challenging than in conventional, non-hierarchic composites such as in extruded plastics. This is due to the FRC complex hierarchic structure, different composition on different length scales, strongly anisotropic properties and presence of several different geometrical interfaces. CF, GRM and polymer matrices can be combined to achieve complex hierarchical structures featuring order on different scales: polymer chains (1-10 nm), GRM nanosheets (10-1000 nm) and mesoscopic glass or carbon fibers (1-1000 μm). The GRM nanosheets can be positioned in the polymer matrix, on the fiber surface, in the pre-peg or in between different FRC layers.

Notwithstanding this additional complexity in manufacturing, the first end-user product containing GRM ever mass-produced was a tennis racket made of FRC. Many other similar FRC-GRM products have been commercialized since then.

Besides applications already commercialised in sport tools, GRM could give massive breakthroughs in key industrial sectors such as aerospace and automotive, potentially allowing to overcome some of the major bottlenecks limiting FRC use. Some of the promising applications discussed are to improve impact strength and lightning strike, add flame retardancy or improve thermal conductivity. A challenging but potentially disruptive breakthrough would be to use the complexity of the hierarchical architectures to enable new functionalities, as example to exploit the hierarchic structure of FRC components to store energy, as batteries, or to sense deformation, pressure, etc. This would foster the diffusion of the internet-of-things (IOT) applications also find important uses in the aerospace or automotive sectors.

6   References

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