



Feature Article

Carbon fiber surfaces and composite interphases

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ABSTRACT

Carbon fiber reinforcements with an excellent mechanical performance to weight ratio are primarily preferred for advanced composite applications. The poor interfacial adhesion between carbon fiber surfaces and polymer molecules caused intrinsically by hydrophobicity and chemical inertness of carbon is a long existing issue to overcome. The article intends to review the research work carried out over the past couple of years in the area of carbon fiber surface modifications and carbon fiber/polymer interfacial adhesion. This paper provides a systematic and up-to-date account of various 'wet', 'dry' and 'multi-scale' fiber surface modification techniques, i.e., sizing, plasma, chemical treatments and carbon nano-tubes/nano-particles coating, for increasing the wettability and interfacial adhesion with polymeric matrices. The review highlights strategies for retaining the carbon fiber mechanical strength after surface modification and stresses its significance.

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Contents

1. Introduction	36
2. Carbon fiber surface modification vs. interfacial adhesion properties	37
2.1. 'Wet' chemical methods	37
2.1.1. Sizing: Application of polymer finish to CF surface	37
2.1.2. Acidic modification	38
2.1.3. Electrochemical modification	40
2.1.4. Electro-polymer coating	40
2.2. Surface modification in 'dry'	40
2.2.1. Plasma surface modification	40
2.2.2. High energy irradiation modification	41
2.2.3. Nickel surface coating	42
2.2.4. Thermal modifications	42
2.2.5. Miscellaneous dry treatments	42
2.3. Surface modification in 'multi-scales'	42
2.3.1. Nano particles modification	43
2.3.2. Carbon nano-tube coatings for carbon fibers	44
3. Surface modification vs. fiber strength	46
4. Conclusions	46
References	46

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1. Introduction

Carbon fiber (CF) reinforcements for polymer matrix composites started to be used for commercial production in the 1960s. For a wide range of potential applications, especially in mechanical engineering, aviation, automotive industries, CF is primarily preferred for composites materials usage due to its excellent properties, such as high specific strength and stiffness, performance to weight ratio, high thermal stability, high conductivity, self-lubrication and corrosion resistance [1–3]. Most significantly, use of CF allows reduction in weight of the equipments or vehicles due to its high strength to weight ratio. CF reinforced polymer composites used for wind turbines applications in automotive energy systems, aerospace efficacies, fuel cells, offshore – deep sea drilling platforms, turbo machinery, compressed gas storage and transportation, antistatic and electromagnetic shielding materials [3,4]. Liu and Kumar have reviewed the existing progress of carbon fiber structure, fabrication and properties including the incorporation of nano-tubes in precursor fiber to improve the mechanical properties [5]. However, the essential mechanical properties of these composites such as toughness, longitudinal and transverse strength limited by the intrinsically poor interfacial adhesion between reinforcing CF surface and polymer materials. It is a long existing critical issue needed to resolve for ensuring the continued development of CF reinforced polymer composites for potential advanced composites applications.

Motivated by this, many researchers focused on probing and understanding the physicochemical interaction at the fiber/matrix interface. For strong interfacial adhesion, the adequate level of van der Waals and hydrogen bond forces between the CF and matrix are required during composite processing [6,7]. In addition, the fiber/matrix interfacial adhesion energy should be higher than the cohesion energy of the matrix [8]. The modifications to CF structure made a big difference in improving the mechanical properties of high performance polymeric composites but the emphasis to control the fiber/matrix interfacial properties is still a major task [9].

CF, by structures has crystallized graphitic basal planes with non-polar surface. The chemical inertness due to the existence of high temperature carbonization/graphitization step during manufacturing [10], surface lipophobicity, and excessive smoothness and less adsorption characteristics of CF leads to weaker bonding with the matrix materials [7,11]. As remedy for CF inertness, modifications at fiber surface needed to execute strong fiber/matrix interfacial adhesion for effective stress transfer at the interface [12–14]. Primarily the alteration in CF surface generally categorized as wet chemical modification, dry modifications and multi-scale modifications. The ‘wet’ methods include applications of polymer sizings, chemical modifications with acids and electrochemical modifications. The ‘dry’ methods includes of plasma treatments, high-energy irradiation and thermal treatments. A ‘Multi-scale’ coating for CF consists of nano-particles/carbon nano-tubes/graphene modifications using eminent techniques such as electrophoretic deposition (EPD), chemical vapor deposition (CVD), and latest methods like dip coating. Most of the aforementioned methods functionalize the highly crystallized graphitic basal plane sites on the fiber surface and increase its surface energy [15]. The fiber surface roughened due to pitting or by adding reactive functional groups, which further leads to enhanced mechanical interlocking between fiber and polymer to impart interfacial strength to the composite materials [16,17]. The efficacy of fiber/matrix adhesion at the interface depends upon simultaneous action of various parameters that entails physical adsorption and chemical interaction [18,19]. In the year 1997, Tang has categorized the conventional methods for carbon fiber surface modification in terms of oxidative and non-oxidative treatment. The results showed that the incorporation of ceramics whiskers on the carbon fiber has improved the fiber/matrix interfacial properties to pronounced level. The work focused on the function of conventional modification methods in the achievements of commercial and particular application [20]. Most conventional carbon fiber treatment methods endorses the fiber/matrix interfacial strength to enhance composites utility, but at the cost of significant loss in single fiber strength; owing to the generation of pits and flaws on the fiber

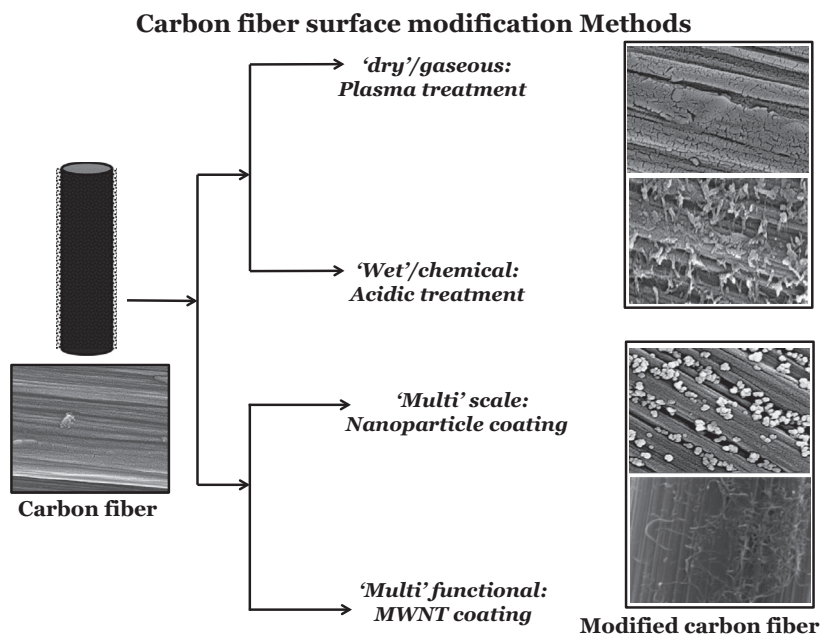


Fig. 1. Schematic for the techniques for surface modifications. The high resolution field emission scanning electron microscope (FESEM) or scanning electron microscope (SEM) images showing of carbon fiber surfaces [23].

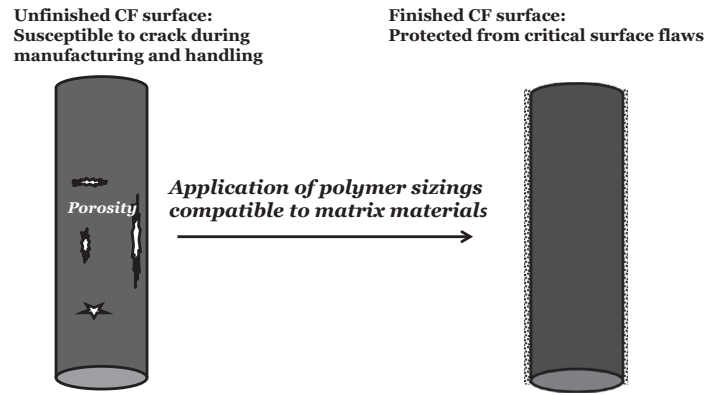


Fig. 2. Schematic for the role of CF sizings to protect fiber from critical surface flaws.

surface, that acts as stress concentration points for crack initiation and propagation [21–23].

