Chapter IV

Multifunctional lube oil additives based on maleic anhydride and 1-decene

2.4.1 Introduction

Engine oils are used to reduce the metal to metal contact of the moving parts in internal combustion engine. With the development of modern engine technology, the demands are being placed to modify engine oils or lubricating oils for automotive engines. Hence much research effort has been committed to develop the lubricating oil. The petroleum based lubricating oil can't satisfy all the requirements of modern engines. Hence, to enhance the characteristic properties, those already present or to impart some new additional properties, a large number of additives are to be added to the lubricating oil.[1]

The most important single property of lubricating oil is its viscosity. Lubricating oils are used in different fields depending on their viscosity and viscosity index (VI) is an important affecting factor on the field of application of lubricant.[2] The variation of viscosity of a lubricant with change in temperature is determined by its viscosity index (VI), which is an arbitrary number calculated from the observed kinematic viscosities at two widely separated temperatures (generally at 40 ^{o} C and 100 ^{o} C).[3, 4] VI improver is added to the base oil to get better VI.[5] Viscosity index improver or viscosity modifier increases the thickness of the base oil and develop the viscosity – temperature characteristic of base oil.[6] A higher viscosity index indicates the less change in viscosity of an oil for a given temperature change.[7]

The pour point of lubricating oil is the lowest temperature at which it cannot flow. Lube oil contains some paraffinic waxes. The solubility of waxes decreases with decreasing temperature. The temperature at which first crystal appears is called cloud point or wax appearance temperature.[8] Below this point, the wax crystals grow up and form three dimensional network. This network traps the oil molecules around it and a gel like structure is made.[9] This gel on further cooling becomes sufficiently dense and the movement of the lube oil get stopped. But when pour point depressants (PPD), also known as lube oil flow improvers (LOFI), are added, they modify the crystal structure of waxes by adsorption and produces smaller and more isotropic crystals which have higher solubility and hence pour point decreases.[10]

Lubricating oils are subjected to oxidation at high temperature in the presence of air or metal and due to oxidation; lube oil decomposes to form some oxidation products, sludge and varnish, dirt etc. and as a result viscosity increases. The oxidation products, sludge particles deposit on the engine parts. Dispersants keep these particles in a dispersed form. Dispersant additive contains a polar head group with an oil soluble hydrocarbon tail, keeps metal surfaces clean by preventing deposition of oxidation products of internal combustion engines.[11, 12] The mechanism of dispersancy is generally described on the basis of adsorption of the additive through its polar ends on the sludge materials.[13, 14]

In the present work, author prepared maleic anhydride -1-decene copolymer by using AIBN as an initiator in toluene solvent and due to insolubility of the copolymer in lube oil, it was aminated with three different long chain amines (n-octyl amine, n-decyl amine and n-dodecyl amine). The efficiencies of the prepared polymers as viscosity index improver, pour point depressant and dispersant in three types of base oils through standard test methods were investigated.

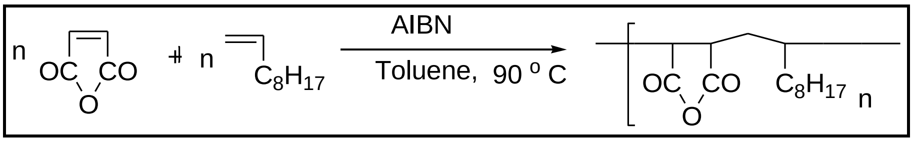
2.4.2 Experimental section

2.4.2.1 Chemicals used

Maleic anhydride (99%, LOBA Chemie, India) and 1-decene (95%, Acros organics) were used without further purification. AIBN (98%, Spectrochem Pvt. Ltd.) was used after recrystallisation from chloroform - methanol mixture. Toluene (Thomas Baker, 99%) was purified by distillation and used as solvent for polymerisation as well as amination of polymer. Octyl amine (Spectrochem Pvt. Ltd., 99%), n- decyl amine (Acros Organics, 99%) and n- dodecyl amine (Sigma – Aldrich, 99%) were used without purification. Methanol (Thomas Baker, 98%) was used after purification by distillation method. Base oils were collected from IOCL and BPCL, India and their properties are given in **table 2.4.1.**

