Chapter III

Copolymer of Rice bran oil with Decyl acrylate and 1-decene as Lube Oil Additives

2.2.1. Introduction

Lubricant oil is well known to reduce the friction between two sliding bodies in contact and thus reducing possible wear and damage to the surface of the moving bodies. In addition to base fluid or base oils they contains about 10–20% of additive package. Viscosity index improver (VII), pour point depressants (PPDs), detergents, dispersants, anti-wear, extreme pressure, antioxidant and corrosion inhibitors are the examples of generally used lubricant additives. Among them most important are PPDs [1]and VMs.[2]

Although lots of additives are in use as PPDs[1, 3, 4] and VMs.[2, 5] But due to potent toxicity most of them are not environmentally benign. Consequently, the development of eco-friendly lubricants has become the major concern of the present decade. Plant oils are known to act as promising base fluid for biolubricants because of their excellent lubricity, biodegradability, and viscosity-temperature characteristics. On the other hand, poor thermal stability has rendered restricted application of them in the lubricant formulations. In consideration of that, their copolymerization with acrylate monomers may be undertaken for the development of some novel polymeric additives in anticipation that they may be used as environmental friendly additives for lubricant formulation.

With this background the present work is intended for the synthesis of copolymer of rice bran oil–1-decene and rice bran oil–decyl acrylate (DA) followed by characterization of them (by thermo gravimetric, gel permeation chromatography [GPC], and spectral analysis) and finally evaluation of their additive performance (as PPDs and VMs) in lubricating oil.

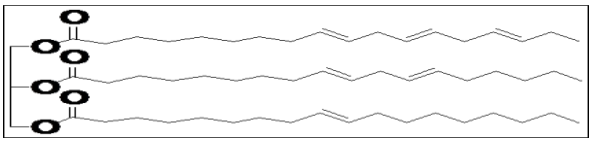


Figure 2b: General structure of triglyceride ester present in Rice bran oil

2.2.2. Experimental procedure

2.2.2.1. Materials and methods

Hydroquinone, Toluene, and H_2SO_4 were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (stabilized with 0.02% hydroquinone monomethyl ether) and decyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Hexane and 1-decene was purchased from S D Fine Chem. Ltd. Rice bran oil was collected from local market and methanol was purchased from Thomas baker Pvt. Ltd. and were used as received. Benzoyl peroxide (BZP) was obtained from LOBA chemicals, which was recrystallized from $CHCl_3$- MeOH before use. Specifications of the chemicals are depicted in Table 1. Two different kinds of base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in Table 2.

2.2.2.2. Esterification: Preparation of monomer

The preparation of decyl acrylate ester from acrylic acid and decyl alcohol was performed by following the procedure described in chapter II of part I and this was also reported in our previous publication.[6]

2.2.2.3. Purification of prepared monomer

The prepared ester was purified according to the procedure described in chapter II of part I.

2.2.2.4. Preparation of copolymers

The rice bran oil–DA and rice bran oil-1-decene copolymers were prepared by using different concentrations of DA and 1-decene (10%, 20%, and 30% [w/w]) with rice bran oil, P-1 to P-3, and P-4 to P-6, respectively. The radical polymerization was carried out following the method as described in chapter II of part II and this was also reported in our previous publication.[7]

2.2.3. Measurements

2.2.3.1. Spectroscopic measurements

The IR spectra of the samples were recorded on a Perkin Elmer FT-IR 8300 spectrophotometer using 0.1 mm KBr cells at room temperature. The NMR (^{13}C and ^{1}H) spectra were recorded in a 300 MHz Bruker Avance FT-NMR spectrometer using 5mm BBO probe. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) was used as reference material.

2.2.3.2. Thermo gravimetric analysis

The thermo grams of the polymer samples in air were obtained on a Mettler TA – 3000 system, at a heating rate of 10K min^{-1}. The samples were heated continuously in a platinum crucible from room temperature to 620 K.

2.2.3.3. Determination of molecular weight by GPC

In GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were measured and 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.[7] The results are represented in table . The whole process was also reported earlier from our laboratory.

2.2.3.4. Biodegradability analysis

The biodegradability of the polymers was tested by (i) disk diffusion method against five different fungal pathogens and by (ii) soil burial test as per ISO 846:1997 method. The samples were recovered after the test for determination of any weight loss. FT IR spectra of the recovered samples were recorded to examine change in IR frequency before and after biodegradability test. Again GPC analysis of the recovered polymers was carried out in an anticipation to see any change of Mn and Mw after biodegradation.

2.2.3.4.1. Disc diffusion method

Disc diffusion test was performed in presence of five fungal pathogens namely *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA), *Colletotrichum gloeosporioides* (CG), and *Curvularia eragrostidis* (CE) as described in Chapter II of Part II and the process was also reported earlier from our laboratory.[5]

2.2.3.4.2. Soil burial test

The soil burial degradation test of polymer sample films was performed as per ISO 846:1997 method according to the procedure described in chapter II of part II and the process was also reported earlier from our laboratory.[5]

2.2.3.5. Evaluation of viscosity index of the prepared additives in lube oil

The viscosity index of the polymer samples was evaluated in two base oils (BO1 and BO2) according to the ASTM D2270 method. The whole procedure is already described in Chapter II of Part I and it was also reported earlier from our laboratory.[8]

Five different concentrations (1 wt% to 5 wt %) of the sample solutions were used to examine the consequence of additive concentration on VI.

2.2.3.6. Evaluation of pour point of the additives in lube oil

The pour point depressant properties of the prepared polymers were tested in two base oils (BO1 and BO2) on a Cloud and Pour Point Tester model WIL-471(India) according to ASTM D 97 method.

Five different concentrations (1 wt% to 5 wt %) of the polymer samples were employed to compare additive concentration with pour point effectiveness.

