

Chapter II

Polyacrylate-Nano Magnetite Composite as a Potential Multifunctional Lube Oil Additive

3.1.1. Introduction

In industry, mainly in machine industry widely utilized materials are lubricants. The proper application of lubricants can improve the efficiency of the engine, prolong the machine life as well as economize on energy. In the last few decades, use of oil-soluble additives in lubricant as effective friction reduction and anti-wear property have been extensively studied in lubrication engineering.¹⁻³ Though, the use of these additives has arisen some troubles, for example pollution, toxicity, waste disposal etc. With the advent of nanomaterials, nanoparticles were incorporated into lubricating oil to improve the tribological properties. In recent years, a great number of studies have been carried out on the effects of a range of inorganic nanoparticles as lubricating oil additives on friction and wear.⁴⁻⁷ Owing to the wonderful tribological properties of nanoparticles and good environmentally benign property, they have been preferred as an exceptional candidate for traditional lubricating oil additives, particularly at high load, high sliding speed and high frictional conditions.⁸⁻¹⁰

Use of graphite nanosheets as lubricating oil additives improves tribological properties of paraffin oil.¹¹ The anti-wear property of paraffin oil was significantly improved by the incorporation of MoS₂ nanoparticles.¹²⁻¹³ Oxide based nanoparticles such as CuO nanoparticles exhibit good anti-wear and friction reduction properties.¹⁴ Cai-Xiang et. al reported the anti-wear and friction reducing properties of CeO₂ and TiO₂ nanoparticles in lubricating oil.¹⁵ All the nanoparticles mentioned above are nonmagnetite and there are few reports on tribological properties of magnetic nanoparticles as lube oil additives.¹⁶ Huang et. al reported the effect of magnetite nanoparticle on tribological property of paraffin oil which disclosed the improvement of load carrying capacity and anti-wear property compared to pure paraffin oil.¹⁶ From the above discussion it is revealed that magnetite nanoparticle and other oxide based nanoparticles are used

only as anti-wear and friction reducing additives in lubricating oil. Furthermore, acrylate based polymers are known to perform as good viscosity index improver (VII),¹⁷⁻¹⁹ pour point depressant (PPD).²⁰ They were not known to act as good anti-wear and friction reducing additives. Hence to impose the multifunctional performance (VII, PPD, anti-wear) into the additives, authors are attempting to prepare those kinds of additives. Keeping this view in mind, we are blending homopoly dodecylacrylate with magnetite nanoparticle to develop multifunctional additives for lubricating oil.

3.1.2. Experimental procedure

3.1.2.1. Materials and methods

Acrylic acid, dodecyl alcohol, BZP and hydroquinone were purchased from Merck specialities Pvt. Ltd. Methanol, hexane and conc. H₂SO₄ were purchased from Thomas baker Pvt. Ltd. BZP was recrystallized from CHCl₃-MeOH. Iron(II)sulphate heptahydrate, potassium nitrate and potassium hydroxide were purchased from Merck specialities Pvt. Ltd. The base oil was collected from IOCL, Dhakuria, Kolkata, India.

3.1.2.2. Preparation of dodecyl acrylate by Esterification

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.

3.1.2.3. Purification of the prepared ester (DDA)

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

3.1.2.4. Synthesis of homo polymer of DDA

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

3.1.2.5. Preparation of magnetite (Fe₃O₄) nanoparticles

Magnetite nanoparticles were synthesized with modification of the method reported by Bruce et al. Solutions of iron(II) sulphate heptahydrate (1.67 g, 6×10^{-3} mol) in 50 ml deionized water, potassium nitrate (1.01 g, 1×10^{-2} mol) in 10 ml of deionized water, and 2.5 M potassium hydroxide were prepared. 1% (w/w) stabilizer (CTAB) was mixed with the iron salt solution under vigorous stirring for two hours. To this solution, potassium nitrate was added and stirring was continued for another half an hour. Then, 10 ml of 2.5 M potassium hydroxide (2.5×10^{-2} mol) was slowly added to the above solution. The reaction mixture was heated to 100°C under nitrogen and maintained at this temperature for two hours. The nitrogen flow was then turned off and the mixture was cooled down to room temperature. After cooling, the black precipitate was repeatedly washed with deionized water, centrifuged and allowed to dry under vacuum at 50°C overnight.²¹

3.1.2.6. Preparation of poly dodecyl acrylate- Fe₃O₄ nanocomposites

PDDA- Fe₃O₄ nanocomposites were prepared by mixing the PDDA/toluene solution and nano-Fe₃O₄ particles. The PDDA- Fe₃O₄ suspension was prepared as follows: 5g of PDDA were dissolved in toluene and required amount (0.5, 1 and 1.5mg) of nano- Fe₃O₄ 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 toluene to evaporate naturally and a semi solid mass of polymer-nanocomposites was obtained.