In the present scenario, where the traditional or conventional fiber treatment methods are well established and extensively used for industrial applications; it is important to draw attentions towards the usage of new developed treatment methods. To deliberate the need of these modified methods, in terms of improved materials (fibers/matrix as well as composites) performance for research and industry adoption, it is high time to symbolize the current review article.

The review covers the major CF surface modification techniques under the three main categories; viz 'wet' chemical, 'dry' and, 'multi-scale'/'multi'-functional modification. Fig. 1 shows the illustration which categories the various carbon fiber surface modification methods commonly used to endorse fiber–polymer interfacial adhesion and strength properties.

Furthermore, the paper highlights the influence of surface modification methods on strength properties of carbon fibers and its composites with polymeric matrices. The papers also communicate attention towards the selection and optimization of appropriate CF modification methods to achieve the excellent interfacial/composites properties, simultaneously at the adequate level of single fiber strength.

2. Carbon fiber surface modification vs. interfacial adhesion properties

2.1. 'Wet' chemical methods

2.1.1. Sizing: Application of polymer finish to CF surface

Sizing is a method to protect filaments (both in roving and fabrics form), which undergoes various contacts during manufacturing [24,25]. It is a stimulating phenomenon in consideration to provide an acceptable surface finish, protection from fluffiness and yarn damage during manufacturing and usage in composites form. The critical surface flaws or notches created during textile processing act as a stress concentrator for crack propagation, which leads to fiber fracture and finally composite failure. The sizing materials (generally, 0.5–1.5 wt.%) protect the brittle fibers from damage, provide suitable strand integrity, improve fiber/sizing/matrix adhesion and composite processibility, which is crucial in generating the pre requested interface properties. The addition of coupling agent along with the sizing materials creates the covalently bonded oxy-carbonated functional groups at the CF surface, that are further responsible for chemical interactions with the matrix polymer [26]. Fig. 2 shows the schematic for the role of polymer sizings to CF to provide adequate surface finish and protection from breakage during handling.

The fiber/sizing compatibility is a decisive factor for final quantification of fiber/matrix interfacial adhesion. However, sometimes the diffusion of the sizing material into the polymer matrix could result into less affected or improved interfacial strength, which depends upon their compatibility. Sporadically, the sizing functional groups preferentially adsorbed onto the fiber surface and obstruct its dissolution in the polymer matrix during composites manufacturing and results in a weak fiber/matrix interface. The sizing development for fibers is a complicated entity. For example, most of the commercially available sizings for CF are compatible to epoxy rather than polyimide matrices. Sizing application to CF improves its abrasion resistance and bending strength, however; it tends to reduce CF compatibilities with the polymer matrix [27–32]. The research on sizing as coupling agents for CF coating to promote fiber/matrix adhesion is in paramount progress [29,33]. The usage of epoxy sizings for CF and their modifications to enhance the fiber surface activities and wettability with the polymer matrix is in progression [34,35]. In advanced composites materials applications such as rocket engines, commercially supplied sizing are refinished or modified to improve fiber thermo oxidative stability and mechanical performance [36]. The optimization of sizing molecular weight is also an important criterion for the enhanced CF surface energies and superlative interfacial shear strength properties of CF/epoxy composites [37]. Daia et al. demonstrated that the CF desizing methods likewise improve composites interfacial strength but sequentially at the cost of decreased single fiber strength. The CF/epoxy composites fabricated with desized CF have less activated carbon atoms with high dispersive surface energy and exhibited higher interfacial strength due to the reduced acidic parameter at the fiber surface [38].

The effect of sizing on interphase behavior of epoxy composites containing carbon and glass fibers was demonstrated for dynamic wetting measurements [39]. The application of silane coupling agent with polyurethane and/or epoxy film formers on glass fiber considerably improved the micromechanical interfacial adhesion and macroscopic fatigue properties. Interestingly the CF sizing in the presence of silane coupling agents increased 15% single fiber tensile strength in addition to increased tensile, flexural and compression shear properties of CF/epoxy composites. The constricted effect on molecular mobility of epoxy matrix showed steadiness with the incremented interface properties and fatigue resistance [40]. The sizing to carbon fibers also affects the fracture toughness of its composites in addition to the interlaminar shear strength (ILSS). Fernandez et al. studied fracture behavior of CF/tetrafunctional epoxy composites by elucidation of the beneficial effect of epoxy sizing to improve their mode-II interlaminar fracture toughness [41].

The carbon fiber interaction with sizing materials is an important factor to control the interlaminar adhesion properties in

Table 1
Sizings for carbon fibers and their influence on properties of CF/polymeric composites.

Coating method	Sizing materials for carbon fibers	Sizing's influence on CF and composites properties	Ref.
Not specified	Poly(thioarylene phosphine oxide) PTPO and polyetherimide	Surface energy decreased with sizing ($\gamma_{CF_{unt}} - 70 \text{ mJ/m}^2$, $\gamma_{CF_{ultem}} - 54 \text{ mJ/m}^2$, $\gamma_{CF_{PTPO}} - 36 \text{ mJ/m}^2$). Polar and dispersive components and the percentage of surface functional groups decreased with CF sizing	[27]
Not specified	PU and polyamide	Sizing reduces the surface energy and covers acid–base sites. Hydroxyl groups on the fiber surface decrease with sizing. Contact angle increased with sizing with decrement in IFSS. (Contact ang., IFSS) – ($\gamma_{CF_{unt}} - 55^\circ$, 28 MPa); ($\gamma_{CF_{polyamide}} - 64^\circ$, 19 MPa); ($\gamma_{CF_{PU}} - 68^\circ$, 14 MPa)	[28]
Aqueous dip coating	Vinyl ester resin emulsion type sizings synthesized by phase inversion emulsification	CF sizing strongly reduces the surface energy of the fibers and increase ILSS to 20.7%	[33]
Not specified	Latent curing agent for epoxy (ethylenediamine with butylacrylate)	CF sizing enhances surface activity and wettability with matrix. 10% increment in ILSS of CF/epoxy composites with improved interface toughness	[36]
Not specified	Epoxy	Epoxy coating improves ILSS and fracture toughness values of woven CF/epoxy composites	[41]
Not specified	Epoxy and polyethersulfone	As compared to CF/epoxy composites, epoxy sizing improves ILSS of CF/PES composites. For CF/Epoxy composites lower M_w epoxy sizings are better than higher M_w epoxy sizings	[42–45]
Polymer grafting	polymethyl methacrylate	25–100% adhesion improvement of CF/polymer	[46]
Not specified	Polyvinyl alcohol sizing modified with oxidative inhibitors SiC, Al_4C_3	Sizing improves resistance to oxidative erosion of CF surface	[48]
Solution dip coating and interfacial polyamidation	Polyamide 6,6	Dip coating with Nylon 6,6 improves ILSS and tensile strength of CF/epoxy composites while interfacial polyamidation deteriorates these properties. Both coating techniques improve fracture toughness of composites	[50]
Electropolymerization	Poly(hydroxyalkyl methacrylates) and Polyaniline	Homogeneous coatings achieved with both materials. Electrochemical studies reveal the dependency of coating on surface properties of the carbon fibers	[52]
Not specified	Beta-tribasic calcium phosphate (β -TCP)	β -TCP sizing to CF/Hydroxyapatite(HAP) composites improve the interfacial bond strength and also eliminate the stresses during cooling	[53]
Electropolymerization	m-Phenylenediamine, phenol and acrylic acid	Contact angle and surface free energy decreased with acrylic acid sizing. (Contact angle, Surf. Free energy) ($\gamma_{CF_{unt}} - 85.6^\circ$, 29.3 mJ/m ²), ($\gamma_{CF_{ac. acid}} - 52.2^\circ$, 33.1 mJ/m ²) Impact str., flexural str. And ILSS of the CF/phenolic composites were improved by $CF_{m\text{-phenylenediamine}} - 44\%$, 68% and 87% $CF_{phenol} - 66\%$, 100%, and 112% $CF_{acrylic acid} - 20\%$, 80% and 100%	[54]
Sol-gel technique	Epoxy/SiO ₂ hybrid	SiO ₂ particles dispersed in the hybrid sizing film homogeneously and improve ILSS, impact strength properties of CF/epoxy composites	[55]
Dip coating	Thermoplastic poly(phthalazinone ether ketone) (PPEK)	CF thermal stability increased (Contact angle, Surf. Free energy, ILSS) ($\gamma_{CF_{unt}} - 97^\circ$, 31.3 mJ/m ² , 42.3 MPa), ($\gamma_{CF_{sized}} - 57^\circ$, 49.9 mJ/m ² , 51.4 MPa)	[56]

