Chapter-III

Olive oil based multifunctional biodegradable lube oil additive

2.3.1 Introduction

Today, petroleum based materials are in widespread use in different industries because of their significant performances in field applications. But, fuels and lubricants derived from renewable sources have also attracted considerable interest in recent years because of the grave environmental related issues of petroleum based products. There is, therefore, a growing urgency to develop and commercialize products and other innovative technologies that can reduce the widespread dependence on fossil fuels. Plant oils have emerged as the chief and the most extensively exploited renewable supplies for the industries due to their unique beneficial properties. They are associated with good low volatility, good lubricity, high viscosity index[1] and many other excellent tribological properties which are taken care of in industrial applications. Biocompatibility and low toxicity are the biggest assets of these bio-based oils. Bio-based composites are already in application in food and agrochemical industry,[2] coating technology,[3] medicine, cosmetics, inks,[4] plasticizers, automotive industry etc.[5,6] Though, it is currently completely difficult to substitute petroleum derived materials, from the standpoint of their competitive performance, but it is a good solution to merge the various features and benefits of both bio-based and petroleum derived materials to reduce the dependence on fossil fuels. Various countries around the globe have pledged to increase the production and market share of these bio-based materials to meet the future energy demands.

Basically, the dominating constituents of vegetable oils are triglyceride molecules of long chain fatty acids. The fatty acids portion of these oils is composed of various levels of unsaturation and this significant level of unsaturations contribute to reduced oxidative and thermal constancy to them.[7] Therefore, prior to any practical application,

curing the oil with suitable reagent or eliminating the unsaturation is absolutely essential to enhance their firmness and mechanical properties. Polymerization can reinforce in them the required rigidity and molecular weight together with incurring some extra advantages like biodegradability when appropriate monomer are selected for copolymerization.

One of the best recognized additive for use in lubricating oils are the acrylate and methacrylate systems.[8,9] Polymethacrylates are among the widespread additive to be used as a pour point depressant (PPD) and viscosity index improver (VII). But, with the current inclination towards green alternatives, people have started producing greener lubricants and lubricant additives to be added to the lube oil.[10-12] This trend has started to limit the extensive application of acrylates in automobile industries. Natural olive oil was selected here as an important monomer for copolymerization with petroleum based products as it is easily procurable, inexpensive and has active unsaturation of around 86%. In this investigation, a thorough study of the polymers synthesized using dodecyl methacrylate (DDMA) and olive oil has been performed to verify their additive performance. Different types of copolymers of DDMA and olive oil were synthesized by altering the ratio (mass) of olive oil.

Structural characterization of the synthesized additives has been performed by IR and NMR analysis. Their thermal response at higher temperature was examined by means of thermo gravimetric analysis and GPC was employed to measure their molecular weight. Evaluation of poly dodecyl methacrylate and DDMA–olive oil copolymers as additive was performed to analyse the contribution of olive oil in the additive framework. Biocompatibility of the additives was also assessed and GPC was used to determine the extent of biodegradability.[13]

2.3.2 Experimental section

2.3.2.1 Materials

Extra virgin Olive oil was collected from a local grocer's shop. Dodecanol, methacrylic acid, H_2SO_4, BZP and hydroquinone were purchased from Merck Specialties Pvt. Ltd., (India). Hexane and methanol were obtained from Nice chemicals Pvt., Ltd. The $CHCl_3$-CH_3OH mixture was used to re-crystallise the initiator BZP and the rest of the chemicals were used as received. Base oil of two different categories (BO1 and BO2) was collected from Indian Oil Corporation Limited, India (Table 2.3.1).

2.3.2.2 Esterification

The ester, dodecyl methacrylate (DDMA), was synthesized by using a molar ratio of 1:1.1 from dodecanol and methacrylic acid. The esterification was performed under nitrogenous atmosphere in toluene (as solvent) using a resin kettle and taking catalytic amount of concentrated H_2SO_4. Hydroquinone was also added to the reaction mixture as polymerization inhibitor. The mixture was steadily heated and the temperature was increased up to 413 K with the help of a thermostat. The measure of the amount of water liberated during the reaction helped in monitoring the extent of reaction.

2.3.2.3 Purification of the prepared ester

The DDMA ester was purified by refluxing it for 3 hours after adding 1 g of charcoal to it. After the stipulated time, the charcoal was filtered off and the filtrate was rinsed in a separation funnel with 0.5N NaOH. The process was repeated a number of

times to ensure the complete removal of any unreacted acids. The ester was then rinsed a number of times with distilled water to eliminate any NaOH (if present in small amount) until it became neutral to pH paper. The ester DDMA was finally left over night on anhydrous $CaCl_2$ for drying. The $CaCl_2$ was then removed by filtration and the toluene was recovered by distillation under reduced pressure. The ester left behind was ready for further use.

2.3.2.4 Preparation of homopolymer and copolymers

The polymerization reactions were performed under microwave irradiation in a focused mono-mode microwave oven (CEM Corporation, USA). The homopolymerization reaction was carried out with dodecyl methacrylate (5.08 g, 0.02mol), applying 300 WT for 15 minute, in the presence of BZP (0.01% w/w, working as an initiator) without any solvent at 90°C. The copolymers were prepared in similar fashion, without any solvent, using dodecyl methacrylate and olive oil (2%, 4%, 6% and 8%, w/w, with respect to dodecyl methacrylate) in the presence of BZP. The designation and composition of the prepared polymer samples are presented in Table 2.3.2.

2.3.3 Measurements

2.3.3.1 Spectroscopic measurements

NMR spectra were recorded in an Avance 300 MHz FT-NMR spectrometer (Bruker Corporation, Germany) using 5 mm BBO probe. $CDCl_3$ was used as solvent and TMS as reference material. IR spectra were recorded on a Shimudzu FT-IR 8300 instrument

(Shimadzu Corporation, Japan) using 0.1 mm KBr cells at room temperature, within the wave number range 400 to 4000 cm^{-1}.

2.3.3.2 Thermo gravimetric study

A Mettler TA–3000 apparatus was employed to calculate the thermo gravimetric results of the polymers in air, with a heating rate of 10 K min^{-1}.

2.3.3.3 Measurement of molecular weight

A GPC instrument (Waters Corporation, USA) was employed to calculate the average molecular weight and the PDI of the polymers at room temperature using polystyrene calibration in THF. The data obtained are presented in Table 2.3.3.

