Chapter 3 Materials and experimental methodology

This chapter provides a comprehensive overview of the materials chosen for the study, sources of procurement, and preparation processes. It details the synthesis procedures for developing hybrid materials, emphasizing precision and reproducibility. Additionally, the chapter outlines the characterization techniques used to analyze material properties to ensure a thorough understanding of their tribological behavior. Testing methods are also discussed, focusing on evaluating performance parameters to meet the study's objectives. Collectively, these elements form the foundation for investigating the properties and performance of hybrid lubricant materials, aligning with the research interest of this work.

3.1. Materials and synthesis

3.1.1. Base oil

The current study focuses on developing vegetable oil-based lubricants for industrial and automotive applications. Non-edible vegetable oils are specifically selected for this purpose. Analytical-grade castor oil (8001-79-01 Sisco Research Laboratory Pvt Ltd) is predominantly used in the study, with extracted Karanja oil (Pongamia pinnata) being explored. Since these oils are non-edible, they are suitable for various engineering applications. Their high availability across the South Asian region ensures that they can be produced in sufficient and quantities, making them a sustainable and viable option to meet specific lubrication requirements. Karanja oil is also chemically modified to enhance its performance and is used for base lubrication as well as functionalizing agent in nano lubricant.

3.1.2. Purification and chemical modification of Karanja oil

Dry seeds are crushed and pressed to extract the oil, which is then passed through coarse and fine strainers to remove finely crushed seed particles mixed with the oil. The water degumming process is employed to remove hydrolytic phospholipids (gum) from the raw oil, as these lipids can negatively affect the epoxidation process. To separate the gum from the oil, 400 mL of cold-pressed oil is mixed with 20-30 mL of deionized water and sheared at 500 rpm at 55 °C. The mixture is then centrifuged at 3000 rpm, allowing the gum to separate. The resulting oil is collected and preheated to 90 °C for an hour under vacuum conditions to eliminate moisture before being cooled and stored. This process ensures that the oil undergoes no chemical changes aside from the removal of gum, which could otherwise interfere with its storage by separating over time. The degummed oil, referred to in the literature as pure Karanja oil (KO), is now ready for further analysis. The process of oil is shown in figure 3.1.

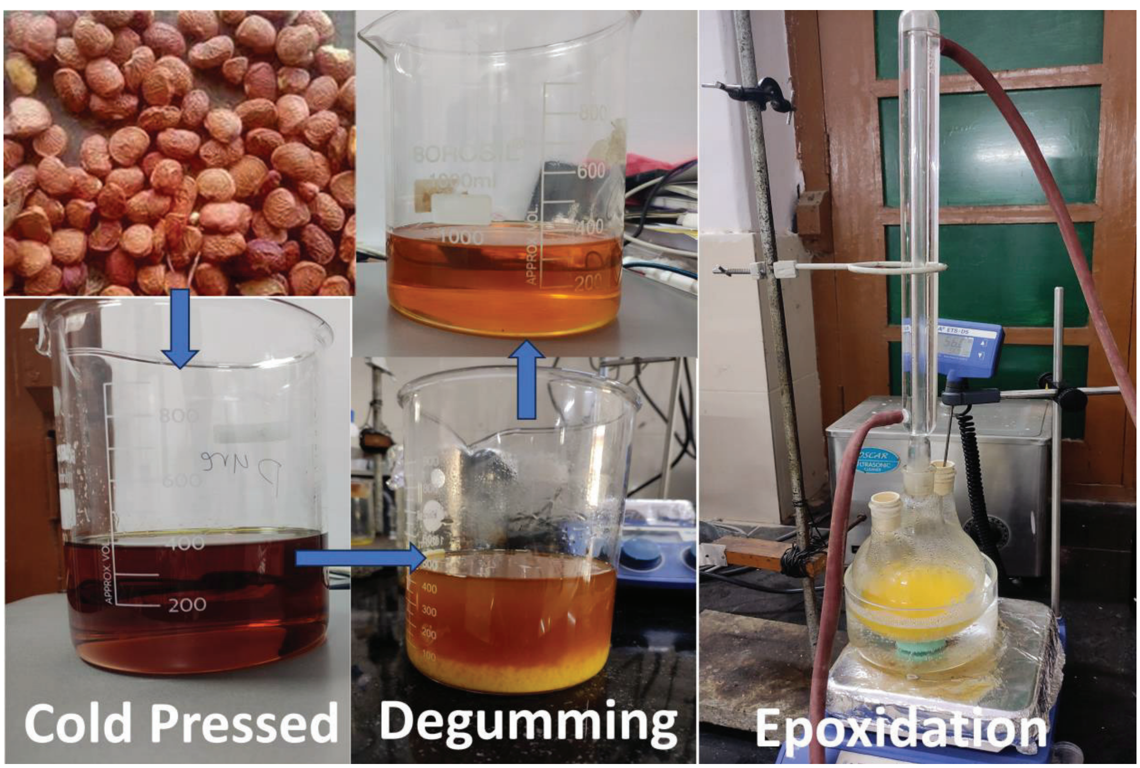

Figure 3.1 Karanja oil at different stages of modification procedure

Epoxidation is a chemical process where alkenes are modified by introducing an oxygen atom in the form of an epoxide, effectively removing unsaturation. To chemical modification of the unsaturated double bonds in Karanja oil (KO), 100 grams of KO was placed in a three-necked round-bottom flask containing 12.58 mL of acetic acid. To accelerate the reaction, 1.2 mL of H_2SO_4 was added. The setup was maintained in an ice bath to keep the temperature below 10 °C. Subsequently, 89.8 mL of hydrogen peroxide was carefully drop wise added to the flask with continuous stirring. The reaction followed a molar ratio of 1:3:8 for Karanja oil, acetic acid, and hydrogen peroxide, respectively. This exothermic reaction was allowed to proceed, and after the addition of hydrogen peroxide, the mixture was processed using water bath at 60 °C for 6 hours to complete the process. The resulting mixture was transferred into a separatory funnel and thoroughly washed with diethyl ether and distilled water to remove any residual free acids. The modified oil was then preheated under vacuum conditions to eliminate any dissolved volatile components. The final product, referred to modified Karanja oil (MKO), was ready for further use. Chemicals used for various purpose are listed in Table 3.1.