2.2.4. Results and discussion

2.2.4.1. Spectroscopic analysis

FT-IR spectra of copolymer of rice bran oil–DA showed absorption at 1733cm^{-1} for the ester C-O stretching vibration along with other peaks at 1457, 1244, and 1171 cm^{-1} and a peak at 723.3 cm^{-1} was due to C-H bending. In its ^{1}H NMR spectra, the polymer exhibited a broad singlet ranging between 4.11 and 4.31 ppm due to the -OCH_2 protons of rice bran oil and DA along with the –CH_3 protons ranging between 0.86 and 0.88 ppm and –CH_2 protons ranging between (1.25 and 1.61) ppm. The synthesis of the copolymer was further confirmed by the nonappearance of sp^2 hydrogen in its ^{1}H NMR and sp^2 carbon in ^{13}C NMR spectrum, respectively and spectra are showed in **figure 2.10**

FT-IR spectra of copolymer of rice bran oil–1-decene exhibited absorption at 1732 cm^{-1} for the ester C-O stretching vibration along with other peaks at 1456, 1378, 1244, 1174, and 724 cm^{-1}. In its ^{1}H NMR spectra, the polymer exhibited a broad singlet ranging between 4.11 and 4.3 ppm owing to the proton of - OCH_2 group of RBO along with the –CH_3 protons at 0.88 ppm and – CH_2 protons spanning between 1.26 and 1.62 ppm. The synthesis of the copolymer was further verified by the nonappearance of sp^2 hydrogen and sp^2 carbon in its ^{1}H and ^{13}C NMR, respectively and spectra are showed in **figure 2.11**

2.2.4.2. Thermo gravimetric analysis (TGA)

Figure 2.14 represents a plot of TGA data which shows a comparison between the thermal stability of rice bran oil–DA and rice bran oil–1-decene copolymers. The analysis discloses that for both set of polymers, thermal stability increases with increasing concentration of 1-decene and DA in the feed and the copolymers of rice bran oil + DA are more stable than the corresponding copolymers of rice bran oil +1-decene.

2.2.4.3. Analysis of biodegradability test

Both sets of copolymers showed significant weight loss against fungal pathogens, *Calletotricheme camellia* and *Alternaria alternata* after Disc diffusion test (**table 2.8a**). Even though the extent of weight loss was less in Soil burial test (**table 2.8b**), the results are still considerable. Again the degradation result was better for Rice bran oil-DA copolymers. The copolymer of 10% Rice bran oil and DA (P-1) found to endure highest weight loss in both the biodegradability tests. Moreover there was considerable shift in molecular weight of the copolymer samples after Disc diffusion test. The result of GPC analysis of the polymer samples before and after biodegradability test is depicted in **table 2.9**. FT-IR spectra of copolymer samples recovered after disc diffusion test were compared with respective spectra before the test and the results are compiled in **figure 2.12 and 2.13**

2.2.4.4. Efficiency of copolymers as viscosity index improver (VII)

The VI values of copolymers in two base oils (determined in six different concentrations) tabulated in **table 2.11** reveals that in both the base oils the values are greater for rice bran oil–DA copolymers than that for respective rice bran oil–1-decene copolymers and for DA copolymers, the VI value increases with increasing RBO concentration in the feed, and similar tendency is also observed for copolymers of RBO–1-decene. This consequence may be explained on the basis of the molecular weight of the polymers. Again, VI increases with increase in concentration of the polymers in solution. The reason may be that although the viscosity of the lube oil gets decreased at higher temperature, the polymer molecules may effectively counterbalance this reduction in viscosity by thickening the oil changing its shape from tight coil to expanded one due to increased polymer-solvent interaction. This in turn increases viscosity of the solution. Again, a higher polymer concentration means increase in total

volume of polymer coils in the solution which imparts a higher VI compared to a low concentrated polymer solution.[2, 5]

2.2.4.5. Efficiency of copolymers as pour point depressant

The pour point (PP) values of the polymers in both the base oils are tabulated in **table 2.10**, which indicates that, their PPD efficiency increases (up to a certain limit) with increasing concentration of the polymer in base oils. Comparison among the PP values indicates that the efficiency of the polymers as PPD is better for DA copolymers than the 1-decene copolymers. Again, the efficiency in base oil, BO1 is better than that of in BO2.

2.2.5. Conclusion

The rice bran oil + DA copolymers are thermally more stable than the rice bran oil + 1-decene copolymers and thermal stability increases with increasing concentration of 1-decene and DA in the copolymers. Performance evaluation of the additives indicates that the rice bran oil + DA copolymers act as better PPD and viscosity modifiers compared to the RBO + 1-decene copolymers. All the studied polymers showed biodegradable property in addition to the multifunctional additive performance (PPD and VM), and so are considered as being more useful in field applications compared to the existing additives.

2.2.6. References

References are given in BIBLIOGRAPHY under Chapter III of Part II (PP 167).

2.2.7. Tables and figures

Table 2.6: Properties base oils

Properties	*Base oils*	
	BO1	BO2
Density, $kg.m^{-3}$ at 313K	836.98	868.03
Viscosity × 10^{-6} , $m^2 \cdot s^{-1}$ at 313K	6.70	24.22
Viscosity × 10^{-6} , $m^2 \cdot s^{-1}$ at 373K	2.00	4.39
Cloud point, ^0C	-10	-8
Pour point, ^0C	-3	-6

Where BO1: base oil type 1, BO2: base oil type 2

Table 2.7: GPC analysis data of the polymer samples (P-1 to P-6)

Polymer samples	M_n	M_w	*PDI*
P-1	35709	43837	1.22
P-2	23332	31234	1.33
P-3	18965	27654	1.45
P-4	16392	23597	1.43
P-5	14815	21230	1.43
P-6	12112	17659	1.45

Where, Mn: Number average molecular weight, Mw: Weight average molecular weight, PDI: Poly dispersity index

Table 2.8 (a): Results of biodegradability test by the disc diffusion method

Sample	*Incubation period (days)*	*Percent weight loss in presence pathogens*				
		CC	FE	AA	CG	CE
P-1	30	33	00	48	00	00
P-2	30	25	00	44	00	00
P-3	30	27	00	37	00	00
P-4	30	23	00	31	00	00
P-5	30	17	00	27	00	00
P-6	30	11	00	28	00	00

Incubated for 30 days at 310K, CC, FE, AA, CG, and CE are the pathogens used. CC= *Colletotrichum camelliae*, FE= *Fusarium equiseti*, AA= *Alternaria alternata*, CG= *Colletotrichum gloeosporioides* and CE= *Curvularia eragrostidis*

Table 2.8 (b): Result of biodegradability test by soil burial method

Weight loss in soil burial test						
Polymer sample	P-1	P-2	P-3	P-4	P-5	P-6
Weight loss (%)	32	28	22	18	15	12

