Chapter III

Multifunctional Additive Properties of Acrylate Based ZnO Nano Composite for Lubricating Oil

3.2.1. Introduction

The lubricating oil is the blood of the machine’s service life and operation and economic efficiency of the machine are relative to the quality, performance and sensible use of the oils.[1-2] The two major constituents of tribology are friction and wear. Thus when these are controlled and reduced, automatically increase the service life of machine. This ultimately saves money. The awareness of the subject, i.e. detection of tribological problems and their solution can give rise to considerable saving. According to some estimation, losses due to unawareness of tribology amount to about 6% of its gross national product in the United States. Thus the significance of friction reduction and wear manage cannot be overemphasized for economic reasons and long term dependability. In these regard peoples are focused on the application of nanoparticles in lubricating oil. Nanoparticles brought into lubricating oils can boost the properties of anti-wear, extreme pressure and friction reducing competency and service life of the machine were also improved.[3] The friction reduction and anti-wear action are relying on the characteristics of nanoparticles, for example size, shape and concentration. One important property that makes nanoparticles dissimilar from other materials is the fact that they have a very large surface area. Due to their very large surface area, nanoparticles are exceptionally reactive compared to its bulk form. Now a day, generally used nanoparticles are oxides based- Al_2O_3, CuO, ZnO, metals- Al, Cu, nonmetals- graphite, carbon nanotubes, layered composites- Al-Al_2O_3, Cu+C, functional nanoparticles etc. Out of the many kinds of nanoparticles, oxides based nanoparticles such as ZnO has been attracting considerable interest because of its unique structure and performance.[4-7] Nano ZnO has huge surface area, high surface energy, high diffusion, strong adsorption, and other wonderful characteristics. Base oil additives of nano sized, which are suitable for the high temperature work, heavy load, low speed, have excellent anti-wear resistance, extreme pressure resistance performance and better lubrication properties. In addition, nano- ZnO is a widely used nano oxides and its preparation scheme is simple. Nano-ZnO used as lube oil additive will not only enhance the tribological properties of base oils, in addition also potentially reduce the cost of lube oil. On the other hand, nano-ZnO is hudrophilic-oleophobic with poor oil solubility. It needs to depend on the role of dispersant, ultrasonic dispersion or strong agitation to disperse nano-ZnO particles in the base oils.[8-12] Again, nano-ZnO particles were not known to show other kind of additive performance other than anti-wear, friction reduction and extreme pressure additive performance. So to disperse nano-ZnO nanoparticle and to meet the purpose of developing multifunctional performance additive, nano-ZnO was dispersed in polymer matrix (acrylate based) by sonication. Since acrylate based polymer were known to perform as good viscosity index improver[13-15] and pour point depressant.[16] The multifunctional performance (tribological performance, viscosity index improver, pour point depressant) of this nano-ZnO/polymer blend was studied.

3.2.2. Experimental details

3.2.2.1. Materials and methods

Acrylic acid, dodecyl alcohol, BZP and hydroquinone were purchased from Merck specialities Pvt. Ltd. Methanol, hexane and conc. H_2SO_4 were purchased from Thomas baker Pvt. Ltd. BZP was recrystallized from $CHCl_3$-MeOH. Zinc chloride and sodium hydroxide were purchased from Merck specialities Pvt. Ltd. The base oil was collected from IOCL, Dhakuria, Kolkata, India.

3.2.2.2. Preparation of monomer

Dodecyl acrylate (DDA) was prepared by esterification of acrylic acid with dodecyl alcohol in the mole ratio of 1.1:1. The detailed process was already described in chapter II of part II.

3.2.2.3. Purification of the prepared monomer

The prepared ester (DDA) was purified according to the process as described in chapter II of part II.

3.2.2.4. Preparation of homo polymer

The homo poly dodecyl acrylate was synthesized and purified according to the procedure described in chapter II of part II.