Table 3.1: List of chemicals used for different purposes

Chemical Name	**Chemical Formula**	**Purpose**	**Manufacturer**
Absolute ethanol	C_2H_5OH	Synthesis	CH-fine chemicals
Acetic acid (Glacial)	CH_3COOH	Modification	SRL Chemicals
Acetone	C_3H_6O	Cleaning agent	SD-fine chemicals
Aminopropyltriethoxysilane	$C_9H_{23}NO_3Si$	Modification	TCI Chemicals
Ammonia (30%)	NH_3	Synthesis	SRL Chemicals
Diethyl ether	$(C_2H_5)_2O$	Synthesis	SD-fine chemicals
Hydrated sodium	$Na_2MoO_4.2H_2O$	Synthesis	Sigma Aldrich

molybdate			
Hydrochloric acid	HCl	Synthesis	Sigma Aldrich
Hydrogen peroxide	H_2O_2	Modification	SRL Chemicals
Hydroxylamine hydrochloride	$HONH_2 \cdot HCl$	Synthesis	Sigma Aldrich
Methanol	CH_3OH	Synthesis	SD-fine chemicals
Monohydrated zinc chloride	$ZnCl_2.H_2O$	Synthesis	Sigma Aldrich
N, N-dimethyl formamide (DMF)	$HCON(CH_3)_2$	Synthesis	CDH Fine Chemical
Potassium permanganate	$KMnO_4$	Synthesis	Sigma Aldrich
Sodium dodecyl sulphate	$NaC_{12}H_{25}SO_4$	Synthesis	SRL Chemicals
Sodium hydroxide	$NaOH$	Synthesis	Sigma Aldrich
Sodium molybdate	Na_2MoO_4	Synthesis	SRL Chemicals
Sulfuric acid	H_2SO_4	Modification	Sigma Aldrich
Tetraethyl orthosilicate (TEOS)	$SiC_8H_{20}O_4$	Synthesis	TCI Chemicals
Thiourea	CH_4N_2S	Synthesis	SRL Chemicals
Toluene	$C_6H_5CH_3$	Synthesis	SRL Chemicals

3.1.3. Nano additives synthesis

*3.1.3.1. **Molybdenum disulphide (MoS_2) synthesis procedure:***

The hydrothermal synthesis of MoS_2 nanosheets was performed utilizing sodium molybdate and thiourea as precursors. To begin, 5 mL of hydrochloric acid (35% aqueous solution) was progressively added to a 20-mL aqueous solution containing 1.21 g sodium molybdate and 0.70 g hydroxylamine hydrochloride. The resulting mixture was swirled at

90 degrees Celsius for 30 minutes. Then, 1.56 g of thiourea was progressively added to the mixture, followed by another 15 minutes of stirring. The produced reaction mixture was then transported to a Teflon-lined stainless-steel autoclave, sealed firmly, and placed in a 230 °C oven. After 24 hours of hydrothermal reduction, the resulting black suspension was separated using a vacuum filtering technique and carefully washed with distilled water until the pH of the decanted water was neutralized. The wet cake thus formed is dried at 100 °C, and then the dried MoS_2 is fined, crushed into a powder using a mortar pestle. These particles are hygroscopic. Thus, they need to be stored in a closed and sealed container.

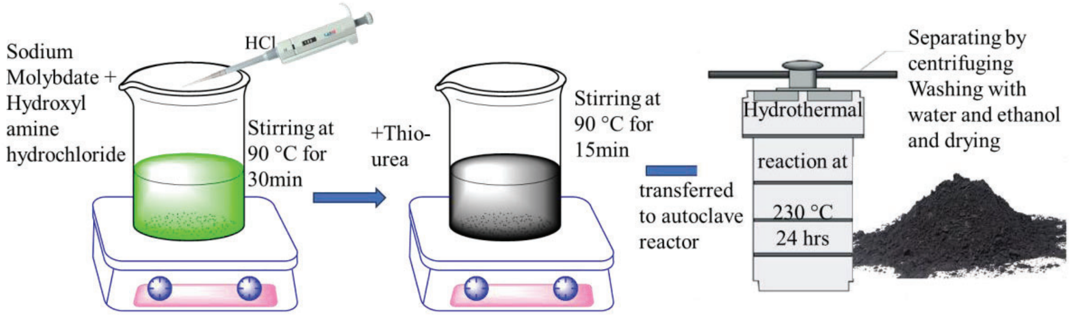

Figure 3.2 Synthesis procedure of MoS_2 nano particles using hydrothermal method

3.1.3.2. ***Silica particle synthesis***

A mixture of distilled water (12 mL), ethanol (80 mL), and 0.1 g of citric acid was prepared. A 6 mL tetraethyl orthosilicate (TEOS) was slowly added to the mixture. After adding TEOS, 2.56 mL of ammonia was gradually added to the solution drop by drop. The addition of ammonia increases the reaction rate. The reaction mixture is allowed for 6 hours for 6 hours stirring. After that, the prepared gel is removed by separating solvents and washed thoroughly using ethanol multiple times. The final formed cakes are dried at 180 °C for 10 min and then finely crushed. After that, the powder is annealed at 300 °C for one hour.

3.1.3.3. ***Synthesis of hybrid MoS_2-SiO_2***

To prepare the hybrid material, 0.25 g of MoS_2 powder was dispersed in a solution containing 40 mL of ethanol and 10 mL of deionized (DI) water, along with sodium dodecyl sulfate (SDS) at a concentration significantly below the critical micelle concentration. The mixture was stirred continuously for 30 minutes, followed by 10 minutes of sonication to prevent particle aggregation. To initiate the gradual formation of siloxane units, 3 mL of TEOS was added to the solution, maintaining a pH of approximately 6. The reaction took place at room temperature (20–35 °C). Ten minutes after adding TEOS, 1.2 mL of ammonia was gradually introduced to accelerate the formation of silica. Smaller silica nuclei formed on the MoS_2 surface tended to cluster, causing the sheets to curl. Ammonia played a key role in promoting the development of spherical silica structures and regulating their quantity [11].

The solution was left undisturbed for 3–4 hours to allow the gelation process to complete. The resulting gels were separated from the mixture and thoroughly washed with ethanol. The drying rate of the hybrid significantly influenced its density. Rapid drying was achieved using a forced convection fan, exposing the sample to high temperatures for a short duration. According to Stokes' law, higher density leads to faster sedimentation velocity [12]. A slower drying process caused the xerogel structure to collapse and shrink, resulting in a dense material that lacked stability even for an hour. In contrast, rapid drying for 10 minutes at 180 °C produced a lightweight MoS_2-SiO_2 hybrid material. Steps followed is also represented in Figure 3.3.