2.4.2.2 Preparation of maleic anhydride - 1-decene Copolymer

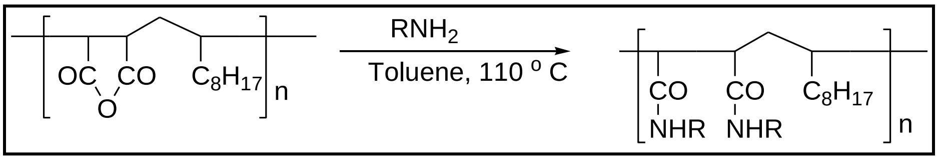
The copolymerization of 1-decene and maleic anhydride was carried out in a three necked round bottom flask fitted with a magnetic stirrer and an inlet for the introduction of nitrogen. Maleic anhydride and 1-decene was mixed in the molar ratio of 1:1 in the presence of AIBN (0.5% w/w, with respect to the monomer) as an initiator and used toluene as a solvent. The reactants were mixed and temperature was kept constant at 90^o C and then AIBN 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 Copolymerization of maleic anhydride and 1-decene

2.4.2.3 Reaction of maleic anhydride – 1-decene copolymer with different amines

The prepared copolymer was reacted with different amines (n-octyl amine, n-decyl amine and n-dodecyl amine) separately in a ratio of 1:1 (w/w) to prepare three polymeric additives designated by A_1, A_2 and A_3 respectively. The reaction was carried out in a three necked round bottom flask fitted with a condenser, a magnetic stirrer and a thermometer and heated for 6 hours in toluene solvent at 110^{o} C. After the reaction time is over, cold methanol was added to the reaction mixture. The amidated copolymer appears as precipitate and finally filtered and dried to obtain the product.



Scheme 2 Amidation of copolymer with different amines. $RNH_2 = C_8H_{17}NH_2$ (octyl amine) gives polymeric additives A_1; $RNH_2 = C_{10}H_{21}NH_2$ (decyl amine) gives polymeric additives A_2; $RNH_2 = C_{12}H_{25}NH_2$ (dodecyl amine) gives polymeric additives A_3

2.4.3 Measurements

2.4.3.1 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.

2.4.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (Waters 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 35 ^{o} C at a flow rate of 1ml/min.

2.4.3.3 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.

2.4.3.4 Performance evaluation as viscosity index improver (VII)

Viscosity index was calculated by dissolving prepared polymer in three types of base oils (BO1, BO2 and BO3) through the viscosity index test according to ASTM D 2270-10. The kinematic viscosity of the polymer doped base oil was determined at 40^{o} C and 100^{o} C.

Different concentrations of additives [ranging from1% - 5% (w/w)] were used, to study the effect of additive concentration on VI.

2.4.3.5 Performance evaluation as pour point depressant (PPD)

Pour point was determined in polymer doped three types of base oils (BO1, BO2 and BO3) through the pour point test according to the ASTM D 97-09 method 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 from 1% - 5% (w/w).

3.4.3.6 Photomicrographic image

The photomicrograph showing wax behaviour of lube oil (BO2, pour point = - 6) without and with 3% (w/w) polymers has been recorded at 0^{o} C temperature. A Banbros polarizing microscope model BPL-400B was used for photographic analysis. The adopted magnification was 200X.

3.4.3.7 Performance evaluation as dispersant

Spot method was applied to determine dispersancy[15]. A few drops of oxidized product of pure lube oil and lube oil containing 3% additive (w/w) were taken from the Indiana oxidation apparatus where samples are oxidized at 165.5 ^{o} C in presence of Fe and Cu strips and after each 24 h intervals of oxidation and up to 72 h to make spots on filter paper (Durieux 122) and dispersancy of the sample was calculated as follows:

$$\% \text{ Dispersancy} = \frac{\text{Diameter of the black spot}}{\text{Diameter of the total spot}} \text{ x } 100$$

An additive having higher value of dispersancy will act as a good dispersant for lube oil.