3.2.2.5. Preparation of ZnO nanoparticle

5.5 g of the zinc chloride was dissolved in 100ml of distilled water in a beaker. This solution was kept under constant magnetic stirring till zinc chloride totally dissolved in the distilled water. The temperature of the solution was raised to 90˚C by electric hot plate heating. Meanwhile 20 g of sodium hydroxide was dissolved in 100ml of distilled water in a separate vessel. From the prepared sodium hydroxide solution, 16 ml of sodium hydroxide is added to the beaker with constant stirring, drop by drop touching the walls of the beaker. The aqueous solution turned into a milky white colloid without any precipitation. The reaction was allowed to proceed for 2 hrs after complete addition of sodium hydroxide. After the complete reaction, the solution was allowed to settle and the supernatant solution was removed by washing with distilled water for 5 times. After complete washing, the nano-ZnO was dried at 100˚C for 30 min. and then it changed into powder form.[17] The reaction involved is given below

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

Scheme: Reaction involved during synthesis of nano-ZnO

3.2.2.6. Preparation of poly dodecyl acrylate- ZnO nanocomposites

PDDA- ZnO nanocomposites were prepared by mixing the PDDA/toluene solution and nano-ZnO particles. The PDDA- ZnO suspension was prepared as follows: 5g of PDDA were dissolved in toluene and required amount (0.5, 1 and 1.5mg) of nano-ZnO particles were added into the PDDA/toluene solution under ultrasonic wave and vigorous stirring to prepare 100, 200 and 300 ppm blend. The suspension was then poured into a glass plate and allows the tolune to evaporate naturally and a semi solid mass of polymer-nanocomposites was obtained.

3.2.3. Measurements

3.2.3.1. Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range of 400–4000 cm^{-1}. NMR spectra were recorded in Bruker Advance 300 MHz FT-NMR spectrometer using 5 mm BBO probe using $CDCl_3$ as solvent and TMS as reference material.

3.2.3.2. Thermo gravimetric analysis (TGA)

The thermal stabilities of the prepared homo polymer and polymer/nano composite were determined by a thermo gravimetric analyzer (Shimadzu TGA-50) using an alumina crucible in air. The system was run at a heating rate of 10 °C/min. The percentage of weight loss (PWL) of the samples with rise in temperature was calculated.

3.2.3.3. Determination of molecular weight by GPC

By GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were determined. The poly dispersity index was also calculated. In this method HPLC grade THF (0.4%, w/v) was used as mobile phase in the water 2414 GPC system (polystyrene calibration) at 35°C with a flow rate of 1 ml/min.

3.2.3.4. Characterization of nano- ZnO by SEM and X-RD

The synthesized ZnO-nanoparticles were characterized by Field Emission Scanning Microscope (FE-SEM, INSPECT F50, FEI) and X-ray diffraction (X-RD, Advance D8, Bruker).

3.2.3.5. Performance evaluation as viscosity modifier

Viscosity index (VI) of the polymeric additives was determined in paraffinic base oil to evaluate the efficiency of the prepared polymeric additives as viscosity modifier (VM). An Ubbelohde OB viscometer was used in this experiment at the temperatures 313K and 373K. The detailed process is previously described in Chapter II of Part I.

Five different concentrations ranging from 1 wt % to 5 wt % of the polymeric sample solutions were used to study the effect of additive concentration on VI.

3.2.3.6. Performance evaluation as pour point depressant

The pour point depressant property of the prepared polymeric additives was determined in base oil by the pour point test on a Cloud and Pour Point Tester model WIL-471(India) according to ASTM D97 method. In this case also five different concentrations of the additives were used for each sample.