* M_w – Molecular weight, CF_{unt} – carbon fiber without sizing, IFSS–interfacial shear stress, ILSS – interlaminar shear stress.

composites, the interaction depends upon the fiber graphitic structure and its properties (strength and modulus) [26]. The fiber surface finish compatibility influence on the interphase properties; for example oxidative treatment improve interfacial strength of CF/epoxy composites almost to double, which was only 25% increment for brominated epoxy sizing. Interestingly the brominated epoxy sizing to CF improves the interlaminar shear strength of CF/PES (carbon fiber/polyethersulfone) composites more promisingly as compared to CF/epoxy composites. In comparison to thermoplastic matrix, epoxy sizing does not dissolve radially in epoxy matrix; consequently, the brominated epoxy coating on the fiber is more compatible with a thermoplastic PES than the epoxy resin. The sizing compatibility with the matrix eases the stress transfer between coated fiber and matrix at the interfacial region [42–44]. The sizing molecular weight (M_w) also influences the interfacial properties; the low M_w polymer sizing creates a soft interface region while the higher M_w sizing is less compatible with matrix and causes more susceptibility to fiber/matrix debonding [37,45]. Polymer M_w influences the fiber matrix interfacial adhesion, low M_w polymer beneficial for adhesion but the segregation of higher concentration of polymer chains at interfacial region deteriorates the mechanical strength properties [46,47]. Clarke and Eitman [48] modified the polyvinyl alcohol sizing for carbon fiber by adding suspended oxidation inhibitors like diamond, boron carbide and silicon carbide, to avoid the oxidative erosion especially in high temperature oxidizing environments. The organic aziridine linking derived from reactive nitrenes was used to size the carbon fiber. The methods do not create any surface defect on to the fiber surface, without affecting the tensile strength properties at the same time [49].

Commonly the treatment methods introduce oxidative functional groups at the fiber surface, while heat treatment to fiber at high temperature (1000–1400 °C) creates desorption of oxidative functional groups [50]. In the former case, the chemical interactions/bonding assumed the basis of interfacial adhesion but in later case due to the high temperature heat treatment most of the functionality removed from the fiber surface. Contrary in latter case also, the functional groups can arise on the fiber surface due to the residual moisture present in the matrix material during composite processing. Hence, it is always very complicate to define the type of bonding (mechanical interlocking or chemical bonding) involved in the interface formation process [51]. In fiber reinforced polymer composites processing and applications; the interdiffusion of fiber sizing and polymer matrix results in the formation of an interphase region that protects the fiber strands and hinders the damage initiation and propagation process.

Table 1 [27,28,19,21,41–56] summarizes the various sizing materials for CF and their influence on polymeric based composites.

2.1.2. Acidic modification

Strong acidic treatment is another wet method for CF modification which corrodes its surface and/or introduces perforations, to improve fiber/matrix interlocking [57,58], simultaneously induced pits, crevasses, expanded micro-voids and flaws on the fiber surface that reduced its single fiber strength [19,20,23]. Researchers have analyzed physicochemical modification on CF surface with a variety of acidic treatments. Surface enhanced Raman scattering [59], X-ray photoelectron spectroscopy (XPS) [60,61], Fourier transform infrared spectroscopy (FTIR) [57] and Fourier transform

infrared-attenuated total reflectance (FTIR-ATR) [58] with other supporting techniques were used to analyze modified CF surface with nitric acid (HNO_3) [57,59–62], maleic anhydride [59] and sodium hydroxide (NaOH) [57]. Raman characterization suggested the two main bands for CF; graphitic band (1350 cm^{-1}) and disorder band (1590 cm^{-1}) modified by maleic anhydride treatment with the vibration modes of $-\text{C}=\text{C}-$, $-\text{CH}_2-$ and $\text{C}-\text{O}$ [59]. The acidic character at fiber surface measured with refluxion in aqueous NaOH after HNO_3 oxidation, which preferentially detaches the partially oxidized, loosely bonded graphitic fragments with higher weight loss [61]. The introduction of phenol hydroxyl group, β -carbon, and bridged structure elucidates the compatibility of modified fiber surface with Bismaleimide (BMI) matrix [59]. Acrylic acid was grafted on CF by free-radical polymerization using redox-induction. The presence of carboxyl groups and increased absorbability at the fiber surface due to the treatment increases its interfacial strength with epoxy matrix [19,63,64]. The electrical conductivity, dielectric strength and flexural strength of CF/phenolic composites containing nitric acid oxidized CF followed by the coupling with glutaric dialdehyde improved significantly [65].

Marieta et al. investigated on CF/cyanate ester composites comprised with HNO_3 treated and plasma oxidized CF surface [66,67]. The interfacial behavior of these composites evident by improved IFSS/ILSS due to CF treatment, along with the thermoplastic (polyethersulfone – PEI) modification of thermoset matrix (cyanate ester) on shear properties and delamination fracture toughness [67]. Fig. 3 shows the perforated CF surface using AFM images. Modifications introduce deep perforations and increased roughness on the acid treated surface. The treatment induced the deeper and narrower ridges on fiber surface at nano-scale, while for unmodified surfaces these very feeble granulations appeared due to the spinning of the fiber precursor during manufacturing [23].

Single fiber pullout tests were performed to analyze the interfacial properties of nitric acid oxidized CF reinforced with maleic anhydride grafted polystyrene composites. Improved interfacial

shear strength permits full utilization of yield strength of thermoplastic matrix [68]. Pull out tests with CF/epoxy composites containing CF modified with maleic anhydride, tetracyanoethylene, and aqueous ammonia, suggested that the modification enhanced fiber/matrix adhesion with interfacial shear strength for composites containing aqueous ammonia treated CF [69,70]. Mechanical in combination with tribological (reduction in friction and improved wear resistance) properties improved for CF/PEI [58,71] and CF/PI [72] composites containing optimized treated carbon fabrics. Deep ridges and a large amount of perforations (AFM studies, Fig. 3 [23]) introduced on the fiber surface due to acid treatment causes improved fiber/matrix interlocking and interfacial strength properties. High shear and tenacious transfer film deposited on counter face; stimulates friction, and wear performance CF/PU coating with HNO_3 and toluene-2, 4-diisocyanate activated CF. The efficient transfer and maintaining of the PU coating film on the metallic counterpart improved wear resistance of composites [73]. 2, 4-diisocyanatotoluene treatment to CF improved tribological behavior of CF/polyurethane composites [74]. Polyhedral oligomeric silsesquioxane coating employed on CF to study interfacial properties of CF/vinyl ester composites, interlaminar shear strength of fiber-coated composites increased up to 38% [75].

Retentivity of fiber mechanical strength is a critical issue for all surface modification methods. Surface fluorination of fiber surface is an efficient technique in this regards to promote fiber/matrix adhesion without compromising the single fiber strength properties. The increased surface polarity of oxi-fluorinated CF promoted its interfacial adhesion with epoxy matrix and low velocity impact properties [76]. XPS elemental analysis confirmed the hydrophilic character of modified fiber surface with the introduction of functional groups; $\text{C}-\text{O}$, $\text{C}=\text{O}$, $\text{HO}-\text{C}=\text{O}$, and $\text{C}-\text{F}$ which improved mechanical performance of composites [77,78]. The toughness of composites estimated with the total energy absorbed during impact. Oxi-fluorination of CF improved the impact behavior of CF/epoxy and CF/polyvinylidene fluoride composites before failure