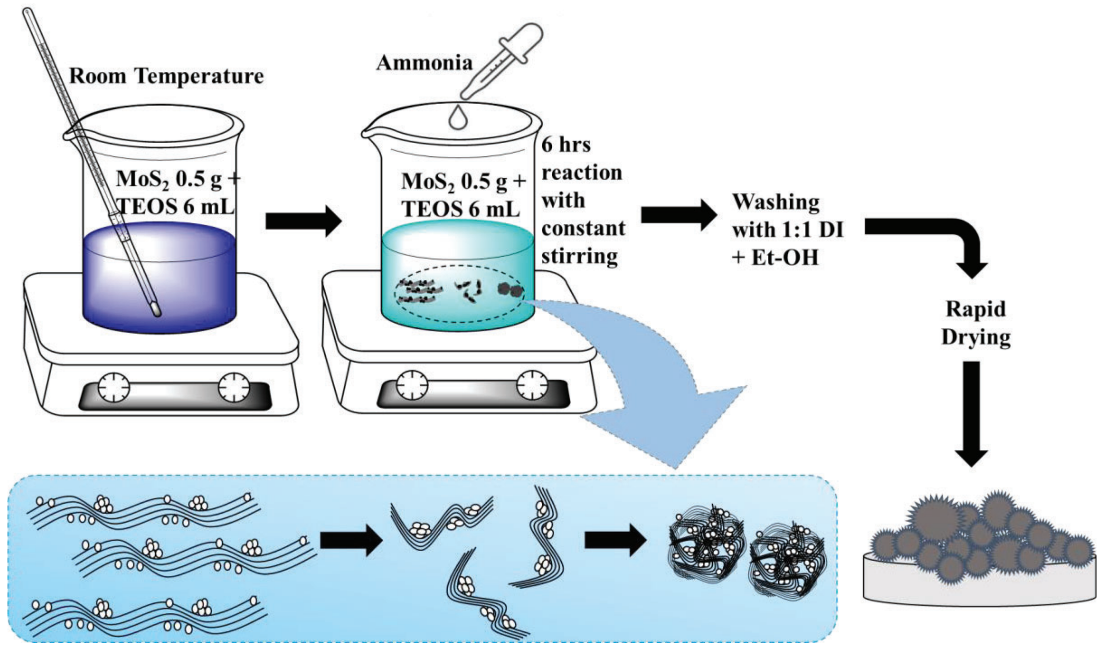

Figure 3.3 Synthesis procedure followed for making of hybrid MoS_2-SiO_2

3.1.3.4. ***Synthesis of graphene oxide***

To synthesize graphene oxide, the process begins with regular graphite powder as the starting material as explained in available study [81]. This powder undergoes a chemical transformation using a combination of powerful oxidizing agents, specifically sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), and sodium nitrate ($NaNO_3$). These chemicals work together to oxidize the graphite, altering its structure and introducing oxygen-containing functional groups. The reaction starts by carefully mixing graphite with concentrated sulfuric acid in a controlled environment. This step is critical because sulfuric acid not only acts as the primary oxidizing medium but also keeps the reaction system highly acidic, ensuring the safe and efficient oxidation of graphite. Next, sodium nitrate is added to the mixture, which enhances the oxidation process, while potassium permanganate is introduced gradually. Potassium permanganate is the main oxidizing agent, responsible for introducing oxygen functionalities in the tightly packed layers of graphite. Since this reaction is highly exothermic (releases heat), it must be conducted at a controlled temperature to prevent overheating or undesired side reactions. Once the oxidation process is complete, the resulting oxidized graphite undergoes exfoliation to transform into graphene oxide. This involves using an ultrasonic probe (a device that generates high-frequency sound waves) to break the graphite oxide into thinner layers, i.e., graphene oxide (GO). The intense vibrations from the ultrasonic waves help to separate the layers of oxidized graphite, resulting in a dark brown aqueous dispersion of graphene oxide.

3.1.3.5. ***Spherical zinc oxide synthesis***

ZnO nanoparticles were synthesized using a simple precipitation method [82]. The procedure involved first adding 5.44 g of $ZnCl_2$ into the methanol (in 100 ml), stirred for 10 min until completely dissolved. A 3.199 g of NaOH was separately dissolved in 100 mL of methanol and stirred for 80 minutes to ensure complete mixing. The NaOH solution was then added drop-wise to the $ZnCl_2$ solution, once both the solutions were prepared. The resulting reaction mixture left for stirring for 2 h. Finally, the precipitate formed are collected via centrifugation process and then dried at 70 ℃, calcinated at 300 ℃ for half an hour. The prepared ZnO having -OH functional group at outer surface, is useful for further modification.

3.1.3.6. ***Hybrid graphene oxide zinc oxide preparation***

A 1 g of zinc oxide (ZnO) was evenly dispersed in 100 mL of toluene. The dispersion was refluxed for 24 h with 2 mL of aminopropyltriethoxysilane (APTES). The prepared product was separated, washed and dried in a vacuum environment at 60 °C. Hydrolysis of silane agent forms the silanol. Silanol can undergo oligomerization and establish hydrogen bonding interactions with the inorganic substrate. Consequently, ZnO reacted with the silane end of APTES, the resulting material is denoted as AZnO. A 71 mL aqueous dispersion of graphene oxide (GO) undergoes a solvent exchange process, where its water is replaced with dimethylformamide (DMF). This exchange is performed using a rotary evaporator at a temperature of 90°C, and a vacuum pressure of 9 millibars. The resulting solution is then diluted with additional DMF to create a total volume of 100 ml. Next, 0.5 g of AZnO is added to the solution and dispersed through sonication for 2 hours. The resulting mixture is centrifuged at 10,000 rpm for 10 minutes. Following this, the material is rinsed several times with ethanol and then washed with hexane. The schematic representation of the steps followed is shown in Figure 3.4.

