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All-carbon multi-scale and hierarchical fibers and related structural composites: A review

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ABSTRACT

Recent advancements in the preparation of all-carbon multi-scale fibers and their use in carbon fiber (CF)reinforced polymer composites are reviewed. A multi-scale or hierarchical structure is the result of a combination of micro-scaled fibers and nano-scaled fillers which are in intimate contact by physical or chemical interactions. Carbonaceous nanofillers, such as carbon black, carbon nanotubes and nanofibers, graphene and its oxidized derivatives, can be deposited on CFs by different strategies. In particular, preformed nanoparticles (indirect methods) or in situ prepared nanoparticles (direct methods) can be used. Multi-scale structuring of the interlaminar region via various deposition techniques is also discussed. An overview of multi-scale fibers and multiscale structured interlaminar layers to improve the load transfer between the matrix (namely thermoset-, thermoplastic- and carbon-based) and the reinforcing (CFs) phase is considered for this review. Moreover, their use to add new functionalities (electric conductivities, sensing, thermal conductivities) to structural composites is also reviewed. Finally, the recent efforts in modeling the mechanical behavior of the interphase and interlaminar regions of all-carbon composites with multi-scale fibers are discussed, along with some notes on future challenges.

1. Introduction

Composites are defined as materials consisting of two or more distinct phases with a well recognizable interphase between them. The matrix is responsible for the spatial positioning of the fibers and for their protection against environment attacks. Fibers are inherently stronger than bulk materials because the probability of critical defects decreases with dimension (volume). The stiffness and strength of the reinforcing fibers, including carbon (CF), are prominently higher than those of polymeric matrices. The matrix transfers the load to the fibers and distributes the stress among the fibers. Prerequisite for an efficient shear transfer under load is therefore the presence of a proper fiber/matrix bonding [1]. The term interphase, meaning a finite interlayer between the fiber and matrix with distinct physico-chemical properties, was introduced in the 1970s [2]. The load transfer capability of the interphase depends on the fiber/matrix adhesion which can be physico-chemical, frictional, or both, in nature [3]. Physico-chemical contributions include chemical bonds, intermolecular interactions,

surface-induced crystallization, phase separation phenomenon, etc. In polymer-based composites, physico-chemical contributions are generally assumed to be more important than the frictional ones. Nevertheless, roughening of the fiber surface and amplification of the difference between the thermal expansion coefficients of fiber and matrix turned out to favor the stress transfer [4]. In most cases, both chemical and frictional components are operative, like in the case of multi-scale fibers and related composites. The term "multi-scale" suggests the presence of a structure arranged in a multiscale morphology spanning over different length scales. In fact, in case of multi-scale all-carbon fibers the surface of the micro-scaled CFs (typical diameter \sim 7 µm) is covered by nano-scaled carbonaceous nanoparticles, such as carbon black, carbon nanotube (CNT), carbon nanofiber (CNF), graphene (GR) and its derivatives, aerogel, etc. Such reinforcements, also termed "hierarchical", "hybrid" or "fuzzy", have pronounced analogies with nature-based multi-scale structures (plant cell walls, skeletons, etc.) where the structure - even if composed of fairly "weak" constituents in multiple length scales – is perfectly "engineered" to fit with the dominant loading situation [5]. Another type of multi-scale fibers are assembled by

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Nomenclature			ICVD	injection chemical vapor deposition
			IFSS	interfacial shear strength
	2D	two-dimensional	ILSS	interlaminar shear strength
	3D	three-dimensional	IPN	interpenetrating networks
	AFM	atomic force microscopy	K-PSMA	potassium-polystyrene-alt-maleic anhydride
	C/C	carbon/carbon	LCP	liquid crystalline polymer
	CF	carbon fiber	MD	molecular dynamics
	CFRP	carbon fiber reinforced polymer	MWCNT	multi-walled carbon nanotube
	CNF	carbon nanofiber	PAN	polyacrylonitrile
	CNT	carbon nanotube	PANI	polyaniline
	CCVD	catalytic chemical vapor deposition	PEI	polyetherimide
	CVD	chemical vapor deposition	PEIm	polyethyleneimine
	CVI	chemical vapor infiltration	PET	polyethylene terephthalate
	DC	direct-current	PMMA	poly(methyl methacrylate)
	DICVD	double-injection chemical vapor deposition	PP	polypropylene
	DMF	dimethylformamide	PSU	polysulfone
	DWCNT	double-walled carbon nanotube	PyC	pyrolytic carbon
	EP	epoxy resin	RCVI	rapid chemical vapor infiltration
	EPD	electrophoretic deposition	RIPS	reaction-induced phase separation
	ESD	electrostatic deposition	RVE	representative volume element
	$V_{\rm f}$	fiber volume fraction	semi-IPN	semi-interpenetrating networks
	FDM	fused deposition modeling	SBS	short beam shear
	FE	finite element	SEM	scanning electron microscopy
	FT-IR	Fourier-transform infrared spectroscopy	SFFT	single fiber fragmentation test
	G _{IC}	critical value of the strain energy release rate under mode I	SHM	structural health monitoring
	GF	glass fiber	SWCNT	single-walled carbon nanotube
	GNP	graphite nanoplatelet	TEM	transmission electron microscopy
	GO	graphene oxide	ToF-SIMS	time-of-flight secondary ion mass spectroscopy
	GR	graphene	UD	unidirectional
	GSD	graphitic structures by design	UP	unsatured polyester resin
	HATU	hexafluorophosphate azabenzotriazole tetramethyl	VE	vinyl ester resin
		uranium	XPS	X-ray photoelectron spectroscopy

Moreover, the use of multi-scale fibers in composite systems may yield additional functional properties, such as mechanical damping, sensing, self-healing, shape memory, morphing [5,17–19].

combining individual units of CNT or graphene. Such fibers, if free of defects and sufficiently long and highly aligned, are expected to generate extreme mechanical and transport properties as well as to possess multifunctional properties for applications in energy harvesting, capacitors or flexible batteries etc [6-15]. However, since this field is still under development and in order to limit the length of this review, such fibers and relative composites are not included.

Depositing carbonaceous nanofillers on CF is an effective method to enhance the fiber surface area thereby supporting the mechanical interlocking (the filler acts as "interlocking agent"). Moreover, gradientlike or local stiffening of the interphase allows a smooth stress transfer and helps to avoid stress concentrations which are the usual sources of premature failure. It has to be underlined that the nanoparticles' dimensions in the nanometric range are fully compatible with the highly packed structure of advanced composites containing high volume fractions of reinforcing fibers. Note that the interphase is a key factor in composite performances both under transverse tensile and in-plane shear loads. In fact, the dominant failure modes in off-axis loaded fiber-reinforced polymers are debonding between fiber and matrix and delamination within (intralaminar) or between (interlaminar) the plies [16]. Accordingly, major benefits of using hierarchical fibers in polymer composites is to improve the matrix-controlled properties, notably the interfacial shear strength (IFSS), transverse tensile strength, the resistance to intra- and interlaminar failures. Another possible benefit is the improvement of the through-thickness properties of advanced composites (composed of plies with unidirectional aligned endless fibers) without compromising the in-plane performance. It is noteworthy that the action traditionally implemented to improve the through-thickness properties (interleaving, z-pinning, stitching, braiding ...) are generally accompanied by a prominent reduction of the in-plane properties.

Though some review papers covering also multi-scale fibers and related composites already appeared [5,17,18,20], none of them focused specifically on all-carbon systems. An additional motivation for the relevance of this topic is given by the ongoing efforts to recover CFs from composite wastes via pyrolysis. This thermal recycling method often generates all-carbon multi-scale fibers. A further aim of this review is to introduce a new classification in order to better distinguish between the various preparation methods of multi-scale fibers. Though the modification of matrices with nanofillers is widely used to improve matrix-dominated properties, this subject is not covered by this review. The same note holds also for multi-scale fibers with the same (e.g. cellulose/nanocellulose) or hybrid constituents (e.g. glass fiber/carbon allotrope). Instead, recent advances in the interphase/interlaminar engineering of all-carbon multi-scale fibers and related composites are addressed. The survey covers also carbon-carbon composites involving multi-scale all-carbon fibers.