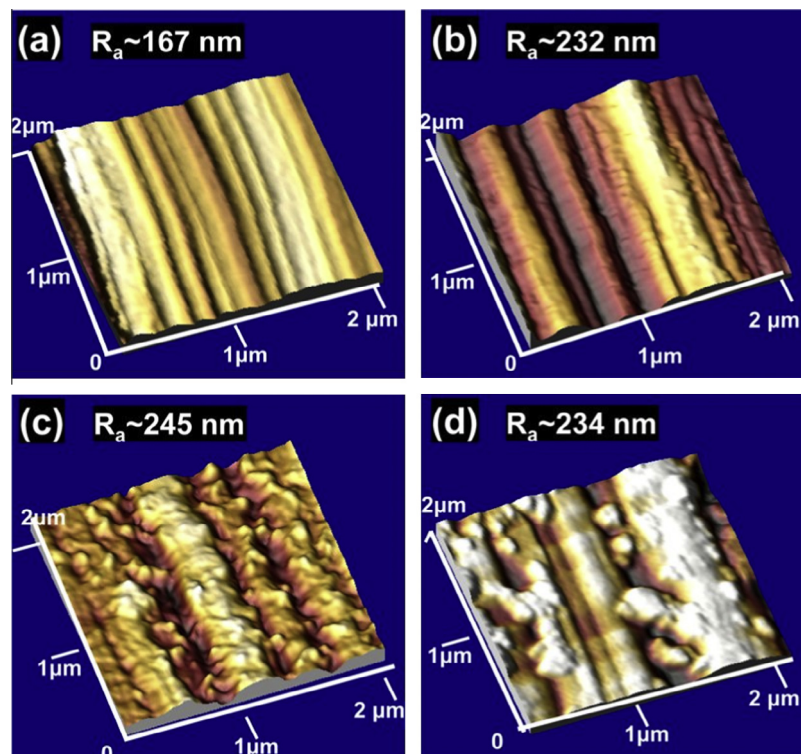


Fig. 3. AFM images of CF: (a) untreated CF. (b) Plasma treated CF with 1% O_2 . (c) HNO_3 treated CF for 90 min. (d) Nano YbF_3 treated CF with 0.3 wt% dose (0.3% YbF_3) [23,71].

due to the interruption by effective hydrogen bonding at the interface [79–81]. In another method, air oxidation at 550 °C, anodization at 6 C/m² [82] and 10 wt.% phosphoric acid [83] treatment for PAN and pitch based high modulus CF were compared to assess interfacial shear strength of its composites with epoxy matrix. Surface oxidation of CF correlated with IFSS values using coulometric method [17], the variation of oxidation in air oxidized slightly higher than the anodized CF. Ozone treatment followed by phenolic coating amends the surface activity of CF to improve the mechanical performance of its composites with polyarylacetylene. Force modulation AFM studies revealed the existence of stiff transition areas at the interface improvement of interfacial performance of composites. The mechanical properties, tensile, compressive and flexural strength of modified CF/PAA composites improved appreciably [84].

2.1.3. Electrochemical modification

The electrochemical surface modification occurs due to electron transfer to alter oxidation state. Electrochemical oxidation commonly employed to functionalize the surface. Functionalities improve surface energy, roughness of CF and significantly improve its adhesion with the matrix polymer. To achieve improved interfacial properties the electrolyte type, concentration, treatment time and conditions are vital parameters. Variety of electrolytes used to create specific functional groups or create deep grooves on the CF surface. Sodium hydroxide, ammonium hydrogen carbonate, ammonium carbonate, sulfuric acid and nitric acid are the commonly used electrolyte used to set up the oxygen functionality on CF surface [85–87]. Electrochemical oxidation coatings employed extensively on CF surface to improve interfacial properties of its composites effectively [88–92]. Electro-oxidative treatment removes weak boundary layers from the CF surface and affects reactivity with the formation of acidic and basic moieties [93]. The electrolyte adsorption increased surface activity by generating extended surface areas via the formation of ultra-micro pores, and/or by introducing polar oxygen-containing groups over extended porous surfaces [89]. The interfacial properties of CF/PA and CF/epoxy composites compared with two CF treatment methods, electrochemical and ozone. The former method inscribed more impact to enhance fiber/matrix interfacial adhesion on both the composites [92]. Three dimensional carbon fabrics intermittently electrochemically treated in both bulk and surface regions. The micro-debond test suggests the uniform fiber/matrix adhesion at different regions of the CF/phenolic composites. The electrochemical treatment has influenced the compressive properties of CF/phenolic composites with 38% increment [94]. The modification effectively improves interfacial properties, however; higher treatment time and electrolyte content can reduce single fiber strength. Hence, precise control and optimization of the electrochemical process parameters is essential.

2.1.4. Electro-polymer coating

Electrochemical method has constraints of reduction in fiber strength. In situ chemical grafting reactions, interfacial polycondensation, plasma polymerization are the other potential techniques used to deposit polymeric coatings on the CF surfaces. Electrochemical polymerization has edge over other techniques with higher controlled conditions the coating thickness and homogeneity maintained over long orders [95]. Hung et al. [96] demonstrated the volumetric scanning electro-polymerization coating techniques for CF to improve the CF/epoxy interface. The morphology and free energy at fiber surface changes due to the introduction of active functional groups —OH, —NH₂, and —COOH, which suggested the improved fiber strength and composites interfacial properties.

Interfacial properties modified by plasma treatment by increasing the concentration of chemical groups. The plasma treatments are beneficial because introduction of chemical functionalities creates changes in outermost layers, however the electrochemical reaction modifies fiber sub layers. This is the reason for reduction in single fiber strength during electrolyte coating on fiber surface. Plasma polymerization can be the solution to introduce selectively coating on carbon fiber surface [50,88].

2.2. Surface modification in 'dry'

2.2.1. Plasma surface modification

The use of plasma technologies for high temperature functional materials applications is a well-established process for metallic [97] ceramic [98,99], alloys [100], and thin film [101] coatings to impart adhesion strength and erosion resistance. Surface modification by cold plasma is vital and gaining potential for widespread applications. For fibrous reinforcements, plasma treatment has revealed predominance behavior to improve the fiber/matrix interfacial properties and composites strength [9]. Plasma modification alter the fibers surface layer physicochemically by introducing excited groups to tailor the fiber/matrix adhesion bond strength, without effecting the bulk mechanical properties. The plasma routes to carbon fiber control the acidic character at its surface for the optimized fiber/matrix adhesion via functionalization of basal plane sites, simultaneously enhancing the surface reactivity [102]. The improvisation on plasma treatment techniques for enhancing fiber/matrix adhesion is unceasingly in progress. In comparison to other classical methods, cold remote plasma treatment for carbon fibers is a less destructive method, which allows greater control over the number of unwanted reaction pathways. The composites comprising cold remote nitrogen oxygen plasma treated carbon fabric with three different special thermoplastic matrices confirm increased interlaminar shear strength and other strength properties [103]. The plasma treatment improved the fiber/matrix adhesion due to the inclusion of various functional groups: hydroxyl, ether, carbonyl on the fibers surface, illustrated by XPS and ATR–FTIR studies [27,103–106]. The reactive functional groups [103,107], improve the surface reactivity and adhesion potential of carbon fibers, [106,108] to boost physical intermolecular bonding and fiber surface wettability with hydrophilic polymer matrix and further the interfacial adhesion strength [109–112].

The demonstration for the role of physicochemical modification to strengthen the fiber/matrix interface by Fitzer and Weiss [111], suggested that the inclusion of functional groups; hydroxyl, ether, aromatic groups or/and increased surface roughness boosted the composite strength, however surface structure has marginally influenced the interface [113,114]. Scanning tunneling microscopy of treated carbon fibers insinuates the subtler local disordering and change in concentration of oxygen functionalities at the surface [115,116]. Stable oxygen and silicon functionalities grafted onto carbon fiber surface by plasma silsesquioxane. XPS studies suggest the plasma grafting to CF surface increased oxygen atomic percent, moreover nanoparticles grafting increases the fiber surface roughness that contrastingly endorses the increase of fiber/matrix interfacial adhesion [9,110,117,118].

Hughes and Dilsiz have reviewed the role of plasma surface modification of carbon fibers to improve fiber/matrix interfacial adhesion, specifically with epoxy matrix [119,120]. Physicochemical properties; surface acidity, and surface tension of high tenacity oxygen plasma treated carbon fibers were investigated using electro kinetic and contact angle measurement. The surface tension measurements augmented with the treatment time. The polar part of surface tension increases strongly as compared to the dispersive part, which imitates the vital features of carbon fibers treatment

[121]. Gao et al. investigated the nanoscopic nature of CF/epoxy interface and its contribution in improving the composites mechanical strength. Moreover, the roles of nanometer/atomic scale finish layer on fiber surface highlighted, together with energy-geometry link the interface fracture toughness by micro-mechanical test [114].

