Chapter- 3

Materials and Methodology

This chapter details the materials and methodologies employed in the fabrication and characterization of various FRPCs. It outlines experimental methodologies for assessing physical, thermal, mechanical, and tribological properties, and also incorporating Taguchi design, ANOVA for statistical significance, and machine learning techniques for predictive modeling.

3.1 Matrix material

This study employs Bisphenol-A ($C_{15}H_{16}O_2$), a thermoset polymer classified as an industrial epoxy resin [171]. Epoxy (Bisphenol-A) is selected for fiber composite fabrication due to its excellent chemical resistance, moisture tolerance, superior thermal stability, and cost-effective. Furthermore, epoxy (LY 556) exhibits good mechanical properties [172]. Its density ranges between 1.1 and 1.3 g/cm^3, while its tensile strength varies from 40 to 60 MPa. Bisphenol-A-Diglycidyl-Ether (BADGE), a compound from the epoxide family, exists in a liquid state but solidifies upon interaction with the hardener HY-917, either with or without external heat application. The LY 556 epoxy resin and its corresponding hardener HY-917 are purchased from Ciba Gaigy Limited, Mumbai, India.

3.2 Fibers used in the present study

3.2.1 Aramid fiber

Aramid fiber, a high-performance synthetic fiber derived from aromatic polyamides, exhibits exceptional strength, thermal stability, and resistance to abrasion and impact. With a superior strength-to-weight ratio, it is widely used in composite applications. Aramid fibers demonstrate excellent heat and chemical resistance, making them suitable for aerospace, ballistic protection, automotive, and sporting applications [173]. Aramid fiber-reinforced polymer composites enhance durability and impact resistance but face challenges such as low compressive strength, and processing limitations. Ongoing research focuses on performance enhancement and hybridization. A 200 Gsm bi-directional plain aramid fiber mat as shown in Figure 3.1 (a), purchased from Arrow Technical Textiles, Mumbai, India, has a density of 1.44 g/cm³, a tensile strength of 2.7 GPa, and an individual fiber diameter of 12 µm, as per supplier specifications.

3.2.2 Carbon fiber

Carbon fiber is a high-performance material composed of thin, strong crystalline filaments of carbon atoms, known for its superior strength-to-weight ratio, high stiffness, and excellent thermal and chemical resistance. It is primarily produced through the pyrolysis of polyacrylonitrile (PAN) or pitch-based precursors, forming highly ordered carbon structures. Carbon fiber is widely used in aerospace, automotive, and precision engineering applications due to its fatigue resistance and low thermal expansion. Carbon fiber-reinforced polymer (CFRP) composites offer enhanced structural integrity with reduced weight [174]. However, high production costs and brittle fracture behavior remain challenges. In this study, a 200 Gsm bi-directional plain weave carbon fiber mat as shown in Figure 3.1 (b), with a density of 1.8 g/cm³, a tensile strength of 3.5 GPa, and a fiber diameter of 8 µm, was purchased from Arrow Technical Textiles, Mumbai, India.

