

Chapter-II

*Myristyl methacrylate based polymers
as performance additives for lube oil*

1.2.1 Introduction

From the time of the advent of the first mechanical device, the desire for the search of newer machineries and robust technologies has always fascinated us. Lubrication, therefore, became a crucial design parameter for developing and improving such equipments. In fact, lubrication technology has always remodelled itself to open up to new possibilities, and to meet the requirements for new applications in accordance to the mechanical systems. Lubricants have been used in the form of gas, liquid or solid, at the interface of two interacting surfaces to improve the energy efficiency of the machines and violating this axiom have resulted in extensive wear and permanent damage to the equipments.

The base fluid is the main ingredient of lubricants but is usually associated with many performance limitations. They are, therefore, blended with specialty chemicals called additives¹, such as cold flow improvers (FI)², viscosity modifiers (VM)³, antioxidants⁴, detergents⁵, corrosion inhibitors⁶ and extreme pressure agents⁷ etc. to impart new performance properties to the finished lubricant. More often additives serve more than one particular purpose and hence, the recent investigations are increasingly focussed toward constructing such type of additives with multifunctional activities. Among the various important design parameters, FIs and VMs are of prime importance for the effective and efficient performance of the lubricant.

Perhaps one of the most important requirements of lubricating oil is that it should be fluid over a wide range of temperature. The pour point (PP) is such an indicator and is the lowest temperature at which the oil will flow while operating at cold conditions.⁸ An additive that effectively improves the fluidity of oil at temperatures much lower than the normal pour point is called cold flow improver (FI), alternatively identified as pour

point depressant (PPD).⁹ At low temperatures, the paraffinic hydrocarbon (present in the base fluid) tends to get separated due to their low solubility. These waxy hydrocarbons, due to Van der Waals force of attraction, get attracted towards each other resulting in the formation of wax crystals.¹⁰ With further drop in temperature, the wax crystals grow in size creating a rigid interlocking crystalline net resulting in all the cold flow problems.¹¹ FIs restrict the wax crystal growth and interfere with the formation of the complex interlocking structures.

Again, the viscosity of fluid is of utmost importance while considering the fluid for different types of machines. Usually, the viscosity varies with temperature and so, a broad range of lubricant viscosities is required between the optimum operating conditions of the piece of equipment under study. If the viscosity becomes too low, the fluid becomes too thin to maintain a proper lubricating film inviting friction and wear of the solid surfaces. Again, lubricants with too high of a viscosity will increase the fluid friction causing reduced energy efficiency. Viscosity modifiers are the additives that help a lubricant to improve the quality and to maintain a proper viscosity over the temperature range of operation.¹² This dependence of lubricant viscosity with temperature is specified in terms of an empirical parameter called Viscosity Index (VI).¹³ It is a crucial parameter that describes the application temperature range of a lubricant. Lubricants with high value of VI have greater resistance to viscosity change with variation in temperature and are usually preferred in most mechanical systems.

Poly alkyl acrylates, poly alkyl methacrylates, styrene butadiene copolymers are some of the widely used additives used in specific composition and architecture for improving the tribological properties of the lubricating oils.¹⁴⁻¹⁶ We also described the introduction of acrylate based polymers several years ago.¹⁷ Going forward with our endeavour to construct the finest multifunctional performance additives for lube oil,

this present work reveals the synthesis, characterization and performance evaluation of additives based on the copolymers of long chain myristyl methacrylate and 1-octene. A comparative assessment of their performances as additive in contrast to the homopolymer of myristyl methacrylate was also studied.

1.2.2 Experimental section

1.2.2.1 Materials

For this study, methacrylic acid was obtained from Sisco Research Laboratories Pvt., Ltd., (India). Myristyl alcohol and hexane were from S D Fine-Chem Ltd., (India). 1-octene was purchased from Acros Organics and methanol was from Thomas Baker Chemicals Pvt., Ltd., (India). Toluene and H₂SO₄ were obtained from Merck Specialties Pvt., Ltd., (India). Azobisisobutyronitrile (AIBN) obtained from Spectrochem Pvt., Ltd., (India) was recrystallized from CHCl₃-CH₃OH before use. Other chemicals were used as received. Mineral base fluid (SN1) was obtained from Indian Oil Corporation Ltd. (IOCL), India. The properties of the base fluid and their specification are tabulated in Table 1.2.1.

1.2.2.2 Synthesis of the ester (methacrylic acid with myristyl alcohol)

The esterification reaction was performed in a resin kettle using 1.1 mol of methacrylic acid and 1mol of myristyl alcohol to prepare the ester, myristyl methacrylate (MMA). The reaction was carried out under a slow stream of deoxygenated nitrogen in 100 mL of toluene, conc. H₂SO₄ as catalyst and 0.25% of hydroquinone with respect to the reactants as polymerization inhibitor. The reactants

were thoroughly mixed in toluene and were heated slowly from room temperature to 403 K using a thermostat and a Dean–Stark apparatus for water separation. The ester was collected after monitoring the amount of water liberated (1 mol) during the reaction.¹⁸