2.3.3.4 Biodegradability test

The biodegradable nature of the polymers samples was evaluated by the following two tests.

(a) Disc diffusion (DD) test

(b) Soil burial degradation (SBD) test

After carrying out tests, the samples collected were analysed for any significant weight loss (measured in terms of PWL) and they were also examined to record any significant shift in their IR peaks.[14-16] Besides, to acknowledge any variation of M_n and M_w values in the polymers after biodegradation, GPC study was also conducted for the recovered polymers.[13]

2.3.3.4.1 Disc diffusion (DD) test

The fungal pathogens employed to perform this test include, *Alternaria alternate* (AA), *Fusarium equiseti* (FE), *Colletotrichum gloeosporioides* (CG), *Colletotrichum camelliae* (CC) and *Curvularia eragrostidis* (CE). For preparing the culture media of fungal pathogens, dextrose, agar powder and potato extract were mixed in Petri dishes in a ratio of 1:1:10 by weight. For this test, 1 g of polymer samples was placed in different Petri dishes and inoculated by spraying the different fungal pathogens. The Petri dishes were then sealed by wax and incubated with fungal pathogens at 310 K in a bacteriological incubator for 30 days. The growth of the pathogens in the culture was ascertained by the gradual transformation in colour from yellow to black. After the required number of days, the polymer samples were recovered from the culture, rinsed with chloroform, filtered with Whatman grade 41 filtration paper and dried in a vacuum oven at 323 K.[14] The PWL was computed for all the samples and they were later analysed through FT-IR and GPC. All the glass apparatus used in this test were autoclaved prior to use.

2.3.3.4.2 Soil burial degradation (SBD) test

The soil for the SBD test was obtained from the campus of North Bengal University (West Bengal, India) with pH 7.2, and before the test its humidity was balanced to around 60% with the help of a humidity chamber. Polymeric films were created separately using the polymeric additives (2g in each case) and buried in the soil in a bacteriological incubator (Sigma Scientific Instruments Pvt., Ltd., India) with temperature 303 K. After a span of 60 days, the polymeric films were reclaimed from

the soil. After recovery, the films were cleaned with chloroform, filtered with Whatman grade 41 filtration paper and dried in a vacuum oven at 323 K.[17] For each of the samples, the weights after drying were recorded to estimate the PWL and they were finally analysed through GPC. The SBD test was here carried out as per the ISO 846:1997 method.

2.3.3.5 Evaluation of pour point

The synthesised polymeric additives were evaluated for their pour points as per the ASTM D97 method in two different oils BO1 and BO2 on a cloud and pour point test equipment (Wadegati Labequip Pvt. Ltd., India). Different percentages (ranging from 1 to 5%, w/w) of the polymers were used for each study.

2.3.3.6 Evaluation of viscosity index

The VI of the two different base oils blended with the polymers was calculated to verify the efficiency of the synthesized polymer as VII. The VI was calculated using an Ubbelohde viscometer which was calibrated at 313 K and 373 K with purified methanol and triply distilled water prior to the experiment.[18] The time taken (t) by the polymer blended solutions to pass through the two calibrated marks in the viscometer was recorded with a digital stopwatch. The VI was evaluated using the kinematic viscosity (ν) of the lube oil samples at the mentioned temperatures from the following equation,

$$\nu = (Kt - L/t)\,\rho \qquad \text{Eq. (1)}$$

where ρ is the density of the polymer blended base oils.[19]

A DMA 4500M vibrating-tube density meter (Anton paar, Austria) was used to compute the densities of the polymer solutions. The instrument was also standardized at atmospheric pressure with distilled, degassed water and dry air before use.[20] The VI was evaluated from the given empirical equation.[19, 21]

$$VI = 3.63(60 - 10^{n}) \quad \text{Eq. (2)}$$

where n is a constant characteristic for each oil and its value is calculated as,

$$n = (\ln\nu_1 - \ln k)/\ln\nu_2 \quad \text{Eq. (3)}$$

Here, ν_1 and ν_2 represents the kinematic viscosity of the lube oil at lower and higher temperatures respectively and k is a function of temperature.[19] Again, different percentages (ranging from 1 to 5%, w/w) of the polymers were used to study the influence of additives on the viscosity index.

2.3.4 Results and discussion

2.3.4.1 Spectroscopic analysis

FT-IR spectra: The FT-IR absorption (Fig. 2.3.1) of P-1 (poly dodecyl methacrylate) showed signal for the stretching vibration of ester carbonyl (C=O) at 1732 cm^{-1} together with the ester C–O–C stretching vibration peak at 1167 cm^{-1}. The absorptions for the C–H bending vibrations of CH_2 and CH_3 groups appeared at 710, 750, 1379 and 1456 cm^{-1} while the another set of peaks which appeared in the regions of 2876 cm^{-1} and at 2942 cm^{-1} were due to the stretching vibrations of the paraffinic C–H bonds.

^{1}H-NMR spectra: In its ^{1}H-NMR spectra (Figure 2.3.2), P-1 exhibited the presence of the protons of –$COOCH_2$ group by appearing as broad peaks in the range of 3.9–4.2 ppm while the other peaks ranging between 1.3–1.9 ppm were for the methylene protons.

The methyl groups of dodecyl and methacrylate chain showed another signal at 0.89 ppm.

^{13}C-NMR spectra: The proton decoupled ^{13}C-NMR spectra of P-1 (Fig. 2.3.3) exhibited peaks between 14.1 and 45.2 ppm for the methyl and methylene carbon atoms. The signals appearing between 64.8 and 65.1 ppm are attributed to the $-OCH_2$ carbons of the polymer while the signal around 177 ppm is attributed to the carbonyl carbons of the ester groups.

The emergence of the copolymers (P-2 to P-5) was also indicated by their ^{1}H-NMR, ^{13}C-NMR and FT-IR spectra. Here, the copolymers also exhibited equivalent spectral outlines. Selecting the polymer P-5 as a standard copolymer, its FT-IR spectra displayed a strong signal for the stretching vibration of ester carbonyl at 1730 cm^{-1}; the ester C–O stretching vibration peak as a band at 1175 cm^{-1} together with the peaks for the C–H bending vibrations at 1464 cm^{-1} and for the stretching vibrations at 2936 cm^{-1} (Fig. 2.3.4).

