CHAPTER 2

The present chapter deals with the experimental details pertaining to the techniques employed for the chemical and structural characterizations of the additives, specification of steel ball bearing and testing methodologies used in the evaluation of lubrication performance of antiwear additives. The techniques used for studying the morphology of worn surfaces and tribochemistry of additives have also been discussed.

2.1. Instrumentation Details

2.1.1. Electronic Absorption Spectra (UV-Visible)

UV-visible spectra of the additives were recorded in DMSO solution in the range 200-1100 nm on a Shimadzu Pharmaspec. UV-1700 model and LAMDA 25 Spectrophotometer Perkin Elmer, Germany.

2.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is one of the most important analytical techniques available to researchers. The FTIR spectra of all samples were recorded using SHIMADZU FTIR-8400S and PerkinElmer 100 spectrum spectrophotometer in the range 4000-400 cm^{-1}. The powder of each sample was mixed with KBr to form the pellets in order to scan FTIR spectra.

2.1.3. Nuclear Magnetic Resonance Spectra (NMR)

NMR spectroscopy is used to confirm the identity of substance and gives distinguishable signals for identical functional groups with different neighbouring substituents. The chemical structure was confirmed by ^{1}H and ^{13}C NMR spectra. NMR spectra of additives were recorded on JEOL AL 300 FT NMR operating at 300 and 75 MHz resonance frequencies for ^{1}H and ^{13}C NMR, respectively using $CDCl_3$ and DMSO-d6 as solvents. All chemical shifts are reported in parts per million (ppm) down field from the internal reference Me_4Si, TMS.

2.1.4. Elemental Analysis

The microanalysis data for C, H and N were obtained using CE 440 Elemental analyser.

2.1.5. MASS Spectrometry

Mass spectrometric analysis of copper complexes was carried out in acetonitrile on a Waters-Q-Tof Premier-HAB213 mass spectrometer.

2.1.6. Powder X-Ray Diffraction Spectroscopy (XRD)

XRD is a rapid quantitative and qualitative technique primarily used to provide information about the phase identification, purity and size of crystalline material. The powder XRD of all nanomaterials were examined using Bruker D8 Advance and XPERT-PRO diffractometer system with Cu Kα radiation (λ= 0.15418 nm). The diffraction data were recorded for 2θ angles between 20° and 80° (step size 0.02, step time 1s) and collected spectra peaks were matched with peaks mentioned in JCPDS files. The d-spacing is calculated from the values of the peaks observed from the Bragg's equation.

$$n\lambda = 2d \sin\theta \qquad 2.1$$

Where, n is the order of reflection and the values are 1, 2, 3,..., λ is the wavelength of the X-ray radiation, d is the interlayer spacing between two successive planes and θ is the angle between the incident ray and the scattering planes. Knowing θ, n and λ, the lattice spacing d can be easily calculated.

2.1.7. Transmission Electron Microscopy (TEM)

TEM is a powerful characteristic tool to observe the morphological features such as shape and size, and crystallographic details of the material at high resolution. To analyse the structural features, dispersion of powdered sample in ethanol was mounted over the carbon coated TEM grid and examined under a Technai-G^2 (FEI, Eindhoven, Netherlands) electron microscope equipped with SIS Mega View III CCD camera (FEI, Eindhoven, Netherlands) at 120 KV. Measurements were done using AnalySIS software (SIS, Muenster, Germany).

2.1.8. Energy Dispersive X-ray Spectroscopy (EDX)

The quantitative information about approximate stoichiometric composition of nanomaterials was investigated using ZEISS SUPRA 40, Oxford Instruments. Besides this, elemental composition of the tribofilm was studied using, ZEISS SUPRA 40

electron microscope Netherlands which gives preliminary confirmation regarding the tribochemical reaction to form *in situ* protective film.

2.1.9. X-ray Photoelectron Spectroscopy (XPS)

XPS is a quantitative and surface sensitive spectroscopic technique that is used to measure the elemental composition of the material and also gives information about the oxidation states of the associated elements. The X-Ray Photoelectron Spectroscopy was used for analyzing the chemical composition of graphene based materials and the tribofilm formed on the worn steel surface. For this purpose, after testing of respective additive in paraffin oil, one of the three lower balls was ultrasonically cleaned in hexane for about 5 min and dried in air. The XPS of tribofilm on wear scar was recorded. Three different XPS spectrometers were used to record the samples. The radiation source Al Kα line with energy of (1486.6 eV) and the binding energy of C1s (284.6 eV) was used for the calibration of the spectrometer, VSW Scientific Instruments photoelectron spectrometer; Sigma Probe and Thermo VG Scientific spectrometer. The radiation source Mg Kα line with pass energy of 29.35 eV was used in case of AMICUS Kratos Analytical, Shimadzu, U.K.

