

Chapter II

Citral-Polyacrylate Based Biodegradable Lube Oil Additives

2.1.1. Introduction

The commercial synthetic acrylate –based additives are non-biodegradable and their widespread use has raised many environmental concerns. Due to increasing environmental pollution the direction towards the development of environmentally benign polymeric additives in the lubricant chemistry is increasing day by day. A recent demand for eco-friendly technology promoted the researchers to develop environmentally benign additives for the lubricant formulation. The use of biodegradable vegetable oils was known from a long time.¹⁻⁴ They not only offers such biodegradable property along with this they can offer significant performances as a pour point depressant, viscosity index modifier and anti-wear additives.

Keeping these mind and in continuation of our studies towards the development of chemical additives for lubricating oil, in the present investigation an attempt has been made to synthesize some copolymer of citral with acrylate ester through the process of copolymerization to getting an ideal blend of performance as well as eco-friendly chemistry. Our present investigation comprises the synthesis of homopolymer of dodecyl acrylate and copolymer of dodecyl acrylate with citral, their characterization, biodegradability test and their evaluation as a pour point depressant, viscosity modifier and anti-wear additives.

2.1.2. Experimental procedure

2.1.2.1. Materials and methods

Toluene, Hydroquinone and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd. Acrylic Acid (stabilised with 0.02% Hydriquinone monomethylether) and dodecyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Hexane was purchased from S D Fine Chem. Ltd. Methanol was purchased from Thomas Baker (Chemicals) Pvt. Ltd. Benzoyl Peroxide (BZP)

obtained from LOBA chemicals was recrystallised from CHCl_3 -MeOH before use. Citral was collected from local grocery shop. The base oils were collected from IOCL, Dhakuria, Kolkata, India. Rest of the materials was used as they were obtained without further purification. All samples were tested before their expiry dates.

2.1.2.2. Preparation of monomer: Esterification

Dodecyl acrylate was prepared by esterification reaction of acrylic acid and dodecyl alcohol with mole ratio of 1.1:1. The reaction was performed in a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone with respect to the reactants as polymerization inhibitor, and toluene as a solvent. The reaction was carried out under nitrogen atmosphere. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of water liberated during reaction to give the ester, dodecyl acrylate (DDA).

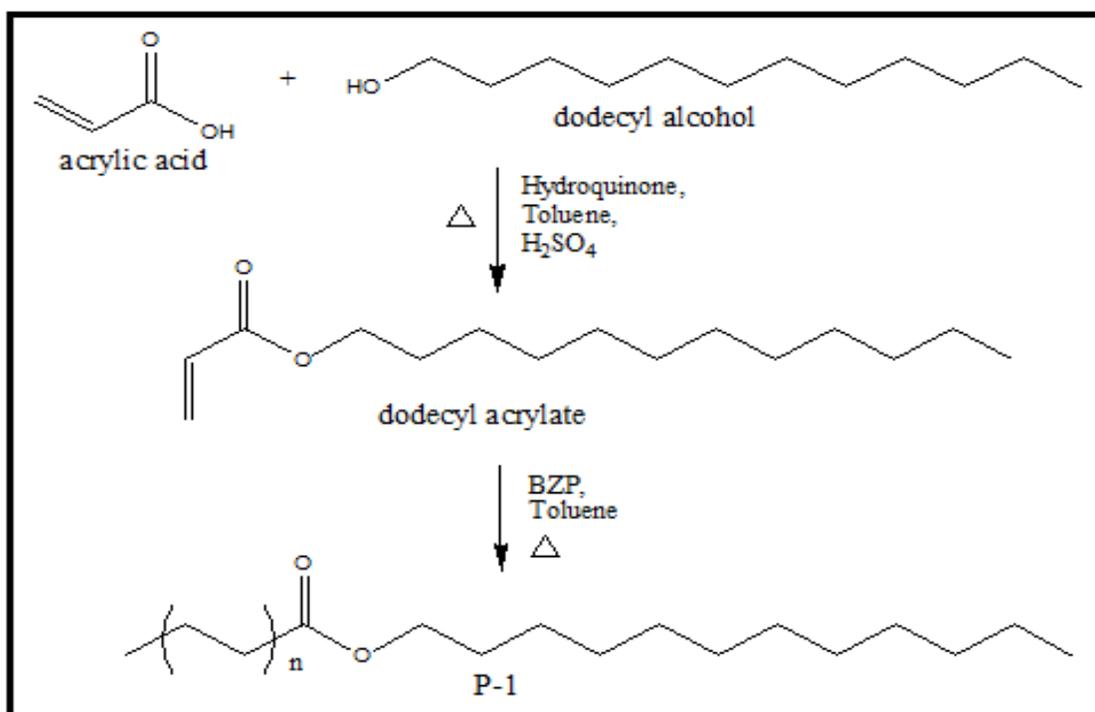
2.1.2.3. Purification of the monomer

In the purification process at first, desired amount of charcoal was added to the ester, followed by reflux for 3 h and then filtered. The filtrate was then washed repetitively with 0.5N sodium hydroxide solution to ensure complete removal of unreacted acid. Then to remove traces of sodium hydroxide, purified ester was washed several times with distilled water. The ester was then left on calcium chloride overnight and recollected by distillation under reduced pressure. This purified ester was then used in the polymerization process.

2.1.2.4. Preparation of homopolymer and copolymer

The polymerization was carried out in a four-necked round bottom flask furnished with a condenser, stirrer, thermometer and an inlet for the nitrogen insertion. Required amounts of dodecyl acrylate and initiator (BZP) were taken in the flask and toluene was also added as

solvent. The reaction temperature was controlled at 353 K for 6 hours. Then the reaction mixture was poured into methanol solvent with stirring to cease the polymerization and a precipitate was appeared. The precipitated homopolymer (P-1) was further purified by frequent precipitation of its hexane solution with methanol followed by drying under vacuum at 313 K. For the synthesis of copolymer a dropping funnel was used for the drop wise addition of required mass of citral in the R.B flask containing DDA, BZP and toluene. The addition was continued under homogeneous stirring for 2 hours. The copolymer of DDA and different percent composition of citral was designated as sample P-2, P-3 and P-4 respectively containing 5%, 10% and 15% citral with respect to DDA. The structures of the prepared polymers are shown in **scheme 1**.



Scheme 1: Preparation of dodecyl acrylate and poly dodecyl acrylate (P-1)

2.1.3. Measurements

2.1.3.1. Thermo gravimetric analysis

The thermal stability of the polymer samples was also determined on a Mettler TA- 3000 systems, at a heating rate of 10 K min⁻¹. All the samples were heated gradually from room temperature to 690 K in a platinum crucible.

2.1.3.2. Determination of molecular weight by GPC method

In GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were measured. 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.

2.1.3.3. Biodegradability analysis

The degree of biodegradability of the polymeric additives was tested by (i) disk diffusion method against fungal pathogens and by (ii) soil burial test as per ISO 846:1997. Polymeric samples recovered after the tests were verified by measuring weight loss and IR spectra was taken to observe any considerable shift of IR frequencies.⁵⁻⁷

2.1.3.3.1. Disc diffusion method

Culture media for fungal pathogens were prepared in Petri dishes by taking suitable amount of dextrose, agar agar and potato extract. All glass apparatus were autoclaved prior to use. Five fungal pathogens were used in this analysis namely *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA), *Colletotrichum gloeosporioides* (CG), and *Curvularia eragrostidis* (CE). The growth of fungal pathogens was confirmed by change in colour of the culture media from yellow to blackish. Specific amount of polymer samples (1g) were added in Petri dishes and incubated for 30 days at 310K in an incubated chamber. After 30 days, polymer

samples were recovered from culture media by chloroform, purified and dried in an open vessel.⁸ The weights of dried samples were taken and FT-IR were taken. The microbial degradation was verified by measuring the shift of IR frequency of the ester carbonyl after biodegradability test.