In the ^{1}H-NMR spectra of P-5 (Fig. 2.3.5), the protons of $-COOCH_2$ group of dodecyl methacrylate and that of olive oil showed broad signals in the range of 3.6–4.3 ppm. The peaks between 2.0 and 2.3 ppm occurred due to the protons of $-OCOCH_2-$ groups present in olive oil. Signals in the range of 1.3-1.6 ppm were for the methylene protons while the signals between 0.86 and 0.88 ppm were due to the methyls of dodecyl, methacrylate and olive oil chain.

The ^{13}C-NMR spectrum of P-5 (Fig. 2.3.6) showed peaks for the $-OCH_2$ carbons of the polymer around 64 ppm while the signals for the carbonyl carbon of dodecyl methacrylate and olive oil appeared between 177.7 and 178.6 ppm. Peaks for unsaturation were not shown by any of the polymers.

2.3.4.2 Thermo gravimetric analysis

The thermo gravimetric analysis showed a gradual increase of thermal stability with increasing concentration of veg oil (olive oil) in the feed (Table 2.3.4). Thus, from the outcome it is obvious that poly dodecyl methacrylate (P-1) is thermally less stable than the copolymers.

2.3.4.3 Performance as viscosity index improver

The effectiveness of the synthesized polymers as VII was analysed by measuring the VI of the base oils blended with the polymers. The measured VI values are plotted in Figs. 2.3.8 and 2.3.9. From the analysis of the graphs it is quite obvious that for all the polymers, the viscosity index values improved with increasing polymer percentage in the base oils. This is in agreement with our previous findings.[22] Again, the analysis of the graphs also revealed that the copolymers acted as a superior VII than the rest. Moreover, with the increase of olive oil percentage in the polymer feed, the VI values also enhanced systematically i.e. a higher viscosity modification of the base oil was achieved by the polymer P-5.

All the above observations can be explained by the fact that the overall size and volume of the polymer micelles is significantly increased by increasing the polymer fraction in the base oil. Also, at higher temperature, when the base oil viscosity decreases, the long polymer chains straighten out and increases the size of the polymer micelles. Hence, the general reduction of viscosity at higher temperature associated with the base oil is compensated by these two reverse situations and a higher polymer percentage exhibits superior viscosity modification.[9]

2.3.4.4 Performance as pour point depressant

The synthesized polymers were analysed for their pour point values in the two base oils and the data are plotted in Figs. 2.3.10 and 2.3.11. A comparative study revealed that poly dodecyl methacrylate is less advantageous as PPD in comparison to the copolymers. Also, the copolymer P-5 was established as the most potent PPD among the other polymers. Moreover, with the rise of additive percentage in the base oil, the pour points improved in all of the cases. The result obtained above is due to more successful polymer–oil association at greater accumulation of the polymer in the base oil.[22,23] The long chain configuration of the polymers have a key role in rupturing the rigid matrix of wax crystal formed at low temperatures. Therefore, the extended chain configuration of the copolymers is possibly more useful in rupturing the rigid matrix of wax crystals present in the base oils in contrast to the methacrylate moiety.

2.3.4.5 Analysis of biodegradability test

The change in weight of the polymer samples after the biodegradability tests are presented in Table 2.3.5. As indicated by the PWL, the fungal pathogen *Alternaria alternate*, brought major degradation to the copolymers of olive oil. Again, in the SBD test, the weight loss, as calculated for the polymers, was lower than the DD test. The polymers collected after the DD test was analysed with GPC and the figures were matched up to with the respective polymers before biodegradation. The comparative GPC data is presented in Table 2.3.6. Analysis of the data showed an appreciable change in their M_n and M_w values and, thus, reveals the biodegradable nature of the synthesised

copolymers. So, the incorporation of olive oil into the methacrylate system has lead to obvious biodegradability into the copolymers.

After the DD test, the spectral data of the copolymers were also taken and analysed to validate their biodegradable nature. The FT-IR signals of polymer P-5 (Fig. 2.3.7) were found to have changed significantly after the test. Moreover, the broad peak ranging between 2847–2956 cm^{-1} also got trifurcated (2868, 2931 and 2944 cm^{-1}) after the test.

The significant weight loss (PWL) of the polymers, variation of M_w and M_n values in the GPC analysis and the shift in their FT-IR signals after biodegradation test clearly pointed out the biodegradable nature of the synthesised copolymers.

2.3.5 Conclusions

The investigation revealed that the newly made copolymers are excellent as PPD and have encouraging VII properties. Their thermal stability too was found to be excellent and the maximum thermal stability was found for the copolymer with highest olive oil percentage. Again, the copolymers displayed remarkable biodegradable quality in contrast to the homopolymer. Hence, the polymers formed by blending DDMA with olive oil can be employed for constructing excellent biodegradable additive for lubricating oils.

2.3.6 References

References are given in BIBLIOGRAPHY under Chapter-III of Part-II (Page No. 218-220).

2.3.7 Tables and figures

Table 2.3.1: Properties of base oils

Properties	***Base oils***	
	BO1	***BO2***
Viscosity at 40 °C in cSt	7.348	23.871
Viscosity at 100 °C in cSt	1.902	3.994
Viscosity index	80	85
Pour point, °C	-3	-6
Density (g cm^{-3}) at 40 °C	0.83827	0.90215

Table 2.3.2: Percentage composition of the copolymers as estimated by spectroscopic method

Polymers	***Mass fraction of the polymers***		***NMR estimation of the mass fraction of olive oil***	***FT-IR estimation of the mass fraction of olive oil***
	DDMA	***Olive oil***		
P-1	1	0	-	-
P-2	0.98	0.02	0.019	0.017
P-3	0.96	0.04	0.036	0.034
P-4	0.94	0.06	0.058	0.056
P-5	0.92	0.08	0.074	0.076

Table 2.3.3: GPC results of the polymers

Polymers	***GPC values of the polymers***		
	M_n	M_w	***PDI***
P-1	21619	35854	1.66
P-2	15432	36138	2.34
P-3	18111	33532	1.85
P-4	20453	34816	1.70
P-5	21835	35675	1.63