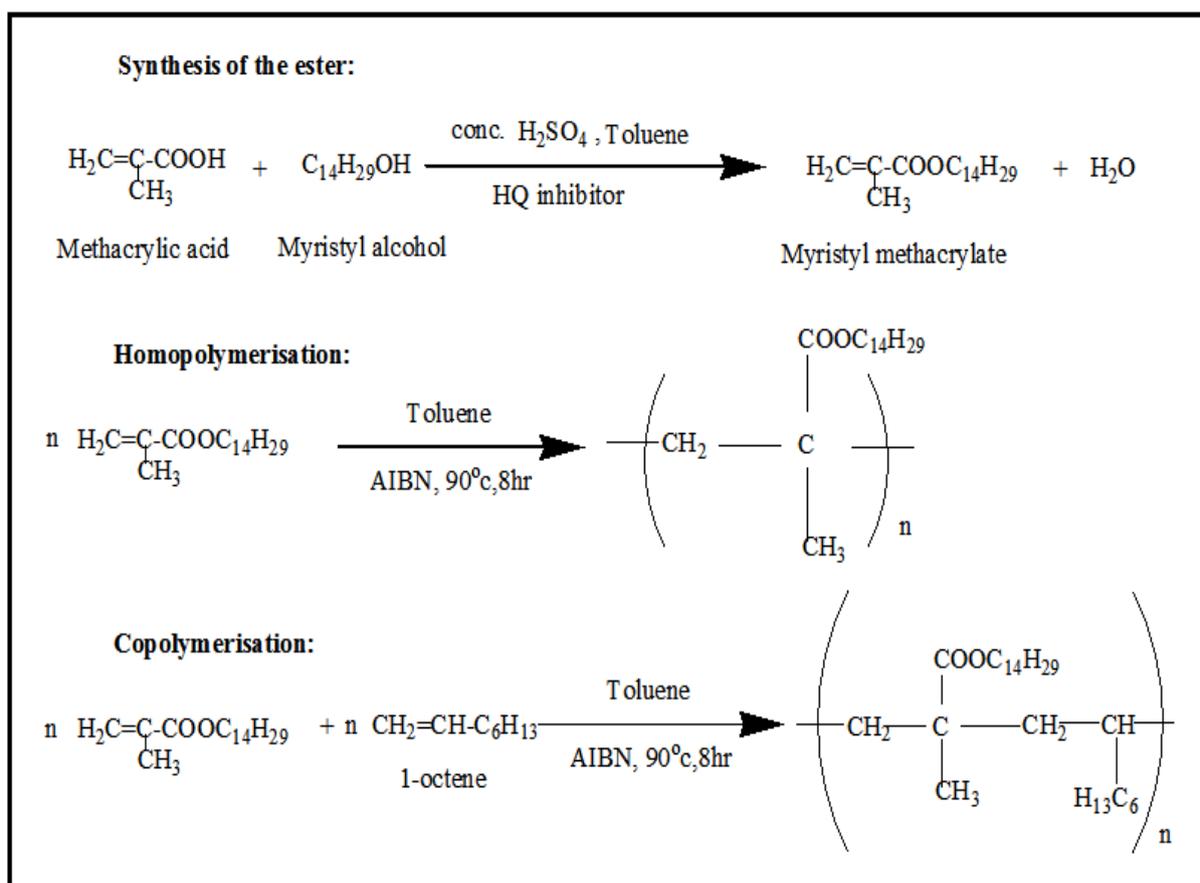
1.2.2.3 Purification of the prepared methacrylate ester

The prepared ester MMA was purified by adding 1 g of charcoal to it and refluxing it for 3 hours. After the stipulated time, the charcoal was filtered off and the filtrate so obtained was rinsed in a separation funnel with 0.5N NaOH. To ensure the complete removal of any unreacted acids, the process was repeated a number of times. The ester was again rinsed a number of times with distilled water to eliminate any NaOH (if left in small amount) until it became neutral to pH paper. The ester MMA was finally left over night on anhydrous CaCl₂. The CaCl₂ was later separated by filtration and toluene was recovered by distillation under reduced pressure.¹⁸ The ester left behind was ready for further use.

1.2.2.4 Synthesis of the homopolymer and the copolymers

The homopolymer of MMA (HMMA) and its copolymers with 1-octene were prepared by thermal polymerization method using a radical pathway. The reaction kettle consisted of a four-necked round bottom flask equipped with a heating jacket system, a thermometer, a mechanical stirrer, a reflux condenser and an inlet for the introduction of nitrogen. 10 g of MMA was placed in the flask with 10 mL of toluene (as a solvent) and it was mixed, gradually heated and maintained at the reaction

temperature (90 °C) for 20 min. The initiator, AIBN, (1% by weight with respect to the monomer) was then added in the flask and the temperature was maintained at 90 °C for 8 hour to prepare the homopolymer. After the reaction time, the mixture was allowed to cool to room temperature. Finally, to stop the polymerization reaction and precipitate the polymer, the mixture was transferred into cooled methanol with continuous stirring. For additional purification of the polymer, HMMA was precipitated by methanol from its hexane solutions repetitively followed by drying in a vacuum oven at 40 °C. Similar polymerisations with 1-octene were carried out for the synthesis of the copolymers, by using 10 g total of MMA with 5% or 10% or 15% of 1-octene. MMA and the initiator (with their required masses) were placed in the reaction kettle, followed by the drop wise addition of 1-octene for 3 hour keeping the other conditions the same.



Scheme 1: Synthesis of the ester, homopolymer and copolymer

The copolymers, so prepared, were also purified under the same conditions as for the homopolymer, for use in reference experiments. Table 1.2.2 reports the composition and designation of the prepared polymers.

1.2.2.5 Preparation of additive based lubricating oil formulations

For the preparation of the additive based lubricating oil formulations, the polymers (additives) were added in varying ratios (1-5%, w/w) to the base fluid SN1. Each solution was stirred for homogenization at a rotational speed of 300 rpm for 2 hour at a temperature of 50 °C. The solutions were then cooled down to room temperature.

1.2.3 Measurements

1.2.3.1 Spectroscopic measurements

For recording the IR spectra, a Shimadzu FT-IR 8300 (Japan) spectrometer was used within the wavenumber range of 400 to 4000 cm^{-1} at room temperature using 0.1 mm KBr cells. The NMR spectra were recorded in Bruker Avance 300 MHz (Germany) FT-NMR instrument using CDCl_3 as a solvent and 5 mm BBO probe.

1.2.3.2 Measurement of average molecular weight

A GPC apparatus (Waters Corporation, USA) was employed to calculate the average molecular weight (number-average and weight-average, M_n & M_w) of the additives using HPLC grade THF as an eluent. The system was fitted with a 2414

refractive index detector (polystyrene calibration) and Waters 515 HPLC pump. The PDI (M_w/M_n) was also calculated by GPC. The data obtained are presented in Table 1.2.3.

