

**INTERFACE STRENGTHENING OF CARBON FIBER-
REINFORCED COMPOSITES USING DIFFERENT
NANO-COATINGS ON THE CARBON FIBER SURFACE**

Thesis Submitted for the Award of the Degree of

DOCTOR OF PHILOSOPHY

**in
PHYSICS**

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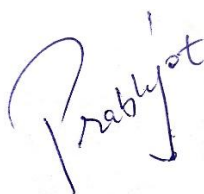


**LOVELY PROFESSIONAL UNIVERSITY
PUNJAB
2026**

DECLARATION

I hereby declare that the work presented in this thesis, entitled “Interface Strengthening Of Carbon Fiber-Reinforced Composites Using Different Nano-Coatings On The Carbon Fiber Surface”, submitted for the award of the degree of Doctor of Philosophy in Physics at Lovely Professional University, Phagwara, Punjab, India, is my original research work carried out under the supervision of Dr. Sahendra Pal Sharma, Associate Professor in the Department of Physics, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara, Punjab, India.

I further declare that this thesis does not contain any part of work that has been submitted for the award of any degree or diploma in this or any other university/deemed university without proper citation or acknowledgment.



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CERTIFICATE

This is to certify that the work reported in the Ph.D. thesis entitled “Interface Strengthening of Carbon Fiber-Reinforced Composites Using Different Nano-Coatings on the Carbon Fiber Surface”, submitted in fulfilment of the requirement for the award of the degree of Doctor of Philosophy (Ph.D.) in Physics, is a Bonafide record of research work carried out by Prabhjot (12116718).

The work presented in this thesis is the original research of the candidate, conducted under my supervision. I further certify that no part of this thesis has been submitted for the award of any other degree, diploma, or equivalent qualification in this or any other institution.



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Graphical Abstract



Abstract

Owing to high strength and low weight carbon fiber-reinforced polymer (CFRP) composites are widely used in aerospace, automotive, sports equipment, and renewable energy sector. But due to weak interfacial bonding between the fiber and matrix the performance of these composites is often limited. As Carbon fibers have a smooth surface, which makes it difficult for the resin to bond effectively. fiber pull-out, delamination, and early composite failure arise because of poor interfacial bonding that reduces load transfer from the matrix to the fibers. Therefore, improving the fiber-matrix interface remains an important area of research.

Present study focusses on utilizing the different nanomaterials, such as multi-walled carbon nanotubes (MWCNTs), graphene, and ZnO nanoflakes for the surface modification of carbon fibers. To enhance the adhesion between fiber and nano-species Polydopamine (PDA) was used as an intermediate coating layer on the fiber surface. The aim was to enhance the interaction between the matrix and fibers, which as a result will enhance the mechanical properties of the composites. PDA was selected because it contains catechol and amine groups which can easily form a thin coating on carbon fibers that promote adhesion. The PDA layer makes the fiber surface active and provide active sites for nanomaterials attachment. As a result, it acts as a coupling agent between the fiber and the deposited particles which made the coating process simpler and helped produce a more uniform surface modification. To remove the commercial sizing and dust particles from the fiber surface the fibers were cleaned using acetone before coating process. Further, to make the surface active and improve PDA attachment the fibers were oxidized with nitric acid. Post PDA coating nano-species; MWCNTs, graphene, and ZnO were deposited onto the fiber surface using dip coating method where fibers were immersed in nanomaterial suspensions, allowing the particles to attach to the surface.

Various characterization techniques were used to study the pristine and modified fibers. FESEM and TEM images confirmed the attachment of MWCNTs, graphene and the flake-like structure of the ZnO coating. EDS mapping displayed the presence and distribution of the deposited elements on the fiber surface. XRD results demonstrated

that the crystal structure of the carbon fibers remained unchanged after surface treatment. FTIR analysis confirmed the presence of functional groups associated with PDA and the deposited nanomaterials. These characterizations confirmed that the modification process affected only the surface and did not damage the fibers.

Dynamic contact angle analyzer was used to examine the contact angle and the surface wettability of fiber. The pristine fibers showed a contact angle of 85.9° which indicates the hydrophobic surface and poor wettability. On the other hand, the surface modified fibers contact angle decreased to 52.8° , indicates hydrophilic surface with high wettability. In result, the surface energy increased from 5.10 J/m^2 to 44.1 J/m^2 . Better wetting allows the resin to spread more uniformly over the fiber surface, improving contact between the two phases and strengthening the interface. Further to analyse the effect of these surface modifications the fabricated CFRP composites were examined through mechanical testing. The results showed that the nanomaterial-coated fibers provided stronger fiber-matrix bonding compared to pristine fiber and improved the overall mechanical performance of the composites.

MWCNT-Modified CFs: Composites reinforced with PDA/MWCNT-coated fibers showed an increase of about 81.4% in flexural strength and 48.2% in tensile strength compared to composites made with untreated fibers. SEM images of the fractured surfaces showed clear differences in the failure behavior. The untreated composites exhibited extensive fiber pull-out and smooth fiber surfaces, indicating weak fiber-matrix bonding. In contrast, the MWCNT-modified composites showed shorter pull-out lengths and more matrix material attached to the fiber surfaces after fracture. Fiber breakage and matrix cracking were also observed more frequently. These observations suggest stronger bonding at the fiber-matrix interface. The MWCNT coating increased the contact area between the fiber and the matrix, enabling the applied load to be transferred more effectively and improving the composite's resistance to fracture.

ZnO Nanoflake-Modified CFs: The composites incorporating PDA/ZnO-coated fibers showed a 48% increase in flexural strength and an 89.4% increase in flexural toughness. The flake-like structure of the ZnO nanoparticles provided a rough surface that improved mechanical interlocking with the polymer matrix. The fracture surface analysis supported these findings, showing reduced delamination and fiber pull-out.

The ZnO nanoflakes increased the interaction between the fiber and matrix and helped slow crack growth during loading. As a result, the composite absorbed more energy before failure, which contributed to the higher toughness observed in the modified composites.

Graphene Coating: Although graphene deposition was attempted using the same PDA-mediated approach, a uniform and stable coating could not be obtained under the conditions used in this study. This could be related to issues during graphene deposition, such as the restacking of graphene sheets or their interaction with the PDA layer. The results suggest that additional work is required to improve the coating process for this nanomaterial.

In conclusion, this study demonstrates mechanical properties of carbon fiber can be improved using bio-inspired surface modification technique. The incorporation of polydopamine (PDA) as a coupling agent enhanced the deposition of MWCNTs, graphene and ZnO nanoflakes uniformly on the carbon fiber surface. Result of different characterization technique such as chemical, surface, and mechanical characterization confirmed that modified fibers showed improved fiber-matrix interface and increased strength and toughness of the composites. The increase in wettability, along with the mechanical interlocking and bridging action of the nanomaterials, improved load transfer between the fiber and matrix and influenced the failure pattern of the composites, enabling them to absorb more energy before failure.

The results obtained in this work could be useful for the growth of advanced composite materials on industrial scale. Carbon fibers with improved interfacial properties could be used for hydrogen storage systems, where strong and stable structures are required. Additionally, it could be explored for energy storage devices and structural supercapacitors and may also be suitable for multifunctional applications. In such systems, the fibers can serve as both a structural material and an electrode, while the deposited nanomaterials may help improve electrochemical performance and electrical conductivity.

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List of Abbreviations

Abbreviation	Full Form
AFP	Automated Fiber Placement
ASTM	American Society for Testing and Materials
ATL	Automated Tape Laying
CMCs	Ceramic Matrix Composites
CVD	Chemical Vapor Deposition
DGEBA	Diglycidyl Ether of Bisphenol A
DI	Deionized
DMF	Dimethylformamide
DSA	Drop Shape Analyzer
FESEM	Field Emission Scanning Electron Microscopy
FRCs	Fiber-Reinforced Composites
MMCs	Metal Matrix Composites
MWCNT	Multi-Wall Carbon Nanotubes
NDT	Non-Destructive Testing
OoA	Out-of-Autoclave
PAN	Polyacrylonitrile
PDA	Polydopamine
PECVD	Plasma-Enhanced Chemical Vapor Deposition
PE	Polyethylene
PEEK	Polyetheretherketone
PMCs	Polymer Matrix Composites
PP	Polypropylene
PPS	Polyphenylene Sulfide
RTM	Resin Transfer Molding
SHM	Structural Health Monitoring
SMCs	Sheet-Moulded Composites
UD-CFRP	Unidirectional Carbon Fiber-Reinforced Polymer
UTM	Universal Testing Machine

VARTM	Vacuum-Assisted Resin Transfer Molding
ZnO	Zinc Oxide

List of SI Units

S. No.	Base Quantity	Base Unit	Symbol
1	Strength	Megapascal	MPa
2	Density	Gram per cubic meter	g/cm ³
3	Temperature	Celsius	°C
4	Modulus	Gigapascal	GPa
5	Length	Nanometre/Millimetre	nm/mm
6	Speed	Millimetre per minute	mm/min
7	Force	Kilonewton	kN
8	Time	Seconds/Minutes	s/min
9	Mass	milligram	mg
10	Volume	Millilitre/Litre	ml/L
11	Molar Mass	Gram per mole	g/mol
12	Viscosity	Millipascal-second	mPa.s
13	Stiffness	terapascal	TPa

Chapter 1

1. Introduction

1.1 Background of Composite

Composites are important materials used in many mechanical engineering applications. These include aircraft structures, electronic packaging, internal combustion engines, machine parts, thermal management systems, trains, and vehicles such as brakes, drive shafts, flywheels, pressure vessels, and tanks. Many natural structural materials are also composites. A composite is formed by combining two or more different materials to produce a new material with different properties. Composites have been used for centuries. One of the earliest examples is the use of mud and straw in house construction. Mud has good compressive strength but low tensile strength, whereas straw improves tensile strength. When combined, these materials provide better overall performance and can be used for floors and walls[1,2].

Modern composites are quite different from those used in the past. Earlier composites were mainly made from natural materials such as clay, straw, wood, and lime, whereas modern composites use materials such as carbon fibers, polymers, and resins. The modern manufacturing techniques involves 3D printing and autoclave processing while traditional methods used simple mixing and layering[3].

The basic concept remains the same like combining different materials to obtain properties that cannot be attained by a single material alone. Despite advancement challenges remain in developing materials with specific properties, improving their performance under demanding conditions and reducing manufacturing costs. Addressing these challenges is very important in aerospace, automotive and biomedical sector, where lightweight, high-performance materials are highly required.

1.2. Classification of Composite Materials

Composite materials can be classified in various ways, based on their scale, matrix materials, and reinforcement materials. The detailed breakdown shown in fig. 1.1 is as follows[4].

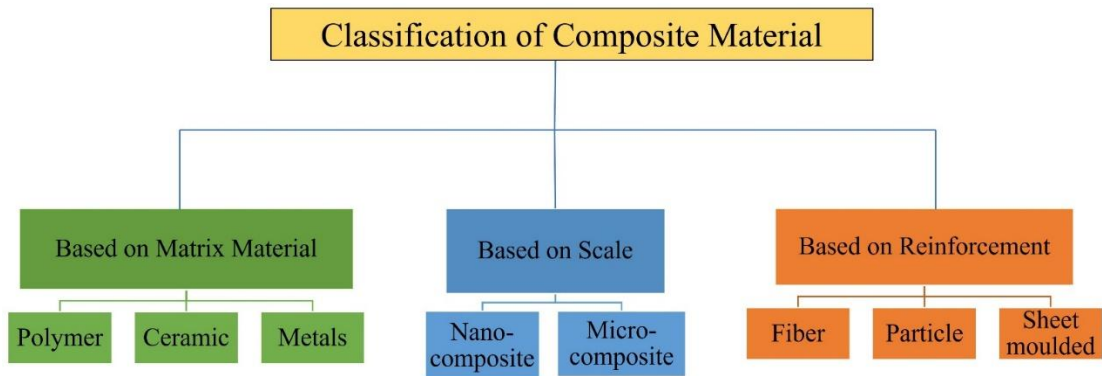


Figure. 1.1. Illustrates the classification of composite material

1.3. Fiber Reinforcements

Continuous fibers, discontinuous fibers, whiskers, and particles shown in fig. 1.2 are the four main forms of reinforcement used in composites. The most effective form of reinforcement is continuous aligned fibers, which are also commonly utilized, particularly in high-performance applications. However, continuous fibers are transformed into a wide range of reinforcing shapes using textile technology for simplicity of manufacturing and to obtain certain qualities, including increased impact resistance. Fabrics with two or three dimensions are important. Fibers are largely responsible for the huge importance of composites and the revolutionary advances in their properties over ordinary materials. The main fibers used in mechanical engineering include glass, carbon (also known as graphite), various types of ceramics, and high-modulus organic fibers[5].

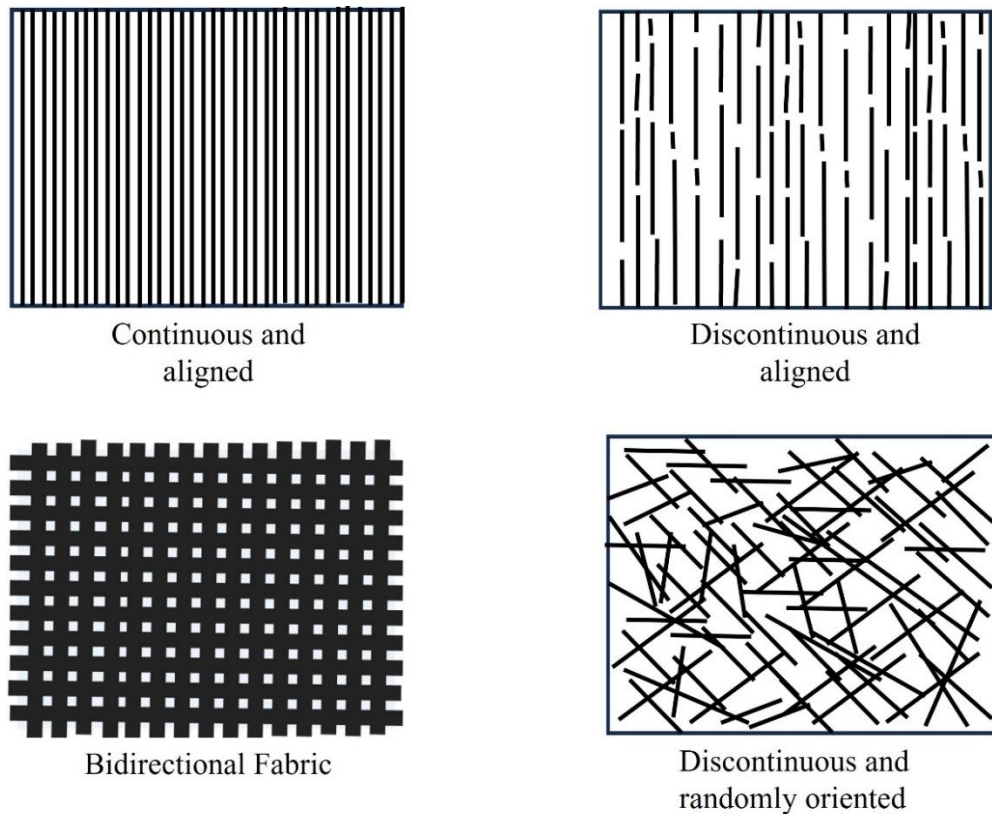


Figure 1.2. Illustrates the types of fiber reinforcement

1.3.1. Types of Fiber Reinforcements

- ***Natural Fibers***

Natural fibers shown in table 1.1 are derived from renewable sources such as plants, animals, or minerals. In (PMCs), plant-based fibers are most commonly used because of their abundance, biodegradability, and low cost. Jute, flax, hemp, sisal, and coir are common natural fibers used in composites. These fibers offer acceptable strength and stiffness and are preferred because they are renewable materials. However, their use is limited because of moisture absorption, variation in fiber properties and lower heat resistance compared with synthetic fibers. To reduce these drawbacks, surface treatments such as alkali or silane treatment are commonly used to improve bonding with the polymer matrix. Natural fiber-reinforced composites are commonly used in automotive interiors, packaging, and eco-friendly consumer products, where

low weight and sustainability are more important than very high mechanical performance.

Table 1.1: Natural Fibers Used in PMCs

Natural Fiber	Source	Tensile Strength (MPa)	Density (g/cm³)	Thermal Stability (°C)	Key Applications	Ref.
Jute	Stems of jute plant	400-800	1.3-1.5	Up to 200	Automotive panels, furniture, packaging	[6]
Flax	Flax plant stalks	500-900	1.4-1.5	Up to 200	Car interiors (BMW, Mercedes), sports equipment	[7]
Hemp	Hemp plant stalks	550-900	1.4-1.5	Up to 200	Biodegradable products, construction panels	[8]
Sisal	Leaves of sisal plant	350-700	1.3-1.5	Up to 200	Ropes, automotive composites, geotextiles	[9]
Coir	Coconut husks	100-250	1.1-1.3	Up to 150	Insulation panels, low-cost roofing	[10]
Bamboo	Bamboo grass	350-500	0.6-1.1	Up to 200	Sustainable furniture, flooring, and textiles	[11]

- ***Synthetic (Man-Made) Fibers***

Synthetic fibers shown in table 1.2 are engineered materials produced through chemical processes that are typically derived from petroleum or mineral sources. These fibers, such as glass, carbon, aramid, and basalt, are designed to provide superior mechanical properties, thermal stability, and consistency compared with natural fibers. Synthetic fibers exhibit high tensile strength, stiffness, and resistance to moisture, chemicals, and extreme temperatures, making them ideal for high-performance applications in aerospace, automotive, marine, and defense industries. However, they are non-biodegradable, energy-intensive, and often expensive. Their engineered compatibility with polymer matrices (e.g., epoxy and polyester) ensures a reliable performance in structural and load-bearing applications.

Table 1.2: Synthetic (Man-Made) Fibers Used in PMCs

Synthetic Fiber	Source	Tensile Strength (MPa)	Density (g/cm³)	Thermal Stability (°C)	Key Applications	Ref.
Glass Fiber	Silica sand, limestone, soda ash	2000-3500	2.5-2.6	Up to 550	Boat hulls, wind turbine blades, automotive parts	[12]
Carbon Fiber	(PAN) or pitch	3000-7000	1.7-2.1	Up to 500	Aerospace, sports cars, bicycles	[13]
Aramid Fiber	Synthetic polymers (e.g., Kevlar)	3000-3750	1.4-1.5	Up to 450	Bulletproof vests, helmets, aircraft components	[14]
Basalt Fiber	Melted volcanic basalt rock	3000-4800	2.6-2.8	Up to 800	Fire-resistant textiles, concrete reinforcement	[15]
Polypropylene Fiber	Petrochemical-derived polymers	400-800	0.9-1.1	Up to 120	Geotextiles, ropes, lightweight composites	[16]

1.3.2. Why Carbon fiber?

Carbon fiber is superior to other fibers owing to its unparalleled combination of a high strength-to-weight ratio, exceptional stiffness, thermal stability, chemical resistance, and design versatility discussed in table 1.3. Unlike natural fibers (e.g., jute, flax), which lack strength and degrade at modest temperatures, or glass fibers, which are heavier and less stiff, carbon fiber boasts a tensile strength of 3,000-7,000 MPa and a density of just 1.7-2.1 g/cm³, outperforming even steel in specific strength. Its high modulus of elasticity ensures minimal deformation under load, which is critical for aerospace and automotive applications, where precision and rigidity are paramount. Unlike aramid fibers (e.g., Kevlar), which excel in impact resistance but soften above 450°C, carbon fibers retain structural integrity up to 500°C in inert environments and resist thermal expansion, making them ideal for high-temperature applications such as rocket nozzles or brake systems. Additionally, carbon fibers are chemically inert, resisting corrosion from acids, alkalis, and solvents, unlike metals or moisture-sensitive natural fibers. Its fatigue resistance allows it to endure cyclic loading without degradation, which is a key advantage for wind turbine blades or aircraft wings. Although costly, the anisotropic properties of carbon fibers enable engineers to tailor fiber orientation for optimized performance in complex geometries, a flexibility unmatched by isotropic materials such as glass or basalt. Finally, its electrical conductivity and electromagnetic shielding capabilities add functional advantages that are absent in nonconductive fibers. Despite higher production costs and environmental challenges, carbon fiber's unmatched performance in strength, weight, and multifunctionality cements its dominance in cutting-edge industries, such as aerospace, motorsports, and renewable energy[17].

Table 1.3: Properties of carbon fiber[18]

Properties of carbon fiber				
Property	Units	Standard modulus	High Modulus	Ultra-high Modulus
Typical tensile modulus	GPa	230-270	350-450	460-935

Typical tensile strength	MPa	3500-5000	2500-4500	2500-4000
Typical elongation at break	%	1.6-2.0	0.5-1.5	0.3-1.0
Tow size examples	K	1,3,6,12,24,30,50	6, 12	1, 2, 3, 6, 12
Reference examples		T300, T700, AS4, HTS40,	M40J, UMT450	M55J, M60J, YSH70
Manufacturer examples		Torey, Teijin, Mitsubishi, Hexcel	Torey, Teijin, Mitsubishi, Hexcel	Torey, NGF, Mitsubishi
Application Examples		Industrial, Aviation, sport	Aviation, motor, sport	Industrial, space, sport

1.3.3. Materials Used in the Production of Carbon Fiber

The production of carbon fiber shown in table 1.4 primarily depends on the type of precursor material used, which determines the final properties of the carbon fiber. The three main precursors are Polyacrylonitrile (PAN), Pitch, and Rayon. Each of these precursors undergoes a transformation process involving stabilization, carbonization, and graphitization to produce high-strength carbon fibers. A detailed explanation of each precursor is provided below[19–22]. The production of carbon fiber from its precursors involves multiple stages of thermal and chemical treatments that transform polymer-based fibers into high-strength carbon structures. The process varies slightly depending on the precursor used ((PAN), Pitch, or Rayon), but all methods follow a general sequence of spinning, stabilization, carbonization, surface treatment, and sizing[23,24]

Table 1.4: Comparison of steps involved in the production of fiber from different precursors[25]

Step	PAN-Based	Pitch-Based	Rayon-Based
Spinning	Wet/Dry-Jet Spinning	Melt Spinning	Wet Spinning
Stabilization	200-300°C in oxygen	250-350°C in oxygen	Chemical pretreatment
Carbonization	1000-1600°C	1000-3000°C	800-2000°C
Graphitization	Optional (for high modulus)	Often used for high thermal conductivity	Not common
Surface Treatment	Electrochemical oxidation	Chemical oxidation	Electrochemical oxidation
Sizing	Epoxy, polyurethane	Epoxy, phenolic	Epoxy, polyester

1.4. Polymer Matrix Material in FRP Composites

The matrix material in FRP composites acts as a binder that holds the reinforcing fibers (e.g., glass, carbon, aramid), transfers load between fibers, and protects them from environmental damage (moisture, chemicals, and abrasion). The choice of the matrix significantly influences the mechanical properties, thermal stability, processing methods, and application suitability of the composite. Two primary types of polymer matrices are used in FRP composites: thermosetting resins and thermoplastic resins[26].

- *Thermosetting Resins*

Thermosetting resins are polymers that irreversibly cure (harden) when exposed to heat, catalysts, or radiation. Once cured, they formed a rigid cross-linked 3D network that could not be remelted or reshaped. They dominate the FRP industry owing to their high strength, chemical resistance, and compatibility with various fibers. Different types of Thermosetting Resins are shown in table 1.5.

Table 1.5: Common Types and Examples of Thermosetting Resins[27]

Resin Type	Description	Examples
Epoxy	Superior mechanical properties, excellent adhesion, and low shrinkage.	Diglycidyl ether of bisphenol-A (DGEBA)
Polyester	Low-cost, fast-curing, but lower mechanical properties than epoxy.	Ortho phthalic, Isophthalic, Vinyl ester
Vinyl Ester	Combines epoxy's toughness with polyester's ease of processing.	Derakane, Hetron
Phenolic	Fire-resistant, high-temperature stability, but brittle.	Bakelite
Polyurethane	Flexible, impact-resistant, and versatile.	Baydur, Isofoam

- *Thermoplastic Resins*

Thermoplastic resins are polymers that soften when heated and harden when cooled, allowing them to be remelted and reshaped multiple times. They are gaining popularity owing to their recyclability, impact resistance, and faster processing times than thermosets. Different types of Thermoplastic Resins are shown in table 1.6.

Table 1.6: Common Types and Examples of Thermoplastic Resins[28]

Resin Type	Description	Examples
Polypropylene (PP)	Lightweight, low-cost, and chemically inert.	Hostacom, Tegriss

Polyamide (Nylon)	High wear resistance and toughness.	PA6, PA66 (e.g., Zytel)
Polyetheretherketone (PEEK)	High-temperature resistance, biocompatibility, and strength.	Victrex, PEEK
Polyethylene (PE)	Excellent chemical resistance and flexibility.	HDPE, UHMWPE (e.g., Dyneema)
Polyphenylene Sulfide (PPS)	High thermal stability and flame resistance.	Ticona, Fortron

1.5. Fabrication of Fiber Reinforced Polymer Composite

Materials made of polymer matrix composites are essential to many industrial sectors, and their impact on the physical characteristics of various matrix-reinforcement combinations is becoming more widely recognized. Because of their widespread use in various electronic industries, it is crucial to design and develop efficient manufacturing procedures. The fabrication of Unidirectional Carbon fiber-reinforced polymer (UD-CFRP) composites involves several methods depending on the application, desired mechanical properties, and production scale. The most common fabrication techniques include the following.

1.5.1. Hand Lay-Up Method

The hand lay-up method shown in fig. 1.3 is one of the simplest and oldest techniques for fabricating UD-CFRP composites. In this process, the carbon fiber fabric or unidirectional fiber tows were manually placed into an open mold in the desired orientation. A liquid polymer resin, typically an epoxy, is then applied using a brush, roller, or spray. A handheld roller was used to ensure proper resin penetration and remove air bubbles. The lay-up was then left to cure at room temperature or under controlled heating. This method is commonly used for prototyping, low-volume production, and large but less structurally demanding components such as marine and automotive parts. However, it has limitations in terms of fiber volume fraction control, consistency, and labor intensity[29].

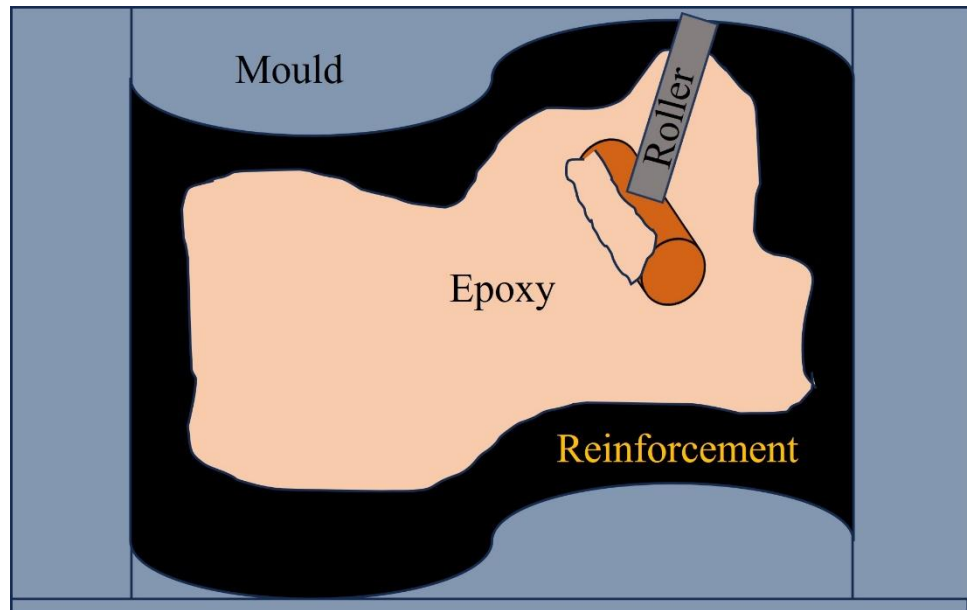


Figure 1.3. Illustrates the hand-layup method of composite fabrication

1.5.2. Resin Transfer Molding (RTM)

RTM is a closed-mold process that enhances the quality and repeatability of UD-CFRP composites. In this method, a dry preform of unidirectional carbon fibers is placed in a sealed mold shown in fig. 1.4, and a thermosetting resin is injected under pressure. The resin infiltrated the fiber network, filled all voids, and ensured a uniform distribution. The RTM is advantageous because it provides better fiber-to-resin ratio control, reduced void content, and improved mechanical properties. It is widely used in the aerospace, automotive, and wind energy industries. However, precise mold design and resin flow control are required to avoid defects such as dry spots or resin-rich areas[30].

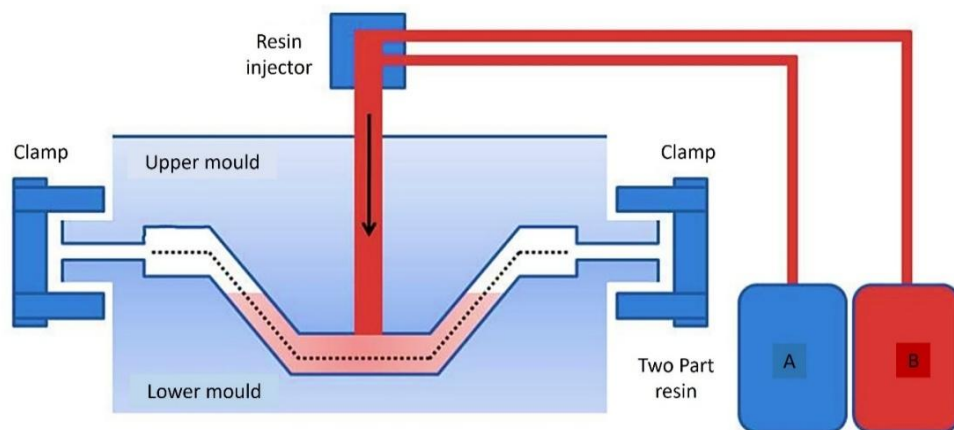


Figure 1.4. Illustrates the Resin Transfer Molding of composite fabrication

1.5.3. Vacuum-Assisted Resin Transfer Molding (VARTM)

VARTM is a variation of RTM that employs vacuum pressure instead of high-pressure injection to draw the resin into the dry fiber preform. The process shown in fig. 1.5 involves placing unidirectional carbon fibers in a vacuum bag or a closed mold, applying a vacuum to create suction, and then allowing the resin to be infused naturally. This method reduces equipment costs compared to RTM while still achieving high-quality laminates with minimal voids. It is particularly useful for manufacturing large, lightweight composite structures such as wind turbine blades, automotive panels, and aerospace components. However, precise control of the resin flow and fiber placement is critical to avoid defects[31].

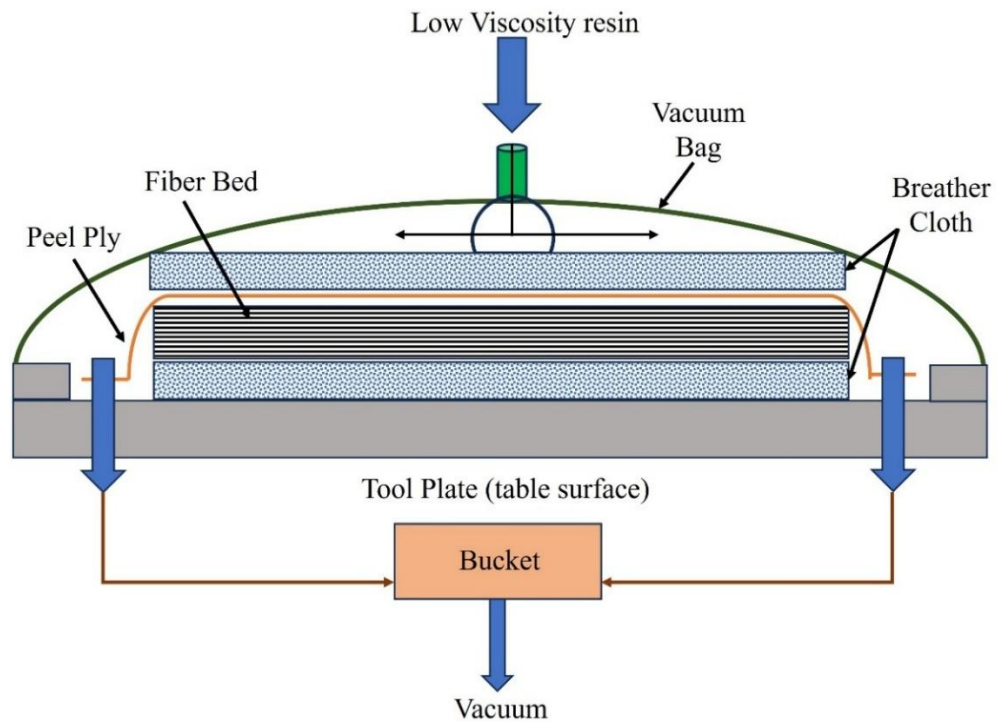


Figure 1.5. Illustrates the Vacuum-Assisted Resin Transfer Molding of composite fabrication

1.5.4. Other Manufacturing Methods

- *Prepreg Lay-Up with Autoclave Curing*

Prepregs are carbon fiber sheets pre-impregnated with a precise amount of resin. In this method, unidirectional prepregs are stacked in the desired orientation,

placed inside a vacuum bag, and cured under heat and pressure in an autoclave. The autoclave ensured uniform consolidation, removed voids, and resulted in superior mechanical properties. This process is widely used in high-performance applications such as aerospace, Formula 1 racing, and defense. The main disadvantages are high equipment cost, long processing time, and the need for refrigerated storage of prepregs before use[32].

