Chapter 2

Experimental

The current chapter delineates the instrumentation details of the techniques employed to characterize the synthesized additives, morphological and analytical studies of worn surfaces. Specification of steel ball bearing, base oil characteristics, testing methodologies used to evaluate the tribological performance of the investigated additives, and various tribological parameters have also been provided.

2.1. Instrumentation used for Characterization of the Synthesized Additives

For studying morphological features of the additives, scanning electron microscopy/high-resolution scanning electron microscopy (HR-SEM) using FEI-Nova Nano SEM 450 and transmission electron microscopy (TEM)/high-resolution transmission electron microscopy (HR-TEM) using FEI-Tecnai-G2 electron microscope were carried out. FTIR spectra were recorded on a *Thermo Scientific* Nicolet iS5 FTIR spectrometer using pellets of samples with KBr. UV-visible spectra of the additives were recorded in the DMSO solution in the range 200-1100 nm on a Shimadzu Pharma spec. UV-1700 model and LAMDA 25 Spectrophotometer Perkin Elmer, Germany. The approximate stoichiometric composition of nanomaterials was investigated by Energy Dispersive X-ray Spectroscopy (EDX)using ZEISS SUPRA 40, Oxford Instruments.

Raman spectral studies were conducted to identify structural features of carbon-based nanomaterials. Confocal Micro-Raman mapping system (UniRAM, employing excitation wavelength, 785 nm laser) was utilized for taking Raman spectra. Powder X-ray diffraction (XRD) studies were performed on Rigaku Miniflex 600, XRD-System using Cu-Kα_1

radiation (λ=1.54˚A) for phase identification, purity, and size of the crystalline material. X-ray photoelectron spectra (XPS) were recorded on PHI 5000 Versa Probe II, FEI, Inc. to find out the chemical composition of the synthesized materials and tribofilm formed on the worn steel surface.

2.2. Antiwear Testing

2.2.1. Base Oil

The lubricating base oil, neutral liquid paraffin oil (Qualigens Fine Chemicals, Mumbai, India) having specific gravity 0.82 at 25 ºC, kinematic viscosity, at 40 ºC and 100 ºC, 30 and 5.5 cSt respectively, viscosity index 122, cloud point -2 ºC, pour point -8 ºC, flash point 180 ºC and fire point 200 ºC, was used without further purification.

2.2.2. Specification of Steel Ball Bearing

The balls of 12.7 mm diameter made of AISI 52100 steel alloy possessing hardness 59-61 HRc were utilized for tribological tests. Before and after each test, balls were rinsed well with *n*-hexane and then properly air-dried.

2.2.3. Test Methodology

The prepared admixtures were sonicated for 1 hour at room temperature. The antiwear tests of the synthesized additives were carried out with the help of a Four-Ball Lubricant Tester (Ducom Instruments Pvt. Ltd., Bangalore, India) following the norms imposed by the American Society for Testing and Materials, ASTM D4172. The test method is used to determine the relative wear preventive properties of lubricating fluids in sliding contact under the prescribed test conditions of applied load 392 N, sliding speed 1200 rpm, time 1 h, and temperature 75 °C according to the manual of Ducom four-ball tester. The wear scar diameter of the three stationary balls were noted, and their mean has been represented as MWD.

Fig. 2.1. Four ball tester machine

At first, concentration optimization tests were carried out for base oil with and without different concentrations of the studied additives according to ASTM D4172 norms. All tribological tests were conducted at the optimized concentration (0.05% w/v) under similar conditions. The step loading test was conducted following ASTM D5183 standards. After the running-in period is over under the test conditions (applied load, 392 N; sliding speed, 600 rpm; temperature, 75 ºC and optimized concentration (0.05 % w/v), increments of 98 N load were added after every 10 min until the seizure of tribo-surface was noted. In general, the tribological testing was repeated three times in every case.

2.3. Tribological Parameters

For each experiment, the arithmetic mean of the diameter of each ball (d_1, d_2, and d_3) was taken as given by equation (**1**). The three stationary balls were not disturbed while taking the readings, and the wear scar diameter was taken by the image acquisition system.

2.3.1. Mean wear scar diameter (MWD)

$$d = \frac{d_1 + d_2 + d_3}{3} \qquad \textbf{2.1}$$

2.3.2. Mean wear volume (MWV)

The MWV data have been calculated from MWD values using Archard wear Equation [Sethuramiah et al. (2015), Kumar et al. (2002)].

