



A review on carbon fiber-reinforced hierarchical composites: mechanical performance, manufacturing process, structural applications and allied challenges

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Abstract

The utilization of carbonaceous reinforcement-based polymer matrix composites in structural applications has become a hot topic in composite research. Although conventional carbon fiber-reinforced polymer composites (CFRPs) have revolutionized the composite industry by offering unparalleled features, they are often plagued with a weak interface and lack of toughness. However, the promising aspects of carbon fiber-based fiber hybrid composites and hierarchical composites can compensate for these setbacks. This review provides a meticulous landscape and recent progress of polymer matrix-based different carbonaceous (carbon fiber, carbon nanotube, graphene, and nanodiamond) fillers reinforced composites' mechanical properties. First, the mechanical performance of neat CFRP was exhaustively analyzed, attributing parameters were listed down, and CFRPs' mechanical performance barriers were clearly outlined. Here, short carbon fiber-reinforced thermoplastic composite was distinguished as a prospective material. Second, the strategic advantages of fiber hybrid composites over conventional CFRP were elucidated. Third, the mechanical performance of hierarchical composites based on carbon nanotube (1D), graphene (2D) and nanodiamond (0D) was expounded and evaluated against neat CFRP. Fourth, the review comprehensively discussed different fabrication methods, categorized them according to performance and suggested potential future directions. From here, the review sorted out three-dimensional printing (3DP) as the most futuristic fabrication method and thoroughly delivered its pros and cons in the context of the aforementioned carbonaceous materials. To conclude, the structural applications, current challenges and future prospects pertinent to these carbonaceous fillers reinforced composite materials were elaborated.

Keywords Mechanical performance · CFRP · Carbon nanotube · Graphene · 3D printing · Hierarchical composite

Abbreviations

0D Zero-dimensional
1D One-dimensional
2D Two-dimensional

3DP Three-dimensional printing
ABS Acrylonitrile butadiene styrene
CCF Continuous carbon fiber

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CCFRP	Continuous carbon fiber-reinforced polymer composite
CFs	Carbon fibers
CFRP	Carbon fiber-reinforced polymer composite
CNTs	Carbon nanotubes
CS	Compressive strength
EPD	Electrophoretic deposition
F-CNT	Functionalized CNT
FDM	Fused deposition modeling
FGO	Functionalized graphene oxide
FM	Flexural modulus
FRP	Fiber-reinforced polymer
FS	Flexural strength
FVF	Fiber volume fraction
GF	Glass fiber
GFRP	Glass fiber-reinforced polymer composite
GO	Graphene oxide
GNP	Graphene nanoplatelet
IFSS	Interfacial shear strength
ILSS	Interlaminar shear strength
IS	Impact strength
KF	Kevlar fiber
KFRP	Kevlar fiber-reinforced polymer composite
MWCNT	Multi-walled carbon nanotube
ND	Nanodiamond
PA6	Polyamide 6
PA66	Polyamide 66
PC	Polycarbonate
PEEK	Polyether ether ketone
PLA	Poly(lactic acid):
PP	Polypropylene
PVA	Poly (vinyl alcohol)
rGO	Reduced graphene oxide
RTM	Resin transfer molding
SCF	Short carbon fiber
SCFRP	Short carbon fiber-reinforced polymer composite
SWCNT	Single-walled carbon nanotube
TM	Tensile modulus
TS	Tensile strength
VARTM	Vacuum-assisted resin transfer molding
VGCNF	Vapor phase-grown carbon nanofiber

1 Introduction

The advent of the cutting-edge engineering era has bound researchers to develop advanced materials with enhanced properties. Recently, composite materials, especially carbon fiber-reinforced polymer composites (CFRPs), are continuously ousting different orthodox metal and metallic alloys owing to their possession of low specific gravity, better strength, higher stiffness, facile fabrication process, higher

corrosion resistance, improved fatigue resistance, extended life cycle property and most importantly convenient-lightweight structure [1–7]. Design flexibility, part consolidation propitiousness and multi-functionalities are yet other incentives that cannot be overlooked [8, 9]. That is why, since their first commercial utilization back in 1960, CFRPs are resonating a seismic effect around the globe in structural applications that run a gamut from aerospace to sports equipment. The global market of CFRP is projected to reach \$ 32 billion by 2025 [10]. CFRP consists of two constituents; a polymer matrix, either thermoplastic or thermoset, and carbon fiber (CF) as reinforcement [11]. In between the two constituents lies a three-dimensional interphase region having discrete characteristics. In addition, a two-dimensional construction marks the contour between these constituents named as interface [12]. Figure 1 portrays a schematic illustration of a CFRP structure.

The primary goal of a CFRP is to create a lightweight material with sublime mechanical traits that individual ingredients cannot achieve. The morphological structure and the mutual interaction in the form of hydrogen bond and van der Waals force between the interface of the reinforcing material and the matrix exert influence over these improved properties [13, 14]. This interaction may revamp the composite's mechanical property when binding energy between the CF and the polymer takes over the resultant cohesion energy of all the individual constituents. For this, the constituents must be physically dovetailed, chemically inert and thermally parallel [15]. These are achieved partly by filler CF which bears the load along with the polymer matrix which secures the fiber and shifts the load towards it. That being said, CFRP is met with difficulties such as delamination, weak interface, low damage resistance to impact, poor wettability and fatigue resistance, inferior strain, mismatch of surface energy between matrix and reinforcement and hence uncompetitive traverse properties [11, 16, 17].

To encounter these issues, attempts were made to employ vapor phase-grown carbon nanofiber (VGCNF) as reinforcement with a diameter of less than 200 nm and seemingly better attribution of mechanical properties than CFRP [18]. However, the disadvantage of VGCNF was its curvy structure which limited the amount of fiber volume fraction

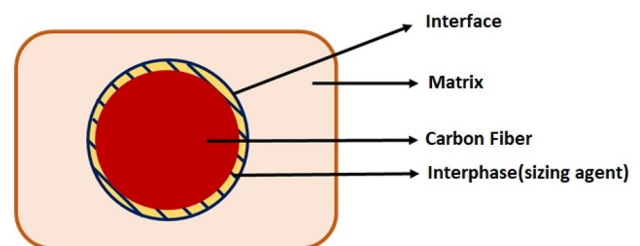


Fig. 1 Schematic illustration of CFRP [12]

(FVF) and homogeneous distribution of resin in composite [19]. Therefore, inevitably it was soon overshadowed by the decisive application of different carbonaceous nanofillers. The current review framed one-dimensional (1D) CNT, two-dimensional (2D) graphene and zero-dimensional (0D) nanodiamond as the most prevailing carbonaceous nanofillers for modifying neat composites' mechanical properties [20]. However, another compelling concept termed nanobifiller will mostly remain out of the scope of this study. In addition, the discussion of hybrid composite will be circumscribed to CF-based fiber hybrid composite, which is a combination of two different reinforcing fibers in a polymeric composite with CF in common.

CNT is the futuristic sibling of CF which was first discovered back in 1991 [21]. Since then, it has forayed into enhancing CFRPs' mechanical characteristics by being a nanofiller in hierarchical composite or three-phase composite (nanofiller, fiber and matrix) [22]. Unlike the orthodox CFRP, hierarchical composites can foster both out-of-plane and in-plane mechanical properties of the composite. This stunning improvement of mechanical properties in hierarchical properties is pivoted upon nanofillers unprecedented aspect ratio, lightweight structure, higher surface area and other noteworthy mechanical characteristics [23, 24]. In hierarchical composite, the minute nanoscale-based nanofiller is combined with regular microscale-based CF reinforcement either by dispersing in the matrix or attaching with CF. That is why it is also known as a multiscale reinforcement structure since a resultant reinforcing effect is produced by the nanoscale reinforcing of carbonaceous nanofiller and microscale reinforcing of CF [25]. Graphene and its associated family members have also spread their wings to harness their nifty integral properties for the sake of mechanical properties improvement of hierarchical composite. Graphene, whose individual existence was first discovered in 2004 by mechanically separating graphene sheets from natural graphite [18]. It is sometimes considered a better nanofiller than CNT because of its high in-plane stiffness, larger surface area from the wrinkled texture of the surface, convenient surface modifiability, bulk production facility at room temperature and lower cost of production [26–28]. Regardless of all the ifs and buts, the application of these carbonaceous nanofillers has gained momentum due to their ability to redress the weak interaction between constituent CF and polymer matrix without supplementing the volume of composites [29].

Over the past 2 decades, numerous reviews have individually summarized mechanical properties at different fronts of carbonaceous reinforcement-based polymer matrix composite such as conventional CFRP [14], fiber hybrid composite [30], hierarchical composite based on CNT [25] and graphene [27] and carbonaceous nanodiamond-based two-phase nanocomposite [31]. However, there remains

no consolidated review paper dissecting, substantiating and then critically assessing the mechanical properties of all these successful materials fronts. Therefore, breaching this research gap by collating these matters into a unified article and critically reviewing them is a worthwhile effort. This review takes a holistic approach to assess the mechanical properties of carbonaceous fillers reinforced polymer composites and their state-of-the-art manufacturing process. Their ubiquitous structural applications, along with the potential challenges, are also underscored. It is anticipated that this research will equip readers with the necessary knowledge, systemic landscape and novel perspectives to design complex carbonaceous reinforcement-based polymer matrix composite structures with enhanced mechanical performance.

2 Principal parameters that control the mechanical performance of CFRPs

The mechanical properties of composites revolve around several aspects. At the outset of this, the followings are considered to be the most influential parameters:

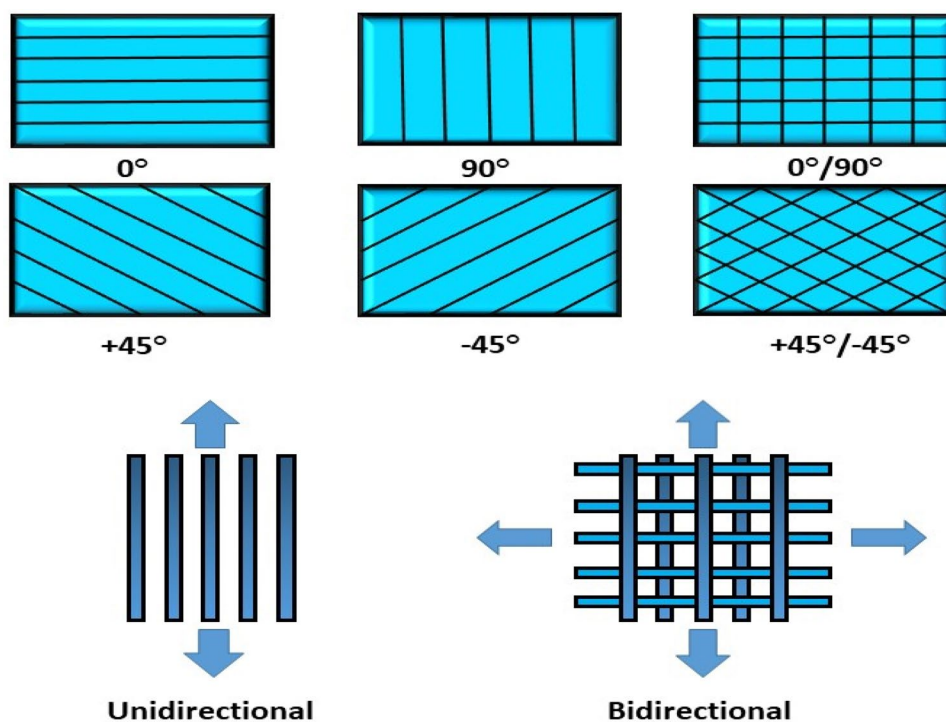
- The void content of the composite structure which negatively affects mechanical property [32].
- Fiber breakage and loading of fiber. Generally, fiber breakage is equivalent to fiber loading [32].
- Aspect ratio (length to diameter) of the reinforcing materials. A lower diameter leads to a higher aspect ratio, which maximizes the transfer of load [33].
- Dispersion homogeneity and interfacial stress shifting [22].
- Chirality and distinguishing structure of nanofiller [33].
- FVF in the composite [34]. There is a linear alliance between FVF and composite's mechanical property [35]. Unfortunately, FVF is constrained by the manufacturing method. For instance, in fused deposition modeling (FDM), any attempt to go over 40~50% of FVF offshoots nozzle clogging [36].
- The degree of crystal plane alignment along the fiber axis [15].
- The waviness of the fiber [37].
- Interaction between reinforcement and matrix which is steered by multiple physical and chemical properties. Based on the study of past decades, Table 1 illustrates the physical properties of carbon fiber along with different carbonaceous micro- and nanofiller reinforcements, including VGCNF, single-walled carbon nanotube (SWCNT), multi-walled carbon nanotube (MWCNT), graphene, graphene oxide (GO) and nanodiamond. Diameter, aspect ratio, surface area, tensile strength and tensile modulus were mainly compared here. The aspect

Table 1 Physical properties of different carbonaceous micro- and nanofillers

Materials	Diameter (nm)	Aspect ratio	Surface area ($\text{m}^2 \text{g}^{-1}$)	Tensile strength (GPa)	Tensile modulus (GPa)
CF	7300 [41]	440 [41]	0.7 [42]	3.8 [41]	227 [41]
VGCNF	50–200 [43]	250–2000 [43]	156 [44]	2.92 [43]	240 [43]
SWCNT	0.6–0.8 [43]	10,000 [43]	415 [45]	50–500 [43]	1500 [43]
MWCNT	12.5 [46]	8,000 [46]	~165.6 [47]	10–60 [48]	600 [49]
Graphene	10 [50]	35,000 [51]	~2630 [52]	130 [26]	1000 [26]
GO	1.2 [53]	3200 [54]	~2391 [55]	112 [56]	~207.6 [57]
ND	2–8 [20]	–	450 [58]	100–150 [31]	900–1250 [31]

ratio and surface area of graphene are clearly higher than both SWCNT and MWCNT. The tensile strength and tensile modulus of graphene are also higher than MWCNT but almost similar to SWCNT. Nanodiamond has slightly better tensile strength and tensile modulus than graphene but has a much lesser surface area. GO, a functional derivative of graphene accounts for a considerably larger surface area than both CNT and ND. In addition, VGCNF outperforms regular CF due to its large surface area. The bond between these fillers and matrices is critical for the composite's performance. The interfacial shear strength (IFSS) and interlaminar shear strength (ILSS) can be used to quantify the mechanical interlocking between constituents. The greater the mechanical coupling between the constituents, the higher these values will be [38].