1.2.3.3 Thermo gravimetric measurements

The thermo-oxidative stabilities (TGA) or the decomposition pattern of the prepared additives in air were determined by a Shimadzu TGA-50 (Japan) thermo gravimetric analyzer, at a heating rate of 10 °C min⁻¹. The percent weight loss (PWL) of mass (of the additives) with rise in temperature was used to measure the thermal stability of the additives. The PWL was measured by the equation,

$$\text{PWL} = [(M_0 - M_1)/M_0] \times 100 \quad \text{Eq. (1)}$$

where M_0 is the original mass taken and M_1 is the remaining mass after the test. The initial decomposition temperature and the temperature of completion of decomposition of the additives were obtained from the TGA curve.

1.2.3.4 Evaluation of pour point

The ASTM D97-09 method was used to evaluate the pour points of the base fluid blended with five different doping concentrations of the prepared additives. A cloud and pour point tester (Wadegati labequip Pvt., Ltd., India) in the temperature range of 0 to -71 °C was used to calculate the pour points.

1.2.3.5 Evaluation of viscosity index

An Ubbelohde viscometer was used here to determine the VI of the polymer doped base fluid. At first, the viscometer was thoroughly dried and calibrated with triply distilled, degassed water and purified methanol at the experimental temperatures (40°C and 100°C) to determine the value of the viscometric constants.¹⁹ The viscometer was filled with the experimental solution and placed vertically in a glass sided thermostat. After reaching thermal equilibrium, the time flow of the solution to pass through the two calibrated marks in the viscometer was recorded with a digital stopwatch. In all the determinations, an average of three measurements was taken and precautions were taken to minimize the losses due to evaporation. The VI, which reflects the variation of kinematic viscosity (ν) of oil with the change of temperature, was evaluated according to ASTM D2270 method at five different doping concentrations (ranging between 1 to 5%) of the polymers according to the equation,

$$\nu = (Kt - L/t) \rho \quad \text{Eq. (2)}$$

where ρ is the density of oil solution, t is the time of flow and K and L are the viscometric constants.²⁰ The values of K and L were found to be 0.0367 cm²s⁻² and 3.0598 cm³ respectively. A DMA 4500 M vibrating-tube density meter (Anton paar, Austria) was used to compute the densities of the oil solutions and the time of flow was recorded with a digital stopwatch. Before use, the apparatus was also calibrated at atmospheric pressure with degassed and distilled water and dry air at 40 °C and 100 °C. The VI was calculated according to the equation,

$$VI = 3.63(60-10^n) \quad \text{Eq. (3)}$$

and n was determined by the equation,

$$n = (\ln \nu_1 - \ln k) / \ln \nu_2 \quad \text{Eq. (4)}$$

where ν_1 and ν_2 are the kinematic viscosities of the polymer doped oil at lower and higher temperature respectively. The value of k was determined to be 2.714 for the given temperature range and is a function dependent solely on temperature.²¹

1.2.3.6 Photo micrograph and wax modification

The effectiveness of an additive in controlling the crystallization of wax can be studied by photo micrographic image of the base fluid. A Banbros polarizing microscope (BPL-400B, India), with magnification 200X, was used here to study the wax modification of the base fluid. The microscope was also attached with a cooling thermostat to control the temperature at 0°C.

1.2.4 Results and discussion

1.2.4.1 Spectroscopic data analysis

FT-IR spectra: In its FT-IR spectrum, the additive HMMA (Fig. 1.2.1) exhibited absorption for the stretching vibration of the ester carbonyl at 1740 cm^{-1} while the peak at 1165 cm^{-1} can be explained considering the C-O (ester bond) stretching vibration. The absorption due to the bending vibrations of the C-H bonds appeared at 722, 1380 and 1456 cm^{-1} . The intense peaks at 2856 and 2927 cm^{-1} were attributed to the presence of stretching vibrations of the C-H bonds.

¹H-NMR spectra: The ¹H-NMR spectrum of the additive HMMA (Fig. 1.2.3) showed broad peaks between 3.94 and 4.14 ppm for the protons of -OCH₂- group of myristyl methacrylate. Peaks in the range of 1.03 to 1.94 ppm were for the methylene protons of

myristyl group while a broad singlet centered at 0.89 ppm was due to the presence of methyl protons.

¹³C-NMR spectra: The proton decoupled ¹³C-NMR of the additive HMMA (Fig. 1.2.5) showed peaks between 178 and 179 ppm for the ester carbonyl carbons. Other peaks between 65 and 68 ppm was for the -OCH₂- carbons of methacrylate chain while the peaks ranging from 14 to 34 ppm indicated the presence of all -CH₃ and -CH₂ carbons of the alkyl chain.

The spectral data of all the other additives (MMAO5, MMAO10 and MMAO15) are almost similar and the spectra of only additive MMAO5 are discussed here. In its IR spectrum, the additive displayed signal at 1736 cm⁻¹ due to the stretching vibration of ester carbonyl group while the another signal for the stretching vibration of C-O bond appeared at 1162 cm⁻¹. Signals for the bending vibrations of C-H bonds appeared at 722, 1378 and 1462 cm⁻¹. The intense peaks at 2855 and 2926 cm⁻¹ (stretching of C-H bonds) were also present in the additive. In the ¹H-NMR spectra, MMAO5 showed broad peaks between 4.16 and 3.94 ppm due to the protons of the -OCH₂- group. Peaks for the methylene protons appeared in the range of 1.03-1.89 ppm while the singlet centered at 0.9 ppm was due to the methyl protons of myristyl and octene chain. The additive, in its ¹³C-NMR, showed the presence of carbonyl carbons by the shift between 177 and 178 ppm. Peaks appearing between 64 and 65 ppm indicated the carbons of the -OCH₂- group; other signals ranging from 14 to 32 ppm were due to all the methyl and methylene carbon atoms.