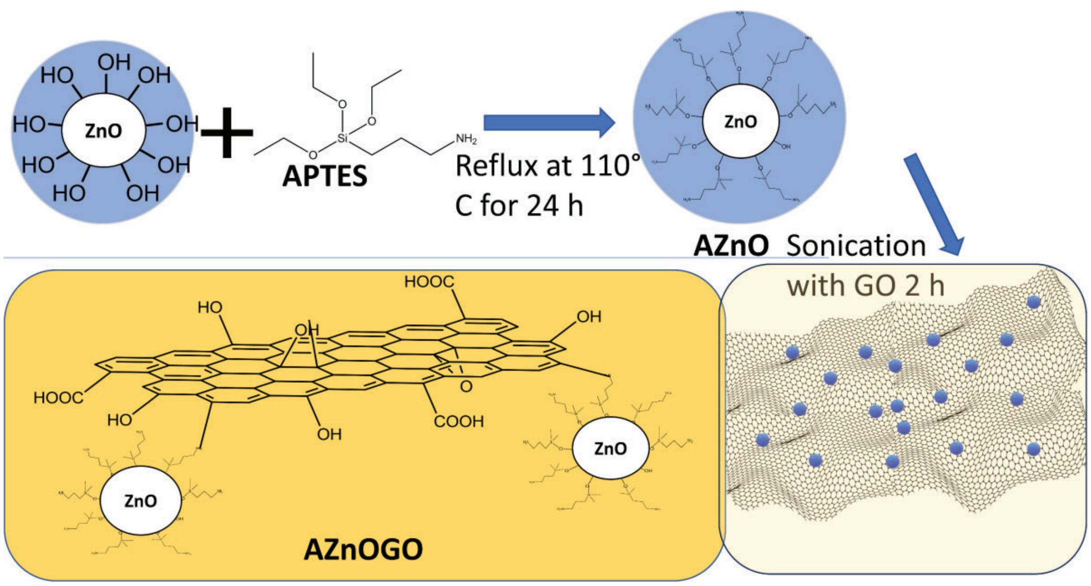

Figure 3.4 Schematic presentation of synthesis procedure followed for AZnOGO

3.1.3.7. ***Preparation of Ti_3C_2Tx MXene:***

Ti_3C_2Tx MXene was synthesized by chemical processing of Ti_3AlC_2 MAX powder using an acidic solution of LiF etchant. First, 3.2 g of LiF was dissolved in 30 mL of 9 M HCl to prepare the etchant in a Teflon beaker. A 0.5 g sample of Ti_3AlC_2 MAX powder was gradually added to the etchant under continuous stirring. The etchant temperature was raised to 40 °C, and the stirring was maintained for 48 hours. After this, the chemically processed material was collected, thoroughly washed with distilled water for several cycles to remove any residual LiF/HCl, and then dried in an oven. To obtain $Ti_3C_2T_x$ MXene, the processed material was submerged in a 2 M KOH solution under continuous stirring for 24 hours to replace the fluorides on the $Ti_3C_2T_x$ MXene surface with hydroxyl groups. The modified $Ti_3C_2T_x$ MXene was washed with distilled water and dried in a vacuum oven at 80 °C [83].

3.1.3.8. ***Synthesis of functionalized $Ti_3C_2T_x$ MXene:***

Functionalized MXene was prepared by modifying the surface of $Ti_3C_2T_x$ MXene with trichloro(octadecyl)silane (OTS). Initially, 0.2 g of $Ti_3C_2T_x$ MXene was dispersed in 10 mL of ethanol. To ensure a moisture-free environment, the ethanol was purged with nitrogen gas for 30 minutes, as the hydrolyzable trichloro groups in OTS are highly reactive to water, which could interfere with the functionalization process. Separately, 0.2 g of OTS was dissolved in the nitrogen-purged ethanol. The two solutions were then combined under a tightly sealed system to prevent any ingress of moisture. This setup ensured that the reaction proceeded without unintended side reactions caused by water.

The reaction mixture was subjected to reflux for 24 hours, facilitating the covalent attachment of OTS molecules to the surface of the MXene via silane bonding. After the reaction, the product was thoroughly washed multiple times, first with water and then with ethanol, to remove residual OTS. Finally, the functionalized MXene was dried in an air oven at 60 °C for 12 hours, yielding a material with improved surface properties, including hydrophobicity. The functionalized MXene holds significant potential for applications in coatings, energy storage, and nanocomposites.

3.1.3.9. ***Synthesis of chemically-functionalized hexagonal boron nitride***

The synthesis began with the vigorous oxidation of bulk h-BN powder (7 g) using $NaNO_3$ (7 g) and 350 mL of H_2SO_4. To maintain the temperature below 4 °C, the reaction vessel (a round-bottom flask) was kept on an ice bath. It was followed by the addition of 42 g of $KMnO_4$ in small portions to the reaction mixture while maintaining constant stirring, as the reaction is highly exothermic. After oxidative process for 24 hours, the vessel was transferred to an oil bath, and 500 mL of distilled water was gradually added into the highly oxidized acidic mixture with a lot of care. The reaction temperature was then raised to 98 °C and oxidation of oxidation of the h-BN powder continued for 24 hours under constant stirring. The reaction mixture was cooled to room temperature, and 84 mL of H_2O_2 was added drop-wise. The oxidized product was washed thoroughly with 49 mL of HCl to remove impurities. Subsequently, the white oxidized h-BN was repeatedly washed with distilled water until the pH of the decanted water became neutral. Finally, the product was dried at 70 °C, yielding oxidized h-BN powder.

To functionalize the oxidized h-BN, 500 mg of the powder was dispersed in 100 mL of toluene under magnetic stirring. The dispersion was transferred into a 500 mL round-bottom flask, where 2 mL of APTMS was gradually added to the reaction mixture and reflux it for 24 hours. Subsequently, the reaction mixture was naturally cooled down. The material was centrifuged to separate the APTMS-functionalized h-BN nanomaterial.

To further enhance the compatibility of the functionalized h-BN with lubricating oils, the wet cake was treated with epoxidized Karanja oil (MKO). For this step, the APTMS-functionalized h-BN was dispersed in 100 mL of toluene, and 2 g of MKO was added to the mixture. The reaction mixture was sonicated for 2 hours to make a stable dispersion, which was then decanted, centrifuged at 10,000 rpm for 10 minutes, and dried in a vacuum oven at 60 °C for 3 hours. The final product, referred to as fh-BN, was ready for application.

3.2. Characterization of nanoparticles

3.2.1. SEM-EDS analyses

The high-resolution scanning electron microscopic (SEM) images were taken for different particles in high magnifications using Nova Nano SEM 450 (FEI USA). The energy dispersive X-ray spectroscopy (EDS) of various particles was taken using the instruments by Team Pegasus Integrated EDS-EBSD with Octane Plus and Hikari Pro by EDAX Inc. The EDS measurements probe the material's elemental composition by detecting characteristic X-rays emitted when a focused electron beam excites atoms in the sample. A silicon drift detector captures these X-rays, generating spectra and elemental maps that reveal the material's composition and spatial distribution for advanced materials characterization and analysis.

3.2.2. TEM

The morphological and nanostructural characteristics of nanomaterials were analysed using a high-resolution transmission electron microscope (TEM; model: JEM 2100, make: JEOL Ltd., Japan). For sample preparation, ethanolic dispersion of each nanomaterial was carefully drop-casted onto the TEM grid made of copper (3 mm in diameter, 100 μm thick, with a 200-mesh lacey carbon coating). The TEM images were captured at a constant voltage of 300 kV under a high vacuum condition, maintained at approximately 10^{-6} Torr.