3.4.4 Results and discussion

3.4.4.1 Spectroscopic analysis

The spectroscopic data of the three polymers A_1, A_2 and A_3 are similar. In the IR spectra (**figure 2.4.1**), a peak at 1644 cm $^{-1}$ indicates the presence of amide group. The presence of two peaks at 2854 cm $^{-1}$ and 2923 cm $^{-1}$ indicate the characteristic of CH_3 CH_2- group. A peak at 1697 cm $^{-1}$ represents the carbonyl group present in amide group. The presence of a broad peak at 3278 cm $^{-1}$ represents –NH group. The disappearance of two peaks for anhydride group indicate that amidation of copolymer was carried out successfully.

In the ^{1}H NMR spectra (**figure 2.4.2**), the methyl protons appear in the range of 0.85 to 0.89 ppm, the methylene protons appear in the range of 1.26 to 1.49 ppm for all alkyl groups. The peaks appear in the range of 2.70 to 2.75 ppm indicate the protons of – CHCO- group. A broad peak at 3.886 ppm indicates the protons of $–NCH_2$ - group. A small peak at 8.85 ppm indicates the proton of – NH group. No peaks in the range of 5-6 ppm indicate that polymerization was carried out successfully.

In the ^{13} C NMR spectra (**figure 2.4.3**), the peak at 176.96 ppm indicates the presence of amide carbonyl carbon. The peak at 41.50 ppm confirms the presence of $–NCH_2$ carbon. The peaks ranging from 14.06 – 32.27 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 atoms and confirms the polymerization.

3.4.4.2 Analysis of molecular weight and TGA values

The experimental values of M_n and M_w of the prepared copolymers (A, A_1, A_2 and A_3) are given in **table 2.4.2**. From the values, it is found molecular weight increases with increasing the alkyl chain length of the amine used in the amidation of copolymers. From the experimental TGA values (**figure 2.4.4**), it is found that polymer A_1 has higher thermal stability than the other two copolymers. It may be due to lower molecular weight and lower PDI value.[16] All the three polymers starts decomposition at 90^o C. In case of A_1, a major decomposition is observed at 300^o C with a 32% weight loss. The thermal stability of A_2 and A_3 are almost same. A major decomposition is observed for these two polymers at 270^o C with a 41% weight loss.

3.4.4.3 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers at a concentrations range of 1% - 5 % (w/w) in three types of base oils. The values are given in **table 2.4.3**. 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, 18] The VI value of polymer A_3 is higher than polymer A_2 and A_2 is higher than A_1 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. [19 – 21] This effect is greater in case of polymer C which may be due to its higher molecular weight.

3.4.4.4 Analysis of pour point data

The polymer doped base oils (BO1, BO2 and BO3) at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **table 2.4.4**.

From the values, it is observed that all the three polymers can be effectively used as pour point depressant and efficiency as pour point increases with increasing the concentration of polymer in base oil up to 3%. This means that at this concentration, the polymer may interact with the paraffinic wax and modify their crystals size.[22, 23] Among the three polymers (A_1, A_2 and A_3), the polymer A_1 is more efficient as PPD in all the three base oils. It may be due to presence of short alkyl chain in polymer A_1. The interaction between the short alkyl chain length and paraffin in the lube oil is more effective than long alkyl chain length and wax crystal formation is prevented.[24] From the experimental values, it is also observed that all the three polymers are more effective as PPD in base oil, BO1. It may be due to lower viscosity of BO1.