No peaks were found to be present between 1600-1680 cm⁻¹ in the IR spectrum and that between 5 and 6 ppm in the ¹H-NMR spectrum. The ¹³C-NMR spectrum also showed no absorptions between 130 and 150 ppm for the additives indicating the complete absence of unsaturation in them (Figs. 1.2.2, 1.2.4 and 1.2.6).

1.2.4.2 Thermo gravimetric analysis (TGA)

The thermo gravimetric analysis (Fig. 1.2.7) of the prepared additives showed a gradual increase of thermal stability with increasing concentration of 1-octene in the additive feed i.e. the copolymers are better in thermo-oxidative stability than that of the homopolymer. The initial degradation of the additive HMMA (i.e. homopolymer of myristyl methacrylate) started around 200 °C with a PWL value of 14 and the decomposition was almost complete around 410 °C with 98% weight loss. At 200 °C, the additives MMA05 and MMA010 have PWL values of 10 and 8 respectively which increased to 82 and 78 at 410 °C. The additive MMA015 showed the most resistance towards thermal degradation, with 98 percent weight loss only at a higher temperature of around 500 °C. The increase in the thermo-oxidative stability of the copolymers is perhaps due to the fact that the homopolymer, which only contain the ester groups, undergo easy degradation by forming gaseous products.²² The narrower molecular weight distribution of the copolymers, as indicated by the PDI values, may also be the reason for their higher thermal stability.²³

1.2.4.3 Analysis of the influence of additives on pour point values

The pour points of the additive doped oils are presented in Fig. 1.2.8. A close investigation of the additives under study revealed that with every increase in the doping percentage, the flow improving efficiency of the additives progressively improved. This improvement in the efficiency of the additives is due to the increased additive-oil interaction as well as an increase in the hydrodynamic volume of the additive.²⁴ A comparative study of the pour point values also confirmed that the

homopolymer (HMMA) exhibited better flow improving performance. The efficiency of an additive as FI is very much dependent on the composition of the base fluid and is credited to its capability to disperse the wax particles.²⁵

Mineral base fluids usually contain a large percentage of waxy paraffinic hydrocarbons dissolved in them whose solubility gets diminished at low temperatures.²⁶ Long-term exposure to low temperature results in crystallization and agglomeration of these waxy hydrocarbons to a gel-like rigid structure. The FI molecule, when added to the base fluid, gets adsorbed on the wax crystals and doesn't allow them to interlock among themselves to form a gel-like structure and, therefore, limit their size.^{27,28} Investigation suggested that the polarity of the additive molecule (with polar functional groups such as ester, amine, amide and hydroxyl groups) may be a decisive factor in restricting the interlocking of wax crystals. A more polar additive fights more efficiently against the creation of crystal wax network and consequently shows greater flow improving ability.²⁹ Due to the presence of only acrylate monomers, HMMA is more polar compared to the other additives (with varying 1-octene concentrations) and hence shows better flow improving ability and greater pour point.

1.2.4.4 Analysis of the influence of additives on viscosity index values

The data presented in Fig. 1.2.9, compared the dependence of the VI values on the additive concentrations, and the results indicated that all the prepared additives effectively modified the viscosity properties of the base fluid. The additive HMMA showed the least viscosity modification and with the increase of octene content in the additive feed, the VI values are found to rise gradually. For any viscosity modifier, the potential to improve the VI relies on the conduct of the additive molecules in the base

fluid, where its molecular weight, solubility and chain topology are crucial parameters.³⁰ Also, the viscosity of the base fluid depends on the temperature, where with an increase in temperature, the viscosity normally decreases.³¹ Various researches suggested that at low temperatures, the additive molecules is poorly soluble in the base fluid and remain in a round coiled up conformation with a minimal effect on the base fluid viscosity.³² But with the increased solubility and interaction between the additive chains and the solvent molecules at higher temperature, the additives change its shape from tightly coiled to inflated spread out ones. This successfully thickens the oil and counters the normal reduction in viscosity of the base fluid with increasing temperature.³³

Here the additive MMAO15 showed the highest VI increment, and this outcome is possibly due to higher degree of solvation and enhanced interaction of the additive having nonpolar ends with the paraffinic base fluid. On the other hand, the additive HMMA, which only consists of myristyl methacrylate monomers, has more polar character compared with the others. Due to this polar nature, the additive has less interaction with the base fluid and, therefore, has a lesser solvated volume, consequently leaving it with the lowest VI among others.³⁴ Moreover, in accordance with our earlier publication, the VI values become more pronounced on increasing the overall additive doping percentage in the base fluid. This is because of the fact that with the enhancement in the percentage of the additive there occur a swelling in overall volume of the polymer coils. These inflated coils, together with their increased interaction with the base fluid leads to greater thickening effect and subsequently increases the viscosity index of the base stock.³⁵

1.2.4.5 Analysis of the photo micrographic images

The photo micrographs of the pure base fluid and with different polymeric additives are shown in Fig. 1.2.10. The original base fluid (pour point = -6°C , Fig. 1.2.10a) shows large rod-shaped wax crystals in its photo micrograph. Upon doping with different additives (4%, w/w solution), the photo micrograph of the base fluid changed significantly with a reduction in the shape and size of the wax crystals. For the additives HMMA (pour point = -16°C , Fig. 1.2.10b) and MMA05 (pour point = -14°C , Fig. 1.2.10c), a major decrease in the wax crystal size has taken place which appeared as a highly dispersed crystals. Additive MMA010 (pour point = -11°C , Fig. 1.2.10d) and MMA015 (pour point = -9°C , Fig. 1.2.10e) also showed reduction in the wax size but to a much lesser extent. Thus, the reduction in the size of wax crystals seems to be responsible for improving the pour point values. Therefore, the pour point values obtained earlier are in complete correlation with the wax modification results.

1.2.5 Conclusions

From the above discussion, it is evident that the pour point and viscosity index results obtained are promising as regard to the design and formulation of polymeric lube oil additives. The thermal stability of the additive increased with the increasing 1-octene percentage and the additive MMA015, with highest 1-octene content, was thermally the most stable one. Moreover, the VI values for MMA015 were also significantly higher compared to other additives. Meanwhile, the additive HMMA showed superior flow improving properties in the base fluid under study. Thus, it can be concluded that all the polymers can be used as effective multifunctional additive for lubricant formulation.