3.2.3. X-ray diffraction

The crystalline phase and lattice structure of the nanomaterials were analysed using an X-ray diffractometer (XRD, Rigaku Miniflex, USA) equipped with Cu–Kα radiation (wavelength 1.54 Å). The diffraction patterns were recorded over a 2θ scanning range of 10° to 90°. When X-ray beams interacted with the powder or thin-film samples, they were diffracted by the crystallographic planes, producing intensity mappings that reflect the sample's structural properties. The instrument was operated at a constant voltage of 40 kV and a current of 15 mA.

3.2.4. Fourier transformed infrared spectroscopy

FTIR spectroscopy was employed to analyze the functional groups present in solid, liquid, and gaseous samples by recording their infrared absorption or transmittance spectra. In the present work, each nanomaterial was individually mixed with dry KBr powder, ground into fine pellets, and used to collect the FTIR spectra. The transmittance spectra were recorded using a Thermo-Scientific Nicolet iS5 spectrometer at a resolution of 4 cm^{-1} across the spectral range of 400–4000 cm^{-1}. This analysis confirmed the chemical functionalities in the materials.

3.3. Nano lubricant formulation and testing

3.3.1. Stirring and ultrasonic mixing

The different solutions and dispersion were prepared by stirring and/or heating using a magnetic stirrer with an inbuilt hot plate (IKA C-MAG HS4 Digital, Germany). This device combines stirring and heating functions, allowing the sample to be heated to temperatures of up to 500 °C.

An ultrasonicator was used to generate ultrasonic pulse waves, ensuring the nanoparticles remained well-dispersed in the oil and prevented agglomeration over an extended period. The device operated at a maximum temperature of 60 °C with a frequency of 40 kHz.

3.3.2. Rheological studies

Viscosity measured using rotational type viscometer with 1 mL of liquid sheared between plates separated by 0.1 mm. With increasing temperature and constant speed of 500 rpm simultaneously collecting data at various temperature. These data are then used for various calculations of film parameters. Stribeck characteristics is tested in MCR 102 rheometer in a ball on three plate geometry shown in Figure 3.5 by Anton Paar with constant loading and variable speed for different lubricant oils with velocity ranges from 0.001 m/s to 1.2 m/s.

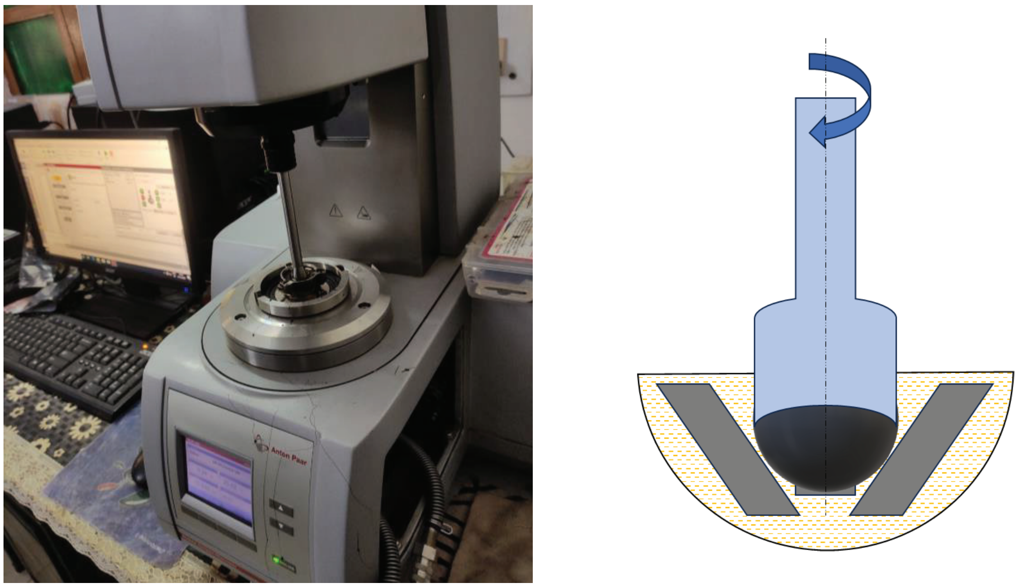

Figure 3.5 Dynamic shear rheometer MCR 102 along with ball on three plate geometry

3.3.3. Film thickness calculation

The minimum film thickness is calculated as per the Hamrock and Dowson's equation by assuming hard EHL (Elastohydrodynamic lubrication) contact.

$$\frac{h_{min}}{R'} = 3.63\left(\frac{u\eta_0}{E'R'}\right)^{0.68}(\xi E')^{0.49}\left(\frac{W}{E'R'^2}\right)^{-0.073}(1-e^{-0.68k}) \quad [3.1]$$

Where:

h_{min}: Minimum film thickness in m;

R': Equivalent radius of contact in m;

u: mean velocity m/s (for one surface fixed $u = u_1/2$)

η_0: dynamic viscosity of lubricant oil in Pa-s;

E': Reduced Young's modulus in Pa;

ξ: Pressure viscosity coefficient (refer to Appendix C)

W: Normal load in N;

k: elliptical parameter (for point contact k=1, for line contact k=0)

3.3.4. Tribological studies

Uniformly dispersed nanolubricants were taken with different concentration ranging from 0.025 to 0.1 wt%. The ball pot, collet and internal setup are cleaned thoroughly before each tribotest. Four balls are taken at a time and degreased using acetone then dried before using in test. Three balls are fitted inside the pot and one fitted into collet. The bias of machine was set at zero then all parameters are configured as per the test standard, shown in Table 3.2.

Table 3.2 Different test standards used for tribological investigation of nanolubricants

Test Method	Speed (rpm)	Load (kgf)	Loading step	Temperature (°C)	Duration (s)
ASTM D-5183	600	10, 20, 30, 40, …	10 kgf/10 min	75	3600 for 40 kgf then till failure
ASTM D-4172B	1200	40	Constant	75	3600
ASTM D-2783	1760	6, 8, 10, 13, 16, 20, 24, 32, 40, 50, 63, 80, 100, 126, 160, 200	constant	Room Temperature	10
DOE	Variable	Variable	Variable	Variable	3600

The test was run for the specified time and the data is collected with time. Frictional torque collected from the sensor is then used to calculate coefficient of friction (μ) as shown in Figure 3.3.

