Chapter II

Synthesis and performance evaluation of maleic anhydride – 1- decene copolymer for lubricating oil

2.2.1 Introduction

Lubricating oil is a complex mixture of paraffinic wax, aromatic and naphthenic hydrocarbons with high molecular weights, very low volatility and with high viscosity index. The proportions of different hydrocarbon components determine the characteristic of the base oil.[1] However, the base oil alone cannot satisfy the requirements of lubricating oil without addition of additives. These additives, commonly known as lube oil additives are oil soluble substances that can improve the properties already present or add some new properties in the base oils. Some additives act to reduce the rate at which undesirable changes take place in the finished product during its service life. Some of the important commonly used additives are viscosity modifier or viscosity index improver,[2] pour point depressant,[3] antiwear,[4] detergents/ dispersants and antioxidants.[5]

The viscosity index is an indicator which indicates the change in viscosity when the temperature is changed. A higher viscosity index indicates the less change in viscosity of an oil for a given temperature change.[6] Viscosity index improvers (VII) or viscosity modifiers (VM) are the polymeric additives that resist the change of viscosity of oil with change in temperature. They are long chain, high molecular weight polymers.[7] It is believed that polymer molecule in lube oil solution exists as a random coil, which is swollen by lube oil solvent at high temperature and produces a network with lube oil and cause a minimal increase of viscosity in engine oil at low temperature but considerable increase at high temperature.[8]

Most of the base oil contains some dissolved paraffinic wax. At low temperature, the wax crystallizes to form a rigid structure that trap the oil in small packets in the structure. With sufficient formation of these crystal structures, the oil will no longer capable to flow.[9] The lowest temperature at which the lube oil just stops its flowing is called pour point. To overcome this problem some high molecular weight polymers are used as pour point depressant (PPD). Pour point depressants, otherwise known as lube oil flow improvers (LOFI), are those additives that improve the low temperature fluidity of the fluid. The pour point depressants function by inhibiting the formation of a wax crystal structure that would prevent the oil flow at low temperatures.[10]

In the present work, author has prepared 1-decene-maleic anhydride copolymer and due to insolubility of the copolymer in lube oil, it was esterified with three different long chain alcohols (isooctanol, n- decanol and n- dodecanol). The efficiency of the prepared polymers has been investigated as viscosity index improver and pour point depressant in three types of base oil through standard test methods.

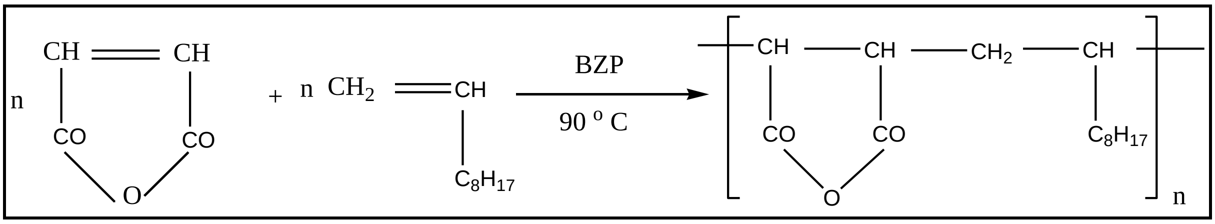
2.2.2 Experimental section

2.2.2.1 Chemicals used

Maleic anhydride (99%, LOBA Chemie, India) and 1-decene (95%, Acros organics) were used without further purification. Benzoyl peroxide (98%, LOBA chemie, India) was used after recrystallisation from chloroform- methanol mixture. Toluene (98%, Sd. fine chemicals, India) was purified by distillation and used as solvent for polymerisation as well as esterification of polymer. P-toluene sulphonic acid (98%, LOBA chemie) was used as catalyst after complete drying. Isooctanol (99%, LOBA chemie, India), 1- decanol (99.1%, Sd. fine chemicals, India) and 1-dodecanol (98%, Sd. fine chemicals, India) were used in esterification without further purification. Base oils were collected from IOCL and BPCL, India. Physical properties of the three base oils are given in **table 2.2.1**.

2.2.2.2 Preparation of 1-decene-maleic anhydride copolymer

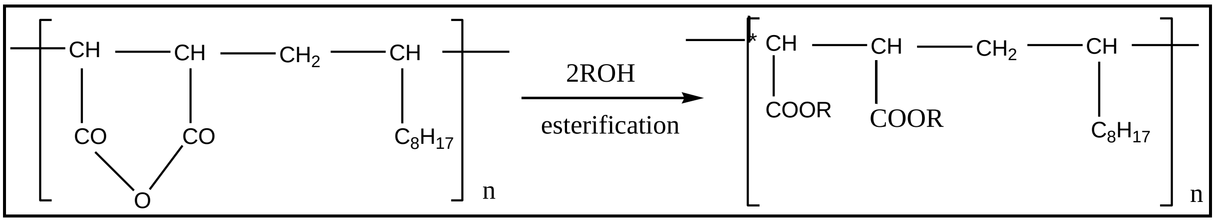
The copolymerization of 1-decene and maleic anhydride was carried out in a three necked round bottom flask fitted with a magnetic stirrer and an inlet for the introduction of nitrogen. 1-Decene and maleic anhydride was mixed in the molar ratio of 1:1 in the presence of benzoyl peroxide (0.5% w/w, with respect to the monomer) as an initiator and toluene used as a solvent. The reactants were mixed and temperature was kept constant at 90^{o} C and then benzoyl peroxide was added and heated for 8 hours. After the reaction is over, the product was put into cold methanol and filtered to obtain the copolymer.