- Length of the fiber. At critical fiber length, the load shifted from the matrix towards the fiber is maximized in CFRP [39].
- Processing parameters (temperature, pressure, humidity) and type of compatibilizer and plasticizer for ramping up interfacial bonding between fiber and matrix [40].
- Stacking sequence and orientation of fibers [8, 12]. Figure 2 provides a glimpse of the different fiber orientations of CFRP. The strength and stiffness of CFRP depend on the proper design of layer orientations. In a unidirectional composite material, the fibers are stretched in one particular direction and strength and stiffness are also converged in that direction. For bidirectional orientation of the fibers, the mechanical properties will be distributed in both longitudinal and traverse directions. The layers should be configured to 0° , $\pm 45^\circ$ and 90° in response to axile, shear and side load, respectively [12].

Fig. 2 Different types of fiber orientations in CFRP [12]

- Fiber packing geometry which controls reinforcing effectiveness and hence mechanical property [28].
- The interaction between CF and manufacturing equipment's surface [15].

3 Mechanical performance of neat CFRP

The mechanical characteristics of polymer matrix have several intrinsic limitations which impair its use in different structural applications. To address these issues, CF can be incorporated with polymer either in short or continuous form, formally known as short carbon fiber-reinforced polymer composite (SCFRP) and continuous carbon fiber-reinforced polymer composite (CCFRP), respectively. Although CCFRP has conspicuously better mechanical properties from higher interfacial interaction and more streamlined orientation of fibers, SCFRP tips the balance owing to its reduced cost and convenient processing technique [59–61]. Quasi-static properties, which comprise tensile strength (TS), flexural strength (FS) and impact strength (IS), are the most vital attributes that need to be addressed during the assessment of the composite's mechanical property [62]. There exists a threshold region of FVF in the composite above which the mechanical traits of composite remain uninterrupted or sometimes undergo adverse transition, let alone resulting in further improvement [63]. The surge of fiber–fiber contact instead of fiber–matrix contact, disruption of the load distribution from matrix to fiber due to fiber agglomeration and the emergence of defective voids within the constituent fibers are responsible for this phenomenon [64]. According to the study of Ning et al. [64], optimum tensile strength, tensile modulus, toughness and flexural strength of thermoplastic-based CFRP can be found at 5, 7.5, 0 and 5% of CF content, respectively, when CF length was 150 μm . But this may vary depending on specific parameters.

3.1 Tensile and flexural strength of CFRP

Considering the composite's properties, Matsuzaki et al. [34] depicted that tensile strength and tensile modulus of composite with continuous carbon fiber (CCF) as the reinforcement and polylactic acid (PLA) as the matrix can be, respectively, 435 and 316% of PLA only structure which are testimonial of proverbial adhesion between CF and PLA matrix. Whereas, the result for the tensile strain to failure of CFRP was diametrically opposite to this, having just 67% of PLA structure mainly for entrenched brittle nature of CFs that will be broadly discussed shortly. Furthermore, Zhang et al. [61] presented a model involving additional attachment of pressure during three-dimensional printing (3DP) of CCFRP. The experimental results predicted that tensile strength and flexural strength could be substantially

increased by 1508 and 585%, respectively, compared to PLA, which is a telltale of CFRPs superiority unfolded by tweaking the process. The higher flexural strength of CFRP originates from the retardation of matrix cracking and delamination by the transition of the fracture mode from compressive to tensile [4]. As a result, in composite, first matrix undergoes fracture by tensile stress followed by fiber pull-out resulting in staunch resistance [65]. Regarding the tensile strength of CFRP, rampant fiber breakage hints at fiber dominant failure mode, which, unlike the matrix failure mode, fuels the seamless transition of load from matrix to fiber while minimizing fiber pull-out [66].

Besides, 40 times better tensile modulus and 3 times better tensile strength were unraveled for 6 CF specimens (6 layers CFRP + 4 layers nylon) than pristine nylon and 2 CF specimen (2 layers CFRP + 8 layers nylon), respectively, through Mark Forged invented 3D printer, presumably owing to the discontinuous reinforcement around the border of latter as they were printed with nylon, not by the CFRP [67]. Furthermore, Dickson et al. [63] hypothesized that 3DP of CF-reinforced with nylon-based matrix produced composites having both greater flexural and tensile strength than Kevlar fiber-reinforced polymer composite (KFRP) and glass fiber-reinforced polymer composite (GFRP), while all the other variables remained identical. This notion has been cemented by other experiments [68, 69]. Based on the findings of Dickson et al. [63], Fig. 3 compares the tensile and flexural strength of composites made of carbon, glass and Kevlar fibers reinforced with nylon matrix utilizing the FDM process. The tensile strength and flexural strength of CFRP were 198 MPa and 250.23 MPa, respectively, representing 21.21 and 44.44% higher TS and 33.74 and 57.39% higher FS than GFRP and KFRP, respectively. In addition to that, Li et al. [70] estimated that 3DP of PLA-based CFRP increases tensile and flexural strength by 185.71 and 11.32%, respectively, over pristine PLA. But interestingly, they found that

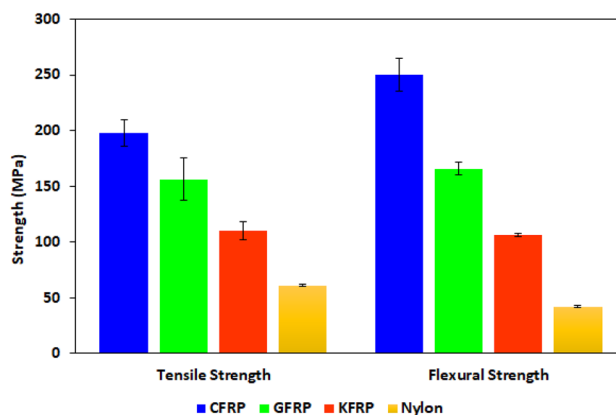


Fig. 3 Tensile and flexural strength comparison of CFRP with other high-performance fiber reinforcement-based composites [63]

by infiltrating PLA sizing substance as a matrix, even better tensile and flexural strength can be obtained, which were 225 and 194.33%, respectively, due to the higher stress transition between bundles of fiber. Table 2 delineates the reinforcing efficacy of CF and VGCNF with different thermoplastic and thermoset-based matrices along with their fabrication methods. Here mainly improvement of tensile strength, flexural strength, tensile modulus and flexural modulus through reinforcement were discussed. Improvement of properties through reinforcement means how the incorporation of reinforcing material (CF) in the matrix develops the mechanical property compared to the neat matrix phase by being transformed into a composite material. In composite materials, dynamics between reinforcement and matrix produce a synergistic effect and thus enhance the mechanical property.

Genel et al. [71] delivered striking findings by distinguishing composites' tensile and flexural properties with different fiber directions of CF reinforcement. It was shown that 0° orientation CFRP produces 22.3-, 15.9- and 4.37-fold higher tensile strength, tensile modulus and compressive strength (CS), respectively, for its relative ductile nature, in comparison to 90° orientation CFRP, which suffers brittle failure traits of matrix region from the increment of CF axis angle [72]. The research also clarified that woven CF-based reinforcement always has better tensile modulus, tensile strength and compressive strength than woven GF reinforcement-based composite. The compressive strength of a CFRP is vital for its structural applications. The micro-buckling of embedded fibers under the matrix is guilty of debilitating the compressive strength of CFRP [73]. Different types of matrix modifications are carried out as countermeasures, which will be discussed later. Apart from that, the higher tensile strength and lower coefficient of thermal expansion of CF than GF and KF yield better compressive strength of CFRP than both GFRP and KFRP [14].

From the findings of Table 2, it is evident that reinforcement, either in short or continuous carbon fiber form, always enhances the mechanical property unless disruption in the internal dynamic occurs accidentally [77]. Sometimes improvement of two properties, especially strength and ductility, become mutually exclusive. It means improving one will result in the downgrading of the other one [78]. Other than that, fabrication method, environmental condition (deposition tension, deposition temperature) and types of materials used have a significant impact on the improvement of properties.

3.2 Impact strength of CFRP

Impact strength occupies a special niche among CFRP structures' mechanical properties. Inept impact strength may usher unavoidable fiber breakage, delamination, matrix cracking and fiber pull-out in the composite's structure,

which eventually succumbs to having depleted residual strength and capacity of load carrying [35, 81]. De-bonding, delamination and matrix crack are likely related to shear rupture [66]. Primarily, the impact strength of CFRP can be construed through two forms of damage. Firstly, fiber prevailing damage caused by fiber breakage and pull-out. Second, matrix prevailing damage from matrix cracking [82].

Generally, failure mode involving cracking of matrix has lower potential impact strength than failure mode involving breakage of fiber since matrix cracking tilts more towards brittle failure than ductile [72]. Therefore, it sparks lower fracture energies in juxtaposition to heightened energy dissipation by ductile failure mode of the fiber. According to Hosseinzadeh et al. [83], CFRP reveals extraordinary performance under low velocity impact without causing any glitches. However, it is prone to collapse when confronted with a higher energy impact. Apparently, GFRP has higher impact resistance than CFRP because of its higher energy absorption and hence prolonged strain to failure as a reinforcement. Concurrently, higher flexural stiffness of CF coupling with its poor wettability results in lower impact resistance property [35]. Figure 4 demonstrates this issue. Surprisingly, CFRPs had impact strength of 57.5, 34.5 and 24.8 kJ/m², representing just 1.43, 1.72 and 1.1 times higher impact strength than nylon, PLA and PA12, respectively [35, 84, 85]. Similarly, while GFRC and KFRC had undergone 575.95 and 212.77% increment, respectively, than pristine matrix, CFRP witnessed barely 43.32% enhancement of impact strength [35].

To overcome these pitfalls of impact resistance and energy absorption capacity, a technique was devised by fabricating both CF and GF together, formally known as fiber hybrid composite. Hosseinzadeh et al. [83] proclaimed that here both CF and GF compensate for each other's intrinsic limitations and thereby fiber hybrid composite maintains proper behavior under both low velocity and higher energy impact. Simultaneously, this type of composite has considerable damage resistance coupled with tolerance. Nevertheless, similar to the tensile and flexural properties, woven CFRP has subsequently higher damage resistance to impact than unidirectional CFRP due to the incorporation of woven plies in upper and lower surfaces, which narrows down the vulnerability of crack formation and propagation [82].

3.3 Ductility and toughness of CFRP

There exists a prevailing notion that any increment of CF% in composite structure compromises its ductile nature and begets brittleness. Following this, Dickson et al. [63] found that, upon using CF as reinforcement, the susceptibility by the brittle failure of composite became dominating as strain values went as low as (≤ 0.1 unit), which is a complete aberration from the previous ductile nature of the matrix. This

Table 2 Mechanical performance of CF- and VGCNF-reinforced polymer composite materials along with their manufacturing methods

Reinforcement	Matrix	Matrix nature	Relevant properties increased by reinforcement	Manufacturing method	Remarks	References
CCF	Nylon	Thermoplastic	Flexural strength, tensile strength	3DP (FDM)	Porosity possessed a significant threat for 3DP-based composite and led to substantial strength loss	[63]
CF	Epoxy resin	Thermoset	Tensile strength, hardness, peak load, yield strength	VARTM	Superior mechanical properties of CFRP in comparison to GFRP	[74]
CF	Copolymerized acrylic	Thermoplastic	Flexural strength, IFSS	Compression molding	The flexural strength of the composite was doubled using HEAA (Hydroxyethyl acrylamide) functional copolymers	[4]
SCF	Acrylonitrile butadiene styrene (ABS)	Thermoplastic	Tensile strength, tensile modulus	3DP	Tensile modulus and strength surged ~700 and ~115%, respectively	[32]
CCF	Onyx (nylon based)	Thermoplastic	Fracture toughness	3DP	Optimization of the deposition tension and temperature can improve reinforcement effectiveness	[75]
CCF	Onyx	Thermoplastic	Compressive and flexural modulus	3DP	Reinforcement type and orientation have a salient impact on compressive and flexural modulus	[76]
SCF	Polycarbonate (PC)	Thermoplastic	Tensile modulus, flexural strength, flexural modulus, micro-hardness	FDM	The addition of SCF decreased the tensile strength rather than boosting it due to matrix failure from misaligned SCF	[77]
SCF	Polypropylene (PP)	Thermoplastic	Tensile strength and tensile modulus	Injection molding	Tensile strength and modulus increased 40.7 and 574.9%, respectively	[40]
CCF	Nylon	Thermoplastic	Tensile strength, stiffness	3DP	Much higher specific strength was achieved for CFRP than pristine nylon at little cost of weight	[69]
CCF	Onyx	Thermoplastic	Tensile strength, flexural strength	3DP	The inclusion of carbon layers increases the strength but at the same time decreases ductility and precipitates crack propagation	[78]
VGCNF	PP	Thermoplastic	Tensile strength, tensile modulus	Injection molding	Tensile strength and tensile modulus were doubled and quadrupled, respectively, for CFRP starkly juxtaposed with a neat matrix	[79]
VGCNF	ABS	Thermoplastic	Tensile strength, tensile modulus, stiffness	Compression molding	VGCNF restricts the polymer's mobility when incorporated into a composite	[80]
CCF	Nylon	Thermoplastic	Elastic modulus	3DP	Elastic modulus of CFRP was 4.25 times and 5.78 times higher than KFRP and GFRP, respectively	[68]
CCF	ABS	Thermoplastic	Flexural strength, tensile strength, tensile modulus, flexural modulus	3DP	ILSS was just 2.81 MPa indicating poor interface characteristics of 3D-printed parts	[65]
CCF	PLA	Thermoplastic	Tensile strength, tensile modulus	3DP	Fiber pull-out caused a fracture, which glorifies the need for interphase modification	[34]