- *Filament Winding*

Filament winding is a highly automated method used to manufacture cylindrical or spherical composite components such as pressure vessels, pipes, and rocket casings. In this process, continuous carbon fiber tows are impregnated with resin and wound onto a rotating mandrel in a controlled manner. The orientation of the fibers can be adjusted to optimize their strength in specific directions. Once the winding was complete, the part was cured at either room temperature or in an oven. Filament winding is highly efficient and produces components with an excellent strength-to-weight ratio. However, it is limited to components with rotational symmetry and requires precise programming for fiber placement[33].

- *Pultrusion*

Pultrusion is a continuous manufacturing process used to create long, uniform cross-section composite profiles such as beams, rods, and tubes. In this method, unidirectional carbon fibers are pulled through a resin bath, impregnated with polymer resin, and then passed through a heated die, where curing takes place under controlled pressure. The resulting composite had a high fiber volume fraction, making it exceptionally strong and lightweight. Pultrusion is ideal for the high-volume production of structural components in the construction, aerospace, and automotive industries. However, it is limited to producing constant cross-sectional profiles and requires specialized equipment[34].

- *Compression Molding*

Compression molding is a high-speed, high-pressure technique used to manufacture UD-CFRP components with complex shapes. The process involves placing pre-cut unidirectional carbon fiber prepregs or sheets into a heated mold, which is then compressed under high pressure to consolidate the laminate and

remove voids. Once the part has been cured, it is removed from the mold and subjected to finishing operations. Compression molding is widely used in automotive and industrial applications because of its ability to produce high-quality, high-strength components with fast cycle times. However, the mold design and material handling require significant expertise[35].

- *Automated Fiber Placement (AFP) and Automated Tape Laying (ATL)*

AFP and ATL are advanced robotic manufacturing techniques used to create highly precise UD-CFRP structures. In AFP, small carbon fiber tows are laid down in a specific orientation by a robotic head, ensuring precise fiber alignment and minimal material waste. The ATL is similar but uses wider carbon fiber tapes instead of tows. Both methods offer excellent repeatability, reduced labor costs, and the ability to manufacture complex geometries with controlled fiber placement. These methods are predominantly used in aerospace and defense applications, such as aircraft fuselages and wing structures. However, they require expensive machinery and skilled programming skills[36].

- *Out-of-Autoclave (OoA) Curing*

OoA curing is an alternative to autoclave processing, which relies on vacuum bagging and oven curing instead of high-pressure autoclaves. This method reduces production costs while still achieving high-quality, void-free laminates. OoA processing is particularly beneficial for large aerospace components and wind turbine blades where autoclave curing may not be feasible. Although it does not always achieve the same level of fiber consolidation as autoclave curing, advancements in resin chemistry have significantly improved its performance[37].

- *3D Printing with Carbon Fiber (Additive Manufacturing)*

3D printing with carbon fibers is an emerging fabrication method that involves depositing continuous or chopped carbon fiber filaments in a polymer matrix through a controlled extrusion process. This method allows for the rapid prototyping and production of lightweight, custom-designed components with complex geometries. Although additive manufacturing is not yet capable of achieving the same mechanical properties as traditional CFRP fabrication methods, continuous advancements in material science and printing

technologies are expanding their potential applications in the aerospace, robotics, and automotive industries[38].

1.6. Failure Mechanisms in Carbon Fiber Reinforced Polymer Composites

Failure of CFRP composites can occur through several mechanisms, as shown in Fig. 1.6, which may act individually or together during service. Fiber breakage is a common failure mode that occurs under excessive tensile loading along the fiber direction and usually results in sudden brittle failure. Matrix cracking can develop due to mechanical loading, thermal expansion differences, or environmental exposure, producing microcracks that grow under repeated loading. Delamination occurs when layers of CFRP separate due to weak interlaminar bonding, impact damage, or out-of-plane shear stresses, thereby reducing the structure's strength. Fiber-matrix debonding results from poor adhesion between the fibers and resin, affecting load transfer and weakening the composite. Impact damage, caused by either low- or high-velocity impacts, may produce hidden delamination or fiber fracture, lowering the remaining strength of the material. Fatigue failure develops under cyclic loading as microcracks grow, fiber-matrix debonding increases, and delamination spreads over time. Environmental factors such as moisture absorption, UV exposure, and temperature changes can weaken the polymer matrix and the fiber-matrix interface, leading to embrittlement and a gradual loss of mechanical properties. Manufacturing defects, including voids, fiber misalignment, and resin-rich or resin-starved regions, can act as stress concentration sites, thereby affecting composite performance. Creep and stress relaxation, particularly at elevated temperatures, may cause time-dependent deformation and reduce the material's stability during long-term use. In addition, fire and thermal decomposition can damage the matrix and fibers, reducing the composite's load-carrying capacity. Since these failure mechanisms can occur simultaneously, proper design, material selection, and manufacturing control are important for improving the service life and performance of CFRP composites in structural applications.[39].

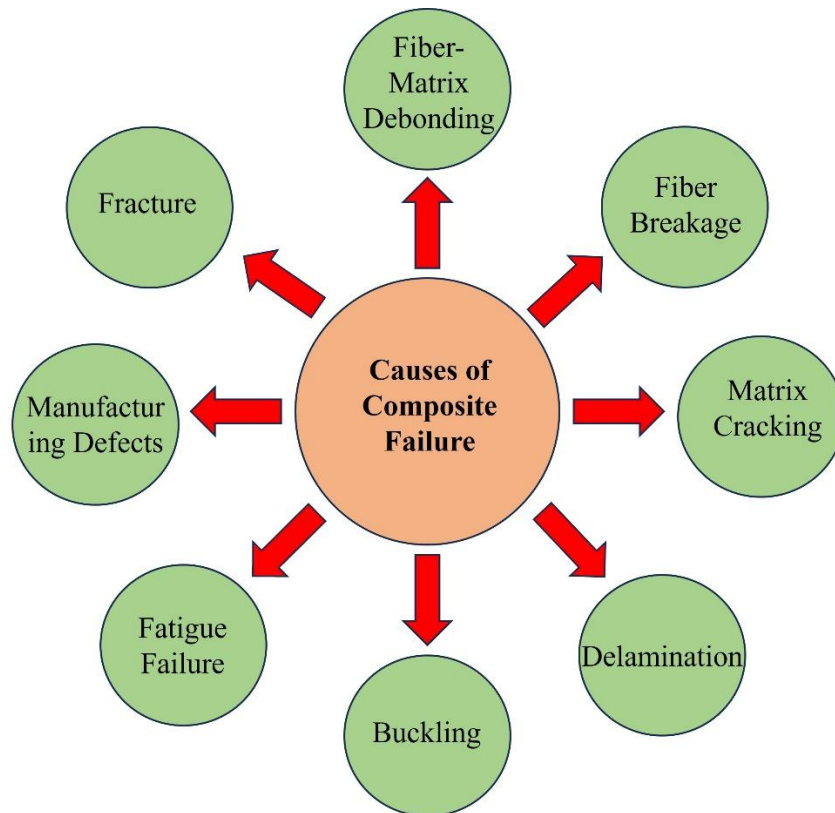


Figure 1.6. Illustrates the causes of composite failure

1.7. Scope of Work

The strength to weight ratio of CFRP composite makes them suitable for plenty of applications in aerospace, automotive, sports industry and structural engineering. One of the main limitations is the weak bonding between the fiber and the polymer matrix. The failures such as delamination, debonding and inefficient load transfer occur due to the smooth and chemically inactive surface of carbon fibers which leads early composite failure. Therefore, improving the fiber-matrix interface is critically important for better mechanical performance and long-term service of CFRPs. This study focuses on developing the surface modification method that will not only preserve the original properties of carbon fiber, but will also improve the adhesion using different interfacial treatments on the fiber surface. Improving the interface can enhance composite performance and support their use in applications that require high strength and long service life.

1.8. Structure of Thesis

The thesis has been divided into 5 chapters and its distribution is as mentioned below.

Chapter -1 deals with introduction, scope of work, aim and objectives of present study

Chapter -2 deals with review of literature.

Chapter -3 deals with Materials and Methods.

Chapter -4 deals with Results and Discussion.

Chapter -5 deals with Conclusion and Future Scope

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Chapter 2

2. Literature Survey

2.1. Background of Carbon fiber

Carbon fiber is a high-performance material renowned for its exceptional mechanical properties, lightweight nature, and resistance to chemical and environmental degradation. The earliest form of carbon fibers can be traced back to the late 1800s, when Thomas Edison used carbonized bamboo filaments in his early electric lamps. Carbon fibers emerged in the mid-20th century as researchers sought high-performance materials for aerospace and military applications. Its development traces back to the 1950s and 60s, when scientists at companies such as Union Carbide pioneered methods to produce lightweight, heat-resistant fibers. The process involves pyrolysis-heating synthetic precursors such as PAN in an inert atmosphere to carbonize the material, aligning carbon atoms into tightly bonded crystals. This results in fibers being renowned for their exceptional strength-to-weight ratio and stiffness. Initially costly and niche, advancements in manufacturing have gradually expanded its use beyond specialized sectors. These days Carbon fiber composites formed by embedding fibers in resins, are widely used in industries such as automotive and sports equipment because they provide lightweight and strong structures with good durability and performance. A breakthrough in carbon fiber technology occurred in the 1950s and the 1960s when researchers developed high-strength carbon fibers by heating PAN in a controlled environment. By the early 1960s, commercial production had begun, and the Royal Aircraft Establishment in the UK developed high-performance fibers that could be used in aerospace components. Over time, production methods have evolved to improve the fiber quality, uniformity, and cost-effectiveness. Table 2.1 highlights the major advancements that have had substantial economic, social, and technological effects resulting in notable accomplishments. On September 3, 2020, Nissan achieved a breakthrough in the production of carbon fiber components. This innovative method allows for the quicker development of parts that enhance safety, fuel efficiency, and driving comfort[1]. In the existing process, the carbon fiber is molded into the desired shape and placed in a die with a slight gap between the upper die and carbon fibers. Resin was then introduced into the fiber and left to solidify.

Table 2.1: Major Breakthrough in the production of Carbon fiber

Sr. No.	Precursor	Scientist	Breakthrough	Year	References
1	Rayon	Thomas Edison	Fabricated the first commercially available carbon fiber for use in incandescent light bulbs.	1879	[2]
		Roger Bacon	First, high-performance carbon fiber with a tensile strength of 20 GPa and a Young's modulus of 700 GPa were discovered.	1958	[3]
		Curry Ford and Charles Mitchell	Heat-treating rayon to temperatures as high as 3,000 °C resulted in the strongest commercial carbon fiber to date. In 1963, carbon fiber was introduced to the "advanced composites" sector.	1963	[4]
		Bacon and Wesley Schalamon	A novel "hot-stretching" technique was developed, employing a temperature of more than 2800°C on rayon to create the first fully high modulus commercial CFs.	1964	[5]
2	PAN	Akio Shindo	Fabricated high strength and high modulus fiber from PAN precursors	1961	[6]
3	Pitch	Leonard Singer	Solved the orientation mystery by revealing that pitch can be polymerized slightly further to orient the molecules in a layered structure	1970	[3]

2.2. Production and Consumption of Carbon fiber Reinforced Polymer Composite

Carbon-fiber-reinforced polymer composites are commonly used as superior performance structural materials in the automotive, aerospace, marine, and energy storage sectors owing to their high strength, modulus, light weight, and improved fatigue resistance. The fig. 2.1 shows the global production and consumption trends of CFRP composites, highlighting data from 2018 and 2020, and projections for 2050. In

2018, demand by application was dominated by Wind Energy (34.2 kt, 24%) and Aerospace (32.8 kt, 23%), with automotive applications showing varied subcategory contributions, including molding Compound (14.3-17.1 kt) and growth rates (8-12%). Regionally, North America led consumption (40%, 57 kt), followed by Europe (29%), and Asia-Pacific (12%). Manufacturing processes were mainly dominated by Pultrusion and Filament Winding (26%, 37.1 kt), while the aerospace sector accounted for 73% of global CFRP sales (US\$18.2 billion). By 2020, pressure vessels (8%, 9.4 kt) and sports goods had become important growing applications. Waste projections for 2050 from the aeronautical sector show that Asia (27%), Europe (23%), and North America (23%) are expected to account for the largest shares, while Oceania (18%) and Latin America (6.7%) are expected to account for smaller shares. These trends show that the aerospace sector is a major contributor to both CFRP sales and future waste generation, while wind energy accounts for the highest material consumption, with noticeable differences across regions.[7][8][9].

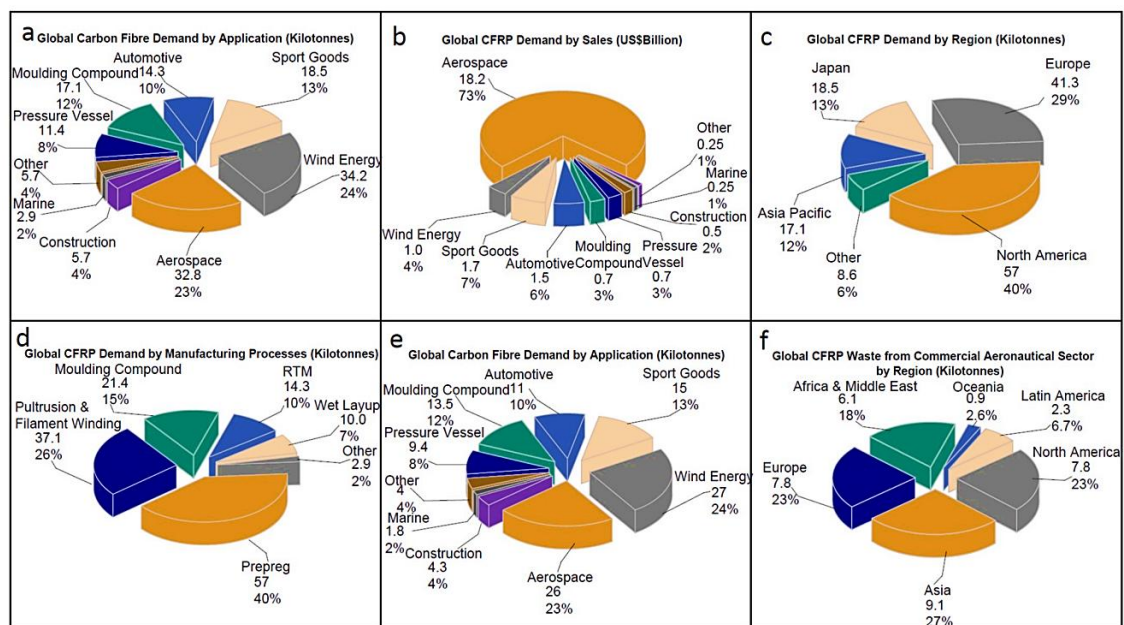


Figure 2.1. Global CFRP consumption in 2018 was categorized as (a) application, (b) sales, (c) region, and (d) manufacturing techniques. Global CF consumption in 2020 (e) by application and (f) estimated worldwide CFRP waste in 2050 from the aeronautical sector by region[10]

2.3. Role of Interface in Carbon Fiber Reinforced Polymer Composite

In CFRP composites, the interface states the boundary region where the carbon fiber and the polymer matrix physically and chemically interact. This region plays an important role in determining the durability, mechanical performance and failure mechanisms of the composites. It is not only a two-dimensional surface but also a three-dimensional interphase zone with different properties that differ from those of the fiber and matrix.

2.3.1. Types of Interfaces CFRP Composite

Mainly there are three types of interfaces i.e. coherent, semi-Coherent and incoherent interface[11].

- **Coherent Interface:** In coherent interface the atomic or molecular structures of the fiber and matrix are closely aligned at the interface. In this case, the lattice structures of both phases remain continuous across the boundary with minor mismatch and there is strong bonding between them. This type of interface helps in stress transfer from the matrix to the fiber more efficiently and improving properties such as tensile strength, stiffness and fatigue resistance. We can achieve coherent interfaces through surface treatments or chemical modification of fibers, hence improving their interaction and bonding with the polymer matrix.
- **Semi-Coherent Interface:** A semi-coherent interface is one where the partial alignment between the atomic structures of the fiber and matrix of CFRP composite. In this case, some of the regions at the interface are well aligned, while others display small mismatches or dislocations. This type of interface offers both bonding strength and a certain degree of flexibility with limited interfacial slip occurring under applied stress. Semi-coherent interfaces provide good stress transfer and modest interfacial bonding between the fiber and matrix. During loading this interface also improve composite toughness by allowing precise debonding and energy absorption. Many of the CFRP composite show semi-coherent interfaces due to limited chemical mismatch between the treated fiber surface and the polymer matrix.

- ***Incoherent Interface:*** Incoherent interface is condition where there is little or no atomic or molecular alignment between the fiber and the polymer matrix of composite. The two materials have limited to van der Waals forces and different lattice structures resulting in weak interfacial bonding. Under mechanical loading stress transfer from the matrix to the fiber is poor due to weak bonding, debonding can occur easily. Fibers which have smooth and chemically inert surfaces have limited interaction with the polymer matrix shows incoherent interfaces. Hence, leads to lower mechanical performance, reduced interfacial shear strength and a high chance of interface failure.

2.3.2. Micromechanical Mechanisms of Interfacial Bonding in CFRP Composite

Interfacial load transfer and durability in composites are governed by three mechanisms: (a) chemical bonding, which involves covalent or polar interactions between fiber surface groups and the resin (b) mechanical interlocking, where surface roughness, pores, or particles help anchor the matrix to the fiber surface and (c) physical adsorption or van der Waals forces. Surface treatments and sizing mainly increase chemical bonding and mechanical interlocking while ensuring proper resin wetting and composite fabrication.[12].

Load Transfer Mechanism

- ***Stress Transfer:*** The primary function of the interface is to transfer the applied loads from the compliant matrix to the stiff, high-strength carbon fibers. Efficient load transfer relies on interfacial shear strength, which is influenced by chemical bonding, mechanical interlocking, and van der Waals forces.
- ***Shear Stress:*** A strong interface ensures effective shear stress distribution along the fiber length, enabling the fibers to bear the maximum load. Weak interfaces lead to fiber-matrix debonding, causing premature failure through fiber slippage or pull-out.

2.3.3. Why the interface is strategically significant in composites?

Because the interface directly controls key composite properties (strength, stiffness, toughness, fatigue life, processability and environmental resistance), small changes in fiber surface chemistry, sizing level, or interphase architecture can produce large

changes in component performance and manufacturability. That makes interface engineering one of the most cost-effective and widely used levers when developing CFRPs for aerospace, automotive, wind, sports and other high-performance applications[13][14].

2.4. Factors Influencing Interface Quality

- **Adhesion:** The adhesion strength of CFRP depends on the interaction between carbon fibers and the polymer matrix. Better bonding between them allows the applied load to move from the resin to the fibers more efficiently. This bonding occurs mainly through chemical bonding and physical locking between the two surfaces. During surface treatment, new functional groups may form on the fiber surface, which can interact with the epoxy resin and enhance the fiber-matrix interface. Epoxy-based sizing materials help bond the carbon fiber and resin during curing. The roughness of the fiber surface also affects bonding by allowing the resin to more strongly adhere to the fiber. Treatments such as plasma and acid oxidation create small irregularities on the fiber surface, which improve contact between the fiber and the matrix. The connection between the fiber and the matrix affects how a composite behaves when a load is applied. A strong bond allows the fibers to carry more of the load, which helps improve the strength of the material. If the bond is weak, the fibers can separate from the matrix or be pulled out more easily, leading to a loss in strength. The nature of this connection also affects how cracks form and grow, making it an important factor in the failure of composite materials[15][16].
- **Wettability:** Wettability refers to the ability of epoxy resin to spread across the carbon fiber surface. When the resin spreads properly, it covers the fibers more uniformly and forms better contact with them. The extent of spreading is influenced by the condition of the fiber surface, the flow characteristics of the resin, and the processing parameters used during fabrication. Surface modification of the fibers often improves resin attachment, while a resin with good flow characteristics can penetrate spaces between neighbouring fibers more effectively. Inadequate wetting may leave voids or trapped air within the composite, creating regions where cracks can initiate more easily. Achieving

proper wetting helps produce a more uniform fiber–resin interface and contributes to improved mechanical performance of the composite material[17].

- **Surface treatments:** Before composite fabrication, carbon fibers are usually subjected to surface treatment to obtain better contact with the polymer resin. These treatments modify the outer layer of the fibers and help the resin remain attached during service. Several approaches are used in practice, including sizing, plasma treatment, and chemical modification. Sizing deposits a thin protective layer on the fiber surface, whereas plasma treatment changes the surface texture and creates additional sites for resin attachment. Chemical modification introduces functional groups that can interact with the surrounding matrix. Silane compounds are frequently used because they can act as a bridge between the fiber surface and the resin, leading to a more stable interface. Surface treatment allows the resin to spread more uniformly over the carbon fibers and limits the formation of voids within the composite. A well-bonded interface reduces the possibility of fiber–matrix separation when the material is subjected to load. As a result, the composite can withstand higher stresses before failure. The influence of surface treatment varies with the treatment method and the intended application. Composites designed for aircraft structures are generally expected to meet more demanding mechanical requirements than those used in many automotive parts[18].

2.5. Strategies for Interface Strengthening

Researchers have explored different ways to reduce failure in CFRP composites. Materials such as high-modulus carbon fibers, epoxy resins, thermoplastic matrices, and nanofillers have been incorporated to obtain stronger laminates and slow crack growth. Attention has also been given to the fiber-matrix interface, since weak adhesion often leads to separation under load. For this reason, fiber surface modification and nanomaterial additions are frequently employed. The arrangement of plies within the laminate is another factor that affects damage behavior. Hybrid stacking and balanced layups are widely adopted because they help limit delamination and lessen the effects of impact loading. Also, the manufacturing quality is equally important, since defects such as voids and uneven fiber distribution can weaken the composite. For this reason,

processing methods such as VARTM, AFP, and autoclave curing are widely used to obtain better laminate quality. techniques such as Z-pinning, stitching, 3D woven composites and toughened interlayers are often introduced between the layers to limit delamination. When higher damage tolerance is required, materials is designed to absorb impact energy, together with self-healing systems and sandwich structures. Selecting suitable fiber orientations and using matrices with good fatigue resistance along with Structural Health Monitoring (SHM) systems with embedded sensors could address long-term loading conditions.

To protect the composite from humidity, sunlight and temperature effects, moisture barriers, UV-resistant coatings and thermal protection layers are commonly applied. To detect internal defects during service and maintenance, non-destructive testing methods such as ultrasonic inspection, X-ray CT scanning and acoustic emission monitoring are used. The usable life of CFRP composite structures can be expended by repair techniques, including bonded composite patches, resin injection, and self-healing materials. These approaches help to improve the durability and service performance of CFRP composites [19][20].

2.6. Different Methods used for Interface Strengthening

The different methods used for interface strengthening in CFRP composite are shown in Figure 2.2

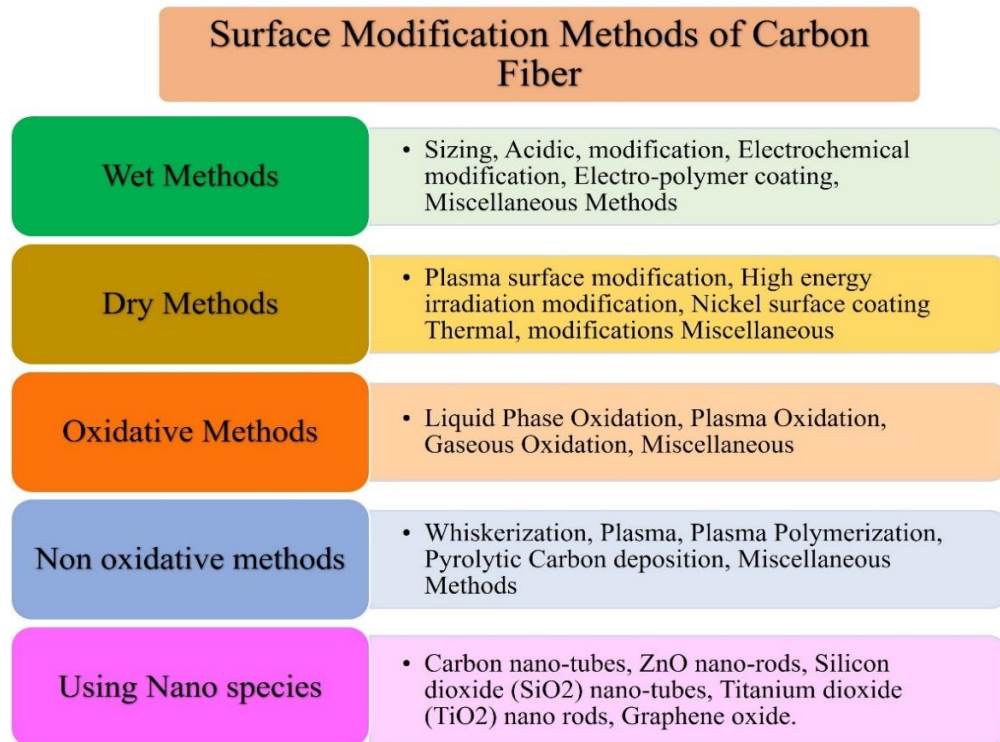


Figure 2.2. Illustrates the surface modification methods of carbon fiber

2.6.1. Wet Methods

Wet methods involve chemical or electrochemical treatments to modify the surface properties of carbon fibers and improve the adhesion between the fibers and polymer matrix.

- **Sizing:** Sizing is a process in which a thin protective layer is applied to carbon fibers to enhance their handling and bonding with resins. Acidic modification uses strong acids, such as nitric acid (HNO₃) or sulfuric acid (H₂SO₃), to introduce functional groups, such as hydroxyl (-OH) and carboxyl (-COOH), on the fiber surface, thereby improving wettability and adhesion. Varelidis et. al. (1999) employed the solution dip-coating method to deposit polyamide 6,6 (Nylon 6,6) onto the surface of carbon fibers to evaluate its effect on the

mechanical properties of carbon fiber/epoxy composites. The dip-coating technique with nylon 6,6 was found to enhance the interlaminar shear strength (ILSS) and tensile strengths of the composites. In contrast, interfacial polyamidation was found to have a detrimental effect on these properties. Nevertheless, both surface modification techniques contribute to an improvement in the fracture toughness of the composites[21]. Dilsiz (1999) did the surface analysis of Poly(thioarylene phosphine oxide) PTPO, polyetherimide sized and unsized fiber, he observed decrease in functional group and surface energy after sizing[22]. Moreover, Dilsiz (2000) investigated the acid-base character and surface energy of PU and polyamide-sized and unsized carbon fibers. He observed an increase in the contact angle; therefore, the number of hydroxyl groups on the surface decreased, which resulted in reduced surface energy[23]. Allred et. al. (2003) investigated the effect of sizing on the durability of high-temperature polymer composites. The results of room-temperature tests conducted after thermal aging indicated that a reactive finish produced a stronger and more durable interface compared to the manufacturer's original sizing. However, under conditions of moisture blistering, the composite with the stronger bond exhibited a tendency to delaminate, a phenomenon attributed to the entrapment of volatiles at the interface[24]. Suping et. al. (2004) examined the impact of beta-tricalcium phosphate (β -TCP) coatings on the mechanical behavior of carbon-fiber-reinforced hydroxyapatite (HAP) composites. The application of β -TCP as a sizing agent enhanced the interfacial bonding strength and contributed to the reduction in the residual stresses generated during the cooling process[25]. Fernández et. al. (2004) investigated the effect of epoxy-based sizing on the fracture behavior of woven carbon fiber-reinforced tetrafunctional epoxy composites. The application of sizing treatments resulted in improved mechanical properties, which were attributed to enhanced fiber–matrix adhesion. Additionally, a decrease in the contact angle was observed, indicating an increase in the surface energy of the carbon fibers, which further contributed to better interfacial bonding[26]. Yang et. al. (2007) examined the impact of emulsion sizing incorporating nano-SiO₂ prepared using the sol-gel method on the interfacial characteristics of carbon fiber/epoxy

composites. SiO₂ nanoparticles were well dispersed in the hybrid sizing layer. Their presence improved the ILSS and impact resistance of the composite. The improvement occurred because the nanoparticles increased bonding between the fiber and the matrix, helping the composite better handle loads[27]. Mäder et al. (2007) examined epoxy composites with single and multiple fibers, each treated with different sizings. They found that polymer sizing improved both static strength and fatigue resistance in glass fiber composites. DMA results also showed that the treated interface reduced the movement of the surrounding polymer, supporting improved bonding and durability[28]. Zhang et al. (2011) developed an epoxy-based sizing formulation for high-modulus carbon fibers using a latent curing agent prepared from ethylenediamine and butyl acrylate. The treated fibers exhibited better resin wetting characteristics than the untreated fibers. As a result, the interlaminar shear strength (ILSS) of the resulting composites increased by approximately 10%. The composites also displayed higher interfacial toughness, indicating a more robust fiber-matrix interface.[29]. Zhang et al. (2012) studied carbon fibers with different sizing contents and evaluated their effect on composite properties. The amount of sizing influenced how the resin spread over the fiber surface. Among the three levels examined (1 wt%, 1.5 wt%, and 2 wt%), the 1.5 wt% sample gave the best overall results in terms of fiber-resin contact and mechanical behavior[30]. Zhang et al. (2013) studied the effect of particle size and particle distribution in sizing emulsions used for carbon fibers. Changes in these characteristics influenced the way the resin spread on the fiber surface. The P2 emulsion gave the highest IFSS among the samples tested. It also showed less deterioration after moisture and heat exposure, suggesting a stronger and more durable bond between the fiber and the resin[31]. Ge et al. (2015) prepared a carbon-fiber sizing agent through the reaction of dodecylamine and tetraglycidylidiaminodiphenylmethane (TGDDM). After applying the sizing to the fiber surface, the authors evaluated abrasion resistance, fluff formation, and fiber stiffness. The coated fibers performed substantially better during abrasion testing, with the highest abrasion resistance being 172.8% greater than that of untreated fibers. Composite samples manufactured with the treated fibers also

exhibited higher interlaminar shear strength (ILSS). The maximum ILSS was 29.16% higher than that measured for the desized composite, reflecting stronger adhesion at the fiber-resin interface.[32]. Ma et al. (2016) used an emulsion-based sizing on carbon fibers before preparing ABS-based composites. The treated fibers bonded more effectively with the matrix than untreated fibers. As a result, the interlaminar shear strength increased by 26.6%[33]. Yuan et al. (2017) used a modified polyacrylate sizing on carbon fibers. The treatment changed the fiber surface and increased the amount of active carbon from 12.65% to 24.70%. The fibers also showed improved wetting with the resin. A 14.2% increase in ILSS was obtained compared with untreated fibers[34]. Zhang et al. (2018) coated carbon fibers with a polyurethane sizing mixed with nano-SiO₂. The fibers with nano-SiO₂ behaved differently from those coated with polyurethane alone. In dry testing, their performance was more than 40% higher. After exposure to heat and moisture, the transverse fiber bundle (TFB) strength showed a small increase. The study shows that adding nano-SiO₂ to the sizing helped the fibers keep their strength in both dry and humid conditions[35]. Hao et al. (2019) coated carbon fibers with a polyimide sizing modified with Fe₃O₄ and reduced graphene oxide (RGO). The coating increased the surface energy and roughness of the fibers. ILSS testing showed a 159.0% increase over the untreated composite, indicating better fiber-matrix adhesion[36]. Eyckens et al. (2020) studied carbon fibers coated with poly(ethylene oxide) (PEO) of different molecular weights. Single-fiber pull-out (SFPO) tests showed higher IFSS values for all PEO-coated fibers than for the untreated fibers. The IFSS of the untreated carbon fiber was about 56.7 MPa. After coating with 1k-PEO and 2k-PEO, the values increased to about 62.6 MPa and 66.8 MPa, respectively. Fibers coated with 5k-PEO and 10k-PEO gave IFSS values of about 62.7 MPa and 63.8 MPa. Among the samples examined, the 2k-PEO coating gave the highest IFSS value. The epoxy resin selected for composite preparation may have influenced this result[37]. Tian et al. (2022) applied a PDA coating to carbon fibers followed by alternating layers of polyethyleneimine and nano-silica. The CF-L5 sample showed the highest IFSS, with a value 99.4% higher

than that of untreated fibers. This surface modification strengthened the connection between the fibers and the epoxy resin[38].