3.2.3.7. Evaluation of tribological performance of prepared additives

The anti-wear performance of the lubricant compositions were evaluated in terms of wear scar diameter (WSD) by Four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method.[18] In this experiment 392 N (40 kg) load was applied at 75°C for 30 min. to measure the wear scar diameter (WSD). The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm, respectively. The details procedure is described in our publication elsewhere.[19]

3.2.4. Results and discussion

3.2.4.1. Spectroscopic analysis

Again in this investigation we were used poly dodecyl acrylate (A) as in the previous study (Chapter-II of Part-III). Here also we observed shifting of IR stretching frequency (**figure 3.9**) of carbonyl group from 1734. 56 cm^{-1} (ester carbonyl) to 1728 cm^{-1}. Hence it can be concluded that, ZnO nanoparticles formed a coordinate type of bond with ester group of A.

3.2.4.2. Thermo gravimetric analysis

The TGA data of the polymer (A) and polymer/ZnO nanocomposites (Z-1, Z-2 and Z-3) are represented in **figure 3.12**. It was seen from the figure that, thermal stability of all nano blended composites is higher than that of A. At 380°C, the percentage of decomposition of the polymer (A) and nanocomposites from Z-1 to Z-3 were 32.42%, 22.88%, 22.09% and 21.29% respectively, whereas at 490°C, the percent of weight loss of A, Z-1, Z-2 and Z-3 were 93.71%, 74.86%, 74.08% and 73.27% respectively. Hence thermal stability of the polymer/ZnO nanocomposites (Z-1, Z-2 and Z-3) was improved by dispersion of the nano-ZnO into the A. This enhancement of thermal stability may be due to the reduction of mobility of polymer chain and the tendency of nanoparticles to remove free radicals.[20]

3.2.4.3. Characterization of nano- ZnO

Figure 3.10 shows the X-ray diffraction pattern of ZnO nanoparticle. The nanoscale range of particles in the prepared materials was indicated by a definite line broadening of the X-RD peaks. The eight most intense diffraction peaks located at 31.84°, 34.52°, 36.33°, 47.63°, 56.71°, 62.96°, 68.13° and 69.18° have been clearly observed which is in good agreement with a research work published elsewhere.[21] Moreover it also suggests that the synthesized nanoparticles was free of impurities as it does not shows any characteristics X-RD peaks other than nano-ZnO peaks.

Figure 3.11 represents the scanning electron micrograph (SEM) of the ZnO nanoparticles at different magnifications. These SEM pictures substantiate the formation of ZnO nanoparticles. These pictures confirm the approximate spherical shape to the ZnO nanoparticles. It also can be seen from the pictures that the size of the nano-ZnO is in the range of 16-18 nm.

3.2.4.4. Efficiency of additive as viscosity modifier

Figure 3.13 represents the viscosity index values of the lubricants blended with the additives. It is observed that, the viscosity index (VI) values of the polymer/nano-ZnO composites of different composition (Z-1, Z-2 and Z-3) at different concentration level are better than the pure polymer (A). Again with both type of additives, there is always a steady increase of VI values with the increase in additive concentration. Increase of concentration of the additives leads to increase in total volume of polymer micelles in the solutions. The additional increase of volume compared to pure polymer may be due to the fact that, the nanoparticles present in the polymer matrix leads to the polymer chain separated from each other.

3.2.4.5. Efficiency of additive as pour point depressant

Different level of percentage concentration varying from 1 wt% to 5 wt% of the additives in the base oil was tested as PPD and the results are depicted in **figure 3.14**. The results showed that the additives (A, Z-1, Z-2 and Z-3) are efficient as PPD and the efficiency decreases with increasing additive concentration. The PPD property of all the blended composites is very similar with that of A. That means, incorporation of nanoparticles into the polymer matrix does not affect the PPD property compared to polymer (A).

3.2.4.6. Tribological performance

The tribological properties of all the lubricant compositions (A, Z-1, Z-2 and Z-3) were determined by measuring WSD by FBWT apparatus employing 40 kg load and the results were depicted in **figure 3.15**. The AW performance of the base oil is significantly enhanced when the additives are blended with it and is indicated by the lower WSD values of the lubricant compositions. The nano-ZnO blended composites exhibited better anti-wear performance compared to only polymer (A) and the performance becomes increasingly better with increasing the amount of nanoparticles in the polymer matrix as is shown in the **figure 3.15**.