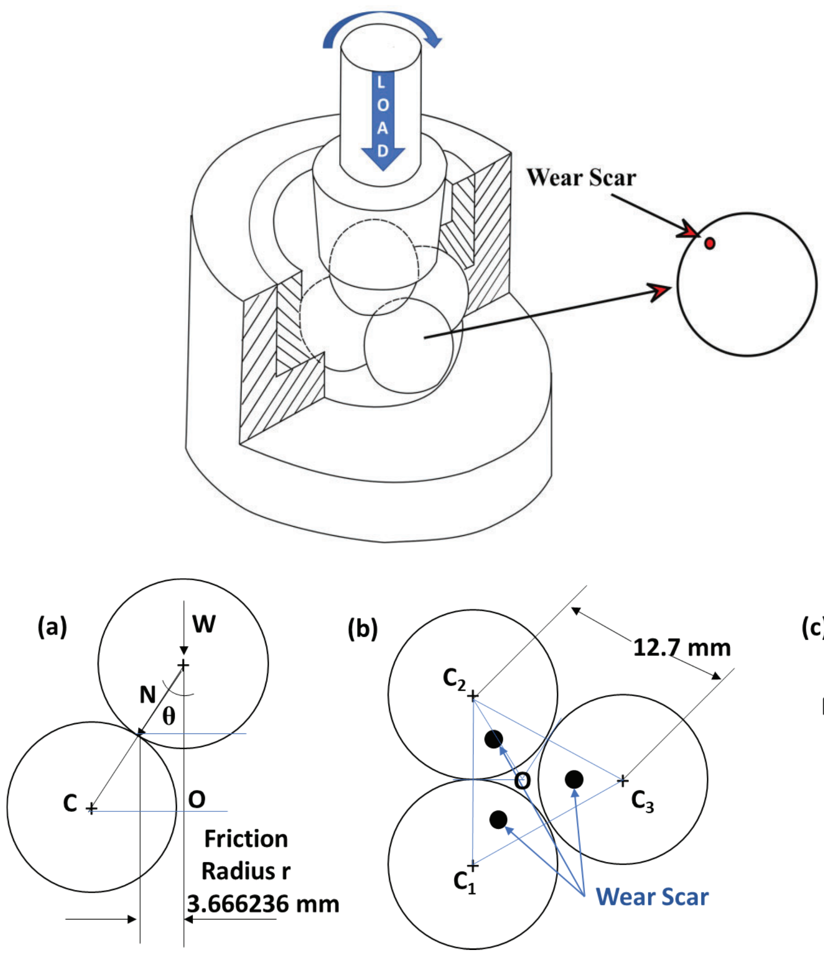

Figure 3.6 Geometric representation of four ball setup for coefficient of friction calculation

Where;

W: applied load in N ($W = N_1 \cos\theta + N_2 \cos\theta + N_3 \cos\theta$)

N_1, N_2, N_3: Normal load on three balls in N

$N = N_1 + N_2 + N_3$: Total normal load in N

C_1, C_2, C_3 are the centres of three balls

θ: angle between loading direction to normal = 35.2644°

O: geometric centre of triangle $C_1C_2C_3$

T: frictional torque collected from machine in N-m

r: Friction radius in m

$$T = \mu N r \quad [3.2]$$

$$\mu = \frac{T \cos\theta}{Wr} \quad [3.1]$$

$$\mu = 222.707\frac{T}{W} \quad [3.2]$$

Equation 3.2 gives values of coefficient of friction from the collected data. The wear volume is calculated from the wear scar diameter (d).

Mean wear scar diameter (d)

$$d = \frac{d_1 + d_2 + d_3}{3} \quad [3.3]$$

Where:

d_1, d_2 and d_3 are wear scar diameter of three stationary balls.

Wear Volume (V) [84]

$$V = \frac{\pi (d_0)^4}{64R}\left\{\left(\frac{d}{d_0}\right)^4 - \left(\frac{d}{d_0}\right)\right\} \quad [3.4]$$

Equivalent radius of contact (R)

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \quad [3.5]$$

R_1 and R_2 are the radius of two contacting balls

Hertzian Diameter (d_0)

$$d_0 = 2\left(\frac{3NR}{4E^*}\right)^{1/3} \quad [3.6]$$

$$\frac{1}{E^*} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \quad [3.7]$$

Where,

E_1, E_2, v_1 and v_2 are young's modulus and poisons ratio of two contacting materials.

N is normal contact load which is 0.408 times the applied load.

After the end of test, the load and thermal connection were removed from the ball pot. While the balls are fixed to the pot the oil filled inside, were cleaned and the surface of the balls were wiped. There after the inclined micrometer is used to measure the wear scar diameter. After that the balls are removed from the ball pot and it is used for further analysis like SEM, EDS of the worn surface.

3.3.5. Sliding reciprocating test

The starved lubrication behaviour of the lubricants is tested with a ball-on-plate geometry on a multifunction tribometer (MFT), using AISI 52100 bearing balls of 6 mm diameter on a 100Cr6 disk (average roughness Ra 0.21 µm) at a maximum Hertzian contact pressure of 2.44 GPa and at room temperature. The data collection rate was set at 1000 samples per second and the data averaging is set to one.

3.4. Friction induced vibration analysis

3.4.1. Analysis of nano-lubricant failure using vibration characteristics

To understand the failure mechanisms of nano-lubricants under operational conditions, vibration characteristics were meticulously analysed. The vibrations, induced by the sliding friction force during the tribological interactions, were measured using a single-axis accelerometer. This sensor was strategically mounted near the friction sensor's loading pin to capture precise vibrational data originating from the system. The accelerometer records the dynamic response caused by the tangential acceleration, which is the primary mode of acceleration considered in this study.

3.4.2. Experimental setup and measurement methodology

The experimental setup involves a ball-on-three-balls configuration, where the fourth ball, attached to the spindle, exerts frictional torque on the other three balls. This torque results in tangential acceleration, generating vibrational signals that are critical for analysing lubricant behaviour. The accelerometer's positioning ensures accurate detection of these signals. However, to account for the geometric configuration of the system, a correction factor of 0.0523 is applied to the recorded acceleration data. This factor is derived from the specific geometry of the ball pot and sensor arrangement, as depicted in 3.7.