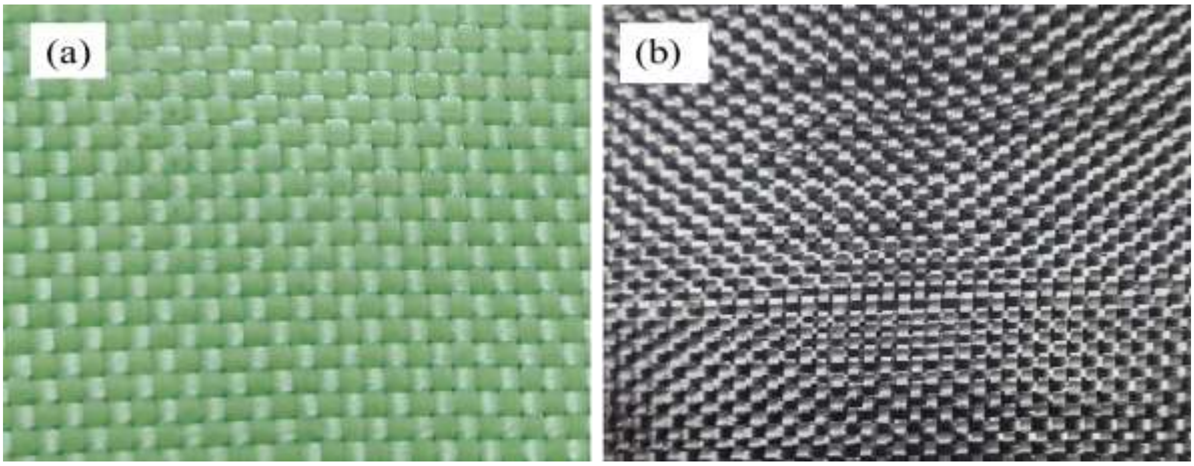

Figure 3.1 Bi-directional woven fiber mat, (a) Aramid fiber, (b) Carbon fiber

3.3 Nanoparticles used in the present study

3.3.1 Carbon nanotubes

Carbon nanotubes (CNTs) are cylindrical nanostructures formed by rolling graphene sheets, exhibiting exceptional mechanical, electrical, and thermal properties. They possess a high aspect ratio, superior tensile strength, and excellent electrical conductivity, making them ideal for applications in nanocomposites, electronics, energy storage, and biomedical devices. CNTs are classified into single-walled (SWCNTs) and multi-walled (MWCNTs) based on their structural layers. Despite their advantages, challenges such as dispersion issues, high production costs, and toxicity concerns limit their widespread use [175]. Ongoing research focuses on scalable synthesis, functionalization, and integration into advanced materials. CNT nanoparticles as shown in Figure 3.2 (a), procured from TUHH, Hamburg, Germany, have a length of ±2 µm, an inner diameter of ±6.5 nm, and an outer diameter of ±40 nm.

3.3.2 Graphene oxide

Graphene oxide (GO) is a single-layer carbon-based nanomaterial synthesized via graphite oxidation, incorporating hydroxyl, epoxy, and carboxyl functional groups that enhance its dispersibility in aqueous and organic media. It exhibits superior mechanical strength, electrical conductivity, and thermal stability, making it suitable for applications in nanocomposites, energy storage, sensors, biomedical devices, and water purification [176]. Research-grade GO nanoparticles as shown in Figure 3.2 (b) (purity: +99%, thickness: 0.8–2 nm, length: 5–10 µm) were procured from Shilpent, Shilpa Enterprises Maharashtra, India.

3.4 Chemicals used in the present study

Sulphuric acid (98% v/v) and nitric acid (69% v/v) were procured from Merck Life Science Private Limited, Mumbai, India, and utilized for fiber and nanoparticle oxidation. Acetone, supplied by Sigma Aldrich chemicals private limited, Karnataka India, served as a cleaning agent. These chemicals were used to enhance surface functionality and purity, ensuring improved compatibility and performance in composite fabrication and material processing applications.