3.1.3. Measurements

3.1.3.1. 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.

3.1.3.2. 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.

3.1.3.3. 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.

3.1.3.4(a). Characterization of nano- Fe_3O_4 by SEM and X-RD

The synthesized Fe_3O_4 -nanoparticles were characterized by Field Emission Scanning Microscope (FE-SEM, INSPECT F50, FEI) and X-ray diffraction (X-RD, Advance D8, Bruker).

3.1.3.5. 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.

3.1.3.6. 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.

3.1.3.7. 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.²² In this experiment 392 N (40 kg) load at 75°C for 30 min. was employed 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.²³

3.1.4. Results and discussion

3.1.4.1. Spectroscopic analysis

FT-IR spectrum of homopoly dodecyl acrylate (A) showed absorption band at 1734.56 cm^{-1} for the ester carbonyl stretching vibration along with other peaks at 1458.40, 1370.18, 1169.67,

1070.96 cm^{-1} . In the ^1H NMR spectra of A showed broad singlet centred at 4.013 to 4.293 ppm due to the protons of $-\text{OCH}_2$ group. Methyl protons of dodecyl chain appeared between 0.866 ppm and 0.878 ppm and the absence of singlet between 5 ppm and 6 ppm implies the absence of any vinylic proton in the polymer. In the ^{13}C NMR spectrum of P-1, the carbonyl carbon appeared at 174.3 ppm along with other SP^3 carbons appeared in the range of 64.72 to 13.94 ppm and it is showed in **figure 3.1**. The FT-IR spectra (**figure 3.2**) of polymer/ Fe_3O_4 nanocomposite showed absorption band at 1726.12 cm^{-1} . This shifting of carbonyl stretching frequency may be due to some association of nano magnetite and poly dodecyl acrylate.

3.1.4.2. Thermo gravimetric analysis

The TGA data of the polymer (A) and polymer/ Fe_3O_4 nanocomposite (F-1, F-2 and F-3) are depicted in **figure 3.5**. It was seen from the figure that, thermal stability of nano blended composites is higher than that of A. Hence, by incorporation of nano- Fe_3O_4 into A increases the thermal stability. At 380°C, the percentage of decomposition of A, F-1, F-2 and F-3 were 32.42% and 21.35% respectively, whereas at 490°C, the percent of weight loss of A, F-1, F-2 and F-3 were 93.71% and 70.56% respectively. The addition of nano- Fe_3O_4 affects the degradation mechanism and as a result improves thermal stability of polymer (A). The decrease of mobility of polymer chain and the tendency of magnetite nanoparticle to eliminate free radicals may be the key effects accountable for this enhancements.²⁴

3.1.4.3. Characterization of nano- Fe_3O_4

Figure 3.3 shows the X-ray diffraction pattern of the prepared magnetite nanoparticle. The six most intense peaks at 30.3°, 35.6°, 43.2°, 53.6°, 57.1° and 62.8° respectively were markedly observed, which was found very similar in a research article.²¹ The purity of the magnetite

nanoparticle was also confirmed by X-RD due to absence of other peaks of iron oxide like maghematite or hematite in samples. Hematite nanoparticles shows nine intense peak in the diffraction angle from 6° to 70° .²⁵

Figure 3.4 shows the scanning electron micrograph of the prepared magnetite nanoparticle and the shape of the particle were also marked in the figure which shows that the particles were nearly spherical. It can be seen from the **figure 3.4** that the particles have an average size of about 29 ± 2 nm.

3.1.4.4. Efficiency of additive as viscosity modifier

Figure 3.6 represents the viscosity index values of the additive doped base oil. It is observed that, the viscosity index (VI) values of the polymer/nano- Fe_3O_4 composites (F-1, F-2 and F-3) doped base oil are better than the pure polymer (A) doped oil at every concentration. 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.

3.1.4.5. 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 3.7**. The results showed that the additives (A, F-1, F-2 and F-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 appreciably compared to polymer (A).

3.1.4.6. Tribological performance

The tribological properties of all the lubricant compositions (A, F-1, F-2 and F-3) were determined by measuring WSD by FBWT apparatus employing 40 kg load and the results were depicted in **figure 3.8**. 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-magnetite 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 3.8**.