Scheme 1 Preparation of copolymer of maleic anhydride and 1- decene

2.2.2.3 Esterification of the copolymer with different alcohols

The esterification of the prepared copolymer was reacted separately with isooctanol, n-decanol and n- dodecanol to prepare three esters of the copolymer. In a four necked round bottom flask fitted with a mechanical stirrer, an efficient condenser with Dean Stark apparatus, a thermometer and a nitrogen gas inlet. The dry copolymer was esterified with different alcohols in the presence of p-toluene sulphonic acid as a catalyst and toluene as a solvent. The copolymer and alcohol were taken in 1:1(w/w) ratio. Reaction mixture was slowly heated up to 130°C until all water of esterification is removed. The esterified product is dried by passing through solid Na_2SO_4 and finally methanol was added to precipitate the polymer and filtered to obtain the product. The designation of the prepared compounds is listed in **table 2.2.2.**



Scheme 2 Esterification of the copolymer

2.2.3 Measurements

2.2.3.1 Spectroscopic measurements

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

2.2.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (polystyrene calibration) equipped with a 2414 detector, waters 515 HPLC pump and 717 plus auto sampler. Sample solutions (0.4% w/v in HPLC grade THF) are prepared by dissolving ~4 mg of polymer per ml THF and filtering (0.45-µm Millipore PTFE) to remove suspended particulates. The pump flow rate is 1.0 mL/min with THF as the carrier solvent, and injection volumes are set to 20 µL. The polydispersity index [11] which indicates the nature of the distribution of the molecular weights in the polymers was also calculated.

2.2.3.3 Determination of Thermo gravimetric analysis (TGA) data

The thermo-oxidative stability of all the polymers was determined by a thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating of rate of 10 °C/min.

2.2.3.4 Performance evaluation as viscosity index improver

Viscosity index (VI) was calculated by dissolving prepared polymer in three different base oils (BOI, BO2 and BO3) using an Ostwald Viscometer (size 200, No 3205), thoroughly cleaned, dried and calibrated at the experimental temperatures (313K and 373K) with distilled water and purified methanol.[12, 13] It was then filled with experimental solution and placed vertically in a glass sided thermostat. After reaching thermal equilibrium, the time flow of solutions was recorded with a digital stopwatch. In all the determinations an average of three measurements was taken into account and precautions were taken to minimize the losses due to evaporation. The kinematic viscosity (ν) of the sample solution, which was used to calculate viscosity Index (VI), was determined at 313K and 373K temperatures from the following equation[14]

$$\nu = (Kt - L/t)\, d \qquad (1)$$

Where K and L are the viscometric constants and their values are 0.06853 $cm^2\, s^{-2}$ and 5.2706 cm^3 respectively, are determined by taking toluene as a solvent, t and d are the time of flow and density of the experimental solution respectively. The densities were measured with a density meter (Anton Paar, DMA 4500M). Before measurements, the density meter was calibrated with distilled water and acetone at the experimental temperature and atmospheric pressure. VI was calculated from the following empirical equation[14]

$$VI = 3.63\,(60 - 10^{n}) \qquad (2)$$

Where n is given by

$$n = (\ln \nu_1 - \ln k) / \ln \nu_2 \qquad (3)$$

Where ν_1 and ν_2 are the kinematic viscosities at lower and higher temperatures respectively, K is a constant which is equal to 2.714 for the temperature range performed and n is the characteristic constant for each oil.[14]

Different concentrations ranging 1% - 6% (w/w) were used to study the effect of additive concentration on VI.

2.2.3.5 Performance evaluation as pour point depressant

Pour point depressants were calculated in polymer doped different base oils (BO1, BO2 and BO3) through the pour point test according to the ASTM D 97-09 method[15] using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging 1% - 6% (w/w).

2.2.4 Results and discussion

2.2.4.1 Analysis of molecular weight and TGA data

The experimental values of M_n and M_w for the polymer A, B and C (determined by GPC) are given in **table 2.2.3.** From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the M_w values decrease but PDI value increases.