The surface modification effectively removes the carbonaceous impurities of ultra-high modulus carbon fiber. At identical matrix strain, the effectiveness of stress transfer estimated from the strain distributions along the fiber length for CF/epoxy composites [122,123]. The fragmentation test conducted with simultaneous collection of Raman shift; implies that at the similar matrix strain value (0.3–0.6%) plasma treated CF/epoxy composites were effectively in transfer the stresses as compared to untreated CF/epoxy composites, for which the transfer mechanism is purely frictional. The interfacial shear stress (IFSS) values of CF/epoxy composites increase from 6 MPa to 42 MPa due to plasma oxidation of CF with increment in structural order parameter ($I_D/(I_D + I_G)$) ratio, which contributes to promote the fiber/matrix adhesion and boost the strength performance of composites [110]. The evaluation of CF/polybenzoxazine composites containing CF modified with two different techniques, plasma oxidation and acid treatment suggests the acid treatment is more effective in improving interfacial strength properties [124]. Ma et al. investigated the effect of plasma oxidization on resin and curing agent non-equilibrium dynamic adsorption process on CF. As compared to the untreated CF, the epoxy resin adsorbed preferentially at the deposited oxygenated functional groups on treated fibers surface, which affects the resin curing process at the interface and the fiber/matrix interfacial adhesion [125].

Lew et al. elucidated the ammonia/ethylene plasma-treatment method for CF to improve and to control fiber/matrix adhesion by dispersing silica nanoparticles to epoxy matrix [126,127]. The load bearing capacity of CF/epoxy composites developed with acetylene plasma treated CF has been determined by calculating the torsional fatigue limit [128], impact strength [129], and shear strength [112,129]. The results indicated the slower rate of accumulated fatigue damage for the plasma-treated composites with remarkable increment in interfacial strength properties [121,128,130–134]. Crack delamination resistance measurements determine the uneven crack growth with purely adhesive failure. Plasma methods for fiber surface modifications suppress the crack initiation process at the interface and promote high bond strength with the cohesive failure mode, which led to the crack propagation within the matrix [135]. The plasma treatment has also influenced the characteristics of CF composites with thermoplastic matrices [130]. Single filament fragmentation test demonstrated that as compared to CF/PA6 composites; the plasma treatment was effectual to improve the interfacial shear strength of CF/PC composites. In another study on thermoplastic matrix composites, the surface energy and ILSS

of inductively coupled plasma treated CF increased marginally for its composites with poly(phthalazone ether sulfone keton) [136].

The interfacial strength evaluated with single fiber pull-out tests to precede the effects of the plasma oxidation on ultra-high modulus (pitch-based) and high strength (PAN-based) fiber with polycarbonate (PC) composites. The incremental interfacial shear strength of CF/PC composites simultaneously supported by inverse gas chromatography results to elucidate physicochemical changes at treated fibers surface [137]. The influence of fiber non-axisymmetry on interfacial properties of CF/PC composites with plasma treated pitch-based and PAN-based carbon fibers explored with fragmentation test. The single filament fragmentation test suggested that the treatment endorses the fiber/matrix adhesion by decreasing the critical fiber length; the improvement in case of pitch-based CF composites is more than in PAN-based CF composites [10]. The improvement in surface functionality at carbon fiber surface was the imperative reason to modify CF-thermoplastic interface properties [138,139]. Fig. 4 shows the FESEM images of carbon fiber impregnated with polyether sulfone before and after plasma modification. In comparison to untreated CF, the matrix pickup is almost 3 times in same conditions for plasma treatment CF.

The mechanical and tribological performance of composites developed with cold remote nitrogen oxygen plasma modified carbon fabric with thermoplastic polymers; polyethersulfone (PES) [140–143], polyetheretherketone (PEEK) [143–145], and polyetherimide (PEI) [146–148] investigated in details. Perforations and increased roughness on the treated carbon fiber, observed by the high-resolution field emission scanning electron microscopy, signposts the improved fiber/matrix adhesion and thus the composites interlaminar shear strength. Physical – void fraction; thermal-heat distortion temperature and mechanical, e.g. interlaminar, tensile and flexural properties of composites boosted due to the plasma treatment [142]. The improved friction and wear performance; adhesive [140,142,144,148], abrasive [141,147], fretting [141,146] and erosive wear [145] of composite with special thermoplastic matrices, signifies the potential use of plasma treated fiber for advanced composite materials for aerospace bearing application particularly in harsh operating environments at high load and elevated temperatures. Fig. 5 confirmed improvement in CF/PEEK interfacial adhesion for composites with plasma modified CF surfaces.

2.2.2. High energy irradiation modification

High-energy irradiation grafting to modify the fiber surface property is an efficient, and environmental friendly pioneered technique, which intensified fiber/matrix adhesion without extensively deteriorating the strength [149,150]. Without any catalyst the chemical reaction induced at fiber surface and affected the crystal lattice, irradiation methods result in changing fiber surface

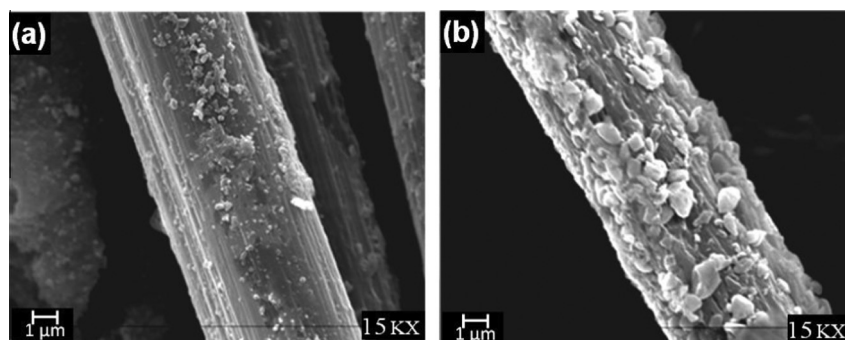


Fig. 4. FESEM images ($\times 15$ K) of CF impregnated with polyether sulphone: (a) before and (b) after plasma modification shows incremented matrix pickup for plasma modified CF [140].

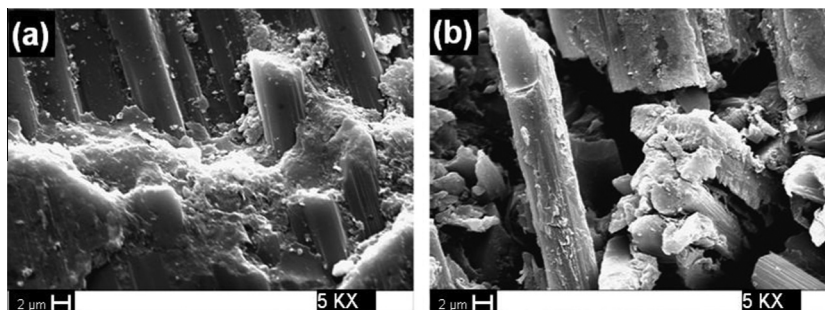


Fig. 5. SEM micrographs for worn out CF/PEEK composites surfaces at the edge of crater after fretting wear (a) CF-PEEK surface with plasma modified CF (b) CF-PEEK surface with unmodified CF (At 600 N, frequency 50 Hz and 1 mm oscillating width) [146].

roughness by displacement of atoms and creating active sites for bonding with matrix functional groups [151]. Physicochemical properties of high energy (0.6–1.4 keV) irradiated Ar⁺ ion CF studied with FTIR technique; the additional carbonyl peak at 1710 cm⁻¹ and broaden -OH peak at ~3300 cm⁻¹, indicated the increased specific polarity and the formation of H-bonding of the carbon fiber surface. The acidic functional groups on fiber surfaces are more efficient to promote interfacial reaction with the epoxy matrix [152]. Pre-radiation (acrylic acid graft-polymerization) and Co-radiation (epoxy resin and chloroepoxy propane) γ -ray grafting method adopted to alter carbon fibers surface [150,153]. Oxygen content and surface roughness of fibers increased with slight increment in single fiber strength and CF/epoxy interfacial strength. The Co⁶⁰ γ -ray irradiation dose at 30 kGy increases surface roughness of fibers, higher irradiation doses are unable to affect the surface and fiber/matrix interfacial strength [154]. Micro Raman studies for γ -ray modified CF showed the increased structural disorder parameter and decreased surface crystallites size with the incremental treatment dose. Enhanced friction and wear properties of CF/PEI composites correlated with the improved interfacial strength of composites [155,156].