3.1.5. Conclusion

In this study nano-Fe₃O₄ was synthesized with better size distribution which was established by SEM and XRD study. The interaction of nano-Fe₃O₄ with PDDA was studied by FT-IR spectral analysis and it suggests that there is definite interaction between them. From the above study it was found that all the nano blended composites showed performance as viscosity modifier and anti-wear additives for lube oil. Moreover the thermal stability of polymer was also improved by the incorporation of nano magnetite into the polymer matrix. This change of properties of polymer is also a proved of nano-polymer interaction. Therefore, the above study is definitely a potential approach to design multifunctional additives for lubricating oil.

3.1.6. References

References are given in BIBLIOGRAPHY under Chapter II of Part III (PP 172-174).

3.1.7. Tables and figures

Table 3.1: Properties of base oil

<i>Properties</i>	<i>Base oil</i>
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 3.2: Designation and Composition of poly dodecyl acrylate-nano magnetite composites

<i>Designation</i>	<i>Composition</i>	
	Polymer in g	Nano (Fe ₃ O ₄) in mg
A	5	0
F-1	5	0.5
F-2	5	1.0
F-3	5	1.5

Figure 3.1(a): FT-IR spectra of polymer (A)

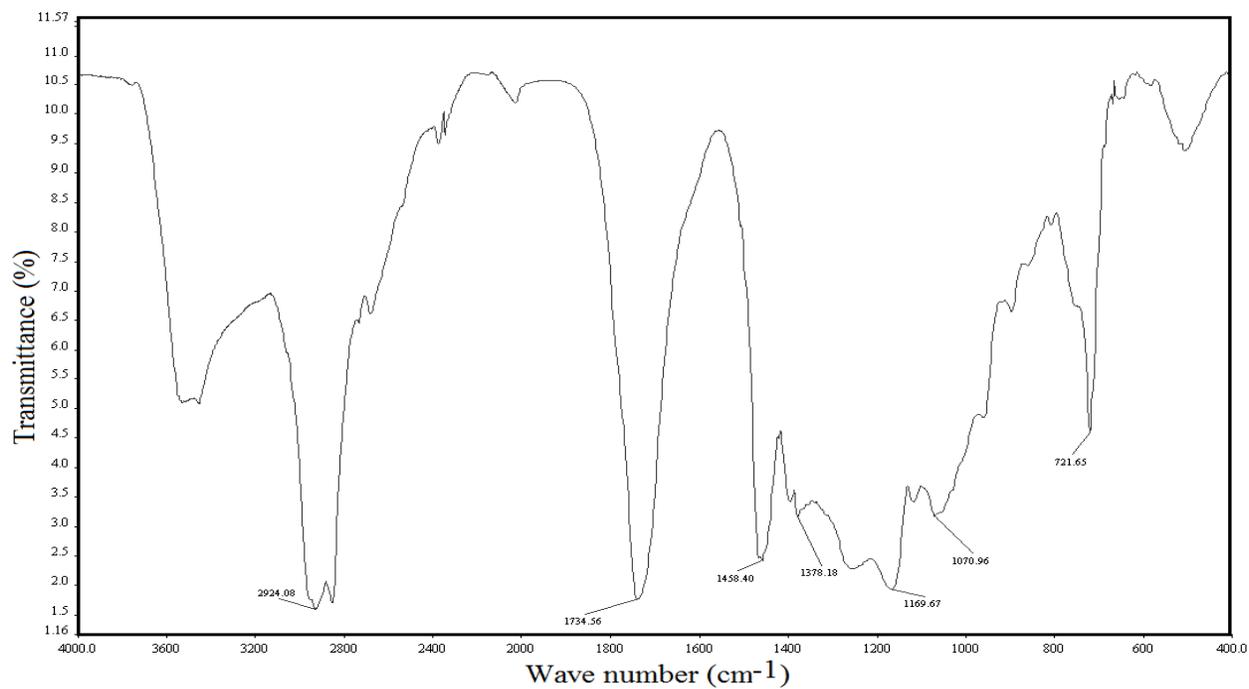


Figure 3.1(b): ¹H NMR spectra of polymer (A)