2.1.3.3.2. Soil burial test

The soil burial test was carried out as per ISO 846:1997 method. Specific amount (1g) of polymer samples were buried in soil collected from University campus (University of north Bengal) in a tray. Prior to use the relative humidity of the soil was adjusted to 50% - 60% and temperature was kept at 303K with a thermostat in a humidity chamber. The buried films were recovered after 60 days, washed with chloroform, purified and dried.⁹ The dried samples were weighed and their FT-IR spectra were recorded.

2.1.3.4. Performance evaluation as viscosity modifier

Viscosity index (VI) of the polymeric additives was determined in two paraffinic base oils (BO1 and BO2) 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.

2.1.3.5. Performance evaluation as PPD

The pour point depressant property of the prepared polymeric additives was determined in two base oils (BO1 and BO2) 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.

2.1.3.6. Performance evaluation as AW additives

The AW properties were assessed by Four-ball wear test apparatus according to ASTM D 4172-94 method ¹⁰ applying two different weight loads, 147 N and 392 N at 75°C for 30 min. with the rotational speed of the ring was 1200 rpm.

The physical properties of the base oils are depicted in **table 3.3**.

2.1.4. Results and discussion

2.1.4.1. Spectroscopic analysis

FT-IR spectrum (**figure 2.1(a)**) of homopoly dodecyl acrylate (P-1) showed absorption band at 1732 cm⁻¹ for the ester carbonyl stretching vibration along with other peaks at 1467, 1271, 1190, 1060 cm⁻¹. In the ¹H NMR spectra of P-1 showed broad singlet centred at 4.02 ppm due to the protons of -OCH₂ group. Methyl protons of dodecyl chain appeared between 0.81 ppm and 0.86 ppm and the absence of singlet between 5 ppm and 6 ppm implies the absence of any vinylic proton in the polymer and it is depicted in **figure 2.1 (b)**. In the ¹³C NMR spectrum of P-1, the carbonyl carbon appeared at 174.4 ppm along with other SP³ carbons appeared in the range of 65.03 to 10.66 ppm and it is showed in **figure 2.1 (c)**.

In the FT-IR spectrum of copolymers, the ester carbonyl appeared at 1731.71 cm⁻¹ along with a peak appeared at 1714.30 cm⁻¹ for aldehyde group of citral. Peak at 1165 cm⁻¹ is due to ester C-O stretching vibration and peak at 2854 cm⁻¹ is due to the aldehydic C-H. In the ¹H NMR of the copolymers, a multiplet in the range of 4.119- 4.402 ppm indicates the -OCH₂ protons. All the SP³ protons appear in the range of 1.259- 1.989 ppm. Two peaks at 5.343 ppm and 5.360 ppm are due to the ethylinic double bond in the citral part of the copolymer. A peak around 10 ppm is due to the aldehydic proton of citral in the copolymer. In the ¹³C NMR of copolymer, the peaks in the range of 167.70- 173.36 ppm indicates the presence of ester carbon and the peaks at 190.81 ppm due to the aldehydic group of citral in the copolymer. The -OCH₂ carbon peak appeared at 68.93

ppm and peaks in the range of 14.09- 34.05 ppm indicate all the SP³ carbons of copolymer and spectra are showed in **figure 2.2**.

2.1.4.2. Thermo gravimetric analysis

TGA data is represented in **table 2.4** for homo and copolymer of dodecyl acrylate. From the data it is found that, the copolymers (P-2, P-3 and P-4) are thermally more stable than the homopolymer (P-1). It was also found that, with increasing citral concentration in the feed, the thermal stability increases.

2.1.4.3. Analysis of biodegradability test

Table 2.3 represents the biodegradability test results obtained by using disk diffusion method and soil burial test. All the copolymers were found to be significantly biodegradable against the fungal pathogen, *alterneria alernata* but the homopolymer was not found to be biodegradable at all. It was further confirmed by the shift of IR frequency of the ester carbonyl from 1731 cm⁻¹ to 1712 cm⁻¹, 1716 cm⁻¹ after the biodegradability test. It was also found that extent of weight loss in disc diffusion method was higher than soil burial test.

FT-IR spectra of the polymer samples, before and after disc diffusion test, were also compared (**figure 2.3, 2.4, 2.5 and 2.6**) to confirm the biodegradable nature of the prepared copolymers. IR peaks of sample P-2 (**figure 2.4**) at 1454, 1161cm⁻¹ has shifted considerably after disc diffusion test. The other copolymer samples (P-3 and P-4) also showed similar pattern of IR shift (**figure 2.5and figure 2.6**).

2.1.4.4. Efficiency of additives as viscosity modifier

The Viscosity index values of the additives doped base oils of all the polymers (P-1, P-2, P-3 and P-4) are presented in the **table 2.5**. Table showed that with increase in the concentration of polymer in the base oils (type BO1 and type BO2) there is a gradual increase of VI values (up to 4%). The increase of concentration of the polymer also leads to an increase in total volume of polymer micelles in the oil solutions. Consequently, a high concentration of polymer will impart a high viscosity index rather than a low concentration of the same polymer.

2.1.4.5. Efficiency of additives as pour point depressant

The experimental data for the PPD values of samples containing different additive concentrations ranging from 1 wt% to 5 wt% are grouped in **figure 2.7(a)** (in the base oil type BO1) and in **figure 2.7(b)** (in the base oil type BO2) which indicates that the prepared additives are efficient as pour point depressant and the pour point values of all the polymer decreases with increase in concentration of the additive. The pour point values of all the copolymers (P-2, P-3 and P-4) are more or less same but lower than the homopolymer (P-1). Hence all the copolymers were excellent pour point depressant additives.

The efficiency of the polymers as effective pour point depressant was also assessed through photo micrographic analysis. The wax crystal size is significantly decreased from large crystal structure (base oil) to very small dots dispersed in the oil phase of the lube oil in case of all the polymeric additives.¹¹ The photo micrographic images (PMI) of all the samples and base oil were depicted in **figure 2.8**

2.1.4.6. Efficiency of additives as AW agents

Decrease in WSD (mm) with increasing concentration of the additives was found in both the base stocks and under both load condition but the decrease was generally greater under 40 kg

load condition (**figure 2.9**), that implies that additives were not so effective at higher load condition. However, beyond 5% additive concentration no significant AW performance was observed. All the copolymers showed better AW property than homopolymer (P-1), this is because of the presence of aldehydic functionality additional to ester functionality of the copolymers.^{5, 6} Hence, the copolymer (P-4), which contain larger proportion citral unit into the polymer matrix showed better performance as AW additives.

2.1.5. Conclusion

The homopolymer (P-1) as well as copolymers (P-2, P-3 and P-4) were showed excellent PPD and AW property. The copolymer showed excellent biodegradable property. Thus it can be concluded that the copolymers can be used as biodegradable PPD and AW additives for lubricating oil.

2.1.6. References

References are given in BIBLIOGRAPHY under Chapter II of Part II (PP 165-166).