2. Multi-scale fibers

Ensuring the stress transfer from matrix to fibers is a crucial role for the interphase. Nanofillers deposited on microscopic fibers can positively contribute in several ways, i.e. by roughening the fiber surface, reducing the stress transfer length (i.e. reduction of the critical aspect ratio of the fiber), and stress redistribution via stress field homogenization (i.e. diminishing stress concentration effects). In fact, stress field homogenization seems to be the main synergism observed in composites with micro- and nano-fillers [21]. Moreover, surface roughening is

beneficial not only for improving the frictional component of adhesion, but also for promoting additional toughening mechanisms. In fact, owing to the presence of nanofiller particles acting as local obstacles, a crack travelling at the interphase is forced to follow a zig-zag route (see Fig. 1).

The use of multi-scale fibers can also offer opportunities to obtain (multi)functional materials. It was recognized that some functionalities could be achieved through straightforward modification of the interphase region. For example, if failure starts in the interphase, then its detection, and possible healing, should also be targeted. Research activities in this field were recently reviewed by Sharma et al. [17] and Karger-Kocsis et al. [18].

2.1. Preparation

To provide a comprehensive overview on the various methods explored for the preparation of multi-scale all-carbon fibers the authors find it convenient to divide the approaches in i) "indirect methods" in which previously formed carbonaceous nanofillers are deposited on the CF surface and ii) "direct methods" in which carbonaceous nanofillers are produced in situ. One would surmise that in the "indirectly" prepared multi-scale fibers only physical interactions exist between the CF and nanofillers, which is, however, not always the case. In fact, to achieve a better anchorage, grafting procedures between the CF and nanoparticles have been developed.

2.1.1. Indirect methods

2.1.1.1. Sizing. All reinforcing fibers used for manufacturing polymer composites are surface treated and/or coated, usually during their production steps. This kind of coating is usually referred as "sizing". Sizing is commonly applied also on CFs. During their production, CFs may be subjected, however, to various surface treatments in order to remove the weak outer layer and introduce oxygen containing functional groups for a better adhesion [1,22]. To generate the functional groups, CFs are electrolytically oxidized in a bath during production. After this anodic oxidation a polymeric sizing is applied to support handling and promote adhesion to the intended polymer matrix [23]. It is intuitive that the most straightforward method for creation a multi-scale fiber is to incorporate the nanoparticles directly in the sizing formulation. The nanoparticles exhibit high aspect ratios having fibrous (needle, 1D) or platelet-like (disk, 2D) shapes. As 1D nanoparticles, carbon nanotubes (CNT) have been used in sizing formulation in various forms, such as single (SWCNT), double (DWCNT) and multi-walled (MWCNT) in oxidized or other functionalized forms [24,25]. As 2D particles, graphene derivatives (generally graphene oxide, GO [26,27]), are preferred in the sizing formulations. Oxidation of the carbon nanoparticles is adopted to promote their dispersion in the sizing bath. An aqueous dispersion is used when silane coupling agent [24,28] and/or aqueous emulsion of the film former (e.g. epoxy- [26], phenoxy-based [29]) are applied. However, when a polymer, such as polyetherimide (PEI), is used as adhesion promoter, the sizing must be deposited



Fig. 1. Schematic of crack bifurcation, deflection mechanisms owing to multiscale all-carbon fibers.

through a proper solvent [27]. Qin et al. [30] used N-methylpyrrolidone (NMP) as solvent for EP-sizing of an UV-ozone pretreated CF. In the sizing solution, exfoliated graphene (GR) nanoplatelets were dispersed by ultrasonication. It is worthwhile to note that the nanofillers are mostly physically adsorbed in the interphase through weak chemical interactions, such as hydrogen bonding.

2.1.1.2. Coating. The simplest way to deposit carbonaceous nanoparticles onto CF is to dip them in a suspension of nanoparticles, or paint the suspension on the CF surface. As suspension media for functionalized CNTs bearing hydroxyl and carboxyl groups, water [31,32], ethanol [33, 34] and acetone [35] are preferred because of their good dispersion ability and easy evaporation upon drying. For GO, usually water [36-38] is selected as suspension medium since the functional groups typically present on the GO surface (hydroxyl, carboxyl, carbonyl and epoxy) can help its easy and fine dispersion. Nonetheless, acetone was also used for GO produced from oxidized expanded graphite [39]. Sonication has been proved to be the right tool to avoid sedimentation and to promote the dispersion of the nanoparticles, sometimes, however, surfactants were additionally applied. Though this is not always explicitly mentioned, the use of ionic surfactants and a proper control of the pH of the aqueous dispersions may facilitate the electrostatic deposition (ESD) of the nanoparticles on the CF surface. Such treatments offered various improvements in different scale depending on the conditions.

Sizing and additional coating with carbon nanoparticles can be combined, and performed even in continuous processes. This possibility was demonstrated by Kamae and Drzal [40] who have shown that MWCNT treated with cationic polymers can be uniformly deposited by ESD on surface oxidized CF having a negative charge followed by a suitable sizing. Between the cationic charged MWCNT particles repulsive forces are acting, whereas between the CF and the MWCNT attractive forces are operative, thus resulting in good dispersion and adhesion. Very high IFSS values (81 MPa) were reached when polyethyleneimine (PEIm) was selected as cationic surfactant. In fact, PEIm was co-reactive with both the sizing and matrix, in this case an epoxy resin (EP). Somewhat similar approach was followed by Yanli [41] using GO nanoparticles dispersed in the coating. This gave, according to the author, a significant ~100% improvement in IFSS of poly(methyl methacrylate) (PMMA) reinforced with carbon fibers.

Infiltration of two-dimensional (2D) or three-dimensional (3D) reinforcing fabrics by infusion with resins containing the dispersed nanoparticles was often unsuccessful because the particles were filtered off. This was the incentive for changing the strategy from bulk toward interphase modification with nanoparticles. A possible way to overcome filtering phenomena is to apply the bulk-modified resin by hand lay-up processes. This is, straightforward when additional effects, such as electrical conductivity, are targeted. Cheng et al. [42] developed a method to disperse GO together with conductive polyaniline (PANI) in unidirectional (UD) CF-fabric reinforced EP composites thereby increasing by more than 100 times their conductivity in alternate current. A bulk/interphase modification strategy was followed also by Bismarck and co-workers [43]. The authors coated CF via a special wet powder coating technique. The powder itself was an EP resin containing a latent curing agent and MWCNT (up to ~6 vol%). The coating compound was prepared by extrusion compounding, thereby avoiding the curing of the EP, followed by pulverization. It was found that the mean particle size of the powder in the slurry strongly affected the impregnation of the CF tow.

2.1.1.3. Spraying. Spraying using different air-brushes under various processing conditions is also a fairly simple technique to generate multi-scale fibers (see Fig. 2). The dispersing media of the (oxidized) carbon nanoparticles are alcohols, and the dispersion is usually promoted by sonication. Methyl alcohol was used for the dispersion of MWCNT [44,



Fig. 2. Schemes of some common indirect methods of producing multi-scale all-carbon fibers by a) immersion deposition, b) electrophoretic deposition and c) spray deposition.