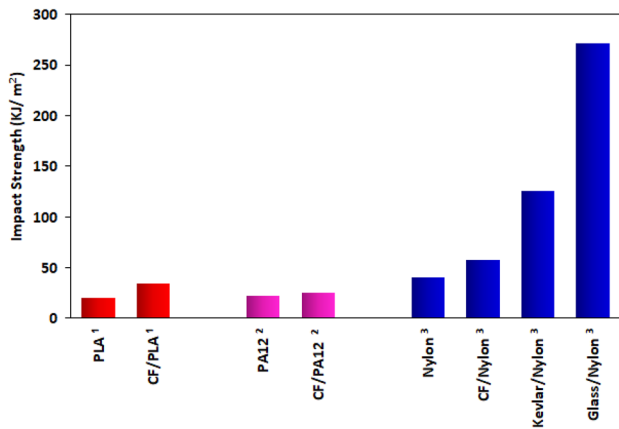


Fig. 4 Graphical comparison of CFRPs impact strength with: PLA¹ matrix [84], PA12² matrix [85], different high-performance fiber reinforcement-based composite³ [35]

finding was reiterated and bolstered by another study based on the composite of SGF/SCF/PP [39]. What happens is that inclusion of CF in the polymeric matrix triggers crack formation upon application of load. With time, this turns into crack propagation, and a chain reaction rages through all the cracks in the vicinity resulting in the brittle nature of CFRP [77]. Figures 5 and 6 depict the co-relation between CF% in composite and its brittle nature. For example, in Fig. 5, five different fiber ratio samples were utilized with a fixed FVF of 25% for all the samples. From sample 1 to sample 5, with the decrement of CF%, the ductile nature of composite got more pronounced. Hence, sample 1 composite had the highest brittleness as it entirely consisted of CF.

Furthermore, Karsli et al. [86] suggested that morphing of ductile CFRP into brittle CFRP during increment of

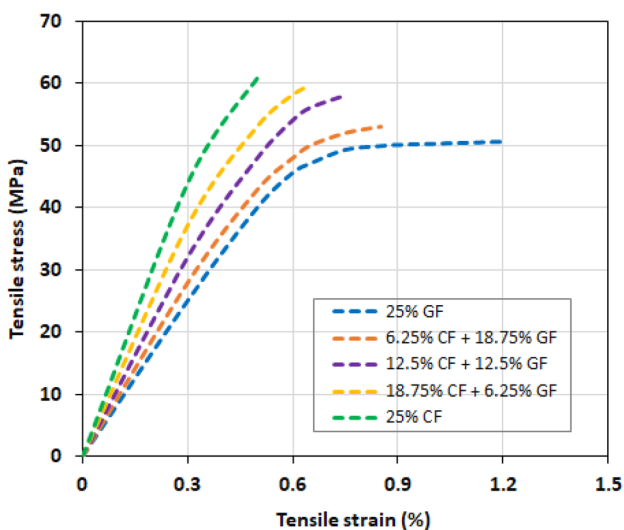


Fig. 5 The tensile stress–strain curve for SGF/SCF/PP composite depicting the brittle characteristics of CFRP [39]

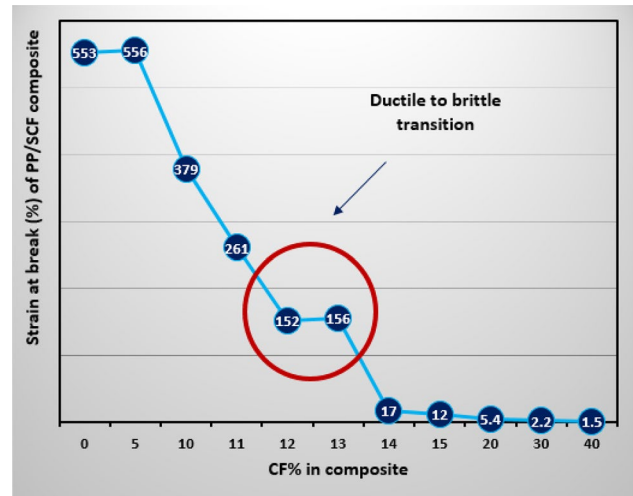


Fig. 6 Relationship of CF% with respect to elongation% in CFRP [40]

CF% encounters an erratic shift at a particular FVF of CF. According to Junaedi et al. [40], as can be seen from Fig. 6, this threshold region was somewhere between 10 and 15% of SCF, where CFRP strain at break decreases drastically from 379 to 12% owing to the disruption of ductile PP matrix continuity from the overwhelming presence of CF and also from its specific concentration regime. More precisely, at 12–13% FVF of CF, the ductile to brittle transition happened for this PP/SCF composite.

Subsequently, Dickson et al. [63] found that CFRP has a lower elongation at break, which explains why it has a lower flexural toughness than KFRP and GFRP. The flexural toughness of GFRP appeared to be the highest. This presumption is pertinent to Goh et al. [66], who claimed that GFRP has 1.19 times higher elongation before rupture than CFRP when nylon matrix is used, which is evident for GF having higher naturally scaled up flexibility than CF. This lower toughness is understandably stemmed from the sudden development of horizontal cracks without necking owing to the tensile rupture [66]. Figure 7 represents a scenario of how the inclusion of CF decreases the toughness of the CFRP. It can be seen here that increment of carbon fiber to 5 and 10% reduces the toughness by about 19.33 and 42.83%, respectively, compared to the 3% carbon fiber in composite mainly for initiation of cracks.

Given these points, it is evident that, although tensile and flexural strength with their respective modulus proportionally increases with the increment of CF% in composite, ductility and toughness give contrasting results by decreasing with the increment of CF% in the composite.

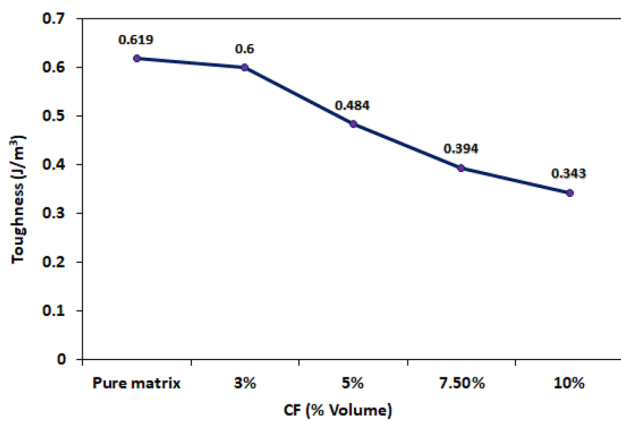


Fig. 7 Influence of CF% on the toughness of CFRP [77]

3.4 Proper selection of polymeric matrix for the higher mechanical performance of CFRP

Previous studies have bolstered that matrix and fiber need to be impeccably interlocked in the composite structure. The polymeric matrix is distinguished into two forms; thermoplastic and thermoset. Amidst the worldwide consumption of polymer matrix, the share of thermoset and thermoplastic are 63 and 37%, respectively [13]. Selecting the perfect utilitarian matrix is a rudimentary practice for generating the utmost possible mechanical properties of CFRP. Thermoplastic matrices are known to have higher fracture toughness and crack growth which aid in the load-bearing function of the structural object. Subsequently, using the thermoplastic matrices is advantageous in terms of recyclability, processing time, ductility and cure reaction. On the other hand, thermosetting polymers are known for their higher modulus, adhesion and dimensional stability. Because of the cross-linking feature, thermoset matrices also have higher mechanical strength, excellent parts design flexibility and efficient resin impregnation than thermoplastic matrices [14, 87, 88].

Regarding the nature of different matrices, PP, a thermoplastic-based matrix, often has a lower modulus of elasticity, which is commonly cited as a critical factor in CFRP's flexural strength. The study by Kishi et al. [4] opined that any copolymerization venture of the matrix via functional copolymers assists in tailoring the mechanical properties of the weak fiber–matrix interface. PLA is a mentionable biodegradable thermoplastic polymer with staggering mechanical properties while having a considerably lower melt temperature that is a very commonplace matrix with CF nowadays [70]. Similarly, thermoplastic-based nylon polymer has arrested attention due to its astounding tensile properties and trouble-free processability, which can be later rendered into CFRP [89]. In addition to that, there has been a prevailing practice of using thermoset-based epoxy resin

owing to its ease of compatibility and processability with CF and for possession of excellent mechanical properties [16].

Other than these, polymers such as thermoset-based phenolic, polyurethanes and thermoplastic-based ABS, PP, polyether ether ketone (PEEK), polyetherimide, polyphenyl sulfide and polyethersulfone are widely used with CF [14, 64]. Among the thermoplastic polymers; PLA, ABS, PEEK, PVA and PA 6 are suitable for the modern FDM-based 3DP method [90]. Besides copolymerization, sometimes necessary conclusive steps are taken to increase the functionality of the pristine matrix of CFRP, such as incorporating thermally expandable microsphere to the thermoplastic matrix for increasing the tensile and compressive strength, reinforcing epoxy resin by rigid nanoparticles for higher compressive and flexural strength and tuning polyphenylene sulfide-based thermoplastic matrix for higher flexural strength of CFRP [73, 91].

3.5 SCFRTP mechanical properties: a new perspective

The research on the mechanical properties of randomly oriented short carbon fiber-reinforced thermoplastic composite (SCFRTP) was started back in 1990 [92]. These discontinuous composite structures are known for their excellent formability and stiffness, cost-effectiveness, easy processability and other noteworthy mechanical characteristics like reducing the considerable weight of parts. On the other hand, the production of CCFRP is highly expensive and not suitable for large-scale production due to low productivity [93]. Besides, unlike the SCFRTP, commercial fabrication methods such as injection and compression molding cannot be utilized for CCFRP production. In addition to that, although CCFRP has superior mechanical performance over SCFRTP, they are also incurred with the inconvenience of constrained geometries with minimal curvatures. For these reasons, SCFRTP is readily transformed into high-cycle complex geometric parts at a high production rate, allowing them to be used in different structural applications [94, 95]. Consequently, this results in increased process efficiency. It is equally important to mention about environmentally friendly nature of the SCFRTP. Utilization of recycled carbon fiber, reduction of structure weight to achieve fuel efficiency and decreasing the carbon footprint in the environment are some points to reflect its environment friendliness [96].

According to the study by Kiran et al. [97], the application of nickel coated SCFRTP can increase the tensile and impact strength up to 68 and 10%, respectively, compared to the untreated matrix. The relatively rough surface of the SCF provides resistance against distortion. Moreover, according to the quantitative analysis through image-based technique by Pei et al. [98], the spatial geometry of SCFRTP and CCFRP contains straight and curved fibers, respectively.

Wan et al. [92] have described the curved section as the weakest point of the composite structure, which is susceptible to delamination from stress concentrations. As a result, failure mode breaches through this weakest resistance path of CCFRP and transmitted towards both the traverse and longitudinal direction. Due to this weakest-link phenomenon, sudden fracture occurs in many instances of CCFRP which is highly unlikely for SCFRTP. Despite of all these benefits, one of the major disadvantages of SCFRTP is their high variability behaviors and hence unavoidable lower load-bearing properties which is of paramount importance from mechanical performance perspective of composite structure. The fiber dimension is an important contributor in the load transfer efficacy between the fiber and the matrix. To confront this issue, researcher has come with the idea of “hybrid fiber architecture” that integrates the performance of CCF and the formability of SCF. Currently, there are numerous researches being conducted on synergistic behaviors, interface behaviors and progression of failure mode of hybrid fiber architecture [94]. Nevertheless, it can be said that SCFRTP materials are increasingly becoming more popular due to the perfect trade-off between mechanical performance, environmental impact and cost.