2.2.3. Nickel surface coating

For improved adhesion, the fiber and matrix should maintain intermolecular equilibrium distance. When the interfacial bond is due to van der Waals physical adsorption, it requires large fiber/matrix interfacial area. In this situation, the surface energy plays a vital role, when fiber surface energy is higher than the polymer; it is advantageous to get proper impregnation of fiber in matrix solution. Due to the introduction of high temperature carbonization and graphitization steps during fiber manufacturing, its surface is highly hydrophobic with surface tension (≈ 40 mJ m⁻²) whilst most polymeric matrices for example phenolic have surface tensions in the range of 35–45 mJ m⁻². Hence, various treatments for carbon fiber surface needed to vary its hydrophobic nature. Metallic Ni-electrolytic plating on the fiber surface employed to improve CF/phenolic interfacial adhesion. The Ni plating is effective enough to increase surface polarity by introducing oxygenated functional groups and increasing the fracture toughness of the composites [157,158].

2.2.4. Thermal modifications

Pyrolyzed materials deposition on fiber surface was removed with cryogenic treatments. The single fiber strength increased due to the removal of amorphous carbon. The pyrolyzed material on the fiber surface act as stress concentrator points and creates weakening during the tensile loading. However, their removal affects the fiber/matrix adhesion strength in composites form. The increase in IFSS values of CF/epoxy composites containing heat-treated CF attribute to the high reactivity of the active sites present on the fiber surface [159]. The fiber tensile strength

improved due to this treatment leading to the basic surface oxides deposition on the fiber surface.

2.2.5. Miscellaneous dry treatments

Other miscellaneous 'dry' modifications for CF/matrix interfacial adhesion improvement are also reported. O₃ treatment for CF/PA6 composites is used to introduce carboxylic groups [160,161], H₂O₂ treatment in supercritical water for CF/epoxy composites to include C=O, COOH, CO₃²⁻ groups, and aqueous ammonia treatment for CF/epoxy composites to introduce carbonyl carbon as quinines or ketones on CF surface [162].

Efforts are continuously going on to improve the fiber/matrix interface. Various methods to modify CF surface are collected to improve the mechanical properties; specifically interfacial strength of their composites with specialty polymers [23,163,164]. Kim et al. applied three treatment methods to CF; plasma, nitric acid, and liquid nitrogen to improve fiber/matrix interfacial strength along with impact and tensile properties of its PA6 and rubber composites. The interfacial shear strength of the hybrid composites with rubber and modified CF improved along with 41% and 106% increment in tensile and impact strength properties; respectively [165].

2.3. Surface modification in 'multi-scales'

The utilization of nano particles for the modification of carbon fiber surface to form thermally stable coatings [118] and/or for improvement of fiber/matrix interfacial adhesion has been recently appraised [166–168]. Carbon nano tubes (CNT) are on the vanguard in this regards, owing to their unprecedented intrinsic properties; such as physical, mechanical, thermal, electrical, optoelectrical and field emission [169–173]. The motivation for using nano additives/nano particles coatings for advanced fiber reinforced polymer composites materials is to mitigate the problems related to the matrix pre dominating properties [166]. The use of CNT as fillers in the bulk of polymer composites is a well proven technique and well exploited by researchers in details [174–181]. Qian et al. have reviewed the improvement in interfacial properties based upon the CNT addition in bulk, and/or on the reinforcement surface of hierarchical polymer composites [166]. The suffusion of CNT on the fiber surface effectively improves the surface area; promotes mechanical interlocking and local stiffening of fiber/matrix interface, which imparts the strength to the interface by enhancing stress transfer from matrix to the fibers [182]. CNT modification forms percolating networks on the fiber surface with CNT loading lower than percolation threshold calculated by the scaling-law [183]. The main challenge in this situation is the homogenous distribution of the CNT on fiber to alter its surface and hence to promote the fiber/matrix adhesion. From processing point of view, surface modification of reinforcement is advantageous, since

Table 2
Interface strength (ILSS/IFSS) enhancement of CF/polymer composites using different techniques.

Treatment method	Fiber and matrix	Improvement in ILSS/IFSS properties	Ref. and year
Plasma	CF/PEI, CF/PEEK, CF/PES	55%	[103], 2011
Plasma	CF/epoxy	6–42 MPa	[110], 2001
Plasma	CF/epoxy	T50-PAN 20–45 MPa P100-Pitch 17–39 MPa P120-Pitch 6–38 MPa	[123], 2002
Plasma, HNO ₃	CF/ polybenzoxazine	CF _{plasma} 170% CF _{HNO₃} 300%	[124], 2000
Plasma	CF/epoxy	37–50 MPa	[125], 2011
Ammonia/ethylene plasma	CF/epoxy	111–146 MPa	[126], 2007
Aq. ammonia	CF/epoxy	24–39 MPa	[127], 2011
Plasma	CF/epoxy	30–45 MPa 50%	[128], 2000
			[132], 1998
			[133], 1987
Plasma	CF/epoxy	23–61 MPa	[131], 1996
Plasma	CF/PC	22–44 MPa CF/PC	[135], 2005
	CF/PA6	17–23 MPa CF/PA6	
Plasma air	CF/PPESK	70–80 MPa	[136], 2007
Plasma	PAN HMCF/PC	24–28 MPa HSCF/PC	[137], 2001
	Pitch HSCF/PC	12–46 MPa HMCF/PC	
Plasma	CF/PAA	34–45 MPa	[138], 2007
Plasma	CF/PC	12–54 MPa, CFP120/PC	[10], 2000
		20–21 MPa, Ctribb /PC	
		24–28 MPa, CFC320/PC	
Aqueous ammonia	CF/epoxy	23–31 MPa	[69], 2002
Polyhedral oligomeric silsesquioxane	CF/vinyl ester	18–22 MPa	[75], 2011
Oxy fluorination	CF/epoxy	55–65 MPa	[79], 2003
Anodization	CF/epoxy	24–76 MPa	[82], 1999
Air oxization		24–60 MPa	
Anodization	CF/epoxy	32–87 MPa	[17], 2000
Anodization 10% phosphoric acid	CF/epoxy	55–65 MPa	[83], 2000
Ozone with phenolic coating	CF/PAA	35–60 MPa	[84], 2008
Plasma polymerization	CF/Epoxy	10–30 MPa	[50], 1997
Acrylic acid	CF/epoxy	16%	[63], 2008
Acrylic acid γ -ray irradiation	CF/epoxy	15%	[19], 2008
HNO ₃	CF/PEI	36–60 MPa	[58], 2011
			[71], 2012
Praseodymium nitrate- γ -ray irradiation, praseodymium nitrate-aqueous immersion	CF/epoxy	13% 8.5%	[15], 2007
γ -ray irradiation	CF/epoxy	75–95 MPa	[186], 2007
γ -ray irradiation	CF/epoxy	37%	[150], 2007
Ar + ion Irradiation	CF/epoxy	5–12 MPa	[151], 2005
γ -ray irradiation	CF/epoxy	62–82 MPa	[152], 2003
γ -ray irradiation	CF/PEI	35–55 MPa	[153], 2010
			[155], 2011
			[156], 2011
Nano YbF ₃	CF/PEI	32–58 MPa	[167], 2011
			[168], 2012
Electrochemical Ozonize	CF/PA	CFElec.chem./PA-16–42 MPa CFElec.chem/epoxy – 37–87 MPa CFozonize/PA – 16–38 MPa CFozonize/epoxy – 37–42 MPa	[92], 1997
Intermittent Electrochemical Electropolymerization	CF/Phenol	Surface 109–142 MPa, bulk 75–134 MPa	[94], 2005
O ₃ Treatment	CF/epoxy	135%	[96], 2008
H ₂ O ₂ Treatment in supercritical water	CF/PA6	60%	[161], 2008
Cryotreatment, Plasma, acid	CF/epoxy	63–100 MPa	[162], 2009
MWNT, CVD	CF/PA6	CF _{unt} – 8.8 MPa CF _{cryo} – 9.5 MPa CF _{plasma} – 9.3 MPa CF _{acid} – 10.2 MPa	[165], 2011
MWNT, CVD, ICVD	CF/PMMA	26%	[195], 2010
	CF/epoxy	175% 71%	[197], 2011
			[198], 2009
MWNT electrophoretic	CF/epoxy	30%	[205], 2007
MWNT, chemical grafting	CF/epoxy	150%	[208], 2009
MWNT, ultrasonic assisted electrophoretic deposition	CF/epoxy	68.8%	[209], 2012
			[210], 2012
MWNT/Cu nano particles, EPD	CF/epoxy	13%	[211], 2011
Graphene oxide, dip coating	CF/Epoxy	36%	[219], 2012

lab-scale success using established coating/sizing application technologies can be easily scaled up to large production.