Table 2.3.4: TGA results of the polymers

Polymers	***TGA values***	
	Decomposition temperature (K)	***PWL***
P-1	441/523	17/92
P-2	463/554	13/90
P-3	491/587	15/92
P-4	505/594	14/93
P-5	498/611	14/92

Table 2.3.5: Results of biodegradability by DD test and SBD test

Polymers	***Number of days of incubation***	***Weight loss (%) in DD test in presence of pathogen***					***Weight loss (%) in SBD test***
		AA	***FE***	***CG***	***CC***	***CE***	
P-1	30	0	0	0	0	0	2.16
P-2	30	54.34	0	0	0	0	33.75
P-3	30	55.67	0	0	0	0	37.31
P-4	30	61.59	0	0	0	0	44.36
P-5	30	64.74	0	0	0	0	51.87

DD test: Incubated at 310 K for 30 days. AA: Alternaria alternate, FE: Fusarium equiseti, CG: Colletotrichum gloeosporioides, CC: Colletotrichum camelliae, CE: Curvularia eragrostidis. SBD test: Incubated at 303K for 60 days.

Table 2.3.6: Comparative average molecular weight values determined by GPC

Polymers	***Molecular weight***			
	Before biodegradation		***After biodegradation***	
	M_n	M_w	M_n	M_w
P-1	21619	35854	21619	35854
P-2	15432	36138	13484	33613
P-3	18111	33532	15344	31261
P-4	20453	34816	17511	30455
P-5	21835	35675	17878	29975