4 Mechanical performance of different carbonaceous composite

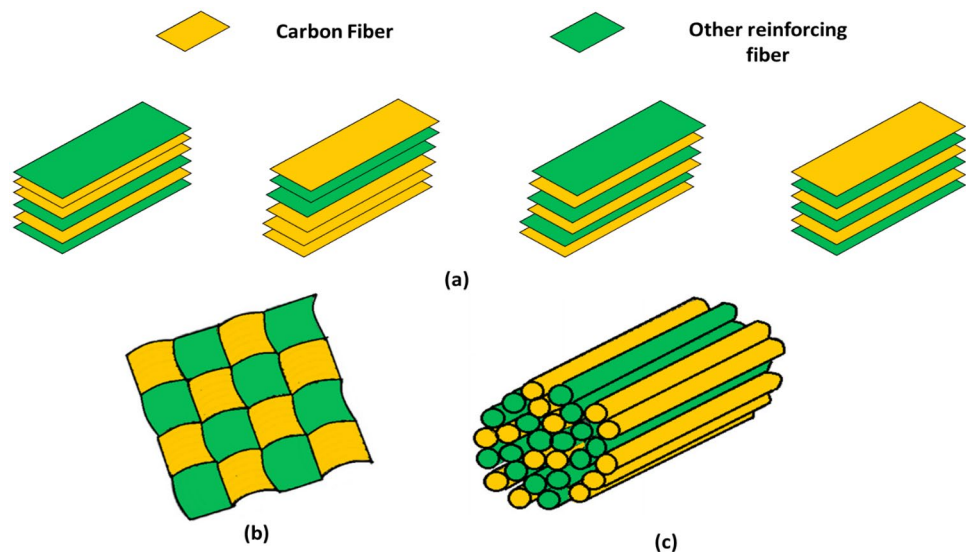
4.1 Carbon fiber-based fiber hybrid composite

The concept of “fiber hybrid composite”, which involves at least two fiber reinforcements with a sole matrix, has its roots in the provision of tailoring the impact strength, ductility and damage resistance of the CFRP at a minimal cost.

Among the two fiber reinforcements, one is low elongation CF alongside a high elongation fiber counterpart. Figure 8 illustrates three basic fiber hybrid composite configuration types: interlayer or layer-by-layer, intralayer or yarn-by-yarn, and intrayarn or fiber-by-fiber. In the interlayer arrangement, two different fiber layers are positioned over one another. This is the most uncomplicated and simplest method for hybrid composite fabrication. In intralayer arrangement, two different types of fibers are blended within the layers. Finally, when two different types of fibers are mixed within the fiber level, it is known as intrayarn hybrid arrangement. Apart from this, further complex hybrid configuration can be formed by combining any of these above two methods [30]. Since CFRP is prone to stress concentration due to the innate brittle nature of CF alongside its costly production, CF is often incorporated with other ductile reinforcements, mainly GF, through immaculate reinforcement across the primary load path, which creates CF-based fiber hybrid composite [8, 99].

Harish et al. [74] looked into the prospects of a fiber hybrid composite with both carbon and glass fiber as reinforcement. Interestingly, conspicuous superiority of CFRP (60% CF) was established over GFRP (60% GF) and hybrid composite (30% CF + 30% GF) during consideration of the mechanical properties, which is understandable from Fig. 9. Compared to fiber hybrid composite, CFRP had undergone a 30, 38.01, 35 and 23% surge of yield strength, tensile strength, peak load and hardness, respectively. Although the uptake of devising hybrid composite seems to impinge on mechanical performance, it can be outweighed if the improvement of ductility, impact strength and the trade-off between certain mechanical properties and cost are considered, which have also been endorsed by previous studies [30, 100]. The re-invigorated synergistic effect between

Fig. 8 Three basic fiber hybrid configuration: **a** layer-by-layer, **b** yarn-by-yarn, and **c** fiber-by-fiber [30]



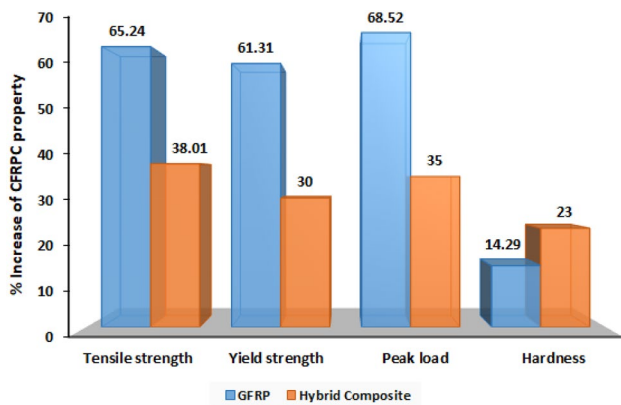


Fig. 9 Mechanical performance comparison of CFRP with GFRP and hybrid composite [74]

reinforcing constituents of the fiber hybrid composite is swayed by better fiber arrangement and reduction of void space [101]. Foremost, CF-based fiber hybrid composite seems to be the best possible solution to disentangle the perpetual conflict between the ductility and strength of the CFRP. That being said, although having different auspicious prospects, the major downside of fiber hybrid composite is

the difficulty it presents to repair [102]. Table 3 presents different prior studies related to CF-based fiber hybrid composite. It can be seen here that carbon fiber was hybridized with different fibers such as glass fiber, Kevlar fiber and different natural fibers. One significant challenge here is predicting the accurate mechanical properties of hybrid composite since they are not always pertinent to the rule of mixture because of the synergistic effect. Although a positive hybrid effect is certain in most instances, there may be some outliers and negative hybridization may happen from method induced damage. Degree of dispersion and inter-laminar bonding are appeared to be the most crucial factors for the hybrid effect [30].

4.2 CNT-based hierarchical composite

The impact of VGCNF reinforcement on increasing the mechanical properties of the composite has been validated by previous studies [43, 79, 80]. However, over time, this concept has been eclipsed by the ubiquitous application of carbonaceous CNT nanofiller through the production of CNT-based hierarchical composite or three-phase composite. The substantial aspect ratio of CNT, combined with its unique one-dimensional spatial configuration, truly sets

Table 3 Mechanical properties and fabrication methods of different CF-based fiber hybrid composites

Matrix	Brittle reinforcement/CF (x)	Ductile reinforcement (Y)	Fiber hybrid composite:CFRP:Y-reinforced composite	FVF in fiber hybrid composite (V_{FVF} : V_X/V_Y)	Fabrication method	References
Epoxy resin	Unidirectional plain weave CF	Chopped GF	TS = 1:1.29:0.77 CS = 1:1.31:0.49 ILSS = 1:0.85:0.95	–	Hand lay-up	[103]
Epoxy	Carbon fabric	Bi-directional Jute fabric	TS = 1:1.74:0.06 FS = 1:1.19:0.27 IS = 1:0.68:1.05	45 (49%/51%)	Hand lay-up	[104]
Epoxy resin	T300 CF 3 K	E-GF	TS = 1:1.61:0.76 CS = 1:1.52:0.68 FS = 1:1.12:0.54	45 (50%/50%)	Hand lay-up	[8]
Epoxy resin	Satin weave T-300 carbon fabric	Plain weave E-glass fabric	TS = 1:1.17:0.74 CS = 1:1.05:0.89	52 (47%/53%)	–	[105]
Epoxy	CF C120-3 K	Woven basalt fiber	FS = 1:1.20:0.6 FM = 1:1.16:0.55	62 (60%/40%)	VARTM	[99]
PP-natural rubber	PAN-based CF	Kenaf fiber	FS = 1:1.89:1.5	20 (50%/50%)	Compression molding	[101]
ABS	SCF	Kevlar fiber	FS = 1:0.95:0.81 FM = 1:1.08:0.75	–	3DP	[102]
Epoxy resin	Unidirectional CF	Unidirectional GF	TS = 1:1.14:0.68 FS = 1:1.21:0.68 Elongation (%) at max. stress = 1:0.91:1.84	48.8 (66.67%/33.33%)	Hand lay-up and vacuum infusion	[106]
PP	SCF	SGF	TS = TS _{CFRP} > TS _{hybrid} > TS _{GFRC} Failure strain = failure strain _{CFRP} < Failure strain _{hybrid} < failure strain _{GFRC}	25 (50%/50%)	Injection molding	[39]

it apart and makes it an excellent deal for this hierarchical composite setup [29, 33]. Homogeneous dispersion of CNT on CFRP stimulates a 3D network structure, which is responsible for bridging microcracks of the interface, crack deflection, effortless load transferring between the fiber and matrix, amplifying the interfacial bonding, increasing the surface area of the reinforcing fibers and squeezing the stress concentrations [26, 42, 107, 108]. All of this ultimately boiled down to a higher magnitude of interfacial bonding, interlaminar shear strength and improved toughness, the likes of which are not present in regular CFRP [26, 109].

Several researchers have shed light on the improvement of mechanical properties of CFRP by amending CF surface through grafting with CNTs [24, 107, 108, 110–114]. While compared to CF/PP composite, CNT-CF/PP composite can have a 104 and 64% improvement in tensile modulus and tensile strength, respectively [114]. Furthermore, Rahmanian et al. [110] investigated and sought out that grafting CNT on CF can cause 57 and 51% improvement of tensile modulus and flexural modulus, respectively, for SCF-based polymeric composite compared to 40 and 36% improvement of SGF-based polymeric composite. These findings justify superior tensile and flexural properties of CFRP than GFRP and simultaneously depict the staggering impact of CNT in the hierarchical composite. Figure 10 presents a scenario where fluorine functionalized CNT (F-CNT) was strategically deposited on CF by spraying technology and latter hierarchical composite was fabricated using VARTM. The experiment was conducted to understand the change in tensile strength and stiffness properties under a hierarchical composite setup. The addition of F-CNT caused covalent bond formation between active sites of treated CF and matrix, which subsequently generated stiff nanoscale teeth. This evolution of the fiber–matrix interface mitigated the delamination and cracking phenomenon resulting in 24 and 18% improvement of the tensile modulus and

tensile strength for 0.5% F-CNT which is discernible from Fig. 10 [111]. In their study, Rahmanian et al. [115] retrospectively found that, although up to 0.3% inclusion of CNT in CFRP increases the strength and modulus of multiscale composite, 0.4 and 0.5 wt.% of CNT happens to reduce the mechanical properties due to aggregation.

The study of Xiao et al. [112] and Zhang et al. [113] suggested that, among the existing method for grafting CF with CNT, aqueous suspension deposition is the most facile and finds better reinforcing efficacy than others due to its feasibility for large-scale production. In addition to a better throughput rate, this method rules out any complex chemical and equipment prerequisite and assures impeccable fiber surface, which prompts better interfacial property. Higher interfacial property can also be achieved by functionalization of the carboxyl group in CNT [116]. Zhang et al. [113] coated carboxyl-functionalized MWCNT on CF, employing both sizing and deposition methods together. The result was startling as a 32.06% increase of IFSS was observed in hierarchical composite compared to raw CFRP, which has its origin in two separate distribution states of MWCNT, triggering a reinforcement layer having gradient discrepancy of modulus, which paves the way for boosted load transfer. Besides compounding interfacial bonding strength, this functionalization is also responsible for stress dissipation and thwarting crack propagation [24].

Following the discussion, two fundamental means for modifying the fiber–matrix interface through carbonaceous nanofiller can be identified. They are either treating the surface of carbon fiber or modifying the matrix. Both cases are depicted in Fig. 11. As it happens that, for both instances, applying optimal CNT concentration is of utmost important since it dictates the mechanical interlocking's uniformity, stability and performance between the fiber–matrix interface [112]. Keeping that in mind, the proverbial superiority of CF-CNT/EP (fiber modification) over CF/EP-CNT (matrix modification) was reverberated by Zhao et al. [108] by showing the rigid dichotomy between the results, which are portrayed in Fig. 12. Interestingly, the TS and IFSS increment of the CNT modified fiber were 24.42 and 45.2%, respectively, in contrast to the 10.41 and 10.14% increment by CNT modified matrix [108]. The reason is deemed to be CNT's vital contribution to prevent stress concentration, pulling-out and debonding through layers of gradient interface on CF surface. On the contrary, the addition of CNT with epoxy stimulates a drastic rise of viscosity of the matrix, which obstacles its flow through reinforcements. As a result, it is axiomatic that the interfacial bonding of matrix with nanofillers remains inherently flawed, resulting in CNTs pulling out rather than fracture [117]. This is understandable from Fig. 12 as the numerical values for FS, FM, IFSS and ILSS were comparatively lesser for matrix modification than fiber modification.