Incubated for 60 days at 303 K and humidity 50-60%

Table 2.9: Comparative GPC data of polymer samples in biodegradability test

Polymer	*Before biodegradability test*		*After biodegradability test*	
samples	M_n	M_w	M_n	M_w
P-1	35709	43837	31421	41238
P-2	23332	31234	19816	28764
P-3	18965	27654	17657	24569
P-4	16392	23597	14710	21056
P-5	14815	21230	12348	19379
P-6	12112	17659	10528	14592

Table 2.10: Dependence of PP (in °C) on the concentration of Additives in BO1 and BO2

Base oil	*Conc., %*	*Sample*					
(PP)		P-1	P-2	P-3	P-4	P-5	P-6
BO1 (-3)	1	-9	-15	-15	-9	-9	-12
	2	-12	-18	-21	-9	-12	-12
	3	-15	-21	-24	-12	-15	-15
BO2 (-6)	1	-12	-15	-18	-15	-21	-18
	2	-15	-18	-21	-18	-24	-24
	3	-15	-24	-27	-21	-18	-24

Table 2.11: Dependence of VI on the concentration of Additives in BO1 and BO2

Base oil(VI)	*Conc.,%*	*Sample*					
		P-1	P-2	P-3	P-4	P-5	P-6
BO1 (85)	1	112	116	119	100	110	118
	2	112	118	125	104	112	122
	3	125	130	132	106	114	128
	4	125	135	138	118	126	135
	5	128	136	145	121	128	138
	6	134	136	146	125	129	137
BO2 (80)	1	95	98	101	98	100	104
	2	97	100	110	109	104	110
	3	102	115	115	115	118	119
	4	105	115	123	118	122	125
	5	115	123	132	131	130	132
	6	116	128	138	137	129	138