2.1.7. Tables and figures

Table 2.1: Properties of base oils

<i>Properties</i>	<i>BO1</i>	<i>BO2</i>
Density(kg.m ⁻³) at 313K	839.98	918.68
Viscosity at 313K	5.97×10 ⁻⁶	20.31×10 ⁻⁶
Viscosity at 373K	1.48×10 ⁻⁶	3.25×10 ⁻⁶
Viscosity index	80.05	89.02
Cloud point (°C)	-10	-8
Pour point (°C)	-3	-6

Table 2.2: Molecular weight characteristics of the samples

<i>Polymer sample</i>	<i>M_n</i>	<i>M_w</i>	<i>PDI</i>
P-1	33789	38412	1.14
P-2	31854	37407	1.17
P-3	25118	30574	1.22
P-4	24272	29872	1.23

Where P-1: Homo poly dodecyl acrylate, P-2: copolymer of dodecyl acrylate+ 5% citral, P-3: copolymer of dodecyl acrylate + 10% citral, P-4: copolymer of dodecyl acrylate + 15% citral

Table 2.3: Results of biodegradability test by disc diffusion method and soil burial test for polymeric additives

<i>Polymers</i>	<i>Disc diffusion method</i>	<i>Soil burial test</i>
	<i>Alternaria alternata</i> Wt. loss (%)	Microorganism Wt. loss (%)
P-1	00	00
P-2	31.60	16.30
P-3	37.70	23.20
P-4	40.30	25.70

Table 2.4: TGA data of polymer samples

<i>Polymer Samples</i>	<i>TGA data</i>	
	Decomposition Temperature (K)	Percent weight loss (PWL)
P-1	513/606	16/96
P-2	523/616	14/95
P-3	533/616	15/92
P-4	543/626	15/95

Table 2.5: Viscosity index value of additive doped Base oil

<i>Sample</i>	<i>VI in BO1</i> <i>Concentration of the additives, % in w/w</i>						<i>VI in BO2</i> <i>Concentration of the additives, % in w/w</i>					
	0	1	2	3	4	5	0	1	2	3	4	5
P-1	80	121	122	123	125	132	89	107	112	117	116	120
P-2	80	113	114	115	119	127	89	101	112	112	119	121
P-3	80	112	113	118	120	125	89	107	106	113	115	117
P-4	80	111	113	119	123	124	89	106	105	112	116	118

Where, P-1: Homo poly dodecyl acrylate, P-2: copolymer of dodecyl acrylate+ 5% citral, P-3: copolymer of dodecyl acrylate + 10% citral, P-4: copolymer of dodecyl acrylate + 15% citral