- **Acidic Treatment:** Chemical treatments are often used to improve the bonding between carbon fibers and thermoplastic matrices. Liang et al. (2009) treated short carbon fibers (SCFs) with chloroform. The available information does not describe the results of this treatment[39]. Zhang et al. (2015) used nitric acid to treat carbon fibers for POM/CF composites. After treatment, the fiber surface became rougher and contained more surface functional groups. The treated fibers also showed a higher level of disordered carbon. Because of these changes, the composites had better flexural strength and modulus than those prepared with untreated fibers[40]. Similarly, Chunzheng et al. (2018) found that acid treatment improved the bonding between ultrahigh-molecular-weight polyethylene (UHMWPE) and CFs[40]. Khan et al. (2016) reported that HDPE composites containing untreated carbon fibers (CFs) showed higher fracture strain, flexural modulus, and strength as the number of carbon fiber layers increased to 20, even without using coupling agents[41]. Shengbo et al. (2019) reported better bonding between nitric acid-treated carbon fibers and the HDPE matrix. This was because the new carboxylic groups formed on the fiber surface could interact with the hydroxyl groups present in the matrix[42].
- **Electrochemical modification** Electrochemical treatment uses an electric current in an electrolyte solution to modify the carbon fiber surface. This makes the surface rougher and improves its bonding ability. In electro-polymer coating, a thin polymer layer is added to the fiber surface. Other wet treatment methods, such as sol-gel coatings and coupling agents, are also used to obtain better bonding between the fiber and matrix[43][44]. Fu et al. (1998) used ozone treatment on carbon fibers and found that it increased the amount of oxygen on the fiber surface. The treated fibers bonded better with the polymer matrix. The treatment also did not reduce the tensile strength of the fibers[45]. Li et al. (2008) also worked on PA6/CF composites. Their results showed that surface treatment of carbon fibers can improve the properties of the composite[46]. Li et al. (2010) treated carbon fibers with ozone and air oxidation before using them in polyimide (PI) composites. The ozone-treated fibers bonded better with

the PI matrix, which reduced fiber pull-out and lowered the wear of the polymer. As a result, the composites showed better wear resistance and longer service life[47]. Li et al. (2011) treated carbon fibers with HNO_3 and found better bonding between the fibers and the ABS matrix. The treated fibers showed stronger attachment to the polymer than the untreated fibers[48]. Shengbo et al. (2019) treated carbon fibers using an electrochemical method. During the treatment, the carbon fiber bundles were connected to the anode and placed in a nitric acid (HNO_3) solution. The treated fibers showed better bonding with the matrix than the untreated fibers[42].

- ***Electro-polymer Coating***

Jin et al. (2006) studied the effect of electropolymerized sizing agents, namely m-phenylenediamine, phenol, and acrylic acid, on carbon fiber-reinforced phenolic resin composites. Among these treatments, acrylic acid reduced the contact angle from 85.6° to 52.2° and increased the surface free energy from 29.3 mJ/m^2 to 33.1 mJ/m^2 , showing better wetting of the fiber surface. All three treatments improved the composite properties. For m-phenylenediamine, the impact strength, flexural strength, and ILSS increased by 44%, 68%, and 87%, respectively. Phenol treatment increased these properties by 66%, 100%, and 112%, while acrylic acid treatment increased them by 20%, 80%, and 100% phenolic resin. Hung et al. (2008) also used electro-polymer coatings on carbon fibers and studied their use in epoxy composites. The coated fibers gave better composite properties than the untreated fibers. The transverse strength increased by about 50%, the longitudinal tensile strength by 64%, and the interlaminar shear strength by 135%. These improvements were mainly due to better bonding between the fiber and epoxy matrix[49].

2.6.2. Dry Methods

Dry surface treatments modify carbon fibers without the use of liquid chemicals. Plasma treatment changes the outer fiber layer and introduces functional groups that promote resin attachment. Radiation-based techniques, including electron beam, gamma-ray, and ultraviolet irradiation, can generate additional active sites on the fiber surface. Nickel deposition forms a thin metallic coating that increases electrical

conductivity and can influence composite performance. Heat treatment carried out under controlled conditions changes surface characteristics such as roughness and surface energy. Other approaches, including laser processing and microwave-assisted treatment, have also been explored for preparing carbon fiber surfaces before composite fabrication[50][51].

2.6.3. Oxidative Methods

Oxidative methods introduce oxygen-containing functional groups onto the carbon fiber surface, improving its compatibility with polymer matrices. Liquid-phase oxidation involves immersing fibers in oxidizing solutions such as nitric acid, potassium permanganate (KMnO_4), or hydrogen peroxide (H_2O_2), which chemically modifies the surface. Plasma oxidation uses oxygen plasma to etch the fiber surface, thereby increasing surface roughness and generating reactive groups. Gaseous oxidation exposes the fibers to oxygen or ozone in a controlled environment, facilitating oxidation reactions that improve the bonding with the resins. Miscellaneous oxidative methods include exposure to supercritical fluids and catalytic oxidation to achieve specific surface modifications[52].

2.6.4. Non-Oxidative Methods

Non-oxidative methods modify carbon fiber surfaces without introducing oxygen-containing functional groups and instead focus on changes in surface structure and composition. Whiskerization involves the growth of nano-sized whiskers (small filaments) on the fiber surface, which improve mechanical interlocking with the matrix. Plasma treatment uses non-oxidative gases, such as nitrogen or argon, to alter the surface characteristics without causing significant oxidation. Plasma polymerization deposits thin polymer films onto the fiber surface through plasma-enhanced chemical vapor deposition (PECVD), improving compatibility with the matrix. Pyrolytic carbon deposition forms a carbon-rich layer through the thermal decomposition of hydrocarbon gases, which helps improve wear resistance and thermal stability. Other non-oxidative methods for specialized applications include doping with metal nanoparticles and chemical vapor infiltration [53].

2.7. Role of Nano-Species in interface strengthening

Nano-species surface modification techniques involve the deposition or integration of nanomaterials onto the carbon fiber surface to enhance the mechanical, electrical, and thermal properties. CNTs are used to increase the electrical conductivity, thermal stability, and mechanical interlocking with the matrix. ZnO nanorods have been introduced to improve adhesion and functionalization for advanced applications such as sensors. Silicon dioxide (SiO₂) nanotubes enhance the hydrophilicity and thermal resistance of composites, making them more durable under extreme conditions. Titanium dioxide (TiO₂) nanorods provide UV protection and photocatalytic properties, which are useful in self-cleaning and high-temperature applications. Graphene oxide (GO) is used to enhance mechanical reinforcement, electrical conductivity, and corrosion resistance in high-performance composites[54].

Table 2.2. Different Techniques used for strengthening interfacial Properties in CF

Technique	Description / Typical Process Parameters	Advantages	Disadvantages	Ref.
CVD / In - situ growth	Nanostructures (e.g., CNTs, graphene) grown directly on CF surface via decomposition of a carbon-source gas at elevated temperature (e.g., 600 °C or higher) with catalyst particles on fibre surface.	Produces strong bonding and good alignment of nano-species; excellent mechanical interlocking.	High temperatures may damage carbon fibre strength, catalyst contamination, high cost, less scalable.	[13,55,56]
Electrophoretic Deposition	A colloidal suspension of charged nanoparticles (CNTs, GO, etc) is deposited	Good control of layer thickness; uniform coatings;	Requires conductive fibres; risk of fibre damage from current;	[57–59]

	onto the conductive CF surface using an electric field (e.g., 20 V for 20 min).	scalable to some extent.	agglomeration, non-uniform deposition possible.	
Dip Coating / Immersion / Sizing with Nanofillers	The fibre tow or fabric is immersed in a suspension containing nanoparticles (e.g., CNFs, CNTs) blended with sizing agent or coupling agent; then dried/ cured. Typical filler loading ~0.1-1 wt% in sizing.	Simple, low-tech, compatible with existing fibre sizing lines; easier to scale.	Control of uniformity is difficult; agglomeration; limited thickness of nano-species; potential for poorer dispersion.	[55,60]
Spray Coating / Aerosol Deposition	A suspension of nanoparticles (CNTs, graphene) is sprayed onto fibre preforms or fabrics (sometimes assisted by electric field or pulsed field) before resin infusion.	Flexible localisation of coating; relatively simple equipment; can deposit low filler contents effectively.	Potential for uneven coating; risk of voids; infiltration of resin may be hindered; additional process step.	[61][62]
Plasma / Electrochemical Surface Functionalisation + Nanoparticle Grafting	Fibre surfaces are activated (e.g., by plasma, acid treatment) to introduce functional groups, then nano-species (metal oxide nanoparticles, graphene oxide) are	Enables strong chemical bonding, improved wettability, tailored surface chemistry; enhanced	Pre-treatment may damage fibre surface; more complex chemistry; may add cost or steps; risk of fibre strength reduction.	[63][64][65]

	grafted or chemically bonded (e.g., via click chemistry) onto fibres. e.g., TiO ₂ nanoparticles grafted via thiol–ene click chemistry improved IFSS by ~78%.	interface performance.		
Magnetron Sputtering Technique	ZnO thin film deposited on carbon fibres via RF/DC magnetron sputtering at ~200–400 °C under Ar/O ₂ plasma. Produces nanocrystalline ZnO coating strongly adhered to CF.	Excellent control of film thickness and stoichiometry; strong adhesion; improves interfacial shear strength and electrical conductivity.	Vacuum equipment needed; moderate temperature may affect sizing; slow throughput.	[66]
Sol-gel Deposition	Nanoparticles (e.g., SiO ₂ , TiO ₂ , Al ₂ O ₃) formed <i>in situ</i> by hydrolysis/condensation of metal alkoxides in sol; CF immersed and then heat-treated at 120–200 °C to form a thin oxide layer.	Low temperature; uniform coverage; tunable chemistry; simple wet-chemical route.	Brittle oxide layer if too thick; drying cracks; needs post-curing.	[67]

2.8. Research Objectives

The main objectives of this study are as follows:

1. Interface modification using different nano-species (CNT, graphene, and ZnO).

2. Microstructure characterization of the pristine and modified fibers.
3. Evaluation of mechanical properties of modified composite.
4. Fractographic analysis of the tested composites to study failure mechanism.

2.9. Research Gap

Although considerable progress has been made in improving the interfacial strength of CFRP composite, several challenges still remain. Many recent studies have explored the modification of carbon fiber surfaces using nanomaterials such as carbon nanotubes (CNTs), graphene oxide (GO), and silica nanoparticles to strengthen the bond between the fiber and the matrix. A number of approaches have been explored for modifying carbon fiber surfaces, such as oxidation, plasma processing, sizing, chemical modification, and chemical vapor deposition (CVD). These methods have produced positive outcomes in many studies. However, obtaining the same level of performance from one batch to another is still difficult. This issue is particularly noticeable when nanomaterials are deposited on carbon fibers. For example, the growth and distribution of carbon nanotubes (CNTs) on the fiber surface are often non-uniform, which can lead to variations in composite properties. Differences in their distribution, alignment, and attachment from one area to another can affect the fiber-matrix interface and lead to variations in the mechanical properties of the composite. In addition, the naturally smooth, hydrophobic, and chemically inert surface of carbon fibers makes it difficult to establish strong bonding with the matrix. Therefore, there is still a need for effective, scalable, and well-controlled surface modification methods that can provide stable and enhanced fiber-matrix interactions for advanced CFRP applications.

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Chapter 3

3. Materials and Characterization Techniques

This chapter outlines the experimental procedures and characterization techniques used to investigate the surface modification and performance of carbon fiber-reinforced composites.

3.1. Material

3.1.1. Reinforcement: Carbon fiber employed was unidirectional T700 grade, produced from PAN-based precursors, comprising 12k filaments (approximate diameter: 7 μm). The mechanical and physical properties of carbon fiber are shown in the table 3.1 and 3.2. Supplied by CF Composite Pvt. Ltd., India. T700S is available in various Tow sizes (6K, 12K, 24K) and sizing types compatible with different resin systems, making it a versatile material for high-performance composite applications. A majority of carbon fibers have a high anisotropy. Thermal conductivity, axial stiffness, tension strength, and compression strength are frequently substantially stronger than their radial direction.

Table 3.1: Physical Properties of Carbon Fiber

Description	Type	Density (g/m^3)	Diameter (μm)	Tow
Carbon Fiber	Non- woven	1.80	7-8	12k

Table 3.2: Mechanical Properties of Carbon Fiber

Description	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
Carbon Fiber	4900	230	2.1

3.1.2. Nano-Species

➤ *Multi-wall Carbon Nanotubes*

MWCNTs utilized in this study were sourced from Techinstro, with the product series designated as TI-MWCNT. These nanotubes were synthesized by CVD using a proprietary method. The MWCNTs exhibit a high degree of purity (99%), and their bulk density is reported to be in the range of 0.20–0.35 g/cm³. The outer diameters of the nanotubes ranged between 5 and 20 nm, with an average length of 10 μm, as confirmed by the datasheet provided by the manufacturer.

MWCNTs are cylindrical nanostructures composed of multiple concentric layers of rolled graphene sheets, typically arranged in a coaxial manner around a common central axis. MWCNTs are carbon nanomaterials made of several graphene layers rolled together. The carbon atoms are arranged in a hexagonal structure with sp² bonding. This structure gives MWCNTs high strength and good electrical and thermal conductivity[1]. The number of graphene layers in MWCNTs usually ranges from 2 to more than 30. Their diameter is typically 2–100 nm, and their length may extend from a few micrometers to several millimeters. MWCNTs have very high mechanical strength, with tensile strength above 60 GPa and a Young's modulus of about 1 TPa. These values are much higher than those of many conventional materials such as steel[2]. MWCNTs are strong because of the strong bonds between the carbon atoms and their tube-like structure. They can flex and recover their shape after loading if they contain few defects. Adding MWCNTs to CFRPs can improve the strength and overall performance of the composites[3,4].

➤ *Graphene*

The graphene powder used in this study was obtained from Techinstro under the Graph-Research series. It has a purity above 99%. Based on TEM observations, the average sheet size is around 60 nm. Its low bulk density of 0.18 g/cc makes it useful for lightweight applications.

Graphene is made of a single layer of carbon atoms arranged in a hexagonal network. It is the main building block of graphite, carbon nanotubes, and fullerenes[5]. Since its discovery in 2004, graphene has been widely used in research because of its useful

electrical, mechanical, and thermal properties. Graphene finds applications in electronics, sensing devices, and composite systems[6]. Its tensile strength is approximately 130 GPa, while its Young's modulus is close to 1 TPa. Despite being only a single atomic layer, graphene can undergo significant deformation without fracture [7]. The combination of high strength and flexibility has led to its incorporation into carbon fiber-reinforced polymer (CFRP) composites, where it is used to modify and strengthen the matrix structure[8][9].

➤ **Zinc Oxide**

ZnO flakes with a size of 15–18 nm were obtained from Techinstro, India. The material has a melting point of 1975°C and a boiling point of 2360°C. Its density is 5600 kg/m³ and its molar mass is 81.40 g/mol. These properties make ZnO suitable for use in composite materials.

ZnO is a compound made of zinc and oxygen. It is used in many areas, including electronics, materials, and composite applications[10]. ZnO usually has a hexagonal crystal structure called wurtzite, which remains stable under normal conditions. It can be prepared in different forms such as nanorods, nanowires, nanoparticles, nanoflowers, and thin films[11]. In CFRP composites, ZnO can improve bonding between carbon fibers and the polymer matrix, thereby enhancing mechanical properties[12][13].

3.1.3. Matrix Material

• **Epoxy LY556/Hardener HY951**

For composite fabrication, LY556 epoxy resin (DGEBA type) was used. The resin provides good strength, chemical resistance, and bonding performance, as shown in Table 3.4. HY951, a low-viscosity aliphatic amine, was used to cure the resin. Its properties are presented in Table 3.3. Supplied by Herenba Pvt. Ltd., India.

Table 3.3: Physical Properties of Resin

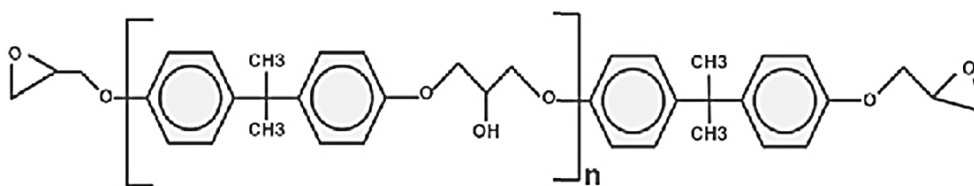
Description	Density (g/m³)	Viscosity (mPa.s)
Epoxy LY556	1.16-120	10350-12000

Hardener HY951	0.97-0.99	10-20
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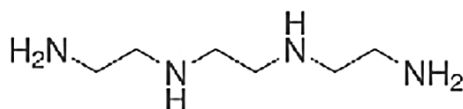
Table 3.4: Mechanical Properties of Resin and Hardener

Properties	Epoxy + Hardener
Tensile Strength (MPa)	52
Tensile Modulus (MPa)	2800
Elongation (%)	6

DGEBA is an epoxy monomer commonly used in adhesives, coatings, and CFRP composites[14]. It is preferred because it cures readily, is easy to process, and provides good strength and chemical resistance after hardening. The molecular formula of DGEBA is $C_{21}H_{24}O_4$, and its molecular weight is about 340 g/mol[15]. As shown in Fig. 3.1(a), DGEBA contains a bisphenol A unit with two glycidyl (epoxide) groups at both ends. The epoxide groups react with amine hardeners such as HY951 during curing, producing a crosslinked polymer network, as shown in Fig. 3.1(b). The aromatic rings present in bisphenol A contribute to the strength and thermal stability of the cured material. DGEBA epoxy resins generally have a glass transition temperature between 100 and 150 °C. They are also resistant to moisture, solvents, and a range of chemicals, which makes them useful in humid and chemically exposed conditions.[16]. DGEBA shows good adhesion with carbon fibers, metals, and ceramic surfaces. In CFRP composites, this helps the resin hold firmly to the fibers. Its liquid form has low viscosity, so it can flow between the fibers during processing and fill the spaces more evenly. DGEBA is also easy to handle and can be stored under normal conditions. For these reasons, it is commonly used in epoxy composites and several industrial products.



(a) Epoxy Resin (LY556)



(b) Epoxy Hardener - Araldite (HY951)

Figure 3.1. Illustrates the (a) chemical Structure of epoxy resin LY556 (b) Hardener HY591

3.1.4. *Coupling Agent*

Dopamine hydrochloride, a compound with a molecular weight of 189.64 g/mol and purity of 98%, was supplied by SRL, India.

Dopamine is a bio-inspired small molecule, structurally similar to the adhesive proteins found in mussel foot pads. Its uniqueness lies in the presence of both catechol (-OH groups on an aromatic ring) and primary amine (-NH₂) groups within the same molecule. This dual functionality allows dopamine to undergo oxidative self-polymerization and adhere strongly to a wide range of organic and inorganic substrates including metals, polymers, ceramics, and carbon-based materials. When exposed to an alkaline environment (typically pH 8.5 in Tris-HCl buffer), dopamine oxidizes and self-polymerizes into polydopamine, which forms a conformal coating on nearly any surface.

Chemical Formula of Dopamine: C₈H₁₁NO₂

Dopamine itself is a small, low-molecular-weight molecule and does not form stable coatings or robust interfaces on its own. While it can adhere to surfaces briefly, it lacks the structural stability and surface coverage needed for composite applications. Upon exposure to mildly alkaline environments, dopamine undergoes oxidative self-polymerization, leading to the formation of PDA, a high molecular weight, amorphous polymer that can form stable, uniform films on virtually all surfaces. PDA coatings are

mechanically robust, chemically active, and capable of serving as an effective interlayer that enhances the adhesion of subsequent nanomaterial coatings.

Moreover, PDA provides a platform for further functionalization, as its catechol and amine groups can chelate metal ions, reduce metal salts to form nanoparticles, and form covalent bonds with other modifiers. This makes PDA not just a passive coating but a versatile chemical bridge between carbon fibers and various nano-species, thereby improving both the chemical compatibility and mechanical integrity of the composite interface.

➤ *Formation of Dopamine to Polydopamine*

PDA formation shown in fig 3.2 begins with the oxidation of dopamine (DA) to dopamine-quinone in an alkaline solution ($\text{pH} > 8$), a process facilitated by oxygen or chemical oxidants. Dopamine-quinone undergoes intramolecular cyclization via a 1,4-Michael-type addition to form leucodopaminechrome, which is further oxidized to dopaminechrome. Dopaminechrome then rearranges and tautomerizes to produce 5,6-dihydroxyindole (DHI). These intermediates (dopamine-quinone, leucodopaminechrome, dopaminechrome, and DHI) polymerize through oxidative coupling, non-covalent interactions (e.g., π - π stacking and hydrogen bonding), and further cyclization, forming the heterogeneous, melanin-like PDA structure. During this redox-driven polymerization, the solution undergoes a distinct color change from colorless to orange, red, burgundy, and ultimately deep brown, reflecting the formation of intermediate products and PDA. When a substrate is immersed in the solution, the adhesive PDA spontaneously deposits, with the coating thickness depending on dopamine concentration and polymerization time. Despite the well-characterized steps, the precise molecular mechanism of PDA formation remains elusive due to the complexity of its structure and pathways.

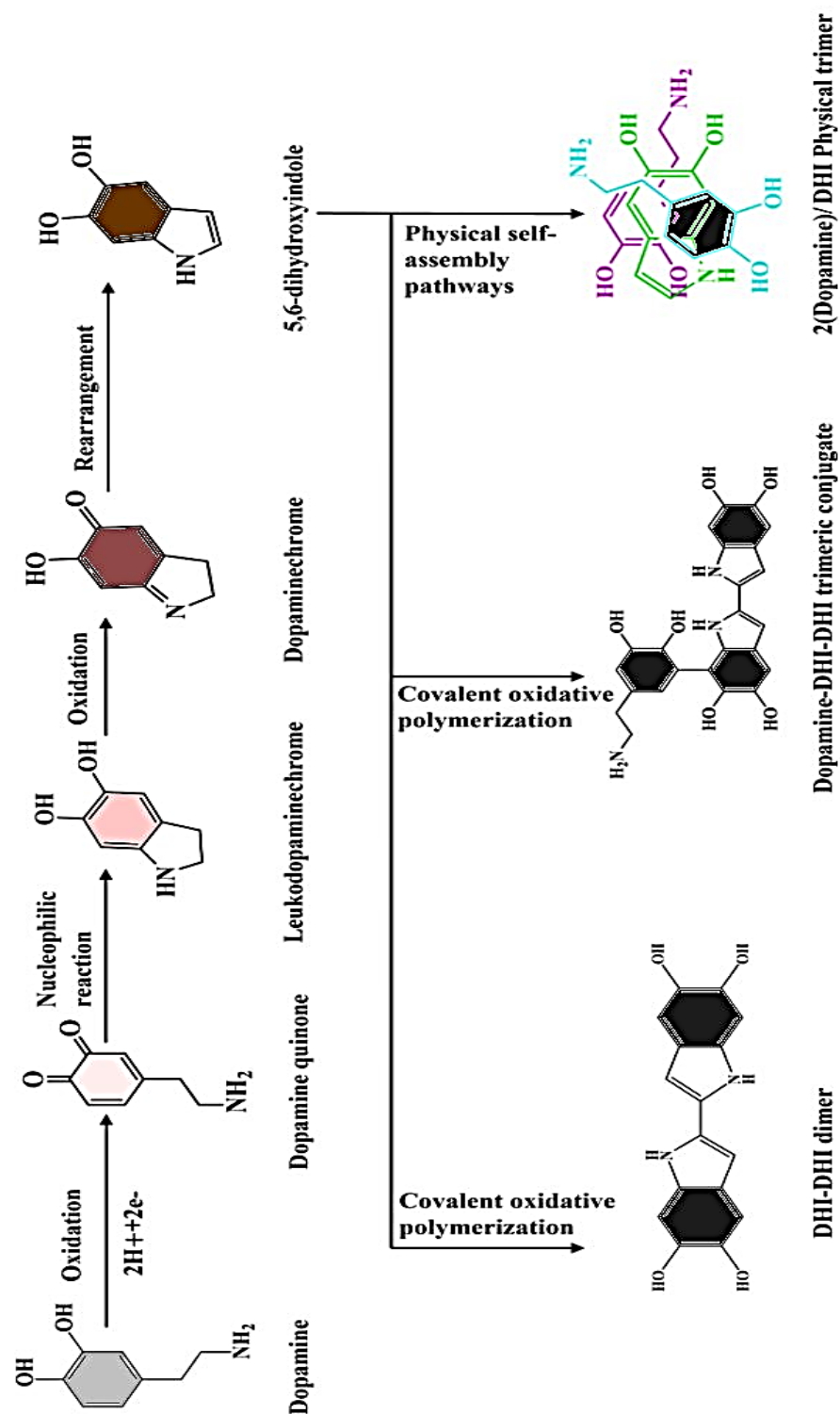


Figure 3.2. Illustrates the polymerization and interaction mechanism of polydopamine from dopamine

3.2. Surface Modification of Carbon fiber

3.2.1. De-Sizing

The initial step involved de-sizing the pristine carbon fiber by immersing it in acetone shown in fig 3.3(a) for 2 h to remove the protective sizing agent, which otherwise hindered surface functionalization and adhesion. Following the de-sizing step, the fiber underwent an oxidation process shown in fig 3.3(b) through acid treatment for 30 min, which introduced oxygen-containing functional groups ($-\text{COOH}$ and $-\text{OH}$) onto the fiber surface. These functional groups significantly enhanced the hydrophilicity and reactivity of the fibers, thereby improving the adhesion of the subsequent coatings. The acid-treated fibers were then thoroughly rinsed with deionized (DI) water until the pH of the washing solution reached neutrality (pH 7), ensuring the removal of residual acidic species and then dried in a vacuum oven at 80°C .

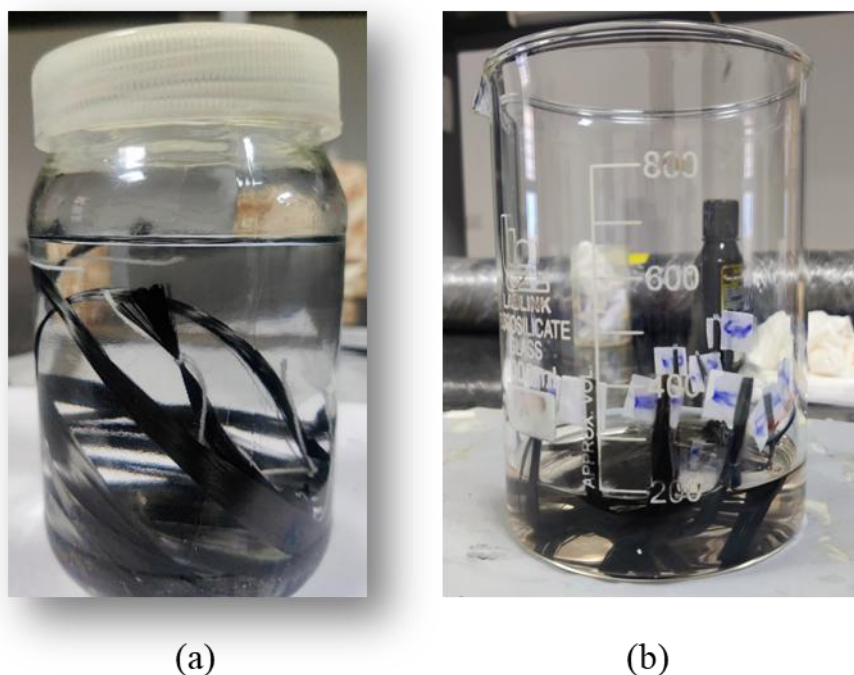


Figure 3.3. Illustrates the (a) desizing of carbon fiber in acetone (b) acidic treatment

3.2.2. PDA Layering

4. PDA layering shown in fig 3.4 was performed to functionalize the surface further. The PDA coating was synthesized using a Tris-buffer solution, where 0.45 g of tris buffer

was dissolved in 125 mL of distilled water and subsequently mixed with 500 mL of DI water containing 0.5 g of dopamine. The acid-treated fibers were immersed in the PDA solution and kept in an incubator shaker for 24 h to allow the self-polymerization of dopamine, forming an adherent PDA coating on the fiber surface. After incubation, the PDA-coated fibers were thoroughly washed with DI water to remove any unreacted or loosely bound PDA particles.

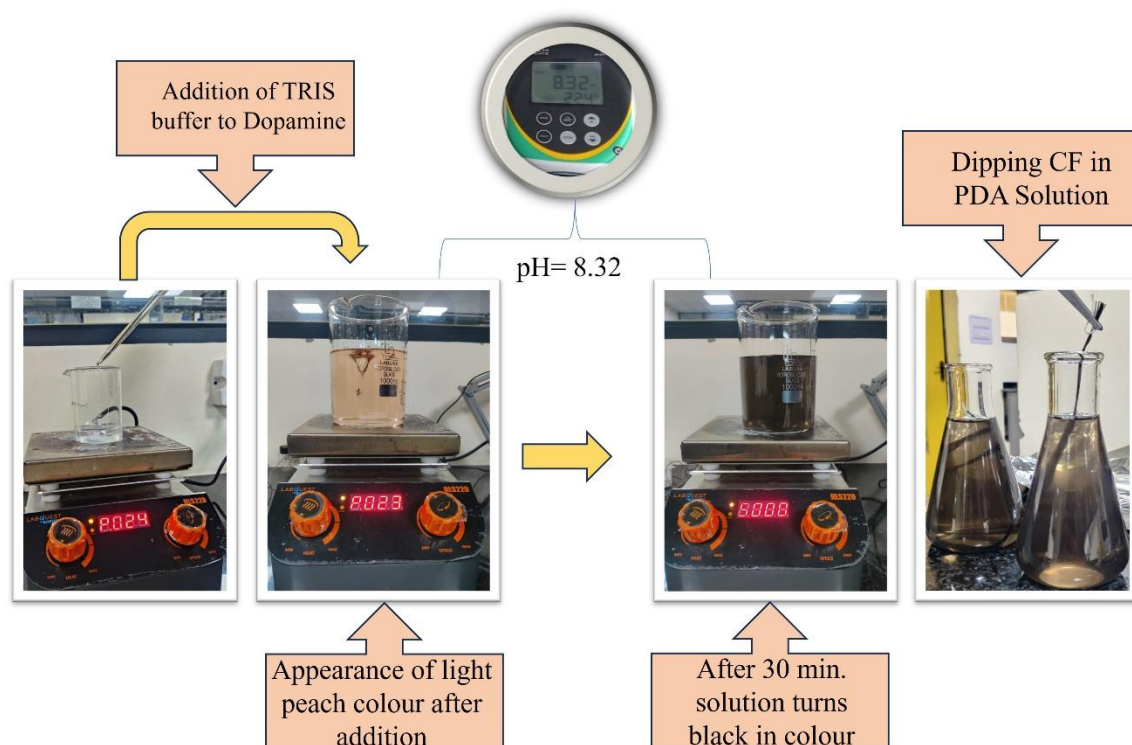


Figure 3.4. Illustrates the formation of polydopamine and its layering on the carbon fiber via immersion method

3.2.3. Nano-species Deposition

In the early stage of the work, carbon fibers were coated by simply dipping them into a suspension containing the selected nanomaterials. This method did not produce a satisfactory coating on the fiber surface. The nanoparticles gradually clustered together and settled in the solution, resulting in non-uniform deposition. As a consequence, some regions of the fibers received a higher coating density, whereas others remained only partially covered, an effect that became more pronounced for longer fiber lengths. Table 3.5 shows the experiment design for optimizing the various parameters.

Table 3.5: Design of Experiment for optimization of Various Parameters

S. No.	Nano-species Used	Quantity of Nano-species (mg)	Solvent Volume (mL)	Immersion Time (minutes)
1	CNT	0.2	100	10
2	CNT	0.2	100	20
3	CNT	0.2	100	30
4	Graphene	2	100	10
5	Graphene	2	100	20
6	Graphene	2	100	30
7	ZnO	2	100	10
8	ZnO	2	100	20
9	ZnO	2	100	30

To overcome this limitation, a secondary strategy was employed involving the use of PDA, a bioinspired adhesive derived from dopamine, known for its exceptional surface modification capabilities and strong interfacial adhesion properties. The application of PDA significantly increased the density of polar functional groups on the inherently smooth and chemically inert surface of the carbon fibers, thereby improving the surface reactivity and facilitating stronger interaction with the nano-species. Following the PDA coating, the modified carbon fibers were immersed separately shown in fig 3.5 into three different beakers containing MWCNTs, graphene, and ZnO each dispersed in 100 mL of dimethylformamide (DMF) solvent. The immersion process was carried out for 30 minutes, after which the fibers were removed and dried in a hot-air oven at 80 °C for 2 h to ensure solvent evaporation and nanoparticle adhesion. To optimize the coating process, immersion durations of 10, 20, and 30 min were tested. However, coatings obtained from 10 and 20-minute immersions were found to be non-uniform and insufficiently adhered, while the 30-minute duration provided the most consistent and homogeneous nanoparticle coverage. This multi-step strategy, incorporating polydopamine as an interfacial layer, proved to be effective in enhancing the dispersion and uniform attachment of nano-species on the carbon fiber surface.