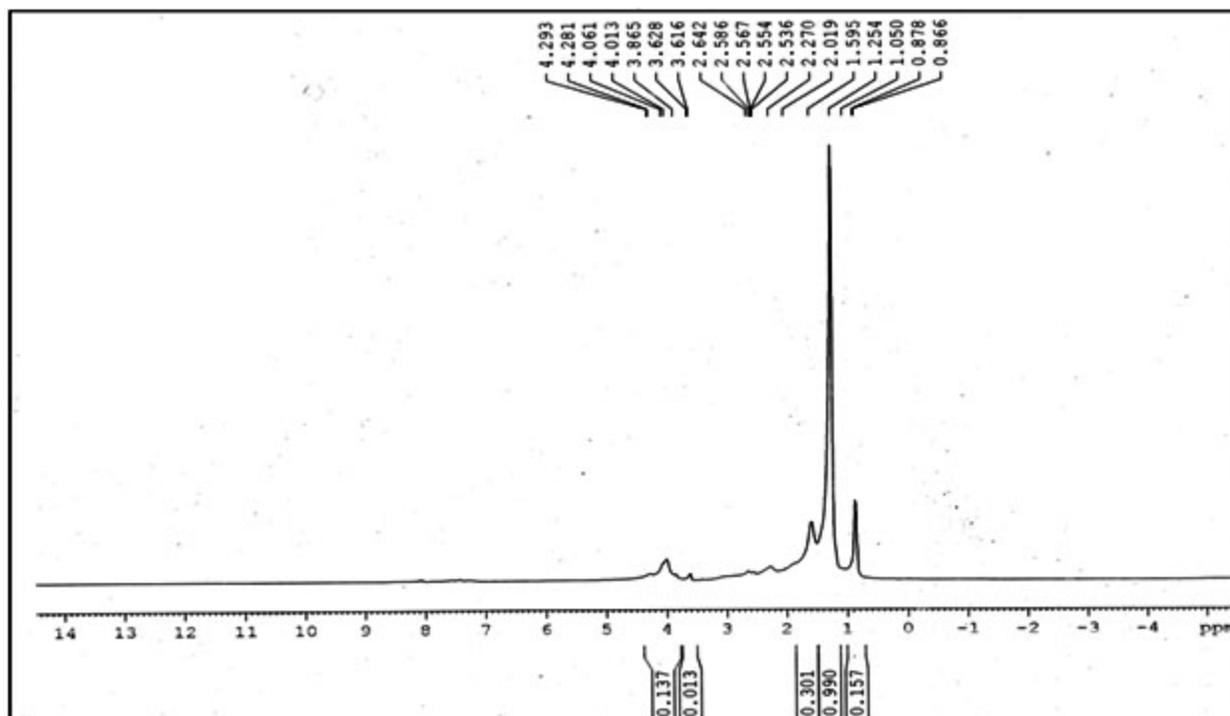


Figure 3.1(c): ^{13}C NMR spectra of polymer (A)