3.2.5. Conclusion

In this study nano-ZnO was synthesized with better size distribution which was established and characterized by SEM and XRD study. The interaction of nano-ZnO with PDDA was studied by FT-IR analysis and it suggests that there is definte interaction between them. All the nano blended composites showed excellent performance as viscosity modifier and anti-wear additives for lube oil but they did not improve the pour point performance compared to polyacrylate. Moreover the thermal stability of polymer was also improved by the incorporation of nano ZnO into the polymer matrix. This change of properties of polymer is also evidence of nano-polymer interaction in the blended composites. Therefore, the above study is definitely a potential approach to design multifunctional additives for lubricating oil.

3.2.6. References

References are given in BIBLIOGRAPHY under Chapter III of Part III (PP 174-177).

3.2.7. Tables and Figures

Table 3.3: Properties of base oil

Properties	*Base oil*
Density(kg.m^{-3}) at 313K	918.68
Viscosity at 313K	20.31×10^{-6}
Viscosity at 373K	3.25×10^{-6}
Viscosity index	89.02
Cloud point (°C)	-8
Pour point (°C)	-6

Table 3.4: Designation and Composition of poly dodecylacrylate-nano ZnO composites

Designation	*Composition*	
	Polymer in g	Nano (ZnO) in mg
A	5	0
Z-1	5	0.5
Z-2	5	1.0
Z-3	5	1.5

Figure 3.9: Comparative FT-IR spectra of polymer (a), polymer/ZnO nanocomposite (b)