(a) (b) (c)

Figure 3.5. Illustrates the nanospecies coating of (a) MWCNT (b) graphene (c) ZnO on the fiber

3.3. Surface morphology Characterization Techniques

3.3.1. *Field Emission Scanning Electron Microscopy (FESEM)*

The surface morphologies of both pristine and modified CFs were examined using field-emission scanning electron microscopy (FESEM, JOEL, JSM 6000). The FESEM was operated at an accelerating voltage of 20 kV under high vacuum conditions with a high probe current. The fibers were coated with gold to prevent charge accumulation during the imaging. Field Emission Scanning Electron Microscopy is a powerful technique that was used to examine the surface morphology of both as-received and coated carbon fibers at very high resolution. In the case of as-received carbon fibers, FESEM provided detailed images that revealed the natural surface features, such as longitudinal striations and smooth textures resulting from the manufacturing process. These images help in identifying surface defects, the presence of sizing material, and any irregularities. Furthermore, elemental mapping, which was performed using EDX, provided a visual distribution of elements across the fiber surface. This mapping technique created color-coded images that display where specific elements are located, allowing to assess the uniformity of the coating.

3.3.2. X-ray Diffraction (XRD)

The crystal structure of the untreated and coated carbon fibers was examined by wide-angle X-ray diffraction (XRD). Measurements were performed using a Bruker diffractometer with monochromatic $K\alpha_1$ radiation. The instrument was equipped with Johansson monochromators for both Co and Cu radiation sources and a LYNXEYE XE-T detector. Diffraction data obtained from the measurements were used to evaluate structural parameters such as the degree of graphitization, interlayer spacing (d-spacing), and crystallite size. These parameters are commonly used to describe the structural characteristics of carbon fibers and are related to their mechanical and electrical behaviour. For the coated carbon fibers, XRD was used to examine the materials deposited on the fiber surface. The diffraction patterns helped verify the presence of the coating and assess its crystalline nature. The technique also allowed the relative amounts of crystalline and amorphous phases to be evaluated. Such information is useful for understanding changes introduced by the surface modification. By comparing untreated and coated fibers, differences in structure arising from the coating process could be identified and related to the behaviour of the fibers in composite materials.

3.3.3. FTIR (Fourier Transform Infrared) spectroscopy

Fourier Transform Infrared (FT-IR) spectroscopy was used to examine the surface chemistry of untreated and coated carbon fibers. The spectra were recorded using a PerkinElmer FT-IR spectrophotometer in the wavenumber range of 4000–400 cm^{-1} . The obtained spectra were analyzed to identify the functional groups present on the fiber surface and to determine changes resulting from the coating process. A comparison of the spectra before and after surface modification provided information on the chemical changes associated with the treatment.

3.3.4. Raman Spectroscopy

Raman measurements were carried out using a WITec Alpha300 R+ spectrometer. A 532 nm laser was selected as the excitation source for spectral acquisition. The measurements were performed with a laser power of 5 mW and a 50 $\times$ objective lens. Each spectrum was collected with an acquisition time of 15 s. To obtain reliable spectra,

three successive scans were recorded and averaged before analysis. The Raman data were used to examine the structural features, bonding characteristics, and phase composition of the samples.

3.3.5. X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out to examine the surface composition of untreated and coated carbon fibers. The spectra were recorded using a Thermo Fisher Escalab XI+ instrument with an Al K α X-ray source. The technique was used to determine the elements present on the fiber surface and their corresponding chemical states. The obtained data were further analyzed to identify changes produced by the coating and surface treatment processes. Comparison of the spectra from untreated and modified fibers provided information on the chemical changes associated with surface modification.

3.3.6. Wettability Tests

Contact angle measurements were carried out for untreated and surface-modified carbon fibers using a Krüss DSA25 Drop Shape Analyzer. The measurements were used to examine the interaction between a liquid droplet and the fiber surface. Contact angle values obtained from the analysis were used to compare the wetting behavior of the different samples. Changes in contact angle after surface treatment provided information on modifications to the fiber surface and their influence on resin spreading during composite fabrication. Therefore, contact angle analysis serves as a simple yet powerful technique to validate surface engineering efforts aimed at optimizing the performance of carbon fiber-reinforced composites.

3.3.7 Transmission Electron Microscope

The high-resolution imaging was done on JEM 2010 from Joel high resolution transmission electron microscope (HRTEM) equipped with field emission gun operated at 200 kV, capable of providing a point-to-point resolution of 0.2 nm and lattice resolution of 0.14 nm. A fine powder of the sample was prepared and subsequently added to methanol. The solution was kept in ultrasonic bath for 15 min to obtain a uniform dispersion. In order to carry out transmission electron microscopy (TEM) analysis a small drop from this uniformly dispersed solution was taken in a capillary tube and poured on a 300-mesh carbon coated grid of 3 mm diameter.

3.4. Fabrication Of Composite

The fabrication of carbon fiber-reinforced composites involves several sequential steps. Initially, carbon fibers were accurately cut according to the dimensions of the mold. The epoxy matrix was then prepared by thoroughly mixing the resin with an appropriate amount of hardener using high-viscosity mechanical stirring to ensure uniform dispersion. Following the preparation of the resin system, the composite laminates were fabricated using the hand lay-up technique. The uncured laminate was subsequently transferred to a compression molding setup to apply heat and pressure for curing. Additional fabrication procedures are detailed in the subsequent section.

3.4.1. Mold Design

As shown in fig.3.6 mold design plays a crucial role in the composite fabrication process. The adjustable nature of the mold through movable screws provides flexibility to accommodate different fabrication requirements. The upper and front views show the arrangement of the samples within the mold. The modified single-tow carbon fibers were arranged systematically to ensure a uniform dispersion within the matrix. Surface-modified fiber composites were fabricated using this mold, where the upper and lower bars provided a uniform pressure distribution across the sample. The structured arrangement ensured the precise alignment of the fibers, promoting efficient stress transfer between the matrix and reinforcement.

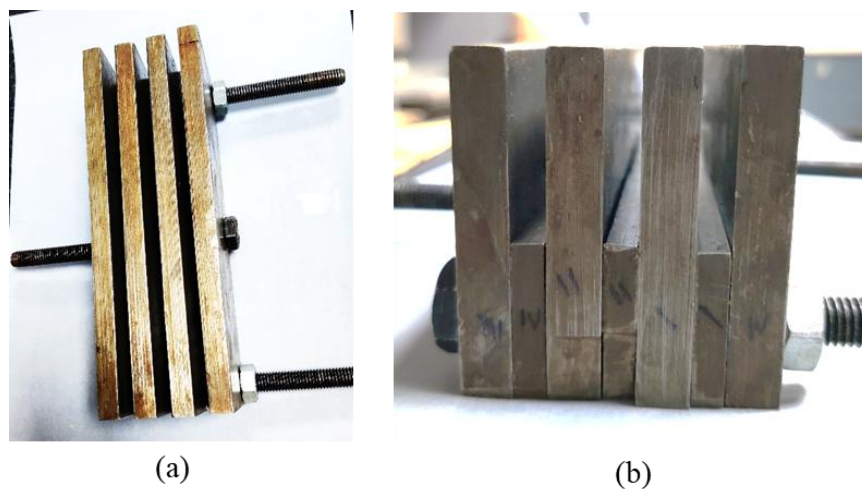


Figure 3.6. Illustrates the mold design (a) upper view (b) side view used for the carbon fiber reinforced polymer composite formation

3.4.2. Preparation of Epoxy Matrix

Matrix processing parameters are shown in table 3.6, to achieve effective reinforcement, a resin mixture prepared in a 10:1 ratio of resin to hardener was applied to the fibers. This step was carried out to reduce air bubbles in the composite, as trapped air can affect its strength. The resin begins to harden soon after mixing due to its high viscosity. For this reason, each composite was prepared individually, ensuring that the fibers were fully covered with resin and that the coated surface was properly wetted.

Table 3.6: Parameters for processing of epoxy/carbon based Composites

Sr. No.	Description	Parameter
1	Mixing Ratio of (epoxy/ hardener)	10:1
2	Mixing Time(for hardener)	5 min
3	Curing temperature	Room Temperature
4	Curing Time (Composite)	24 h

3.4.3. Hand Layup Technique

Carbon fiber composite laminates were fabricated by the hand layup technique. Carbon fiber sheets were first cut according to the required dimensions and arranged on a mold surface coated with a release agent. The epoxy resin and hardener were mixed and then applied to the fiber layers. A roller was used to distribute the resin throughout the laminate and remove trapped air. Successive layers were placed one over another until the desired laminate thickness, based on ASTM specifications, was obtained. After layup, the laminate was left for curing before further testing. Owing to its simplicity and low equipment requirement, the hand layup process is widely adopted for laboratory-scale composite fabrication and prototype development.

3.4.4. Compression Molding

Compression molding was carried out using a 30 MT hydraulic press (Model: DES/CMP/01, Serial No.: 25022023/01, Panel No.: 062304) available at Lovely Professional University, India. During molding, a pressure of 1 MPa was applied to the laminate. The molded assembly was maintained under these conditions for 12 h to allow resin curing. After completion of the curing process, the composite

laminates were removed from the mold and cut into the required dimensions for characterization and mechanical testing.

3.4.5. Indexing of CFRP Composite Samples

The sample codes used in this work are listed in Tables 3.7 and 3.8. Table 3.7 contains the codes for the untreated carbon fiber and the nanomaterial-coated fibers. Table 3.8 lists the codes for samples prepared with a PDA layer prior to nanomaterial coating. The PDA layer was used to improve the bonding between the fiber and the coating.

Table 3.7: Indicates the Sample IDs of the reference CF and nanospecies-coated carbon fiber.

Sr. No.	Sample ID Reference sample	Sample ID CNT coated sample	Sample ID Graphene coated sample	Sample ID ZnO coated sample
1	CF1	CF+CNT1	CF+G1	CF+ZnO1
2	CF2	CF+CNT2	CF+G2	CF+ZnO2
3	CF3	CF+CNT3	CF+G3	CF+ZnO3
4	CF4	CF+CNT4	CF+G4	CF+ZnO4
5	CF5	CF+CNT5	CF+G5	CF+ZnO5
6	CF6	CF+CNT6	CF+G6	CF+ZnO6

Table 3.8: Indicates the Sample IDs of the PDA layered and nanospecies-coated carbon fiber samples.

Sr. No.	Sample ID CNT and PDA coated sample	Sample ID Graphene and PDA coated sample	Sample ID ZnO and PDA coated sample
1	CF+CNT+PDA1	CF+G+PDA1	CF+ ZnO+PDA1
2	CF+CNT+PDA2	CF+G+PDA2	CF+ ZnO+PDA2
3	CF+CNT+PDA3	CF+G+PDA3	CF+ ZnO+PDA3

4	CF+CNT+PDA4	CF+G+PDA4	CF+ ZnO+PDA4
5	CF+CNT+PDA5	CF+G+PDA5	CF+ ZnO+PDA5
6	CF+CNT+PDA6	CF+G+PDA6	CF+ ZnO+PDA6

3.5. Mechanical Property Analysis

3.5.1. Universal Testing Machine (UTM)

Mechanical tests were carried out using an electronic universal testing machine (UTM). The same setup was used for both untreated and modified CFRP composite samples. During testing, load was applied to the specimen and the corresponding deformation was recorded. The data obtained from these tests were used to compare the mechanical response of the different composites and to assess the effect of surface modification.

3.5.2. Flexural Strength Analysis

Flexural testing was done on a 1000 kN universal testing machine at a crosshead speed of 2 mm/min. The three-point bending test was used to measure the flexural strength and modulus of the composite samples. This method was selected because the specimens failed at strains below 5%.

➤ Procedure for Three-Point Bending Flexural Test Using UTM

The flexural properties of the CFRP composites were measured using a three-point bending test. A universal testing machine (UTM) with a bending fixture was used for the test, as shown in Fig. 3.7. The testing procedure is described below:

- *Specimen Preparation:* Test samples were prepared according to ASTM D790. Each sample had a width of 8 mm and a length of 150 mm. The thickness varied depending on the fabrication process.
- *Fixture Setup:* The three-point bending fixture was mounted on the UTM. The sample was placed on two support rollers with a 15 mm overhang on each side.
- *Positioning the Loading Nose:* The loading roller was positioned at the center of the sample between the two supports.
- *Machine Configuration:* The crosshead speed of the UTM was set to 2

mm/min and kept constant throughout the test.

- *Initiating the Test:* The test was started by moving the crosshead downward. The loading roller pressed on the center of the sample until failure occurred or the required deflection was reached.
- *Data Recording:* Load and displacement values were recorded by the UTM software during the test. These readings were later used for flexural calculations.
- *Observation:* The sample was checked for visible damage such as cracks, layer separation, or other changes during loading.
- *Test Completion:* The test was stopped after sample failure or after reaching the specified deflection. The recorded data were then used for further analysis.

Five or more specimens were tested for each sample set. The reported values are the averages of these measurements. The carbon fiber fraction remained around 42% across all specimens, maintaining the composite composition nearly constant throughout the study.

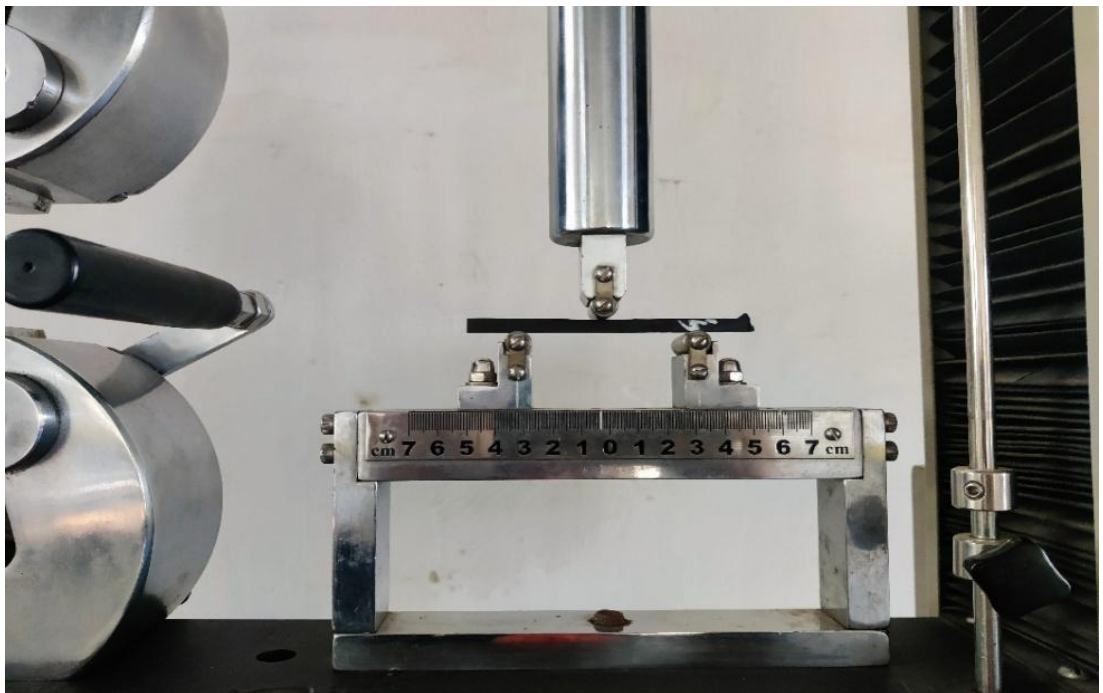


Figure 3.7. Illustrates the evaluation of flexural strength by three point bending test

3.5.3. *Tensile Strength Testing*

To analyse the tensile strength of CFRP composites the specimens were prepared according to ASTM D3039 standardized dimensions.

➤ *Procedure for Tensile Testing of CFRP Composites Using UTM*

The tensile properties of the CFRP composites were measured using a universal testing machine (UTM), as shown in Fig. 3.8. The procedure is as follows:

- *Specimen Preparation:* Samples were prepared according to ASTM D3039. The dimensions of the specimens followed the standard requirements.
- *Mounting the Specimen:* Each specimen was fixed between the upper and lower grips of the UTM. Care was taken to keep the sample straight during mounting, and the grips were tightened to avoid movement during testing.
- *Machine Configuration:* The crosshead speed was set according to the ASTM standard and remained unchanged during the test.
- *Initiating the Test:* After setting the test conditions, the machine was started, and a tensile load was applied to the specimen.
- *Data Acquisition:* Load and extension values were recorded automatically by the UTM software during the test.
- *Monitoring the Test:* The specimens were examined during loading for visible changes such as cracks, layer separation, or fiber pull-out.
- *Test Completion:* Testing continued until the specimen broke or the preset displacement limit was reached. The recorded values were then used to calculate the tensile properties of the composites.

This tensile testing method provides a clear understanding of the load-bearing capacity and failure characteristics of CFRP composites under axial loading conditions.

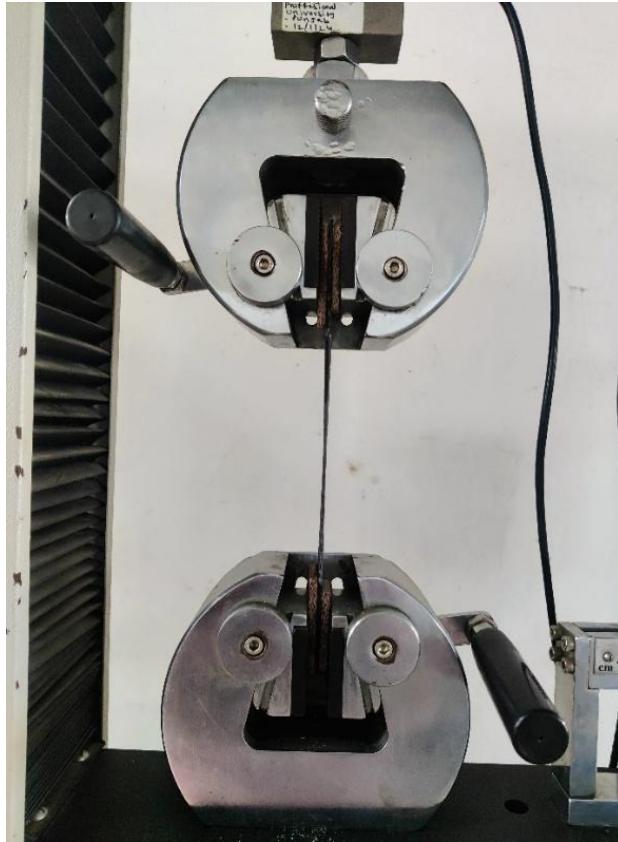


Figure 3.8. Illustrates the evaluation of tensile strength

3.6. Fractography Analysis

After mechanical testing, the fractured CFRP specimens were examined using field emission scanning electron microscopy (FESEM). Images collected from the fractured surfaces were used to study features such as fiber pull-out, matrix cracking, fiber breakage, voids, and interfacial debonding. The observations helped in understanding the fracture pattern of the composites and the effect of fiber–matrix interaction on the failure process. Differences in the fracture surfaces were compared with the mechanical test results. Flexural test specimens exhibited a combination of tensile and compressive failure features on opposite sides of the fracture cross-section. The tensile side demonstrated fiber breakage and matrix cracking, while the compressive side revealed fiber buckling and matrix deformation. Delamination between adjacent fiber plies was also detected, highlighting poor interfacial adhesion or resin-rich regions that acted as weak interfaces under bending loads.

3.7. Zeta Potential Particle Size Analyzer

Particle size and zeta potential measurements were carried out for ZnO, MWCNTs, and graphene dispersed in DMF. The measurements were performed using a Malvern analyzer equipped with a 633 nm He–Ne laser. Before analysis, the dispersions were sonicated and then transferred to the appropriate sample holders. Disposable cuvettes were used for particle size measurements, while zeta potential measurements were performed using folded capillary cells. The obtained data were used to examine particle distribution and surface charge characteristics of the dispersed materials. The cell was inserted into the instrument, where an electric field was applied across the sample for zeta potential analysis. The movement of charged particles under this field (electrophoretic mobility) was measured and subsequently converted into zeta potential values using appropriate models. Particle size was determined based on dynamic light scattering (DLS), where fluctuations in scattered light intensity due to Brownian motion of particles were analyzed to obtain the hydrodynamic diameter.

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Chapter 4(a)

Enhancement of Interface Adhesion in Carbon Fiber-Reinforced Composites through Polydopamine-Assisted Nanomaterial Coatings

4.1. Morphology of the Nanoparticles

The TEM micrographs shown in fig. 4.1 illustrate the structural characteristics of CNTs, ZnO, and graphene nanoparticles. In fig. 4.1(a) (5 μm scale), CNTs appear as entangled, tubular structures with well-defined walls and consistent diameters, extending several micrometers in length. Some smaller particles, residual catalysts, and impurities are attached to the tube surfaces. fig. 4.1(b) (5 nm scale) shows ZnO nanoparticles with spherical to slightly irregular shapes, clustered due to high surface energy, with individual particles in the nanometer range. Finally, fig. 4.1(c) (500 nm scale) displays wrinkled and layered graphene sheets with a flake-like morphology, where thin, semi-transparent sheets overlap in a random stacking pattern, providing a large surface area and flexibility.

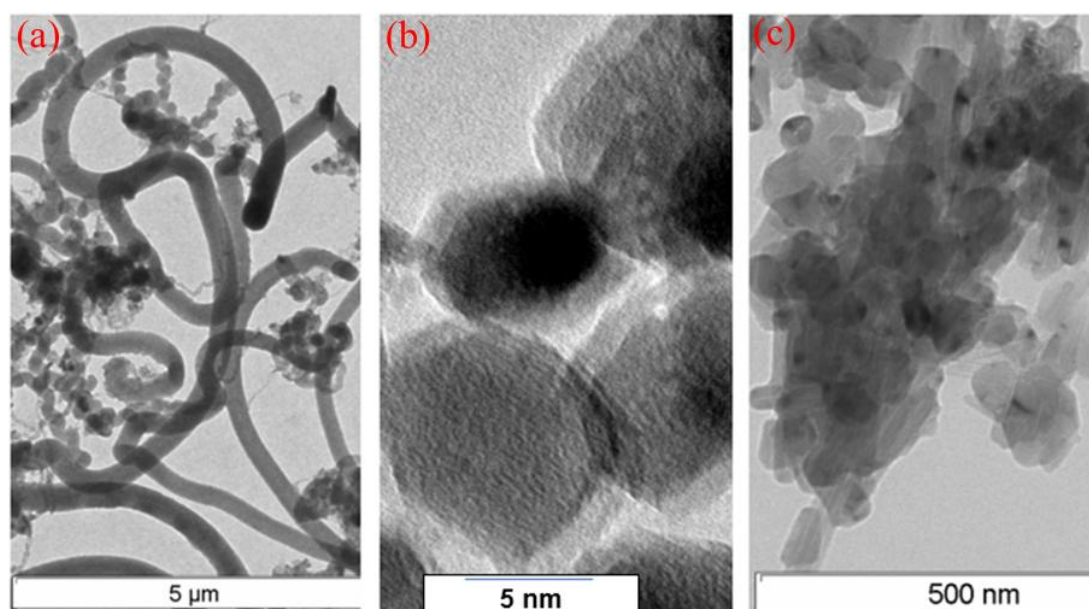


Figure 4.1. Illustrates the TEM images of (a) MWCNT, (b) ZnO, (c) Graphene

4.2. Zeta Analysis of the Nanoparticles

The zeta potential values presented in Fig. 4.2 provide information about the surface charge and dispersion behavior of ZnO, MWCNTs, and graphene (G) in DMF. Among the three materials, ZnO shows the lowest zeta potential value (-8.77 mV), indicating weak repulsive forces between particles and a greater likelihood of particle aggregation. Graphene showed a little higher negative value (-11.0 mV), suggesting better dispersion, but the stability in the solvent remains limited. MWCNTs have the high negative zeta potential (-19.4 mV), which indicates stronger electrostatic repulsion and relatively improved stability. But this value is still below the commonly accepted range of ± 30 mV required for highly stable suspensions. Based on these results the dispersion stability of the materials follows the order: ZnO < Graphene < MWCNTs. All three samples showed a tendency to form aggregates because the repulsive forces between particles were not strong enough to keep them separated.

Fig. 4.2 shows the particle size distribution of ZnO obtained from intensity measurements, most ZnO particles were found in the range of 10–100 nm, along with a few larger particles near 1000 nm. The larger size values are due to the formation of particle clusters. A broad peak is observed in the case of graphene between 1000 and 10000 nm, suggesting the formation of large agglomerates in the suspension. MWCNTs also displayed two peaks, one conforming to individual nanotubes in the 10–100 nm range and another near 1000 nm, which can be attributed to bundled or aggregated nanotubes. The results demonstrates that aggregation occurred in all three materials, with graphene showing the largest agglomerates, whereas ZnO and MWCNTs contain a mixture of well-dispersed particles and larger aggregated structures.

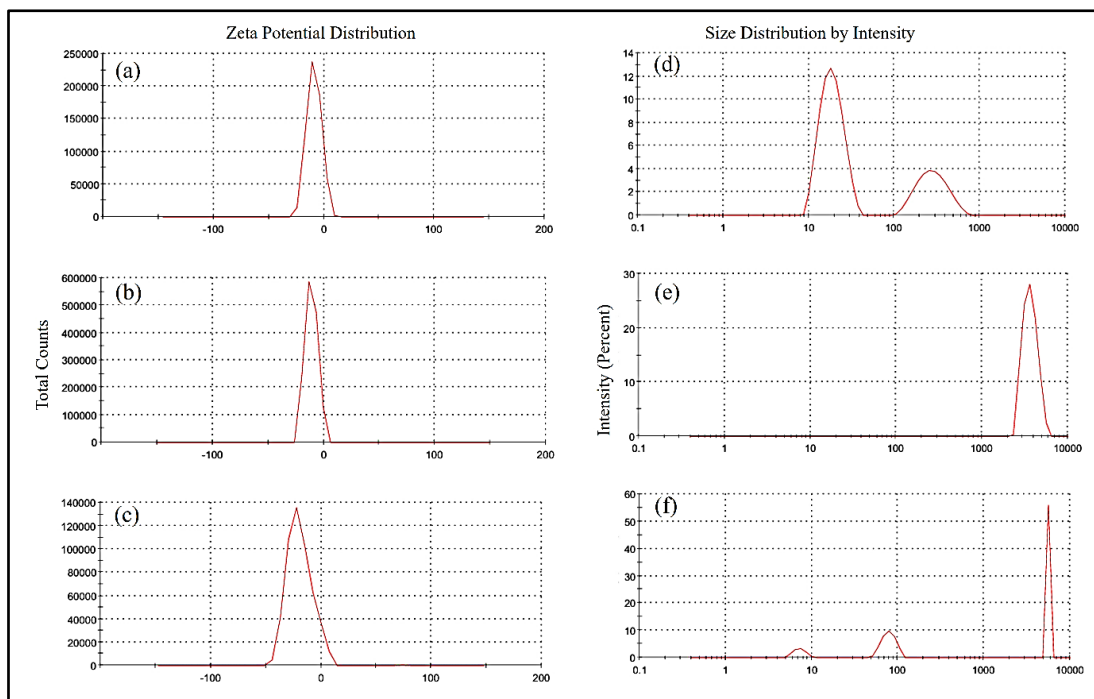


Figure 4.2. Illustrates the zeta potential of (a) ZnO, (b) G, (c) MWCNT and particle size distribution of (d) ZnO, (e) G, (f) MWCNT

4.3. Surface Morphology of CNTs, ZnO, and G coated Carbon fiber

The different stages of carbon fiber are shown in fig. 4.3 from the pristine to acid treated fiber including coatings and depositions. Where fig. 4.3 (a) shows a smooth and untreated carbon fiber surface and the greenish indicates the natural state of the fiber with no visible surface modifications or coatings. Fig. 4.3 (b) indicates that after cleaning the carbon fiber appears smoother with fewer surface impurities. The reddish tone shows the surface cleanliness with acid and the removal of initial sizing and contaminants. Further, fig. 4.3 (c) demonstrates the carbon fiber that has been coated with polydopamine in which surface seems more slightly rougher compared to the pristine fiber reflecting the presence of a coating layer. ZnO nanoparticles coating could be seen Fig. 4.3 (d) and (e). Image (d) shows a zoomed-out view of the ZnO coating, while (e) shows a magnified area, highlighting the dispersion of ZnO particles on the fiber's surface (with the blue arrows pointing at areas of interest). Fig. 4.3 (f) shows the distinct structure of MWCNTs. The fiber like nature of the nanotubes is visible,

suggesting a porous, fibrous network. Fig. 4.3 (g) represents a magnified image of ZnO nanoparticles separately, exhibiting a granulated texture. The green hue highlights the distinct particulate nature of the nanoparticles. Fig. 4.3 (h) shows CF coated with MWCNTs appears to have a more fibrous and rough surface texture, suggesting successful deposition of the nanotubes over the fiber substrate. Fig. 4.3 (i) shows the morphology of G, where the surface seems flaky and layered, indicative of graphene's thin sheet-like structure. Fig. 4.3 (j) displays carbon fiber coated with graphene. The fiber surface has a textured, rough appearance due to the graphene flakes adhered to it. Each micrograph highlights a different stage or type of modification to the carbon fiber, illustrating the changes in surface morphology as various coatings are applied.

[Note: The colors used in the FESEM micrographs are applied solely for visual differentiation between various treatments and coating processes. They do not carry any intrinsic or scientific significance. Instead, the color variations are artificially added to help distinguish different processes and coatings in the micrographs for easier interpretation.]

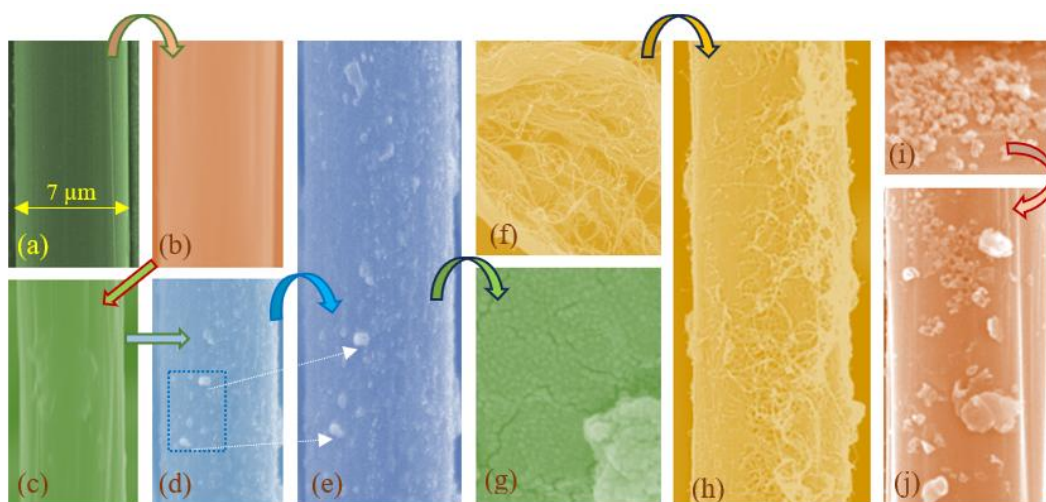


Figure 4.3. FESEM micrographs of carbon fiber prior and post-processing (a) Pristine carbon fiber (b) Cleaned carbon fiber (c) PDA coated carbon fiber (d), (e) ZnO coated carbon fiber (f) MWCNTs (g) ZnO nanoparticles (h) MWCNTs coated carbon fiber (i) Graphene (j) graphene coated carbon fiber.

The dipping time was adjusted from 10 to 30 minutes, and after 10 minutes, only minimal coating was observed, but after 30 minutes, coatings were visible. Although the particles were not uniformly distributed on the surface of the CF. However, after the catalyst coating, efficient growth of nanomaterials was achieved as PDA formed a strong adhesive layer on the CF surface due to its robust adhesion properties, which mimic the adhesive proteins found in mussels. This PDA layer provides a versatile platform for the subsequent attachment of ZnO, MWCNTs, and G. PDA coating contains abundant functional groups, such as amine and catechol groups, these functional groups facilitate strong covalent and non-covalent interactions, improving the uniformity and stability of the nanomaterial coating. The dip coating method made an equally uniform coating of ZnO, MWCNTs, or G on the fiber surface. Fig. 4.5 (a), (b) shows the uniform coating of ZnO at magnification (1000x), (3000x). Similarly, Fig. Fig. 4.5 (c), (d) shows the uniform coating of MWCNTs and Fig. 4.5 (e), (f) shows the G-G-coated CF at (1000x), (3000x) magnifications. The coating of ZnO shows the maximum bonding on the other hand CNTs make a continuous and branched network on the fiber surface. In contrast, the surface of G-coated CF displays hills and flattened patterns due to the size difference of G nanoparticles. That's why it's hard to see the uniformity at 1000x or 3000x magnifications because many of the particles are much smaller in size which can only be observed at higher magnification. Therefore, the difference in the morphologies can be seen at the particular magnifications as the CNTs have wire-like structures and ZnO and G possess different sizes of nanoparticles.