From TGA values of all the three polymers (**table 2.2.4**), it is seen that polymer C is thermally less stable than polymer A and B. Thermal stability of polymer A and B are almost same. Therefore, it is expected that polymer A and B are more linear than polymer C.[16]

2.2.4.2 Spectroscopic data analysis

The spectroscopic data of the three polymers A, B and C are similar. In the IR spectra (**figure 2.2.1**), the peak at 1736 cm^{-1} indicates presence of ester carbonyl group. The peak at 2854.5 cm^{-1} and 2924 cm^{-1} is the characteristic of CH_3CH_2- group. The peaks at 1465.8, 1404, 1373, 1211.2 and 1165 cm^{-1} due to CO stretching vibration and absorption bands at (810 cm^{-1} and 725 cm^{-1}) were due to bending of C-H bond. The disappearance of two anhydride peaks indicates that the esterification of copolymer was carried successfully.

In the ^1H NMR (**figure 2.2.2**), the methyl protons appear in the range of 0.88 to 0.92 ppm, the methylene protons in the range of 1.27 to 1.30 ppm for all alkyl groups. A broad peak at (4.17 ppm and 4.19 ppm) indicates the protons of $-OCH_2$ group. Absence of peak in the range of 5-6 ppm indicates the disappearance of C=C bond and confirms the polymerisation. In the ^{13}C NMR (**figure 2.2.3**), the peak at 165.27 ppm indicates the presence of ester carbonyl carbon. The peak at 65.35 ppm confirms the presence of $-OCH_2$ carbon. The peaks ranging from 14.03 – 32.62 ppm represents all sp^3 carbon atoms of alkyl groups. No peak in the range of 120-150 ppm indicates the absence of sp^2 carbons and confirms the polymerization.

2.2.4.3 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers at a concentration range of 1% - 6 % (w/w) in different base oils. The values are given in **table 2.2.5**. From the experimental data, it is found that VI values increase with increasing the concentration of polymer in base oil. The higher concentration of polymer increases the total volume of polymer micelles in the oil solutions and hence increases the VI.[17] The VI value of polymer A is higher than polymer B and C in all the three base oils. The lube oil viscosity decreases with increasing temperature but expansion of polymer molecules increase with increasing temperature. As a result, the hydrodynamic volume increases and micelle size of the solvated polymer molecule also increase and resists the reduction of the viscosity of lube oil with temperature.[18, 19] This effect is greater in case of polymer A and may be due to its higher molecular weight. From the

figures 2.2.4, 2.2.5 and **2.2.6**, it is found that all the polymers are more effective in BO2 and least effective in BO3 as VII.

2.2.4.4 Analysis of pour point data

The polymer doped base oils (BO1, BO2 and BO3) at different concentration ranging from 1% - 6% (w/w) were tested for pour point and experimental values are given in **table 2.2.6**. From the values, it is observed that all the three polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oil. It may be due to decrease in solvation power.[20, 21] Among the three polymers (A, B and C), the polymer C is more efficient as PPD in all the three base oil. It may be due to decrease in molecular weight and increase in polydispersity index.[22, 23] Pour point of polymer A and B are not so much different in BO1 but in BO2 and BO3, the pour point of polymer B is higher than polymer A (**figures 2.2.7, 2.2.8 and 2.2.9**). From the values of ΔPP, a critical observation can be taken that in most of the concentrations ΔPP value is higher in case of base oil BO1. This indicates that the polymers are more effective in case of BO1 i.e. in the lower viscous base oil.

2.2.5 Conclusions

From the above study, it is found that all the prepared polymers are effective as VI and PPD. In case of VI, polymer A is more effective than B and B is more effective than C. This indicates that with decreasing the alkyl chain length in alcohols used for esterification, the VI property increases. The polymer C has highest PPD property than A and B, therefore, with increasing the alkyl chain length in alcohols used in esterification, the PPD property improves. Therefore, carbon chain length in polymer has a significant role when added in the lube oil to act as a VII and PPD.

2.2.6 References

References are given in the bibliography section under Chapter II of Part II (Page No. 186 - 188).

2.2.7 Tables and figures

Table 2.2.1 Physical properties of the base oils

Base oil properties	Base oils		
	BO1	BO2	BO3
Density (g cm^{-3}) at 40 ^{o} C	0.83	0.84	0.87
Viscosity at 40 ^{0}C in c St	7.102	23.502	107.120
Viscosity at 100 ^{0}C in c St	1.850	3.98	10.322
Viscosity index	84.56	85.15	81.5
Pour point (^{o} C)	-3	-6	-0.5
Cloud point (^{o} C)	-1	-4	+2

Table 2.2.2 Polymer code of the prepared compounds (esters)

Copolymer + Alcohol	Code
1-Decene-maleic anhydride copolymer + Isooctanol	A
1-Decene-maleic anhydride copolymer + n- decanol	B
1-Decene-maleic anhydride copolymer + n- dodecanol	C

Table 2.2.3 Molecular weight of A, B and C (determined by GPC)

Polymer code	M_n	M_w	PDI
A	19,327	19,496	1.02
B	15,883	18,056	1.14
C	9,105	14,472	1.59