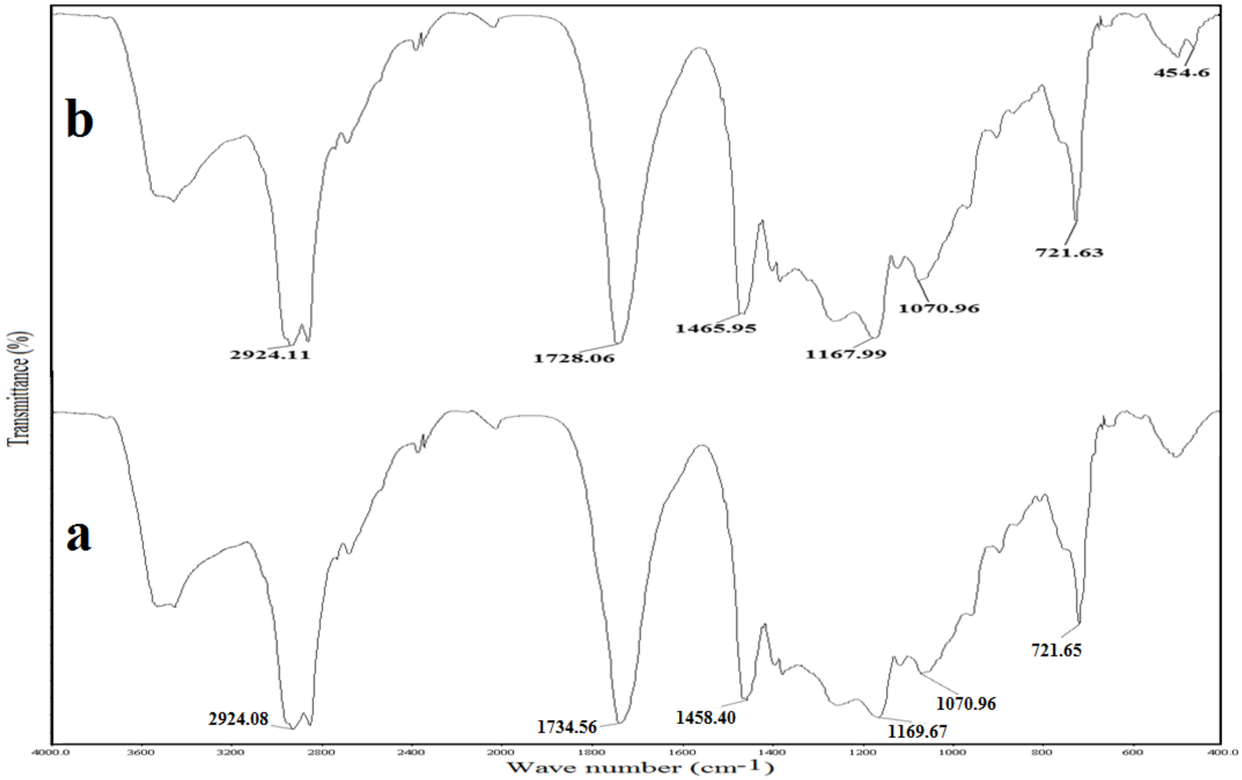

Figure 3.10: X-RD spectra of prepared ZnO nanoparticle

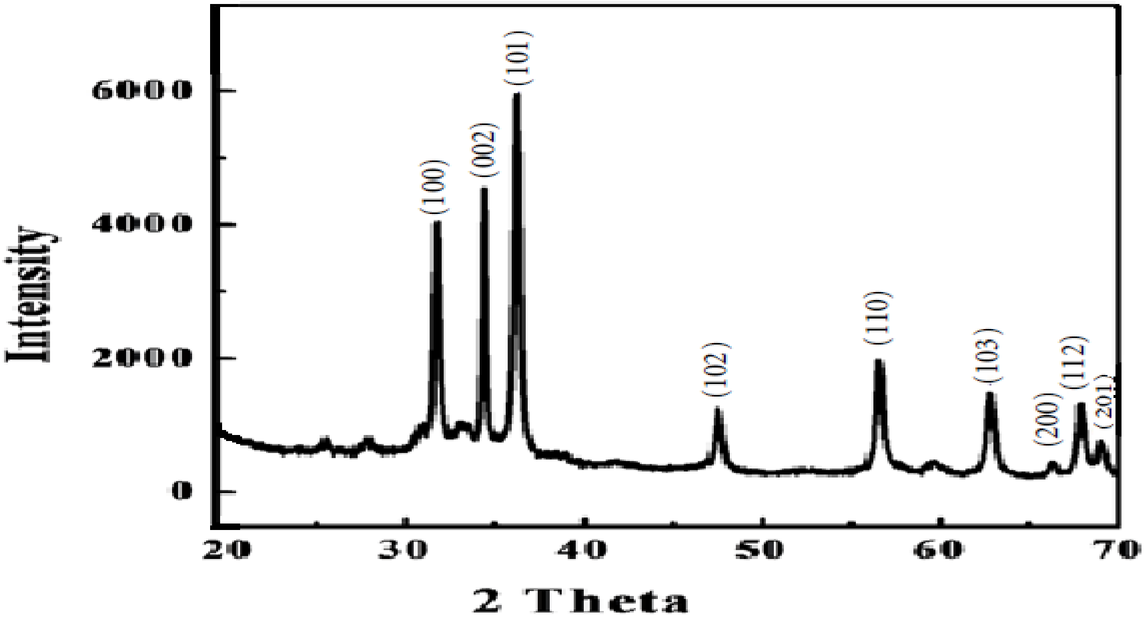

Figure 3.11: SEM pictures (a, b, c and d) of prepared ZnO nanoparticle at different magnifications