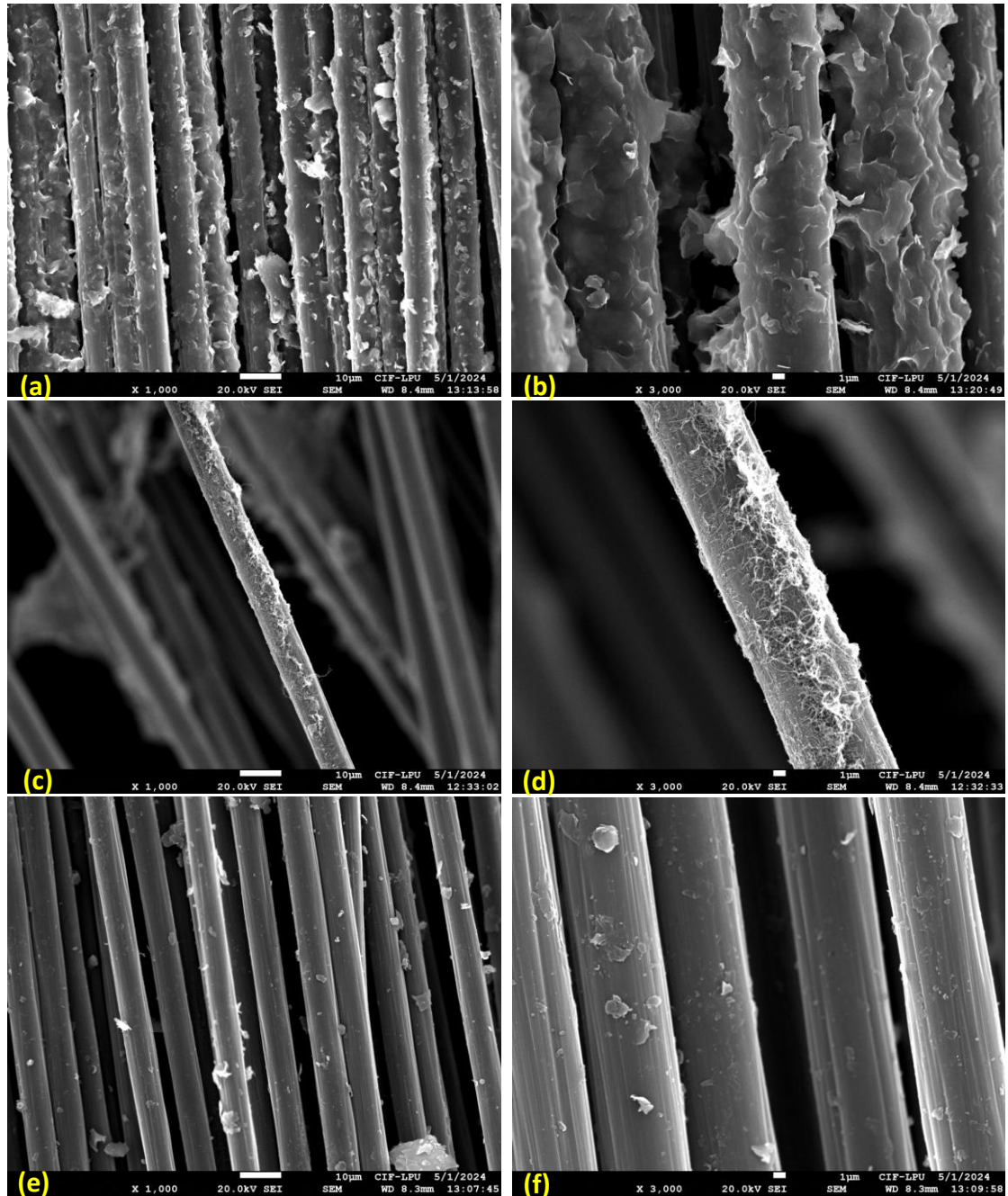


Figure 4.5. Illustrates the SEM images comparison of (a)-(b) ZnO, (c)-(d) MWCNTs, (e)-(f) Graphene Coated Carbon fiber at two different magnifications

The EDS energy spectrum analysis shows the distribution of nanomaterials on fiber surface. Fig. 4.6 (a) presents EDS, Fig. 4.6 (b) (c) shows the elemental mapping analysis of CF coated with G, and Fig. 4.6 (d) (e) shows the elemental mapping analysis of CF coated with MWCNTs. The EDS spectrum features a significant peak at 0.3 keV confirming that carbon is the predominant element in the samples, with a weight

percentage of 100%, indicating the high purity of the G and MWCNT coatings. The other peak at ~ 2 keV represents the gold, as the samples were gold-coated to avoid charge accumulation during observation. The absence of other notable peaks suggests the samples are primarily composed of these carbon-based nanomaterials. The SEM images show the surface morphology of the coated fibers: the G-coated fiber exhibits a smooth, continuous layer with visible texture, while the MWCNT-coated fiber shows a network of entangled nanotubes providing a dense coating. The elemental mapping shows the fiber surface covered with graphene and CNTs, the image is entirely red which indicates the distribution of carbon.

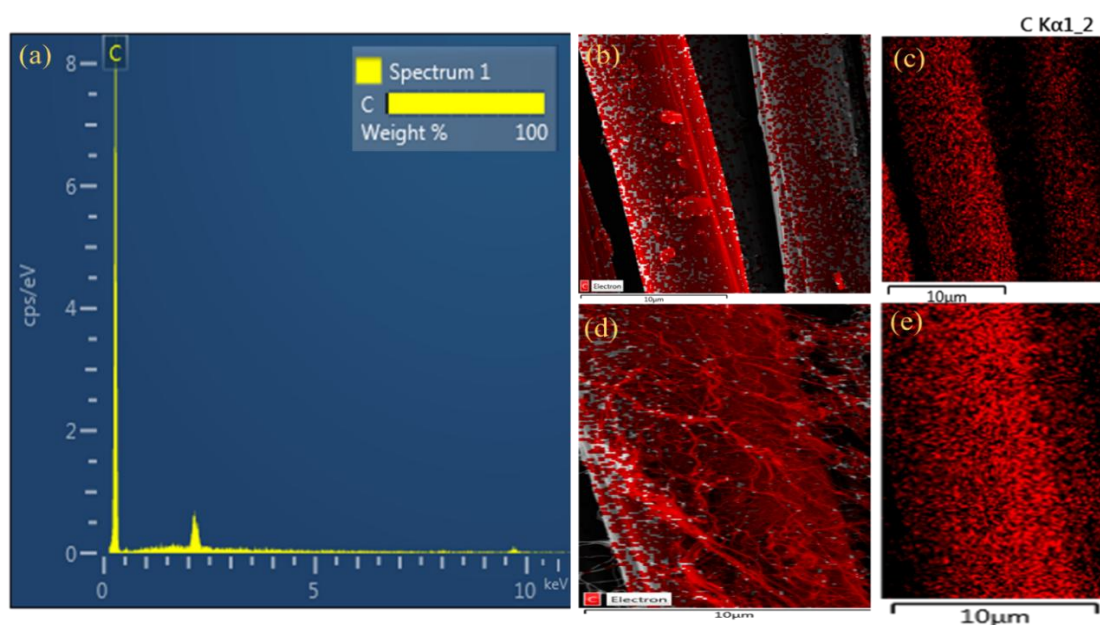


Figure 4.6. Illustrates the (a) EDS spectrum and elemental mapping of (b), (c) Graphene coated CF, (d), (e) MWCNTs coated on CF

Fig. 4.7(a) shows the EDS spectrum, while Fig. 4.7(b) shows the elemental mapping of the ZnO-coated CF. Fig. 4.7(c), (d), and (e) represent the distribution of zinc, carbon, and oxygen, respectively. The EDS spectrum shows peaks for carbon, oxygen, and zinc, indicating their presence in the sample. The peak near 0.3 keV is associated with carbon, the main constituent of the carbon fiber. A peak around 0.5 keV corresponds to oxygen, which is attributed to the ZnO coating. Peaks at higher energies (~ 1 keV and ~ 8.6 keV) indicate the presence of zinc, confirming the presence of ZnO nanoparticles.

Each colour corresponds to a specific element, green dots representing zinc, showing the distribution of Zn, and blue dots representing oxygen (O₂), indicating regions where ZnO or other oxides are present. The red dots represent carbon (C), showing the underlying CF structure.

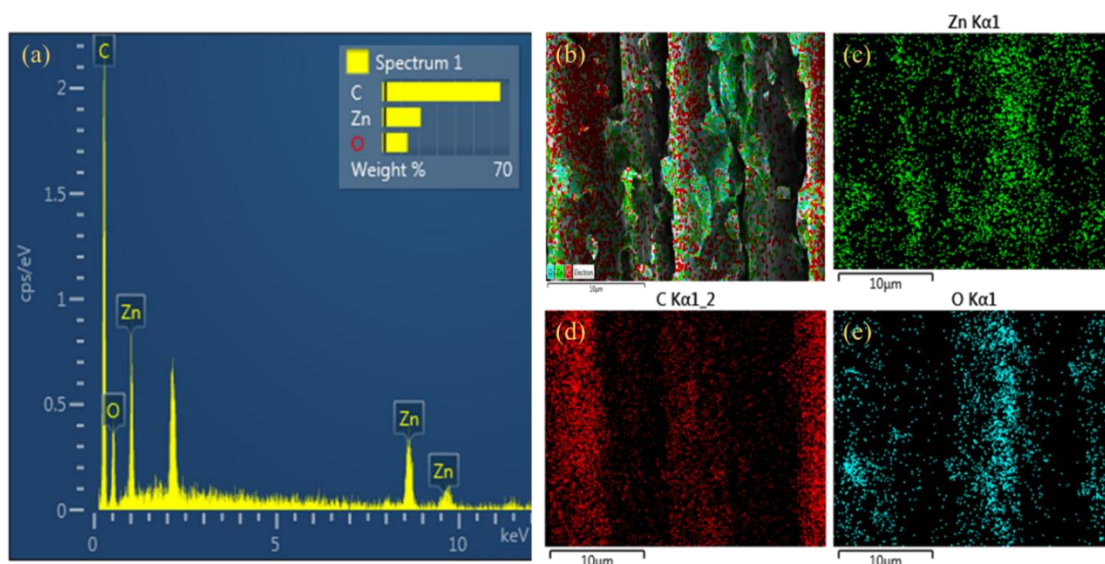


Figure 4.7. Illustrates the (a) EDS spectrum, (b) elemental mapping of Zinc Oxide coating on CF, (c) highlights the zinc, (d) highlights the carbon, and (d) highlights the oxygen

4.3.1. FTIR Analysis

A clear distinction is observed between the FTIR spectra of pristine fiber (P-CF) and nanomaterial-coated CF as shown in Fig. 4.8. In the spectrum of P-CF, a peak at 1061 cm⁻¹ indicates the C-O stretching which shows the presence of primary alcohol groups. Conversely, in the spectrum of the coated fiber, a sharp peak at 1034 cm⁻¹ shows the CO-O-CO stretching which indicates the presence of anhydride groups. The peak at 1404 cm⁻¹ in the P-CF shows the O-H stretching indicating carboxylic groups, while the peak at 1534 cm⁻¹ in the coated fiber indicates the N-O stretching that shows the nitro compounds. Additionally, the peak at 2321 cm⁻¹ in the P-CF shows the presence of cyano groups, whereas the peak at 1631 cm⁻¹ in the coated fiber indicates the C=C stretching which shows the presence of alkenes. The peaks between 2911-2975 cm⁻¹ in the P-CF and the peak at 2921 cm⁻¹ in the coated fiber both signify the C-H stretching

shows the presence of alkanes. Furthermore, a broad peak at 3683 cm^{-1} in the P-CF indicates the O-H stretching which shows the presence of alcohol. While the peak at 3274 cm^{-1} in the coated fiber indicates the O-H stretching which suggests the presence of carboxylic acid groups. Similar peaks are observed in MWCNTs, G, and PDA-coated CF; however, the ZnO-coated fibers exhibit fewer sharp peaks, though the appearance of the peaks is comparable to the other coatings. The reactive functional group enhances the fiber's surface reactivity and adhesion potential, thereby improving surface wettability and overall interfacial adhesion strength.

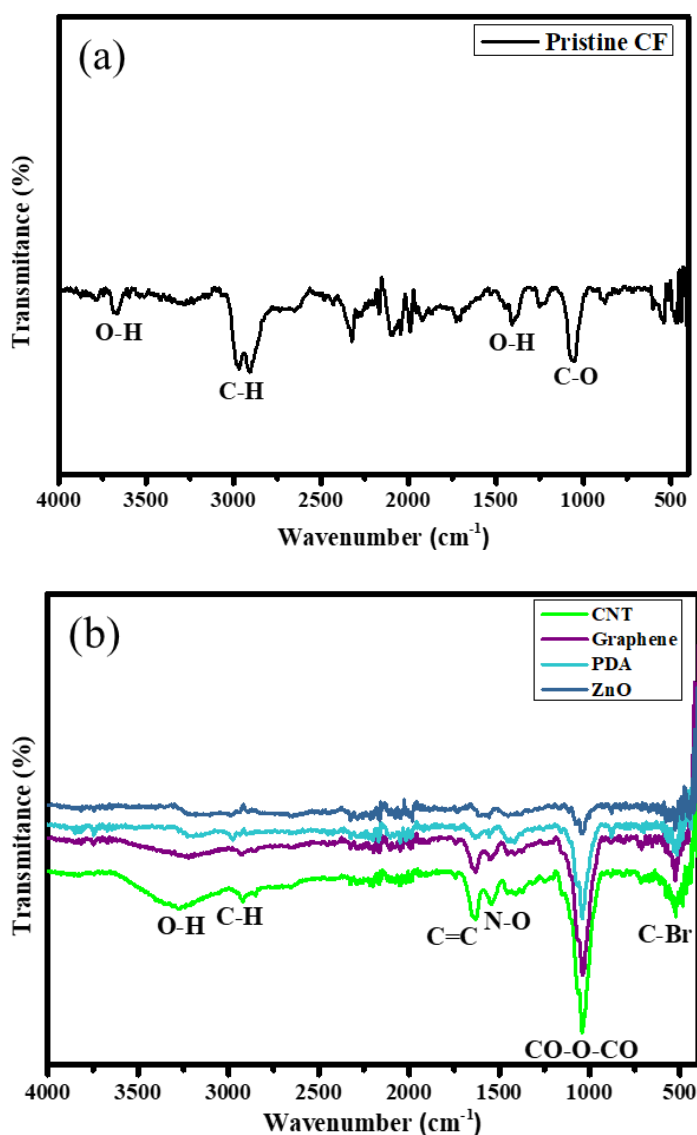


Figure 4.8. Shows the FTIR spectrum of (a) Pristine CF (b) Nanomaterials coated CF

4.3.2. XRD Characterization

The change of any carbon crystal by the dip coating method was analyzed by XRD. The provided XRD pattern compare the diffraction patterns of P-CF with those coated with various nanomaterials such as (CNT+PDA, G+PDA, ZnO+PDA). Fig. 4.9 (a) shows the P-CF pattern and in Fig. 4.9 (b) purple line indicates the ZnO+PDA, Fig.4.9 (c) red line indicates the CNT+PDA and in Fig. 4.9 (d) green line indicates the G+PDA coated CF. The P-CF XRD pattern exhibits a peak around $2\theta = 16.95^\circ$, 31.74° and a broad peak around 25.6° , which is characteristic of the (001), (111), and (002) plane of graphite, indicating the graphitic structure of the CF, while the broader peak at 43° represents in-plane structure and disordered in the graphitic carbon. In contrast, the XRD pattern of the nanomaterial-coated CF shows additional distinct peaks corresponding to the specific nanomaterials deposited: The ZnO peaks typically appear at certain 2θ values such as 31.8° , 34.6° , and 36.4° , which correspond to the (100), (002), and (101) planes of hexagonal ZnO.

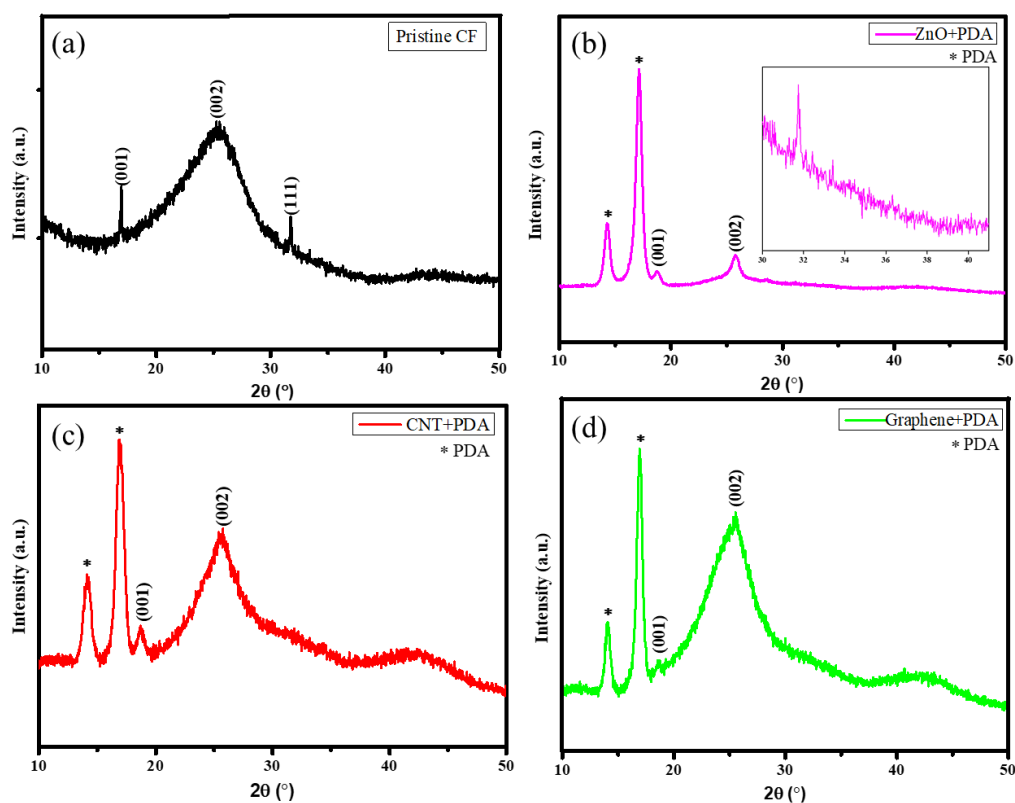


Figure 4.9. Illustrates the X-ray diffractogram of (a) Pristine CF, (b) ZnO+PDA coated fiber, (c) CNT+PDA coated fiber, (d) Graphene coated fiber

Additionally, the presence of the PDA layer and the carbon fiber substrate contribute to peak broadening and overlapping, which reduces the visibility of these ZnO peaks in the presented pattern. As a result, the peaks in this region are not distinctly observable. The presence of these peaks indicates the successful deposition of ZnO on the CF. The ZnO peaks are hidden due to overlapping sharp peaks of polydopamine at $2\theta = 14.27^\circ$ and 17.14° as the intensity of the polydopamine peak is very high. For the CNT-coated CF, the CNT+PDA shows a broad hump between 20° to 30° , which is characteristic of disordered carbon or amorphous carbon regions. The broad peak at around 26° is visible, indicating the presence of graphitic planes. However, the intensity is lower than in P-CF, suggesting the interaction between CNT and CF reduces the degree of crystallinity or creates more disordered carbon structures. The additional sharp peaks in the CNT-coated CF samples confirm the successful deposition of the PDA catalyst, enhancing the structural complexity and potential functional properties of the CF compared to the P-CF. Similarly, the broad peaks observed in the XRD pattern for G-coated CF are at around 25.6° , which are characteristic of the (002) planes of graphite. These peaks indicate the presence of G on the CF. There are no changes through the calculation of the interplanar distance (d_{002}) and the crystal structure of CF has not changed.

4.4. Wetting Properties of CF

The contact angle of epoxy LY556 with CF can vary depending on several factors such as surface treatments of the CF, the method of measurement, and environmental conditions. Generally, untreated CF has relatively high contact angles with epoxy resins, indicating poor wettability. Surface treatments lower the contact angle, improving the adhesion between the epoxy and the CF.

The Wenzel model used to relate the apparent contact angle on a rough surface (θ_w) to the contact angle on a smooth surface (θ) through the roughness factor (r):

$$\cos \theta_w = r \cos \theta \quad (1)$$

The surface energy (γ_s) of a solid surface can be related to the contact angle (θ) of a liquid droplet on that surface using **Young's Equation**. This equation expresses the balance of forces at the contact line where the liquid, solid, and vapor phases meet[1]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (2)$$

where: γ_{SV} is the surface energy of the solid-vapor interface,

γ_{SL} is the surface energy of the solid-liquid interface,

γ_{LV} is the surface tension of the liquid-vapor interface

θ is the contact angle.

Table 4.1: Show the comparison of contact angle, surface roughness and surface energy of pristine and coated fiber

Sr No.	Sample	Contact Angle (°)	Roughness Factor(r)	Surface Energy (J/m ²)
1	P-CF	85.9±0.08	1	5.10
2	PDA-CF	52.8±1.12	6.98	44.1
3	CNT+PDA-CF	66.6±0.24	4.54	29.0
4	G+PDA-CF	72.4±0.29	3.42	21.6
5	ZnO+PDA-CF	78.4±0.30	2.34	14.5

Table 1 compares different CF samples, including P-CF, and those coated with PDA, CNT, G, and ZnO. Each sample's contact angle, surface roughness, and surface energy are measured. P-CF exhibits a high contact angle (85.9°), indicating hydrophobicity, with the smoothest surface (roughness factor of 1) and the lowest surface energy (5.10 J/m²), indicating poor adhesive properties. PDA-CF shows increased hydrophilicity with a significantly lower contact angle (52.8°) and higher roughness (6.98), but increased surface energy (44.1 J/m²). The CNT+PDA-CF sample offers moderate wettability, roughness (4.54), and surface energy (29.0 J/m²) which is beneficial for adhesion. Additionally, G+PDA-CF maintains moderate roughness (3.42) and surface energy (21.6 J/m²). On the other hand, ZnO+PDA-CF achieves a moderate contact angle (78.4°) with relatively low roughness (2.34) and moderate surface energy (14.5 J/m²), indicating slight adhesive properties. High surface roughness generally correlates with increased adhesive properties and improved bonding between the CF and matrix material, as observed with PDA-CF, which has the highest roughness and high surface

energy, enhancing its interaction with the matrix material. Thus, the choice of coating material significantly influences wettability, roughness, and surface energy, impacting the CF's adhesion and surface interaction properties. Fig. 4.10 shows the graphical representation of the contact angle of the pristine and coated fiber. The blue bar shows the P-CF angle which is higher as compared to coated fiber but after the PDA coating, the angle decreased indicating the good adhesive properties of PDA. Fig. 4.11 shows the roughness factor and surface energy variation with a change in contact angle.

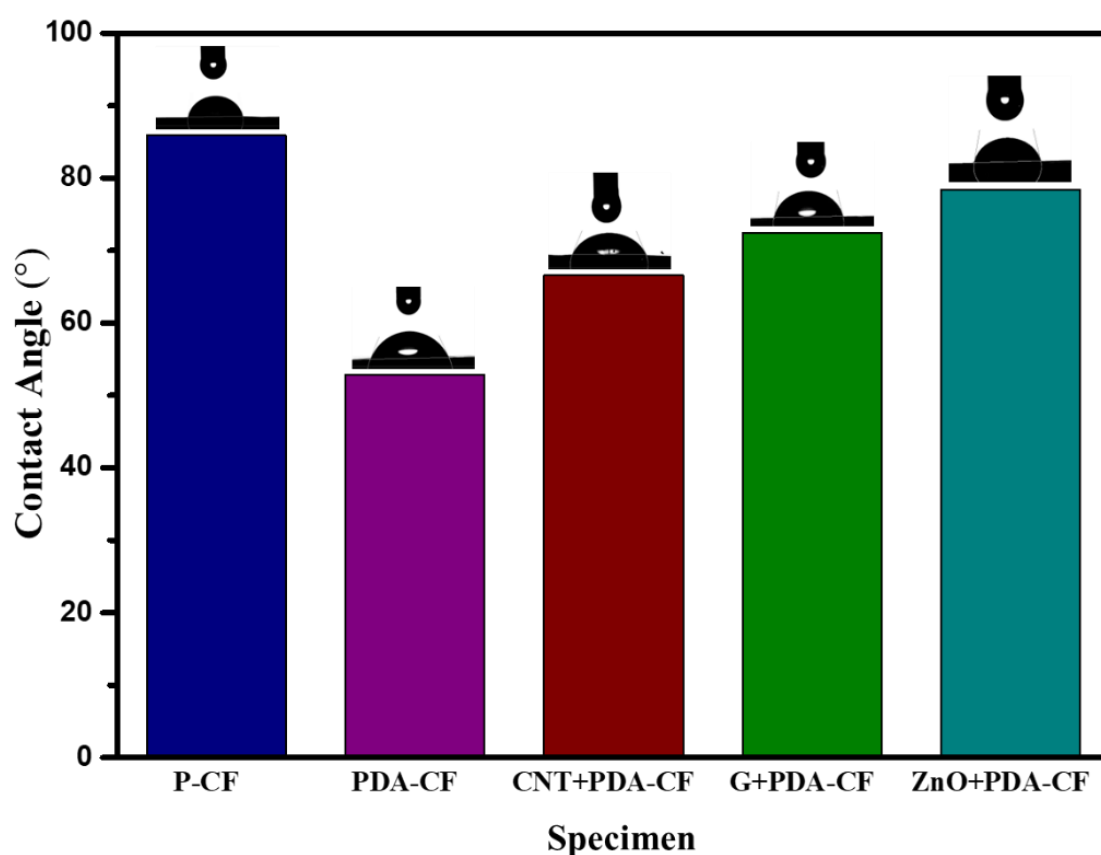


Figure 4.10. Illustrates the graphical representation of dynamic contact angle before and after coating the carbon fiber.

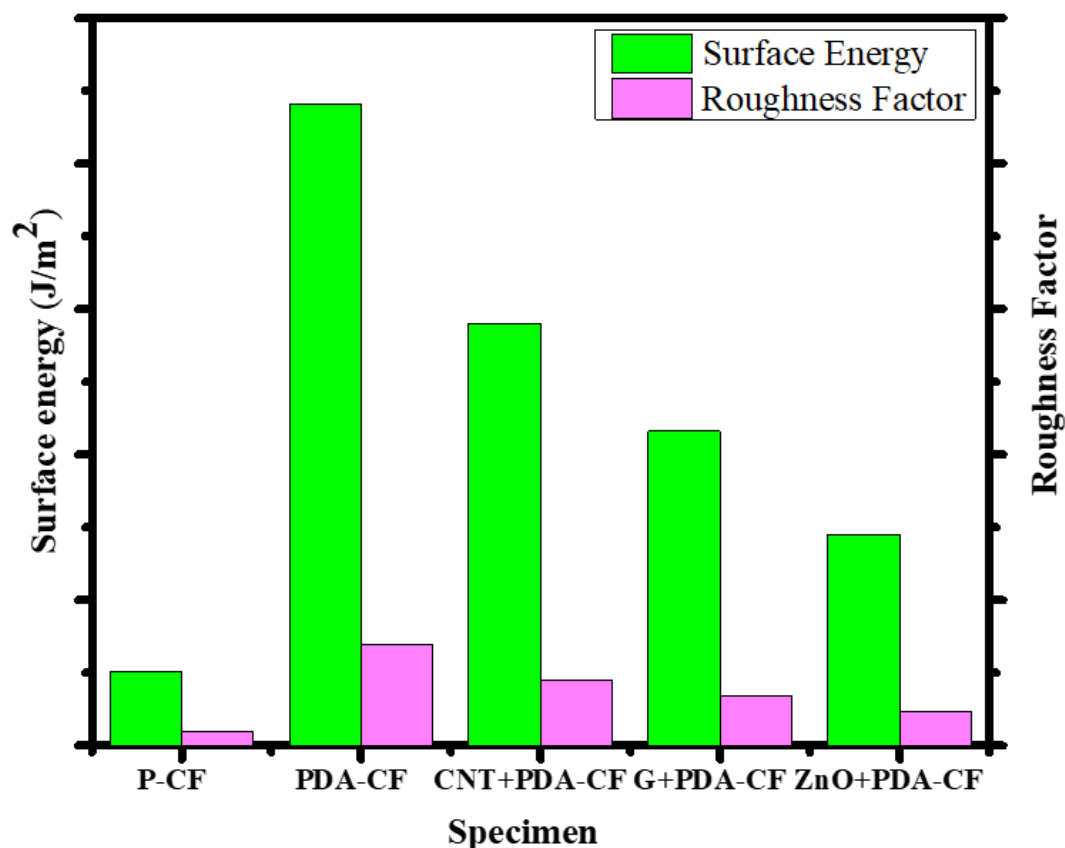


Figure 4.11. Illustrates the graphical representation of surface energy and roughness factor

4.5. Discussion

The FESEM analysis of CF revealed that the as-received fiber had a smooth, shiny surface due to the presence of epoxy sizing, which was removed by acetone and acid cleaning, leaving a clean surface with small grooves. After nitric acid treatment, the CF surface became oxidized, forming -COOH groups. However, in the absence of functional groups, coating the nanomaterial on the fiber surface was difficult due to the smoothness and hydrophobic nature of the fiber. Therefore, with PDA coating, a robust adhesive layer formed morphological features allowing uniform deposition from the colloidal particles of ZnO and MWCNTs also reported by wang et al.[2] and other researchers[3,4][5]. On the other hand, despite treating the CF surface with acetone and nitric acid, a uniform coating of G was not achieved using the dip-coating method. This discrepancy occurred due to the weak bonding of graphene with carbon fibers arises

from its chemically inert, smooth, sp²-hybridized surface, which lacks functional groups for covalent bonding, leading to poor interaction with the similarly non-reactive carbon fiber surface. This results in bonding that relies primarily on weak van der Waals forces or mechanical interlocking, which are far less effective than the strong covalent bonds achievable with functionalized materials like graphene oxide (GO). The low surface energy and hydrophobic nature of pristine graphene can make its attachment to carbon fibers difficult. Differences in the surface characteristics of graphene and carbon fibers may reduce their interaction. In addition, sizing agents or protective coatings already present on the carbon fiber surface may affect graphene deposition and reduce bonding between the two materials. The surface treatment used in this study may not have been adequate to reduce the hydrophobic nature of graphene or to achieve good adhesion on the carbon fiber surface. The other reason is due to the aggregation of G nanoparticles in the solution which hindered its coating on the fiber surface. Though the uniform coating of GO was reported in the literature using electrophoretic deposition and the pristine G is used as a filler in the matrix material [6–9]. Bridging this gap with functionalized pristine graphene or innovative deposition techniques could open new pathways for achieving uniform, strong coatings in carbon fiber-reinforced composites. Moreover, FESEM analysis and elemental mapping confirmed the uniform coverage of the MWCNTs and ZnO on the fiber surface. The FTIR spectra revealed increased surface reactivity and adhesion as dopamine-coated fiber, attributed to its oxidative properties. Therefore, it showed the enrichment in the functional groups that interacted with those on the CF surface, promoting the formation of C=O bonds[10]. The oxidation of dopamine occurred due to the interaction between the aldehyde (–CHO) and ketone (C=O) groups present in dopamine and the functional groups available on the carbon fiber surface[11]. The zeta potential values obtained for MWCNTs, ZnO, and graphene dispersed in DMF were comparable with previously reported values. However, the measured values were less negative which indicates limited stability of the suspensions. ZnO generally shows zeta potential values between –10 mV and –30 mV in polar solvents such as DMF. In this study, the ZnO suspension showed a value of –8.77 mV, suggesting weaker charge-based repulsion between particles and a higher chances of aggregation [12,13]. MWCNTs, value -19.4 mV, match well with reported values[14,15] (ranging from -15 mV to -30 mV) for

unmodified MWCNTs in organic solvents, showing better colloidal stability compared to ZnO. Graphene, showing -11.0 mV, which is on the lower end of the literature range[16,17] (-10 to -30 mV for pristine graphene) and indicates minimal functionalization or partial exfoliation. XRD analysis after deposition there is no harm to the crystal structure and mechanical properties of the fibers[18]. The results show that the crystalline structure of the carbon fiber remained unchanged after the dip-coating process. This indicates that the coating treatment did not affect the original properties of the carbon fiber, including its strength and mechanical stability. The increase in surface energy was due to the increased number of polar components on the fiber surface[19]. The wettability and interfacial properties obtained using the dip-coating method improved by approximately 38.53%. This increase in wettability suggested that the surface modifications achieved by dip coating with nanomaterials, such as ZnO, MWCNTs and G led to enhanced interaction between the CF surface and liquids. Wettability can vary depending on the deposition method and the type of nanomaterial applied to the CF surface. Different deposition techniques reported in the literature showed varying contact angle results, influenced by the type of liquid used as the drop analyzer [19][20][21][20]. Lastly, adhesion is greatly improved with PDA, as it acted as a molecular "glue" that bonded nanomaterial like ZnO, MWCNTs, or G to the CF surface. In the absence of PDA, nanomaterial coating was not achieved due to differences in surface chemistry or physical properties of both fiber and coating material. PDA helped improve the bonding between the nanomaterials and the carbon fiber surface. The functional groups present in PDA formed connections with both materials, which improved coating adhesion and reduced coating detachment during loading. The modification of carbon fiber surfaces with MWCNTs, graphene, and ZnO nanoparticles can be useful for hydrogen storage and energy storage applications. Changes to the fiber surface may improve its performance in these areas. A stronger bond between the fiber and matrix is important for hydrogen storage systems because these materials must bear high pressure during hydrogen storage. The modified carbon fibers may also be used in structural supercapacitors and batteries as the nanomaterial coating changes the fiber surface, which can help electron movement and increase energy storage capability[22–26].