Figure 2.1(a): FT-IR spectra of homo poly dodecyl acrylate

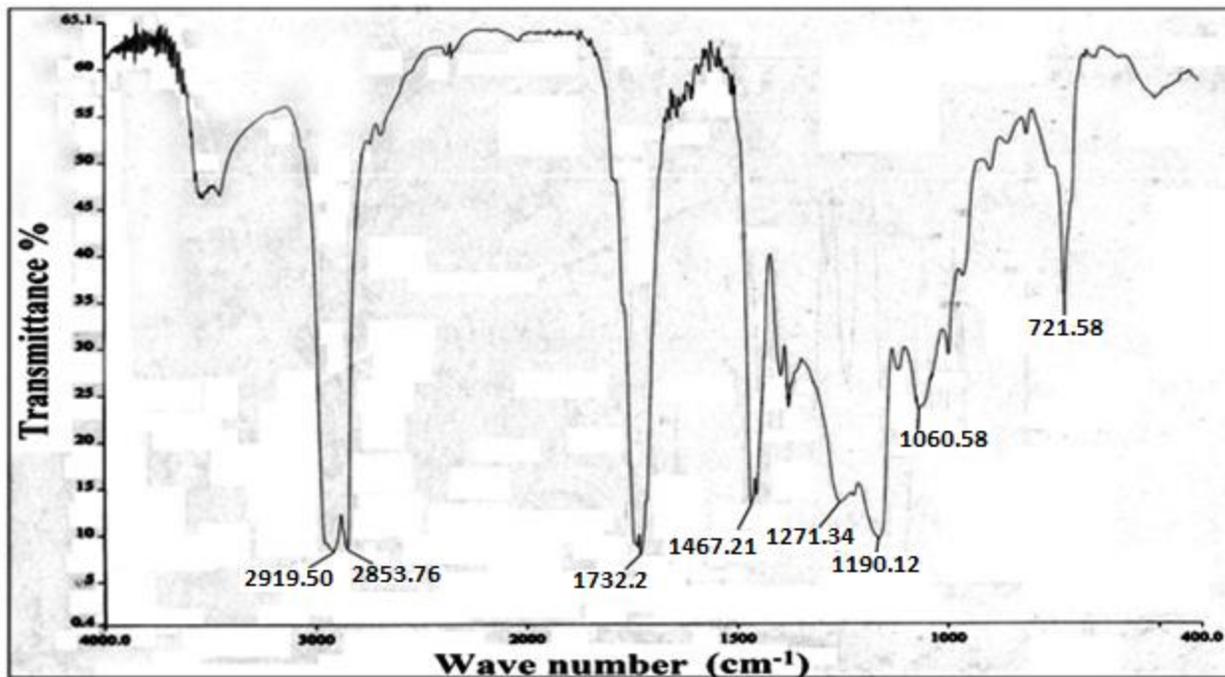


Figure 2.1(b): ¹H NMR spectra of homo poly dodecyl acrylate

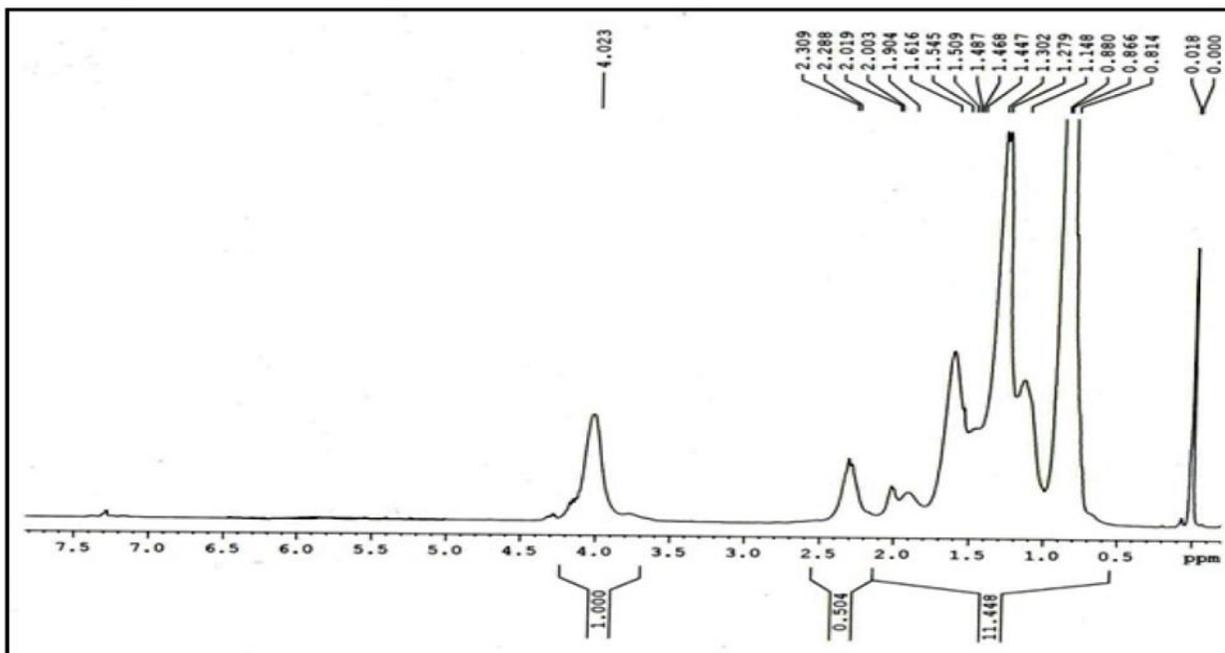


Figure 2.1(c): ^{13}C NMR spectra of homo poly dodecyl acrylate

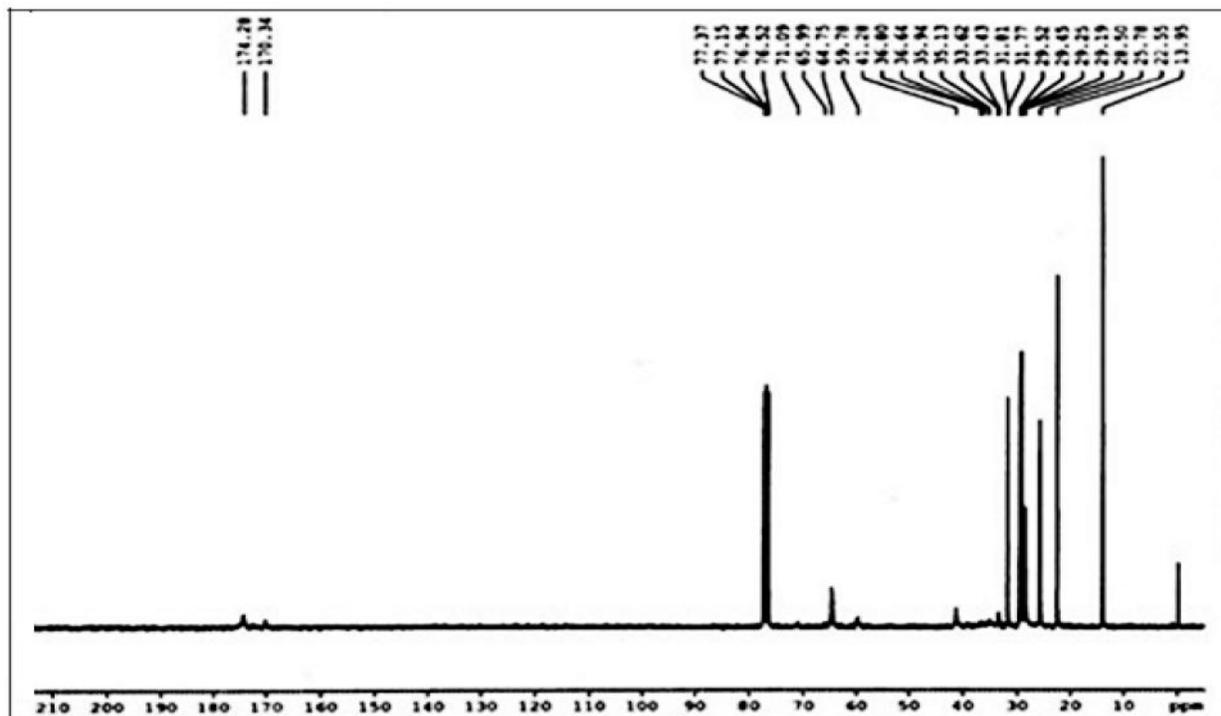


Figure 2.2(a): FT-IR spectra of copolymer of dodecyl acrylate with citral

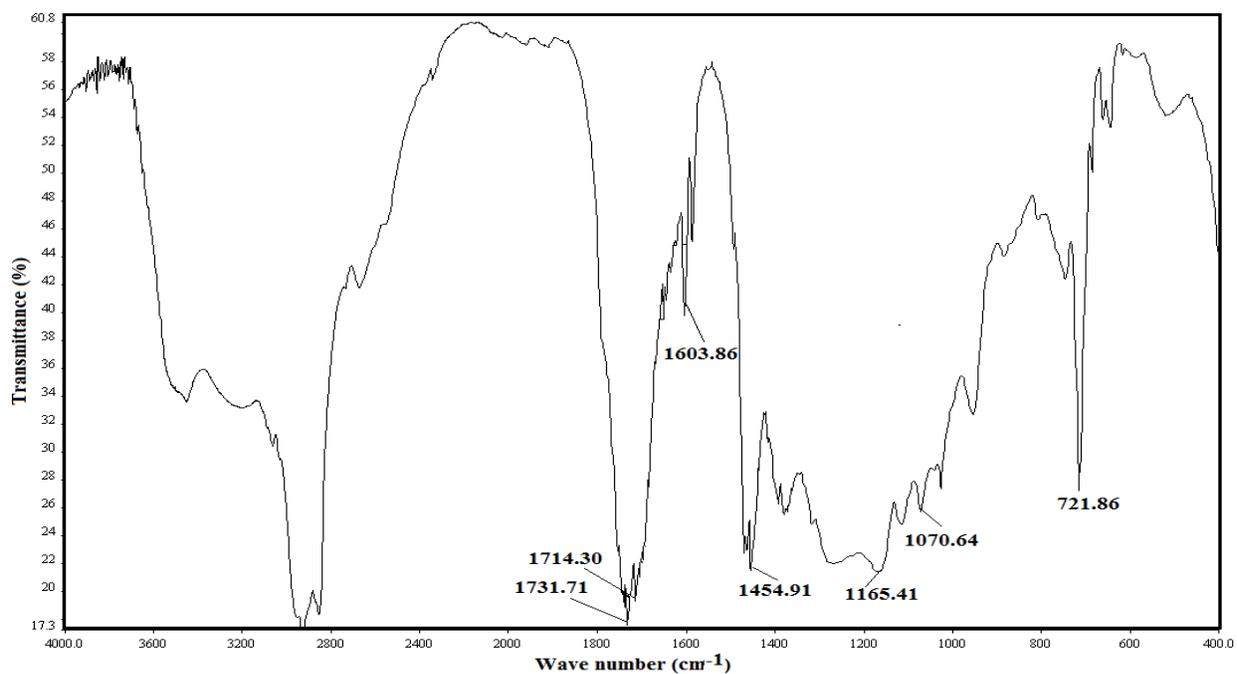