Figure 2.10 (a): FT-IR spectra of copolymer of Rice bran oil-DA

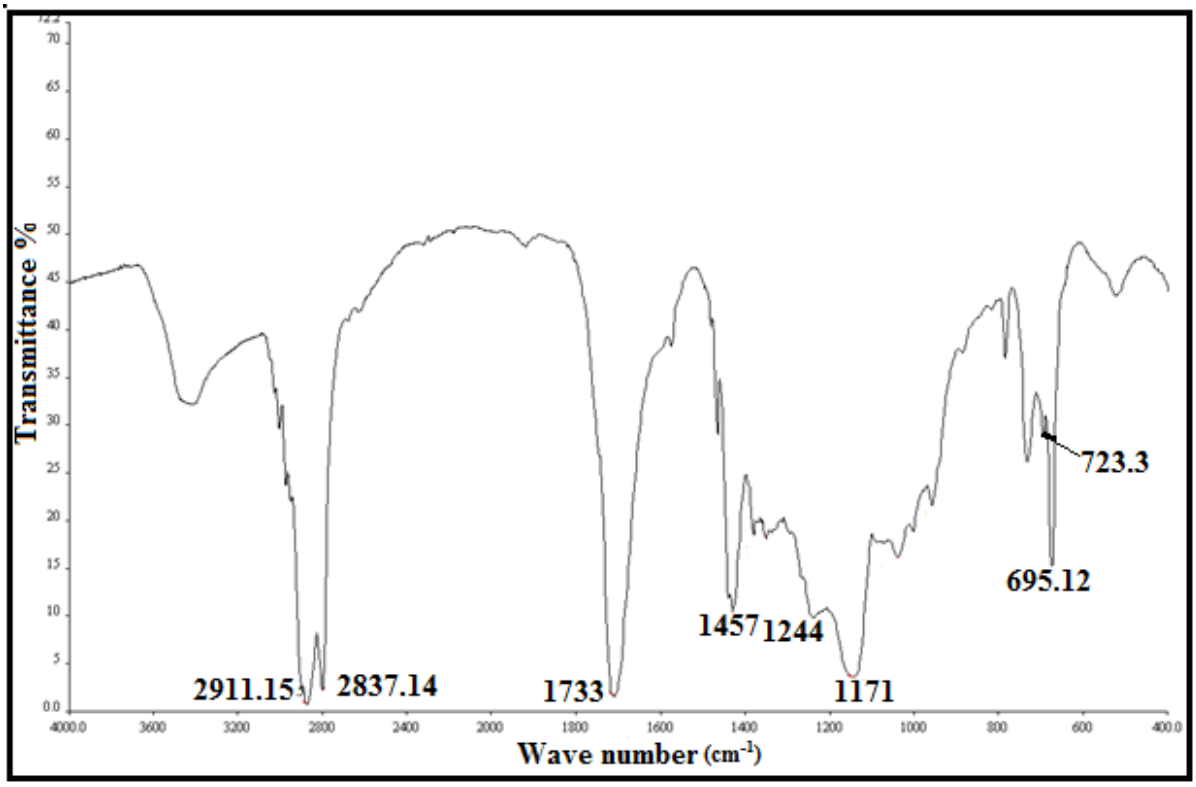


Figure 2.10 (b): ^{1}H NMR spectra of copolymer of Rice bran oil-DA

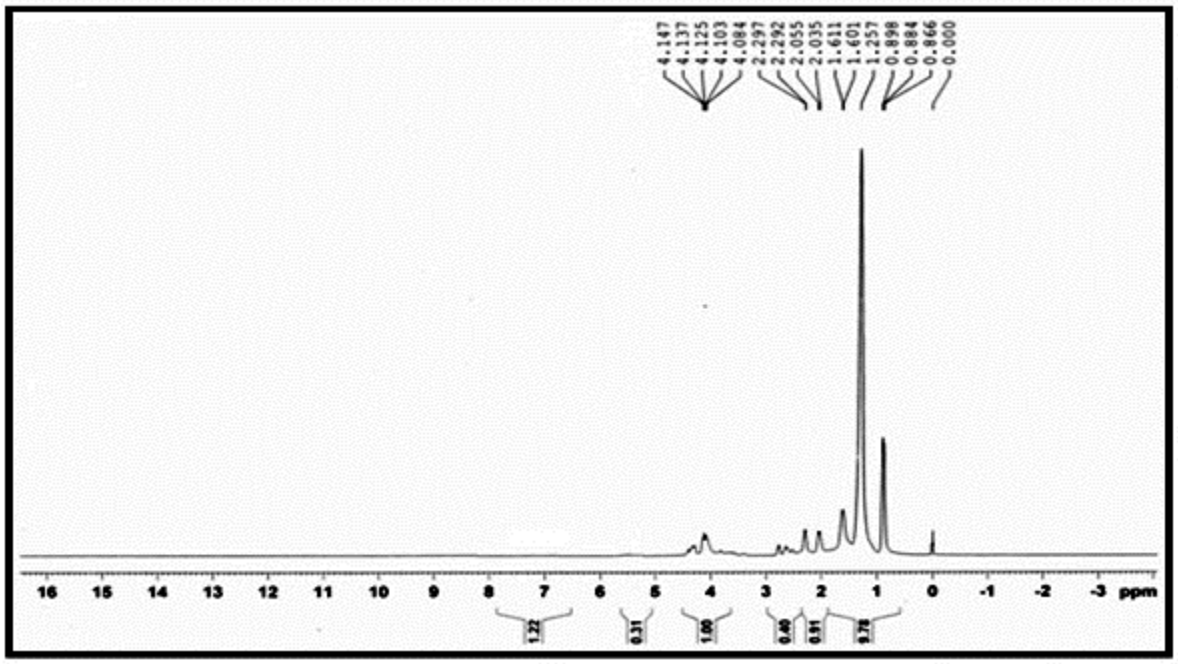


Figure 2.10 (c): ^{13}C NMR spectra of copolymer of Rice bran oil-DA

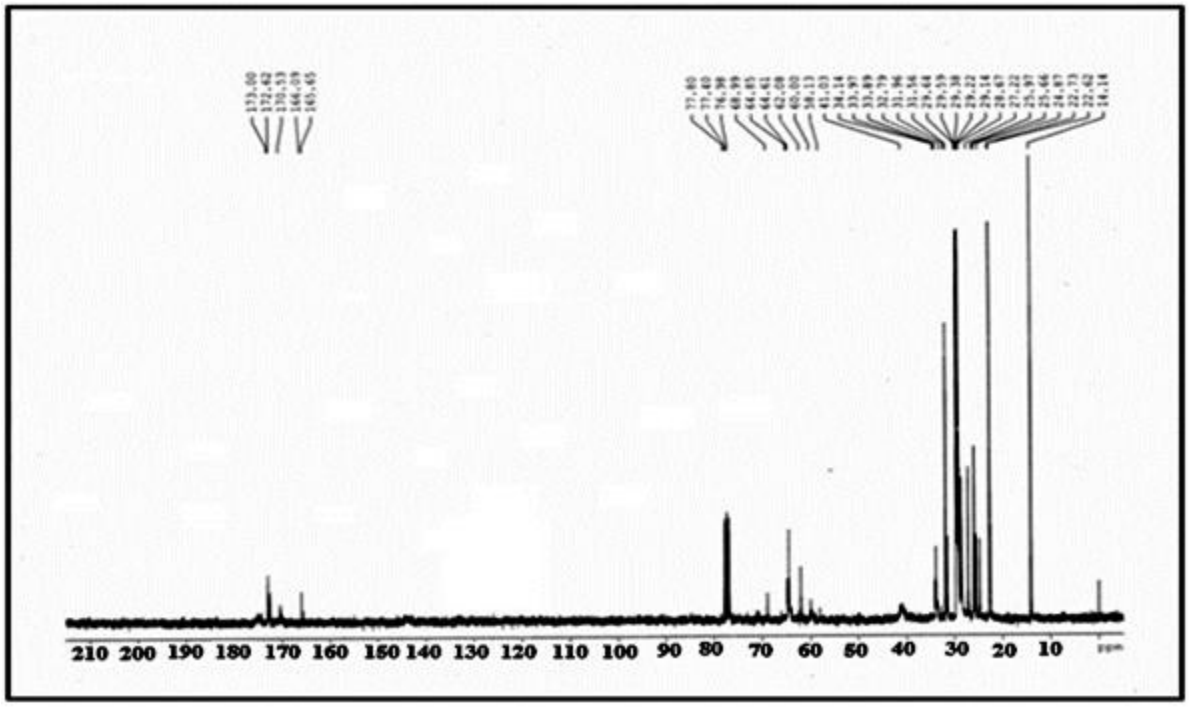