The 'multi-scale' nanoparticles attachment on the fiber surface is an approved technique for improving fiber/matrix interface properties. In one way the fiber surface modification done with simple dip coating method by dipping the fiber in suspension containing nanoparticles/CNT/graphene in water, other way is the direct grafting of these nano additives on fiber surface by

deposition techniques, such as CVD/ICVD. Both the techniques have their advantages and limitations, for example latter is influential in improving the fiber/matrix interfacial adhesion strength but reduced the single fiber strength properties.

2.3.1. Nano particles modification

Rare earth particle attachment for carbon fibers surface modification were conducted by dip coating method. These particles

adsorbed on fiber surface, which enhance its chemical reactivity via incorporation of oxygenated functional groups: sulfonic, carbonyl, hydroxyl, carboxyl [184,185]. The selection of type and size of rare earth particles is an important criterion in improving the fiber/matrix adhesion properties. Nano rare earth coatings to fibers are effective as compared to micro coating due to their ability to provide higher surface area to volume ratio, which further acts as a driving force to enhance the interface strength. Nano YBF_3 coatings, due to highly electronegative F^- atom demonstrate enhanced surface reactivity of CF and improved interfacial strength and wear resistance properties of CF/PEI composites [167,168]. Surface physicochemical properties of CF altered with praseodymium nitrate rare earth and γ -ray treatment to carbon fibers. Oxygen content and praseodymium both influentially enhance fiber surface roughness. In comparison to rare earth immersion method, γ -ray treatment method for fibers surface modification was effective in increasing the interfacial strength properties of CF/Epoxy composites [15,186]. Micro sized Lanthanum chloride coating to CF, improved bending ($\sim 18\%$) and tensile ($\sim 14\%$) strength of CF/PTFE composites; marginal increase in flexural strength ($\sim 11\%$) of CF/PI composites along with wear resistance in dry and lubrication conditions [187,188].

2.3.2. Carbon nano-tube coatings for carbon fibers

The research on CNT grafting on CF surface is in its swing and well adopted for the interface modification of polymer based composite materials [166]. A key challenge in this regards is the homogeneous distribution of CNTs on the CF surface. The CNT coating for CF applied to electrodes for super capacitors, fuel cell electrodes and/or conductive layers in composite fabrication to boost fracture toughness and interfacial strength [177,189–191]. Different techniques for deposition of multi-walled CNT (MWNT) on CF such as; chemical vapor deposition (CVD), injection chemical vapor deposition (ICVD) [181,190–201] hot filament chemical vapor

deposition (HFCVD) [202] and chemical vapor infiltration (CVI) [203] as well as electrophoretic deposition (EPD) [204–211], coating by chemical/electrochemical grafting [212–217], and dendrimers [218] have been adopted by the researchers.

CVD is frequently used to modify carbon fiber surface [192–194], the nano-tubes layer grafting on CF increased fiber surface area and interfacial shear strength of CF/PMMA along with tensile and compressive strength of CF/epoxy composites [181,195–201]. However, the single fiber strength of fibers reduced marginally due to the adsorption of iron particles on the fiber surface [190–192]. The increased specific surface roughness and capillary action due to the MWNT grafting on carbon fiber surface, improved the interfacial properties of CF/epoxy composites. The fragmentation test suggests an enormous increase in IFSS due to the exact control on orientation and length of aligned CNT [197]. The tensile strength and modulus of CF/PP composites increased with vapor grown CNT on CF surface [198]. Using thermally evaporated CNT functionalized on woven carbon fibers, fracture toughness and fatigue durability of CF/epoxy composites improved almost 50% without compromising the structural stiffness [199].

EPD techniques for deposition of CNTs on conductive surfaces reviewed in details [204,205,207]. The techniques governed by motion of dispersing charged particles, which move towards the substrate under the applied electric field. The out-of-plane electrical conductivity and the ILSS enhanced for multi and single walled CNT deposited CF epoxy composites using electrophoretic technique [205]. Recently Guo et al. applied ultrasonically assisted electrophoretic CNT deposition on CF; the results showed increased single fiber tensile strength, Weibull modulus and IFSS of CF/epoxy composites. Ultrasonic aid to EPD process creates homogenous coating and reduces the adverse effect of water electrolysis on deposition quality [209,210]. Table 2 summarizes the different techniques for CF surface modification and their influence to enhance interface strength of CF/polymer composites.

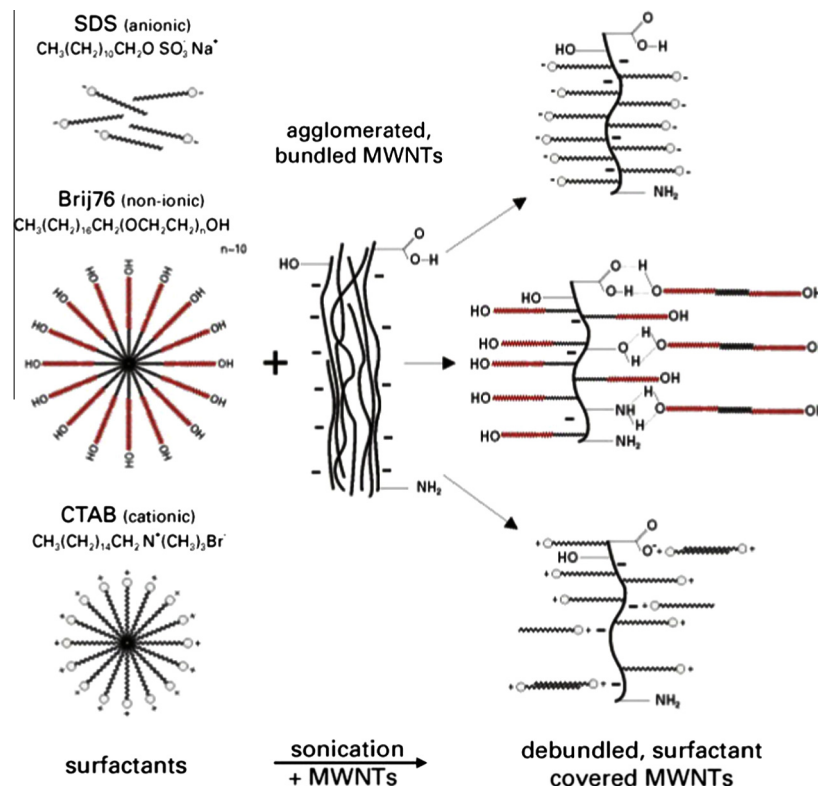


Fig. 6. Interaction between MWNTs and different surfactants during sonication. Chemical structures of the surfactants used are shown below the corresponding abbreviation (scheme not to scale) [221].

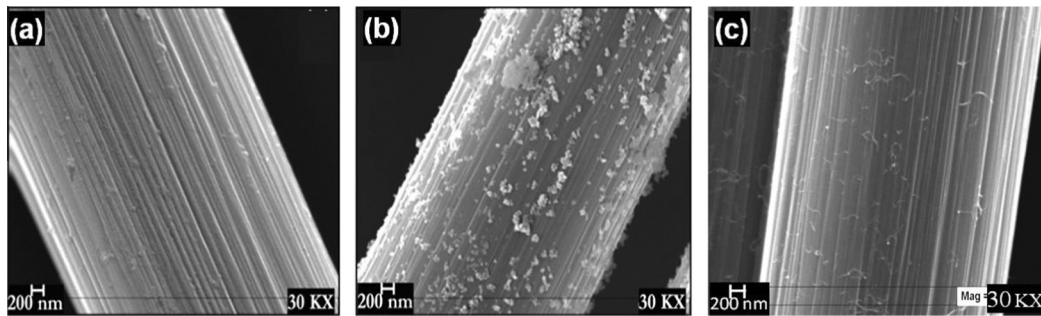


Fig. 7. SEM micrographs ($\times 30$ k) of carbon fibers: (a) without sizing, (b) sized with nano rare earth particle modification, and (c) sized with MWNTs.