Figure 2.3.1: FT-IR spectra of polymer P-1

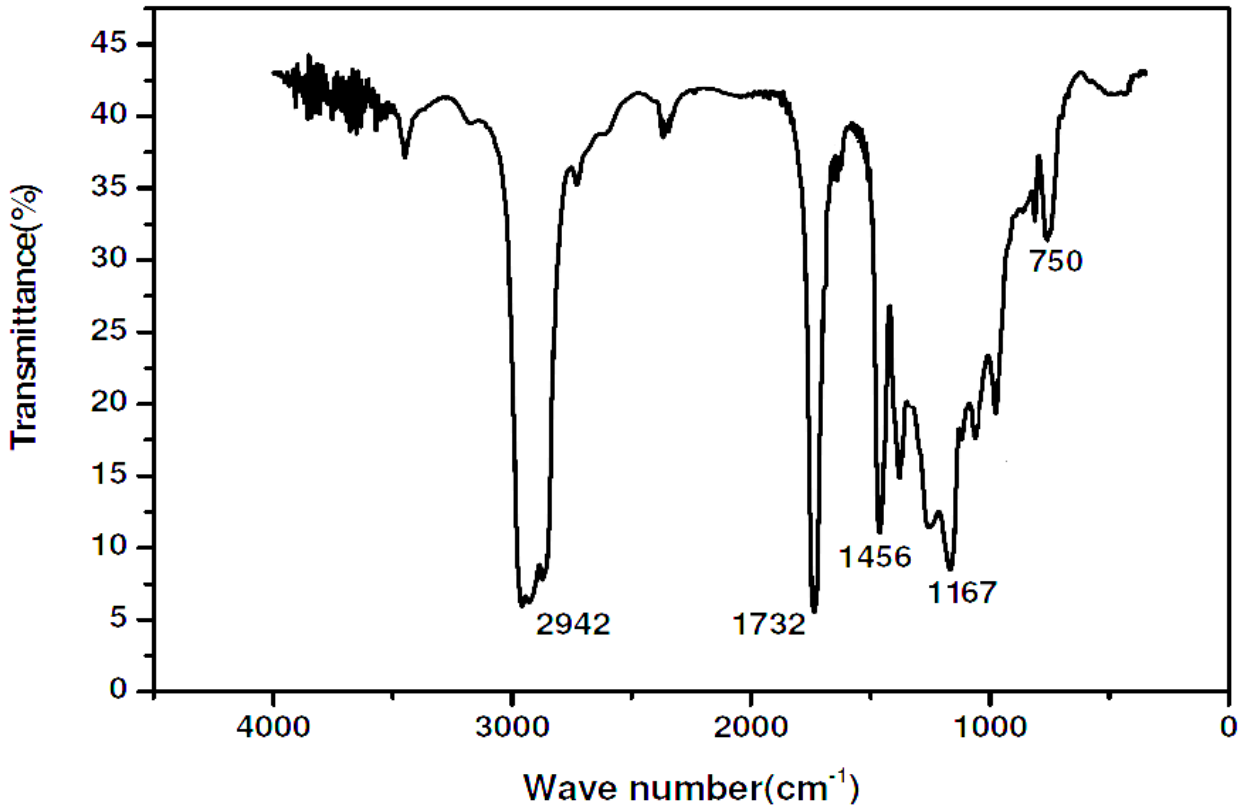


Figure 2.3.2: ^{1}H-NMR spectra of polymer P-1

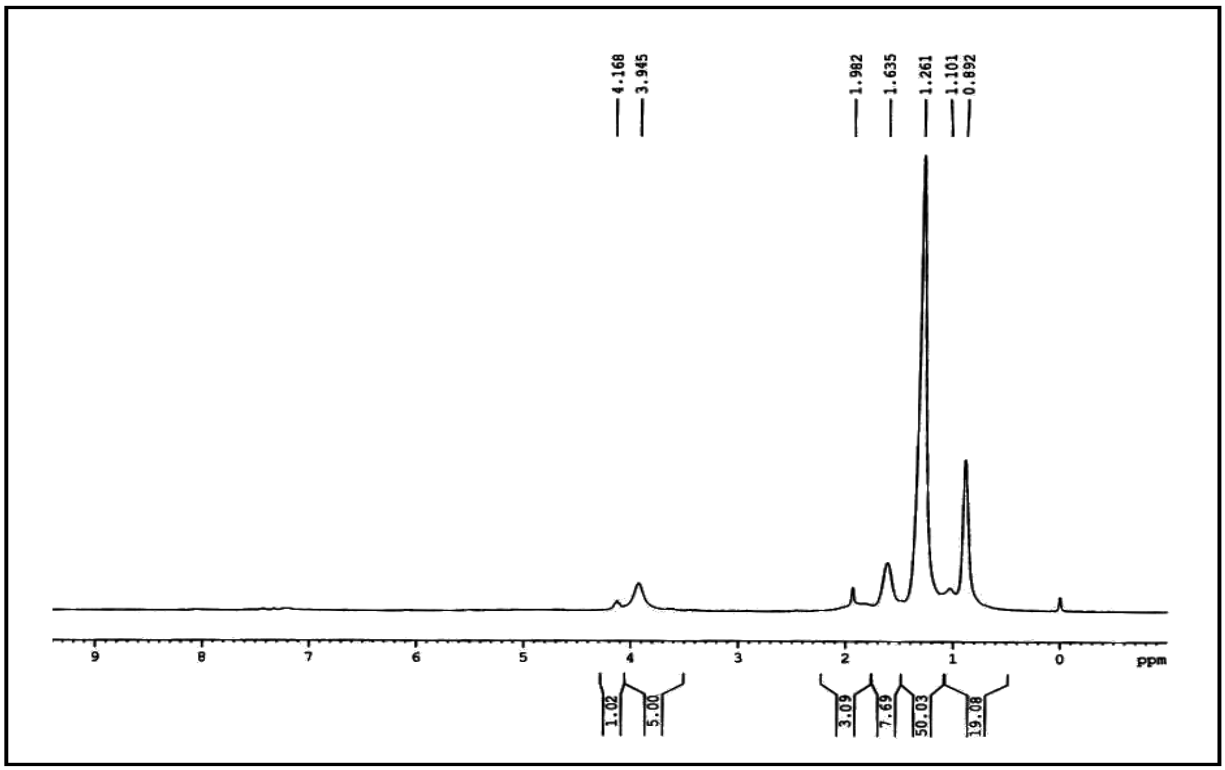


Figure 2.3.3: ^{13}C-NMR spectra of polymer P-1