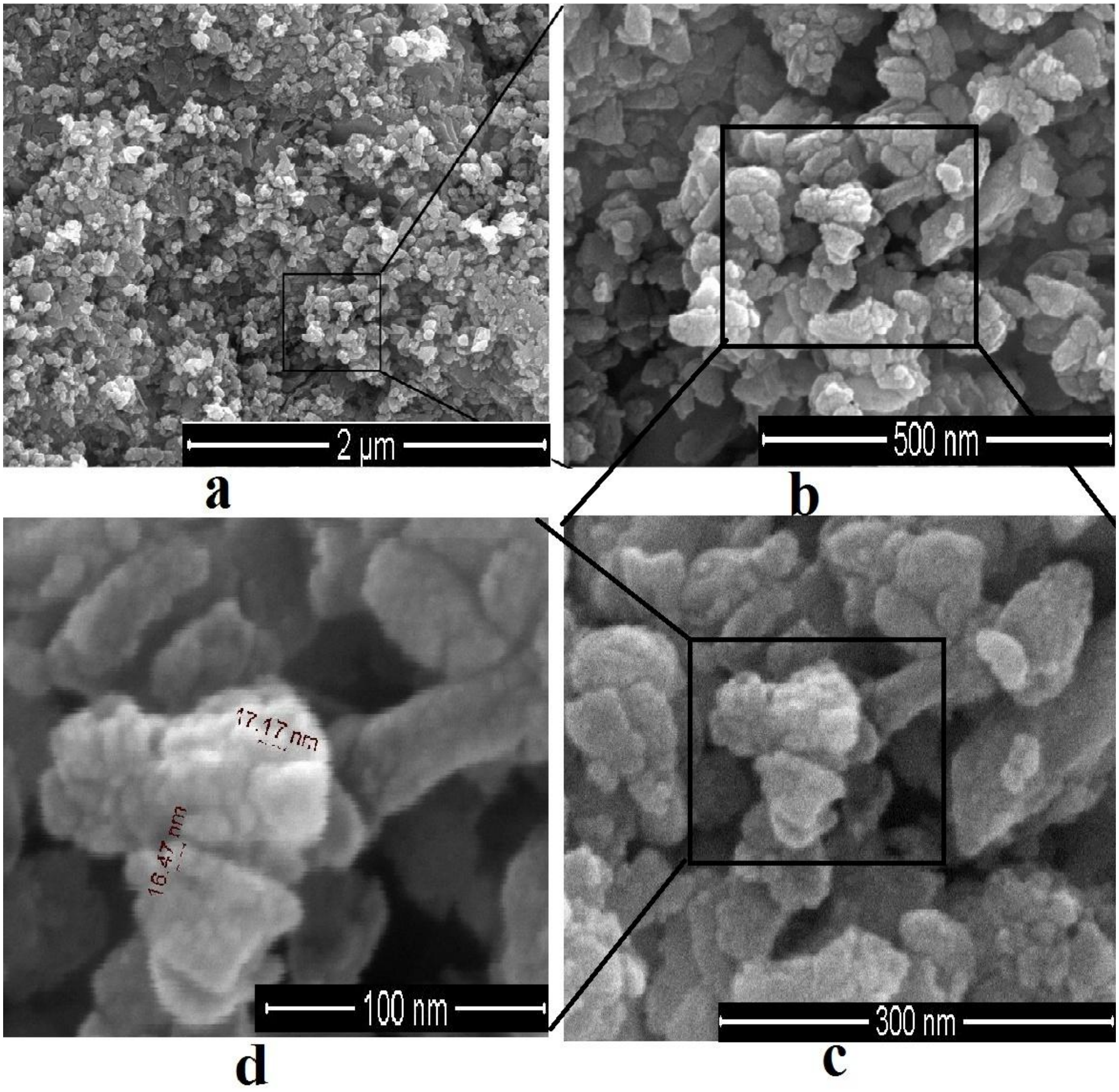

Figure 3.12: TGA data of polymer (A) and polymer/ZnO nanocomposite (Z-1, Z-2 and Z-3)