45], ethyl alcohol for oxidized MWCNT [46,47], isopropyl alcohol for GR [48] and water for oxidized MWCNT [49] prior to spraying on the CF reinforcement or prepreg layers, the latter of which gave doubling and tripling of electrical conductivity level on in-plane and out-of-plane respectively at just 1 wt% MWCNT content. An advanced method in this field is represented by the electro-spraying (electro-hydrodynamic atomization) which produces a fine aerosol from the nanoparticle-containing suspensions which can be directed onto a target CF (neat or prepreg) applying a high-voltage electric field. Upon leaving the spray nozzle, the positively charged drops are broken into smaller droplets due to electrostatic repulsion. While travelling toward the grounded target the droplets become smaller and smaller, the solvent evaporates, and the charged nanoparticles deposit on the substrate without agglomeration. This electrospray deposition is more efficient than the traditional spraying. It was adapted by Li et al. [50] to create multi-scale CF fibers using a mixed solvent composed of N, N-dimethylformamide (DMF), tetrahydrofuran and a surfactant.

In the above examples the multi-scale structures were stabilized by physical interactions. However, physico-chemical interactions can also be triggered. Yao et al. [51] grafted MWCNTs with poly (styrene-co-maleic anhydride) or poly(glycidyl methacrylate) via radical polymerization, suspended in ethyl alcohol. The grafted nanotubes were then spray coated on a CF fabric. Another possibility is to graft the carbon nanoparticle or carbon precursor directly onto the CF surface. Lavagna et al. [52] deposited oxidized MWCNT from an acetone dispersion onto oxidized CF, evaporated the solvent, and subjected this agglomerate to thermal treatment (200 °C for 5 h) thus promoting chemical reaction. According to the method of Lee et al. [53], CNT-grafted CFs were produced by using a spray solution of dimethylformamide (DMF) containing functionalized MWCNT and polyacrylonitrile (PAN). Desized CF fabric was spray-coated by this solution and the grafting of CNTs occurred by the thermal stabilization process of PAN in a furnace at 300 °C for 3 h.

One interesting study was recently performed by Vázquez-Moreno et al. [54] in which the spraying of carbon nanoparticles (CNT or graphene dispersed in ethanol) was done on carbon fiber and the properties of the obtained composites were compared with those of composites fabricated by traditional mixing process using exactly the same nanofiller and concentration. In both cases the composites were produced by vacuum-assisted resin infusion molding (VARIM). The author claimed that the mixing method presented the limitation of increasing the viscosity of the resin which hence caused problems during the infusion stage, whereas the spraying process produced agglomeration on the fiber surface. Although the reported tensile properties of the 90° laminates with respect to fiber direction had limited variations (max. 8% of tensile strength improvement in case of CNT sprayed on CF), shear modulus increased by 20% in the case of fiber orientation of $\pm 45^{\circ}$. Moreover, 15% of improvement in ILSS was claimed due to the larger contact area between the carbon fiber and the matrix when carbon nanotubes were used as a reinforcement. The variation in each property had significant effect by the type of reinforcement as well as the concentration used.

2.1.1.4. Electrostatic and electrophoretic deposition. Immersion coating and spaying techniques generally did not yield a uniform and homogeneous distribution of the nanofillers on the CF surfaces. Though some improvements were reached with sonication, still a homogeneous sizing dispersion remains a challenge. To overcome this problem, electrostatic deposition (ESD) and electrophoretic deposition (EPD) methods were investigated (see Fig. 2). ESD differs from EPD due to the fact that in the latter the required electrical charging of the reinforcement is achieved by coupling to an electrode (cathode, anode) the potential of which depends on the charge of the corresponding nanofillers. As a consequence, in contrast to ESD, the ionic movement in EPD is forced. In these deposition processes, charged particles are deposited on the CF having opposite electrical charges. Attractive forces between positively charged nanoparticles and negatively charged reinforcing materials (or vice versa), were exploited to obtain a homogeneous deposition of nanofillers. Anionic CF can be easily obtained via suitable oxidation treatments. On the other hand, nanofillers, such as CNT, can be rendered cationic using cationic polymers as polyelectrolytes. This concept was investigated by Drzal and coworkers [40].

Unlike ESD, EPD has received more attention for nanofiller deposition on the surfaces of CF reinforcements. Similar to ESD, the electrical charge of the nanofillers is achieved by functionalization. For this purpose, CNT, CNF and GR derivatives are generally oxidized to generate carboxyl and hydroxyl groups on their surfaces. It is noteworthy that the purification processes, used to eliminate amorphous carbon and catalytic residues in CNTs and CNFs, are oxidative ones and the related oxidized products are commercially available. In most research papers, oxidation of the carbonaceous nanoparticles occurred by wet chemistry in oxidative acidic media [55]. A more environmental friendly method compared to the acidic ones is represented by ozonolysis [56]. Prerequisite of a successful EPD is the preparation of a stable suspension of the particles in suitable solvents. Therefore, in both aqueous and non-aqueous EPD dispersions, various surfactants can be used. Exhaustive reviews on the EPD of CNTs and graphene-related materials were published by Boccaccini et al. [57] and Diba et al. [58], respectively. Jiang et al. [59] quoted that not only the EPD suspension but also the surface modification of the CF (in this case electrochemical oxidation of the CF prior to EPD) affect the efficiency of deposition of GO, with reported improvement in the ILSS by 60%. Similarly, Mei et al. [60] reached similar conclusions by using acidic treated CFs thus obtaining an enhancement in elastic modulus, strength and failure strain by around 70%, 34% and 21%, respectively. It is also noteworthy, that the original sizing of the CF has to be removed because it may act as an insulating layer during electrophoresis. For this task, washing in acetone or immersion in acidic solution are preferred. Sonication is performed to avoid the settling of nanofillers in the coating dispersions, to facilitate the penetration of the nanoparticles into the CF tow, and to reduce the bubbling induced by water electrolysis. It is, however, accompanied by other phenomena (e.g. change in the movement of the charged particles) which are topics of ongoing research. Interestingly, few reports are available on the systematic variation of the conditions of EPD, such as sonication, applied voltage, distance between the electrodes and the acidity of the bath [61,62]. EPD was successfully used to coat single CFs [63], CF tows [64-68] and CF fabrics [69-74] with functionalized CNT and GO nanoparticles. Even if carboxyl functionalization of the carbon nanoparticles were preferred, examples of amine-functionalization have been also reported [69,70]. For the EPD coating of CF tows, continuous deposition lines were realized [65,67,68,73]. The deposited carbon particles are physically adsorbed on the CF surface, eventually with some hydrogen bonding. In order to trigger their chemical coupling several approaches were followed. Wang et al. [66] subjected the CF on which GO was deposited via EPD to a thermal treatment at 150 °C for 1 h. This resulted in a chemical coupling of GO onto CF through ester linkages hence enhancing the IFSS significantly. Wang et al. [75] were capable to obtain a partial healing of the surface cracks on CF by electrochemical deposition of silver nanoparticles before starting the EPD with GO. This approach resulted in an improved tensile strength of the multi-scale CFs.