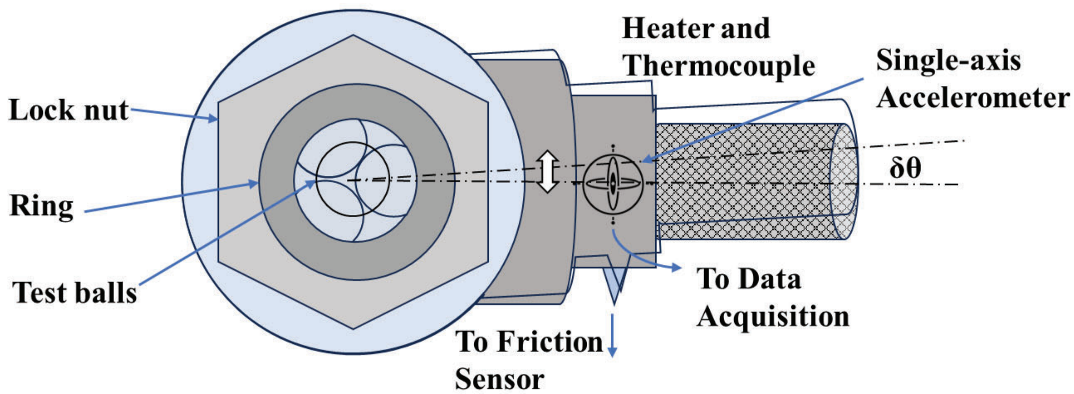

Figure 3.7: Placement of accelerometer on ball pot

The vibrational method has been widely adopted in tribological studies to evaluate lubricant performance. By comparing the amplitudes of captured vibration signals, researchers have demonstrated the effectiveness of various lubricants under different conditions [85,86]. In this study, the focus is on leveraging vibration signals to detect the onset and progression of lubricant breakdown. The data provides insights into how the nano-lubricants behave as they transit from effective lubrication to failure, offering a dynamic perspective on their performance.

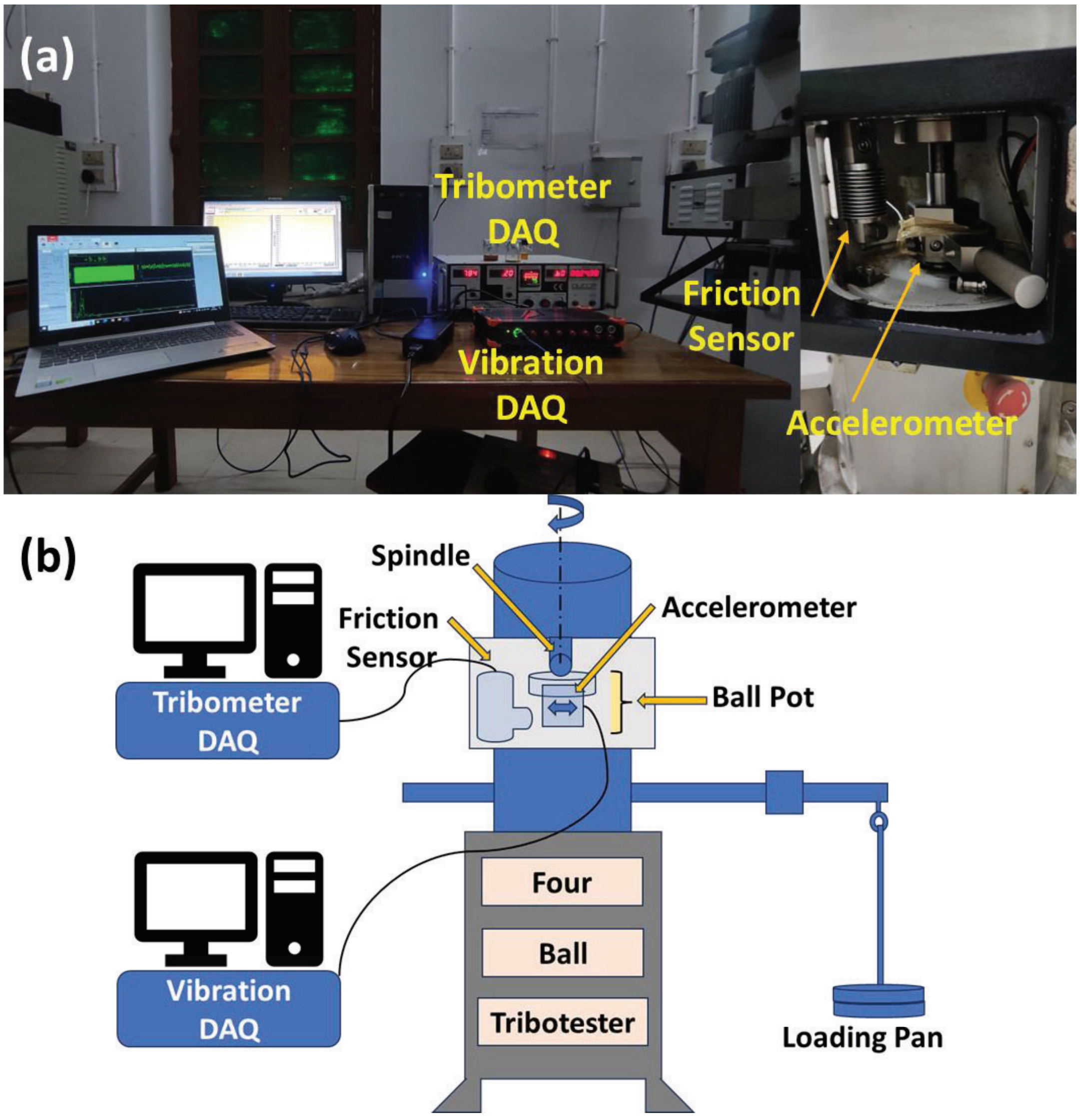

Figure 3.8 Setup used to collect vibration signature from the friction induced signals (a) digital image of actual setup, (b) schematic representation of the setup

3.4.3. Signal acquisition and processing

The vibration signals were recorded synchronously at a high sampling rate of 50,000 Hz, ensuring that even subtle variations in the signal are captured. The accelerometer used in this setup has a sensitivity of 101.1 mV/g, which allows for precise quantification of the vibrational forces. The geometric factors were applied during data analysis to accurately scale the recorded signals to the system's physical parameters.

To interpret the vibration data effectively, the signal captured during failure is transformed into relative time data. This transformation is critical for aligning the vibration characteristics with the operational timeline, and facilitating the identification of failure points.

3.4.4. Spectral analysis using time-frequency representation

The spectral analysis of the vibration data was conducted using the Short-Time Fourier Transform (STFT), a technique renowned for its ability to represent non-stationary signals in the time-frequency domain. Moosavian et al. [87] demonstrated the utility of time-frequency representations in comparing vibration signatures of malfunctioning and healthy systems. In this study, STFT is employed as the primary analysis tool due to its simplicity, computational efficiency, and ease of interpretation.