Archard Wear Equation

Wear volume, $$\mathrm{V} = \frac{\Pi\, \mathrm{d}_0^4}{64\,\mathrm{r}}\{(\frac{d}{d_0})^4 - (\frac{d}{d_0})\} \qquad \textbf{2.2}$$

Hertzian diameter, $$\mathrm{d}_0 = 2(\frac{3\,\mathrm{Pr}}{4E})^{\frac{1}{3}} \qquad \textbf{2.3}$$

Where, $$\frac{1}{r}=\frac{1}{r_1}+\frac{1}{r_2}$$

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

Where, E^* = Resultant modulus of elasticity

v = Poisson's ratio

r = Radius of steel ball

$E_1 = E_2 = 206$ GPa

$v_1 = v_2 = 0.3$

d = mean wear scar diameter of steel ball (mm)

d_0 = Hertzian diameter of circular contact supporting the load before wear (mm)

2.3.3. Coefficient of Friction (*μ*)

The coefficient of friction for different antiwear additives is obtained directly from the software of four-ball tester using equation (4)

$$F=\mu\times N \qquad \textbf{2.4}$$

Where μ = Coefficient of friction, F = Frictional force, and N= Normal force

2.3.4. Wear rate

Overall, running-in and steady-state wear rates have been calculated on the basis of observed mean wear volume data at different time intervals. Mean wear volumes at different times

(0.25, 0.5, 0.75, 1.0, 1.25, and 1.5 h) for each experiment were plotted with time, and a linear regression model was fitted on the points, including origin, to find out the overall wear rate.

$$\frac{V}{l} = K\frac{P}{H} \qquad \textbf{2.5}$$

V = mean wear volume

l = sliding distance (2πr.N)

K = wear coefficient

H = hardness of steel ball (59-61 HRc)

P = applied load (0.408×392 N)

P = Actual load in Newton on each of the three horizontal balls that is 0.408 times of applied load.

2.4. Analysis of Worn Surface

Scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDX) was applied for providing surface magnified images of wear scar of 12.7 mm diameter steel balls and elemental compositions of tribofilm formed on the wear scar respectively using a scanning electron microscope (ZEISS SUPRA 40 electron microscope). A contact mode atomic force microscope (Model no. BT 02218, Nanosurf easyscan 2 Basic AFM, Switzerland) was used to investigate the roughness of the worn surfaces with the Si_3N_4

cantilever (Nano sensor, CONTR type) having a spring constant of approximate 0.1 Nm^{-1} and tip radius more than 10 nm. X-ray photoelectron spectroscopy (K-alpha X-ray photoelectron spectrometer) was used for analyzing the chemical composition of the tribofilm formed on the worn surface.

2.5. Hamrock–Dowson equation

For determining the lubrication state of the tribosystem, at first minimum film thickness was calculated according to Hamrock–Dowson equation [Hamrock et al. (1978)].

$$\frac{h_{min}}{R'} = 3.63\left(\frac{u\eta_0}{E'R'}\right)^{0.68}(\xi E')^{0.49}\left(\frac{w}{E'R'^2}\right)^{-0.073}\left(1 - e^{-0.68k}\right) \qquad \textbf{2.6}$$

Where h_{min} is the minimum film thickness, u is the mean velocity (m/s), η_0 is the dynamic viscosity of lubricant (PaS), E' is reduced Young modulus (Pa), R' is the reduced radius of curvature (m), ξ is pressure viscosity coefficient (m^2/N), w is contact load (N), k is the elliptical parameter. The calculated minimum film thickness was obtained as 0.027 μm for paraffin oil. The λ ratio was computed (i.e., $\lambda = \frac{h_{min}}{\sigma^*}$) by using values of σ^* and h_{min}. The σ^* is composite surface roughness (i.e. $\sigma^* = \sqrt{\sigma_1^2 + \sigma_2^2}$) where $\sigma_1$and σ_2 are the surface roughness of two mating bodies. The computed value of λ was 0.0949. Its value <1 indicates that the operating lubrication regime was boundary or thin-film lubrication [Hamrock et al. (2004)]. where a thin film of the adsorbed lubricant reduces friction. Further, the average coefficient of friction for paraffin oil was observed as 0.0756, which is very well within the limits of boundary lubrication.