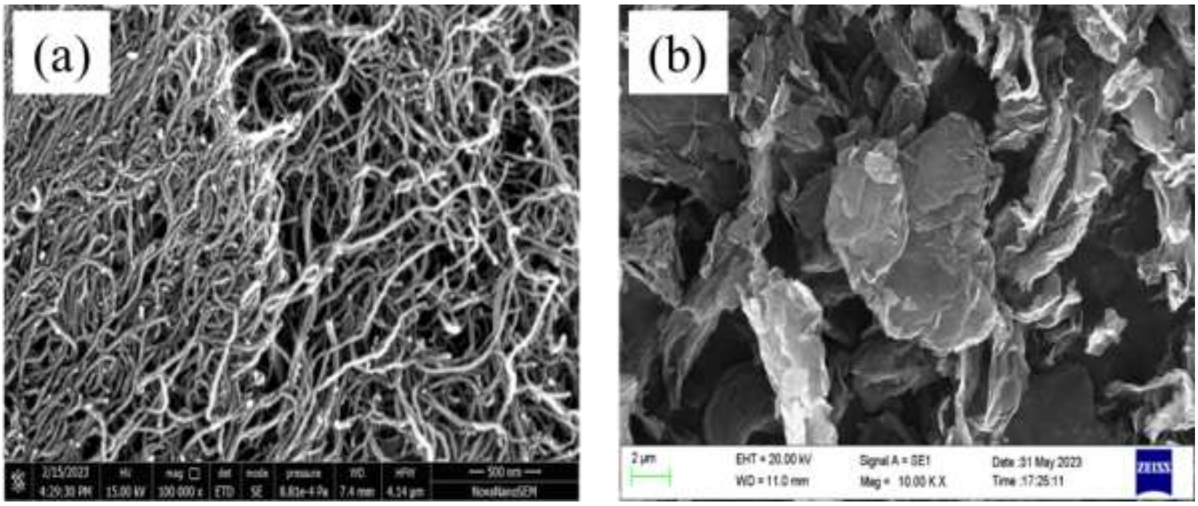

Figure 3.2 SEM image of (a) CNTs and (b) GO

3.5 Functionalization of CNTs

A 100 ml of acid solution was prepared by mixing 10M sulphuric and 10M nitric acid in the ratio (3:1 v/v) for the functionalization of CNT [177]. Typically, 1 gram of untreated CNT was mixed in acid solution by magnetic stirring a mixture on a hot plate for 15 minutes at a temperature of 60°C. The mixture was then sonicated in a conventional ultrasonic bath for 2 hours. During the sonication process, approx. 60°C temperature was maintained. Once the process was complete, the functionalized CNT slurry was filtered and washed with distilled water using a vacuum filtration process. To ensure no acid was left in the filtered slurry, the pH of the outlet water was continuously measured using a pH paper until it reached 7. Finally, the filtered slurry containing the powder of functionalized CNT was dried in an oven at 120°C for 4 hours. After that, the dry functionalized carbon nanotubes (FCNT) were pulverized in ball-milling.

3.6 Surface treatment of aramid fiber

Just before the chemical treatment, the aramid fiber was treated with acetone to remove the sizing agents. Then, it was repeatedly washed in deionized water and dried at ambient temperature to obtain the desized aramid fiber.

3.6.1 Chemical treatment of aramid fiber

The aramid fiber modification was carried out by dipping the fiber in a 3 M mixture of sulphuric and nitric acid in the ratio (3:1 v/v) for 1 hour. After that, the aramid fiber was cleaned with distilled water until all of the acid content had been eliminated, and it was confirmed by the pH paper, which showed the value 7. The fiber was then dried for two hours in an oven at 120°C. The intended impact of this procedure is to modify the amorphous portion of the aramid fibers by breaking the amide bonds located in the fiber structure backbone. This process results in the creation of carboxyl and amide groups in fiber segments [178]. With the carboxyl and hydroxyl groups on the previously oxidized CNTs, these newly created functional groups can establish hydrogen bonds [179].

3.6.2 Coating of CNTs on aramid Fiber

The process described involves functionalizing CNTs and attaching them to a fiber surface through dip coating. Initially, 1 gram of previously functionalized CNTs was added to 1000 ml of acetone in a container. The mixture was then stirred using a magnetic stirrer for 10 minutes to ensure that the CNTs were evenly dispersed in the solvent. After the stirring, the mixture was subjected to a bath sonication process for 1 hour. This process involves immersing the container in a water bath and using high-frequency sound waves to break up any agglomerates that may have formed and ensure proper dispersion of the CNTs in the acetone. Once the sonication process was completed, a fiber was immersed in the mixture and sonicated for an additional hour. This allowed the CNTs to attach to the fiber’s surface and was dried in an oven at 120°C for 2 hours.

3.7 Surface treatment of carbon fiber

Before undergoing chemical treatment, the carbon fiber was first cleaned with acetone to eliminate surface sizing agents. It was then repeatedly washed with deionized water and air-dried at room temperature to obtain desized aramid fiber.

3.7.1 Chemical treatment of Carbon fiber

The surface modification of carbon fibers was performed by immersing them in a 3 M acidic solution composed of sulphuric acid and nitric acid in a 3:1 volume ratio for 1 hour. After the treatment, the fibers were thoroughly washed with distilled water until neutrality was confirmed using pH paper (pH = 7). Subsequently, the fibers were oven-dried at 120 °C for 2 hours. The oxidative treatment induced the formation of oxygen-containing functional groups, primarily carboxyl and hydroxyl, thereby generating active sites on the carbon fiber surface. Additionally, acid etching increased the specific surface area and surface roughness, further enhancing interfacial compatibility [180, 181].