The spectrogram function was used to generate STFT graphs, providing a detailed visualization of the signal's frequency content over time. The following parameters are used to ensure accurate and meaningful results:

- **Window Function**: A Hanning window is applied to reduce spectral leakage and improve frequency resolution.
- **FFT Points**: The number of Fast Fourier Transform (FFT) points is set equal to the window length, ensuring a balanced trade-off between time and frequency resolution.
- **Overlap**: A 50% overlap is employed between successive windows to minimize pixel distortion and maintain continuity in the time-frequency representation.

The uniformly spaced time intervals on the spectrogram's abscissa are converted to relative time using the sampling frequency. This conversion ensures that the results align with the actual timeline of the tribological interactions, allowing for precise correlation between the vibration characteristics and lubricant breakdown events.

Applications and perceptions

The vibrational analysis provides a robust method for detecting lubricant failure. The STFT-generated spectrograms reveal critical changes in the vibration signatures, such as shifts in dominant frequencies, amplitude increases, or the emergence of new frequency components. These changes serve as indicators of lubricant degradation, such as the formation of wear debris, loss of protective films, or thermal instability. By analysing these signatures, the study aims to develop a comprehensive understanding of the failure mechanisms in nano-lubricants, enabling the design of more effective and durable lubrication systems.

In conclusion, the combination of high-resolution vibration data, geometric correction factors, and advanced spectral analysis techniques provides a powerful framework for evaluating the performance and failure characteristics of nano-lubricants under operational conditions.

3.5. Worn surface analysis

3.5.1. Scanning electron microscopy

The SEM images of the worn scars obtained after conducting the four-ball test were captured using an EVO 18 Scanning Electron Microscope (SEM) by CARL, Germany. During the imaging process, the operating voltage was consistently maintained at 20 kV, while the working distance between the electron gun and the specimen was carefully controlled within the range of 10 to 10.5 mm. Elemental analysis of the worn samples was conducted using Energy Dispersive Spectroscopy (EDS) using the 51N1000 system from Oxford Instruments Nano Analysis, UK.

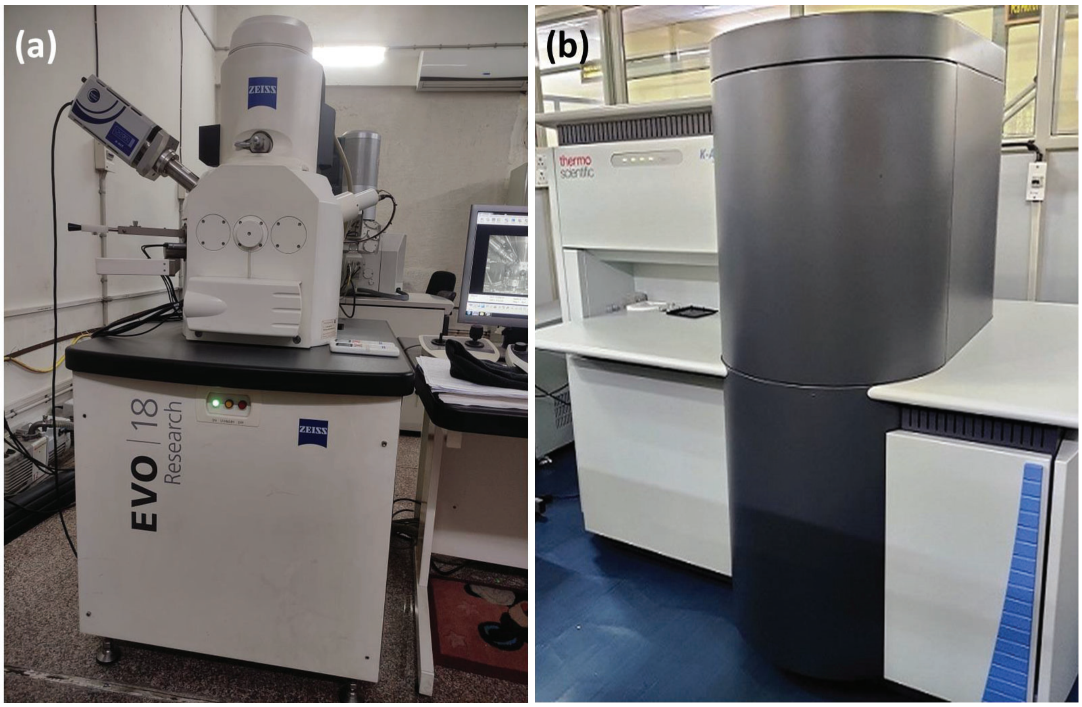

Figure 3.9: (a) Scanning electron microscope EVO MA15/18 by CARL ZEISS MICROSCOPY LTD combined EDS system 51N1000 by Oxford Instruments Nanoanalysis (b) X-ray photoelectron spectroscopy by Thermo Fisher Scientific

3.5.2. X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) analysis was performed using a state-of-the-art XPS microscope (Thermo Fisher Scientific, Waltham, MA) equipped with an aluminum (Al Kα) X-ray source. This technique was employed to investigate the surface chemistry of the samples, enabling the identification of elemental composition, chemical states, and bonding environments. The high-resolution capability of the instrument ensured precise surface characterization, providing insights into the chemical interactions and modifications, in speciation.

3.5.3. Profilometry (optical 3D/ Line 2D/ AFM)

The profilometry data for the worn surfaces were collected using Atomic Force Microscopy (AFM) for samples with relatively smooth surfaces. However, for surfaces with higher roughness, AFM was not suitable due to its limitations in handling highly uneven textures. For such rough surfaces, a stylus-type line profilometer and an optical profilometer were employed to capture the surface profile data effectively. The roughness values obtained from profilometry were calculated after removing the major form or shape of the surface, ensuring that only the texture-related features were analysed. To ensure consistency and standardization, the extracted surface texture data were processed in accordance with ISO 4287:1997 standard. This approach enabled a detailed and reliable analysis of the surface texture parameters, providing valuable insights into the surface characteristics and wear behaviour of the samples.

3.6. Wear debris analysis

The separation and analysis of debris from tested lubricating oils provide valuable insights into the mechanisms of lubrication and wear. To isolate the debris, the oil is diluted using solvents like acetone or hexane, which effectively reduce its viscosity, enabling easier filtration. The diluted oil is then passed through a cellulose membrane filter, which captures the wear particles and other solid residues. After drying, the debris is analysed using techniques such as SEM, EDS, and XRD. These analyses reveal the composition, morphology, and size of worn particles, offering crucial information about the wear mechanisms, such as adhesive, abrasive, or oxidative wear. Additionally, the debris provides clues about the performance of additives and the presence of contaminants. This process helps diagnose wear-related issues, optimize lubricant formulations, and improve tribological performance, contributing to enhanced machinery reliability and durability through predictive maintenance and informed design strategies.