Figure 2.11 (a): FT-IR spectra of copolymer of Rice bran oil-1-Decene

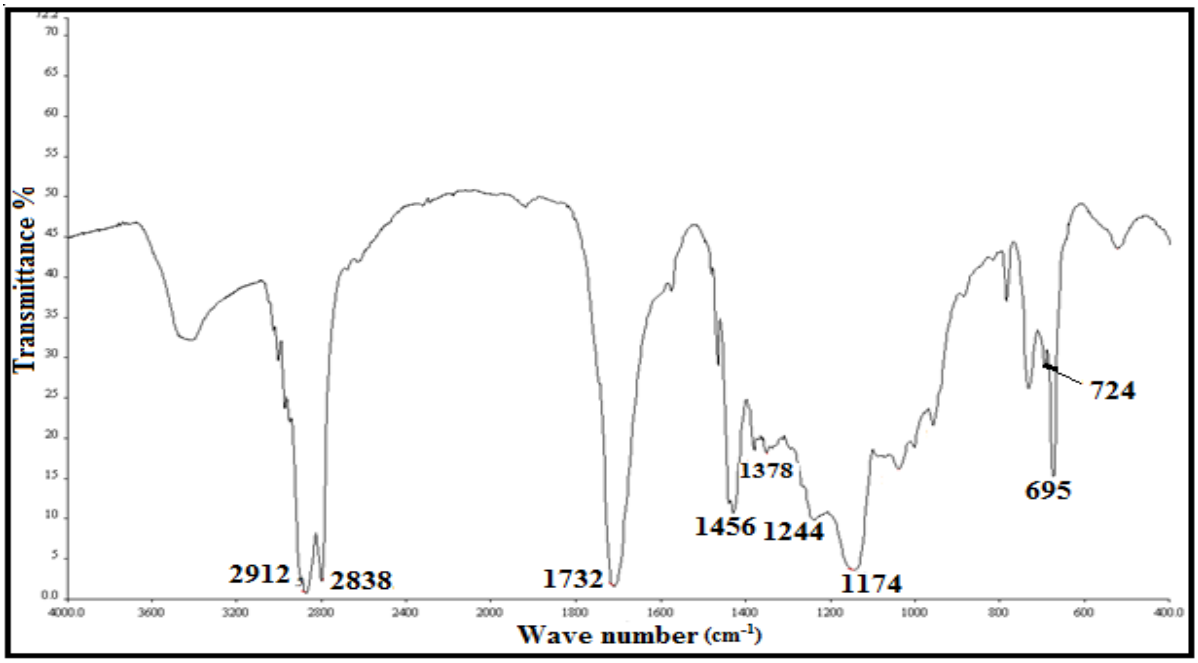


Figure 2.11 (b): ^{1}H NMR spectra of copolymer of Rice bran oil-1-Decene

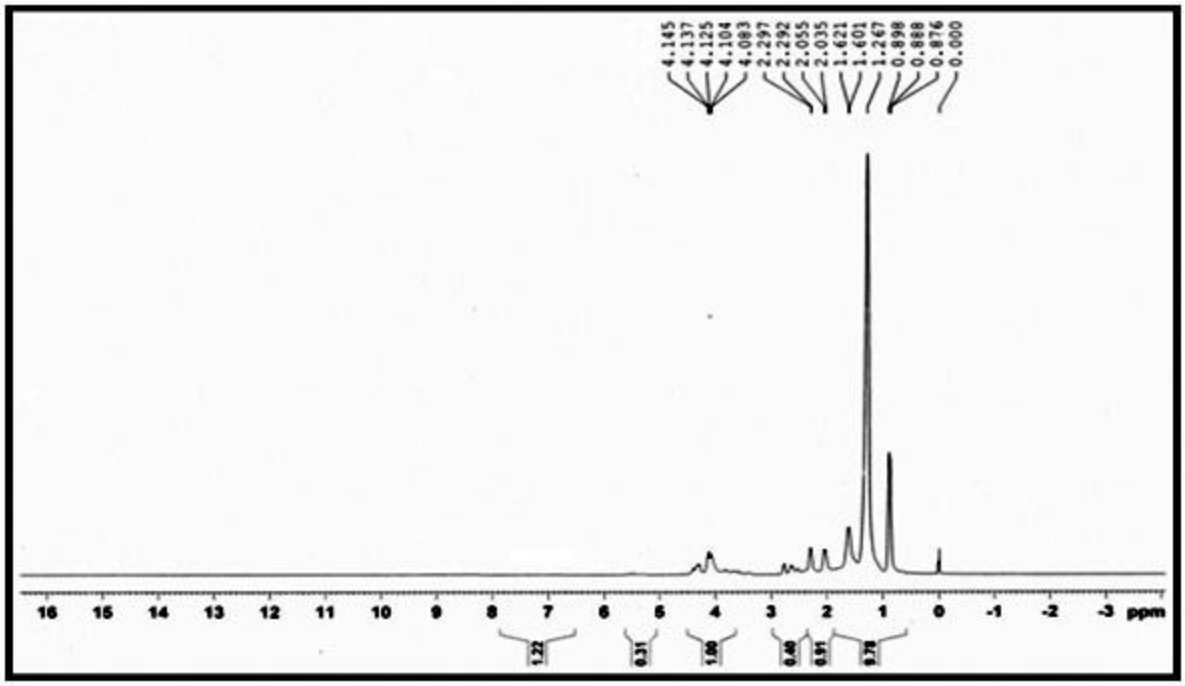


Figure 2.11 (c): ^{13}C NMR spectra of copolymer of Rice bran oil-1-Decene