2.1.10. Raman Analysis

Raman spectroscopic measurements are carried out to confirm chemical and structural features of graphene-based nanomaterials. Raman spectra were obtained with a micro-Raman setup (HR LabRam inverse system, JobinYvon Horiba), the 532 nm line from a frequency doubled Nd:YAG laser (Coherent Compass) was used as excitation wavelength.

2.1.11. Scanning Electron Microscopy (SEM)

In order to understand the lubrication mechanism and morphological features of the worn surface, SEM is a very prominent technique. Scanning electron microscope (SEM) images of the worn surface areas of the steel balls were taken using a ZEISS SUPRA 40 electron microscope.

2.1.12. Atomic Force Microscopy (AFM)

Contact mode Atomic Force Microscope (Model No. BT 02218, Nanosurf easyscan2 Basic AFM, Switzerland) was used to investigate roughness of the worn

surfaces with Si_3N_4 cantilever (Nanosensor, CONTR type) having spring constant of ~0.1Nm^{-1} and tip radius more than 10 nm.

2.2. Theoretical Studies

Density Functional Theory (DFT) is found to be a suitable method for theoretical calculations of electron densities at various centres of a molecule. The geometry optimizations of Schiff base ligands and copper complexes were performed on a computer using atomic coordinates from ChemDraw structure as input, employing the G03, D.01 suite of programs [Frish *et al*.(2004)]. Ligands were treated as a closed-shell system using spin restricted DFT wave functions (rB3LYP), i.e. the Becke's three-parameter exchange functional (B3) in combination with the LYP correlation functional of Lee, Yang and Parr with 6-31G++(d,p) basis set. Complexes were treated as an open-shell system using uB3LYP for C, H, N and O atoms, and effective core potentials basis set LanL2DZ (Los Alamos National Laboratory 2 double zeta) for Cu atom in the complexes. The B3LYP method is commonly used for DFT calculation of transition metal complexes because of close relation of calculated geometrical and spectral parameters with experimentally observed results. DFT optimized calculations were carried out in states with spin multiplicity S=2, and the optimized structures were confirmed to be local minima by performing harmonic vibration frequency analyses (no imaginary frequency found). No symmetry constraints were applied and only the default convergence criteria were used during the geometric optimizations.

2.3. Tribological Characterization

2.3.1. Steel ball

The balls of 12.7 mm diameter made up of AISI 52100 alloy steel having hardness 59-61 HRc were used for the tests. Before and after each test, balls were cleaned with n-hexane and thoroughly air-dried.

2.3.2. Base oil

The lubricating base oil, neutral liquid paraffin oil (Qualigens Fine Chemicals, Mumbai, India) having specific gravity 0.82 at 25 ^{o}C, kinematic viscosity at 40 and

100 ^{o}C as 30 and 5.5 c*S*t respectively, viscosity index 122, cloud point -2 ^{o}C, pour point -8 ^{o}C, flash point 180 ^{o}C and fire point 200 ^{o}C, was used without further purification.

2.3.3. Tribological Test

The antiwear tests were performed using Four-Ball Lubricant Tester (Stanhope-Seta, London Street, Chertsey, U.K. in case of third to fifth chapters) at 1475 rpm (equivalent to a sliding speed of 567 mm/sec) 392N load for 60 min. time duration according to approximately similar ASTM D4172 procedure. The tribological testings were performed in case of sixth chapter according to ASTM D4172 and ASTM D5183 standards using Four-Ball Tester, Ducom Instrument Pvt. Ltd., Bangalore, India. Besides this, in order to calculate wear rate the tribological tests have been also performed at different time intervals 15, 30, 45, 60, 75 and 90 min respectively at 392N load. Load carrying ability of the additives was determined by varying load for 30 min. test duration.