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Chapter 4(b)

Effect of Polydopamine-Assisted Carbon Nanotube Grafting on the Mechanical Properties of Carbon Fiber-Reinforced Polymer Composites

4.6. Surface Analysis of CNT Coated CF

4.6.1. Raman Spectroscopy Analysis

Raman spectra of P-CF and CNT-coated carbon fiber is compared in Fig. 4.12, which reveals the change in structural characteristics Post CNT deposition. The spectra are mainly characterized by three peaks: the D-band ($\sim 1346\text{ cm}^{-1}$), G-band ($\sim 1585\text{ cm}^{-1}$), and 2D-band ($\sim 2700\text{ cm}^{-1}$). P-CF, the CNT-coated sample shows a higher D-band intensity, as D-band signifies the defect and disorder in carbon material. After CNT coating the G-band shifts slightly toward a higher wavenumber, it could be related to the strain caused during deposition or this shift recommend change in the local electronic environment which represents to the vibration of sp^2 -bonded carbon atoms shifts. Further the presence of 2D band confirms the structural modification of fiber surface. To evaluate the degree of order in carbon-based materials we use the intensity ratio of D-band to the G-band (ID/IG). In general, a lower ID/IG ratio indicates a more graphitic and ordered structure, while a higher value reflects a greater level of disorder. The pristine carbon fiber exhibited an ID/IG ratio of 1.5, suggesting the presence of a relatively large number of structural defects. Significant improvement in structural order was observed as ratio decreased to 0.5 after CNT coating, it is possible due to highly graphitic nature of deposited CNTs. While the pristine fibers contain defects such as edge imperfections and amorphous carbon regions that donate to a stronger D-band, but the well-formed CNTs possess a more ordered sp^2 carbon network. As a result, lower ID/IG ratio was observed due to the dominance of the G-band. The measured signal is strongly influenced by the CNT coating rather than the underlying carbon fiber because Raman spectroscopy mainly probes the near-surface region of the sample. The Raman spectrum suggests that the CNT layer has a higher degree of crystallinity. The ID/IG ratio mainly depends on the defect content of the CNTs rather than their

alignment. Although the CNTs were not uniformly aligned on the fiber surface, the lower ID/IG ratio suggests fewer structural defects and a more ordered graphitic structure. The changes observed in the Raman peak positions and intensity ratios indicate a strong interaction between the CNT coating and the carbon fiber surface. The Raman spectra shown in Fig. 4.12 show clear differences between the untreated and CNT-coated carbon fibers in both peak position and peak intensity. The CNT coating increased the defect content of the fiber surface, but it also created additional active sites that can improve interaction with the matrix material.

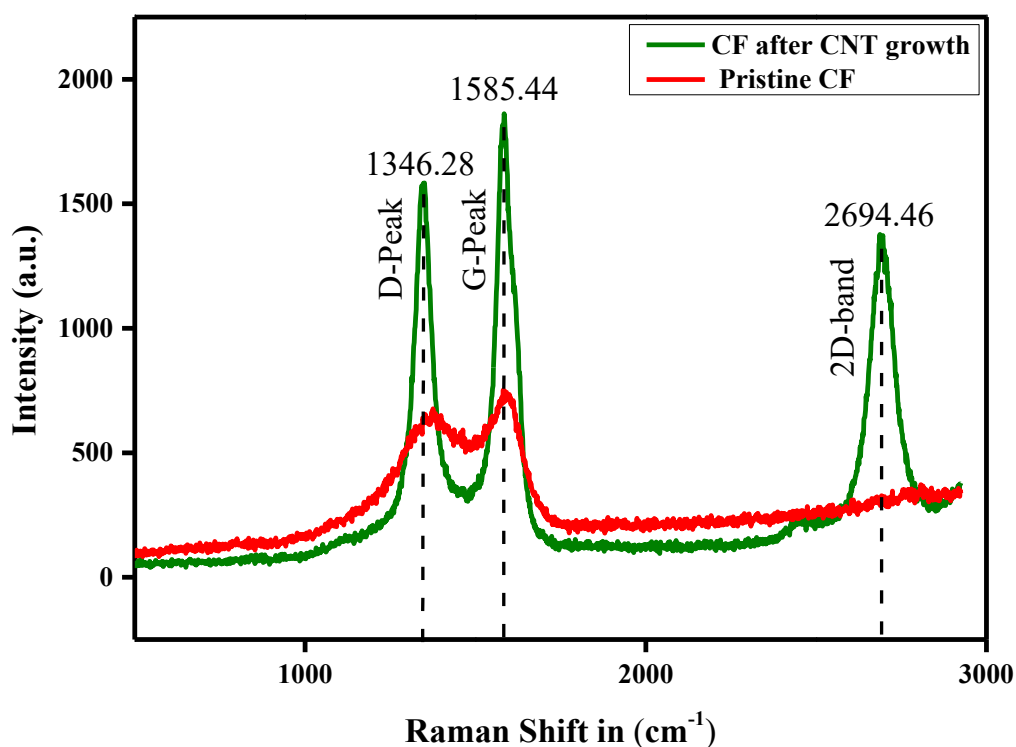


Figure 4.12. Illustrates the Raman shift of pristine and CNT modified CF

4.6.2. X-Ray Photoelectron Spectroscopy

The provided XPS characterization of (P-CF) in Fig.4.13 (a) includes survey spectrum and Fig.4.13 (b) shows the high-resolution spectra for the C 1s and Fig.4.13 (c) indicates O 1s regions. In the survey spectrum, significant peaks corresponding to the C 1s (~284 eV) and O 1s (~532 eV) binding energies confirmed the presence of carbon and oxygen on the surface of the sample. The high-resolution C 1s spectrum shows

deconvolution into multiple peaks, indicating the presence of various carbon species, such as sp^2 hybridized carbon (C=C), sp^3 hybridized carbon (C-C), and functional groups such as C-O, C=O, and O-C=O. The high-resolution O 1s spectrum revealed peaks attributable to oxygen-containing functional groups, such as hydroxyl (-OH), carbonyl (C=O), and ester or carboxylic groups (O-C=O). These results indicate that the P-CF surface exhibits a combination of graphitic carbon and oxygen-containing functional groups, which could contribute to its surface reactivity and potential for functionalization.

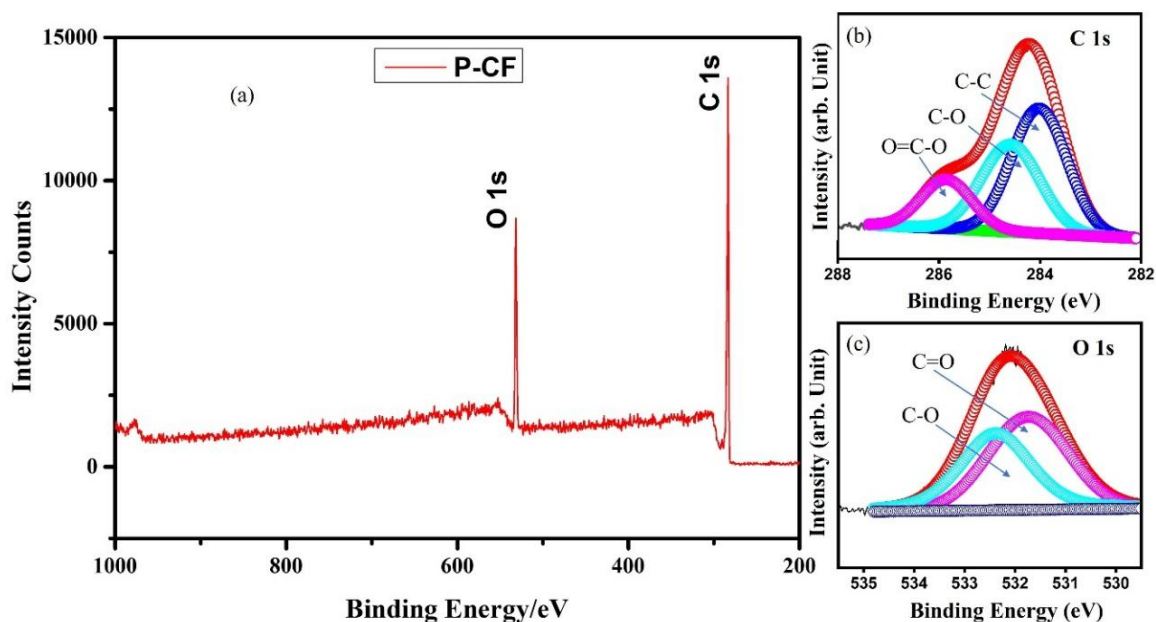


Figure 4.13. Illustrates the X-ray Photoelectron spectroscopy (a) survey spectrum of pristine carbon fiber (b) deconvolution peaks of carbon (c) deconvolution peaks of oxygen

The XPS characterization of the PDA+CNT-coated carbon fiber in Fig. 4.14 reveals significant differences compared to P-CF, particularly in the chemical bonding on the surface. The survey spectrum in Fig. 4.14 (a) shows prominent peaks for C 1s (~284 eV) and O 1s (~532 eV), similar to those of P-CF, indicating the dominant presence of carbon and oxygen. However, the high-resolution C 1s spectrum in Fig. 4.14 (b) shows an increased contribution from oxygen-containing functional groups, including peaks

for C=C (sp^2 carbon), C-C (sp^3 carbon), C-O, and O=C-O, which suggests successful surface modification with PDA and CNTs. The increased intensity and distinct deconvolution peaks for C-O and O=C-O compared to those of P-CF reflect the introduction of new functional groups via PDA deposition and CNT attachment. In Fig. 5(c), in the O 1s region, the peaks corresponding to C=O and C-O bonds exhibit higher intensities, further corroborating the presence of oxygen-rich functionalities. This indicates enhanced surface reactivity and chemical heterogeneity owing to the coating process, which introduces polar groups suitable for potential interactions, adhesion, and functionalization. Compared to P-CF, which shows only slight oxidation, the oxygen-containing groups in the coated sample were introduced to improve adhesion.

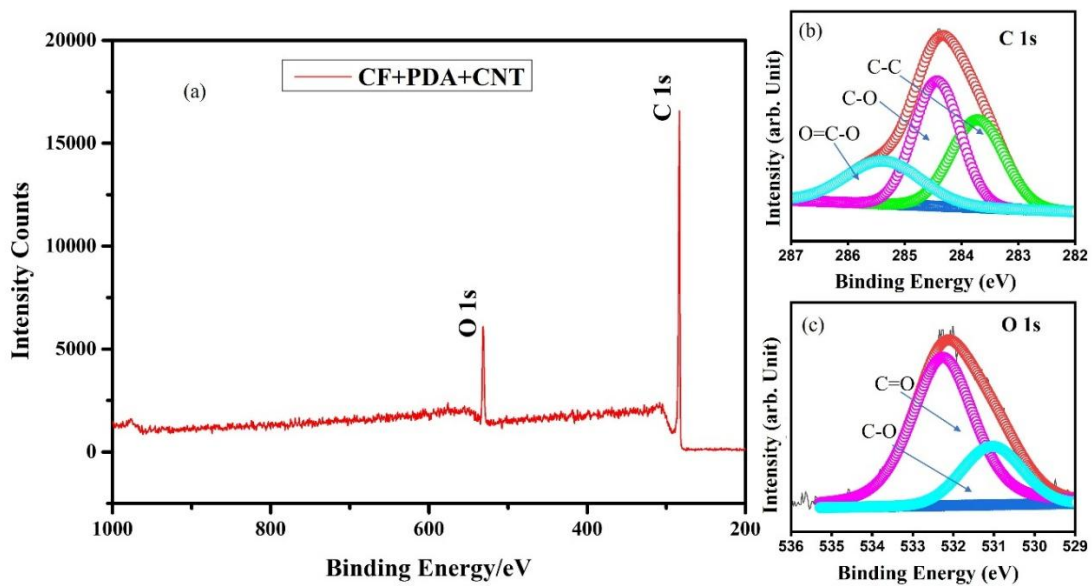


Figure 4.14. Illustrates the X-ray Photoelectron spectroscopy (a) survey spectrum of PDA+CNT coated carbon fiber (b) deconvolution peaks of carbon (c) deconvolution peaks of carbon oxygen

4.7. Mechanical Testing

4.7.1. Three Point Bending test

Flexural testing of the CFRP composites was done according to ASTM D790, to compare the impact of surface modification on the mechanical performance of the

composites. The flexural strength results shown in Fig. 4.15 shows a clear effect of fiber surface modification on composite performance. The P-CF composite displayed a flexural strength of 284.75 ± 8.06 MPa, this low value is due to weak bonding between the carbon fibers and the polymer matrix, which limits effective stress transfer during loading. CNT modified CFRP composites flexural strength increased to 342.41 ± 12.84 MPa, i.e. 20% improvement compared to the P-CF composite. FESEM micrographs confirmed that CNT deposition has increased the surface roughness of the fibers. This roughened surface likely contributed to improved mechanical interlocking with the epoxy matrix in the modified composites at the fiber-matrix interface. Although a noticeable improvement was observed, the interfacial interaction was still not fully improved. PDA and CNTs coated fiber showed the larger improvement. The CF+PDA+CNT composite touched a flexural strength of 516.69 ± 15.51 MPa, which is approximately 81.4% higher than that of the P-CF composite. The enhanced flexural strength may be related with the PDA-mediated attachment of CNTs, which improved fiber-matrix interaction as well as transferred the stress throughout the composite. The error bars shown in Fig. 6(a) represent the standard deviation of the measured values. With fiber modification the flexural modulus also changed significantly, demonstrating that the interfacial structure strongly influenced the stiffness of the composites. Due to inefficient stress sharing between the fibers and the matrix P-CF composite showed the highest modulus, approximately 87.2 GPa. This indicates high stiffness also suggest a more brittle response. The modulus of CNT modified CFRP composite decreased to 46.5 GPa this reduction may be related to non-uniform CNT distribution or limited bonding between the modified fiber surface and the matrix. In contrast, the CF+PDA+CNT composite displayed a modulus of about 69.3 GPa. The improvement compared with the CNT-coated sample indicates that the PDA layer enhanced compatibility between the fibers, CNTs, and matrix, resulting in stronger interfacial bonding and more effective stress transfer.

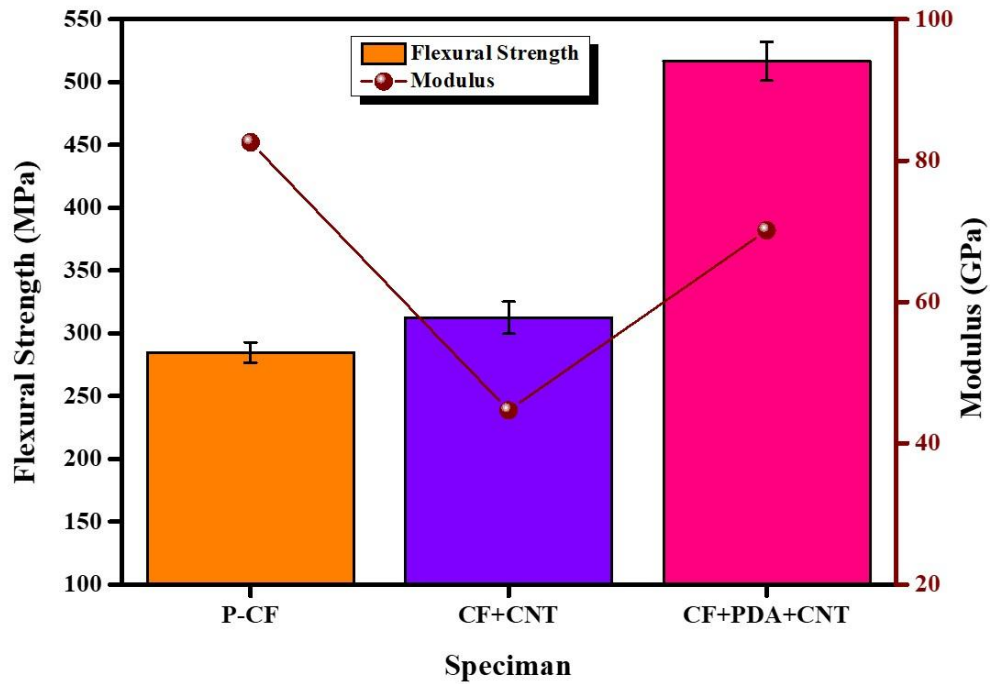


Figure 4.15. Illustrates the enhancement in the flexural strength variation in the flexural modulus of CFRP before and after surface modification

4.7.2. Tensile Testing

The tensile strength and tensile modulus of modified and unmodified CFRP composites is shown in Fig. 4.16. The unmodified composite (P-CF) showed a tensile strength of 293.52 ± 7.12 MPa mainly due to the limited bonding between the carbon fibers and the polymer matrix, which restricts efficient load transfer during tensile loading. CNT modified composite shown 362.87 ± 10.23 MPa tensile strength which is approximately 23.6% higher compared to the unmodified composite. This increase in the strength could be credited to CNT coating as it provided the higher surface roughness and larger contact area, which improved stress transfer across the interface and enhanced fiber-matrix interaction. Further when CNT was layered on PDA modified fiber, the tensile strength 434.98 ± 9.85 MPa was observed in CF+PDA+CNT composite which is about 48.2% higher than that of the P-CF composite. This result highlights that PDA adhesive layer promoted uniform CNT attachment and strengthened the interaction between the fiber and matrix, resulting in improved mechanical performance of composite. The

tensile modulus did not change in the same way as tensile strength. It increased from 13.2 GPa in P-CF to 16.4 GPa in CF+CNT, showing that CNTs made the composite more rigid. The tensile modulus of the CF+PDA+CNT composite decreased to 12.8 GPa. This reduction could be possible due to the polymeric nature of PDA layer, that might have caused some flexibility at the fiber-matrix interface. The decreased stiffness and the significant increase in tensile strength suggests that the modified interface was more effective in carrying and distributing applied loads. The findings suggest that modifying the fiber surface enhances the tensile performance of CFRP composites. The variation in modulus shows a balance between composite stiffness and a tougher fiber-matrix interface.

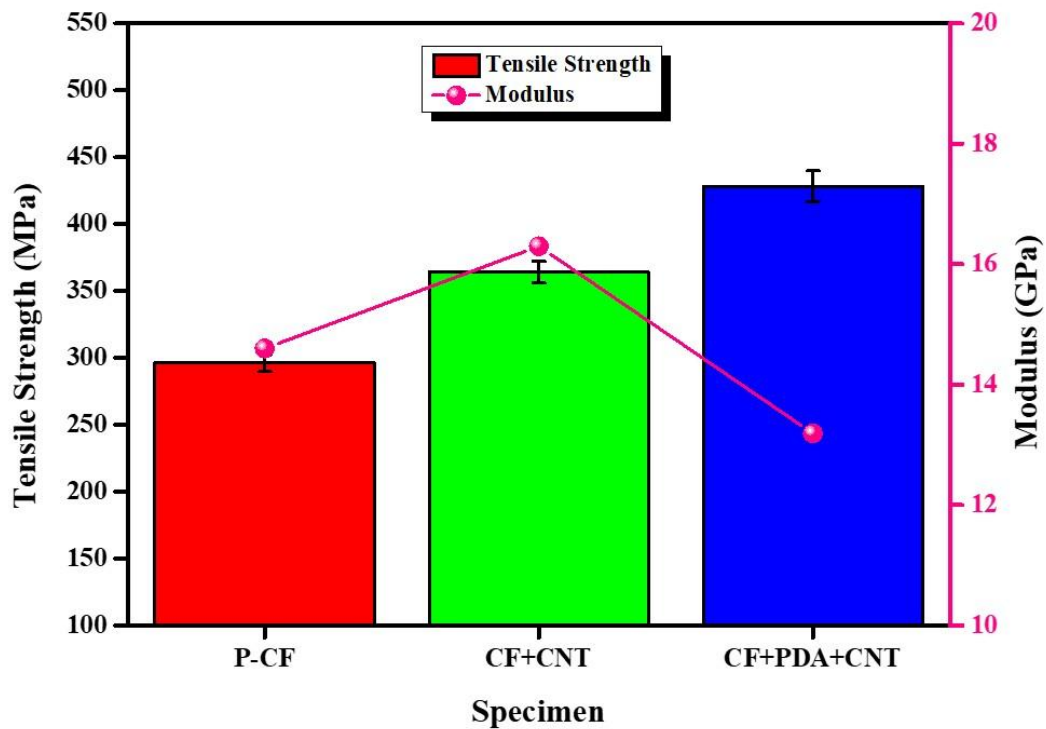


Figure 4.16. Illustrates the enhancement in the Tensile strength and variation in the tensile modulus of CFRP before and after surface modification

The load-displacement curves obtained from (a) tensile and (b) flexural tests for the pristine and PDA, CNT modified composites is shown in Fig. 4.17. Fig. 4.17 (a) shows that the CF+PDA+CNT composite achieved the highest peak load of approximately

349 kg, whereas the CF+CNT and P-CF composites reached about 296 kg and 187 kg, respectively. The progressive increase in peak load confirms that surface modification improved the load-bearing performance of the composites. A similar trend was observed during flexural testing in Fig. 4.17 (b) the CF+PDA+CNT composite reached the highest peak load of nearly 140 kg, whereas the CF+CNT and P-CF composites touched 100 kg and 60 kg approximately. These results confirm that the combined PDA and CNT treatment provides the significant improvement in flexural performance.

The failure behavior of the composites is provided by the tensile load-displacement curves. Under tensile loading stress is distributed throughout the gauge section of the specimen. After the composite reaches its maximum load, small cracks begin to form at the fiber-matrix interface and some fibers start to fail. As the damage develops, the material gradually loses its ability to carry the applied load. This behavior can be seen in the load-displacement curve, where matrix cracking, fiber pull-out, local deformation, and failure at the fiber-matrix interface occur before the final fracture.

Whereas, in a three-point flexural test the stress is non-uniform i.e. it is zero at the neutral axis, maximum in the outer tensile fibers and compressive on the opposite face. As the tensile side begins to crack the compressive side and the sustained fiber near the neutral axis continue to carry load for a short range of increasing deflection. Therefore, after reaching the initial peak the flexural load-displacement curve continues to carry the load producing a slight outward bend before final failure. The failure behavior during bending differs from that under tensile loading. While tensile stress often causes damage to concentrate in a small region, leading to a rapid loss of load-carrying capacity, bending allows stresses to be distributed between the tension and compression sides of the specimen. This improves load redistribution and results in a smoother, more gradual failure after the peak load.

Area under the load-displacement curves was used to determine the toughness of the composites, a clear improvement in toughness was observed after surface modification. Under tensile loading, the toughness for the P-CF composite was 374 kg·mm, the dramatic increase (858 kg·mm) in toughness was observed for CF+CNT composite and for CF+PDA+CNT the it increased to 960 kg·mm. These values correspond to increases of about 129% and 156%, respectively, compared with the unmodified composite.

Further similar trend was Detected in the flexural tests, the flexural toughness increased from about 50 kg·mm for P-CF to 110 kg·mm for CF+CNT and further to 180 kg·mm for CF+PDA+CNT. This demonstrated improvements of approximately 120% and 260%, relative to the pristine composite.

From the above result it is witnessed that combining CNTs with a PDA interlayer is highly operative in improving the toughness of CFRP composites. The enhancement is mainly visible under tensile loading, where the modified composites absorbed more energy before failure. These findings demonstrate that surface modification not only increases the strength of the composites but also improves their ability to absorb and disperse energy under both tensile and flexural loading conditions.

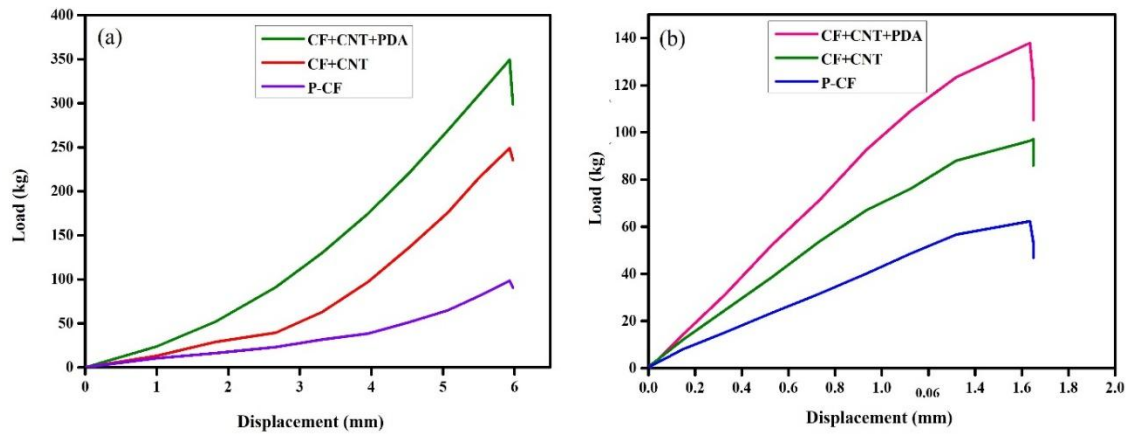


Figure 4.17. Illustrates the (a) tensile and (b) flexural load-displacement curves for pristine carbon fiber, CNT-modified fiber, and CNT+PDA-modified fiber

4.7.3. Statistical Analysis

To determine the statistical significance of differences in the mechanical properties of the CFRP composites, a two-factor analysis of ANOVA without replication was performed using Microsoft Excel. Each composite group (P-CF, CF+CNT, and CF+PDA+CNT) was evaluated based on three measured parameters: Tensile and flexural strength, modulus, and standard deviation.

The ANOVA results in table 4.2 indicate that the effect of composite type (surface modification) on the overall measured properties is not statistically significant ($F = 2.37$, $p = 0.173 > 0.05$). This suggests that, when all parameters are considered collectively,

there is no strong statistical evidence to conclude that the different composite modifications lead to significantly different overall performance.

In contrast table 4.3, the effect of property type (Tensile and flexural strength, modulus, and standard deviation) is found to be statistically significant ($F = 28.21$, $p = 0.00061 < 0.05$). This indicates that the measured values differ significantly across the different mechanical parameters.

Table 4.2. Two-way Anova

Summary	Count	Sum	Average	Variance
P-CF	4	671.5199	167.879975	20973.65
CF+CNT	4	733.97	183.4925	32542.49
CF+PDA+CNT	4	1030.65	257.6625	63341.83
Tensile Strength	3	1088.51	362.8366667	4370.351
Flexural Strength	3	1113.85	371.2833333	16048.59
Standard Deviation	3	36.4099	12.13663333	14.24704
Modulus	3	197.37	65.79	373.9876

Table 4.3. Two-way ANOVA results of CNT modified CFRP composite

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	18407.78884	2	9203.894422	2.379644	0.173422	5.143253
Columns	327367.3457	3	109122.4486	28.21334	0.000619	4.757063
Error	23206.56797	6	3867.761329			
Total	368981.7026	11				

4.7.4. Failure Analysis

The failure mechanisms observed in the CFRP composites (Fig. 4.18) were subjected to mechanical testing. In Fig.4.18 (a), significant delamination is observed in the

pristine CFRP, and Fig.4.18 (b) shows the crack propagation in the impacted area, indicating weak interfacial bonding between the fibers and matrix. The fibers were visibly detached, and the extensive delamination highlighted the brittle nature of the uncoated composite. In contrast, the CNT-coated composites exhibited an improved damage tolerance, as shown in Fig. 4.18 (c) and 4.18 (d). As shown in Fig. 4.18 (c), brittle matrix fracture occurred; however, the damage was more localized, reflecting the enhanced interfacial strength owing to the CNT coating. The failure pattern in Fig. 4.18 (d) is mainly characterized by fiber breakage, indicating that the fibers were strongly bonded to the matrix. Because of this strong interface, the applied load was efficiently transferred to the fibers, preventing excessive matrix damage. The presence of CNTs further enhanced the fiber-matrix interaction, leading to improved load transfer and the composite performance. Therefore, this change indicates that CNTs strengthened the fiber-matrix interface compared to the pristine composite which showed severe delamination to more localized damage in the CNT-modified samples.

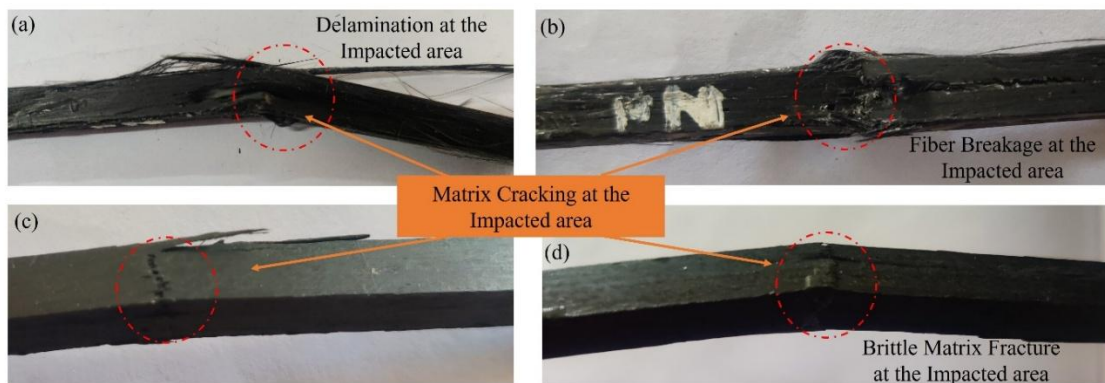


Figure 4.18. Illustrates the type of failure that occurred after mechanical testing: (a) delamination in the pristine CFRP composite and (b-d) CNT-modified composite

4.8. Fractography Analysis

It was observed that the main failure mechanism in fractured CFRP specimens were fiber pull-out, matrix cracking and delamination. The fracture behaviour and the effect of surface modification on the fiber-matrix interface was clearly observed from the FESEM micrographs. Fig. 4.19 (a) shows the fracture surface of the pristine CFRP composite where extensive fiber pull-out, smooth fiber surfaces, and several voids on the fracture surface is visible, similarly presents in the PDA+CNT-modified composite

shown in Fig. 4.19 (b). This indicates the weak bonding between the carbon fibers and the polymer matrix. Therefore, the applied load could not be transferred efficiently from the matrix to the fibers, causing interfacial debonding and fiber pull-out during failure. Fig. 4.19 (a) and 4.19 (c) confirms the poor interfacial adhesion in pristine composite due to the presence of empty cavities after fiber extraction. Additionally, matrix cracking was observed, suggesting that cracks could propagate more easily through the material. On the other hand, the PDA+CNT-modified CFRP displayed a much rougher fracture surface with fewer pulled-out fibers. Many fibers remained embedded within the matrix, indicating stronger interfacial bonding. The CNT coating increased the bonding area between the fibers and the matrix and provided more anchoring for the materials to attach. This enhanced interfacial contact, improved load transfer, and delayed failure at the interface. As shown in Fig. 4.19 (d), much less fiber pull-out occurred compared to the untreated composite, showing that the CNT layer improved the bonding strength. CNTs reduced crack growth and matrix cracking during loading. The untreated CFRP showed more fiber-matrix separation, whereas the CNT-modified composite showed more matrix fracture. After CNT modification fewer gaps were observed between the fiber and matrix. The fracture surface was more intact showing better contact between the two phases this stronger bonding helped the composite carry higher loads before failure

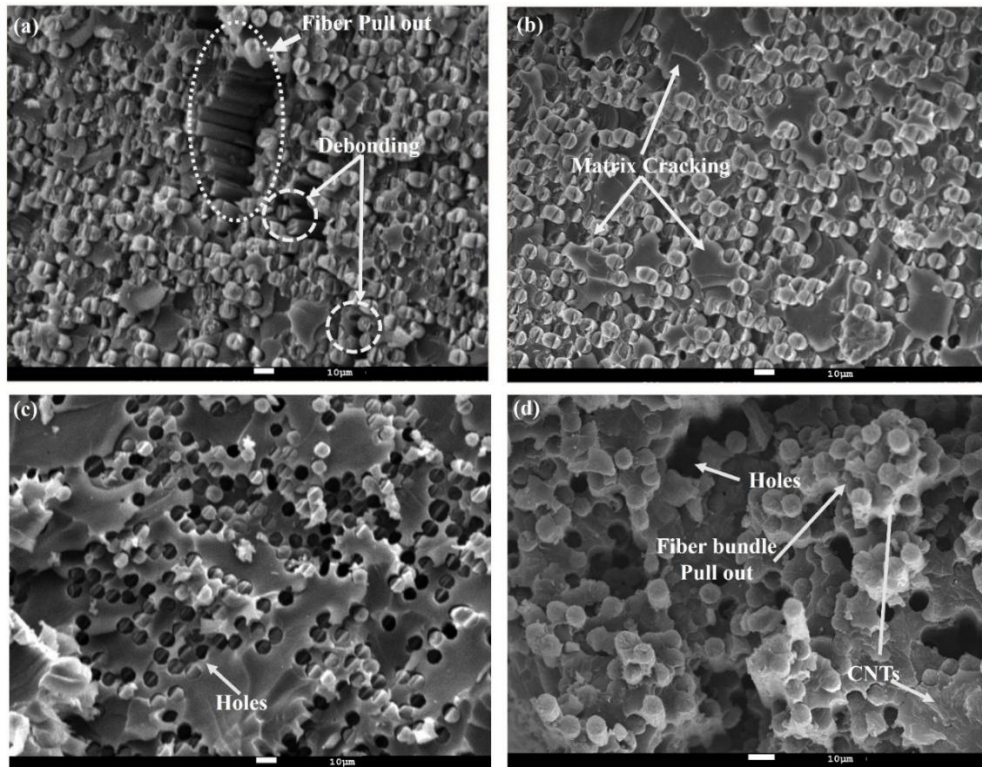


Figure 4.19. Illustrates the comparison of fractographic analysis of (a), (c) pristine CFRP and (b), (d) CNT-modified CFRP

Figure 4.20 compares the untreated and CNT-coated carbon fiber composites. The untreated fibers shown in Fig. 4.20(a) have a relatively smooth surface with no additional coating. Because of the limited contact between the fiber and epoxy, separation can occur more easily during loading. In Fig. 4.20(b), CNTs are attached to the fiber surface and are also present in the matrix. The coating makes the fiber surface rougher than that of the untreated sample. More matrix material remains in contact with the coated fibers, and the CNTs within the resin may help reduce crack growth. These differences help explain the better mechanical properties obtained for the CNT-coated composites. Fig. 4.20 (c) indicates that the post-failure analysis revealed that the CNTs still adhered to the fiber surface after the pull-out. This indicates a strong interfacial bonding between the CNTs and the fiber. The failure mechanism likely occurred at the CNT-matrix interface or within the matrix itself, rather than at the CNT-fiber interface. This behavior suggests that CNT coatings improve toughness by requiring additional energy to de-bond CNTs from the matrix during fracture. In Fig. 4.20 (d), the CNTs are observed to span the gap between the fiber and matrix, forming a physical bridge. This

CNT entanglement + PDA-induced covalent bonding mechanism enhances the stress transfer from the matrix to the fiber, mitigates crack propagation, and increases fracture toughness. The two distinct interfaces- fiber-CNT and CNT-matrix create a graded transition zone, optimize the load distribution, and reduce the stress concentrations at the primary fiber-matrix interface. The dual interfacial zones work synergistically: the fiber-CNT interface ensures strong adhesion to the fiber, while the CNT-matrix interface promotes energy dissipation through CNT pull-out and matrix deformation. The combination of these structural features delay damage and improves the resistance of the composite to failure.