Figure 2.2(b): ^1H NMR spectra of copolymer of dodecyl acrylate with citral

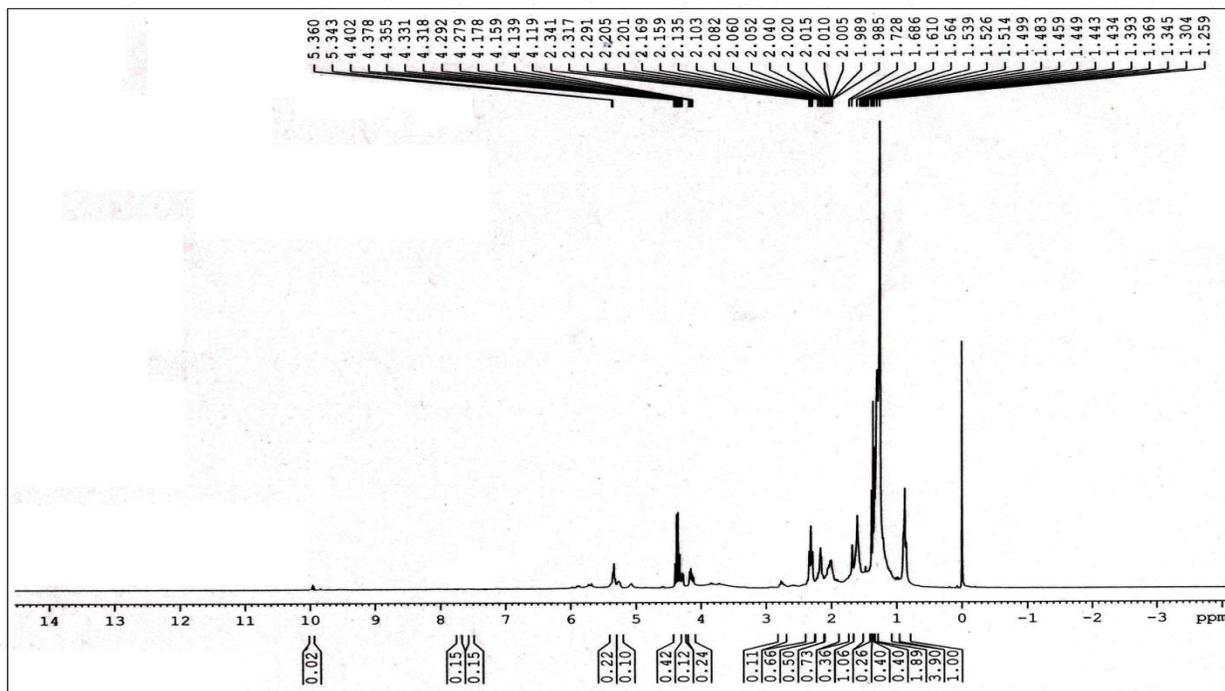


Figure 2.2(c): ^{13}C NMR spectra of copolymer of dodecyl acrylate with citral

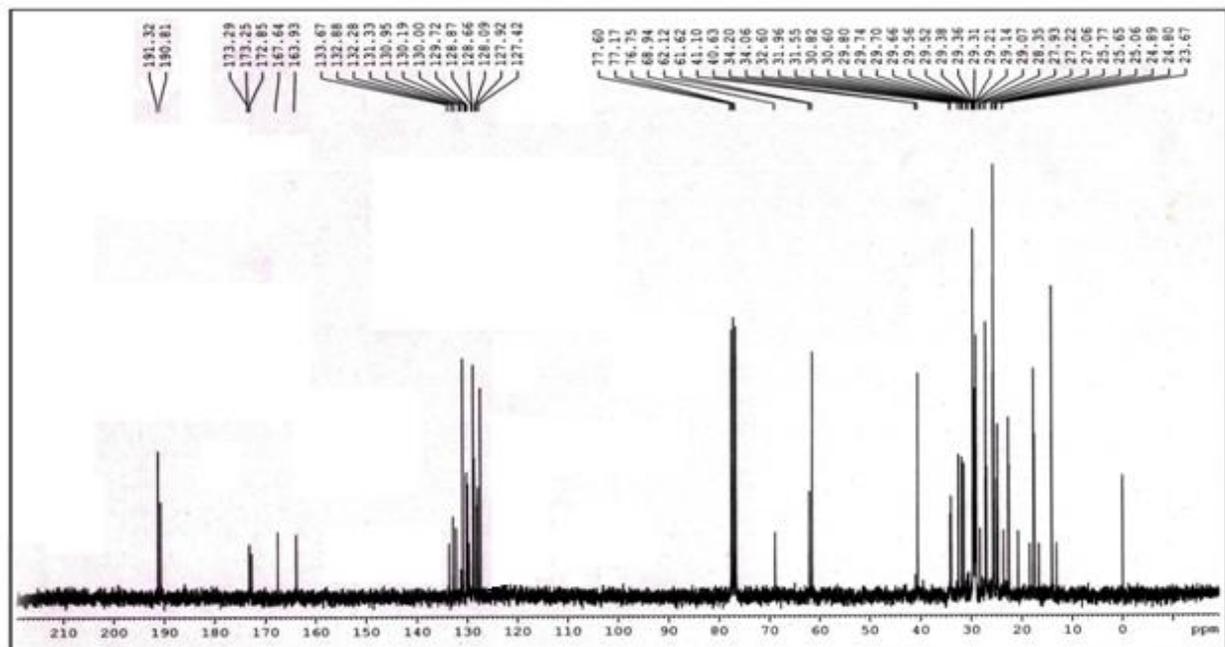


Figure 2.3: Comparative FT-IR spectra of P-1 before and after disc diffusion test

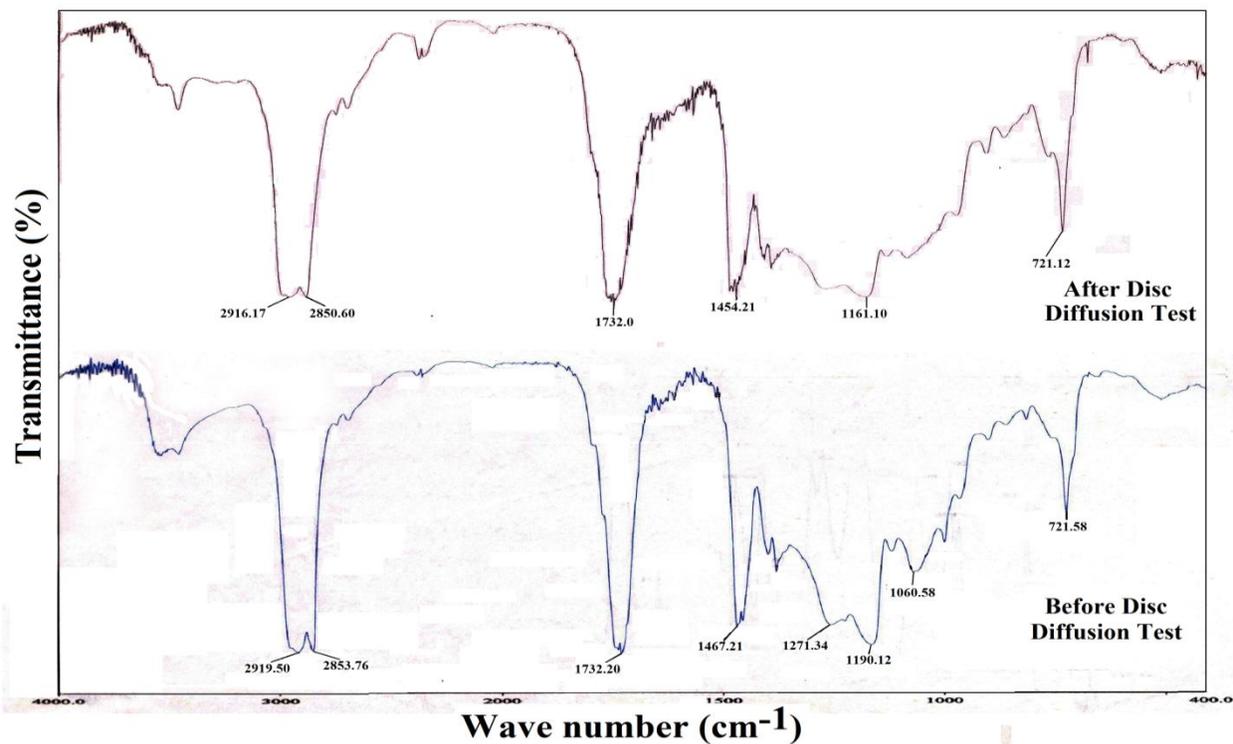


Figure 2.4: Comparative FT-IR spectra of P-2 before and after disc diffusion test