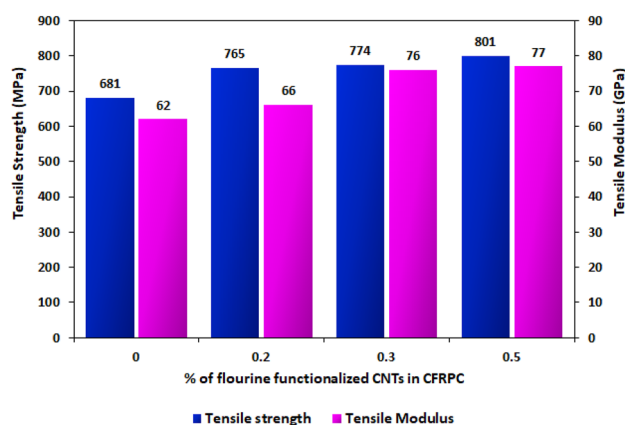


Fig. 10 Improvement of CFRP tensile properties by addition of functionalized CNT [111]

Fig. 11 Schematic illustration of CNT-based hierarchical polymer composite [108]

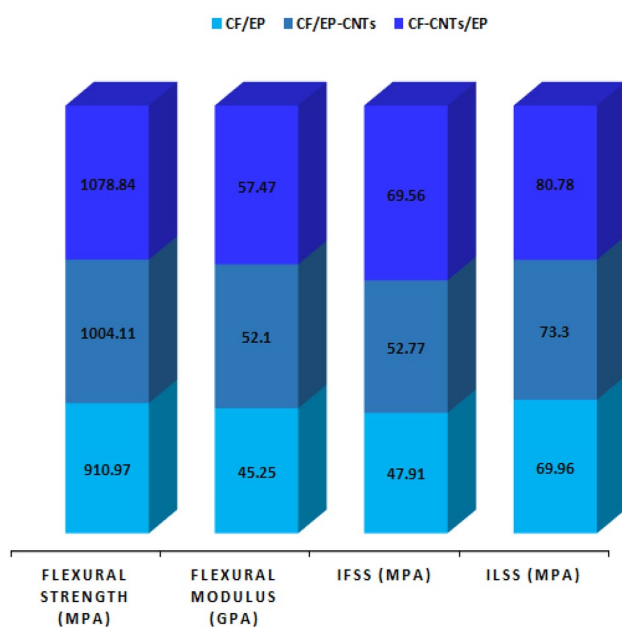
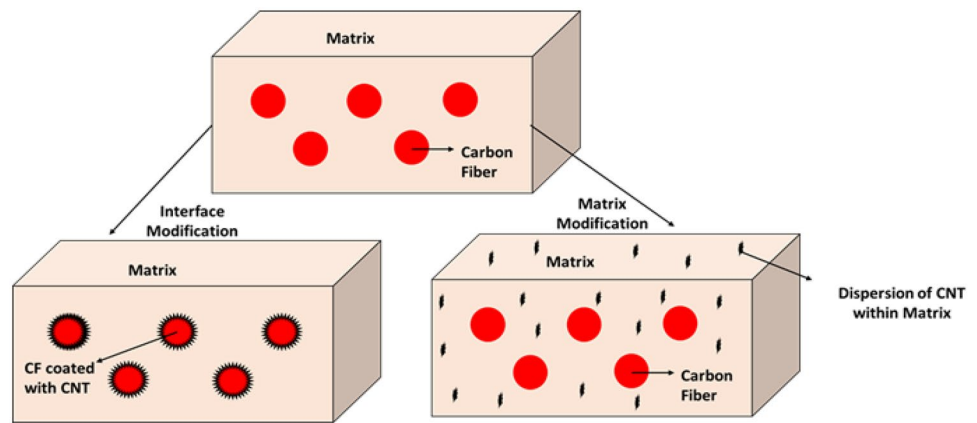


Fig. 12 Comparison of mechanical performance between CNT aided interface-modified hierarchical composite and matrix-modified hierarchical composite [108]

Eventually, applying different types of CNT nanofiller significantly reduces damage unfolding and consequently increases the durability and other mechanical properties of hierarchical composite [111]. However, CNT has a threshold value upon transcending which the mechanical properties of hierarchical composite become desensitized to any further improvement. It mainly arises from CNT's powerful inherent van der Waals force, which tends to entwine one another, forming a cable like shape. Hence, homogeneous dispersion becomes nearly impossible. Putting that aside, CNT provides decisive reinforcing efficacy in hierarchical composite, which covers a broad spectrum from low density to high fracture tolerance ability [43, 118].

In addition, the formation of voluminous fibers of CNT around CF by dipping and retracting in a CNT-based suspension has been a successful expenditure that leverages the composite's ingredients through enhanced agility and maximized anisotropy without compromising their strength and stiffness. Furthermore, the homogeneous distribution of CNT is a critical issue for improving reinforcing efficacy since any disorientation of nanotubes degenerates the composite's mechanical properties. Moreover, there is a debate around which one is better among single-walled carbon nanotubes and multi-walled carbon nanotubes. MWCNT is comparatively low cost, commercially available and provides leniency in dispersion, while SWCNT has a lower diameter, lower presence of impurities and provision of maximizing the interaction with matrix from highly crystallized structure [16, 22, 25]. Table 4, based on the study of the past decade, provides a glimpse of different CNT-based nanofiller efficacy in increasing the mechanical property of CFRP by forming hierarchical composites. Improved properties that were discussed here are tensile strength, flexural strength, impact strength, IFSS and ILSS. Apart from that, the fatigue life of the material was also maximized for this hierarchical composite setup. Most importantly, the addition of CNT caused both in-plane and out-of-plane improvements in mechanical properties.

4.3 Graphene-based hierarchical composite

Graphene is a carbonaceous 2D nanofiller with a very high aspect ratio that has lured a great deal of attention because of its remarkable mechanical properties [125]. It is sometimes regarded as the 2D counterpart of CNT but proven to have superior reinforcement efficacy than CNT. Pristine graphene itself cannot form a bond and thus indispensably exfoliates into functionalized sheets [126]. For instance, the existence of oxygen-containing functional groups in derivatives of graphene such as graphene oxide (GO) and reduced graphene oxide (rGO) provide

Table 4 Mechanical performance improvement of CFRP by incorporating CNT in hierarchical composite

Reinforcement	Matrix	Relevant CFRP properties increased by CNT	Composite manufacturing method	Remarks	References
CF-CNT	Epoxy resin	ILSS	VARTM	The addition of CNT did not compromise any in-plane mechanical performance	[109]
CF-SWCNT	Epoxy resin	Flexural strength, flexural modulus	Hand lay-up	Flexural modulus and strength were enhanced by 16 and 22%, respectively	[119]
CF-SWCNT	Epoxy resin	Impact resistance	Autoclave molding assisted by vacuum bagging	Impact resistance of modified CFRP was improved by 44 and 9.8%, respectively, at parallel and perpendicular to the fiber	[117]
CF-SWCNT	Epoxy resin	Impact resistance	Autoclave and hand lay-up with vacuum bagging	13 and 28% improvement of two different modes of fracture toughness	[16]
CF-MWCNT	Epoxy	ILSS, flexural strength	Hand lay-up aided by vacuum bagging	The critical rate of loading was 100 mm/min, at which the properties were maximized	[38]
CF-MWCNT	Epoxy	Flexural strength	Hand lay-up	The weight of Nickel, which was used as a catalyst for attachment of CNT, affected the purity of CNT and lattice size of graphite	[11]
CF-MWCNT	Phenolic resin	Flexural strength	Compression molding	Flexural strength and modulus increased at 1% content of MWCNT but decreased at 2%	[107]
CF-MWCNT	Epoxy resin	Flexural strength, tensile strength	Compression molding	The addition of MWCNTs above 0.25% caused moderate improvement of properties	[120]
CF-MWCNT	Epoxy resin	Fracture energy, tensile strength	Hand lay-up	The highest fracture energy and tensile strength were found for 1% wt. of MWCNT. Whereas best young's modulus outcome came at 0.5% wt. of MWCNT	[121]
CF-amine functionalized SWCNTs	Epoxy resin	Strength, stiffness, fatigue life	VARTM	Strength and stiffness have improved to a satisfactory level, but long-term fatigue life has improved dramatically	[122]
CF-amine functionalized MWCNT	Epoxy resin	Tensile strength, flexural strength	Filament winding	Beyond optimum MWCNT %, inter-face toughness gets declined, and so did TS and FS	[123]
CF-carboxylic acid functionalized MWCNT	Epoxy resin	IFSS, ILSS, tensile strength	VARTM	Resin toughening, interfacial friction and chemical bonding are liable for hierarchical composite's mechanical property	[124]

Table 4 (continued)

Reinforcement	Matrix	Relevant CFRP properties increased by CNT	Composite manufacturing method	Remarks	References
CF-acyl chloride functionalized MWCNT	PA66	Tensile strength, tensile modulus, elongation %	Compression molding	The hierarchical composite setup maximized the fatigue life	[17]

unrivaled dispersibility, solubility and stability [52]. GO is at the forefront of graphene-based materials due to the rolling out of outstanding mechanical properties, which are predominantly stemmed from its propensity towards homogeneous dispersion as a nanofiller [127]. The fused functional oxygen group in the structure is catalytic for this homogeneous dispersion, which gives ease to process, quells the propagation of cracks and improves the hierarchical composite's strength compared to the CFRP [128].

Previous studies have described how GO coating on CF surface plays a decisive role in increasing the surface roughness, area and energy [129], forming the covalent bond between CF and matrix [130], retarding the opening of cracks by impeccably bridging the microcracks on CF surface [131], restricting the drifting of a considerable volume of polymer branches by swelling the wettability and chemical bonding of CF and sometimes even by changing the surface morphology [132]. For these reasons, the multiscale reinforcement employing GO amplifies interfacial bonding between CF-matrix through enhanced mechanical interlocking, which substantiates the hierarchical composite's higher mechanical property. Besides, it becomes difficult to distort the hierarchical composite since more energy is required to pull-out CF from the matrix [131]. Furthermore, the implementation of functionalized GO (FGO) also ameliorates the interfacial bonding for most situations, if not in all situations. FGO harnesses immanent functional groups such as epoxide, carbonyl and amine. Thus, GO or FGO on CFRP can reduce the stress concentration and improve the bulk mechanical performance by boosting the properties such as IFSS, ILSS, tensile strength, flexural strength and others [133]. Table 5 illuminates different graphene affiliated nanofiller-based hierarchical composite's mechanical properties over pristine CFRP's mechanical properties. The improvement of hierarchical composite properties can widely vary. For instance, from Table 5, we found the increment range of tensile modulus can vary from 20.3 to 800. The improvement is dictated by the proper dispersion of reinforcing fillers up to the saturation point. The saturation point refers to the tipping point above which inclusion of GO in CFRP results in aggregation of GO nanosheets because of van der Waals force [131]. As a result, debonding energy among the constituents of the three-phase composite decreases and stress concentration becomes endemic, resulting in reduced mechanical properties. Sometimes, there can also be poor wetting of GO from its higher than optimal content %, further deteriorating the composite's property, let alone strengthening it [134]. It is also evident from Table 5 that among the different deposition methods of GO, the electrophoretic deposition method (EPD) is most prevalent because of its homogeneous dispersion, less susceptibility to agglomeration, gauging precise thickness and simple prolific deposition mechanism [126, 127, 132, 135].

Table 5 Mechanical performance improvement of CFRP by incorporating graphene-based nanofiller

Filler	Matrix	Graphene-based nanofiller	FVF%	Nano-filler vol.% ^a wt.% ^b	Composite manufacturing method	Nano-filler deposition method	Highest increase % of properties	References
T700 CF 12 K	polyphenylene sulfide	Graphene sheet	15	0.5 ^b	Injection molding	Solution mixing	IFSS: 20	[136]
Woven CF 6 K	Epoxy-amine	GO	34	0.5 ^a	Hand lay-up	EPD	ILSS: 34 FS: 14	[127]
UCF T700S 12 K	Epoxy resin	GO	40	0.1–0.5 ^b	Hand lay-up	Chemical grafting	TS: 22.4 TM: 800 FS: 76	[133]
PAN-based T300 CF 3 K	Polyurethane	GO	1	0.1–0.3 ^b	VARTM	EPD	IFSS: 74.4 TS: 46.4	[134]
PAN-based T700 CF 12 K	Epoxy resin	GO	–	0.25 ^a	VARTM	EPD	ILSS: 55.6	[135]
Pan-based unidirectional CF	Epoxy resin	GNP	66	3 ^b	Hand lay-up and autoclave molding	Continuous solution coating	ILSS: 19 FS: 51	[137]
SCF	Polyethersulfone	GO	12.5	0.05–1 ^b	Injection molding	Dip coating	TS: 12.06 YM: 31.6 FS: 15.5 FM: 31.2	[138]
Plain weave mat CF 3 K	Epoxy resin	Graphene carboxyl	–	1 ^a	Hand lay-up	EPD	FS: 9.6 ILSS: 22.9	[126]
Uniaxial CF 12 K	Epoxy resin	Thermally exfoliated GO	70	0.02 ^b	VARTM	Electro spraying	FM: 31.1 FS: 51.2 TM: 20.3 TS: 19.4 IS: 29.9	[129]
Carbon Fabric T700S CF 12 K	Epoxy resin	Partially rGO	14 layers	0.0007 ^b	VARTM	EPD	ILSS: 14	[139]
SCF T300	Epoxy resin	GO	45–50	5 ^b	VARTM	Dip coating	IFSS: 35	[131]
UCF T300	Epoxy resin	GO	62.6	0.1 ^b	Compression molding	Aqueous solution	ILSS: 14.7	[140]
UCF T300	Epoxy resin	GO	63–65	0.05–0.4 ^b	VARTM	Dip coating	ILSS: 11 IFSS: 32	[141]
Unidirectional carbon fabric	Epoxy resin	GNP	8 plies	0.3 ^b	VARTM	Spray coating	FS: 27.2 ILSS: 24.5	[142]
SCF	PES	GO	12.5	0.2–0.5 ^a	Injection molding	Dip coating	TS: 17.77 FS: 28.76	[143]
UCF 12 K	Epoxy resin	Silane-functionalized GO	50–55	0.2–1 ^b	VARTM	Dip coating	TS: 15 FS: 15 IFSS: 60 ILSS: 19	[144]

4.4 Two-phase composite: impact of carbonaceous nanodiamond reinforcement on the polymeric matrix

Nanodiamond (ND) is a sophisticated carbonaceous nanofiller that has recently been a cynosure to composite-based materials research. Unlike the aforementioned 1D CNT and 2D graphene, ND is a 0D nanofiller. As deposition of ND on CF surface is hardly feasible, it is prevalently employed as a carbonaceous nanofiller with a polymeric matrix to produce two-phase composite or sometimes in conjugation with other nanofiller (CNT, graphene, GO), which gives away

synergistic bifiller composite [20]. What sets it apart is its discrete ability to attack a specific point on a polymer chain rather than the whole length of the chain; supplemented by its enormous surface area, thicker interphase than CNT and GO, minuscule particle size, spontaneous transformation into other nanocarbon fillers, provision of convenient surface functionalization, possession of ample functional groups predominately of oxygen-based (hydroxyl, ether, carboxyl, ketone) on the surface, high capacity of adsorption and not to mention the perfect microcosm of bulk diamond properties. Because of these extraordinary characteristics, incorporating ND with matrix yields a sharp increase in

mechanical properties of composite [20, 31, 145]. These include a substantial development of the tensile property, flexural property and toughness. Table 6 covers the prospect of enhancing the mechanical properties of carbonaceous nanocomposites associated with ND compared to pristine matrix. The rich common functional groups of ND couple with its spherical shape in the structure caused outstanding swelling of properties (Table 6). It was also noticeable that mechanical mixing and solution mixing are the best methods for processing ND with polymers.