1.2.6 References

References are given in BIBLIOGRAPHY under Chapter-II of Part-I (Page No. 195-198).

1.2.7 Tables and figures

Table 1.2.1: Physical properties of base fluid

Properties	Method	SN1
Viscosity at 40 °C in cSt	ASTM D445	23.518
Viscosity at 100 °C in cSt	ASTM D445	3.979
Viscosity index	ASTM D2270	86
Pour point, °C	ASTM D97	-6
Density (g.cm ⁻³) at 40 °C	ASTM D4052	0.85521

Table 1.2.2: Monomer ratio and designation of the prepared additives

Polymers	% of monomers in the polymers		Solvent, Initiator
	Myristyl methacrylate	1-octene	
HMMA	100	0	Toluene, AIBN
MMA05	95	5	Toluene, AIBN
MMA010	90	10	Toluene, AIBN
MMA015	85	15	Toluene, AIBN

HMMA: Homopolymer of myristyl methacrylate, MMA05: Copolymer of myristyl methacrylate + 5% 1-octene, MMA010: Copolymer of myristyl methacrylate + 10% 1-octene, MMA015: Copolymer of myristyl methacrylate + 15% 1-octene.

Table 1.2.3: Average molecular weight of the additives determined by GPC

Polymers	Average molecular weights		
	M_n	M_w	PDI
HMMA	24946	39416	1.58
MMAO5	24829	31277	1.26
MMAO10	24622	30481	1.24
MMAO15	24401	30107	1.23

M_n = Number-average molecular weight, M_w = Weight-average molecular weight, PDI = Polydispersity index.

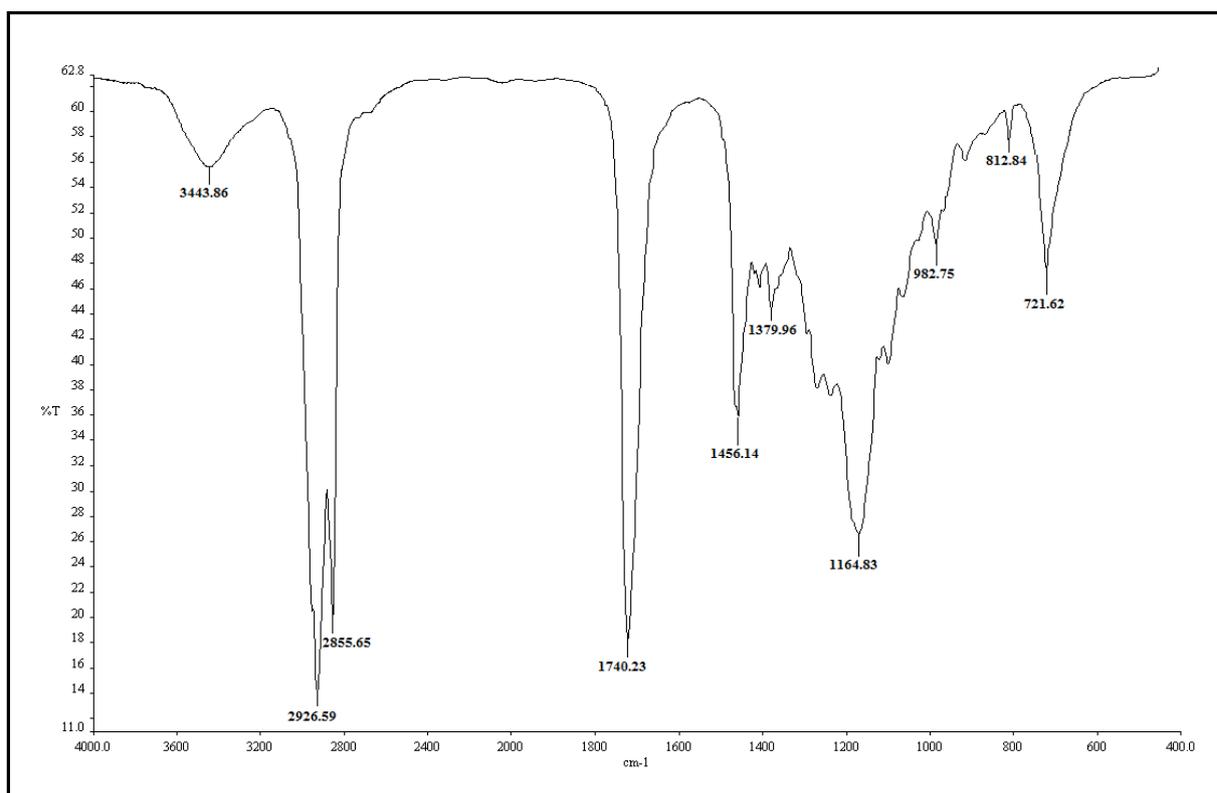
Figure 1.2.1: FT-IR spectra of the additive HMMA