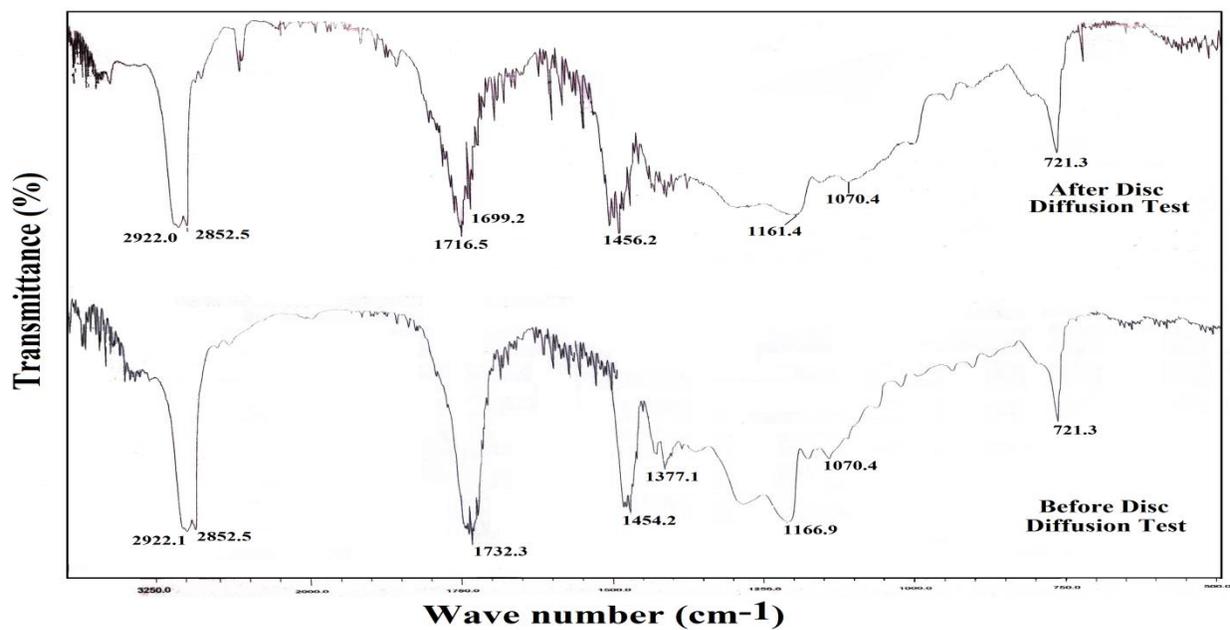


Figure 2.5: Comparative FT-IR spectra of P-3 before and after disc diffusion test

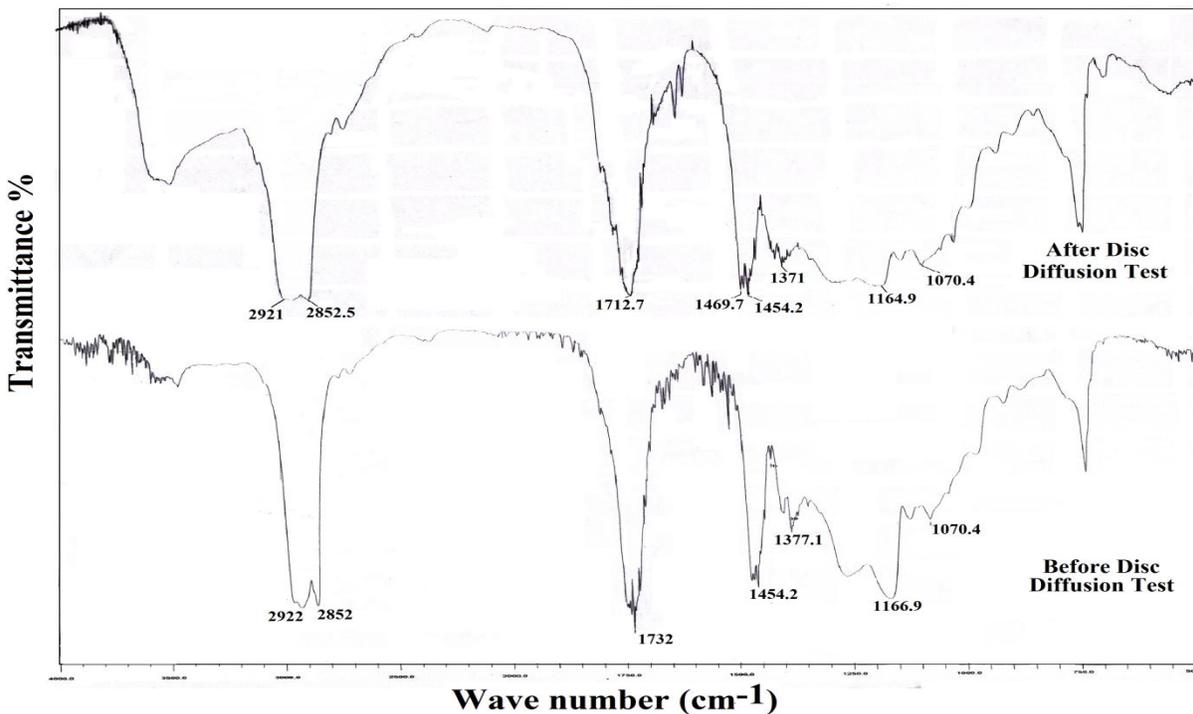


Figure 2.6: Comparative FT-IR spectra of P-4 before and after disc diffusion test

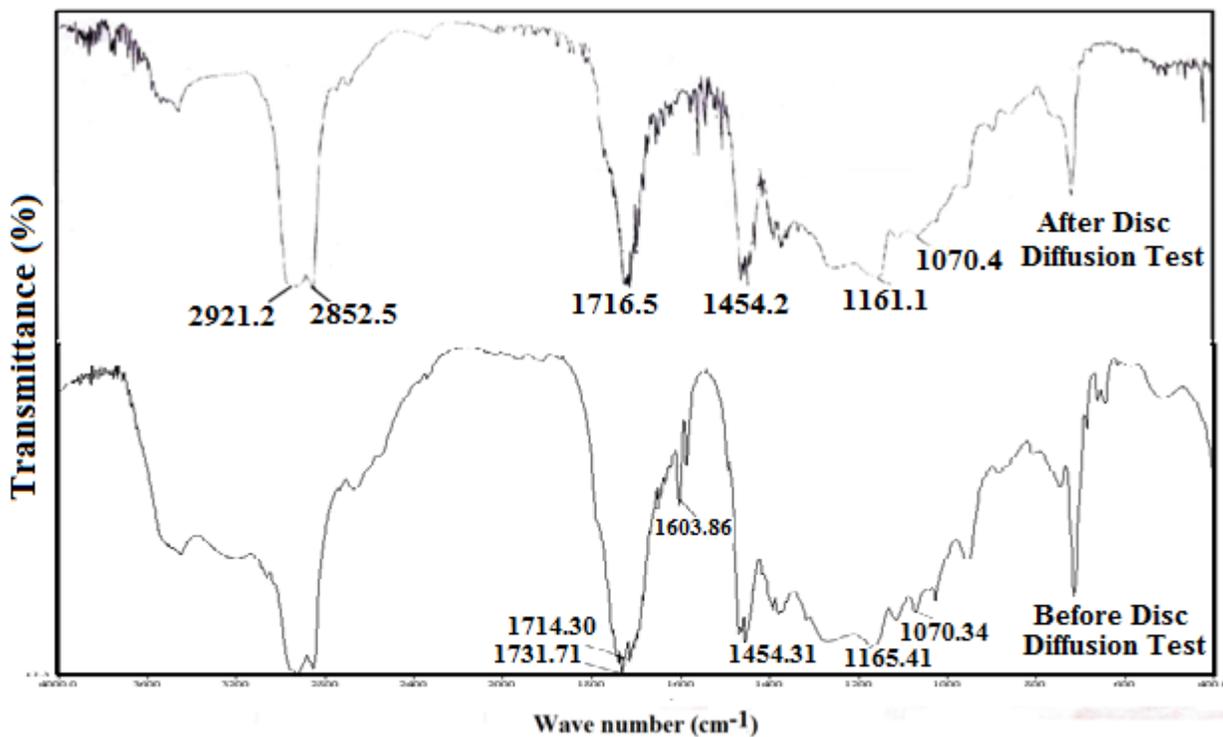


Figure 2.7(a): Plot of pour point of formulated lubricants as a function of additives concentration (w/w) in base oil BO1