3.4.4.5 Photo micrographic analysis

Photo micrographic analysis was used to study the pour point and its mechanism of the lube oil without and with polymeric additives. The photograph of lube oil (BO2) without and with different additives is shown in the **figure 2.4.5(a-d)**. The figure 2.4.5a is the photograph of lube oil (pour point = $-$ 6^{o}C) without any additives where there is large number of rod shaped wax crystals. The photo micrographic images of lube oil with 3% (w/w) of A_1, lube oil with 3% (w/w) of A_2 and lube oil with 3% (w/w) of A_3 are shown in the figures 2.4.5b, 2.4.5c, and 2.4.5d respectively. A significant wax crystal modification is observed in figure 2.4.5b (pour point = $-$19 ^{o} C). This is in agreement with the pour point values determined by ASTM D97-09 method.

3.4.4.6 Analysis of dispersant data

The lube oil (BO1, BO2 and BO3) and lube oil with 3% (w/w) polymer of each were subjected to severe oxidation conditions using the Indiana test method as described in experimental section, in which dispersant additive increases the diameter of the black spot. This is due to the enhanced capability of the doped oil to carry the oxidation products to a longer distance from the centre of the spot. It may be due to the fact that the –NH groups form hydrogen bonds with the polar end of oxidation products like alcohol, aldehyde, ketone, acids etc.[25, 26] Moreover, the presence of amine part present in the prepared additives neutralizes some of the acidic products formed during oxidation. It is observed that efficiency as dispersant increases with increasing the molecular weight of polymers and with increasing alkyl chain length. Among the three base oils (BO1, BO2 and BO3), the polymers are more effective as dispersant in base oil BO1 (**table 2.4.5**).

3.4.5 Conclusions

From the above study it is found that the prepared copolymers are effective as viscosity index improver, pour point depressant and dispersant for lube oil. The molecular weight of the prepared polymers increases with increasing the alkyl chain length of the amines used in amidation of copolymer. The efficiencies as VII and dispersant increase with increasing the molecular weight as well as with increasing the alkyl chain length of the polymer. Whereas, the efficiency as a pour point depressant increases with decreasing molecular weight of the prepared polymers and with the decreasing the alkyl chain length. Therefore, molecular weight and alkyl chain length of the polymers have a significant role for acting as a lube oil additives.

3.4.6 References

References are given in the bibliography section of Chapter IV of Part II (Page No. 190 - 192).

3.4.7 Tables and figures

Table 2.4.1 Physical properties of the base oils

Base oil properties	Base oil		
	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 2.4.2 Monomers, polymer code and M_n, M_w and PDI values of copolymers

Monomers	Polymer code	M_n	M_w	PDI
M.A + 1-D	A	16641	20559	1.24
M.A + 1-D + OAM	A_1	16047	23118	1.44
M.A + 1-D + DAM	A_2	11637	27190	1.93
M.A + 1-D +DDAM	A_3	15335	30330	1.97

M.A = Maleic anhydride; 1-D = 1- Decene; OAM = Octylamine; DAM = Decylamine; DDAM = Dodecylamine; M_n = Number average molecular weight; M_w = Weight average molecular weight; PDI = Polydispersity index.

Table 2.4.3 Viscosity index values of polymers of A_1, A_2 and A_3 at different concentrations (% in w/w) in different base oils (BO1, BO2 and BO3)

	Base	VI of Polymer doped base oil (conc. in %, w/w)					
Polymer	oil	0%	1%	2%	3%	4%	5%
A_1	BO1	84.6	92	98	104	109	116
	BO2	85.2	90	98	104	108	114
	BO3	81.5	90	92	98	106	109
A_2	BO1	84.6	93	99	108	115	119
	BO2	85.2	92	100	102	112	118
	BO3	81.5	90	95	102	112	116
A_3	BO1	84.6	98	104	112	118	124
	BO2	85.2	98	104	110	120	126
	BO3	81.5	95	100	109	116	120

Table 2.4.4 Pour point values of polymers A_1, A_2 and A_3 at different concentrations (% in w/w) in different base oil (BO1, BO2 and BO3).