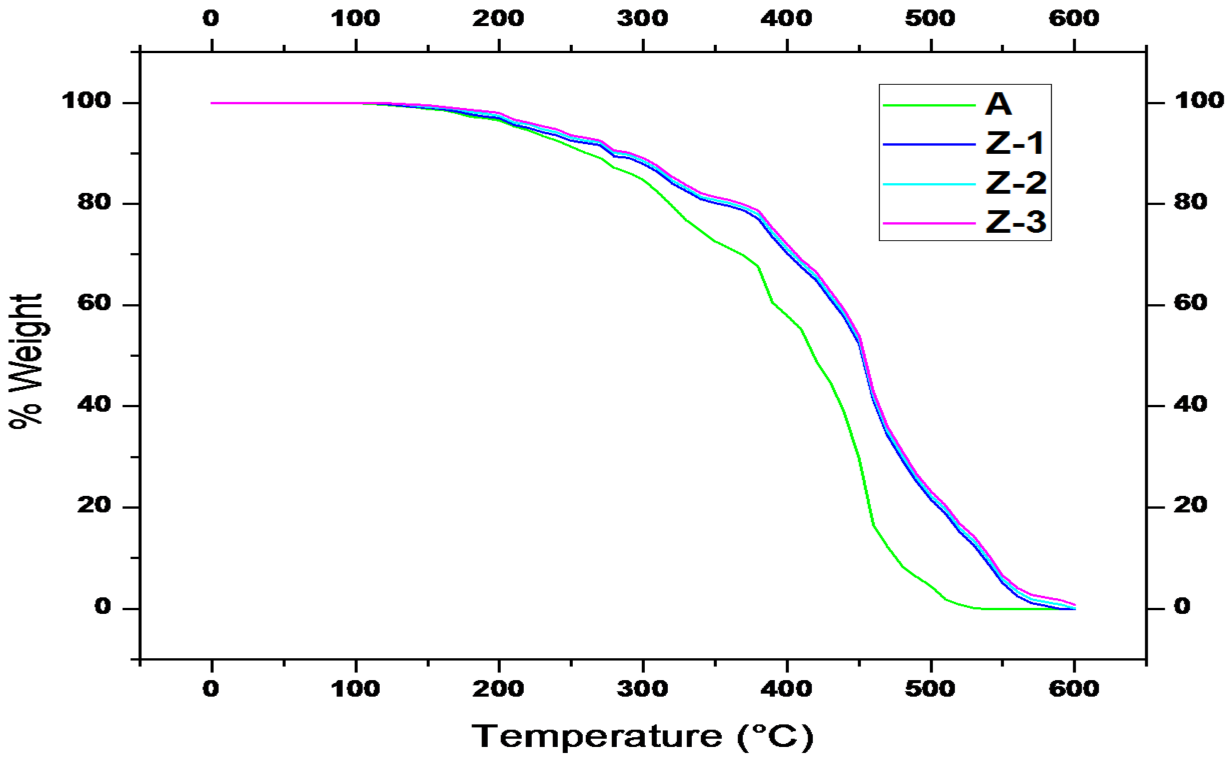

Figure 3.13: Plot of viscosity index of the additives (A, Z-1, Z-2 and Z-3) doped base oil with additive concentration