3.7.2 Coating of CNTs, GO, and hybrid (CNTs/GO) on Carbon Fiber

The three distinct solutions were prepared by mixing 1 mg/ml of functionalized CNTs in acetone, 1 mg/ml of GO in acetone, and a combination of 1 mg/ml of CNTs/GO hybrid (in ratio 1:1) in acetone. The stirring process, facilitated by a magnetic stirrer, lasted for ten minutes to ensure uniform dispersion of nanoparticles in the solvent. Subsequently, the mixture underwent a 1-hour bath sonication process, and utilizing high- sound waves frequency to disperse any agglomerates and achieve proper dispersion of nanoparticles in acetone. Nanoparticles were deposited onto a carbon fiber substrate measuring 20 cm by 20 cm utilizing a high atomizing spray cannon connected to an air compressor, equipped with a nozzle of 0.5 mm diameter. To ensure even dispersion, the spray cannon was positioned perpendicular to the fiber during the coating process. The distance between the spraying nozzle and the carbon fabric was consistently maintained at 12 cm to maintain uniformity, and the optimal air pressure for spraying was set at 3.0 bar. After the spray coating, the solvent was removed through drying, leading to the immobilization of nanoparticles on the carbon fiber surface. Three different types of coatings were applied to the carbon fiber: (1) a 1 wt.% concentration of CNTs, (2) a 1 wt.% concentration of GO, and (3) a 1 wt.% concentration of CNTs/GO hybrid (in ratio 1:1).

3.8 Composite fabrication

3.8.1 Aramid fiber-reinforced epoxy composites

The fabrication process of fiber-reinforced polymer composites was done by hand lay-up process. The two different samples were prepared; in the first sample, here six layers of the aramid fiber were used as a reinforcement and matrix as epoxy called aramid fiber reinforced epoxy composite (AF/epoxy); in the second sample, six layers of the functionalized CNT-coated aramid fiber as a reinforcement and matrix as epoxy called as functionalized CNTs coated on chemically treated aramid fabric reinforced epoxy composite (CAF-FCNT/epoxy). In the hand lay-up process, a carefully measured mixture of epoxy and hardener is prepared in a beaker with a 10:1 ratio by weight. This ensures that the proper chemical reaction occurs when the mixture is applied to the fiber mat. Next, a plastic sheet is placed on a flat surface, and the epoxy resin mixture is applied. Then, the fiber mat is carefully laid on top of the resin, on which the resin is manually applied using a roller for the uniform distribution of resin, and the process is repeated with additional layers of resin and mat until six layers are in place. Ensuring the adhesion of carbon nanotubes (CNTs) to aramid fibers (AF) during resin application is a methodical process. Initially, both CNTs and AF undergo surface treatment through a chemical functionalization process. This treatment leads to the functionalization of surfaces for both CNTs and AF. Importantly, it enhances mechanical interlocking between the CNTs and the fiber, establishing a strong bonding capability. This heightened bonding becomes pivotal during the subsequent CNT coating process onto AF. To ensure the proper distribution of the epoxy resin and prevent the formation of dry fiber patches, a pressure of 15 kPa is applied to the top of the sample. This helps to evenly distribution of the resin throughout the fiber mat and promote a strong bond between the layers. It was then left to cure for 24 hours in a natural setting. Finally, the sample is cut according to desired dimensions for the different tests.

3.8.2 Carbon fiber-reinforced epoxy composites

Four distinct polymer composite samples were created: Carbon Fiber Reinforced Epoxy (CFRE), Carbon Nanotubes Coated Carbon Fiber Reinforced Epoxy (CCFRE), Graphene Oxide Coated Carbon Fiber Reinforced Epoxy (GCFRE), and Hybrid (CNTs/GO) Coated Carbon Fiber Reinforced Epoxy (HCFRE). Each sample consisted of six layers. The fabrication process involved preparing a precisely calculated blend mixture of epoxy and hardener in a beaker, maintaining a weight ratio of 10:1. This ensured the initiation of the appropriate chemical reaction when applied to the fiber mat. The hand lay-up method was employed in the fabrication process of the polymer composites. During this process, epoxy resin was systematically applied to each layer sequence for all samples. A pressure of 15 kPa was applied to the samples on the upper face in order to stop the epoxy resin from depositing and make sure there were no dry fiber patches. Subsequently, the samples underwent compression for 24 hours during the curing phase. This meticulous process aimed to produce polymer composite with specific properties tailored to each type of coating.