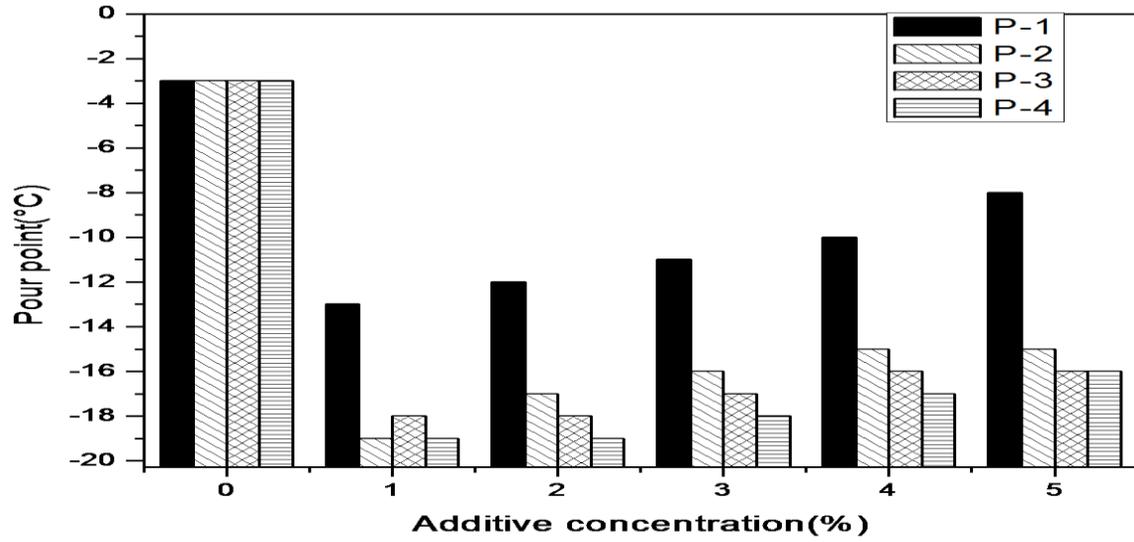


Figure 2.7(b): Plot of pour point of formulated lubricants as a function of additives concentration (w/w) in base oil BO2

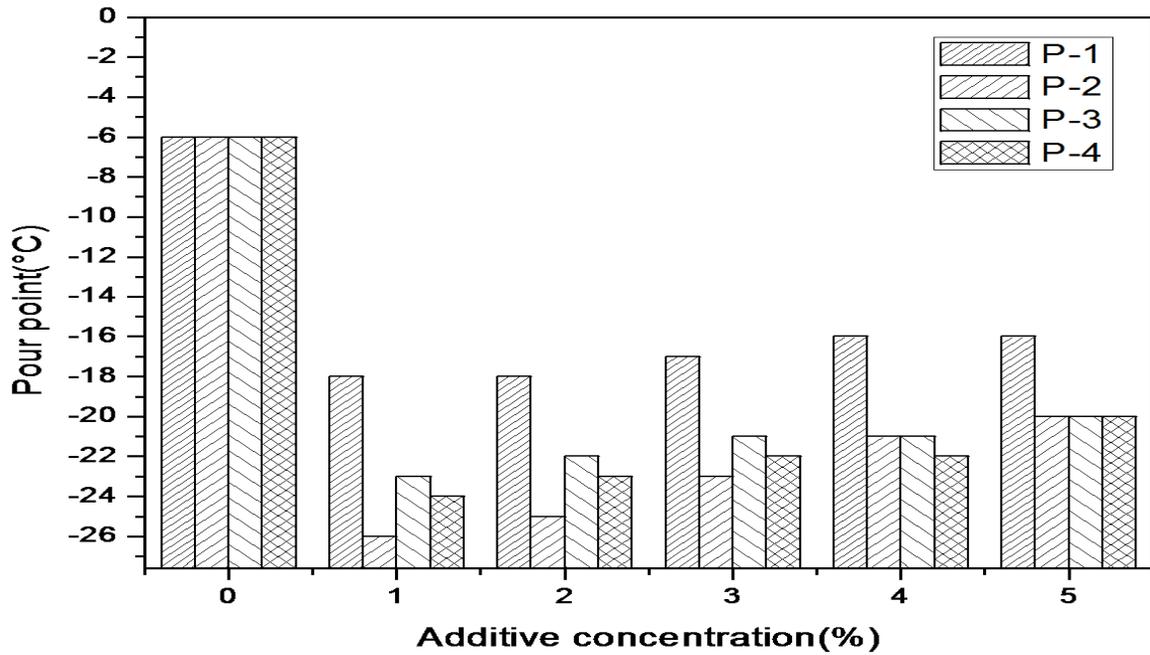


Figure 2.8: Photomicrographic images of base oil (left side) and additive (P-1, P-2, P-3 and P-4) doped base oil (right side)

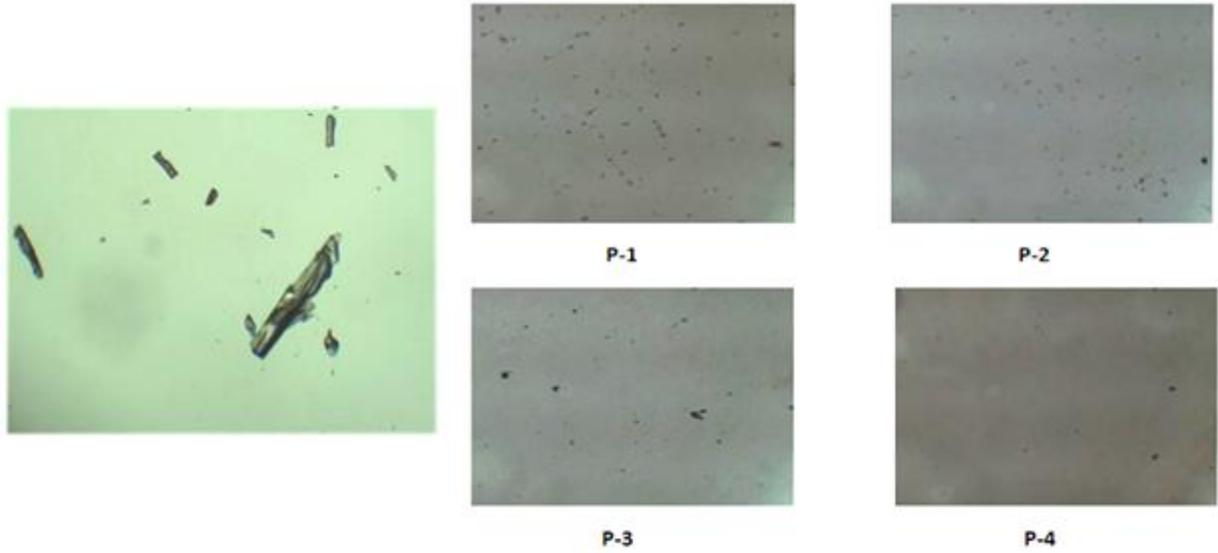


Figure 2.9(a): Plot of wear scar diameter vs. additive concentration in base oil BO1 at 20 kg load condition