M_n = Number average molecular weight, M_w = weight average molecular weight, PDI = Polydispersity index

Table 2.2.4 TGA data for the polymers A, B and C

Polymer	Decomposition temperature/ ^{o} c	Percent weight loss(PWL)
A	203/365	26/44
B	195/ 360	27/48
C	183/309	32/53

Table 2.2.5 Viscosity index of polymer of A, B and C at different concentrations in different base oil (BO1, BO2 and BO3)

Polymer	Base oil	VI of Polymer doped base oil						
		0%	1%	2%	3%	4%	5%	6%
A	BO1	84.6	94	97	99	102.6	104.5	114
	BO2	85.2	102.3	106	108	112.4	124	124
	BO3	81.5	87.5	93.4	98.5	104	109	109
B	BO1	84.6	92.3	95	98.7	102.7	104.7	109.8
	BO2	85.2	92.5	106	106	112	120	124
	BO3	81.5	88	88	94	104	107	108
C	BO1	84.6	89	94.6	94	99	103	103.7
	BO2	85.2	93	94	100.5	110	116	117
	BO3	81.5	87	90	91	98	103	106

Table 2.2.6 Pour point (PP) and difference in pour point of pure lube oil and polymer doped lube oil (ΔPP) of polymer A, B and C at different concentrations (w/w) in base oils (BO1, BO2 and BO3

Polymer code	Base oil	PP	ΔPP	PP	ΔPP	PP	ΔPP	PP	ΔPP	PP	ΔPP	PP	ΔPP
		1%		2%		3%		4%		5%		6%	
A	BO1	-10	7	-10	7	-8	5	-8	5	-6	3	-6	3
	BO2	-10	4	-10	4	-9	3	-8	2	-7.5	1.5	-7.5	1.5
	BO3	-6	5.5	-5.5	5	-5	4.5	-5	4.5	-3.5	3	-3.5	3
B	BO1	-10	7	-8	5	-8	5	-7.5	4.5	-5.5	2.5	-5.5	2.5
	BO2	-12	6	-11	5	-11	5	-11	5	-8	2	-8	2
	BO3	-6	5.5	-8	7.5	-6	5.5	-5.5	5	-4	3.5	-4	3.5
C	BO1	-14	11	-12	9	-12	9	-9	6	-9	6	-8.5	5.5
	BO2	-12	6	-14	8	-14	8	-11	6	-10	4	-10	4
	BO3	-9	8.5	-8.8	8.3	-8.8	8.3	-7	6.5	-6	5.5	-6	5.5