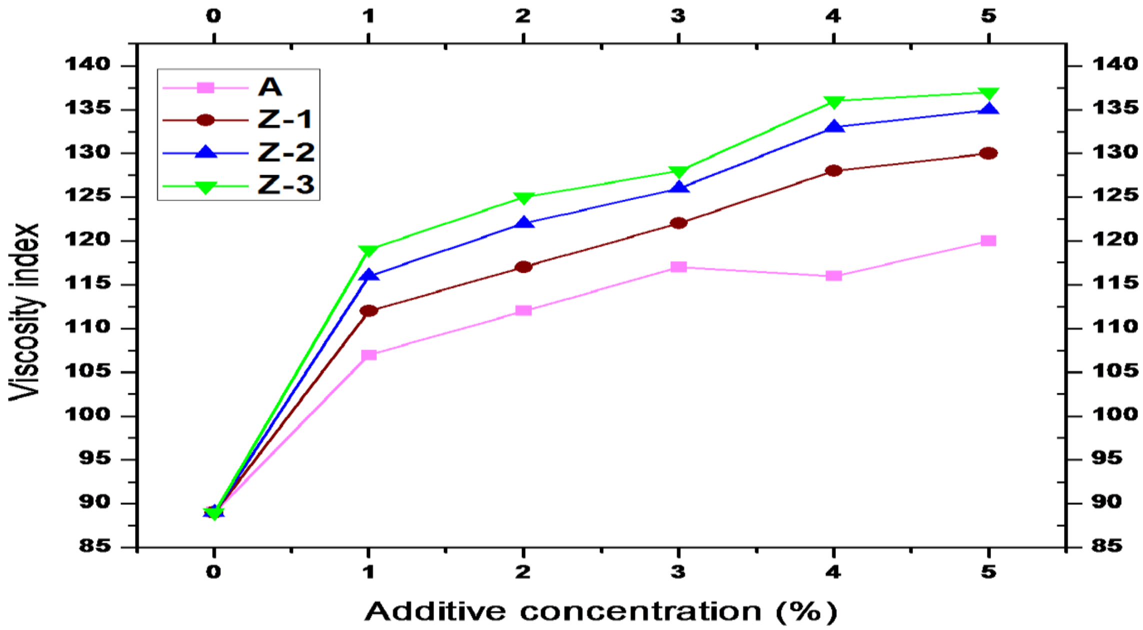

Figure 3.14: Plot of pour point of the additives (A, Z-1, Z-2 and Z-3) doped base oil with additive concentration

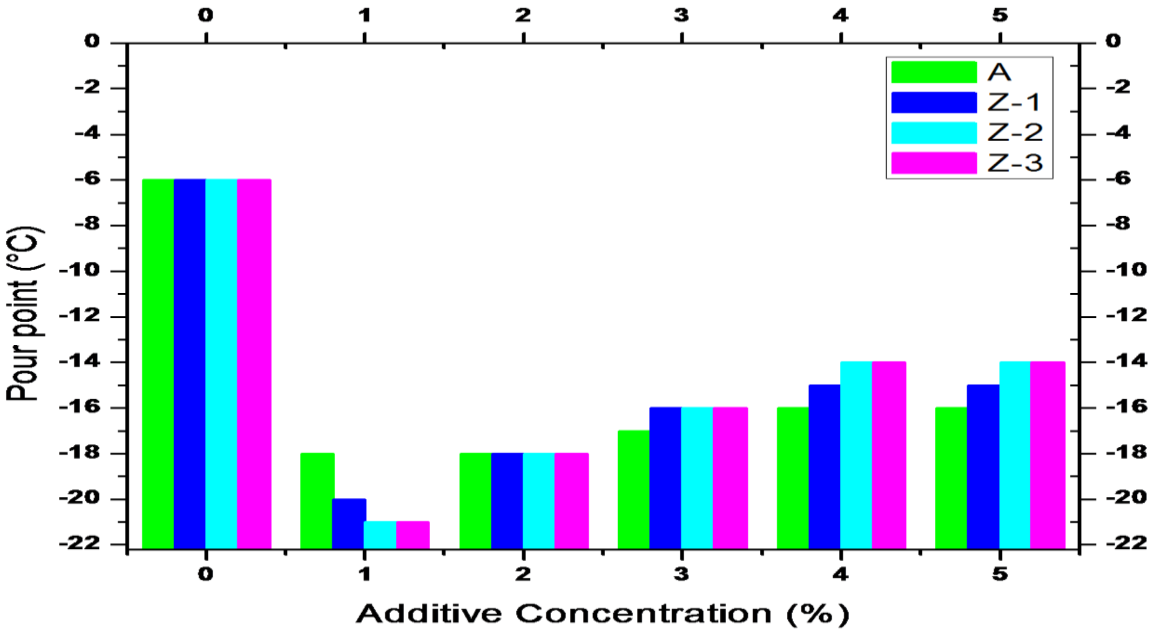

Figure 3.15: Wear scar diameter (WSD) of the lube oil blended with additives (A, Z-1, Z-2 and Z-3) at different percentage (w/w)