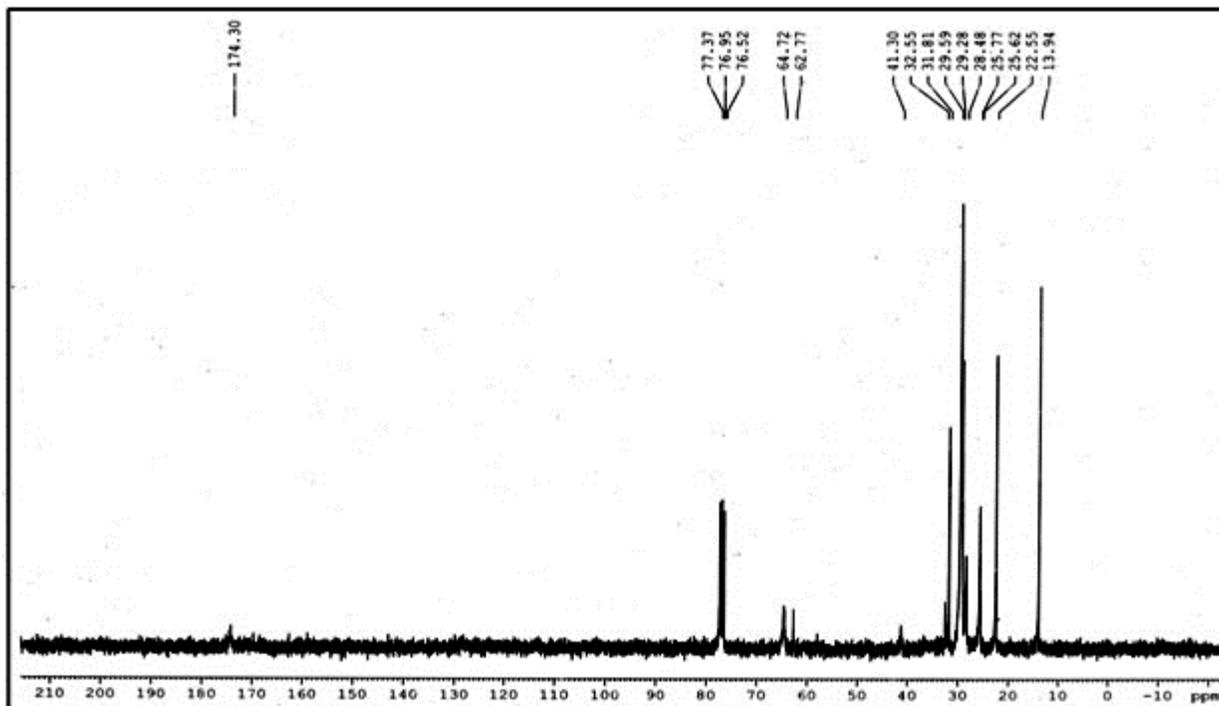


Figure 3.2: Comparative FT-IR spectra of polymer (a), polymer/ Fe_3O_4 nanocomposite (b)