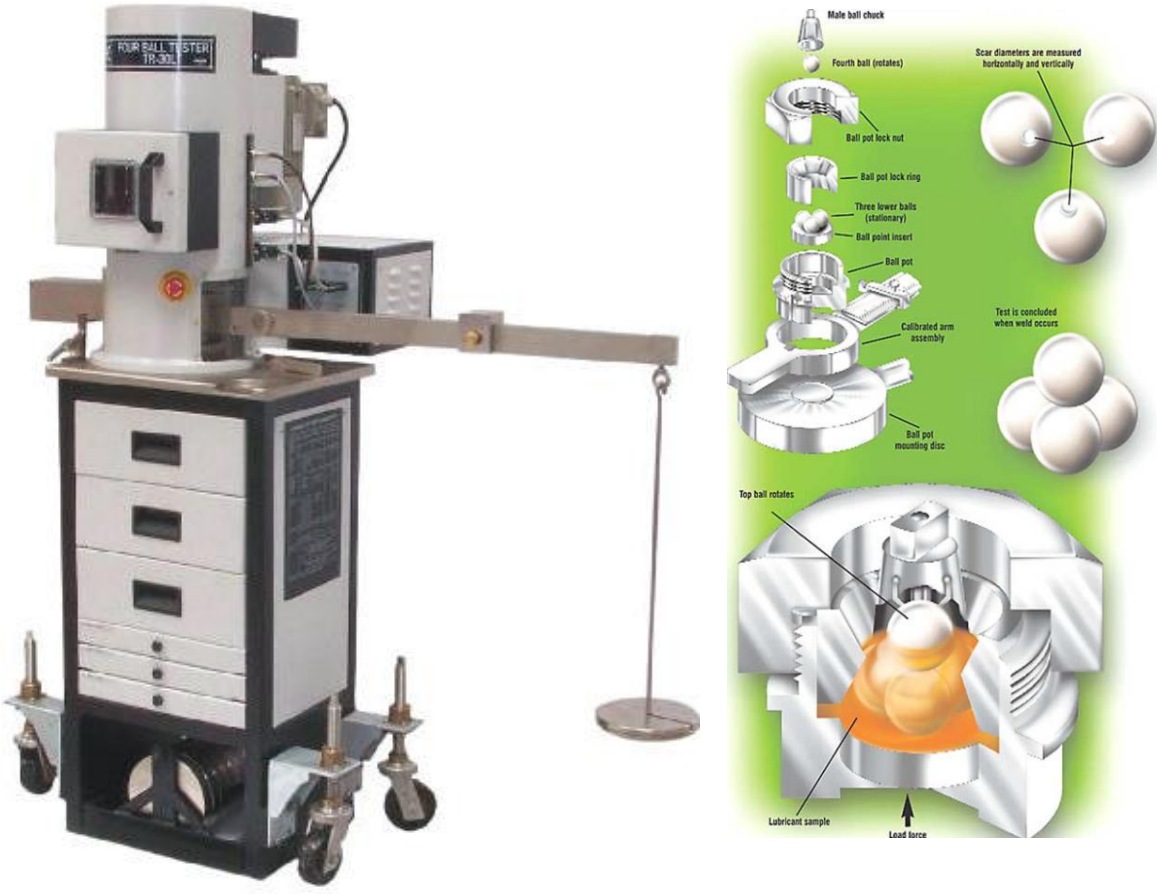

Figure 2.1. Four-ball lubricant tester

2.3.3.1. Tribological Parameters

2.3.3.1.1. Mean wear scar diameter (MWD)

The wear scar diameter of each of the three horizontal balls was measured in two mutually perpendicular directions, one in the sliding direction (d_s) and the other perpendicular (d_p) to it using an optical microscope. Geometric mean of the two perpendicular diameters on the same ball was taken as given by the equation 2.2.

$$d_1 = \sqrt{(d_s d_p)} \tag{2.2}$$

$$d = \frac{d_1 + d_2 + d_3}{3} \tag{2.3}$$

For each experiment arithmetic mean of the above diameter of each ball (d_1, d_2 and d_3) was taken as given by equation 2.3. The three stationary balls were not disturbed while taking the readings and the wear scar diameter was taken by tilting eye piece of the microscope at an angle of 35.26^o making it perpendicular to the surface of the scar. All of the antiwear and load bearing tests were performed in triplicate and their mean values were used.

2.3.3.1.2. Mean wear volume (MWV)

$$\text{Wear volume,} \qquad V = \frac{\Pi\, d_0^4}{64\, r}\{(\frac{d}{d_0})^4 - (\frac{d}{d_0})\} \tag{2.4}$$

$$\text{Hertzian diameter,} \qquad d_0 = 2(\frac{3Pr}{4E})^{\frac{1}{3}} \tag{2.5}$$

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 = Poissons ratio

r = Radius of steel ball

$E_1 = E_2 = 206$ GPa

$v_1 = v_2 = 0.3$

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

2.3.3.1.3. Friction coefficient (μ)

The coefficient of friction for different antiwear additives is calculated from the pattern observed on the friction paper with the help of equation 2.6.

$$\mu = \frac{0.00223fL}{P} \tag{2.6}$$

Where, f = Friction force exerted on the indicator spring, N

L = Length of the torque-lever arm, cm

P = test load, kg

2.3.3.1.4. Wear rate

Mean wear volume in absence and presence of different additives at 392N load for paraffin oil was plotted as a function of time and a linear regression model was fitted to find out overall, running-in and steady-state wear rate.