Figure 1.2.2: FT-IR spectra of the additive MMA05

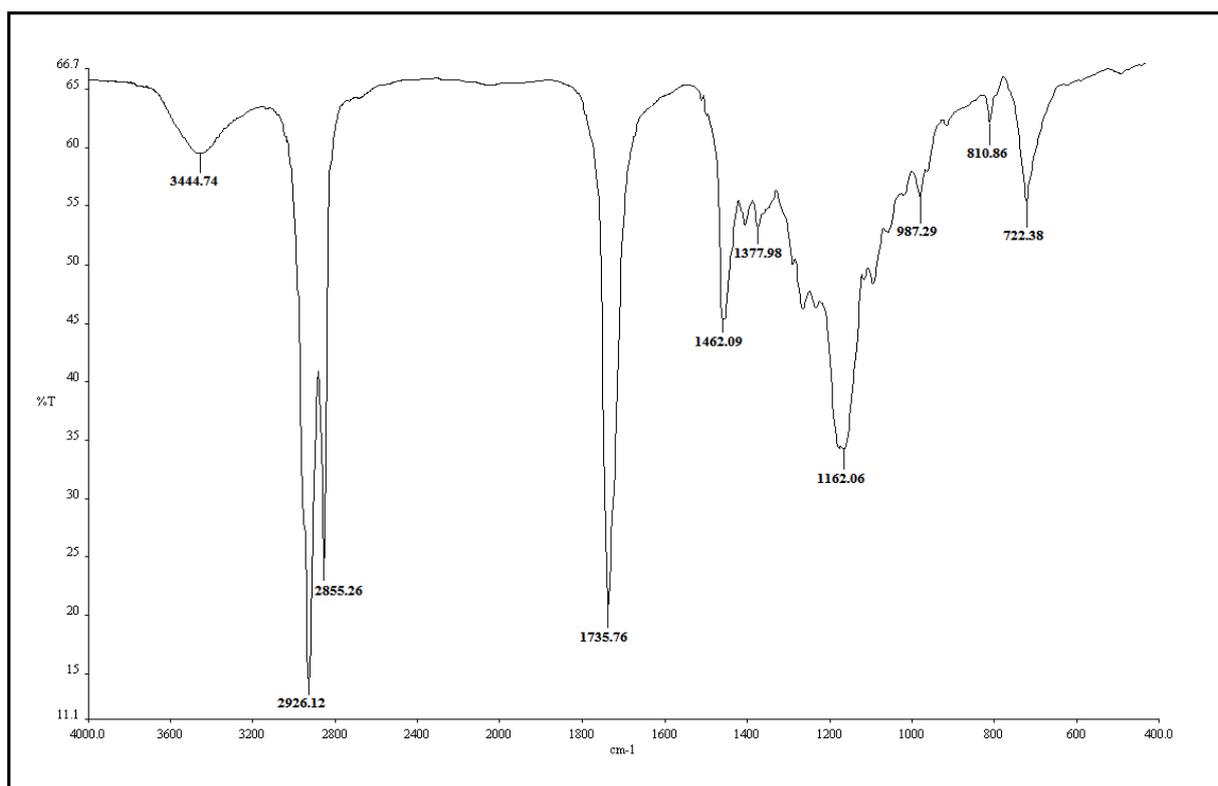
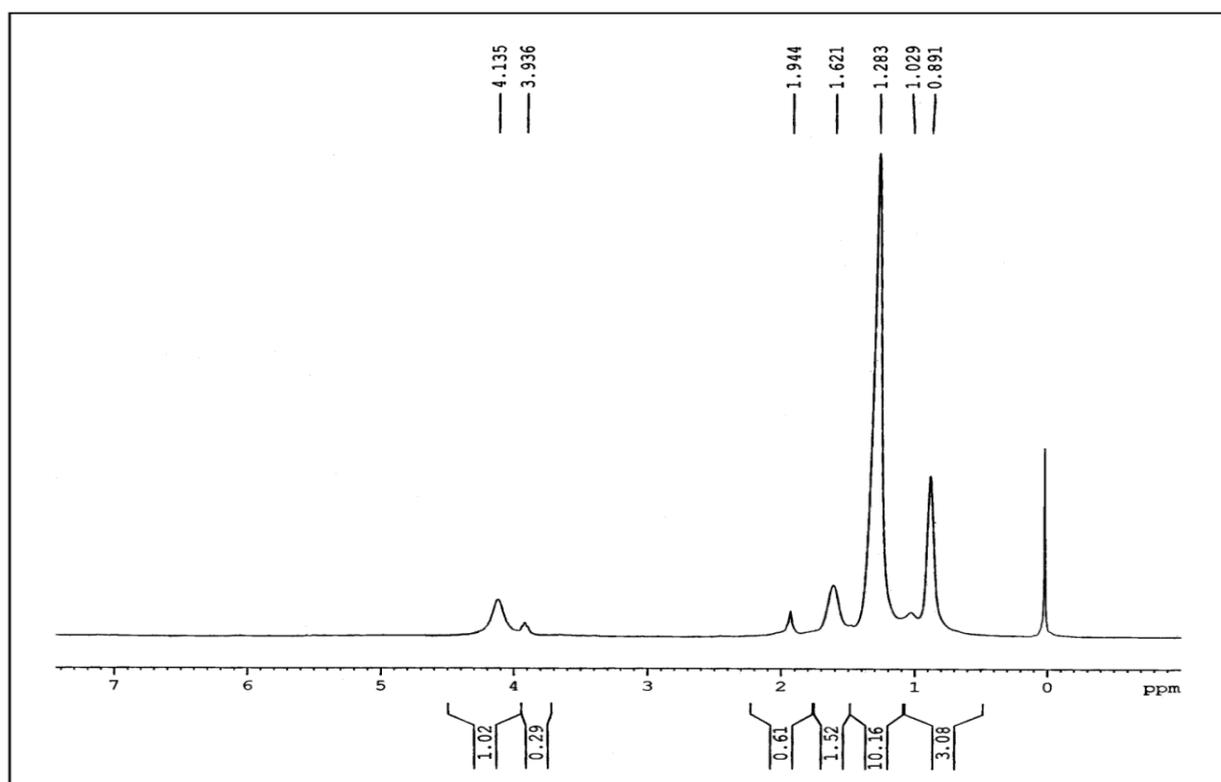
Figure 1.2.3: ¹H-NMR spectra of the additive HMMA