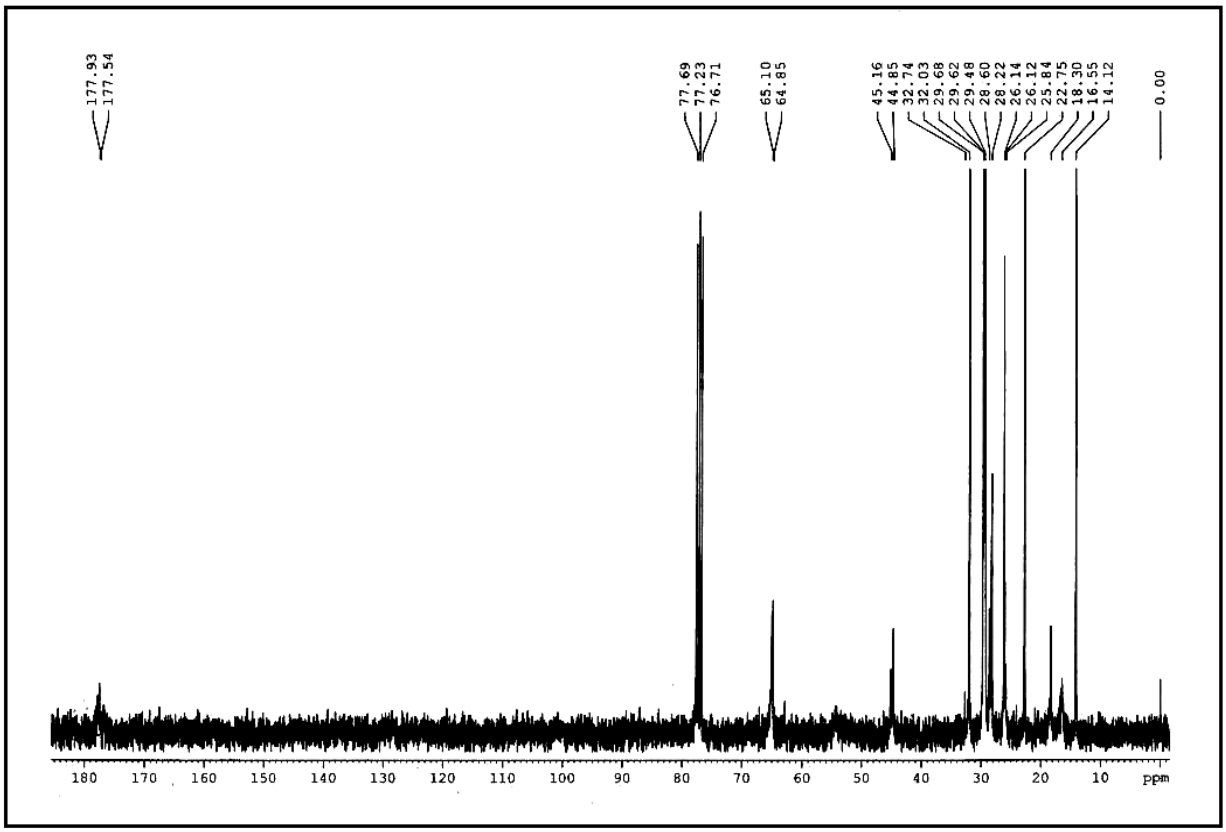


Figure 2.3.4: FT-IR spectra of polymer P-5

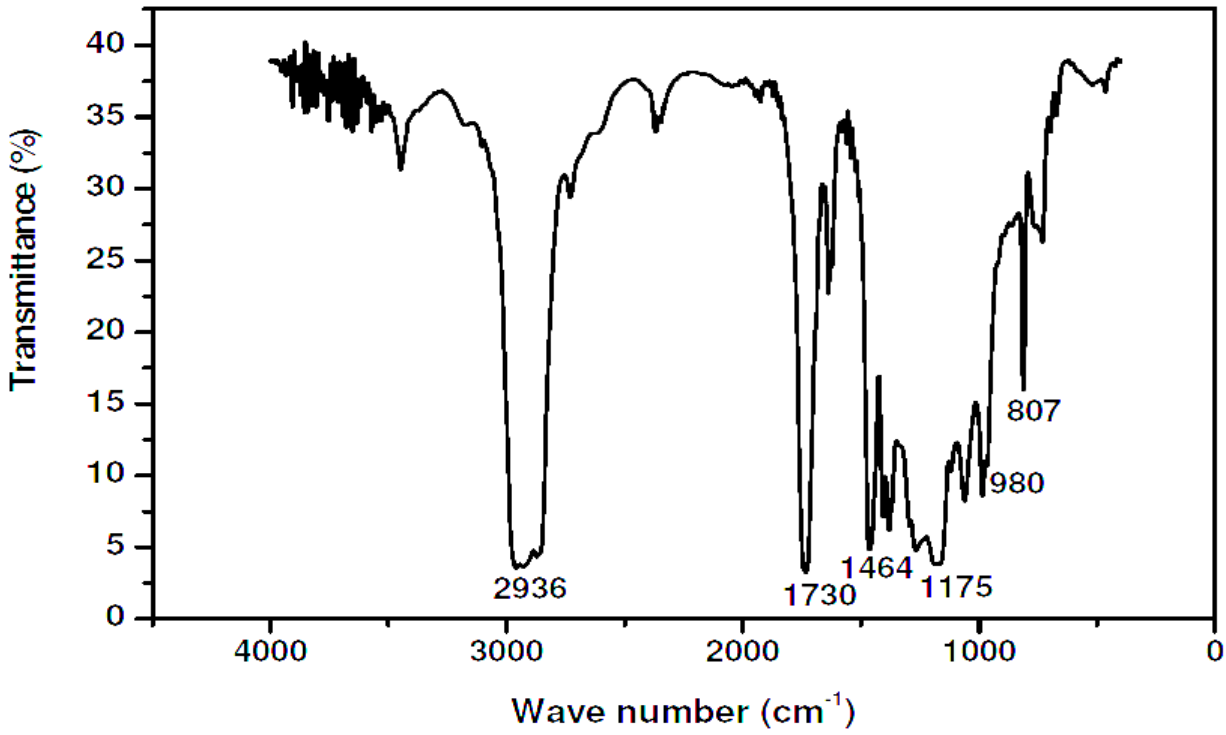


Figure 2.3.5: ^{1}H-NMR spectra of polymer P-5

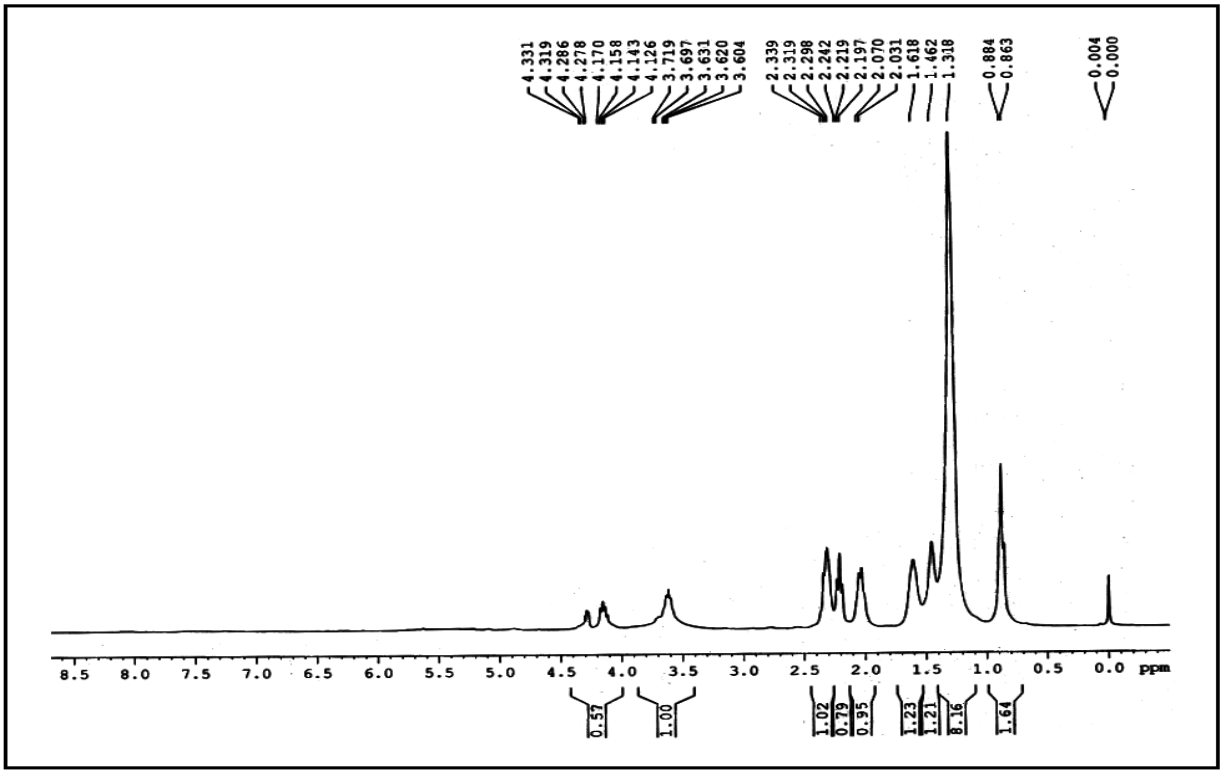


Figure 2.3.6: ^{13}C-NMR spectra of polymer P-5