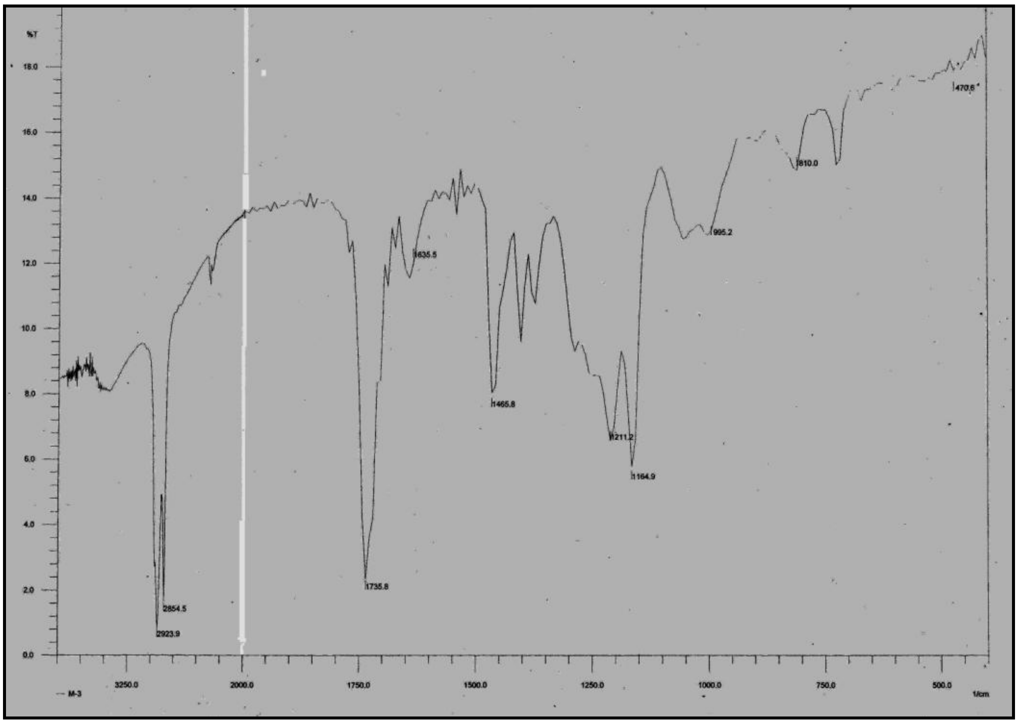


Figure 2.2.1 IR spectra of polymer C

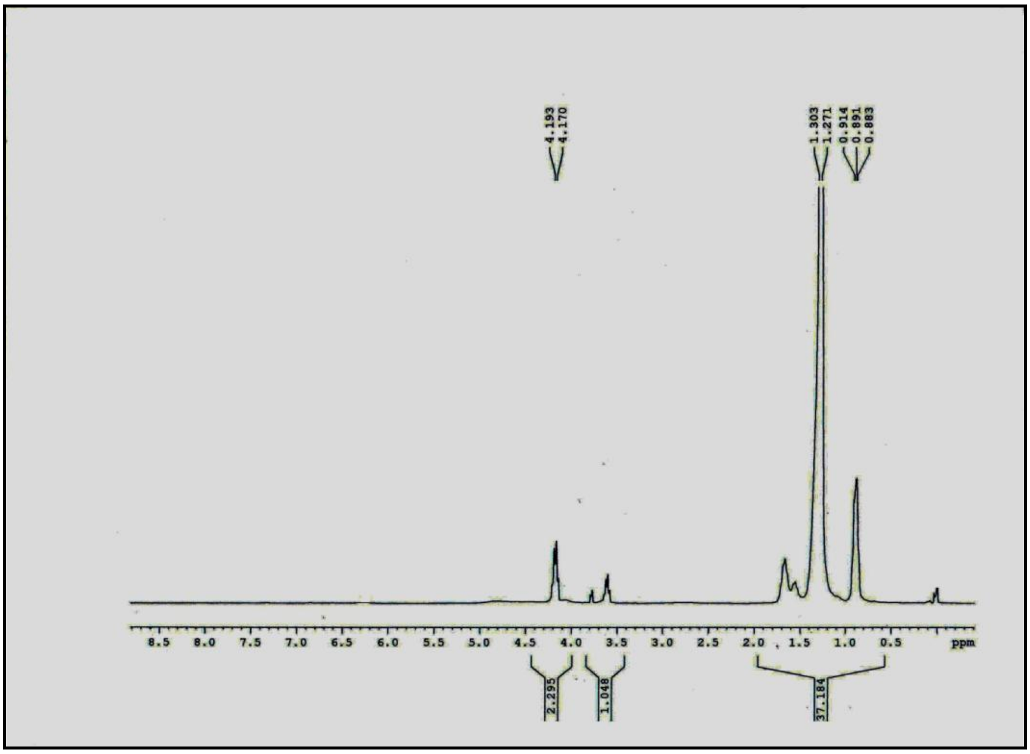


Figure 2.2.2 ^{1}H NMR of polymer C

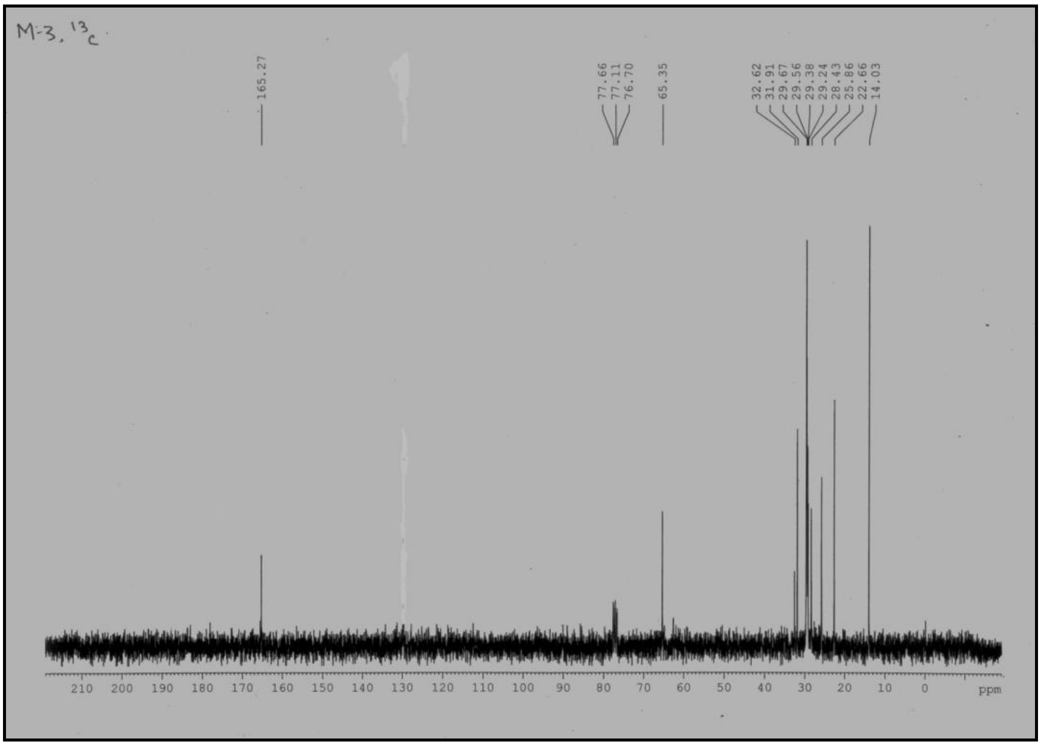


Figure 2.2.3 ^{13}C NMR of polymer C