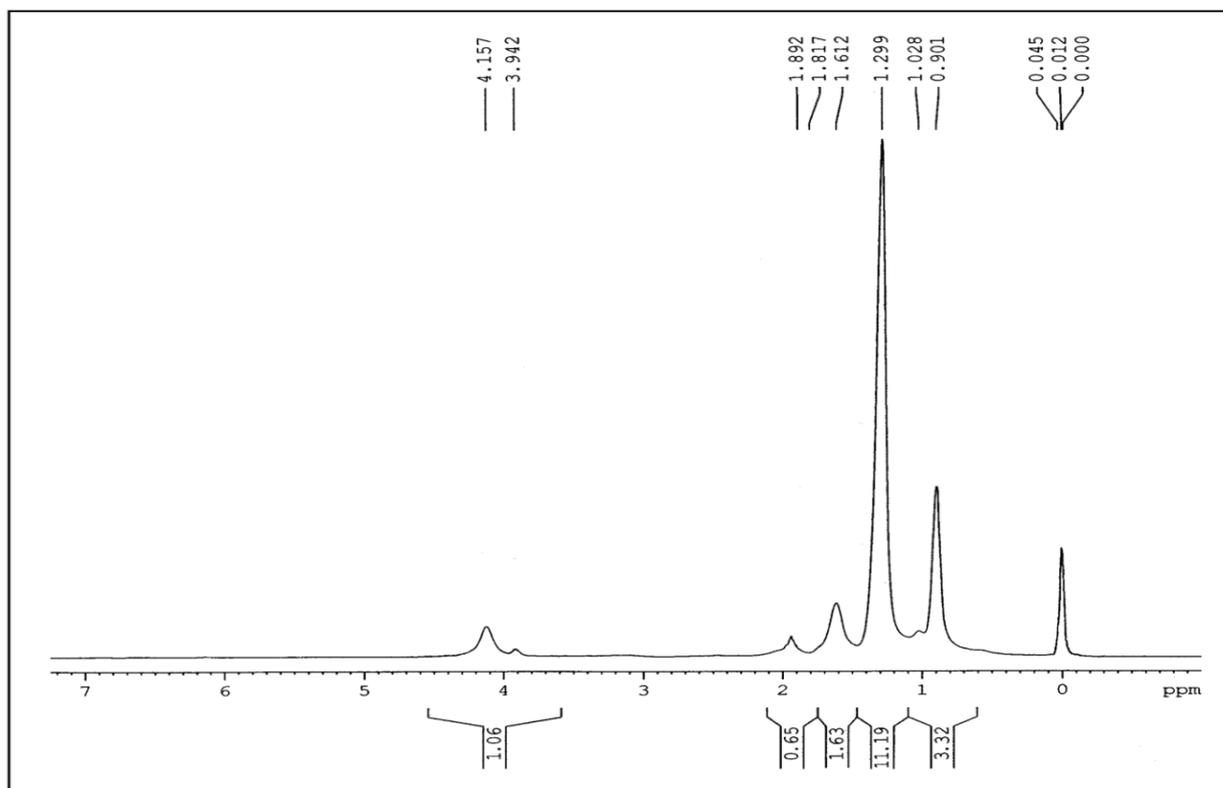
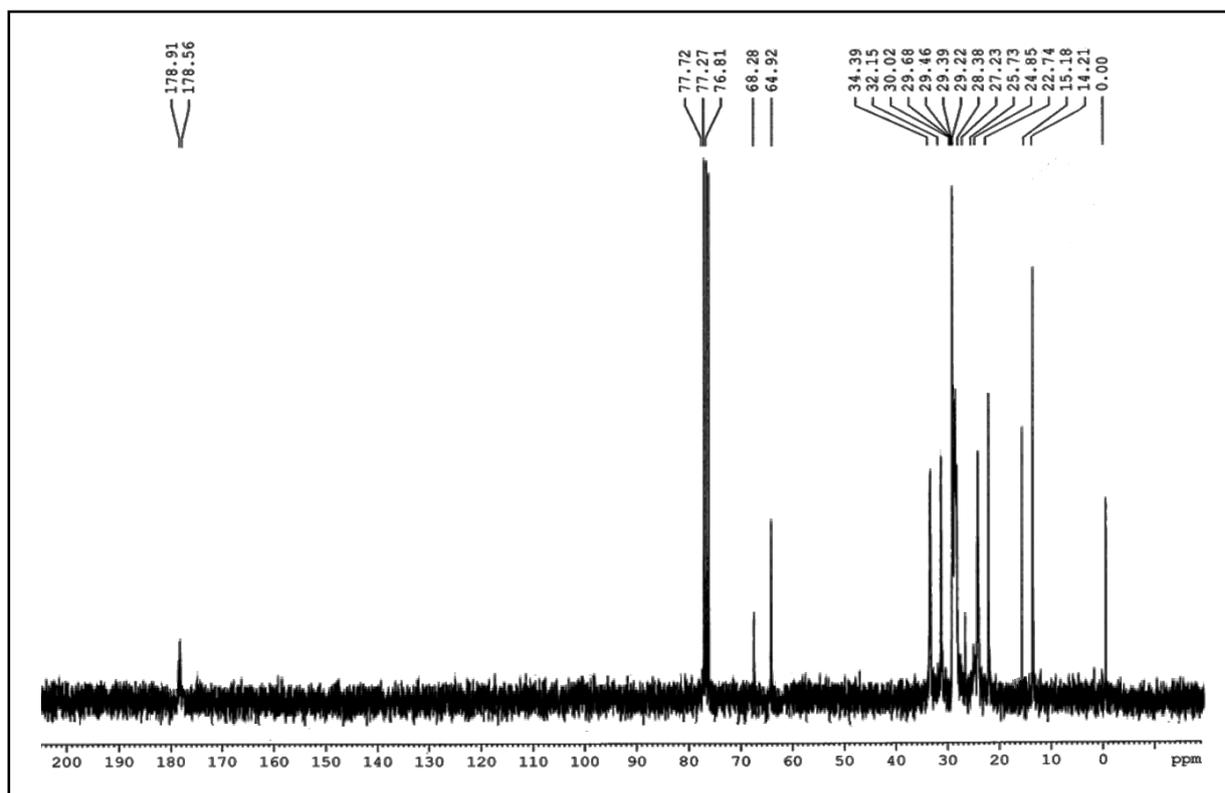
Figure 1.2.4: $^1\text{H-NMR}$ spectra of the additive MMA05Figure 1.2.5: $^{13}\text{C-NMR}$ spectra of the additive HMMA