3.9 Physical and thermal characterization of fibers and nanoparticles

3.9.1 Scanning electron microscopy (SEM)

SEM analysis was conducted using an EVO-SEM MA15/18 (Carl Zeiss Microscopy Ltd.) as shown in Figure 3.3 to investigate the morphological characteristics of uncoated and nanoparticle-coated fibers, as well as untreated and chemically modified nanoparticles.

3.9.2 Fourier Transform Infrared spectroscopy (FTIR)

FTIR was used to examine the functional groups in untreated and chemically treated for both fibers and nanoparticles. A Nicolet iS5 spectrophotometer as shown in Figure 3.4 from THERMO Electron Scientific Instruments LLC, with a scanning range of 4500 cm^{-1} to 550 cm^{-1} and a resolution of 2 cm^{-1}, was used to collect the infrared spectra of the unmodified and modified fibers and nanoparticles. Using the attenuated total reflectance (ATR) mode, the fibers were examined, whereas the nanoparticles were analyzed using a Potassium Bromide (KBr) mode.

Figure 3.3 EVO-SEM MA15/18 (Carl Zeiss Microscopy Ltd.)

Figure 3.4 Nicolet iS5 spectrophotometer

3.9.3 Thermogravimetric analysis (TGA)

The thermal stability of fibers and nanoparticles coated fibers was analyzed using a TGA-50 instrument from Shimadzu Asia Pacific Pvt Ltd as shown in Figure 3.5. TGA curves were created by subjecting samples weighing a few milligrams using a heating rate of 10°C per minute, reaching a temperature range of 24 to 800°C, while maintaining an inert atmosphere with nitrogen gas. This analysis allowed for the investigation of the behavior of the samples under different temperatures and conditions.

Figure 3.5 TGA-50 instrument (Shimadzu Asia Pacific Pvt Ltd)

3.10 Physical, mechanical, thermal, and tribological tests of fiber-reinforced epoxy composites

3.10.1 Density calculation

Following the ASTM D792-13 standard was followed in order to calculate the sample density. The mass of the sample was measured using a digital weighing machine having an accuracy of 0.1 mg. The density was then determined by applying Archimedes' principles and the sample mass. This process yielded standard values for different samples' masses and the calculated density.

3.10.2 Vickers Microhardness testing

Microhardness testing of polymer composite samples was performed using a micro-indentation tester as shown in Figure 3.6 following the ASTM E384 standard. A 25 g load with a dwell time of 10 seconds was applied to generate indentations. Each polymer composite sample underwent five Microhardness measurements, and the average value was recorded for analysis.

Figure 3.6 Vickers micro hardness instrument

3.10.3 Tensile testing

A computer-controlled Instron universal testing machine as shown in Figure 3.7 with a 100 kN load cell was used to perform tensile tests on the composite specimens. The testing followed the guidelines as per ASTM D-3039 standard, employing test specimens measuring (150*15*2) mm in dimensions. The testing process was conducted with a cross-head speed of 2 mm/min and at room temperature. Each polymer composite sample underwent three test, and the average value was recorded for analysis.

Figure 3.7 Universal Testing Machine

3.10.4 Flexural testing

Following the ASTM D-790 standard, the flexural tests of the composite specimens were performed using a computer-controlled Instron universal testing machine. The flexural characteristics of composite specimens and were evaluated at a span length of 60 mm, width of 15 mm, thickness of 2 mm and a cross-head speed of 1 mm/min.

The formula as given below is employed to calculate the flexural strength of the FRPC specimen [182]:

$$\text{Flexural strength} = \frac{3FL}{2bd^2} \tag{3.1}$$

Maximum load is denoted by the symbol F (N), the length of the span is denoted by the symbol L (mm), and the width and thickness of the FRPC specimens are denoted by b and d, respectively (both in mm).

The below-mentioned formula can calculate the value of the Flexural modulus [182]:

$$\text{Flexural modulus} = \frac{mL^3}{4bd^3} \tag{3.2}$$

Where m is the slope of the tangent of the load-deflection curve (N/mm).

3.10.5 Short beam shear test

The composite specimens' Interlaminar Shear Strength (ILSS), with dimensions of 15mm in width, 2 mm in thickness and 30 mm in length, was assessed through short beam shear testing conducted on an Instron universal testing machine. The cross-head speed was adjusted to 1 mm/min during the testing process, which adhered to the parameters specified in the ASTM D-2344 standard.