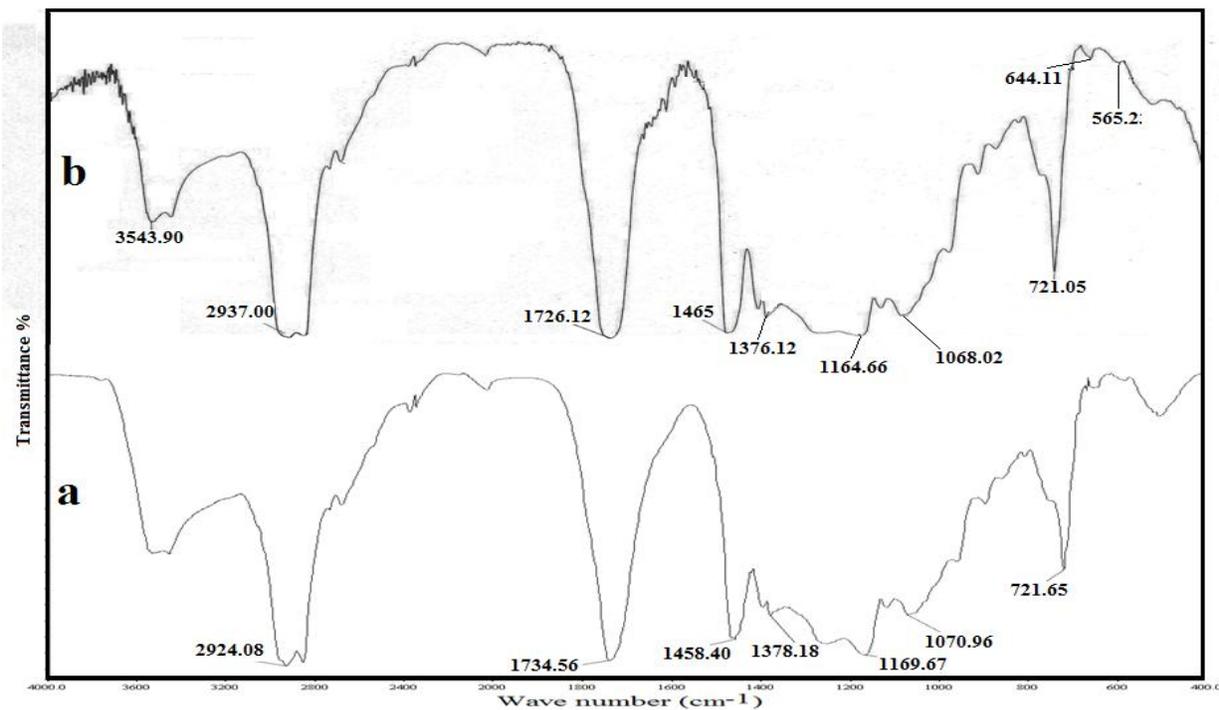


Figure 3.3: X-RD pattern of prepared nano-Fe₃O₄

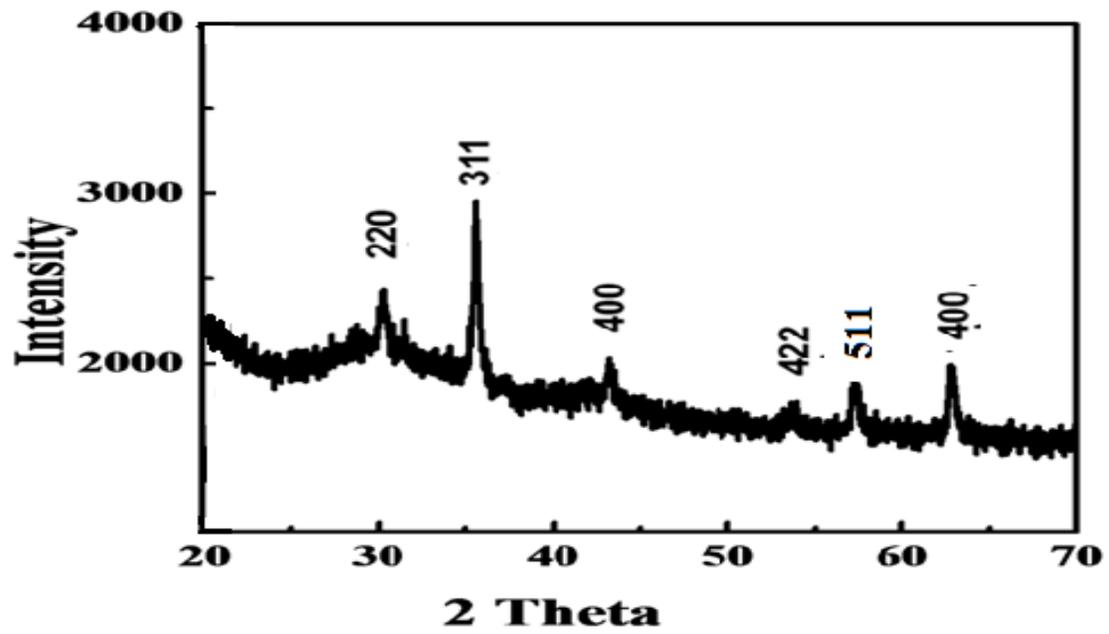


Figure 3.4: SEM images of prepared nano-Fe₃O₄ at different magnifications

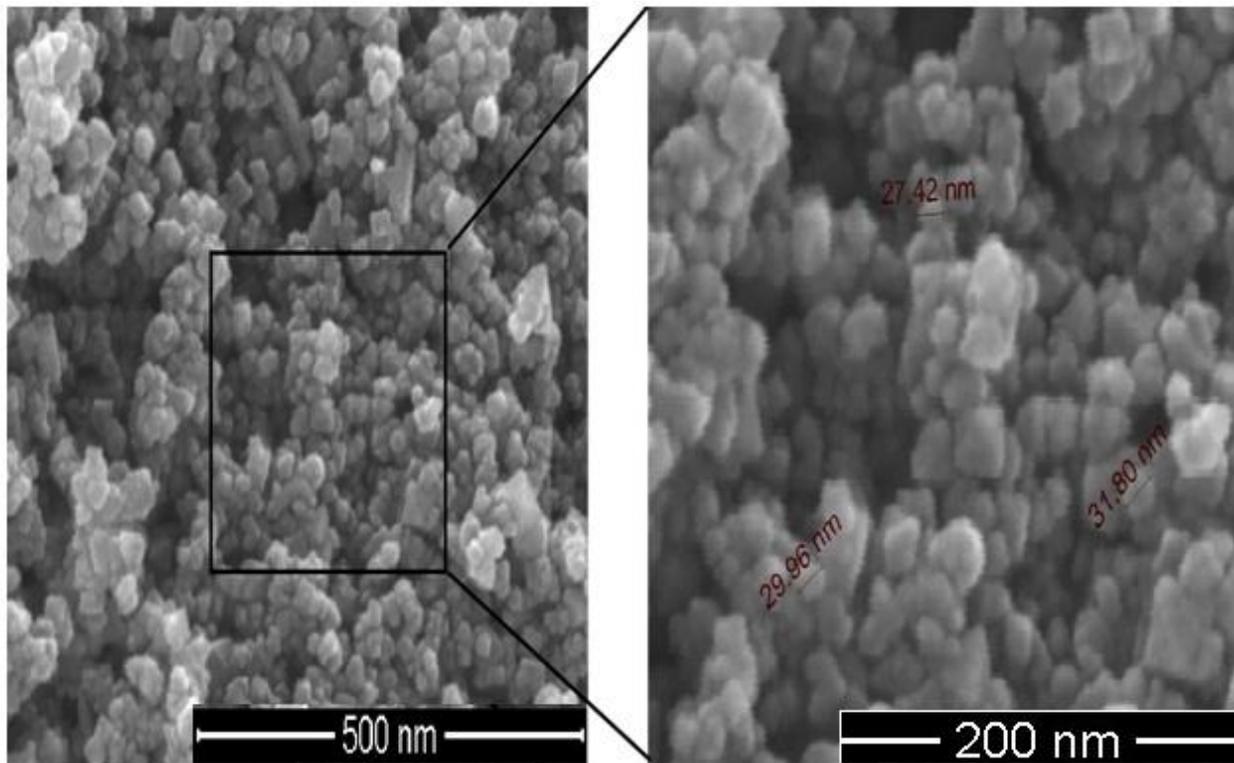


Figure 3.5: TGA data of polymer (A) and polymer/Fe₃O₄ nanocomposite (F-1, F-2 and F-3)