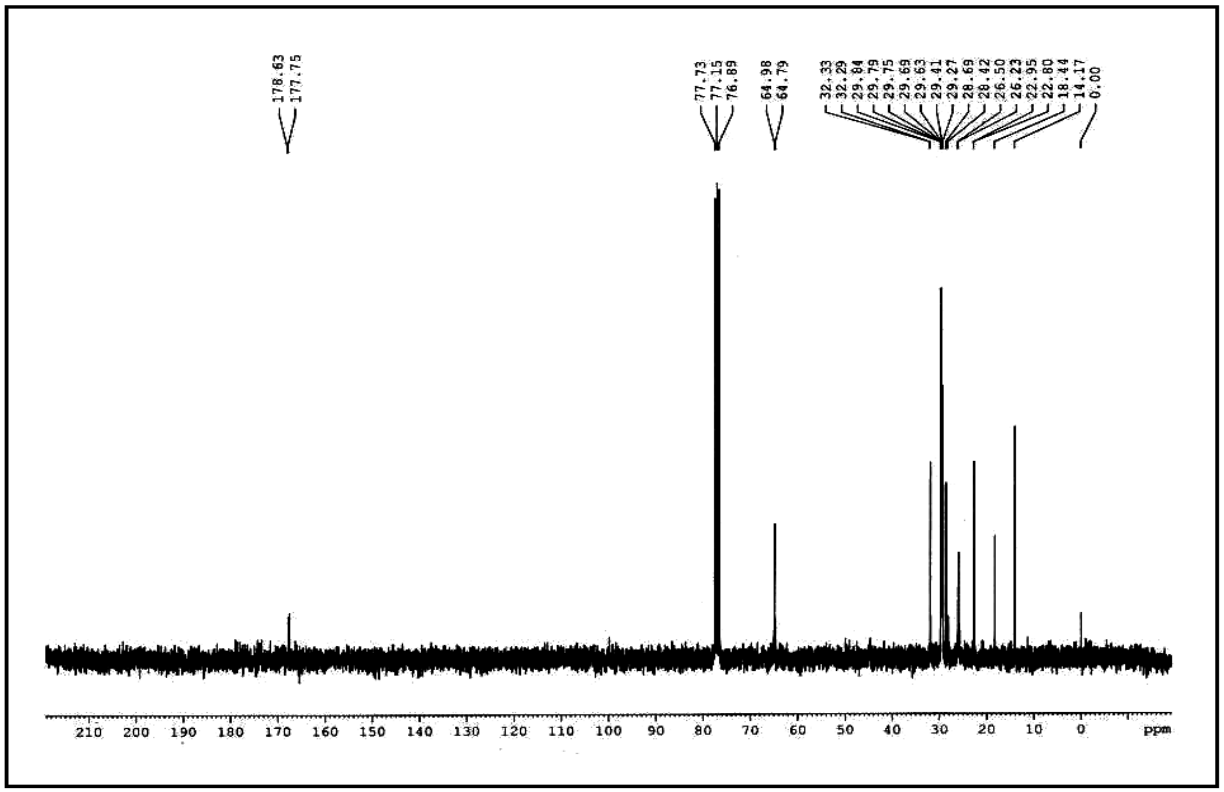
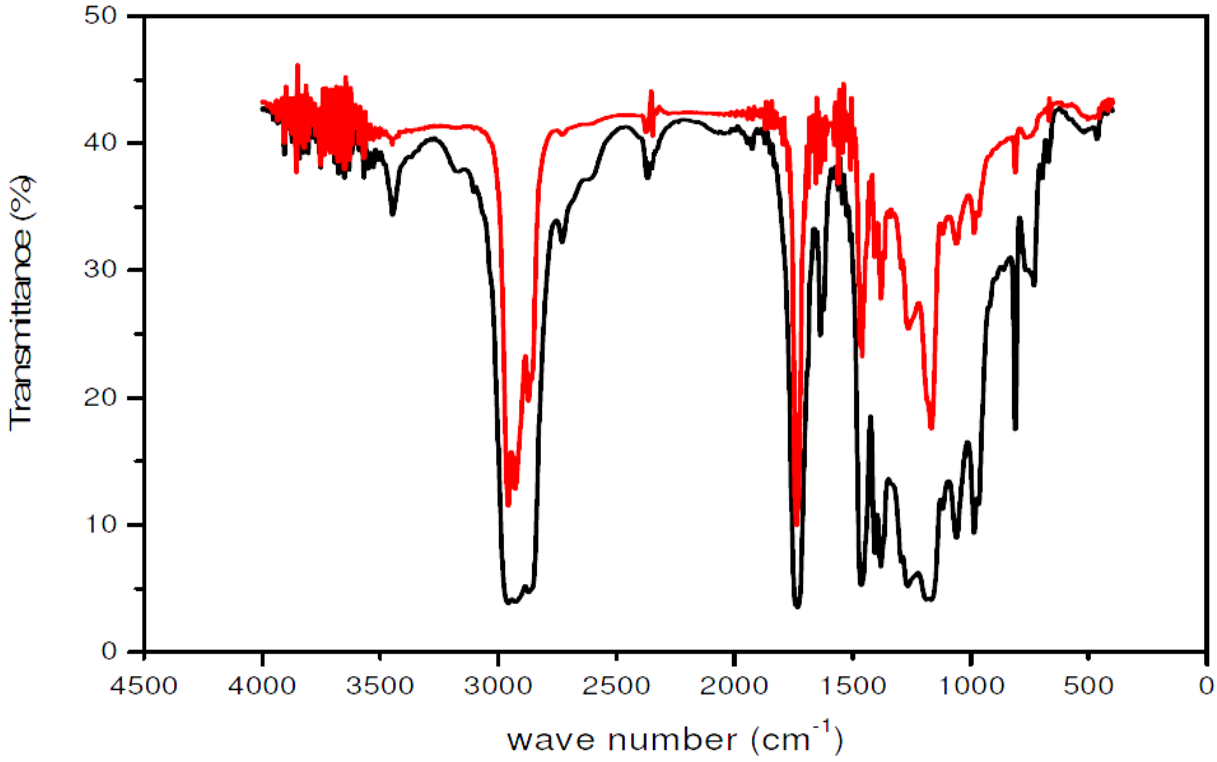


Figure 2.3.7: IR spectra variation of P-5 after the DD test



Black line: IR spectra before the test, Red line: IR spectra after the test.