ILSS of the composite samples are calculated from the following equation [183]

$$\text{ILSS} = \frac{3F}{4bd} \tag{3.3}$$

3.10.6 Izod impact test

Izod impact testing used a Resil Impactor-50 model from CEAST, S.p.A., Italy as shown in Figure 3.8. The specimen size of (64*12.7*2) mm and the test parameters included an impact length of 0.327m and a velocity of 3.426 ms^{-1}. A hammer with a mass of 0.932 kg was dropped onto the specimens, and impact strength was determined according to ASTM D256 standards. The specimens were positioned in the testing machine so that the notch root aligned with the vice, and the hammer impacted the notched face.

Figure 3.8 Impact Testing Machine

Figure 3.9 TPS 500 thermal conductivity analyzer

3.10.7 Thermal conductivity test

The polymer composites' thermal conductivity (k), arranged in a stacked configuration, was measured using a TPS 500 thermal conductivity analyzer as shown in Figure 3.9. This instrument provided a direct assessment of the thermal conductivity (k) value at ambient room temperature.

3.10.8 Tribological testing

Tribological testing was performed to analyze the wear and frictional characteristics of polymer composites. The evaluation involved measuring friction coefficients, wear rates, and material degradation under different conditions.

3.10.8.1 Reciprocating wear test

Wear tests using linear reciprocating motion were conducted in accordance with ASTM G133 guidelines. A square sample, 20 mm by 20 mm in size and 2 mm thick, was used for the testing. Polymer composite specimens that were fixed were subjected to the reciprocating friction test. The counter surface material was a 62 HRC chrome steel ball that reciprocated on the stationary sample. The experiments utilized a reciprocating friction monitor (TE 200ST) sourced from Magnum Engineers, Bangalore, India as shown in Figure 3.10. The stroke length stayed at 1.5 mm throughout the testing period. Various tests were conducted under different loads, temperature, and sliding frequency. The test period was 20 minutes for each test, during which the wear loss and coefficient of friction were carefully examined.