Polymer	Base oil	Pour point of polymer doped base oil (conc. in %, w/w)					
		0%	1%	2%	3%	4%	5%
A_1	BO1	-3	-15	-16	-18	-18	-17
	BO2	-6	-16	-17	-19	-19	-19
	BO3	-0.5	-7	-7	-10	-10	-10
A_2	BO1	-3	-15	-15	-16	-16	-16
	BO2	-6	-15	-15	-17	-17	-16
	BO3	-0.5	-7	-8	-9	-9	-9
A_3	BO1	-3	-15	-15	-16	-16	-15
	BO2	-6	-14	-14	-15	-15	-15
	BO3	-0.5	-7	-8	-9	-9	-8

Table 2.4.5 Dispersancy of the lube oils (BO1, BO2, BO3) and their blends containing polymers (A_1, A_2 and A_3) after different oxidation periods

Sample	Dispersancy time, (in hour)		
	24	48	72
Lube oil (BO1) only	40	42	45
BO1 + A_1	60	67	68
BO1 + A_2	63.6	68	70
BO1 + A_3	64	73	75
Lube oil (BO2) only	30	32	45
BO2 + A_1	58	63	65.5
BO2 + A_2	62	66	68
BO2 + A_3	65	69.5	72
Lube oil (BO3) only	25	27	28
BO3 + A_1	54	60	62
BO3 + A_2	56	61	65
BO3 + A_3	56	64	65.5