Figure 2.3.8: Viscosity index of the polymer blended BO1 in various percentages

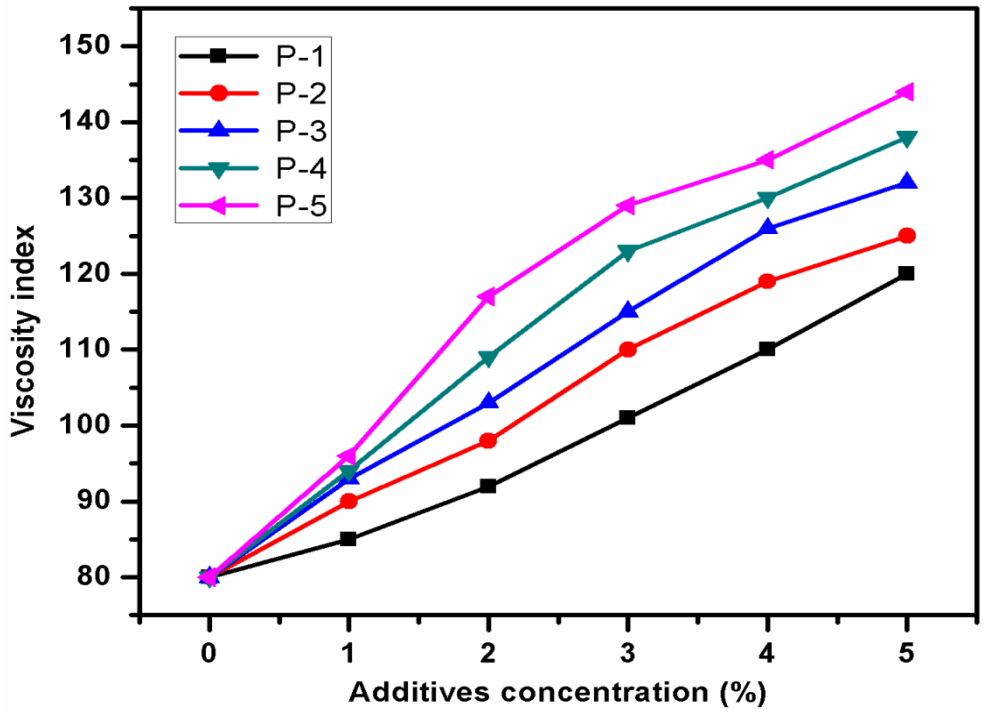


Figure 2.3.9: Viscosity index of the polymer blended BO2 in various percentages

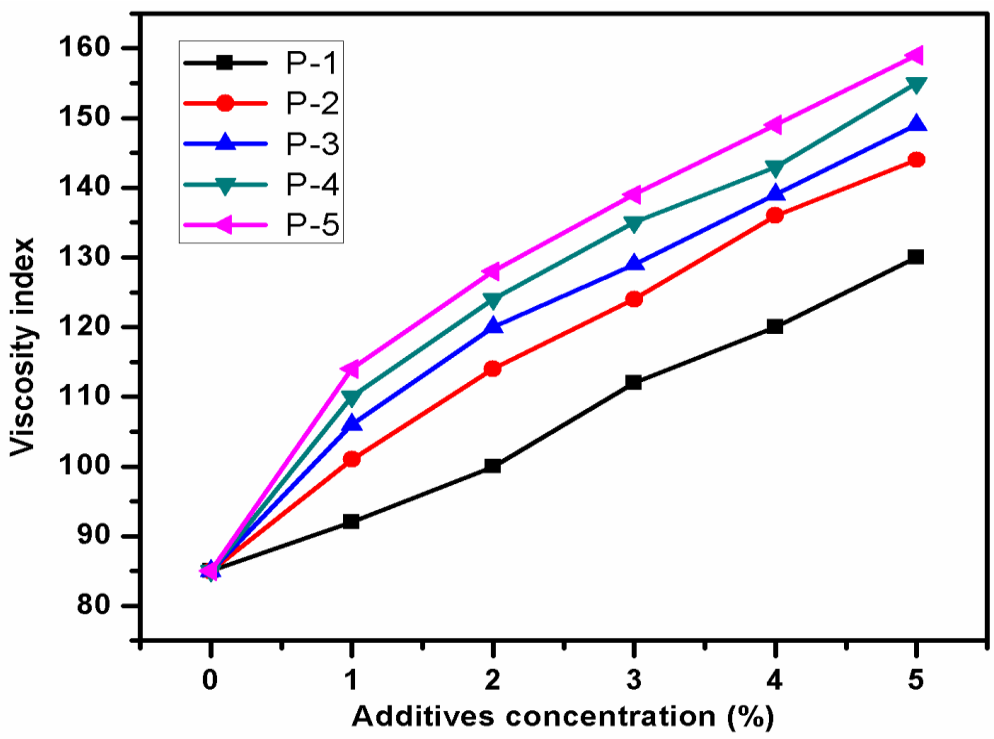


Figure 2.3.10: Pour point of the polymer blended BO1 in various concentrations

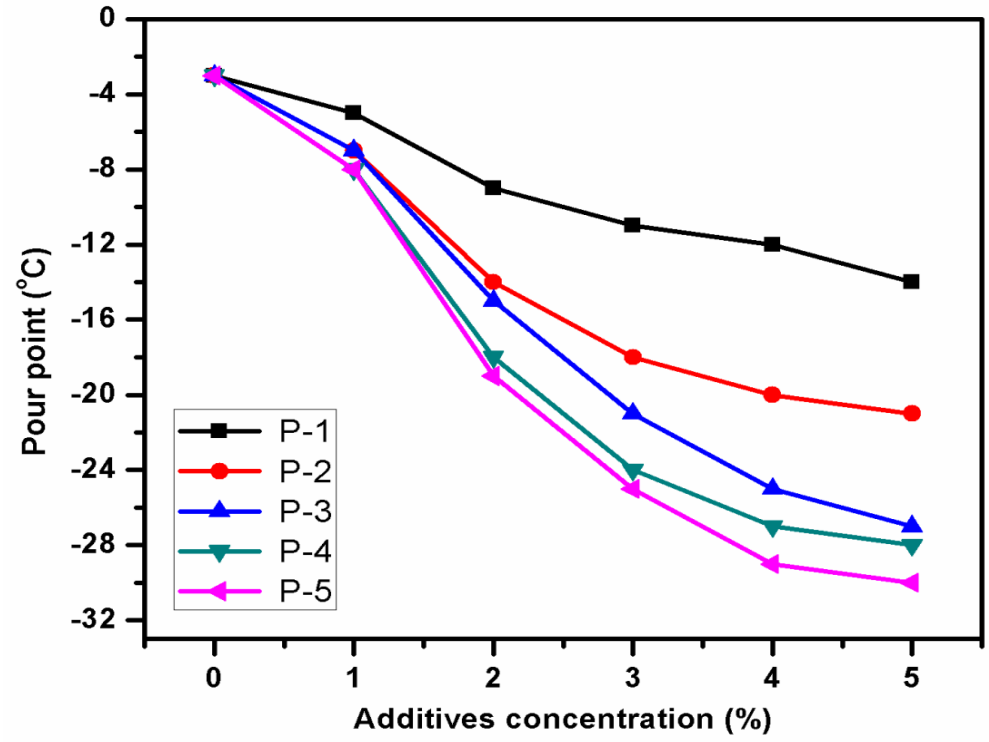


Figure 2.3.11: Pour point of the polymer blended BO2 in various concentrations