However, a higher amount of ND may prompt agglomeration like other nanofillers. This higher proportion of ND in the composite may instigate poor ductility, which cannot be disregarded in terms of nanocomposite performance [146]. Numerous papers have analyzed the mechanical properties of CNT-ND-based nanofiller. One such study by Subhani et al. [147] exhibited appealing results as 0.2% weight of ND and CNT in matrix caused 84, 70, 56, 104 and 161% improvement of tensile modulus, tensile strength, flexural modulus, flexural strength, impact strength, respectively, in comparison to the pristine matrix. This hybrid arrangement fetched uniform dispersion of nanofillers and improved the composite's property, which was even economically feasible to scale up. Consequently, the existence of active van der Waals force and covalent bonds between the nano-constituents further fueled effortless load transfer [148]. A similar result was found for epoxy matrix reinforced with GO-ND

(GN)-based hybrid filler. Properties portrayed by the addition of 0.1% wt. of GN were much higher than the 0.2% addition of GO alone, indicating the auspicious reinforcing efficacy of ND [149]. For both instances, ND prevents the aggregation of GO and CNT.

5 Manufacturing techniques of CFRP

A variety of conventional molding processes are being used to manufacture CFRP. For instance, open molding processes include hand lay-up, vacuum bagging, spray-up, autoclave molding, pultrusion and closed molding processes such as resin transfer molding and compression molding, to name [160]. Currently, there is a prevailing practice of a modern CFRP manufacturing technique, commonly known as 3DP or additive manufacturing which is getting ubiquitous popularity for its versatile use.

5.1 Hand lay-up

Hand lay-up is the simplest composite fabrication process comprising several simple processing stages and infrastructures but primarily restricted to thermosetting polymers. It is a manual process where each carbon fiber sheet is placed by hand in the desired orientation layer by layer up to the preferred thickness and resin is used between the layers

Table 6 Mechanical performance improvement of various polymer matrices through incorporating ND

Polymer matrix	ND modification	ND wt. %	Polymer-ND processing method	% Increase of composite's property than pristine matrix	References
Epoxy	Air oxidization and acid treatment	0.1–0.4	Solution mixing	TS: 81 Toughness: 87 TM: 80	[150]
Epoxy	Amine functionalization	0.1–0.5	Mechanical mixing	TM: 14.51 TS: 12.17	[151]
Epoxy	Air oxidization and acid treatment	1–30	Mechanical mixing	TM: 150 TS: 49.18	[152]
Epoxy	Acid treatment	0.01–1	Solution mixing	TS: 52.7 TM: 54.2	[153]
Polyamide 66	PA66 grafting of ND	1–3	Melt mixing	TS: 11.6 TM: 20.8	[31]
PA 11	Air oxidization	20	Electrospinning	TM: 300	[154]
PVA	Acid treatment	0.1–5	Solution mixing	TM: 186.48 TS: 30.52	[155]
PVA	Acid treatment	0.2–0.6	Solution mixing	TM: 98.50	[156]
PA6	Diamination	0.25	Melt mixing	TS: 11.55 TM: 27.30 IS: 29.82	[157]
Polycarbonate	Amine functionalization	5	Solution mixing	TM: 67	[158]
Silicone rubber	–	0.5–2	Solution mixing	TS: 147 TM: 80	[31]
Epoxy	Amine functionalization	7	Solution mixing	TM: 50	[159]

through rollers and brushes [161]. However, this is a labor-intensive process and complex structures like aircraft components can hardly be made through this process. Moreover, the composites fabricated by this technique are inflicted with poor impact resistance and flexural strength due to weak bonding at the interface. Using the vacuum bagging method, the entrapped air bubble can be reduced considerably and mechanical properties can be improved to some extent [162]. The mechanical properties of manually processed CFRPs depend on the void percentage, the magnitude of fiber alignment, the resin used, optimum temperature, roller pressure and friction between fibers [161].

5.2 Resin transfer molding (RTM)

RTM is a pressure-injected closed molding fabrication process that injects a low-viscosity thermoset into the mold. At first, the reinforcements are placed between two molds as “preform” according to the desired shape. Then the resin is heated in the transfer chamber and finally graduated to the mold cavities by applying pressure [163]. This method is renowned for large-scale production and maintaining the smooth surface of objects. The process is also neither labor-intensive like hand lay-up nor initial cost-intensive like compression molding [164]. Although RTM can be used to produce hierarchical composites, VARTM appears to offer more pragmatic process routes to device hierarchical composites since it discards the prerequisite of staunch solid mold and high pressure of injection. It also reduces the voids and hence improves impregnation [25].

5.3 Compression molding

Compression molding is desirable for its short cycle time and imparts higher impact strength in the structure while maintaining dimensional accuracy [164]. The manufacturing technique comprises three basic steps, which are as follows: (1) loading the raw material into the mold, (2) compression and (3) removal of the produced parts [165]. Compression molding can be a hot or cold process depending on whether the fabrication is carried out at high temperatures or room temperatures [164]. In pursuit of attaining better mechanical performance in CFRP, recently, a technique has been devised which ensures the optimal combination of both RTM and compression molding process, altogether known as compression-resin transfer molding [166].

5.4 Autoclave molding

Autoclave molding is an extended version of the vacuum bag process. The distinguishing curing process carried out in this method is the significant difference between the two. This method is known for conferring higher FVF and protean

fiber orientation in CFRP. The process includes a prepreg set in the mold system, followed by vacuum bagging the system and finally applying distinguishing high pressure and temperature in the autoclave. The curing in the autoclave imparts exceptional structural homogeneity and intensification, while the vacuum bagging exhausts the trapped air inside the mold and ensures minimal void and debonding areas inside the composite [160, 164].

5.5 Pultrusion

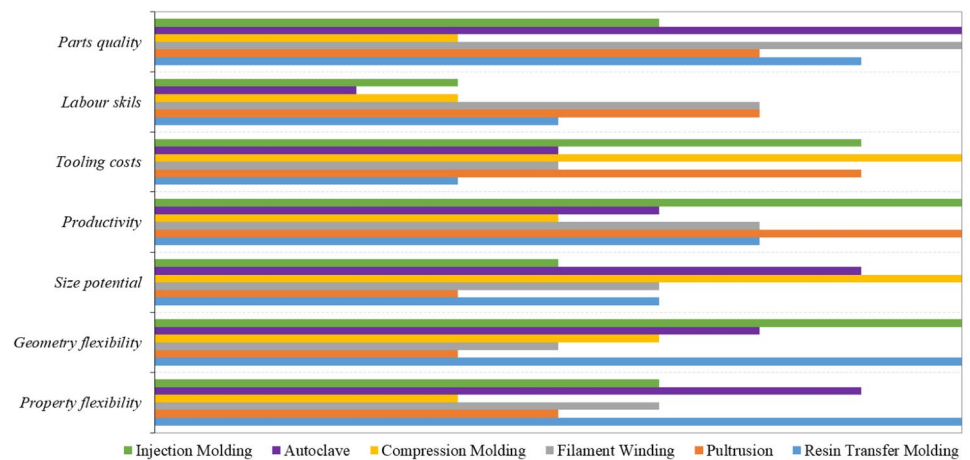
Pultrusion is a continuous fabrication technique to produce CFRP with a close-dimension and uniform cross-section. The process includes continuous fibrous materials that are shaped and organized by passing through guides, followed by impregnation with a resin and finally continuous pulling of the profile through a premeditated shaped die. As a result, profiles have limited geometrical choices, which is a crucial drawback of this process. The advantages of pultrusion are high production rate, high degree of automation, energy efficiency and cost-effectiveness, provision of imparting higher FVF and dimensional tolerance in the structure. The quality of the CFRP primarily depends on the die's temperature and the fiber's passing speed [167].

An ideal fabrication process must possess unique properties such as a short cycle period, provision of incorporating complexity, minimal labor cost, precise final product and a wide range of materials processability. However, there is no such fabrication process as flawless and inherits all these properties at the same time. Nevertheless, Fig. 13 takes a step to compare the aforementioned characteristics of some widely pervasive CFRP fabrication processes in industry. As can be seen that filament winding process ensures the best quality of CFRP parts. On the other hand, injection molding is regarded as the most productive; compression molding accounts for the lowest tooling cost and RTM imparts the greatest flexibility to the structure [160].

5.6 Additive manufacturing process/3D printing

Additive manufacturing is an advanced manufacturing technology that is popularly known as 3D printing. Whereas machining and cutting of substrates are required to get any shape in conventional composite manufacturing techniques, 3DP has eliminated such prerequisites by introducing precise CAD designing tools. 3DP covers a vast horizon of technologies, including FDM, selective laser sintering (SLS), stereolithography (SLA) and laminated object manufacturing (LOM) [168]. According to Yan et al. [169], the SLS-based 3DP method can be used for CFRP production. Likewise, according to Ning et al. [64] and Shofner et al. [80], FDM is another promising 3DP method successfully implemented for CFRP manufacturing. As the SLS method is focused

Fig. 13 Comparison of different CFRP fabrication processes according to labor skills, productivity, part's quality, etc. [160]



on powder-based material, it is unwise to use it in CFRP manufacturing since creating a homogeneous mixture of fiber-powder is challenging and often impossible [170]. That being said, irrespective of the pros and cons of different 3D printing methods, it can be noted that all methods can yield intricate objects without unwanted material wastage [168]. Apart from being inherently sustainable, 3DP also stands out in terms of competitiveness from other conventional composite fabrication methods due to the leverage of mass customization, viability to use in a wide array of fields that stretch out from prototyping to advanced bulk productions, provision of relentlessly maintaining the least number of processing steps along with optimal time and cost while not compromising quality and durability of the structures and finally for ensuring ergonomic fabrication process [59, 62, 171].

Nevertheless, 3DP technology arrives with some pitfalls such as voids forming and imputing lower fiber content during composite fabrication that cannot be amended afterward [34]. Regarding 3DP, it is hardly possible to achieve FVF above 40–50%, whereas the typical FVF for CFRP used in the aerospace application is 67% [172]. This lower FVF arises from the embedded characteristics of 3DP to consume a higher amount of matrix constituents than the conventional CFRPs manufacturing methods [173]. Figure 14 also reflects higher energy consumption by 3D printing, which is another downside. In 3D printing, energy consumption is heavily dependent upon printing speed. Energy consumption reduces with the increase of printing speed. According to Fig. 14, at the initial stage, energy consumption by the 3DP method is 3.47 times higher than in the injection molding process. But when the printing speed was increased, 3DP consumed almost similar energy to the injection molding process. But higher printing speed means less time for fiber impregnation than before, which can impair interfacial bonding and hence mechanical properties of CFRP. Therefore, an optimum balance should be maintained between energy

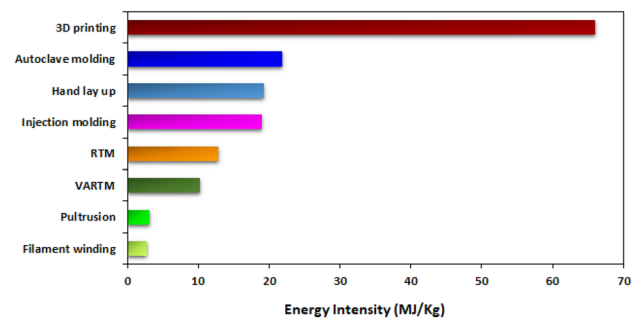


Fig. 14 Comparison of energy consumption between different CFRP fabrication techniques [84, 174]

consumption and impregnation time of fibers. Nevertheless, injection molding and the RTM are thought to provide the best balance between mechanical properties and energy consumption [84, 174].