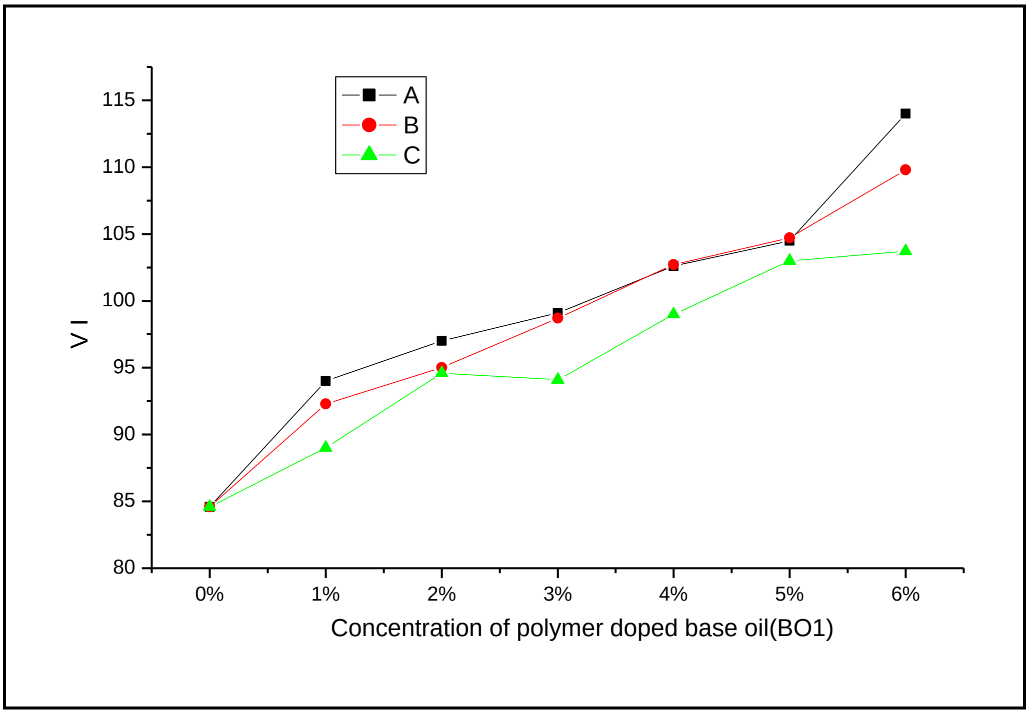


Figure 2.2.4 Comparison of VI values of three polymers in base oil, BO1

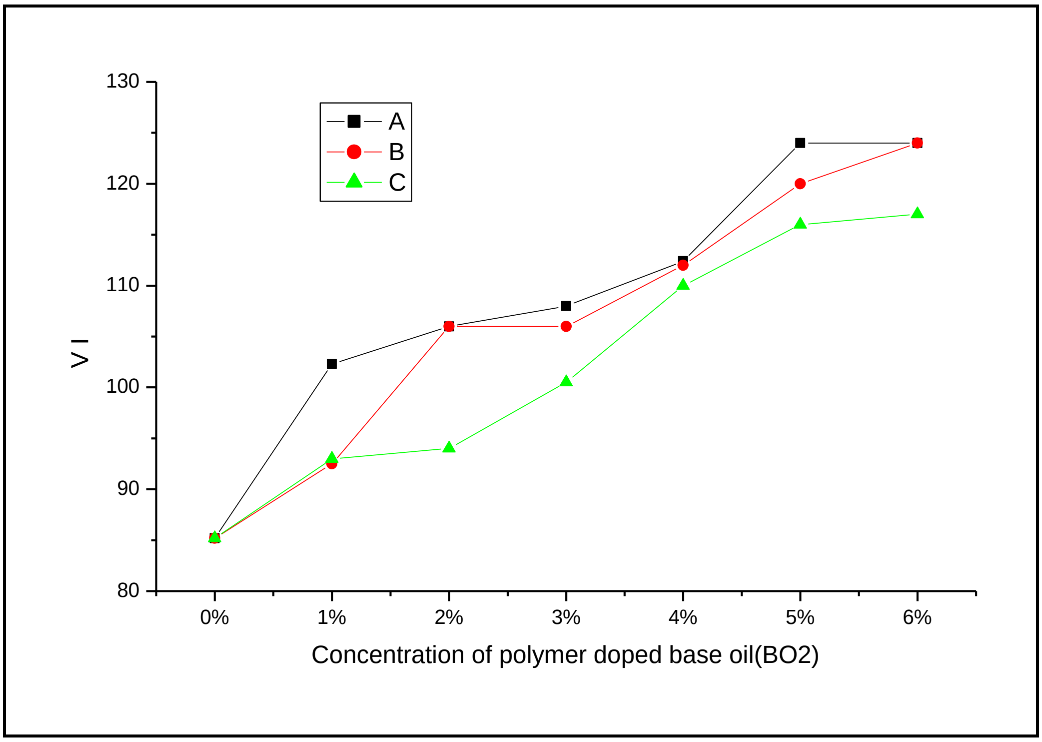


Figure 2.2.5 Comparison of VI values of three polymers in base oil, BO2