2.1.1.5. Chemical grafting. The possibility to anchor the nanofillers on the fiber surface by triggering suitable chemical reactions has been also explored. The possibility to have functionalized CNT to react with CF was already demonstrated in the section about spraying. This method was originally proposed by Laachachi et al. [76] who supposed that chemical grafting between the functionalized nanotubes and functionalized CFs occurs by esterification, anhydridation and amidization reactions. This method was adapted by Lavagna et al. [77]. The esterification reaction between CNT and CF can also be selectively triggered. Islam et al. [78] first prepared carboxyl functionalized CNT and CF by the traditional wet chemical oxidation using HNO₃ solution. Afterwards, the -COOH functional groups of the CF surface were converted into -OH groups by reduction with BH₃. Finally, the carboxyl functionalized CNT was grafted onto the hydroxyl functionalized CF via esterification. Another possibility is to attach the nanofillers onto CF via chemical linkages with and without additional coupling molecules or polymers. The above-mentioned processes are often termed as

"grafting". Liu et al. [79] used a DMF-based sizing solution which contained amine-functionalized MWCNT to coat the CF tows. MWCNT was first oxidized and its carboxyl groups reacted with an aromatic diamine thus forming amide linkages. The free amine groups of the grafted amine were foreseen to react with the EP thereby enhancing the adhesion between the matrix and the multi-scale fiber. The amide coupling between CF and GO was reached by Wang et al. [80] in an elegant way. CF was first oxidized to bear carboxyl groups. These groups were reacted with a long chain diamine (traditional used as a hardener of EP). The free terminal groups of the diamine served to couple with suitable reactive groups (carboxyl, epoxy) of the GO. In this reaction, a further coupling agent, i.e. hexafluorophosphate azabenzotriazole tetramethyl uranium (HATU) was used. By selecting different centrifuged GO fractions, the authors were able to graft the surface of the CF with GO in different patterns. In a follow-up work, CNTs were grafted onto CFs through a layer-by-layer deposition [81]. In this case the carboxylated CF was first reacted with melamine, then with carboxylated CNT under the action of HATU. Note that melamine coupled both functionalized CF and CNT via amide linkages. The free carboxyl groups of the first layer CNTs were subsequently reacted with melamine and then again with carboxylated CNT. Several layers of CNT could be grafted onto the CF surface by this layer-by-layer procedure. Luo et al. [82] prepared petal-like GO on the CF surface using epoxy-functionalized GO. Phenolic hydroxyl groups were first generated on the surface of CF which then reacted with hexachlorocyclotriphosphazene. Afterward, it was partly crosslinked and amine-capped by an aromatic diamine that served for the chemical bridging with epoxy-functionalized GO. Gao et al. [83] succeeded to produce multi-scale CF with both grafted GO and CNT. The chemical pathway in this case was as follows: carboxylated CF was reacted with thionyl chloride yielding -CO-Cl functionalities which were then reacted with ethylenediamine. The resulting amine-functionalized CF was then reacted with the thionyl functionalized GO and afterward with amine-functionalized CNT. The latter was produced in a way similar of that followed to obtain amine-functionalized CF. Surprisingly, the polyurethane chemistry, which is one of the most versatile ones, was not extensively explored so far. Ma et al. [84] grafted hexamethylene diisocyanate cyclic trimer onto the surface of GO or oxidized CF both bearing abundant -OH groups. Urethane coupling occurred between the residual -NCO groups of the cyclic trimer and the -OH groups of the GO or CF, respectively, resulting in GO-grafted multi-scale CF. The most important grafting reactions are summarized in Fig. 3.

2.1.1.6. Selective placement. A multi-scale structure at a nano-scale can also be achieved when the nanoparticles are selectively positioned by various different methods. These methods can be grouped into wet, dry and sacrificial methods, as described next. One will recognize that there is a clear analogy to the interleaving concept, however, using new materials. A simple way is to place the nanoparticles, dispersed in the matrix resins with or without additional solvent, or in a suitable dispersing medium (wet techniques), between the reinforcing layers by brushing, rolling, or other mechanical methods. This approach was adapted by Ma et al. [85] and Lee et al. [86] depositing CNF and silane-functionalized GO, respectively, in the interlaminar regions of structural composites. Marriam et al. [87] adapted the same method, however, only for CNT-modified EP. In the dry techniques free-standing assemblies of carbon nanoparticles in form of film, mats or webs are positioned in the interlaminar regions of composite laminates. Hamer et al. [88] used a MWCNT nanofibrils mat as an interleaf to enhance the resistance of CF/EP composites in mode I and mode II loading. Pan et al. [89] prepared an ultrathin (thickness 12 µm) CNT film by floating catalyst chemical vapor deposition (CVD), and placed it without and with subsequent epoxidation in different positions between UD CF/EP prepreg layers. Epoxidation of this CNT interleaf yielded to a better load transfer and increased the resistance to delamination. UD compacted CNT fibers positioned in the middle layer were used to enhance the



Fig. 3. Most common direct and indirect grafting reactions.

in-plane fracture behavior of laminates composed of UD CF/EP prepregs by Mikhalchan et al. [90]. Sun et al. [91] used electrostatic flocking of short pitch-based CF, graphite flake and vapor-grown CNF to improve the out-of-plane thermal conductivity of CF fabric-reinforced EP. Nanowebs, nanofiber assemblies (novel ultrathin interleafs), produced by electrospinning, proved to be suitable delamination suppressors in composites [92]. It is rather easy to disperse CNT or other nanoparticles in a polymer solution suitable for the electrospinning process. This method was followed by Eskizeybek et al. [93] who produced a carboxylic functionalized CNT-containing polyacrylonitrile (PAN) nanoweb and placed it in the interlaminar region of CF fabric/EP composites. Li et al. [94] elaborated an interesting approach to create a multifunctional interleaf via direct electrospinning of a non-woven mat on a UD CF/EP prepreg. In this case, polysulfone (PSU) served as polymeric carrier for the epoxidized MWCNT in the electrospinning solution. Note that polysulfones can be well dissolved in EP and yield a dispersed (below a given content) phase after reaction-induced phase separation

(RIPS) [95]. The dispersed thermoplastic phase acts as impact modifier (toughening agent) in EPs. The combined effect of MWCNT and PSU domains lead to enhanced stiffness, strength and toughness compared to the reference CF/EP composite. It has to be mentioned that, using epoxidized MWCNT, a direct chemical reaction between the amine hardener of the EP and MWCNT can be promoted and thus chemical interactions were also involved. The work of Zhang et al. [96] moves along the same direction and may be termed as sacrificial placement (see Fig. 4). The authors used an EP dissolvable thermoplastic (phenoxy) interleaf for the localization of CNTs. Thin phenoxy interleaves (30 µm in thickness) with 1 wt% MWCNT contents were prepared by both solution casting and hot pressing and positioned in the mid plies of CF fabric/EP composites. Phenoxy, being enriched in the interphase, underwent phase inversion and became the continuous phase locally in the EP matrix. The properties of the resulting CNT structure were exploited for damage sensing, measuring the volumetric electrical resistance, under mode I loading.



Fig. 4. Scheme of "sacrificial" interleaving with a EP soluble CNT-containing thermoplastic polymer.

Damage sensing/location and self-healing are hot topics in the field of advanced laminate composites, including thermoplastic-based ones. Joo et al. [97] demonstrated that addressable conducting network (ACN) is a promising method for damage sensing of polypropylene (PP)-based composites. This technique utilizes as sensor an electrically conductive network embedded in the composite itself. Structural delamination or matrix cracking can be evaluated through resistance changes induced by the interruption of the through-thickness electric current flow. Metallic line electrodes were arranged in a grid pattern on the top and bottom of the composite laminate and served to detect the change in the resistivity. To set the required through-thickness electric conductivity, carbonaceous fillers may be dispersed in the matrix or placed between the UD-CF laminae. It is noteworthy that composites containing both traditional fibrous and nanoscale reinforcements are referred to as multi-scale, multiscale or fuzzy composites. The beauty of this ACN approach is that it may work also for self-healing of the related composites triggered by resistive heating. It was shown that damage sensing was possible with high accuracy and the self-healing efficiency, measured in flexural tests, was as high as 96% [97]. It is worth mentioning that sensing via aligned CNT sheets [98] or SWCNT-coated single fibers different from CF [99], embedded in the interlaminar region of glass fiber fabric/EP composites, also worked properly. A further novelty in sacrificial placing of carbonaceous nanoparticles is given by the possible variants of the manufacturing methods. Fused deposition modeling (FDM) is suitable for such task since the fillers can well be incorporated into polymer filament and various resins dissolvable polymers may be selected as "matrix carriers". There are some further benefits in this technique: i) the orientation of anisometric particles can be obtained upon fused deposition of a filament in which they were already aligned, ii) semi-interpenetrating networks (semi-IPN) in which both thermoplastic and thermoset phases are continuous can be created thereby bypassing the thermodynamics governing the RIPS process from blends, and iii) the locally enriched thermoplastic phase may work for self-healing, and even for shape memory performance. All these aspects, explicitly or implicitly, were recently summarized in a concept paper [100].