The potential damage of CF during the CNT grafting/graphene (for example using CVD techniques) was potentially avoided by the use of other promising techniques (dip coating methods [212–217,219]). However, the exact control on the CNT orientation and alignment is an important criterion. With dip coating method the CNT/finish dispersions with defined surface charge were used to modify the fibers surface and also its composites with the polymer matrix [220]. The dispersibility of the CNT can be improved by covalent physical adsorption of surfactants. Sonication methods are commonly used to break and improve dispersions of entangled CNT by providing suitable mechanical energy. The multi-scale coating has been grafted on carbon fibers using hexamethylene diamine functionalized CNTs [212]. Grafting process increased the fiber weight, which indicates the CNTs intake onto the fiber surface. Fig. 6 represents the possible interaction mechanism between the different surfactants upon sonication [221]. Chemical grafting by nucleophilic substitution of functionalized CNT on to the CF surface improved the interlaminar properties of their polymeric composites. To enhance the

efficiency and processability of CNT coating, the process of chemical functionalization and non-covalent modification are employed, to improve their dispersion, either in organic solvents or in aqueous media.

The interaction of CNTs with fibers was promoted by chemical functionalization method but at the cost of affecting their intrinsic structural properties [208,214–216,222–225]. In contrast non-covalent methods including surfactant assisted solubilization [220,226], linear synthetic polymers [227] or bio-macromolecules (such as proteins [228] and celluloses [229–231]) wrapping, and aromatics π -stacking [232] well known to persevere nearly all the intrinsic features of CNTs. The quest of new modification methods for carbon fibers without compromising its strength is always a topic of interest for the researchers. Figs. 7 and 8 show the SEM and AFM images for sized with nano particles in comparison with unsized carbon fiber surfaces. The CNT/nano particle coating is a promising resolution for multifunctional polymer composite applications, but the selection of accurate technique and its optimization is still a matter of expertise.

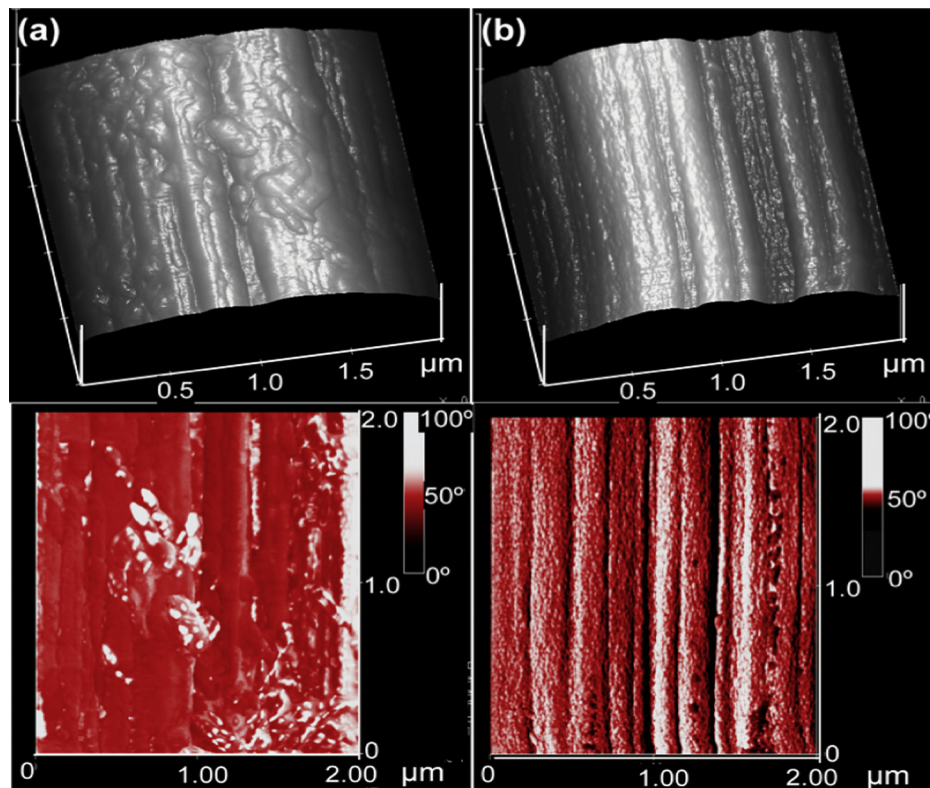


Fig. 8. AFM Tapping Mode images of carbon fiber surfaces (a) with sizing and MWNTs; (b) without sizing; top: 3-dimensional height images (Y axis scale: 600 nm), bottom: phase images.

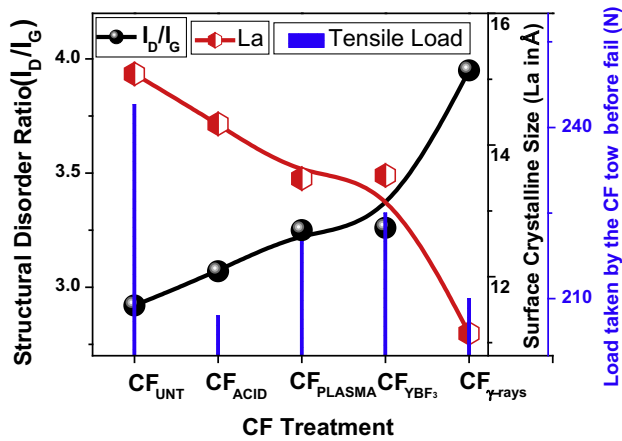


Fig. 9. Raman studies for untreated CF and various treatments (HNO₃, Plasma, Gamma ray, nano rare earth), shows variation of structural disorder parameter (I_D/I_G) and surface crystalline size (La) with optimized CF treatments [23].

3. Surface modification vs. fiber strength

The theoretical strength of graphite single crystals is far higher than the experimentally achieved carbon fiber strength (up to 20%) [233]. The estimated theoretical strength of carbon fiber would be around 100 GPa, whereas the commercially achieved is 7 GPa for high strength carbon fibers. The compressive strength of carbon fibers reaches only 50% of its tensile strength [234,235]. There are numbers of aspects, which affect the fiber and ultimate composites strength. The resin and fiber strength, fiber to stress alignment, fiber volume fraction, residual stresses, and stress concentrating effects are the main causes [119]. To overcome the deprived single fiber tensile strength, selective chemical modification and coating techniques needed to explore in depth [221]. The development of convenient methods for fiber surface modifications with optimized irradiation doses and conditions without sacrificing the longitudinal fiber strength is an essential confront for the advancement of high performance composites materials [16,236].

Advanced AFM mapping techniques have suggested new opportunities to determine property profiles across the interface [114,237,238]. The alteration in surface roughness and morphology of 'wet' treated carbon fibers surface quantified by increased etching on its surface (AFM studies, Fig. 3). Enhanced fiber surface energy led to increase its reactivity towards matrix, and endorses higher fiber matrix mechanical interlocking through a stronger interface [136]. The Raman spectroscopic studies (Fig. 9) for CF surface reveal the increased structural disorder parameter (I_D/I_G) and decreased surface crystalline size (La) due to various treatment methods which specifies the distortion in its graphitic structure as submitted by high resolution transmission electron microscopy for cold plasma treated carbon fibers [23,163]. The treatment method indubitably increases the fiber/matrix interfacial strength but at the worth of decreased single fiber strength properties. Majority of treatment methods distort fiber surface and increase its roughness by jurisdictionally introduction of specific functional groups in compatibility with the polymer matrix, for example; as compared to other epoxy systems generally do not strongly bond with carbonyl groups, hence for CF/epoxy composites, it is beneficial to minimize the carbonyl groups during fiber surface modification.

4. Conclusions

We reviewed the techniques based on 'wet', 'dry' and 'multi-scale' carbon fiber surface modifications, along with the summary of precise increment in interfacial strength properties of its

composites with different polymeric matrices. The 'multi-scale' modification methods by attaching CNT/nanoparticles at the CF surface are current and promising as compared to the formerly employed 'wet' and 'dry' methods. The progression of 'multi-scale' methods to analyze and to promote the fiber/matrix interfacial characteristics is continuing. It is in its establishment for the improvement of CF/matrix interfacial adhesions using multi scaled nanoparticles/CNT coatings. For carbon fiber reinforced polymer composites, interfaces behave with vast assortment in construction and properties. The information on the role of carbon fiber modification on strengthening the interface properties is inadequate. The studies on physical and mechanical properties of nano-scale interphase and underlying mechanism by using advanced characterization techniques, such as; atomic force microscopy based mechanical/electrical/thermal mapping; will perceptibly be a valuable addition. The investigations on molecular rearrangement in interfaces during CF-CNT/nano-particles network formation and its potential applications in composite form is an area of interest. It is required to explore and put emphasis on CF-CNT network and its characterization with advanced tools in materials science. One open question is related to the exploration of new modification methods for carbon fibers without compromising its strength.

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