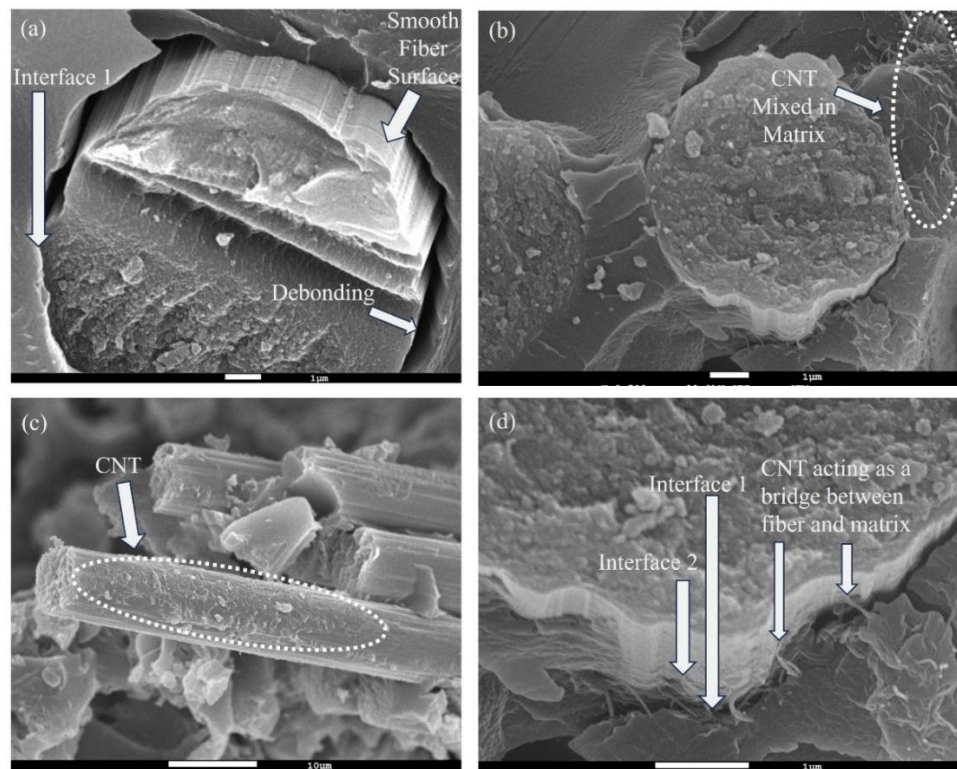


Figure 4.20. Illustrates the high magnified FESEM micrographs of CFRP composite (a) fiber without coating (b) CNT coating and presence of CNT in matrix (c) Presence of CNT on the fiber surface after mechanical testing (d) two interfaces between fiber-CNT-matrix.

4.9. Discussion

It was observed that both PDA and CNT-coated CFRP showed a flexural strength value of 516.69 MPa, demonstrating an enhancement of approximately 81.4% compared to

P-CF. However, the increase in tensile strength was ~48.2%, which was comparatively lower than the flexural strength. Additionally, the tensile modulus decreased to 12.8 GPa compared that with of P-CF. The dopamine layer itself is a polymer; therefore, it may act as a softer interphase between the stiff carbon fiber and the matrix. Even though it improves adhesion, the PDA layer could be less stiff than the original fiber-matrix interface, leading to a lower overall modulus. Moreover, the PDA layer enhances energy dissipation through viscoelastic deformation, thereby increasing toughness and ductility. This promotes plastic deformation rather than brittle fracture, increasing the tensile/flexural strength, but reducing the stiffness. CNTs are particularly effective at resisting crack growth under these complex stresses, but the flexibility of the interface from dopamine lowers the modulus. While CNTs are intrinsically stiff, their random orientation and interface flexibility (owing to PDA) limit their ability to enhance the modulus. The modulus depends on the initial resistance of the composite to deformation, which is compromised by the compliant PDA interphase.

Flexural failure is often due to delamination, particularly in layered composites. The CNTs grafted axially might bridge the layers, making it harder for cracks to propagate between them. In addition, during bending, the outer layers are in tension and the inner layers are in compression. CNTs can provide better resistance to compression by stabilizing the fibers against buckling. Flexural loading concentrates the high stresses near the outer surfaces of the composite beam. The CNT-rich surface region helped sustain and distribute these high local stresses more effectively, thereby delaying the onset of failure during bending. In addition, the flexural strength is influenced by the ability of the material to handle stress gradients. CNTs might be more effective in redistributing stress in a nonuniform stress state (such as bending) compared to uniform tension. The ductile interphase could absorb more energy during flexural deformation, leading to higher strength gains.

The mechanical properties of the composites are significantly influenced by the robustness of the fiber-matrix interface. Chang Li et al. coated a porous carbon network onto woven CF after applying a PDA coating. The combined effect of porous carbon and PDA improved the mechanical properties of the composite the bending strength increased from 104.7 MPa to 138.9 MPa, which corresponds to an increase of 32.7.[1].

32.32% increase in flexural strength was observed using two step modification method for CNT grafting on unidirectional CFRP composite[2]. Chufan Xiao et al. used an aqueous suspension deposition method to coat MWCNTs onto the surface of CF. This process improved mechanical strength from 714 MPa to 822 MPa, i.e. 15.1% increase. The results also demonstrated a significant increase in the surface energy of the CFs after MWCNT deposition[3]. Caminero investigated the flexural damage behavior of composite laminates by analyzing two primary lay-up configurations: unidirectional laminates and multidirectional laminates. The study revealed that the flexural strength and stiffness of the laminates significantly decreased compared to the $[0]_{12}$ laminate. Furthermore, all the tensile specimens failed within the gauge length, except for the unidirectional $[0]_{12}$ laminate[4].

When CNTs are oriented in the same direction as CFs, they enhance directional strength and stiffness by efficiently transferring loads along the axis. Studies have confirmed that aligned CNTs enhance the tensile strength and stiffness in the alignment direction, while random distributions offer more balanced, albeit lower, performance peaks[5–7]. Overall, the FESEM image confirms that the CNTs are well distributed around the carbon fiber surface, increasing the effective interfacial area and enhancing the load transfer primarily where the interfacial shear and through-thickness stresses control the failure mode; hence, the flexural strength is larger than the tensile strength. However, the PDA layer and CNT grafting introduced a more compliant interface or matrix regions, and CNT misalignment reduced the overall stiffness (modulus).

In composites with both microscale CF and nanoscale CNT reinforcements, such as those based on multiscale architectures, the fracture processes occur at both scales. Fractographic examinations of the multiscale composites revealed three distinct fracture mechanisms: fiber pullout, debonding, crack propagation, and fiber fracture. The addition of CNTs within the matrix and at the fiber-matrix interface enhances crack resistance by impeding crack initiation and propagation through crack-bridging mechanisms[8–10]. This phenomenon increases the ability of the material to resist crack growth, thereby improving its overall toughness and energy absorption capacity.

Raman spectroscopy of CNT-coated CFs reported the presence of D and G peaks[11]. However, in this study, further analysis identified a 2D band, indicating the graphene sheets. This finding confirmed the successful deposition of high-quality CNT coatings.

The failure and fractography results clearly show the positive effect of CNTs on the bonding between the fiber and matrix. The failure modes such as delamination, fiber pull-out, and matrix cracking were observed in the untreated composites due to weak interfacial bonding. The stronger interactions at the interface and better mechanical interlocking improved due to the addition of CNTs. In some cases, functionalized CNTs can form bonds with the surrounding materials. CNTs present at the fiber-matrix interface provide additional contact between the two phases, allowing the applied load to be transferred more easily. Their high surface area increases the interaction between the fiber and matrix, which reduces crack formation and improves the overall behavior of the composite during loading.

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Chapter 4(c)

Effect of Polydopamine-Assisted ZnO Nanoflakes Coating on the Mechanical Properties of Carbon Fiber-Reinforced Polymer Composites

4.10. Surface Analysis

4.10.1. Raman Spectroscopy

Figure 4.21 shows the Raman spectra of the P-CF and ZnO + PDA-modified samples, which were used to study the changes in the carbon fiber surface after modification. A 532 nm laser was used as the excitation source because it is commonly used for carbon materials and provides clear D and G bands in the Raman spectrum. The laser power was kept at 5 mW to prevent heating or damaging the sample during testing while still obtaining a clear signal. A 50X objective lens was used to focus the laser on a small area of the sample for accurate measurements. Each spectrum was collected with an exposure time of 15 seconds to ensure sufficient signal intensity. To obtain reliable results and reduce background noise, three scans were recorded and then averaged to generate the final spectrum.

The Raman spectra show two primary peaks the D-band and the G-band characteristic of carbon-based materials: around 1351 cm^{-1} and 1592 cm^{-1} characteristic of carbon-based materials. The D-band is due to the vibrational modes of disordered carbon arising from defects such as sp^3 -hybridized carbon and edge imperfections, while the G-band corresponds to the in-plane stretching vibrations of sp^2 -hybridized carbon atoms in graphitic domains. The G-band is sharp in the P-CF spectrum, indicating a relatively ordered graphitic structure with minimal defects. In contrast, the intensity of the D-band is high in CF + PDA + ZnO spectrum. The $I_{\text{D}}/I_{\text{G}}$ ratio of P-CF was 0.84, while that of CF + PDA + ZnO was 0.91, indicates increase in surface defects or disorder, which is typical when nanomaterials such as ZnO are deposited onto carbon fibers. The PDA coating and ZnO nanoparticles introduced additional defect sites, interrupt the graphitic structure and enhancing the surface reactivity. Despite these changes, the G-band remained strong in the modified sample, indicating that the

graphitic backbone of the carbon fiber was largely preserved, ensuring the holding of its intrinsic mechanical and electrical properties. The CF + PDA + ZnO spectrum open up additional features in the low-frequency region ($\sim 400\text{--}800\text{ cm}^{-1}$), which are absent in the pristine carbon fiber. These peaks are linked with the vibrational modes of the ZnO nanoparticles, confirming their successful incorporation onto the carbon fiber surface. The magnified Raman spectroscopy analysis of P-CF and ZnO and PDA-modified carbon fiber provides deeper understanding into the structural changes introduced by ZnO incorporation. The absence of ZnO-related vibrational modes was confirmed as olive-colored spectrum show no distinct peaks in the $400\text{--}800\text{ cm}^{-1}$ range. The pink spectrum shows peaks associated with ZnO a peak at about 430 cm^{-1} is assigned to the $E_2(\text{low})$ mode of ZnO. Another peak appears near 570 cm^{-1} and is related to the $A_1(\text{LO})$ phonon mode, which is commonly associated with oxygen vacancies. A peak around 660 cm^{-1} indicates the presence of defects or changes in the ZnO structure. The modified sample show the broader intensity in the range $\sim 700\text{--}750\text{ cm}^{-1}$ may reflect vibrational contributions from the PDA layer or interactions between PDA and ZnO. The Raman spectrum of the coated carbon fibers was different from that of the untreated fibers. A noticeable rise in the D-band intensity was observed after PDA and ZnO deposition, which points to changes on the fiber surface. In addition, peaks related to ZnO appeared in the lower wavenumber region, confirming that ZnO particles were present on the fibers. These results show that the coating process changed the surface characteristics of the carbon fibers. The G-band position and intensity did not change significantly, indicating that the graphitic framework of the fibers remained largely unaffected. Thus, the surface became more active after coating, while the basic structure of the carbon fibers was retained.

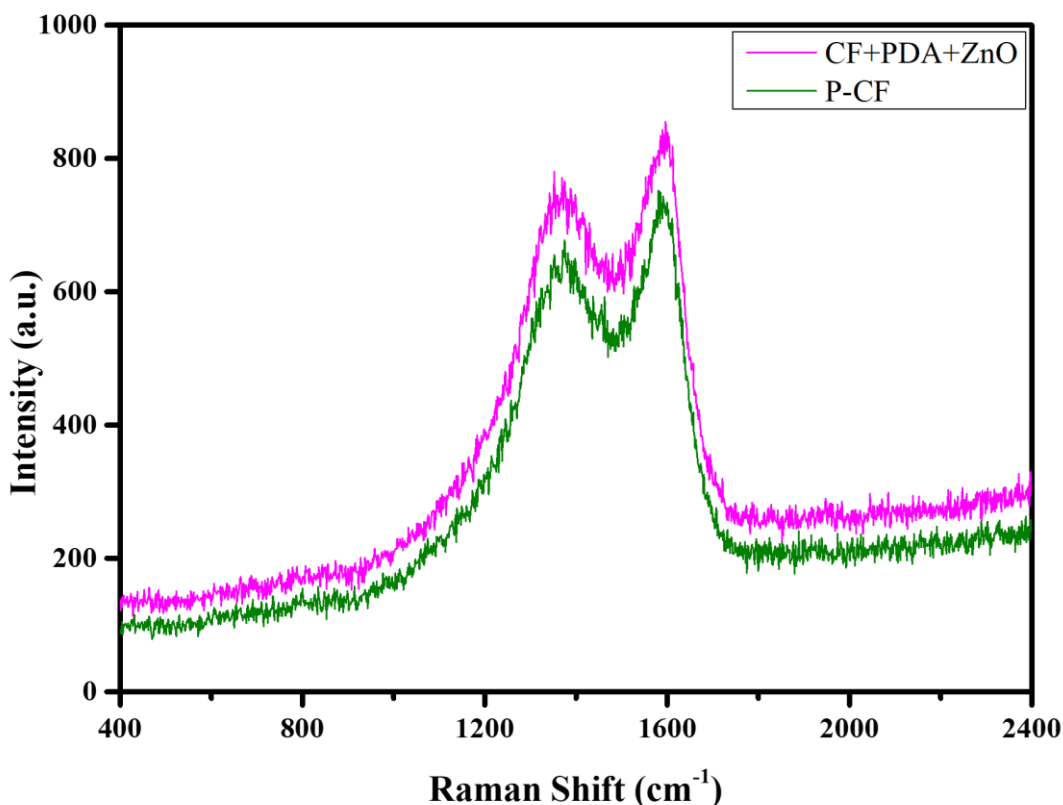


Figure 4.21. Illustrates the Raman spectra of pristine carbon fiber and ZnO+PDA-modified CF showing D and G bands, with enhanced intensity after surface modification, the inset highlights additional peaks in the low-frequency region (~ 400 – 800 cm^{-1}) for CF+PDA+ZnO

4.10.2. XPS Analysis

The XPS characterization reveals the surface chemistry of the as-received carbon fiber, shown in Fig. 4.22. The survey spectrum Fig. 4.22 (a) highlights the elemental composition of the sample. Carbon and oxygen are the major elements on the surface of the carbon fiber confirms with the presence of dominant peaks C 1s and O 1s. The contributions from different chemical states were observed in Fig. 4.22 (b) which shows the deconvoluted peaks for the C 1s region. The C 1s spectrum shows a major peak near 284.9 eV, which is related to carbon-carbon and carbon-hydrogen bonds present in the carbon fiber structure. Another peak appears around 283.8 eV and is associated with carbon bonded to oxygen, suggesting the presence of oxygen-based groups on the fiber surface. The deconvoluted O 1s spectrum shown in Fig. 4.22(c) contains several

components, indicating that different types of oxygen species exist on the modified fiber surface. The peak at approximately 531.5 eV corresponds to C=O bonds, suggesting the presence of carbonyl groups, whereas the peak at approximately 533 eV is attributed to C-O bonds, indicative of hydroxyl or ether functionalities.

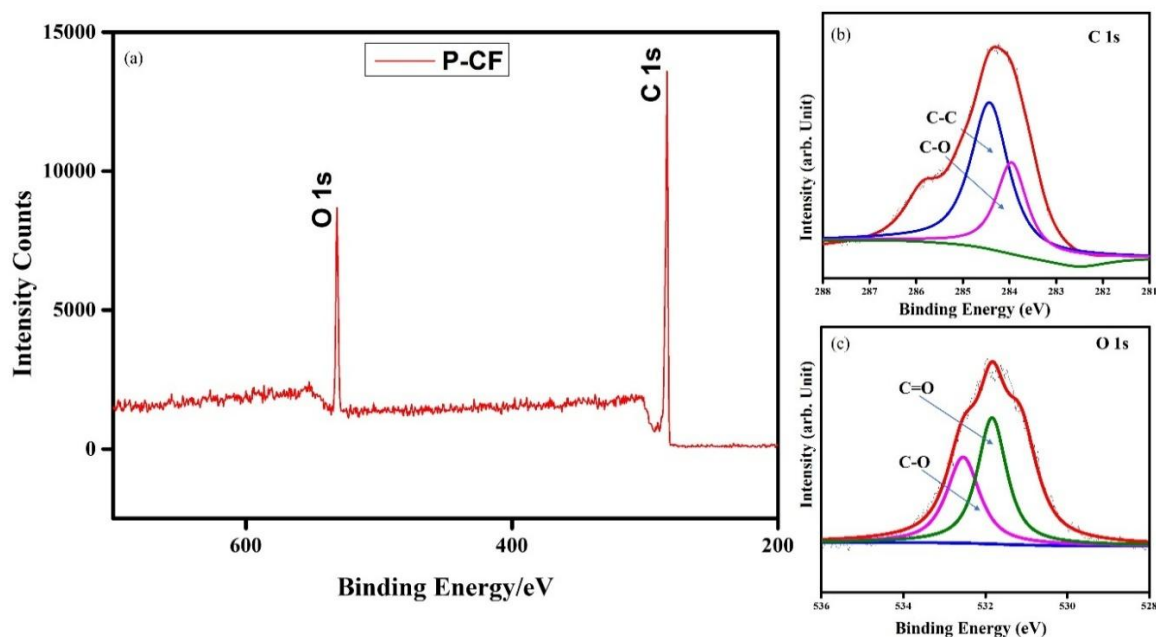


Figure 4.22. Illustrates the XPS spectra (a) survey of the as received carbon fiber (b) deconvolution peaks of C 1s (c) deconvolution peaks of O 1s

The XPS analysis of carbon fiber coated with PDA and ZnO nanoflakes, shown in Fig. 4.23, was used to study the surface composition and chemical bonding of the modified fiber. The survey spectrum in Fig. 4.23(a) shows clear Zn $2p_{3/2}$ and Zn $2p_{1/2}$ peaks at around 1022 eV and 1045 eV, confirming that ZnO nanoflakes were successfully formed on the carbon fiber surface. Peaks corresponding to C 1s (~284 eV), O 1s (~531 eV), and N 1s (~400 eV) are also present, indicating the presence of PDA and oxygen-containing groups on the surface. The high-resolution C 1s spectrum shown in Fig. 4.23(b) contains several peaks. The main peak at about 284.8 eV is assigned to C–C/C–H bonds. Additional peaks at around 286 eV and 288 eV correspond to C–O and O=C–O bonds, while a smaller peak near 285.5 eV is related to C–OH groups. These results suggest that PDA treatment and ZnO coating introduced additional oxygen-containing groups onto the fiber surface. The increase in these functional groups indicates that

PDA helped modify the surface, which may improve the attachment and stability of the ZnO nanoflakes on the carbon fiber.

The hybrid nature of the coatings were confirmed as the O 1s spectrum in Fig. 4.23 (c) shows distinct contributions from C=O (~532 eV), C-O (~531.2 eV), and Zn-O (~533 eV). The presence of zinc in the material confirmed by the Zn 2p spectrum Fig. 4.23 (d) that exhibits sharp.

Compared with the pristine fiber analysis, the spectrum of the modified fiber (CF+PDA+ZnO) showed significant differences. While the pristine fiber primarily exhibits peaks for C 1s and O 1s with contributions from the C-C and C-O groups, the modified fiber includes additional peaks for Zn 2p and N 1s, confirming the incorporation of ZnO and PDA. The peak at ~531 eV in the O 1s spectrum of both P-CF (Fig. 4.22 (c)) and CF+PDA+ZnO (Fig. 4.23 (c)) originates from the oxygen bonds inherently present in the carbon fiber (CF) structure, such as C=O and C-O functional groups. Because ZnO is coated onto CF in CF+PDA+ZnO, these pre-existing oxygen bonds in CF persist, leading to a similar peak in the ZnO-coated sample. However, in CF+PDA+ZnO, an additional contribution from the Zn-O bonding slightly modifies the peak intensity and shape. This suggests that while ZnO introduces new oxygen interactions, the dominant contribution at ~531 eV originates from the intrinsic oxygen-containing functional groups in the CF. The O 1s peak appears in both samples, which shows that the carbon fiber itself contributes to the oxygen signal. After adding the ZnO coating, the O 1s spectrum changes because of the formation of Zn-O bonds. The PDA layer contains catechol and amine groups that help the coating attach to the epoxy matrix and also help hold the ZnO nanoflakes on the fiber surface through Zn-O-C/N interactions. The C 1s and O 1s spectra of the coated fiber also show new oxygen-containing groups such as C=O and Zn-O, which are not seen in the untreated carbon fiber. These results show that the carbon fiber surface was successfully modified with PDA and ZnO nanoflakes, giving the coated fiber different surface and chemical properties compared with the uncoated fiber.

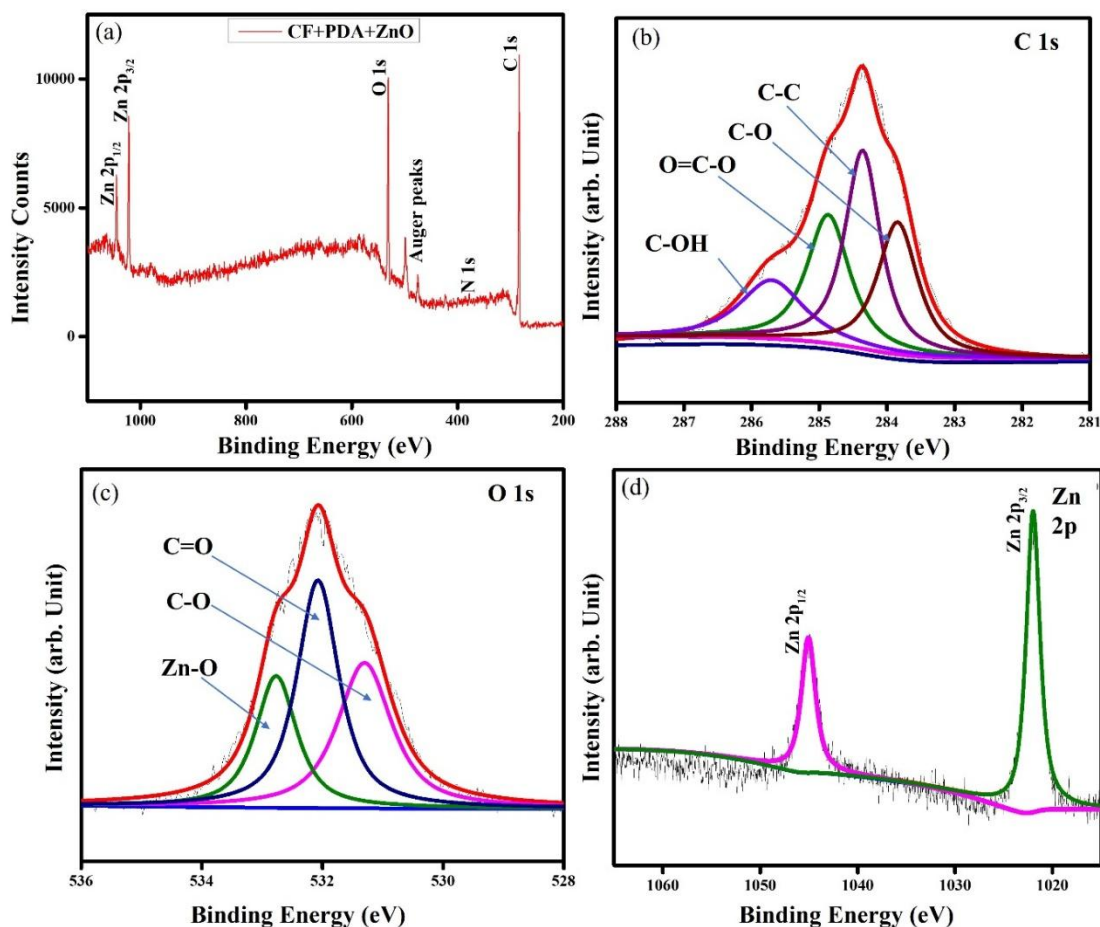


Figure 4.23. Illustrates the XPS spectra (a) survey graph of ZnO and PDA coated carbon fiber (b) deconvolution peaks of C 1s (c) deconvolution peaks of O 1s (d) deconvolution peaks of Zn 2p

4.11. Mechanical Testing

4.11.1. Flexural testing

The flexural test was carried out to evaluate the bending performance of the composites. As shown in Fig. 4.24(a), the P-CF sample showed a flexural strength of 271.05 ± 11.07 MPa. After coating with ZnO, the flexural strength increased to 306.78 ± 8.06 MPa, which is about 13.18% higher than that of P-CF. The CF+PDA+ZnO sample showed the highest value of 401.85 ± 5.93 MPa, giving an increase of 130.8 MPa compared with P-CF. The increase in flexural strength after ZnO coating may be related to the reinforcing effect of the ZnO particles, which help transfer the applied load more effectively. The increase was observed after

PDA treatment as PDA layer helped ZnO to attach more strongly to the fiber surface, resulting in uniform distribution of stress and better bonding. The better bending performance of the carbon fiber composites due the surface treatment given to the fiber. There was an increase in the flexural modulus from P-CF to CF+PDA+ZnO, as shown in Fig. 4.24(a). It signifies that the modified composites became more resistant to deformation under load. The combination of PDA and ZnO coating improved both strength and stiffness of the composite.

The effect of the surface modifications on the stress-strain curves of flexural behavior of the composites is shown Fig. 4.24(b). The untreated CFRP specimen showed a maximum stress of about 50 MPa and fractured at a strain of around 0.1-0.2. The sample broke soon after reaching its peak load, indicating that the fiber-matrix adhesion was not strong enough to transfer the applied stress efficiently. The fiber and matrix were not bonded strongly in the untreated composite. As a result, cracks developed more easily and the sample fractured sooner. The stress-strain curve also covered a smaller area, showing that the material could not take up much energy before failure.

Larger strain range of around 0.3-0.4 and higher stress values of about 57-58 MPa was observed in CF+ZnO composite. By filling small gaps between the fiber and matrix and providing better contact the ZnO particles improved the interaction between the two phases. The improved bonding between the fiber and matrix allowed the composite to carry a higher load before failure. However, the strain value showed only a small change, which means that the composite still fractured without much deformation.

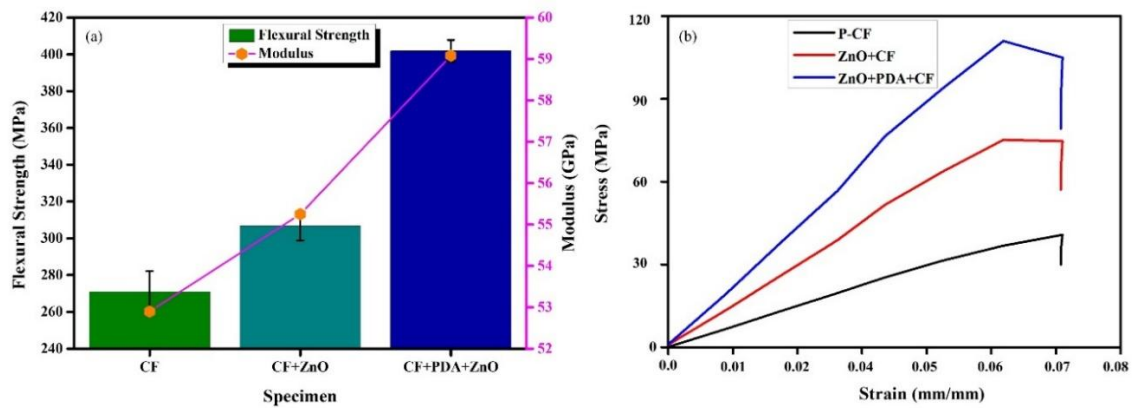


Figure 4.24. Illustrates (a) the flexural strength and modulus (b) stress vs strain of pristine CFRP composite, ZnO modified and ZnO+PDA modified CFRP composite

Among all the samples, the CF + PDA + ZnO composite showed the highest stress and strain values, reaching about 110 MPa and 0.6. The improvement can be linked to the combined role of PDA and ZnO at the fiber-matrix interface. PDA helps the resin to stick more strongly to the fiber surface, while ZnO particles provide additional resistance to crack growth. The larger area under the stress-strain curve also shows that the material could absorb more energy before failure compared to the other samples.

Variations in the interfacial adhesion, defect density and energy absorption mechanisms cause differences in the peak stress and strain between the specimens. Low toughness in untreated CFRP is due to inherent defects and poor bonding. The composite containing only ZnO showed improved strength, but its ability to deform before fracture remained low. A different behavior was observed when both PDA and ZnO were present. The combination provided stronger fiber-matrix bonding and reduced the rate of crack propagation during loading. This led to better mechanical properties and a higher amount of energy absorbed before the sample fractured. The toughness of each composite was directly proportional to the area under its stress-strain curve, with CF+PDA+ZnO achieving the highest value.

Composite design is influenced by the actors such as the nanoparticle dispersion, PDA coating uniformity and curing conditions. These results verifies that for advance application of CFRP composite treatments play a major role in increasing the stiffening and toughening mechanisms.

4.11.2. Statistical Analysis

Microsoft excel shown in table 4.4 was used for two-factor analysis of variance and to determine the statistical significance in the mechanical properties of the CFRP composites. Each composite group (CF, CF+ZnO, CF+PDA+ZnO) was tested with three specimens ($n = 3$), and the measured parameters included flexural strength, modulus, and standard deviation. The ANOVA results, summarized in Table 4.5 , indicates that the effect of composite type (i.e., surface modification treatment) on overall mechanical performance is statistically significant ($F = 58.31$, $p = 0.0011 < 0.05$). In contrast, differences across property types (flexural strength, modulus, standard deviation) were not statistically significant ($F = 1.02$, $p = 0.437 > 0.05$), suggesting consistent improvements across all measured parameters.