2.1.2. Direct methods

The creation of multi-scale fibers by directly growing CNTs, CNFs and GR or GR-derived nanofillers onto the fiber surface has many benefits. The advantages include the enhancement of the fiber surface area, the possibility of mechanical interlocking, capillary sorption of the liquid matrix, and local reinforcement of the interphase. All the aforementioned aspects contribute to a better stress transfer from the matrix to the fibers. As emphasized before, major goal of composites containing multi-scale fibers is the improvement of the out-of-plane (transverse) properties without sacrificing the in-plane ones. Radially grown CNTs, CNFs or GR with a suitable length and surface coverage may work for transverse reinforcement, with effects on both inter- and intra-laminar properties.

CVD growth of nanotubes, nanofibers, and nanowires can be considered as a development of the whiskerization process developed from the mid-1970s [101]. Instead of generating silicon carbide or nitride single crystals at high temperatures (1300°-1800 °C), CVD results in nanoscale fibrous structures at much lower temperatures (600-800 °C). For in situ growing of carbon nanoparticles catalytic and thermal (pyrolytic) CVD processes are used. A catalytic CVD (CCVD) process is typically based on the following two steps: i) coating of the fibers (in strand or fabrics) with a proper catalyst, and ii) growth of the nanotubes or nanofibers on the fiber surface in a reactor using various hydrocarbon sources. CCVD employs usually nanoscale metal particles as catalysts. They can be produced separately from the CVD process or in situ. The growth mechanism is that carbon diffuses into the metallic particles and segregates from them at specific orientation on the CF surface forming CNT or CNF. Depending on the adhesion between the catalyst particles and CF, the particles either remain at the CF surface or move with the tip

of the growing carbonaceous nanostructure [102]. The resulting morphology of the grown carbon may be very different [101]. Selection of a suitable metal catalysts and its homogenous deposition at a nanoscale are challenging tasks. Ni and Fe are the preferred catalysts but many other transition metals have been tried alone or in combination. Ni (III)- [103-107], Fe(III)- [108,109] and Co(II,III)-salts (nitrates, sulphates, chlorides) alone (monometallic) or in combinations (bimetallic catalysts [110,111]) are usually applied onto CF surface from aqueous solutions prior to reduce them by hydrogen or wet chemical methods. The catalyst deposition prominently affects the growth, therefore research efforts have been focused on its optimization as demonstrated by the example of wet Ni-coating [102,112]. Before CVD, the sizing is generally removed from CF by different methods, even if the possible effects of a sizing have been recently investigated [113]. The catalyst can be deposited onto the CF surface also by techniques different from wet chemistry. Thostenson et al. [114] created a Fe-catalyst layer by magnetron sputtering, Kim et al. [115] adopted electron beam evaporation. Felisberto et al. [116] deposited Ni particles by dual direct-current (DC) sputtering in Ar atmosphere. It was, however, early noticed that the tensile strength of the CF was reduced owing to the CVD treatment. The reduction varied between 10% and 33%. This negative effect was attributed to the penetration of the catalysts in the CF, to the catalyst induced erosion of the CF surface with the reactive gases [113], and to morphological damages in CFs induced by the high temperature of the CVD process. In a systematic study, De Greef et al. [111] demonstrated that the temperature of the CVD process was a key factor which negatively affected the tensile strength of CF. Low CNT growth temperatures (of about 500 °C) did not cause degradation of the tensile strength of the individual CFs. Researchers explored several possibilities to overcome the abovementioned problems, such as optimization of the CVD process parameters [117] and creation of a buffer (heat shielding) layer between CF and CVD grown particles to protect the CF substrate. In the work of An et al. [117], the protective layer was constituted by Al₂O₃ (obtained via reduction of aluminum nitrate followed by oxidation) while Pozegic et al. [118] deposited a 35 nm thin Al film onto the CF surface through DC magnetron sputtering (the same technique was used for generation of Fe catalysts). A peculiar multilayer structure, composed of SiC, SiO₂ and Al₂O₃, was prepared on the CF surface by Kim et al. [115] followed by deposition of the Fe catalyst by electron beam sputtering. Tehrani et al. [119] covered CF by a 75 nm thick SiO₂ layer before placing a 2 nm Ni catalyst layer using magnetron sputtering for both layers.

The catalyst deposition and CNT (or CNF) growth steps may be, however, merged. In the so-called injection CVD (ICVD) process, the deposition of a catalyst containing solution (precursor generally ferrocene) and pyrolysis of the hydrocarbon source take place simultaneously. This technique was explored in several works [22,120-122]. In order to reduce the thermal degradation of the grafted CF during CCVD, Pozegic et al. [118] developed a photothermal CVD process in which only the top of the fibers was subjected to higher temperatures due to radiation heat. In the flame growth process, CNTs can be in-situ generated on the CFs at low temperatures (~450 °C) [123,124]. To grow the CNTs, the CF fabric wetted with NiCl₂ catalyst precursor was mounted on a metal frame of woven mesh structure and then put into the flame of burning ethanol at \sim 25 mm distance. Due to the heat sink effect of the metal frame, the detected temperatures were in the range of 450–520 °C. Note that this temperature range is much lower than the usual temperature required for CCVD. It is worthwhile to mention that uncatalyzed thermal CVD processes, requiring thermal treatments up to 1000 °C, were also attempted to create multi-scale fibers. In this case, no oriented growth of the carbon deposit could be achieved. Instead, carbon black or graphene-like structure could be resolved on the surfaces of the grafted CFs [125,126].

Though CVD is a very promising approach for interphase engineering, there are several challenges with the catalytic CVD processes. The growth temperature of the CNTs is quite high and thus it should be reduced in order to minimize fiber damage. Several attempts were already made to reduce the CVD temperature. Some of the catalysts and carbon sources (especially in ICVD) are toxic and thus should be replaced. The interaction of the CF with the catalysts (dissolution, eutectic formation) under the CNT growth conditions should be better understood. Moreover, in practically all works introduced above, the production of multi-scale all-carbon reinforcements occurred in batch (discontinuous) CVD processes which are not suitable for an industrial scale-up.

A novel method has been recently introduced by Zheng et al. [127] who developed a scalable route for the manufacturing of multi-scale CFs using the CVD technique. The production process (see Fig. 5) involved the followings steps: i) desizing of the CF by heat treatment, ii) electrochemical anodic oxidation of the CF, iii) deposition of the catalyst (Co) by wet treatment, iv) pulling the CF through to an open-ended CVD furnace. The process was operated at 450 °C in order to first reduce Co (II) to Co with the help of hydrogen (residence time 5 min), before rising the temperature in the furnace to 600–750 °C and introducing a carbon source (H₂/C₂H₂). The residence time for CNT growth was varied in the experiments between 3 and 20 min. Note that the duration of the CVD treatment may be even longer. Microdebonding test evidenced an enhancement of IFSS by approximately 84%.

A breakthrough in this field for high-yield growth of aligned CNTs on aerospace-grade carbon fibers (CFs) was recently proposed by Li et al. [128]. The proposed method for CNT growth is based on non-covalent functionalization of CF and low-temperature. Unsized CFs were dip-coated in 0.25 wt% potassium-polystyrene-alt-maleic anhydride (K-PSMA) solution for 5 min, spread over smooth rollers to remove excess liquid, and dried in a vacuum heating chamber at ~ 80 °C. A catalyst solution of 0.05 M Fe(NO3)3.9H2O in isopropanol was mixed and stirred for 1 h to develop iron oxide particles in solution. Fe^{3+/}K-PSMA coated tows were inserted into a fused quartz tube. Argon was first flushed into the tube for 2 min before flowing H₂ and Ar. Iron catalysts were then reduced during temperature ramp (50 C/min) to 480 C before growth was started by switching off H₂/Ar, and flowing CO₂/10% C₂H₂ in Ar. This development circumvents the drastic in-plane strength reductions, which have limited the full potential for multi-scale composite integration into structural composites.