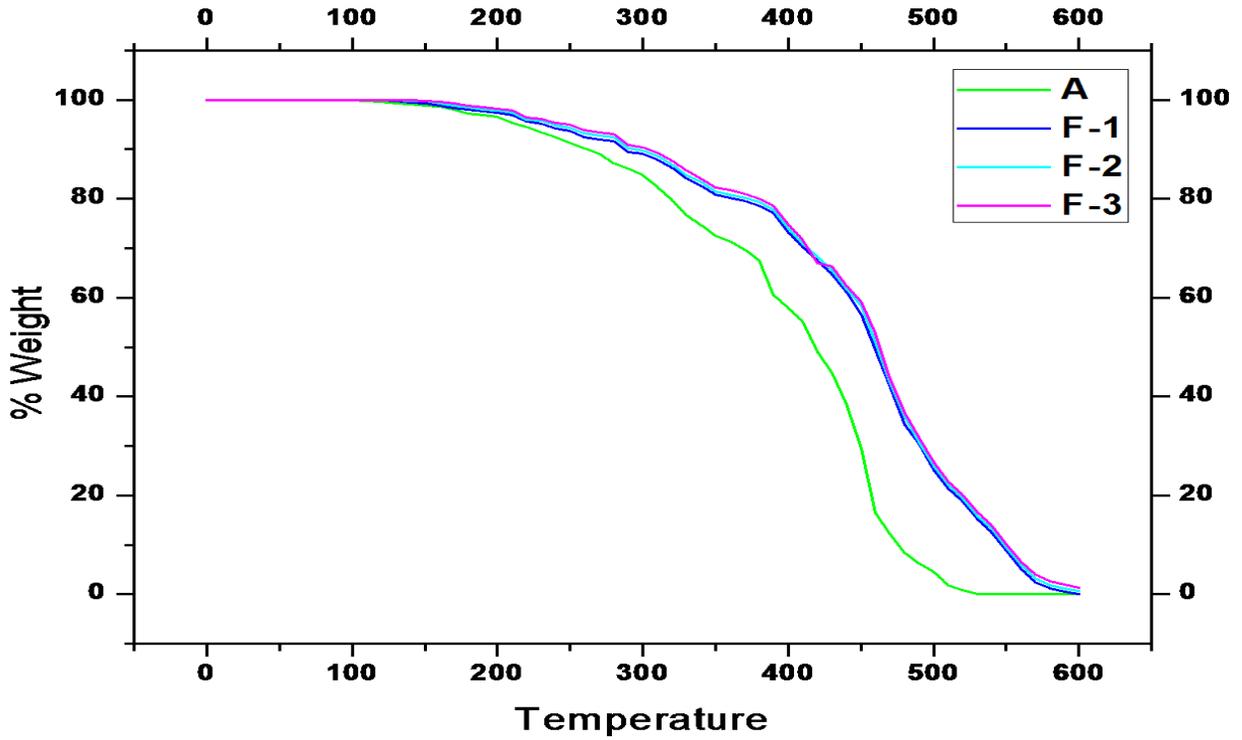


Figure 3.6: Plot of Viscosity index of the additives doped base oil with additive concentration