Table 4.4. Two-way ANOVA

Summary	Count	Sum	Average	Variance
CF	3	335.02	111.673	19488.13
CF+ZnO	3	370.09	123.363	25787.98
CF+PDA+ZnO	3	466.86	155.62	46178.14
Flexural Strength	3	979.68	326.56	4570.596
SD	3	25.06	8.35333	6.669433
Modulus	3	167.23	55.7433	9.730633

Table 4.5. Two-way ANOVA results of ZnO modified CFRP composite

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	3108.458156	2	1554.23	1.024958	0.437141	6.944272
Columns	176842.9618	2	88421.5	58.31076	0.0011	6.944272
Error	6065.534578	4	1516.38			
Total	186016.9545	8				

4.11.3. Failure Analysis

Fig. 4.25 shows the failure modes of the different composite materials under mechanical stress. In Fig. 4.25 (a), the unmodified composite exhibits significant fiber breakage and delamination, indicating poor interfacial bonding between the fibers and the matrix, leading to catastrophic failure under load. In Fig. 4.25 (b), the ZnO nanoflake-modified composite shows signs of delamination, buckling, and crack propagation, which suggests an improved but still insufficient load distribution, leading to structural instability and failure under compressive forces. In Fig. 4.25 (c), the ZnO and PDA-layered modified composites show brittle failure behavior, indicating enhanced stiffness but reduced ductility, due to enhanced matrix cross-link density. Among the three samples, the unmodified composite shown in Fig. 4.25(a) experienced the most damage, with noticeable fiber breakage and layer separation. This indicates weaker mechanical performance than the modified composites. In comparison, the composites coated with ZnO and PDA, shown in Fig. 4.25(c), showed less fiber damage and reduced delamination. However, these surface treatments also made the material more brittle, causing it to break with less deformation before failure.

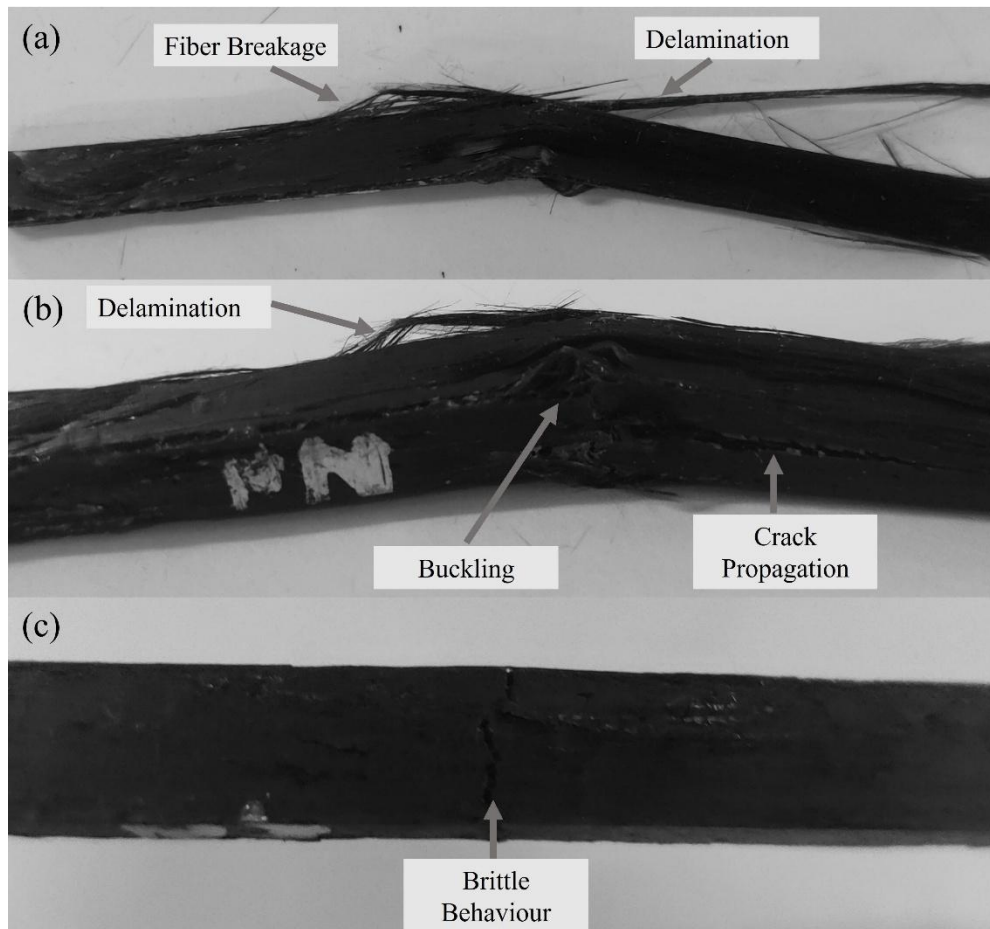


Figure 4.25. Illustrates the failure modes of (a) unmodified composite, (b) ZnO nanoflakes modified composite, (c) ZnO and PDA layered modified composite

4.12. Fractography Analysis

The FESEM images show the fracture surfaces of untreated and ZnO/PDA-coated CFRP composites after the three-point bending test. During the test, the upper side of the sample was under compression, while the lower side experienced tension, which led to crack formation and fracture. The fracture topographies of the untreated CFRP composite are shown in Fig. 4.26(a), (c), and (e) in which the fiber surfaces appear smooth which indicates weak bonding between the carbon fibers and the epoxy matrix. Cracks and voids were observed in the matrix, as shown in Fig. 4.26(a). These defects indicate that damage had already developed within the composite during loading. Weak bonding between the fibers and epoxy caused early damage in the untreated composite.

During fracture, the fibers separated from the matrix and created visible gaps. Fiber pull-out can be seen in Fig. 4.26(c), while Fig. 4.26(e) shows empty regions where fibers were completely detached from the resin. After ZnO and PDA treatment, the fracture surfaces changed. More matrix material remained attached to the fibers, and fewer areas of complete separation were observed. The fibers in Fig. 4.26(d) stayed embedded in the matrix even after failure. This shows that surface treatment improved the bonding between the carbon fibers and epoxy. The improved adhesion reduces fiber pull-out and helps the composite withstand higher loads before failure.

Finally, Fig.4.26 (f) confirms the presence of ZnO bonding between the fiber and matrix, ensuring strong adhesion and an effective load distribution across the composite. In the pristine CFRP, these stress concentrations caused rapid fiber debonding and brittle fracture, whereas in the ZnO and PDA-modified CFRP, the improved interface mitigated such failures by enhancing the load-bearing capacity and reducing premature matrix cracking.

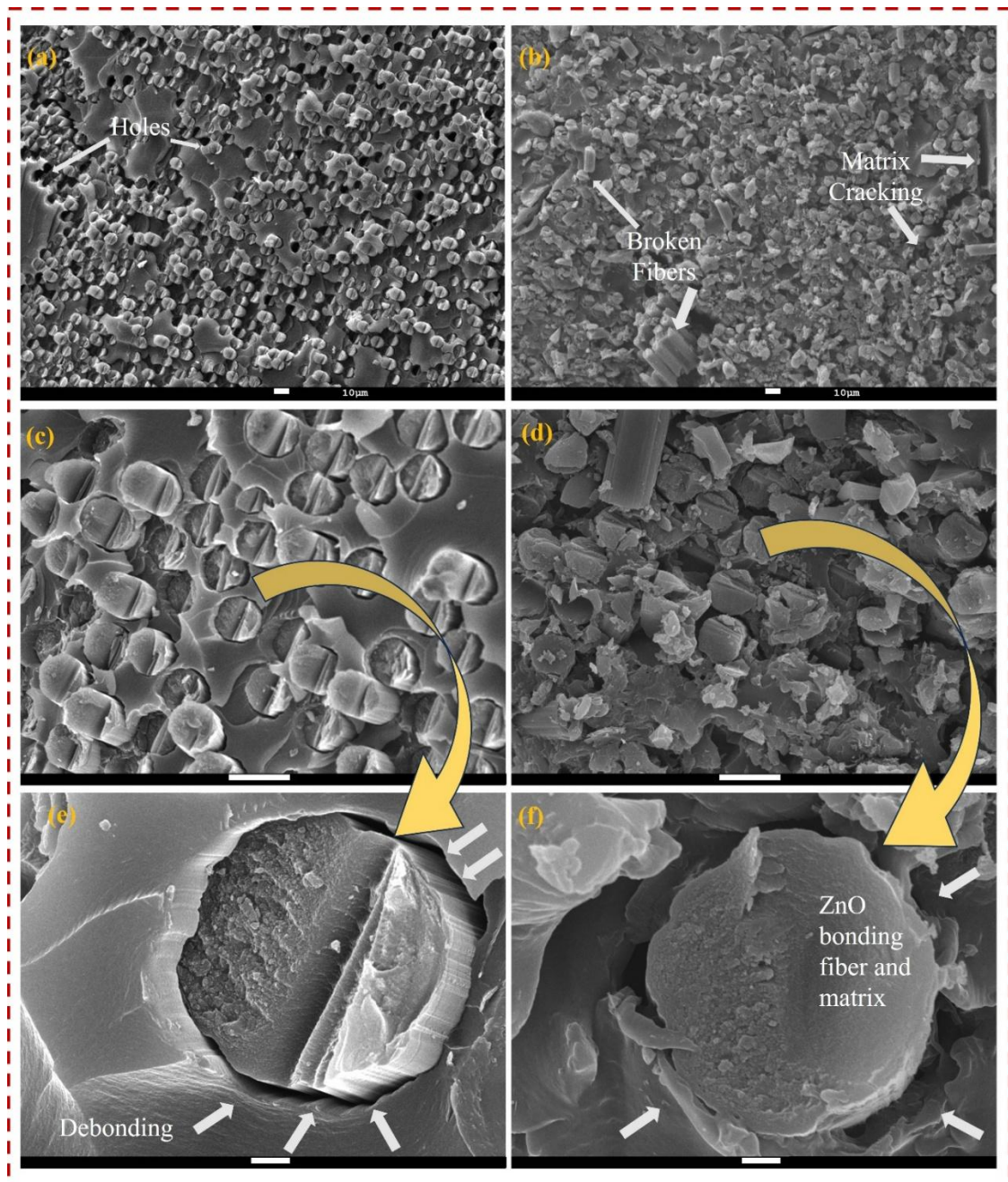


Figure 4.26. Illustrates the FESEM micrographs of fracture behaviour of (a) (c) (e) CFRP and (b) (d) (f) ZnO and PDA modified CFRP shows the improved fracture behaviours

4.13. Discussion

Our findings are supported by earlier XPS survey scan data from other researchers, which showed that the fiber surface has no notable elemental peaks other than carbon

and oxygen[1][2]. Potential structural configurations are limited by the atomic composition, which shows that surface carbon primarily forms carbon-oxygen or carbon-carbon bonds. Although surface functional groups are naturally present in carbon fibers, these groups can adopt a vast diversity of molecular configurations, each of which exhibits distinct chemical characteristics. Because of its intrinsic limitations, XPS cannot accurately determine molecular structures; however, it can provide useful information regarding the bond polarity. Although XPS is widely used to study surface chemistry, it has certain limitations. Since the technique detects core-level electrons, it cannot directly identify the exact nature of covalent bonds. But it helps identify changes caused by surface treatments and provides useful information about the chemical environment of atoms present on the surface[3]. In future studies XPS can be combined with other characterization methods to obtain a more complete understanding of carbon fiber surface chemistry. From literature it is noted that ZnO plays an important role in improving the interaction between fibers and polymer matrices. Brendan A. Patterson found that ZnO contributes significantly to interfacial interactions between the reinforcement and matrix using AFM-based adhesion measurements[4]. The effect of ZnO depends on the type of structure formed on the surface. The size and shape of ZnO particles affect their bonding with the matrix and the overall performance of the composite. Various ZnO morphologies, including rods, spheres, and flower-like forms, have been used in composites, and different results have been reported for each type[5][6]. Poulami Banerjee et al. deposited ZnO nanorods on the fiber surface using an in-situ growth method. After the modification, they observed an increase of 43% in flexural strength and 39% in interlaminar shear strength[7]. Guipeng Quan et al. adjusted the pH during the ZnO synthesis process to form rod-like and flower-like structures. They found that these two morphologies improved the flexural strength by 40.8% and 39.8%, respectively[8]. In the present work, ZnO nanoflakes were selected as the surface modification material. The flexural strength increased by 48.27% compared with the untreated carbon fiber composite. This improvement is higher than many values reported for other ZnO morphologies. The shape of the nanoflakes may have contributed to the improved flexural properties. Their thin and wide structure provides a larger contact area with the epoxy matrix. This can help strengthen the connection between the filler and the matrix. Crack growth also becomes more difficult

because the flakes act as obstacles within the material. In comparison, rod-shaped particles mainly reinforce the material along one direction. The nanoflakes interact with the matrix from several directions, which can be beneficial when the specimen is subjected to bending loads.

The fracture observations further supports the mechanical test results as the untreated composite failed primarily by fiber-matrix interface separation. FESEM images showed that after fiber removal empty cavities left behind and fiber pull-out, matrix cracking also visible. These indicate weak bonding between the carbon fiber and epoxy matrix. When the load was applied cracks formed at the interface and spread quickly leading to early composite failure. As the fibers were not strongly attached to the matrix, the applied stress could not be transferred efficiently from one phase to the other.

The fracture surface of the ZnO-modified composite was different from that of the untreated sample. Most fibers remained embedded in the matrix, and signs of fiber-matrix separation were less evident. Matrix residues remained on the fiber surface after fracture, indicating stronger adhesion between the two components. The SEM images in Fig. 4.27 further support this observation. In Fig. 4.27(b), detached ZnO nanoflakes can be seen within the epoxy matrix rather than on the carbon fiber surface. This indicates that the bond between ZnO and epoxy was stronger than the bond between ZnO and the untreated fiber. During fracture, separation occurred primarily at the fiber-ZnO interface, leading to partial removal of the coating from the carbon fiber surface.

The fracture features of the PDA + ZnO coated fibers were different from those of the ZnO-coated sample. In Fig. 4.27(c), the ZnO nanoflakes were still present on the fiber surface after fracture. This indicates that the coating remained attached during loading. The PDA layer helped hold the ZnO coating on the carbon fiber surface and limited coating separation. In addition, the ZnO nanoflakes remained embedded in the surrounding epoxy, showing good interaction between the coating and matrix. The PDA and ZnO coating changed the fracture behavior of the composite as cracks did not spread as quickly as in the untreated sample. In many areas, the fibers remained attached to the surrounding matrix hindering crack growth. Because of this, the sample was able to absorb more energy before breaking. This behavior is consistent with the improved flexural strength observed during mechanical testing. The fracture analysis

showed clear differences between the untreated and treated composites. Samples with weaker fiber-matrix bonding exhibited crack formation and fiber pull-out at earlier stages of loading. After PDA and ZnO treatment the fibers remained more strongly attached to the matrix and fewer interfacial defects were observed. These changes were lead to better flexural performance and delayed fracture under bending conditions.

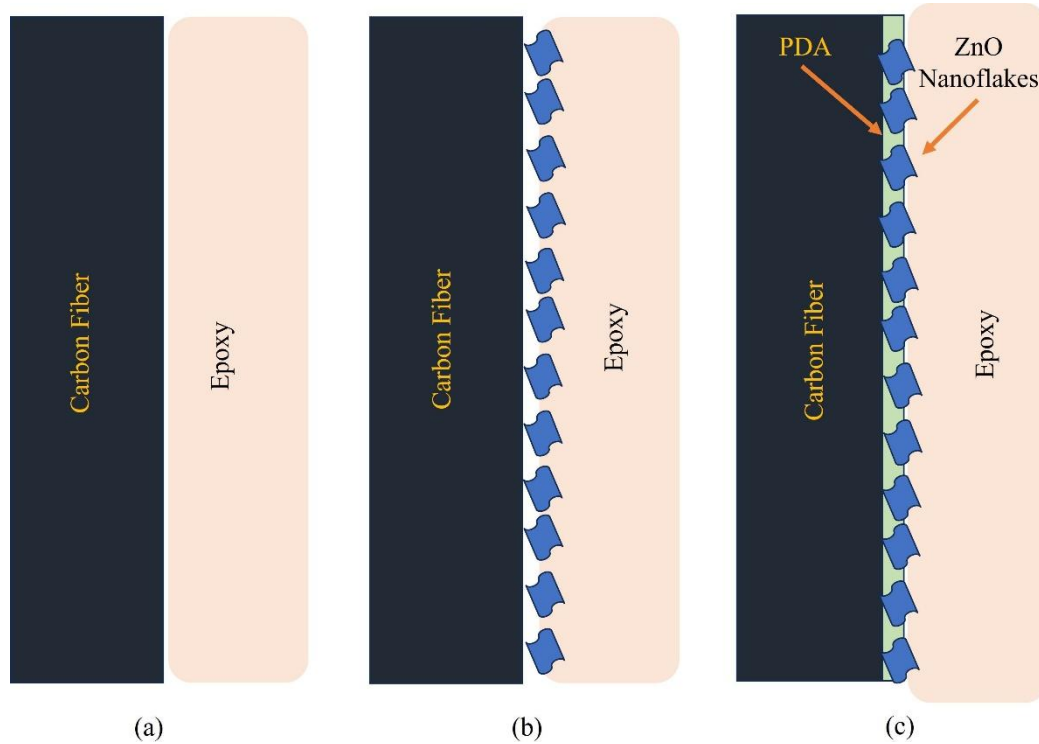


Figure 4.27. Illustrates the (a) lack of bonding between fiber and epoxy (b) ZnO interlocking the fiber and epoxy after PDA layering

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Conclusion

The work carried out in this study focused on the region where the carbon fibers and epoxy matrix come into contact known as interface. The experimental results showed that modifications made to the fiber surface enhanced the mechanical strength of the CFRP composites. Since the interface is responsible for transferring stress from the matrix to the fibers, improving this region directly affects the strength, stiffness, and failure behavior of the composite.

In this work, PDA was applied to the carbon fibers before coating them with MWCNTs and ZnO nanoflakes. The PDA layer remained attached to the fiber surface and provided suitable locations for the nanomaterials to attach. This made the deposition process more effective and helped keep the coating on the fibers during later processing steps. Compared with many traditional surface treatment methods, the PDA coating procedure was simple and easy to carry out. A uniform layer was formed on the fiber surface, which helped maintain the stability of the deposited nanomaterials.

The mechanical properties of the composites varied depending on the surface treatment applied to the carbon fibers. The highest flexural and tensile strengths were obtained for the PDA-assisted MWCNT coated samples. Compared with the untreated composite, the flexural strength increased by about 81.4%, while the tensile strength increased by nearly 48.2%. The presence of MWCNTs at the fiber surface may have improved the interaction between the carbon fibers and epoxy matrix. As a result, the composites sustained higher loads during testing and showed improved resistance to damage.

The ZnO-coated composites performed better than the untreated composites during flexural testing. The flexural strength increased by 48.27%, while toughness increased by about 89.4%. This improvement may be linked to the flake-like shape of the ZnO particles. Because nanoflakes cover a larger area, they remain in contact with more of the surrounding epoxy. Crack growth became less direct in the presence of these particles, and fracture occurred after a longer period of loading therefore composites absorbed more energy before failure.

The EDS maps showed that the coating was present across the fiber surface. FTIR and XPS results confirmed the presence of PDA and the deposited nanomaterials on the carbon fibers. The XRD patterns of the untreated and modified fibers showed no noticeable changes. This suggests that the surface treatment affected the fibers outer surface while the original carbon fiber structure remained intact.

The untreated carbon fibers showed a contact angle of 85.9° , whereas the modified fibers exhibited a lower value of 52.8° . The surface energy also increased from 5.10 J/m^2 to 44.1 J/m^2 after modification. These values suggest that the epoxy resin spreads more easily on the treated fiber surface. Better wetting can reduce interfacial voids and improve contact between the fibers and the surrounding resin.

The fracture analysis helped to explain the improved performance of the modified composites. In the untreated composites, failure mainly occurred through fiber pull-out, matrix cracking, and interfacial separation. These features indicate that the bond between the fiber and matrix was unable to withstand the applied stress. Once a crack formed at the interface, it could grow rapidly, leading to premature failure. The smooth fiber surfaces observed after fracture further suggest that little resistance was offered during fiber pull-out.

The fracture surface of the modified composite differed from that of the untreated composite. Even after failure resin was still attached to the fibers in many areas. Fiber pull-out was observed less, and fewer gaps were present at the fiber-matrix interface. Some ZnO nanoflakes remained within the epoxy after fracture, while others stayed attached to the fiber surface. The PDA layer appeared to improve coating attachment to the carbon fibers, and less coating separation was observed during fracture.

The results obtained for the different coatings were not the same as graphene coating was less stable on the carbon fiber surface, whereas the MWCNT and ZnO coatings remained attached more successfully. Composites prepared with MWCNTs and ZnO showed better mechanical performance than those containing graphene. This comparison shows that both the type of nanomaterial and its attachment to the fiber surface influence the behavior of the final composite.

The behavior of the composites was closely linked to the changes made at the fiber surface. The PDA layer helped to hold the nanomaterials on the carbon fibers, and the deposited MWCNTs and ZnO reformed the interaction between the fibers and the epoxy. Compared with the untreated composite, the modified samples showed better mechanical performance and fewer signs of interfacial failure.

5.1. Future Scope of the Work

Further work is needed to improve the coating process of graphene and understand the factors affecting graphene deposition. The graphene coating used in this study did not coat well and not formed stable layer on the carbon fiber surface.

Future studies can focus on using reduced graphene oxide (rGO) and graphene oxide (GO) because their surface functional groups may provide better interaction with the PDA layer. Different solvent systems such as water and DMF can also be studied to improve graphene dispersion and coating uniformity.

Electrophoretic deposition (EPD) can be used in future studies to deposit graphene on carbon fibers surface. Parameters such as voltage, deposition time and particle concentration can be changed to identify suitable coating conditions. After deposition, the coated fibers can be characterized and tested using IFSS and ILSS to examine the effect of the coating on fiber-matrix interaction.

Further investigation of coating formation and adhesion on the carbon fiber surface may assist in improving the stability of graphene coatings. This could contribute to stronger fiber-matrix interaction and better mechanical performance of CFRP composites.

List of Publications

S. No.	Paper Title	Journal/Indexing	Status
1	Enhancing Interfacial Adhesion in Carbon Fiber-Reinforced Composites through Polydopamine-Assisted Nanomaterial Coatings	Polymer Composite I.F: 4.7 Scopus/WOS SJR: 0.8	Published
2	Performance Analysis of CFRP Composite Interface Engineered with Bioactive Polymer- Supported ZnO Nanoflakes Coating for Improved Bending Strength	Polymer Composite I.F: 4.7 Scopus/WOS SJR: 0.8	Published
3	Enhanced Mechanical, Electrochemical, and Thermal Stability of CFRP Composites through Interfacial Modification Using CNT- Grafted Carbon Fibers	Polymer I.F: 4.5 Scopus/WOS SJR: 0.843	Submitted
4	Surface Engineering of Jute Fiber-Polymer Composites using p-dopamine and ZnO Nanocoating for Superior Mechanical Performance	Journal of Thermoplastic Composite Materials I.F: 3.4 Scopus/WOS SJR:0.756	Submitted

List of Book Chapter

S. No.	Title	Status
1	One book chapter published “Perovskite and emerging future technology” in Advanced Materials for Next-Generation Technologies (2023), ISBN: 9781774917800.	Published
2	Impact of Precursors on Carbon Fiber Properties and Applications	Submitted

List of Patent Published

S. No.	Title	Status
1	Surface Modification of carbon fiber PyC deposited on CNT	Published
2	CNT-MXENE Nanocomposite for Enhanced Water Purification	Published
3	Method of Enhancing Interfacial Bonding in Fiber Reinforced Composites Via Hybrid Nanocoating	Published
4	Enhancing Interfacial adhesion in Carbon Fiber-Reinforced Composites Through Polydopamine-Assisted	Published

List of Conferences

1	Conference	4 th International Conference on Recent Advances in Fundamental and Applied Sciences, [2023]	Paper Presented
2	Conference	5 th International Conference on Recent Advances in Fundamental and Applied Sciences, [2024].	Paper Presented
3	Conference	International Conference on Polymer Composite and Nano-composite, Mahatma Gandhi University, Kerala	Paper Presented
4	Conference	International Conference on Recent Advances in Composite Materials 2024 (ICRAM 24), Chinmaya Vishwa Vidyapeeth, Kerala	Paper Presented

List of Workshops

1	Hands-on Training	Level:2 “Hands-on Training on Fabrication & Characterization Facility for Nanotechnology” held at IIT Kharagpur”, during 26 Aug - 4 September, 2024.	Attended
2	Workshop	Level: 1 “9th User Awareness Workshop on Fabrication & Characterization Facility for Nanotechnology” held at IIT Delhi during 23 - 24 September, 2023.	Attended
3	Workshop	National Workshop on X-Ray Diffraction and Particle Size Analyzer held at LPU on 26-27 th April, 2024	Attended
4	Workshop	Workshop on intellectual Property Right on green technology and innovation. 20 th Aug, 2024, LPU	Attended
5	Hands-on Training	Microscopy School Inter University Accelerator Centre (IUAC), New Delhi, Dec 9-12, 2024	Attended

Annexure-I

Supplementary Data

(a) Lack of Graphene Coating

Figure 1 shows that a uniform graphene coating was not formed on the carbon fiber surface, even after using the PDA layer. In Figure 1(a), the SEM image shows uneven coating coverage. Some regions appear to contain graphene deposits, while other areas of the fiber surface remain exposed. Figure 1(b) provides a closer view of the surface. Graphene is seen as small clusters and flakes instead of a continuous layer. The grooves of the carbon fiber are still visible, indicating incomplete surface coverage. Some flakes also appear loosely attached, suggesting weak bonding between the graphene and the fiber surface. Figure 1(c) shows that the graphene coating is not evenly distributed on the carbon fiber surface. Some areas contain graphene clusters, while other regions show little or no coating. The darker regions indicate exposed fiber surfaces. Figure 1(d) shows a closer view of the graphene deposits on the fiber. In some locations, small gaps can be seen between the graphene flakes and the fiber surface, suggesting weak attachment. The images indicate that graphene did not spread uniformly over the carbon fiber and instead formed clusters. This may be related to the tendency of graphene sheets to stack together and the limited interaction between graphene and the PDA layer under the conditions used in this work.

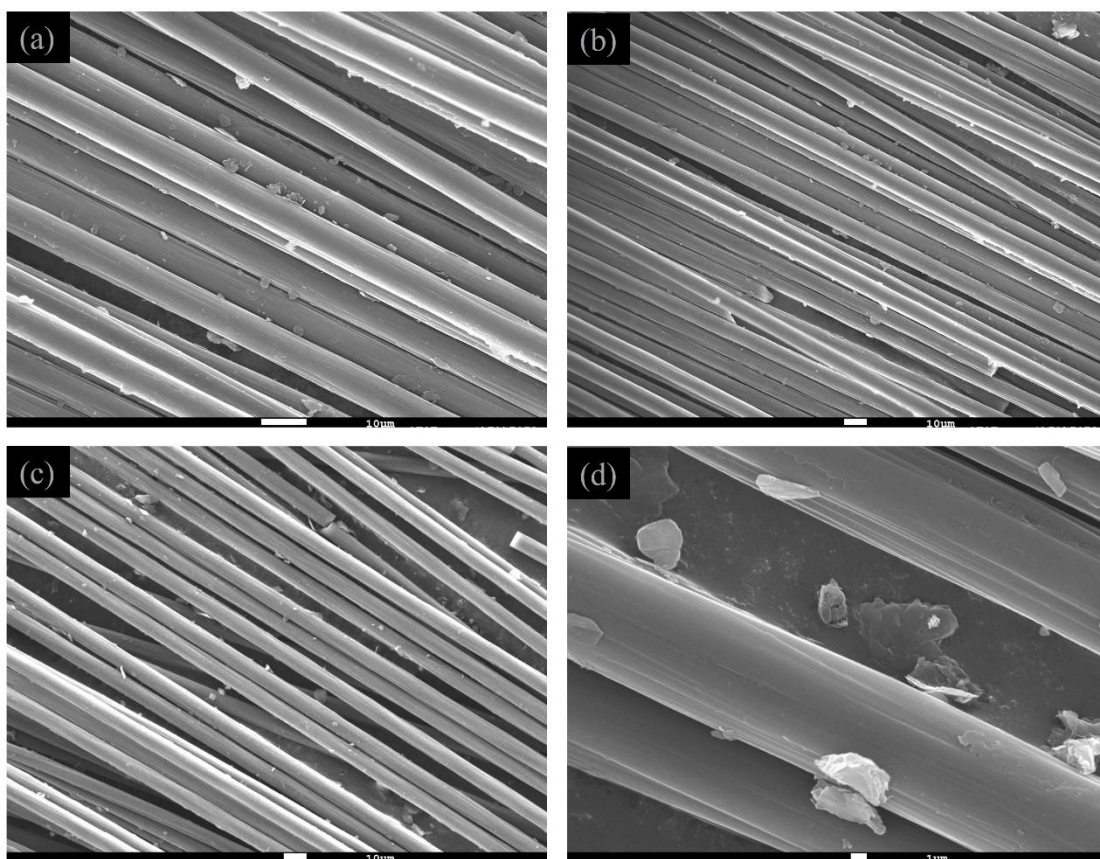


Figure 1. Illustrates the lack of graphene coating on carbon fiber

Appendices

Publication

Paper 1: Enhancing Interfacial Adhesion in Carbon Fiber-Reinforced Composites through Polydopamine-Assisted Nanomaterial Coatings

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RESEARCH ARTICLE

Enhancing interfacial adhesion in carbon fiber-reinforced composites through polydopamine-assisted nanomaterial coatings

Prabhjot Sharma, Sahendra P. Sharma 

First published: 04 January 2025 | <https://doi.org/10.1002/pc.29479> | Citations: 1

Abstract

This study explores the surface modification of carbon fiber (CF) with multi-walled carbon nanotubes, graphene, and zinc oxide nanoparticles to improve interfacial adhesion in carbon fiber-reinforced composites. A polydopamine (PDA) layer was used as a coupling agent to enhance the deposition and uniformity of the nanomaterial coatings on CF. The novelty lies in using PDA, which mimics mussel adhesive proteins, offering robust adhesion due to its amine and catechol functional groups. Elemental mapping through energy dispersive x-ray spectroscopy, along with Fourier transform infrared (FTIR) and x-ray diffraction analyses, confirmed the successful nanomaterial deposition while preserving the CF's graphitic structure. Nanoparticle structures at the nano-level were examined under a transmission electron microscope. Contact angle measurements showed improved wettability, decreasing from 85.9° to 52.8°, and increasing surface energy from 5.10 to 44.1 J/m², indicating better adhesion potential. The modified CF surface demonstrated improved interfacial bonding between the matrix and CF making them promising candidates for applications in hydrogen storage systems and energy storage devices, such as structural supercapacitors and batteries.

Paper 2: Performance Analysis of CFRP Composite Interface Engineered with Bioactive Polymer - Supported ZnO Nanoflakes Coating for Improved Bending Strength

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RESEARCH ARTICLE

Performance Analysis of CFRP Composite Interface Engineered With Bioactive Polymer-Supported ZnO Nanoflakes Coating for Improved Bending Strength

Prabhjot Sharma, Sahendra Pal Sharma✉

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ABSTRACT

This research explores the integration of ZnO nanoflakes in a dual-layer format using a bio-adhesive polymer on carbon fibers to improve the interlocking between the fiber and matrix in carbon fiber-reinforced polymer (CFRP) composites. A systematic approach to surface preparation was employed, which included the removal of polymer sizing, oxidative treatment, and the preparation of polydopamine (PDA) from dopamine to enhance ZnO adhesion. X-ray photoelectron spectroscopy indicated improved surface functionalization, while Raman spectroscopy verified the successful deposition of ZnO and structural changes. The innovative two-step process involving PDA layering followed by ZnO flake deposition led to a significant increase in flexural strength and toughness, with improvements of 48% and 89.4% compared to untreated fibers. Fractography analysis showed that ZnO nanoflakes improved interfacial bonding, minimized fiber pull-out and delamination, and altered failure modes to matrix cracking and fiber breakage. ZnO nanoflakes functioned as nanoscale bridges, enhancing stress transfer and energy absorption.

Conference

Presented Paper at 4th International Conference on Recent Advances in Fundamental and Applied Sciences, [2023]



Paper Presented at 5th International Conference on Recent Advances in Fundamental and Applied Sciences, [2024]



Paper Presented at International Conference in Polymer composite, Nanocomposite and Biocomposite (ICPCNB-2024)



Paper Presented at International Conference on Recent Advances in Composite Materials 2024 (ICRAM 24)