2.2. Characterization

A plethora of physical and chemical methods have been used to assess and quantify the surface characteristics of the all-carbon multiscale fibers. Among the microscopic techniques, scanning electron microscopy (SEM), scanning transmission electron microscopy (TEM) [129] and atomic force microscopy (AFM), along with their various versions, are preferentially used to demonstrate the presence of multiscale morphology. Electron microscopes, equipped with energy dispersive X-ray analysis (EDS or EDAX), enable the detection of foreign elements due to the production of CF or its coating/grafting. AFM proved to be the right tool to quantify the surface topography (roughness) of multi-scale CFs [23].

AFM offers, however, further possibilities. It may be used to estimate the thickness of the interphase (phase constrast, peak force quantitative nano-mechanics [23]), and even to measure directly the adhesion level between individual CNT and CF. He et al. [130] have shown these possibilities using a nanomanipulator equipped AFM with a highly sensitive load cell. The CNT was grafted onto the CF surface by amidation reaction. The pull-out of the CNT from the CF surface occurred in the chamber of a SEM allowing to visualize the full process. Adhesion bonding between the CNT and the tip of the instrumented AFM cantilever was achieved by using in situ polymerization of a glue through electron beam. The authors measured 5–90 MPa grafting strength values which were attributed to van der Waal's forces and chemical bonding. Nanoindentation tests are also suitable to detect the interphase in all-carbon multi-scale polymer composites [131].

X-ray photoelectron spectroscopy (XPS) is a very powerful surface chemical analysis. In fact, the functional surface groups on CF or on carbon nanoparticles can be determined by fitting the narrow band C1s spectra by convolution lines representing the chemical shift owing to oxygen-containing groups [23,132,133]. In case of chemical anchorage of carbon nanoparticles to CF via molecular bridging, Fourier-transform infrared spectroscopy (FT-IR) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) may deliver further insights. Major benefit of ToF-SIMS over FTIR and XPS is that they concurrently provide information at a molecular level and not only hints on the chemical environment.

For crystalline carbonaceous materials, Raman spectroscopy can provide precious information. In fact, the Raman shifts and their changes may inform us about alterations in the sp^2/sp^3 hybridization, wall structuring in CNTs, etc. The strain-sensitivity of a suitable Raman band of CF and CNT may serve for mapping the interfacial shear transfer in model composites [134].

Surface thermodynamics [132] of multi-scale CFs and their assemblies are of great relevance with respect to their wettability by the polymer matrix. This is assessed in static and dynamic contact angle measurements (sessile drop and Wilhelmy plate techniques). The Wilhelmy balance may be used to assess the wettability of both single fibers [135] and fiber bundles [136]. Determination of the electrokinetical or zeta potential [136] is very helpful when ESD or EPD techniques are adopted for the deposition of carbonaceous nanoparticles onto the CF surface.

It is of paramount importance to check how the strength of the CF is affected by the generation of the multiscale morphology. The strength of carbon fibers is generally investigated by single fiber tensile test that is also standardized (ASTM C1557). The test results are usually interpreted using the Weibull statistics which deliver further information on the inherent flaws in the fibers [137].



Fig. 5. Scalable manufacturing of CNTs on continuous carbon fibers surface: a) device for a unique CVD system, b) temperature profile along the center of the furnace heated zone (650 °C) {taken from Ref. [127]}.

2.3. Multifunctionality in all-carbon composites

Beside the mechanical improvements, multi-scale CF fibers may be used also to induce functional properties in composite materials, such as improvements in the through thickness electrical conductivity, mechanical and acoustic damaging and even damage sensing. Bekyarova et al. [71] selectively deposited MWCNT and SWCNT on woven CF for which EPD technique was employed. The incorporation of the carbonaceous nanofiller in the matrix-rich regions significantly improved the out-of-plane electrical conductivity of the epoxy/CF composites compared to the base composites. The increased conductivity was higher for SWCNT than for MWCNT (~100% and 30%) when ~0.25 wt% of filler with regard to carbon fabric was deposited. The authors deduced the difference based on the different thicknesses of the composite specimen or due to different morphology of the deposited MWCNT and SWCNT on the fabric. It is hence critical to note that the selection and type of material and method of creating hierarchical composites determine the magnitude of final properties. Poegic et al. [138] reported a method for the growth of carbon nanotubes on carbon fiber using a low temperature growth technique. Such method created fuzzy fiber plies which were used to create laminates that showed a 510% out-of-plane electrical conductivity. The same group used the same method to create fuzzy fiber plies on CF without any polymer sizing and showed an out-of-plane conductivity of 450% however they did not explain the reason for decrease of the conductivity as compared to the previous work [139]. Shin et al. [140] used three fabrication methods to create hierarchical composites using CNTs on CF i.e. 1) CNT mat (1.06 wt%) inserted between CF plain-weave fabric, 2) CNT mat (1.53 wt%) and buckypaper (3.73 wt%) inserted between CF woven prepreg laminates and 3) CNTs grown directly on CF plain weave fabric (2.56%). The out-of-plane electrical conductivities increased for each case where for the first case, the increase was in the factor of 2.9 times. For the second case, the electrical conductivity values found were 2.8 times higher than when CNT mat was used in prepreg composites but with buckypaper this increase was 5 times as compared to baseline. Lastly, the hierarchical composites showed 40 times and 56.2 times increase (polished and unpolished specimens) over control composites. The justification given by the authors was that the unpolished specimens had lower sheet resistance since CNT forest was present in the epoxy layer on the out surfaces hence resulted in lower contact resistance between the terminals and the specimen.

The possibility of strain sensing by following the Raman shift of highly crystalline CF, CNT and GR was demonstrated by several authors [141,142]. Failure/damage sensing based on the electrical conductivity of the bulk matrix doped with CNT was proposed by Fiedler et al., in 2004 [143] and boosted the research efforts targeting on-line structural health monitoring (SHM) in composite structures [144,145]. Recognizing that fiber/matrix debonding is one of the early failure events in composites, its monitoring was attempted by registering the disruption of an electrically conductive percolation network of carbon nanoparticles at the interphase [146]. Promising results were achieved with non-conductive multi-scale fibers, such as glass (GF) and natural fibers (NF). Park et al. [147] demonstrated that multi-scale structuring of CF in single CF/EP model composites may be exploited for damage sensing. The authors coated a single CF with a CNT-containing electrically conductive EP, and embedded it into a neat EP matrix (dual-matrix). This single CF composite was subjected to repeated subcritical tensile loading in a pull-out type configuration. Zhang et al. [44] followed the failure during mode I test in a double cantilever beam (DCB) specimen by sensing the crack propagation through a spray deposited CNT web. The authors found that the collected signal showed a good correlation between crack propagation and electrical resistivity [44,148]. CNT localization in the interlaminar region through a dissolvable thermoplastic interleaf containing CNT worked also for damage sensing. According to the authors, the sensing signals reflected well the initiation and propagation stages of the delamination [96]. Interestingly enough,

no work addressed the task to exploit the sensing capabilities of composites containing all-carbon multi-scale fibers produced via direct and indirect coating methods.