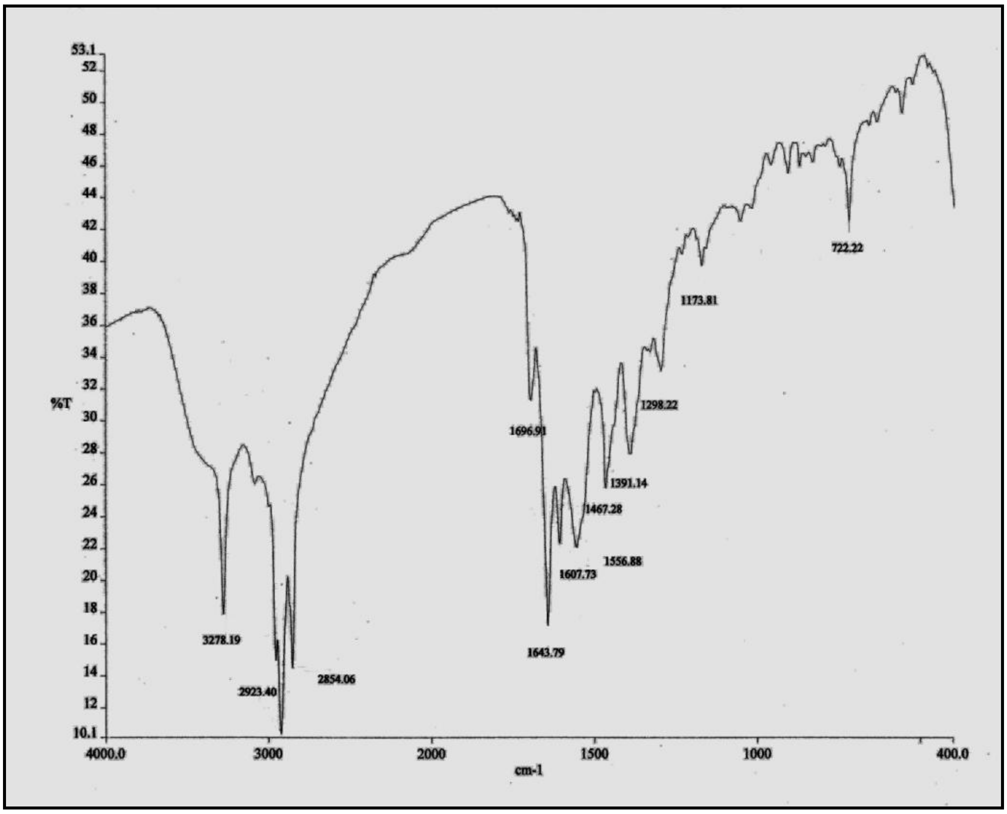


Figure 2.4.1 IR spectra of polymer A_1

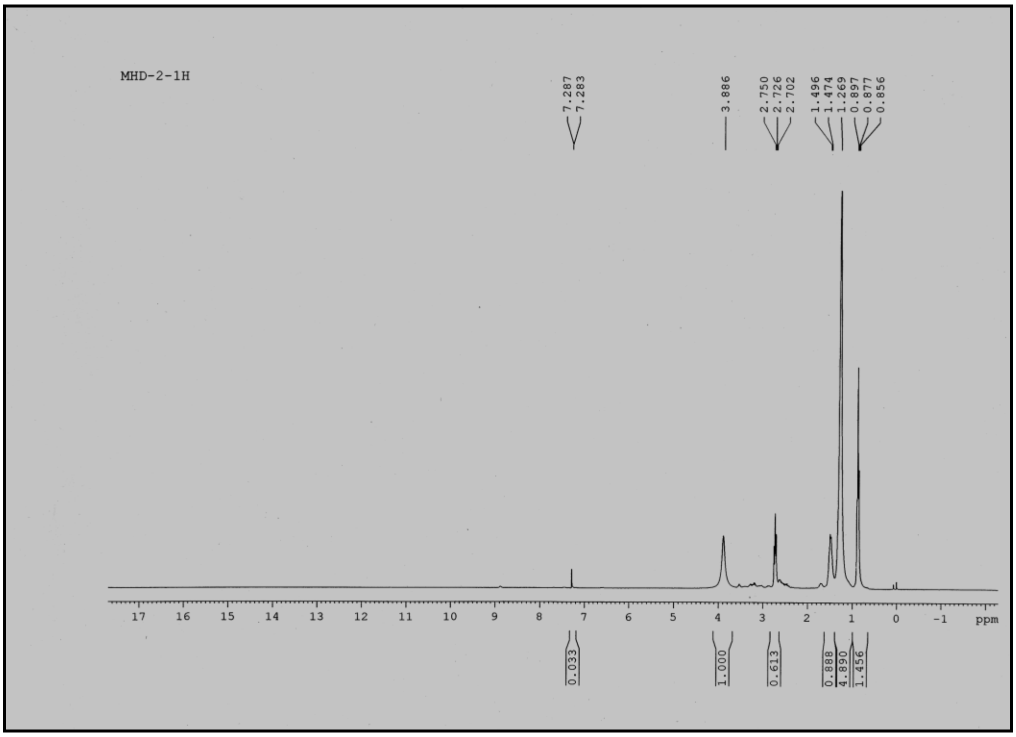


Figure 2.4.2 ^{1}H NMR spectra of polymer A_1

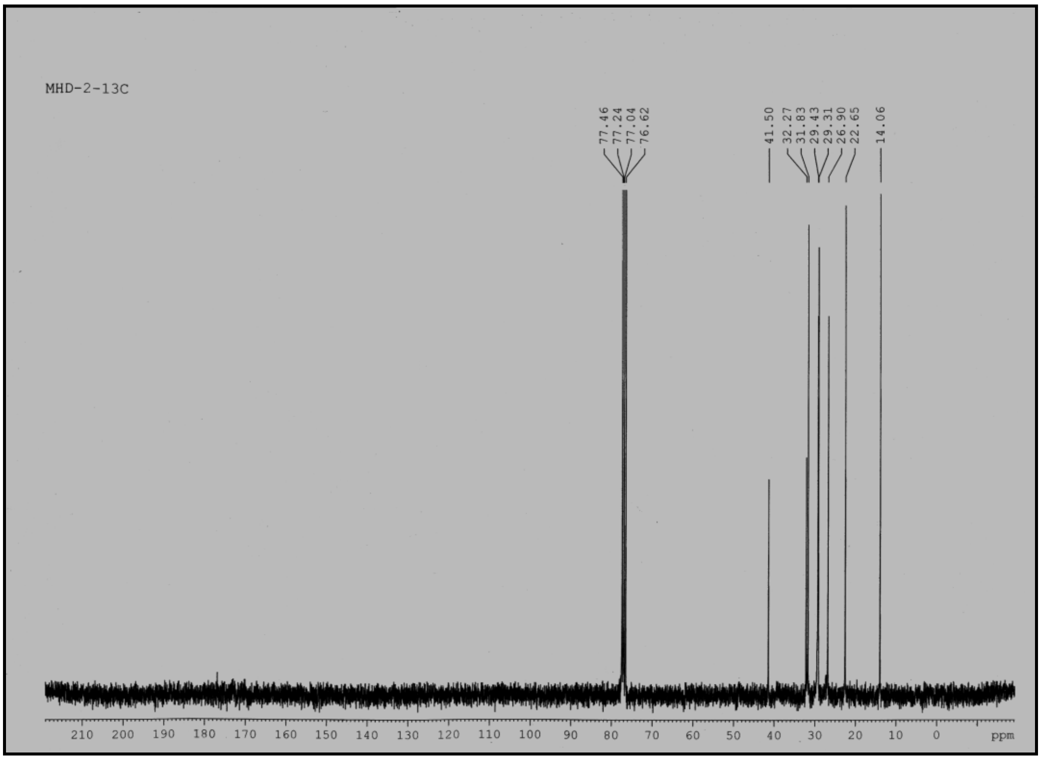