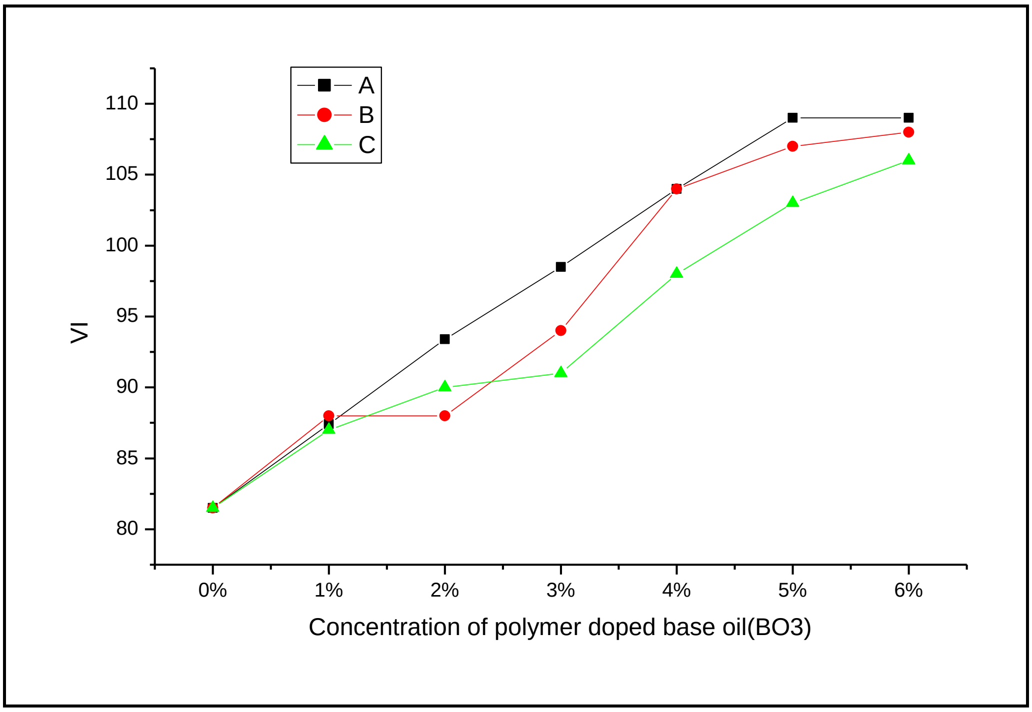


Figure 2.2.6 Comparison of VI values of three polymers in base oil, BO3

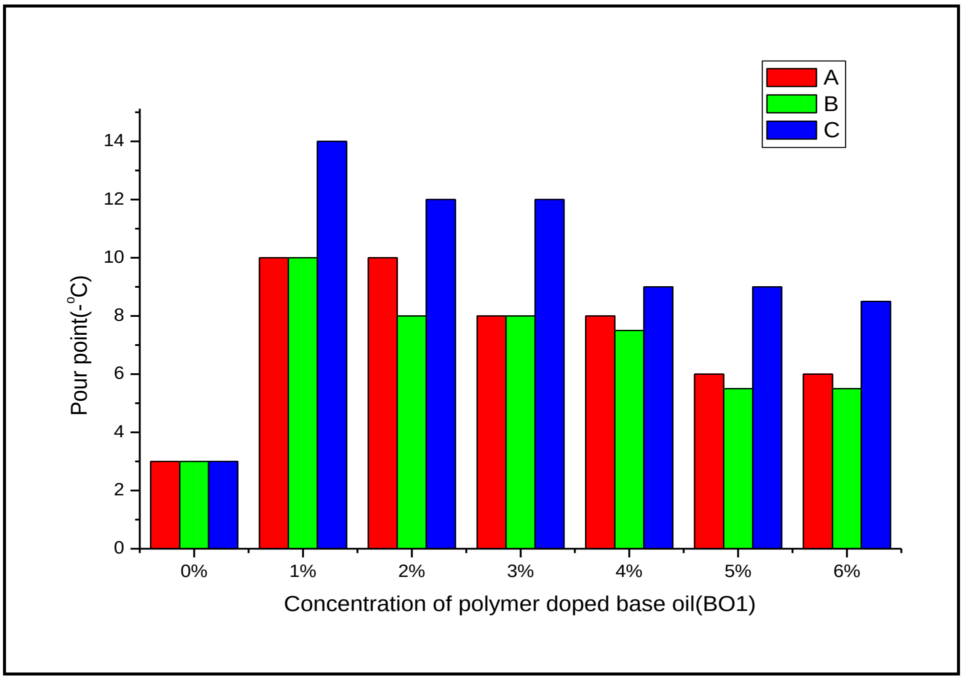


Figure 2.2.7 Comparison of pour point values of three polymers in base oil, BO1