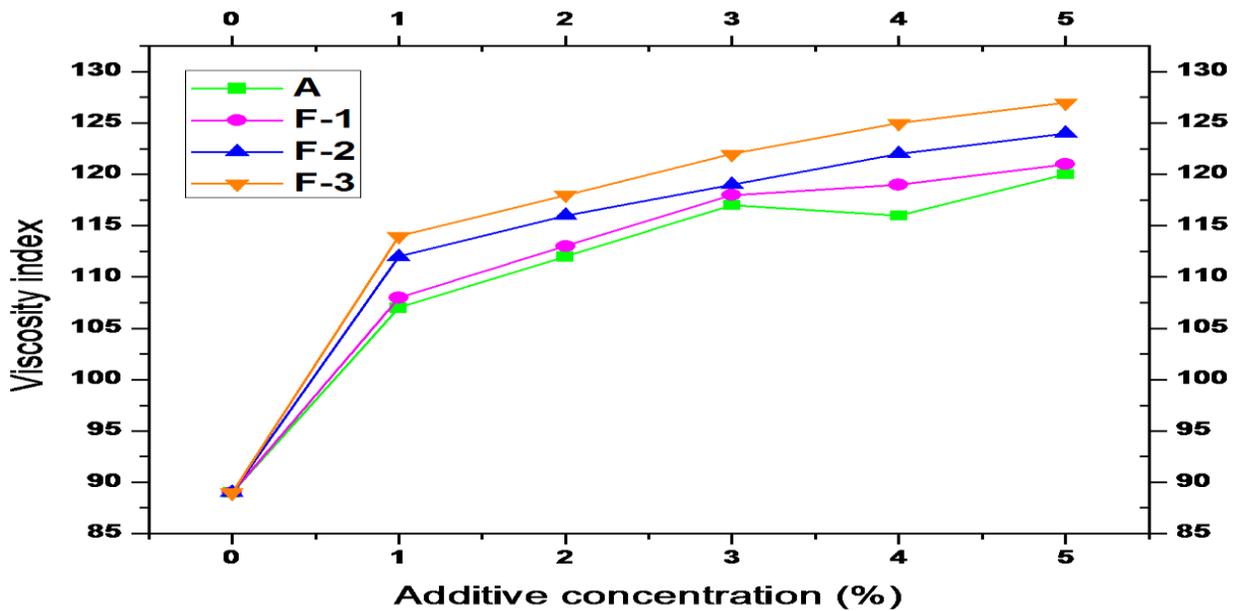


Figure 3.7: Plot of pour point of the additives doped base oil with additive concentration

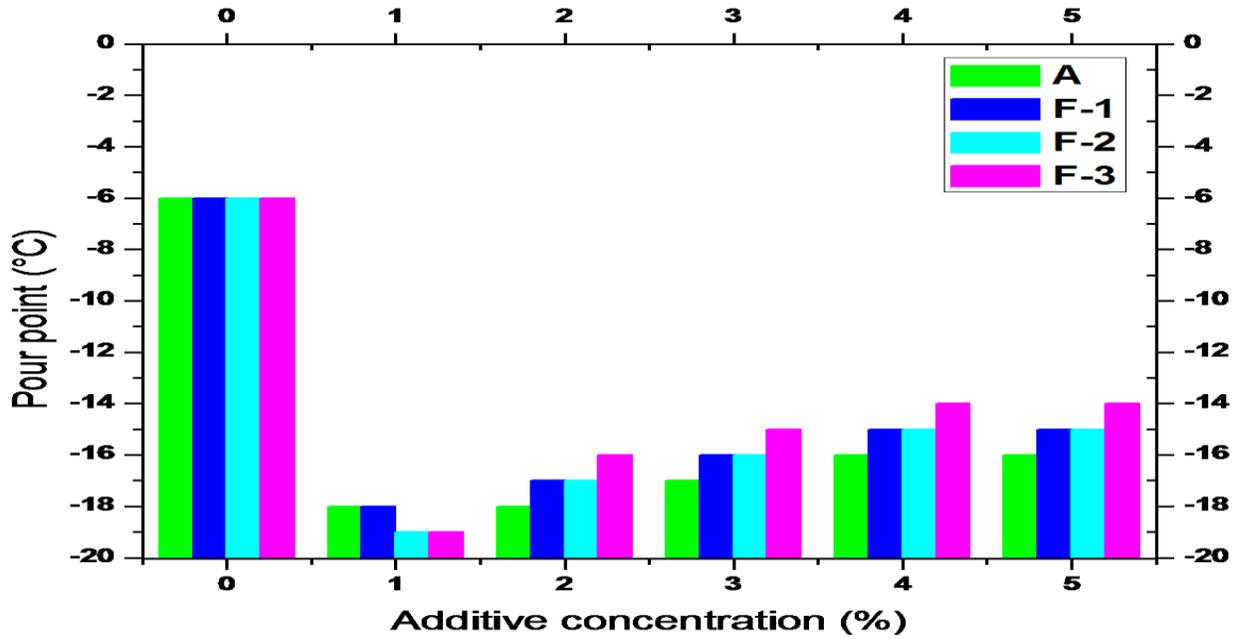


Figure 3.8: Wear scar diameter (WSD) of the lube oil blended with additives at different percentage (w/w)