Figure 2.4.3 ^{13}C NMR spectra of polymer A_1

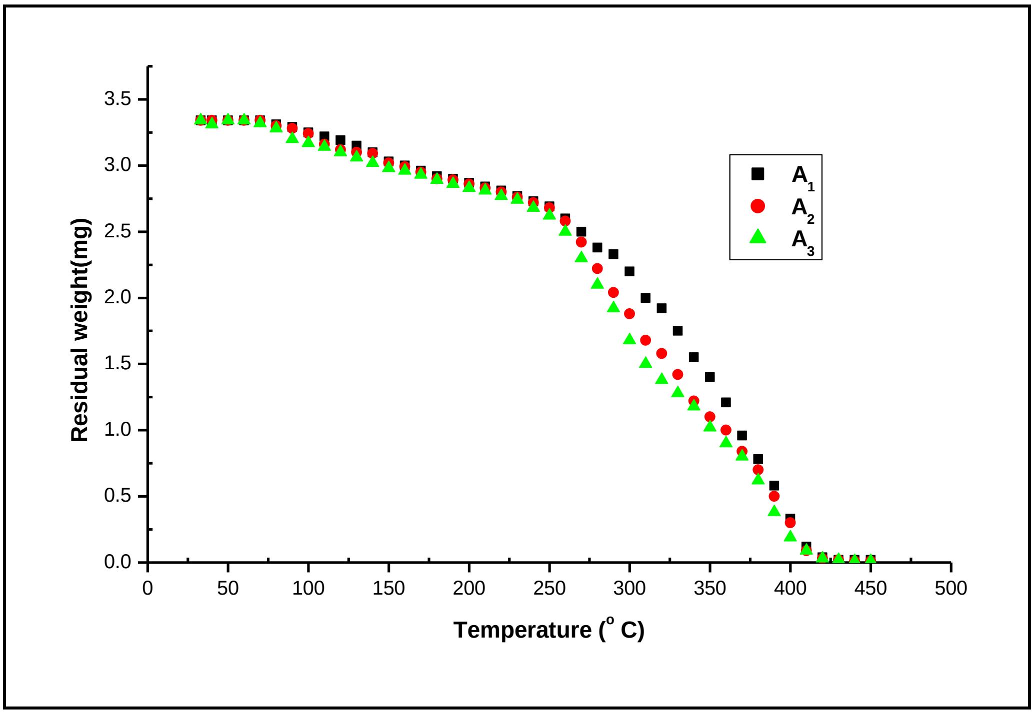
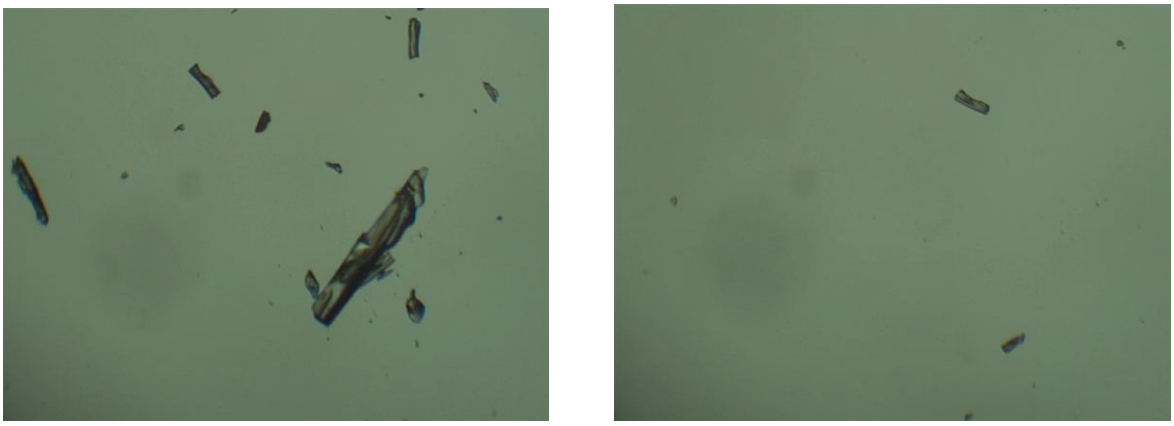
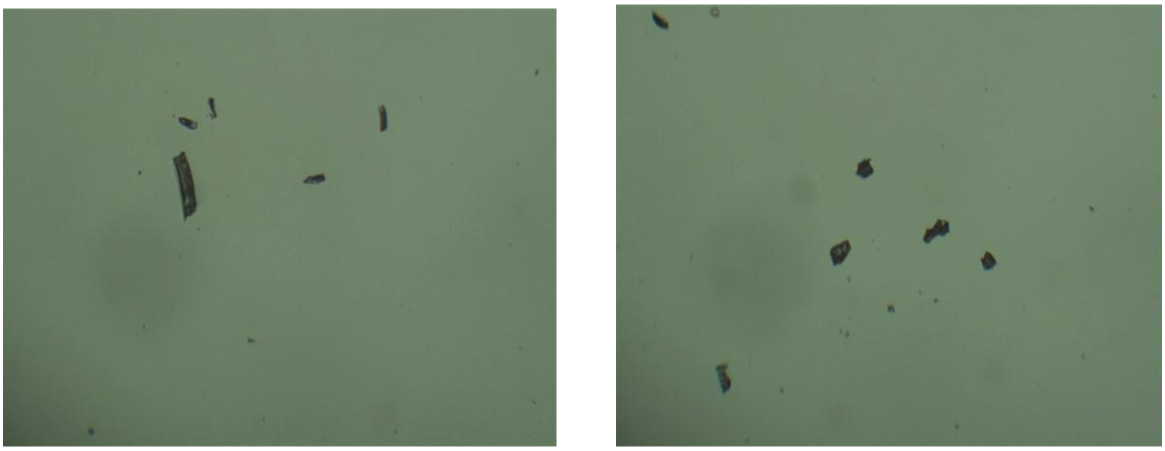


Figure 2.4.4 Thermal degradation of polymers A_1, A_2 and A_3



a. (pour point = -6 ° C)

b. (pour point = -19 ° C)



c. (pour point = - 17 ° C)

d. (pour point = - 15 ° C)

Figure 2.4.5 Photomicrograph images of a) Pure lube oil b) lube oil + 3% (w/w) of A_1 c) lube oil + 3% (w/w) of A_2 d) lube oil + 3% (w/w) of A_3