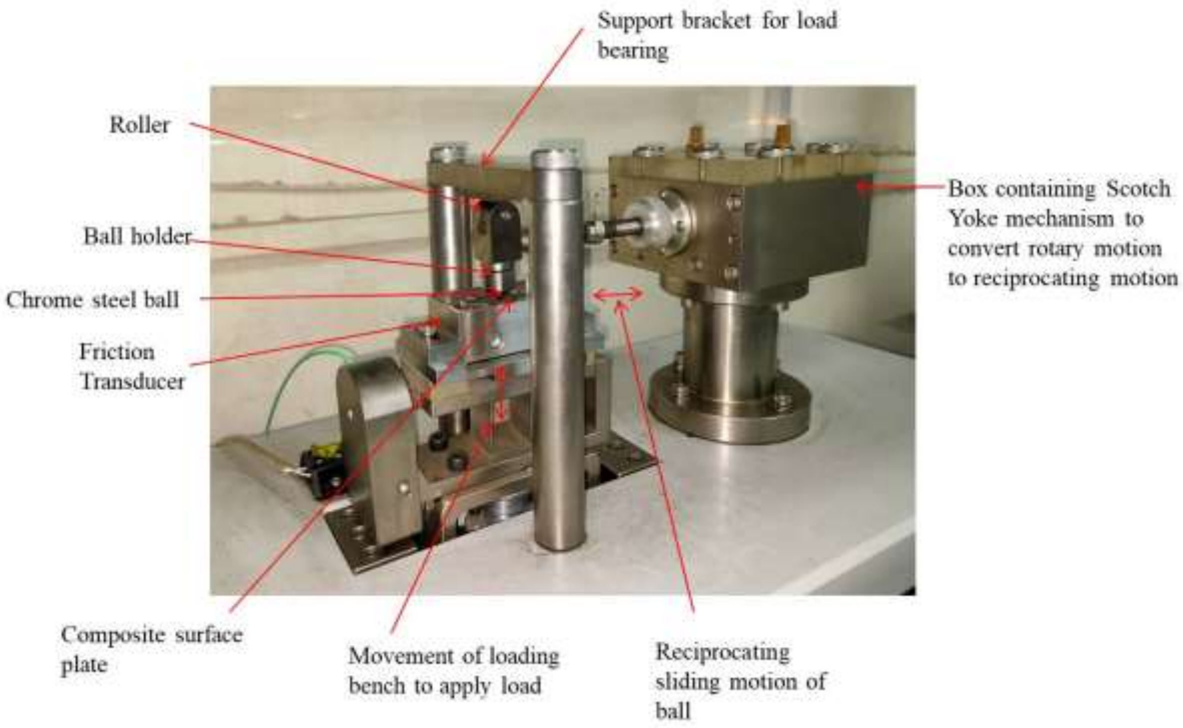

Figure 3.10 Reciprocating Friction Monitor

3.10.8.2 Erosion wear test

Erosive wear occurs when solid particles suspended in a fluid stream, whether liquid or gas, collide with the surfaces of elements, causing material loss over time. To evaluate composite specimens' erosion wear characteristics, an air-jet erosion tester (TR-471-800) manufactured by Ducom Instruments in Bangalore, India, was employed as shown in Figure 3.11. A device comprising three primary elements: an air compressor, an air-particle blending chamber, and an acceleration segment. The erosion test utilized a nozzle with an orifice radius of 0.75 mm and a standoff distance of 60 mm. Test duration was maintained at a constant 10 minutes. Sample dimensions varied depending on the impingement angle: 25 × 20 mm for 15° and 30° angles and 25 x 25 mm for 60° and 90° angles.

Figure 3.11 Air-jet Erosion Tester (TR-471-800)

3.11 Surface morphology tests

The surface morphology of the worn composite surfaces was analyzed using a scanning electron microscope (EVO-SEM MA15/18, Carl Zeiss Microscopy Ltd.).

3.12 Taguchi experimental design

The Taguchi method and ANOVA selection for statistical analysis are justified by their effectiveness in optimizing experimental design and identifying the most significant control factors influencing erosion wear. The Taguchi method, with its orthogonal array approach, efficiently analyzes multiple variables without requiring exhaustive testing of all possible combinations, enhancing experimental efficiency. ANOVA further validates the statistical significance of each factor by quantifying their contributions and interactions, ensuring robust conclusions. These statistical techniques are widely used to enhance product and process quality by systematically identifying and analyzing the impact of multiple experimental variables. The experimental procedure for solid particle erosion is a prime example of a process where numerous control parameters interact to influence the performance outcome, such as the erosion rate [184]. The Taguchi method serves as a strategic framework for designing and executing experiments aimed at exploring processes influenced by numerous variables and inputs [185]. It allows for a comprehensive investigation of these elements without the need for exhaustive testing of all possible combinations, thus optimizing efficiency. In the erosion wear test, a Taguchi (L16) orthogonal array was utilized, incorporating four factors with four levels each. The resulting experimental data were transformed into signal-to-noise (S/N) ratios and interpreted based on the desired output results. Specifically, in this scenario, a "smaller the better" preference for the S/N ratio was favoured to minimize the erosion rate [186]. The calculation of the S/N ratio for erosion wear rate was carried out using Equation (3.4), and the values were presented in decibels (dB) as a standard unit of measurement.

$$\frac{S}{N} = -10 \log \frac{1}{n} \sum [y]^2 \qquad (3.4)$$

The output erosion wear rate mean-square deviation is represented by $[\frac{1}{n}\sum[y]^2]$: where 'n' stands for the number of observations and 'y' for the average of the observed data. Furthermore, an analysis of variance was used to determine the most significant control factors and their interactions, with a significance level of 0.05 ($p < 0.05$).

3.13 Machine Learning (ML)

This study utilized a machine learning (ML)-based data-driven approach to predict the coefficient of friction (COF), a critical parameter in Tribological and Industrial applications. The methodology encompassed systematic data collection, pre-processing, optimization, model training, and evaluation to enhance predictive accuracy. Pre-processing ensured data integrity, while optimization refined model performance. Predictive models were developed using previous tribological, mechanical, and thermal data, employing three ML algorithms: Artificial Neural Network (ANN), Gradient Boosting Machines (GBM), and Random Forest (RF). The study aimed to establish a robust computational framework, reducing experimental efforts and improving tribological analysis efficiency. The ML models demonstrated high precision in COF estimation, contributing to advanced material design and economic decision-making.