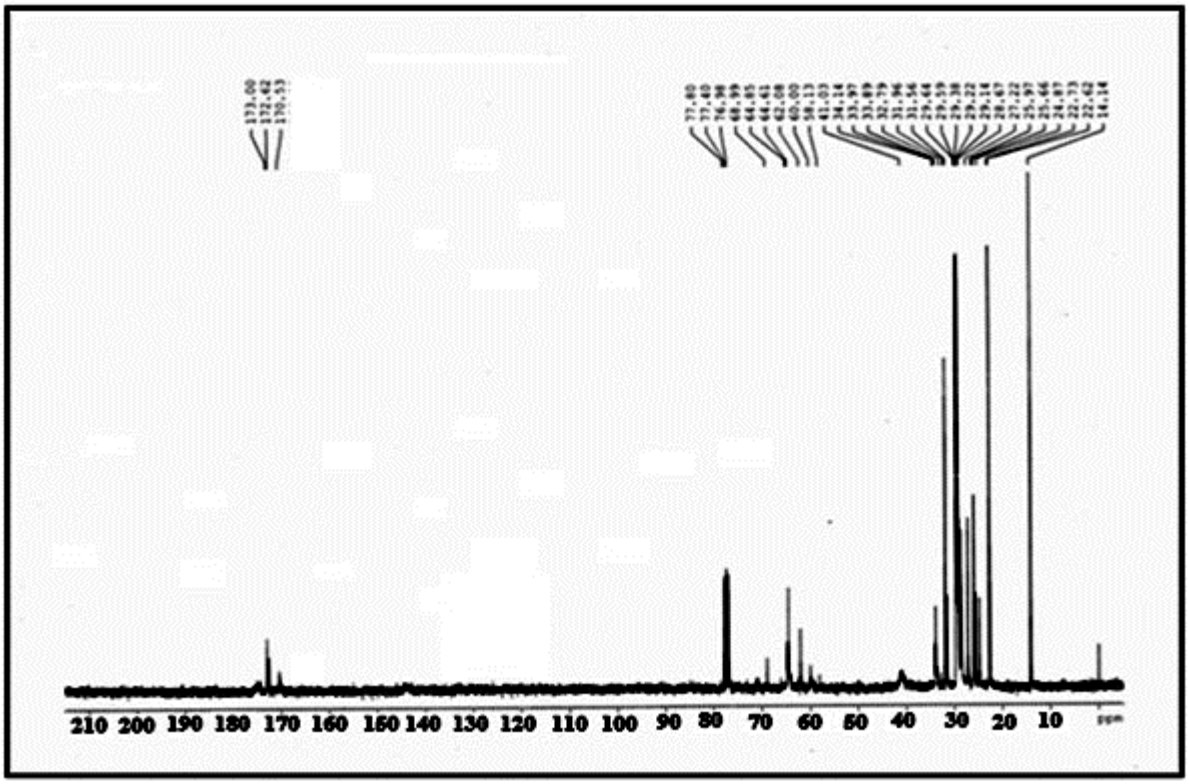


Figure 2.12: Comparative FT-IR spectra of copolymer of of Rice bran oil-DA

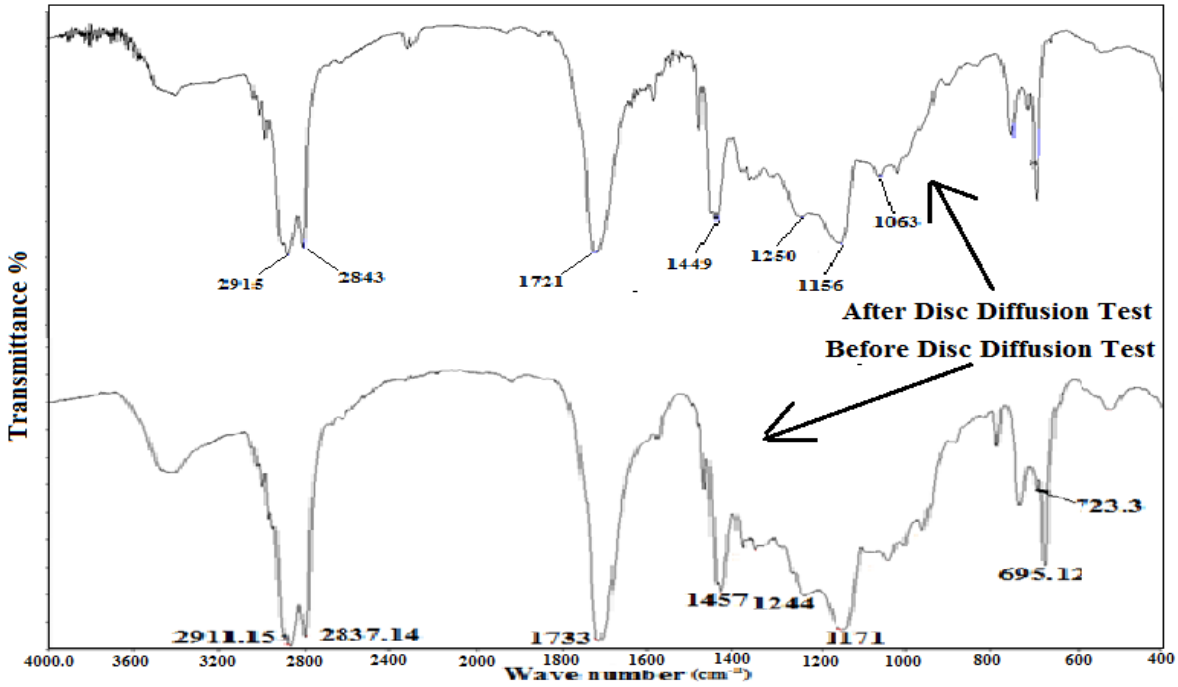


Figure 2.13: Comparative FT-IR spectra of copolymer of of Rice bran oil-1-Decene

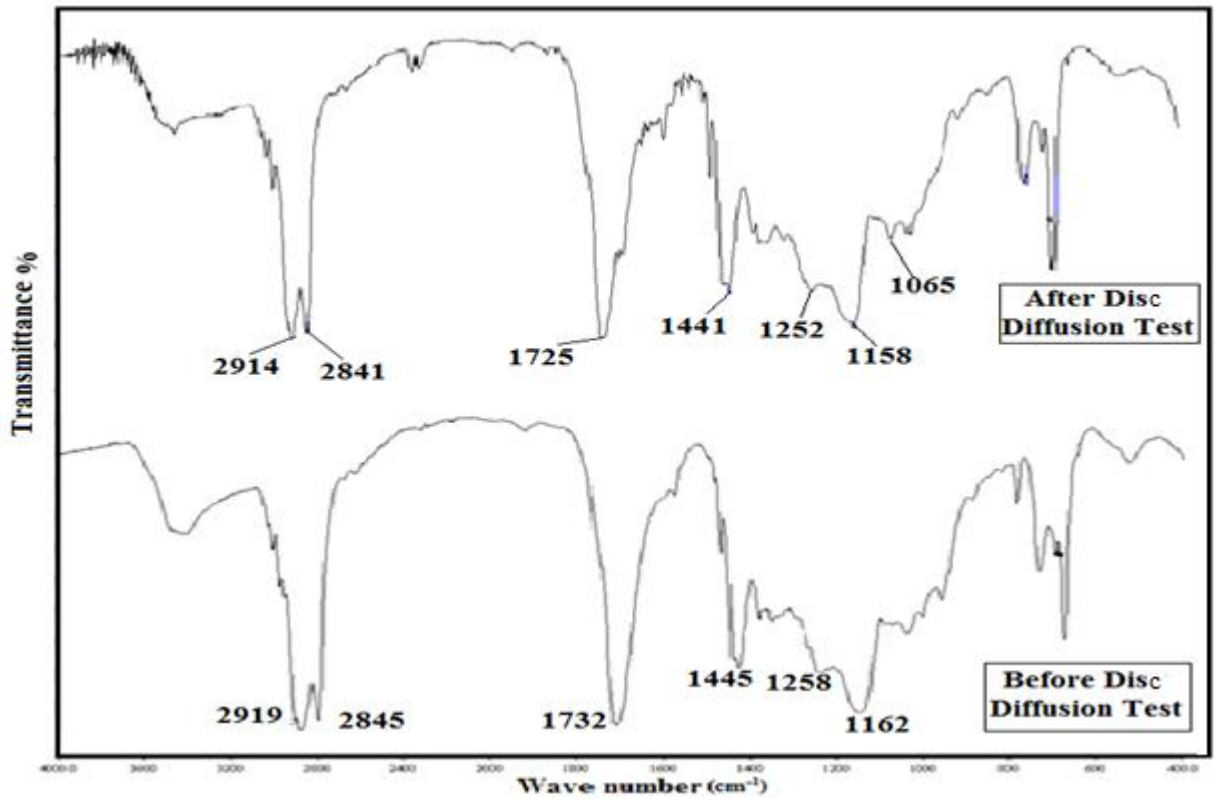
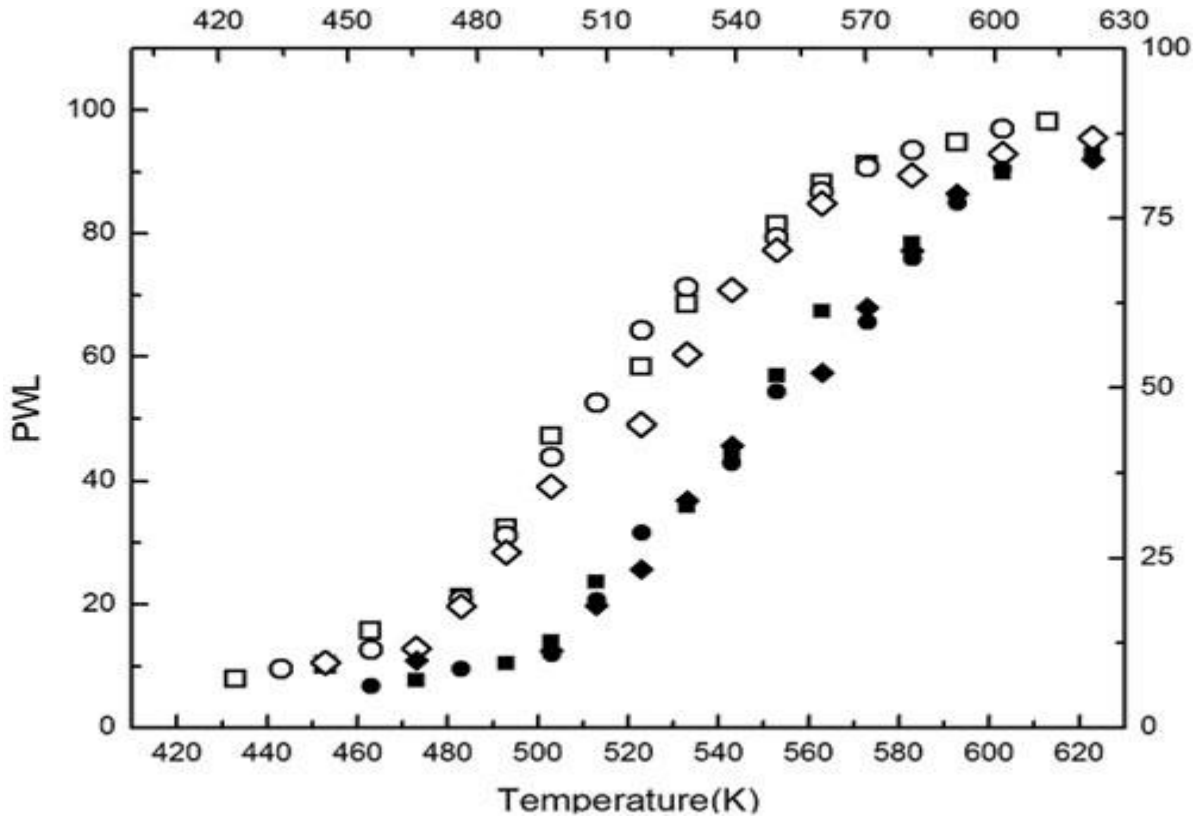