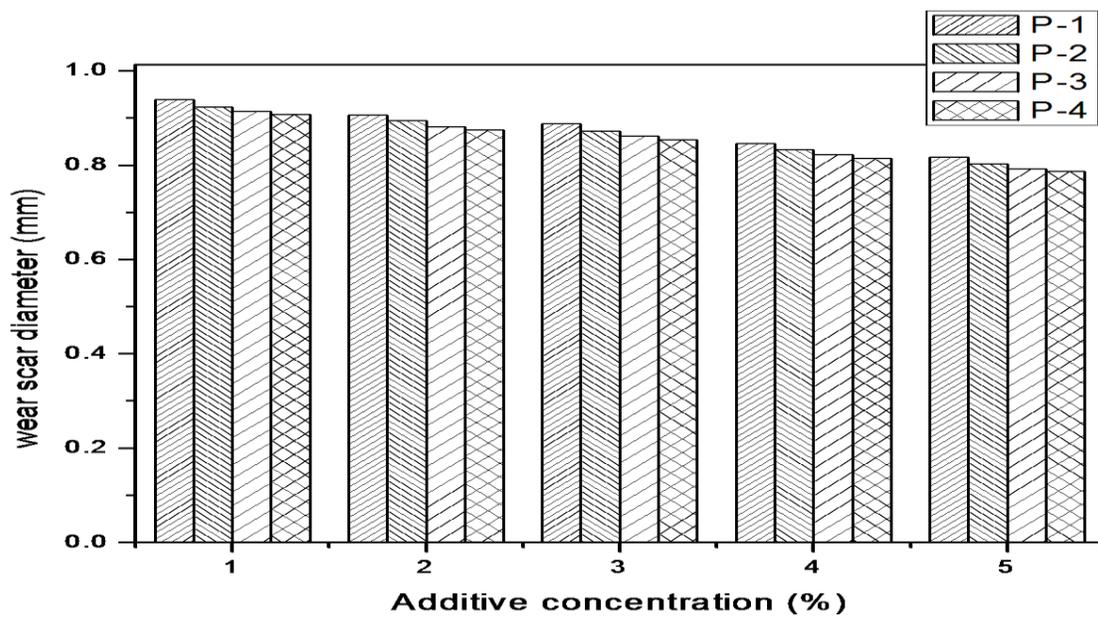


Figure 2.9(b): Plot of wear scar diameter vs. additive concentration in base oil BO1 at 40 kg load condition

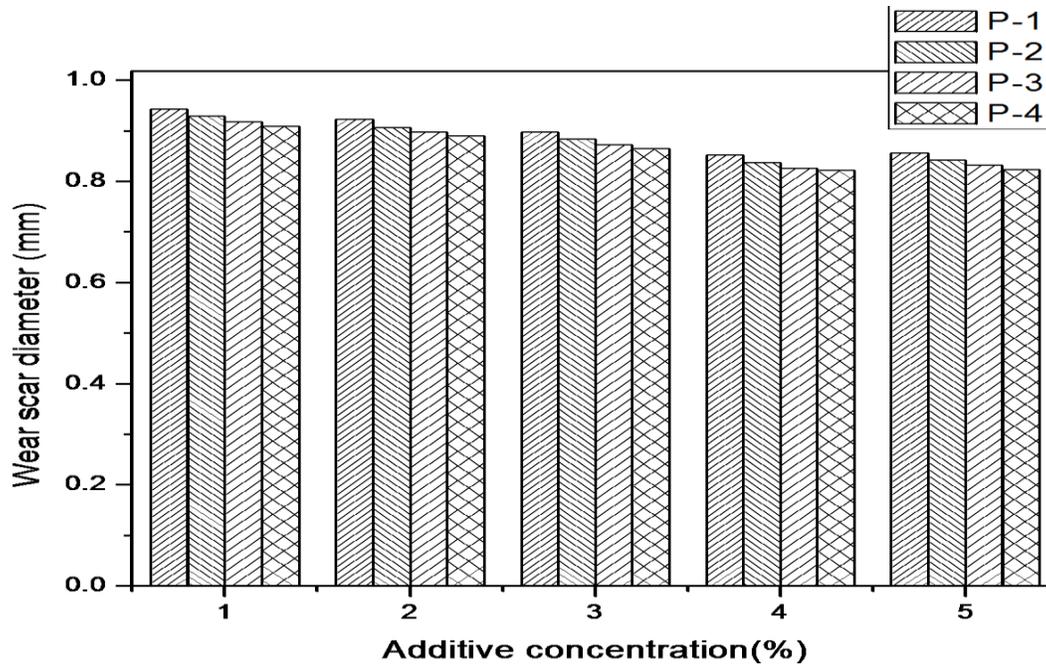


Figure 2.9(c): Plot of wear scar diameter vs. additive concentration in base oil BO2 at 20 kg load condition

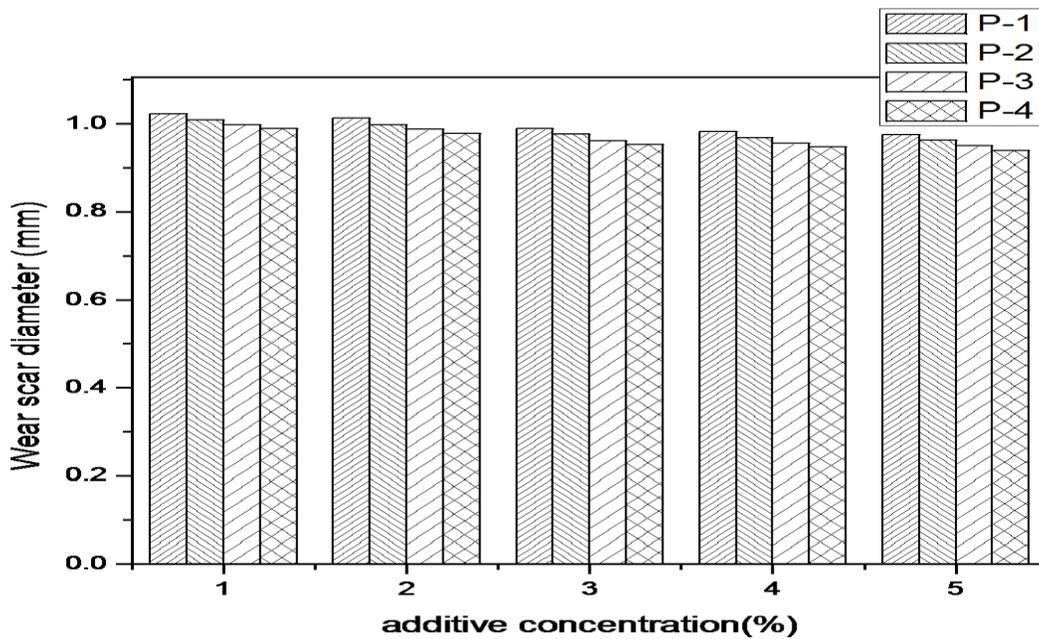


Figure 2.9(d): Plot of wear scar diameter vs. additive concentration in base oil BO2 at 40 kg load condition