Previous studies validated that polymer-based products engineered by 3DP always have less strength than conventional fabrication methods [69, 175]. Although FRP has improved the context to some extent, still 3DP-based fabrication method remains far behind the traditional fabrication method in terms of contribution towards strength in composite, which can be understood from Fig. 15. It originates from the inherent limitation of the 3DP method. Whereas the conventional pultrusion method can impart 85% FVF in the structure, 3DP can hardly impart more than 40% FVF [165]. As a result, discontinuous short carbon fiber-based 3D-printed products always have inferior mechanical properties than conventional manufacturing methods, as shown in Fig. 15. Continuous carbon fiber-based 3DP products have relatively high mechanical properties due to proper alignment and higher surface area in the structure. But they are also susceptible to lower mechanical properties than conventional fabrication-based CFRP [176]. The same resultant lower property of 3D-printed CFRP has been rendered by

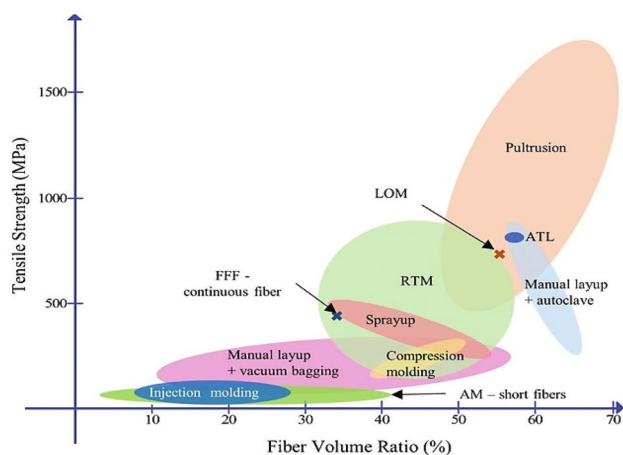


Fig. 15 Relationship between tensile strength and FVR for different conventional and 3DP-based CFRP manufacturing methods [176] (applied for permission)

previous studies [60, 177]. High porosity combined with the poor interfacial and interlaminar bonding, inadequate infusion of the matrix and the geometry of the nozzle were the impeding factors [62]. However, the silver lining is that there has been a significant improvement of this situation through 3DP of CCFRP instead of SCFRP [78, 178]. That being said, 3DP of CCFRP is still in its embryonic stage since it is only available for FDM and SLS techniques [66].

There are some pros and cons of every fabrication method. In addition, the application suitability of different fabrication methods for producing various composites (SCFRP, CCFRP, hybrid composite, hierarchical composite) depends on the nature of the fabrication method. Table 7 presents a comprehensive overview of different fabrication methods, including their pros and cons, process parameters, structural applications, processable composites and also future directions.

Selecting the proper manufacturing method is crucial since it determines the mechanical property, cost and quality of the final product. From Table 7, it can be noticed that injection molding and compression molding are the two widely used methods for fabricating SCFRP. Among them, Injection molding is the most prevailing in structural application. Injection molding process enables the production of larger and numerous CFRP parts at little cost in comparison to other expensive production methods. In this method, mass production, high aspect ratio and high fiber concentration are not mutually exclusive and can exist at the same time [94, 165]. On the other hand, pultrusion is the most feasible method for the production of CCFRP. By this method, faster impregnation and high fiber content of up to 85% can be achieved, ensuring supreme strength in the longitudinal direction. Moreover, latest individual brake control feature for controlling the tension of reinforcement fiber and low

rejection are further incentives for using this method [160, 165].

RTM, VARTM and filament winding are the most prevalently used methods for hierarchical composite fabrication. High injection pressure and robust molding are the prerequisites of RTM. For these constraints, VARTM is suitable for producing large and intricate hierarchical composite structures. Unfortunately, a common disadvantage of both RTM and VARTM processes is that the addition of carbonaceous nanofiller can cause a filtering effect against the CF, resulting in nanofiller depletion and segregation. The drum winder mechanism in the filament winding method has the potential to deter this issue and has since been considered an ideal method for hierarchical composite fabrication [25]. Furthermore, from the literature, it can be seen that hand lay-up, injection molding, compression molding, pultrusion, etc., are being used for hybrid composite fabrication. But among them, pultrusion is regarded as the best method for fiber hybrid composite fabrication since it produces an unparallel compounding reinforcing effect by establishing a proper synergistic relationship between CF and other reinforcing fiber and hence increases the mechanical property massively [160].

6 Applications of CFRP

The use of CFRP materials is not new to human history. Coming to the current twenty-first century, it is perceivable from their rapid exploration through all the realms of structural applications, ranging from land to sky, from small playing kits to gigantic space shuttle [117, 179]. Their outstanding specific strength, specific stiffness and corrosion resistance have outspokenly set them apart from other counterparts [3]. Over the last decade, there has been an exponential growth of global CFRP demand. From 2010 to 2022, the global CFRP demand is expected to have a compound annual growth rate of 11.98% [9]. Recently, there has been prevailing use of CFRP in aerospace, defense and automotive industry. Conventional metallic structures are continuously superseded by these CFRP-based modern structures predominantly for their lightweight properties. Figure 16a presents a thriving CFRP market from 2015 to 2024 in a percentage of billion USD. Although COVID-19 has plunged through this booming market by disrupting the supply chain and financial flaws, the situation is expected to be changed in the upcoming days. Nevertheless, this rapid growth of the CFRP market has simultaneously led to the increased consumption of CFRP worldwide and hence greater production. The global production of CFRP is expected to reach 199 Kt in this current ongoing year. Figure 16b describes the global production trend of CFRP. In contrast to the year 2010, the composite market will likely witness about 3.90 times higher

Table 7 Comprehensive comparison of different CFRP fabrication methods [160, 165]

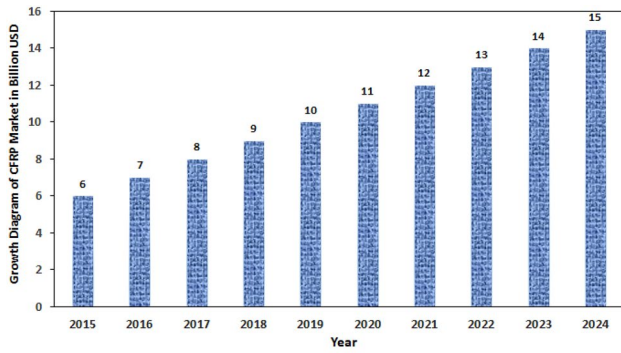
Fabrication method	Advantage	Disadvantage	Process Parameters	Processable composites	Future direction	Application
Injection molding	Produces high-quality duplicated CFRP parts ranging from very small to extremely large in shortest time, cost effective for bulk production, seldomly requires machining in post-production phase, possibility of full automation	Higher initial investment in creating the mold, not commercially feasible for production of fewer than 100 parts, short lifespan of aluminum mold, potential defects such as jetting, fiber exposure, warpage, and weld lines	Screw pressure, barrel temperature, cooling time	SCFRP, hybrid composite	Achieving uniformity of fiber dispersion in the matrix, identifying optimal cooling period, pressing force and injection period, prolonging the lifespan of the mold, performing molding at high speed	Aerospace (rocket cover), defense, automotive (air intake manifolds, cooling module), construction, sport
Compression molding	Produces high-strength CFRP panels and electric impeccable complex parts in a large quantity, offers competitive cost, attributes for easy automation, dimensional stability and higher productivity, reduces wastage generation	High susceptibility to surface imperfection such as pitting and waviness, can only be employed with thermosetting resin, potential defects such as voids, blisters, delamination, sink marks, residual stress and fiber separation	Molding time, temperature of the mold, external pressure, placement of the precharge in the mold	SCFRP, hybrid composite	Finding the exact quantity of material required, identifying minimal energy and time required, selecting a correct heating method and optimum pressing force, devising a sustainable design for rapid cooling	Automotive industry (spoilers, hoods, fenders, bumper beams, front end module of the car)
Resin transfer molding	Produces high-strength lightweight complex 3D parts at minimal resultant void, reduces material and handling cost, offers effortless surface finish, emits minimal volatile by-products, produces sophisticated small parts with minute details	Slow pace of curing, misalignment of reinforcement fiber during the resin transfer, inconsistency in repetition, only low-viscosity resins are employable, lengthier production cycle	Resin flow and injection, injection pressure, fastness of molding and demolding, curing period	Hierarchical composite, CCFRP	Addressing part-to-part inconsistency, devising a feasible modeling system that requires minimum resources and time, employing thermoplastic resins having low viscosity	Truck panels, boat hulls, wind and aerospace turbine blade

Table 7 (continued)

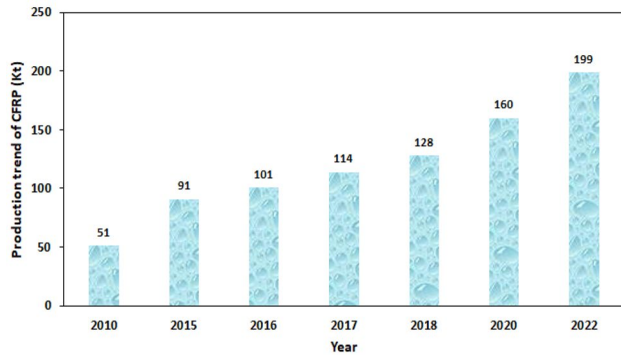
Fabrication method	Advantage	Disadvantage	Process Parameters	Processable composites	Future direction	Application
Vacuum-assisted resin transfer molding	Flexible material selection and tooling design, requires low injection pressure, utilizes vacuum to maintain an uninterrupted flow of resin, produces high-performance complex parts at lower cost, offers a high degree of freedom in altering molding geometry, imparts high FVF with nearly zero void	Origination of voids owing to fluctuating resin flow pressure or change in temperature can result in premature failure	Pressure gradient and positions of resin inlet, volume fraction, varying part thickness, infusion speed, lay-up configuration	Hierarchical composite, hybrid composite	Fine-tuning the design of the preform, conceiving a novel resin system with viscosity and curing kinetics, improving the fusion time, enhancing the reliability in detecting the internal system leaks	Aircraft fuselage, landing gear, wind turbine blades, marine
Hand lay-up process	Simplest and least expensive CFRP manufacturing process, utilized for low volume assembling of large structures, engages manual rolling which releases away the entrapped air and improves the fiber-matrix interaction, easily modifiable design	Requires secondary processing, less production, accidental entrapment of air drastically reduces the strength of structure, higher manual labor	Curing times, volume fraction, quantity of applied resin and catalyst	Hybrid composite, hierarchical composite	Identifying the accurate itinerant of entrapped air and gas bubble inside interphase, determining optimum curing time and resin amount, mitigating the risk associated with manual handling	Car body panels, wind turbine blades, boat hulls, prototyping of large structures
Pultrusion	Highly automated technology, produces CFRP parts with uniform cross-section profile, precludes the need for post-production process, excellent productivity and quality, cost-competitive, imparts high strength to weight ratio in the structure, lowers the labor cost for high volume production, low rejections	Higher initial investment, limited choice over parts geometry, constant cross-section only in the direction of longitude, scarcity of the standards of the structure hampers market recognition, lower strength in cross-direction of CFRP parts comprising solely unidirectional fibers	Die's temperature, method of preheating, fiber passage speed	CCFRP, hybrid composite	Improving pultrusion technology for simultaneously producing large complex parts and maintaining good product quality, sustainable approach to incorporate cleaner energy, novel approach towards addressing the limitation of profile geometry	Complex parts of vehicles, aircraft components, sports (skis, flagsticks of golf course, hovel constructions), marine construction

Table 7 (continued)

Fabrication method	Advantage	Disadvantage	Process Parameters	Processable composites	Future direction	Application
Filament winding	Introduces automation, imparts incredibly high tensile strength, produces high-quality duplicated structure, provides freedom to maintain optimum fiber orientation which is conducive to higher mechanical strength, provision of using a wide range of matrices, offers higher freedom of design	Only applicable for convex-shaped composites, arising of difficulties during positioning the fiber across the length of composite, mandrel cost is very high for large composite, produced parts are esthetically unattractive	Mandrel temperature, dipping time, process velocity, winding pressure and angle, fibers' tensions, resin's temperature and content	CCFRP, hierarchical composite	Finding methods to eliminate residual stress formed in the structure, pressing demand to introduce highly accurate temperature manageable automation process, improvement of simulation tools, enhancing the component quality, processing of high viscosity thermoplastic polymer	Fuel storage, chemical tanks, pressure vessels, rocket motor cases, drive shafts, tanks, bicycle rims and forks, axially symmetrical structures
Autoclave molding	Provides versatile orientation of fibers, imparts higher FVF and lower content of voids, removes air and other volatile products from CFRP parts, utilization of inert gas pressure maximizes structural efficiency, delivers dimensional accuracy and higher geometric flexibility	Prepreg substrates have to be preserved in a cold shielding, prohibitive initial cost, lower production, overall expensive, limited part dimensions imposed by closed autoclave, residual stress generations during curing	Autoclave pressure, vacuum pressure, curing conditions of material	CCFRP, hierarchical composite	Increasing productivity, decreasing tooling cost, increasing the commercial feasibility of smaller CFRP structures, properly defining a procedure of bagging for getting undistorted, cured and void free parts in shortest time	Aerospace components where dimensional accuracy is very crucial
3D printing	Reduction of material waste, imparts great durability and mechanical strength in CFRP parts, highly automated process, elimination of different intermediate processes such as cutting and tooling, coalesces sporadic behavior in a single CFRP part	Slower production, impossible to process large volume, formation of voids, difficulty in joining the separated parts due to their tiny contact area, requires skilled operators, lower mechanical property attribution due to anisotropy	Fiber content, forming pressure, nozzle and bed temperature, infill orientation, layer thickness, speed of printing	CCFRP, SCFRP, hybrid composite	Recycling of 3D-printed CFRP parts, producing more adaptive and interactive CFRP structures, creating a standard procedure for devising hierarchical composite which will conform to ideal mechanical properties	Bicycle frames, wind energy, automobiles, aerospace



a Growth diagram of the CFRP composites market from 2015 to 2025 [163]



b World Production trend of carbon fiber reinforced polymeric composite [183]

Fig. 16 a Growth diagram of the CFRP composites market from 2015 to 2025 [160]. b World production trend of carbon fiber-reinforced polymeric composite [180]

production of CFRP in the year 2022. This scenario will likely continue in the upcoming years and new structural branches will be included under the sphere of influence of CFRP [160, 180].