Figure 2.14: Comparative TGA data of copolymer of Rice bran oil-DA (P-1, P-2, and P-3) and Rice bran oil- 1-Decene (P-4, P-5 and P-6)



Where, PWL= percent weight loss. Temperature is in K. ■, P-1; ●, P-2; ♦, P-3; □, P-4; ○, P-5; ◊, P-6.

Figure 2.15 (a): Dependence of viscosity index on additive concentration in base oil BO1

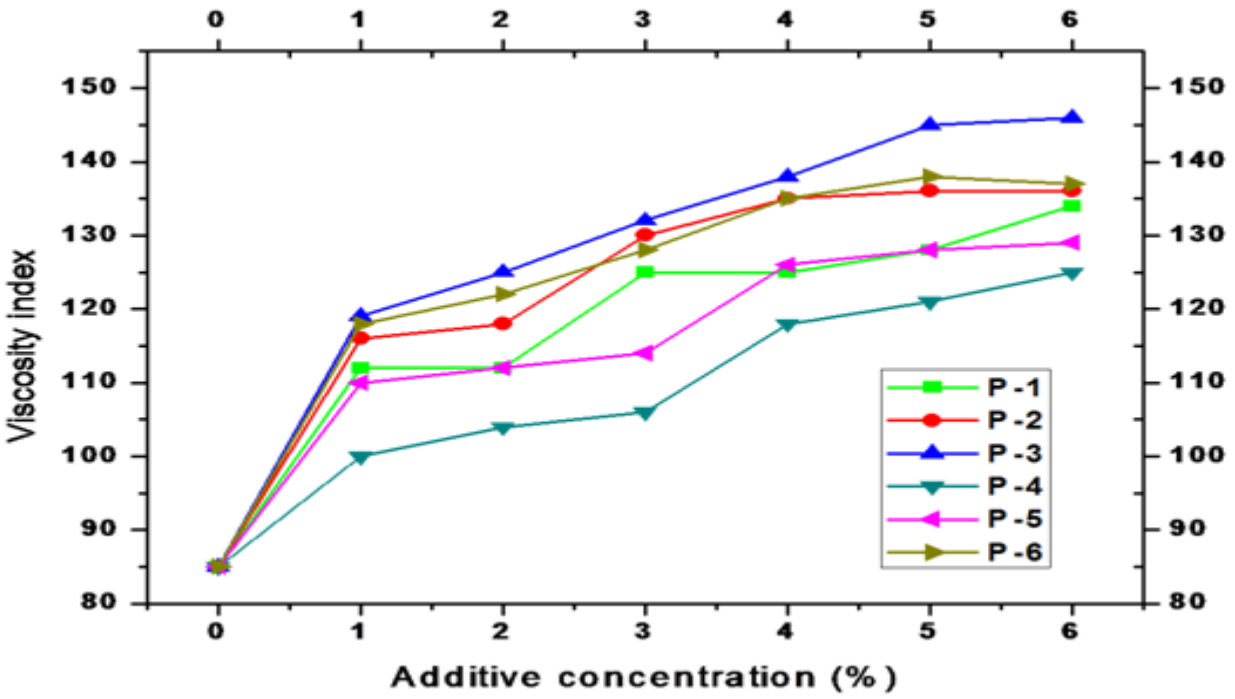


Figure 2.15 (b): Dependence of viscosity index on additive concentration in base oil BO2