Carbon fiber reinforced polymers (CFRPs) suffer from poor thermal conductivities especially in the out-of-plane direction which does limit their advantages in specific applications such as in de-icing components for airplanes. Beside the improvement of electrical conductivities, a few of the works reported demonstrate the usefulness of carbonaceous nanofillers in the development of high thermal conductivitiy in hierarchical composites. The improvement of through-thickness thermal conductivity in all carbon composites was first demonstrated by the use of carbon black by Han et al. [149]. The method used was to disperse a carbon black on the fiber surface by immersing the carbon fiber prepreg in a bath containing carbon black and ethylene glycol monoethyl ether. The latter was used to remove the epoxy from the interface of the fiber and let the carbon black settle on the surface. The author reported an increase in the thermal conductivity by 115% and 212% for unidirectional and cross-ply composites with just 0.8 wt% of carbon black. Shin and co-workers also reported a similar 175% increase of out-of-plane thermal conductivity when a CNT mat was added between the CF fabric to prepare the composites [140]. A CNT interphase deposited on carbon fiber by CVD showed relatively less improvement of thermal conductivity i.e. 107% as compared to base composites [139].

3. Carbon-carbon composites

Carbon/carbon (C/C) composites exhibiting a unique combination of outstanding mechanical (under compressive loads), chemical (inertness), thermal (conductivity, ablation resistance), electrical (conductivity, shielding) and tribological (low friction and wear) properties. For these reasons, C/C composites are extensively used in application fields like aviation, aerospace, nuclear power engineering. The largest application volume is, however, high-performance brake disks, such as those used in aircrafts. The carbon reinforcement in C/C composites is usually constituted by CF in various textile arrangements, though nowadays efforts are in progress to replace it by CNT assemblies [150]. The carbon matrix is created by polymer impregnation followed by pyrolysis or chemical vapor infiltration yielding pyrolytic carbon (PyC).

Carbonaceous nanoparticles (usually CNT, CNF, GR or GO) can be placed on the CF by various techniques before and during densification. Densification means the creation of a carbon matrix or its precursor before additional graphitization takes place. Incorporation of carbon nanoparticles into the interphase of C/C composites targets the improvements of both fiber- (modulus and strength) and matrix-dominated (compression strength, flexural bending, ILSS) mechanical properties. Note that C/C composites have excellent specific modulus and strength values but rather poor compression and interlaminar properties, ductility and toughness [151]. As a consequence, C/C composites are prone to catastrophic brittle fracture under unconstrained loading conditions. To overcome these limitations of C/C composites, investigations are ongoing to incorporate carbon nanoparticles selectively at the interphase. The related approaches differ from one another whether CNT, CNF or GR nanofillers are deposited indirectly (via coating) or directly (via CCVD) on the CF surface - cf. section 2.1 of this review.

Jie et al. [152] deposited CNFs onto UD CF clothes by immersion in a mixed solvent (EP/alcohol) containing CNF. C/C was produced after densification through CVD ending with a graphitization step at 2500 °C. The authors found that CNF induced an ordered deposition of PyC during CVD. Compared to the reference C/C composite the CNF modified one exhibited improvements in the flexural strength when tested transversally (~46%) or longitudinally (~57%) to the UD aligned CFs in the composite specimens. It was early recognized that for better properties improvements both the interphase and matrix should be "nanoreinforced". This implies the radial growth of CNTs on CF for which CCVD processes are predestinated. Researchers in this field experienced the same problems which were already noticed for polymer-based

composites containing in situ grown multi-scale fibers, i.e. deterioration of the CF tensile properties due to the catalyst dissolution in CF along with the related annealing process. To overcome this problem, approaches very similar to those listed in section 2.1.2. were tried. This fact is a clear proof of the steady knowledge transfer between the fields dealing with traditional polymer– and carbon matrix-based systems.

Li et al. [153] first grafted GO onto carboxylated CF through esterification reactions at 150 °C. Afterwards, Ni catalyst particles were generated on the surface of this GO-grafted CF before CNT growth started in a CVD reactor. Densification of the composite took place at 1100 °C for 10 h. The tensile properties of the resulting C/C composites were 32% and 87% higher than that of neat C/C (without CNT particles) and C/C doped only with in situ grown CNT (no GO protective layer), respectively. To build a protective layer, Song et al. [154] coated the CF preform with PyC prior to CCVD and completed the process with a graphitization step at 2500 °C. This treatment resulted in a prominently enhanced mechanical behaviour under compressive (both transverse and parallel to the UD CF direction) loads. In fact, both compressive strength and strain at break were enhanced, and also ILSS improved (threefold increase). A similar strategy was followed by Feng et al. [151] who produced a protective PvC layer by isothermal chemical vapor infiltration (CVI) at 1080 °C prior to perform a double-injection chemical vapor deposition (DICVD) process. In this DICVD process, first the catalyst precursor (Fe(III) nitrate) was injected and then the injection of the carbon source and CNT growth promoter was performed. The radially grown CNTs markedly enhanced the stiffness and toughness characteristics of the resulting C/C composites. In fact, flexural strength, flexural ductility, compressive strength and ILSS were enhanced by 31.5%, 118%, 81.5% and 82%, respectively, compared to the reference C/C composites. Moreover, the failure mode changed from brittle to



Fig. 6. Effect of CNT on the microstructure of pyrocarbon in composites. (a) The mechanism of carbon molecules depositing on CNT, (b) CNT influencing the microstructure of pyrocarbon in C/CNT/C composites. {taken from Ref. [155]}.

pseudo-ductile type in the flexural test.

Efforts are ongoing to manufacture multi-scale CF containing CC composites in an eco-friendly way. Yang et al. [155] started from oxidized PAN fibers (precursor of the PAN-based CF) and used the CO, evolved during its carbonization, as reducing gas for the Ni catalyst, introduced in Ni(II) nitrate form. CNT growth was induced in CCVD using natural gas as carbon source at ~1100 °C. For the densification at ~1100 °C, rapid chemical vapor infiltration (RCVI) was used using natural gas and propane. Final graphitization occurred at 2400 °C for 2 h. It was demonstrated that CNT triggered an ordered growth of PyC acting like nucleation sites (see Fig. 6). The flexural strength was improved by ~35%, the thermal conductivity in plane direction by ~15%, the friction coefficient was reduced by ~40% and the wear resistance by ~20% with respect to the reference C/C composite.

Deng et al. [156] produced nanofilamentous carbon reinforced C/C composites by floating catalyst chemical vapor infiltration and tested them to assess their tribological behaviour. It was found that the mean coefficient of friction and wear rate were reduced in a given range of the catalyst content (ferrocene content of 0.5–0.8 wt%) when the graphitization at 2300 °C took place. The wear rate increased, however, when the catalyst content and the graphitization temperature were higher and this was ascribed to the development of isotropic PyC and limited formation of carbon nanofilaments.

4. Modeling

Modeling of the mechanical and functional (thermal and electrical conductivities) properties of composites with all-carbon multi-scale fibers is a very challenging task. On the other hand, it may convey useful advices with respect to multiscale structuring of composites to target specific applications. Numerous approaches, based on simple phenomenological to highly sophisticated 3D models, were proposed to describe the properties of multi-scale composites [157]. An exhaustive survey of these methods is not feasible in this review. Instead, we will focus only on the most recent models which explicitly tackle effects of the nanostructured interphase in polymer-matrix composites and thus help the reader to reach a better understanding of the stress transfer and damage phenomena in these novel composites. Recall that exactly these properties were the most influenced/improved by the incorporation of multi-scale fibers in composites.