The potential use of CFRP is not only limited to automobile and aerospace but also sprouting to many other high-performance structural applications such as solar energy, sports goods and even space shuttle. The main reason lies underneath in their ability to cater diversified material properties. Figure 17 depicts a simple overview of structural applications of CFRP in different sectors. The most important applications are automobiles, aerospace, wind energy and sporting goods.

Aviation and aerospace sector are massively dominated by the application of CFRP. Figure 18 portrays the present global demand and turnover scenario of CFRP in different structural applications. It is noticeable that aviation and aerospace industries alone are responsible for 36% of demand and 56% of worldwide turnover. High quality composite materials mimic diversified properties in end aerospace products. Automotive industry is the second largest since it is liable for 24% of global demand and 18% of global turnover. CFRP materials have also made a firm establishment in the sports sector. The demand and turnover produced by it

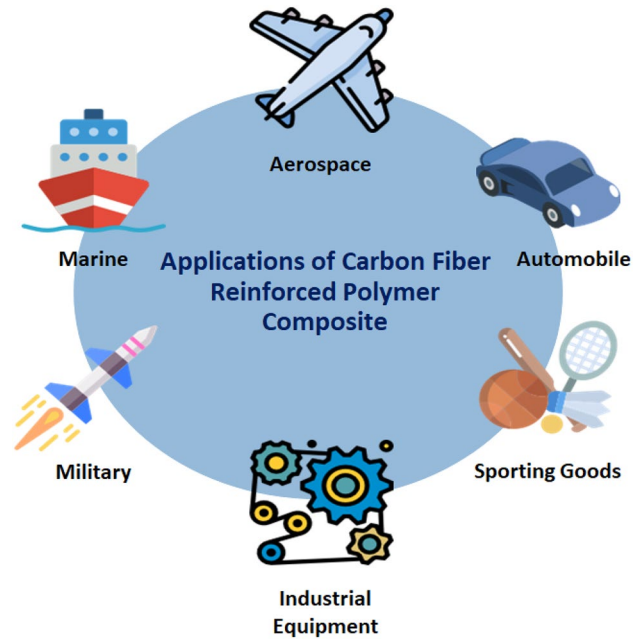


Fig. 17 Structural applications of CFRP

are 13 and 11%, respectively [180]. The important structural application sectors of CFRP are described as follows.

6.1 Automobile

CFRPs are widely used in automobiles to achieve fuel economy, extract the best performance out of the car and most importantly ensure passenger safety. A wide array of components of modern cars, including chassis, suspension system, engine, gearbox, driveshaft, bonnet, roof panels, side door and wheels are made out of CFRP [14, 181]. Formula 1 is the epitome of CFRP applications in the modern-day automobile industry. After the first introduction of CFRP-based

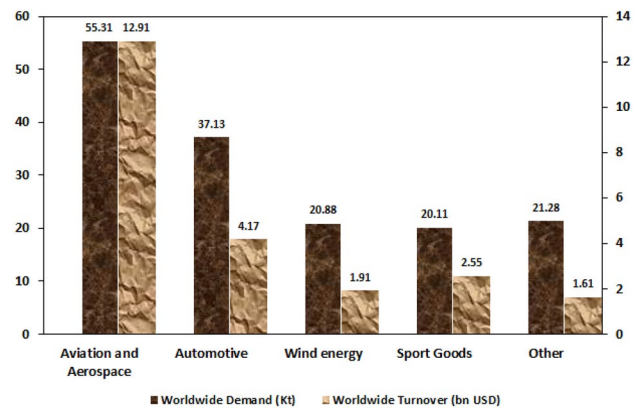


Fig. 18 Recent global demand and profit scenario of CFRP in structural applications [180]

monocoque chassis in 1980 by the McLaren F1 team, CFRP covers almost 85% of modern F1 cars [182]. CFRPs are 60–80% lighter than steel [183]. Study shows that a 10% reduction in weight can result in 6–8% better fuel economy [184]. That is why automobile manufacturers have centered their thoughts on increasing the presence of CFRPs in regular road cars. Out of this ambition, BMW-i3, LandRover, Audi R8 model cars were sculpted from CFRP [185]. It has been found that, in 2021, the global demand for CFRP in the automobile sector valued \$ 6.3 billion, which happens to be 162.5% higher than in 2015 [186]. CFRP is also utilized in the bumper as it remains stoic under tensile and compressive pressure and displays agility to change into convenient shapes under heavy impact due to the high energy absorption capacity that can protect the passenger from the impact of an accident [3, 187]. Generally, thermoset-based CFRPs are used for primary build purposes, whereas thermoplastic-based composites are utilized for secondary parts [13].

6.2 Aerospace

Aluminum was used in the initial beginnings of aircraft technology, followed by Titanium alloys. However, the pressing demand to address different technical issues such as fatigue resistance, fracture resistance, static resistance, corrosion resistance, engine noise reduction and fuel consumption have given rise to the application of CFRPs in the aerospace industry [187, 188]. Figure 19 compares the relative structural efficiency of aluminum (7075-T6), CF-reinforced epoxy composite and Ti–6Al–4 V alloy. Among all three components, carbon-epoxy resin-based composite has excellent static and fatigue efficiency, which is a telltale of the superior structural efficiency of CFRP over other metal and metallic alloys.

Primarily, CFRP presides over metals and metal-based alloys because of weight reduction, high load-bearing capacity and fuel efficiency phenomenon. CFRPs occupy 50% of the total weight of the latest Boeing 787 Dreamliner and Airbus A350. Aerospace components developed by the CFRP include aircraft doors, brakes, clips, fuel tanks, fuselages,

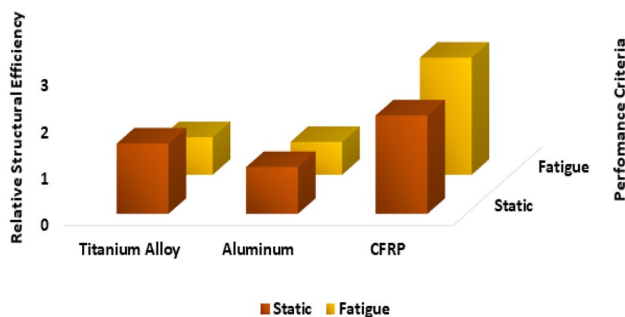


Fig. 19 Comparative efficiency of different aircraft materials [188]

fuselages cockpit, ribs, wings, landing gears, spoilers, keel beam, tail assemblies, horizontal and vertical stabilizers. Reduction of CO₂ emission is another driving factor for this increased usage of CFRP [12, 27, 189]. Besides the regular civil aviation industry, epoxy-based carbon fiber composites have been used in space shuttle and satellite structure development [14]. In a bid to reduce the cost, some researchers have also attempted to use thermoplastic PES- and PEEK-based CFRP in place of thermosetting epoxy resin-based CFRP [109, 190].

6.3 Wind turbine blades

The world is thriving toward renewable energy. As a result, the application of turbine blades is on the rise, and so is the use of CFRP, which is expected to touch the \$ 4 billion landmark in 2022 [191]. CFRPs and their graphene and CNT nanofiller-based hierarchical composites are widely being used in the manufacturing of wind turbine blades mainly for their resistance to fracture, fatigue failure and leverage of attaining a high degree of energy by changing their shape while not compromising the stiffness and stability [27, 192]. Although epoxy-based thermoset composites provide better strength and stiffness, in practice, thermoplastic polymer-based composites are widely used to avoid intermittent disposal of blades [14].

6.4 Sports equipment

CFRP's multifunctional property is a boon to the sports equipment market. Nowadays, sports equipment such as ski boards, rackets, fishing rods, golf clubs, bows and arrows, bicycles, baseball bats, yachts, ice hockey and rowing are made with it [193]. Its market value is expected to reach \$ 2.4 billion by 2022 [191]. Each sporting good has unique structural criteria that need to be checked by the CFRP and hierarchical composite. For instance, in golf balls, composites improve the damping performance, reduce the dead weight and thus increase the ball's durability. Similarly, the racket is provided with high specific strength and modulus along with tighter string by composite structure to serve at higher speed and absorb shock during rebuffering. For bi-cycle, CFRPs ensure immaculate shock absorption and maximization of speed at little effort [187, 194]. Moreover, in the terrain racing cycle's wheel, there has been an innovation named "NAWASTich", which employs CNT with CFRP to increase the strike damage resistance and strength over conventional CFRP [195]. It happened due to improved buckling resistance nature at the interior of rims under high compression phenomenon. In this way, CFRPs are exploiting all realms of sports equipment.

7 Challenges and future research

Although carbonaceous filler-reinforced polymer matrix composites have arrested salient attention, there are some flaws that need to be unearthed and solved through future research. One of them is the debacle of achieving optimum strength and ductility in the same CFRP structure [102]. It handicaps the design and functionality freedom of the structures. That is why it is challenging to implement CFRP for energy absorption purposes and translate multifunctionality heritage into the structures [10]. Fiber hybrid composite can be a potential solution. However, the literature does not adequately define the fabrication, repairing, modification and other aspects of this material. In addition, there are looming dangers of fake graphene that various studies have discussed recently, which endangers hierarchical composite's mechanical performance [196].

Different carbonaceous materials are vulnerable to skin and can cause respiratory disease by generating noxious by-products such as ammonia (NH_3), carbon dioxide (CO_2), hydrogen cyanide (HCN), carbon monoxide (CO) and nitrogen oxide (NO_x) during production [197, 198]. Concomitantly, the required energy intensity by CFRP is very high, predominantly for higher energy consumed by CF during production compared to glass fiber, stainless steel, copper, zinc and even to some extent, aluminum [174, 183]. This is the plausible reason why CFRPs costs are higher than other fiber-based composites and metallic alloys. This situation can be overcome by establishing effective recycling routes. Then again, this presents another seemingly insurmountable challenge of establishing an economically viable, mechanically competitive and cradle-to-cradle loop for recycling and waste management of CFRP, which should be a focus of research in the future [9, 199]. The inclusive application of thermoplastic matrix instead of thermoset for structural applications should also be addressed in these future studies.

Consequently, the anisotropic characteristic of CFRP results in low machinability, which prompts structural defects and health issues that are even more pronounced for hierarchical composites [12]. This anisotropic property, combined with the formidable task of achieving various geometrical interfaces in the same structure, throw a monumental challenge to the efficient large-scale production of hierarchical composite [28]. Most importantly, the exorbitant cost of nanofiller like CNT has even pushed formula 1, one of the most extravagant sports globally, to ban CNT [194]. Moreover, the chemically grafting of CF with CNT or graphene can cause surface distortion. Besides, engineering an optimum amount of nanofiller deposition to avoid agglomeration is extremely difficult [11]. In the future, more research should be carried out in

quest of economically viable and repercussion free fabrication routes of carbonaceous nanofillers. A mathematical model can be designed to validate the findings.

Regarding the manufacturing process, despite the revolution brought by 3DP, much work still needs to be done to dispel the inconvenience of hybrid and hierarchical composite fabrication, increase the FVF, decrease the void, avoiding large anisotropies formation inside objects and scale up the production [62, 200]. In addition, research should be focused on making 3DP a more energy efficient method. Currently, only a few thermoplastic polymers can be used as matrices during the 3DP of CFRP and prospects for other matrices remain unexplored [32]. That is why this futuristic manufacturing process's full potential and commercial feasibility are yet to be known.

8 Conclusion

This study has thoroughly reviewed the contemporary progress in the field of carbonaceous fillers reinforced polymer matrix composites' mechanical properties, their structural applications and critically analyzed some widely used manufacturing methods. At first, the mechanical performance of carbon fiber-reinforced polymer composites was analyzed, compared with the high-performance glass and aramid fiber-based composites and the summary was recorded. Carbon fiber-reinforced polymer composites have higher tensile and flexural strength but translate lower impact strength and higher brittle characteristics in the composite structure. Fiber volume fraction, critical fiber length, fiber orientation angle, void percentage and fabrication method are the most vital attributes of polymeric composite's mechanical performance. The dwelling issue of lower ductility is resolved by fiber hybrid composite where low elongation CF is coupled with a high elongation fiber reinforcement. The other pitfalls of polymer composites, including frail fiber–matrix interface, pull-out of fibers and lack of traverse properties, are addressed by CNT or graphene-based three-phase hierarchical composite or nanodiamond-based two-phase nanocomposite. These carbonaceous nanofillers have discrete configurations, stupendous aspect ratios and colossal surface area. As a result, these nanofillers improve IFSS, ILSS, toughness and delamination resistance of the composite. Some derivatives of these nanofillers are rich in functional groups, which further bolster the mechanical interlocking. There is an ambiguity in concluding whether the SWCNT or MWCNT produces better hierarchical efficacy. However, it can be undoubtedly said that GO and functionalized GO provide better reinforcing efficacy than graphene itself. Dispersion homogeneity is deemed to be the most vital issue for these nanofillers. Furthermore, 3D printing was dictated as an avant-garde technology to manufacture carbon fiber-based

polymeric composites regardless of their strength and energy issues. To sum up, aerospace, automobile, sporting goods and wind energy sectors were enlisted as the major focus of the structural application by CFRP. Based on the current progress, it can be extrapolated that the exponential growth of global carbonaceous fillers reinforced polymer composites demand will continue in the upcoming days.

Author contributions AS main idea; literature search; formal analysis; writing—original draft; writing—review and editing; visualization. ANMMR conceptualization and design; writing—original draft; writing—review and editing; visualization; supervision. MSR writing—review and editing. SAS supervision. FA supervision. MFR visualization. MH conceptualization. MOF visualization.

Declarations

Conflict of 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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