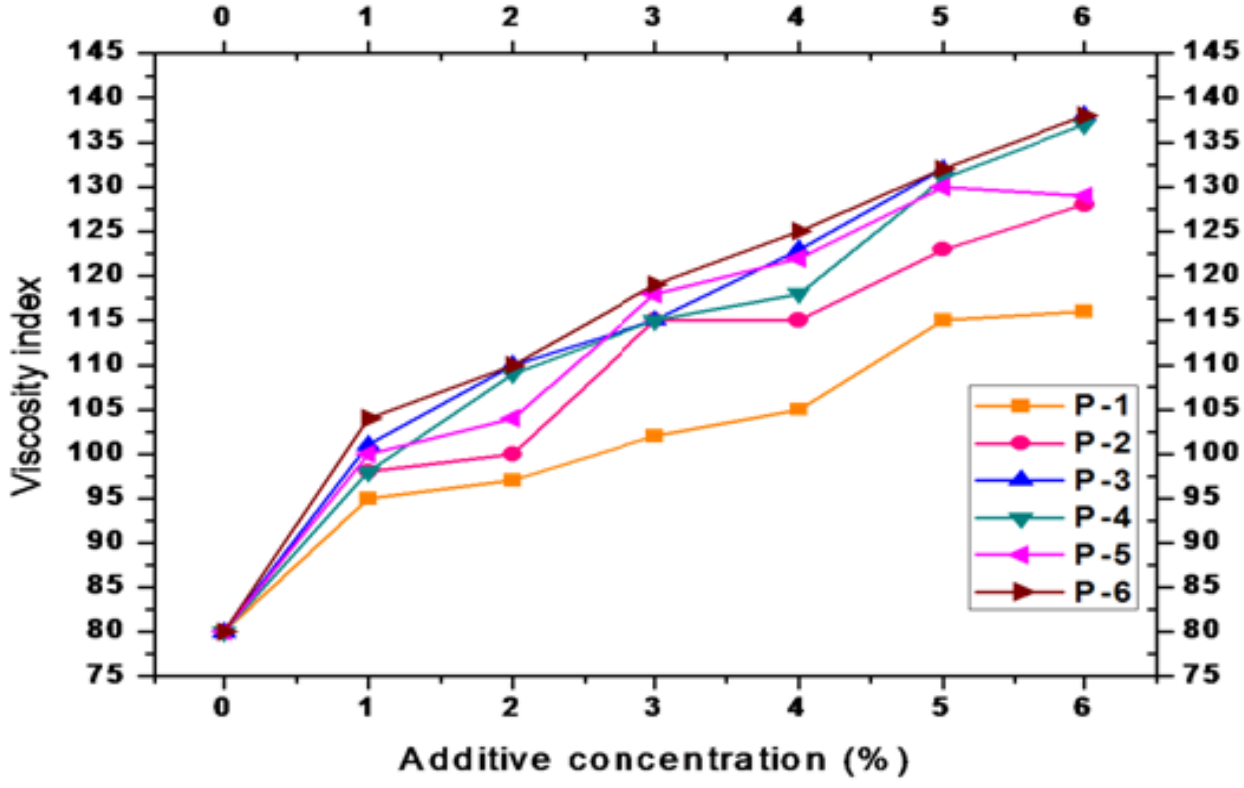


Figure 2.16 (a): Dependence of pour point on additive concentration in base oil BO1

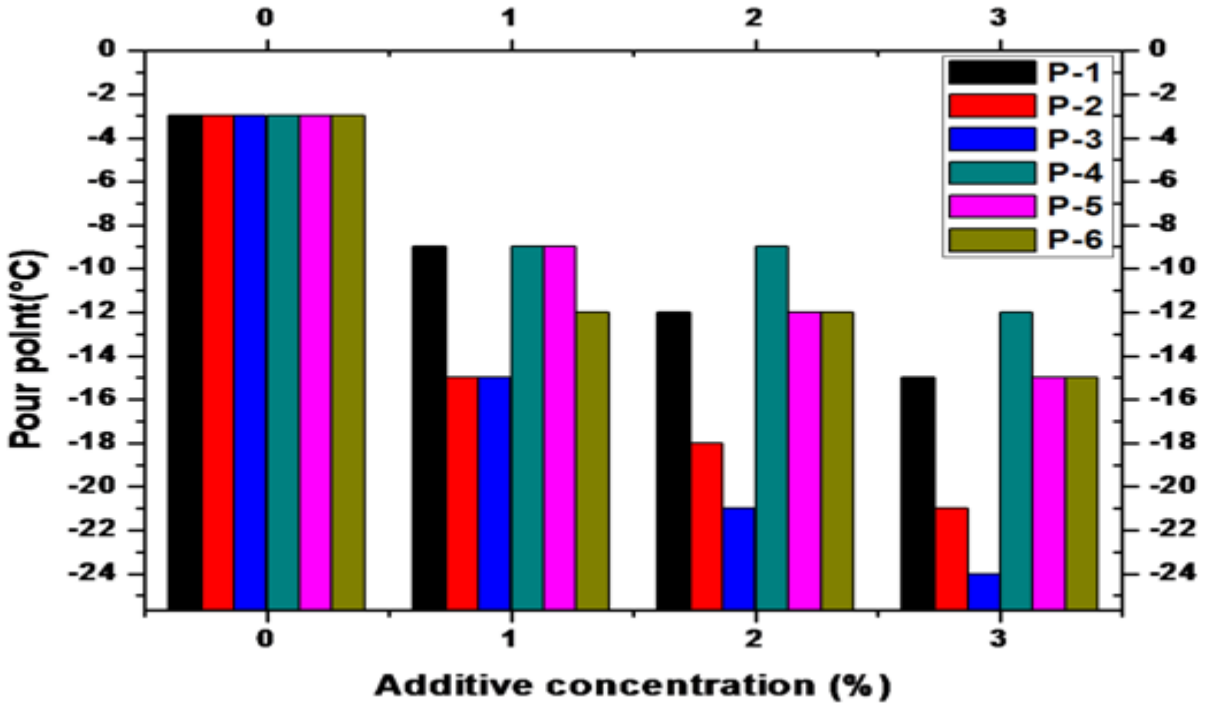


Figure 2.16 (b): Dependence of pour point on additive concentration in base oil BO2