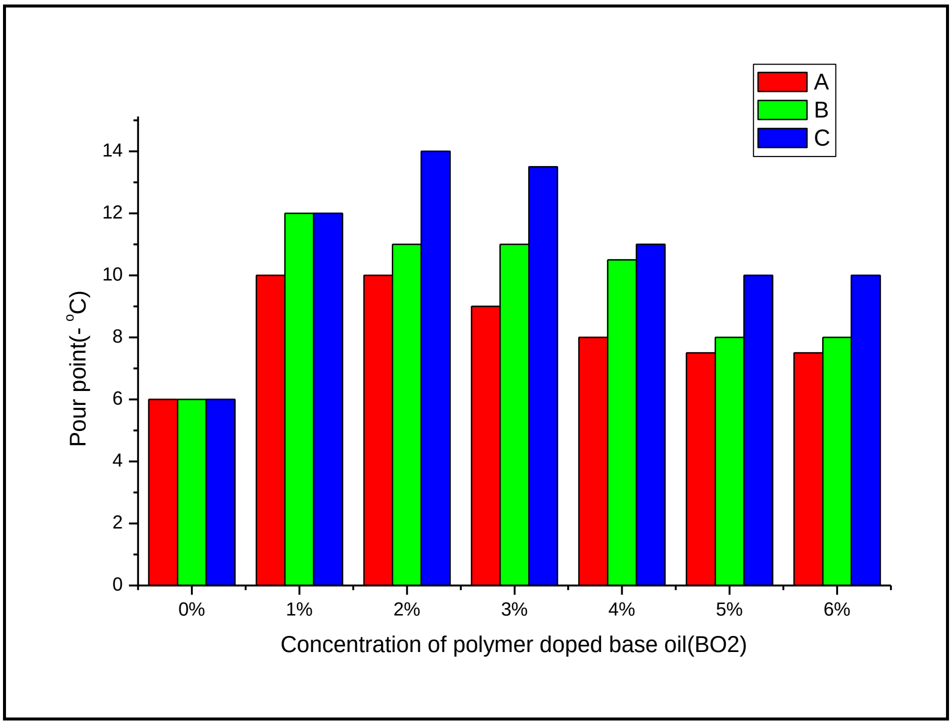


Figure 2.2.8 Comparison of pour point values of three polymers in base oil, BO2

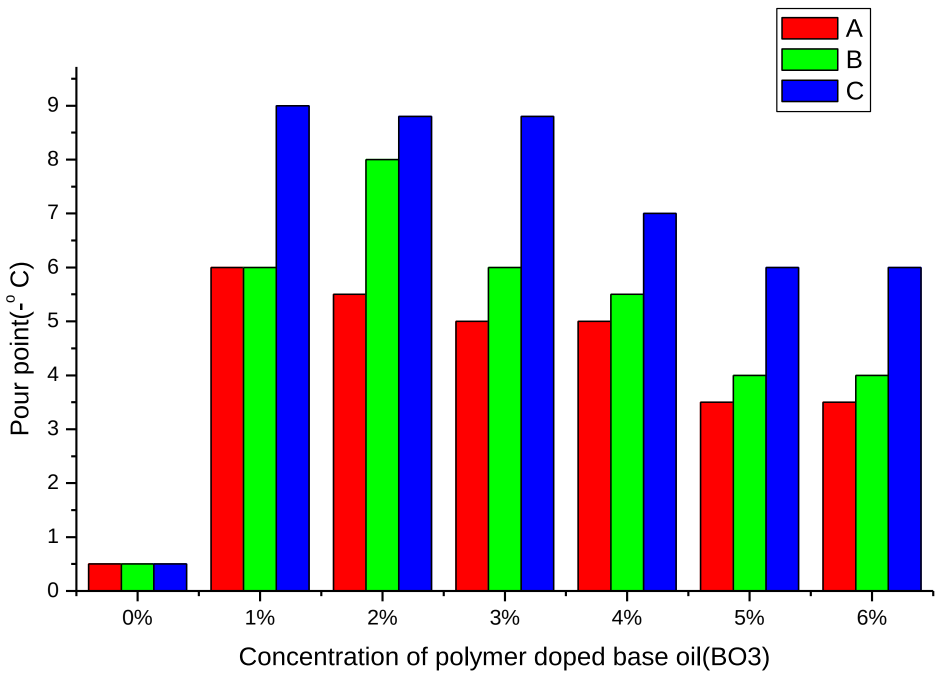


Figure 2.2.9 Comparison of pour point values of three polymers in base oil, BO3