Sun et al. [158] performed multiscale computational analysis based on representative volume element (RVE) modeling and molecular dynamics (MD) simulation for UD CF reinforced composites. The presence of a 0.2 µm thick interphase formed during EP curing was characterized by MD. It was found that the interphase has higher stiffness and strength than the bulk with a gradual change from the CF surface towards the bulk. The model of Subramanian et al. [159] addressed the interphase mechanics of composites containing CFs with radially grown CNTs. The authors termed this all-carbon multi-scale fiber as "fuzzy fiber", a terminology which is frequently used especially in the modeling field [160, 161]. In the atomistic model of Subramanian et al. [159] a functional polymer coating served to trigger the CNT growth which, according to us, may be not physically correct. Nevertheless, results from the simulation of virtual deformation in various space directions of the multi-scale CF/EP were useful to understand the local failure mode. Main conclusion of the authors was that incorporation of multi-scale fibers enhanced the out-of-plane properties while the in-plane ones are maintained. This suggests that the delamination behavior is suppressed as experimentally proven in several of the references cited in this review. A further result of the simulation work was that a polymeric surface coating in which the nanoparticles are dispersed, may improve also the in-plane performance. This information may push the future research to use sizing with and without additional chemical grafting. Wang et al. [162] modeled the effects of interphase in UD CF composites with a fiber volume fraction (V_f) of 50% assuming an interphase thickness of 0.1 μ m. Nanoparticles (spherical) were assumed within, in the boundary, and



Fig. 7. Contour plots of the maximum principal stress in the matrix for composites without CNTs (bottom right), with random CNT forests of LCNT = $0.7 \mu m$ and $0.5 \mu m$ (bottom left), with aligned CNT forests of LCNT = $0.7 \mu m$ and $0.5 \mu m$ (top left); with CNTs in the fiber coating of thickness $0.2 \mu m$ containing of 1500 and 500 CNTs. The applied displacement is in the x-direction. {taken from Ref. [168]}.

outside of the interphase based on their scaling. Moreover, their density, elastic modulus and even the number of the interphase layers were variable in the corresponding finite element (FE) model. Major outcomes of this modeling were that i) the transverse tensile strength and the tensile modulus of the composites increased with increasing density or number of nanoparticle layers, ii) the transverse tensile strength of the composites increased with decreasing tensile modulus of the particles, and iii) strength improvement was accompanied with extensive crack bifurcation - especially in case of the interphase with several layers. The latter finding is in good agreement with results deduced from 3D multiscale FE models by Mishnaevsky and co-workers [163,164] who concluded that the crack deviation probability is 50-85% higher when the anisometric particles (platelet in this case) are located in the interphase and not in the bulk. It is noteworthy that agglomeration of the nanoparticles, which is a crucial issue in bulk polymer nanocomposites [165,166], may also be considered in the interphase. To take possible agglomeration effects into consideration, Shin et al. [167] proposed a percolation-based FE model.

An advanced 3D multiscale FE model was developed by Romanov et al. [168–170]. In the unit cell of this model different alignments and deposition possibilities (direct grown, indirect coating) of CNTs were also considered. The grown CNTs were considered as radial, quasi-straight and randomly oriented, wavy forests in different densities and lengths. Similarly, the work of Shishkina et al. [171] also used either the direct growth of CNTs on the carbon fiber or the dispersion of CNT in the fiber sizing hence producing different alignment, orientation and concentration of CNTs in a composite.

Fig. 7 shows the contour plots of the maximum principal stresses in the matrix ligaments with and without CNTs. High stresses can be detected locally around the individual CNTs. These nanoscale stress concentrations, which do not lead to localized cracking and thus microscale damage, depend on the CNT density, orientation (respective to the applied load), and waviness. CNT orientation proved to play a decisive role to redistribute the stresses in the matrix (both radial and transverse shear). Non-overlapping CNT forests may create stress concentration sites. When they are long enough to overlap, the stresses in this section are suppressed but enhanced in a larger area. CNTs deposited by coating behaved differently since their stress-redistribution capability was lower than the one reached with CVD grown ones.

Numerous approaches reported in this review specifically tackled the suppression of interlaminar delamination by different multi-scale structuring. Because in many of the related works mode I fracture toughness was used to quantify the delamination resistance, its modeling should also be introduced. Menna et al. [172] developed a micromechanical model thereby adapting the analytical framework elaborated for the toughness assessment of discontinuous fiber-reinforced composites [173]. In this model, CNT fracture and pull-out events, along with the corresponding energy absorption mechanisms were considered. The authors pointed out that the relative orientation of CNTs and their length distribution should be considered with proper probability functions in order to obtain simulation results matching with the experimental data. According to us, the above approach can be easily transferred to multi-scale structures with other particles such as GR or GO. Moreover, other energy absorbing mechanisms such as debonding and matrix deformation (voiding) may also be considered. This possibility was already demonstrated for the mode I fracture energy estimation of EP, bulk modified with CNF and GR [174].

5. Summary

Carbonaceous nanofillers can be conveniently deposited on the surface of CF and related fabrics by different techniques. In this review, these techniques were grouped into i) indirect methods using preformed particles and ii) direct methods in which nanofillers are in situ generated on CF. The stability of multi-scale structures is based on physical, physico-chemical and chemical interactions. It is noteworthy that, for nanostructuring an interlaminar layer, various selective placement techniques may also be adopted.

The scientific papers cited in this review highlight that multi-scale structuring of the interphase and interlaminar regions is an efficient approach to improve the out-of-plane properties of composites without compromising or even improving the in-plane ones. Despite the fact that, at present, the main attention has been focused on the improvement of mechanical property, also enhancement of electrical and thermal conductivities can be exploited. As far as the creation of all-carbon multi-scale fibers is concerned, hardly any reliable prediction can be tempted for the industrial implementation of one or other of the reviewed methods. The methodologies for multiscale and hierarchical structuring most compatible with the current fiber production technologies are those involving sizing procedures. Another viable industrial option could be the electrophoretic deposition (EPD) during which oxidation of the CF tow, sizing and/or doping with carbonaceous nanoparticles can be performed continuously in line. Note that these processes do not yield, however, a preferred radial alignment of CNTs and CNFs. Therefore, further efforts are needed to develop quasicontinuously chemical vapor deposition processes operating at lowtemperature.

6. Future trends

Additional and not yet explored possibilities can be predicted for allcarbon multi-scale and hierarchical fibers, such as direct conversion of CF into a core-sheath type multi-scale fiber under suitable conditions in analogy to the concept proposed by Ji et al. [175]. A further challenging task is connected to the pyrolytic recycling of CF-based composites [176]. It would be an upgrading option to control the pyrolysis conditions in such a way that the resulting reclaimed CFs result in a multi-scale structure by the presence of pyrolytic carbon (PyC) residues on their surfaces. Moreover, a change from structural toward functional properties can be predicted with respect to the target applications.

All-carbon multi-scale fibers are naturally predestinated to be used in carbon-carbon (C/C) composites. In this field vigorous research and development activities, supported by modeling [177], are expected. The development of all-carbon CF-based composites will follow guidelines deduced from extensive modeling works. Multiscale FE models seem to be the most suitable to clarify open issues related to the effects of hierarchical structuring of the interphase and interlaminar regions. Interestingly, the experimental and modeling works on the damping performance of these novel composites are far behind the expectations, though multi-scale CFs are very promising intrinsic damping elements. Selective placement of free-standing nanostructured assemblies (interleaf concept) into the interlaminar region will be further explored. In this respect, the research will likely focus on dissolvable polymer carriers (as bulk or foam materials [178,179]) of the nanoparticles which may work after curing for toughening, shape memory behavior [180], self-healing (for example by using nanoreinforced self-healable interleaving films [181]). For the production of such interleaves additive manufacturing and electrospinning methods appear as appealing tools. Sensing for structural health monitoring whereby exploiting the beneficial properties offered by all-carbon multi-scale fibers will remain under spot of research interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Note by Alessandro Pegoretti and Haroon Mahmood.

This manuscript is one of the last contributes of prof. Joseph Karger-Kocsis in the field of composite science and technology before his premature death on 13th December 2018. The idea behind this work emerged during several fruitful discussions we had with him during the period he spent at the University of Trento as a visiting professor in May 2018. During his stay at the University of Trento he prepared a first draft of the manuscript.

Prof Karger-Kocsis had received outstanding achievements in basic, applied research and innovation, and he had been able to combine them, as evidenced by 35 patents, 4 professional books, 50 book chapters, nearly 500 journal articles and countless invitations as guest speaker. The quality of his professional work is evidenced by more than 20,000 citations received for his articles, with makes him one of the most renowned researchers in the field of polymer matrix composites.

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