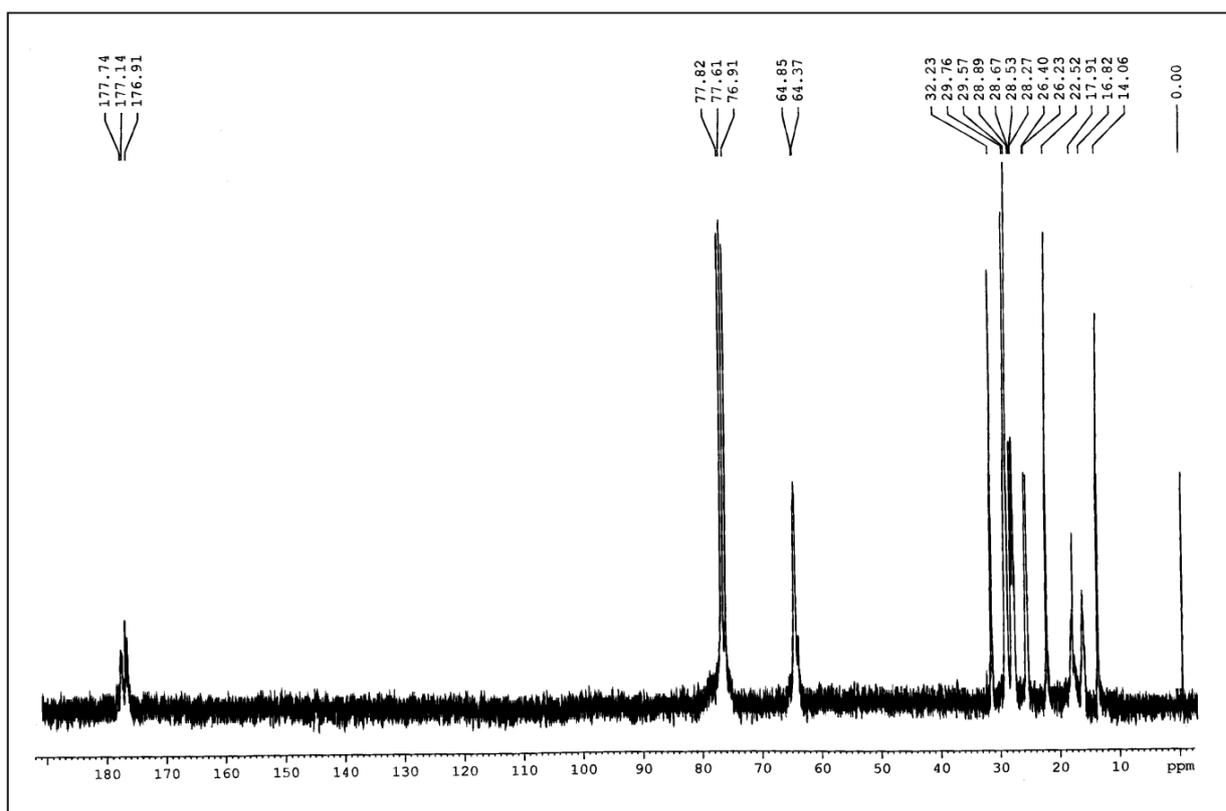
Figure 1.2.6: ^{13}C -NMR spectra of the additive MMAO5

Figure 1.2.7: Thermo gravimetric analysis of the additives

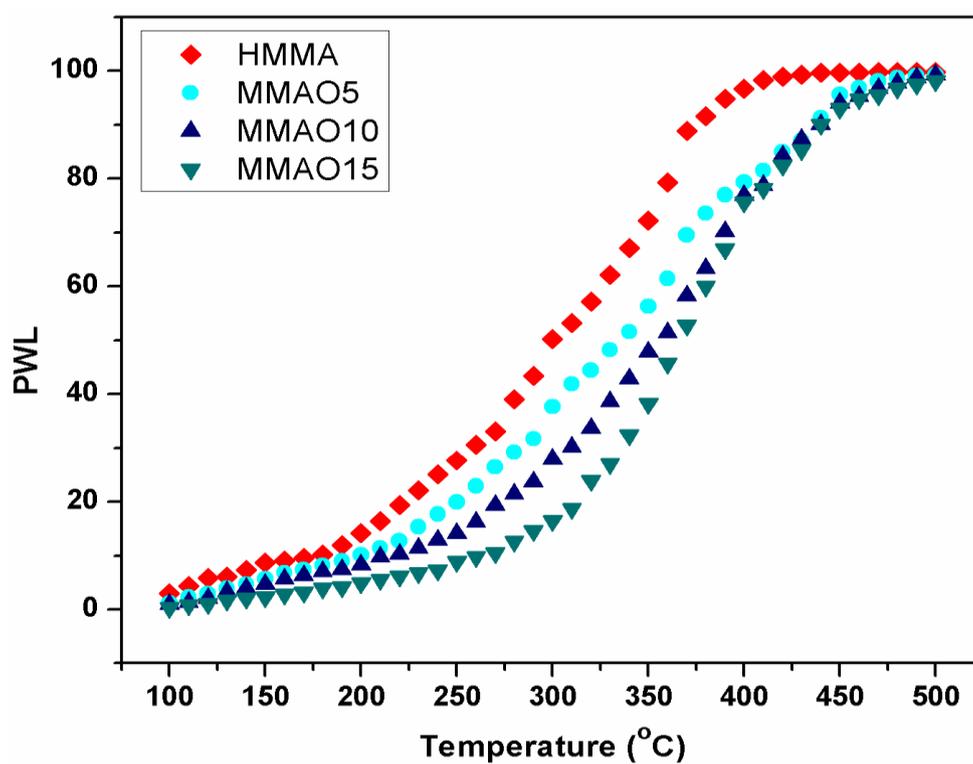


Figure 1.2.8: Variation of pour points of the base fluid doped with additives at different concentrations

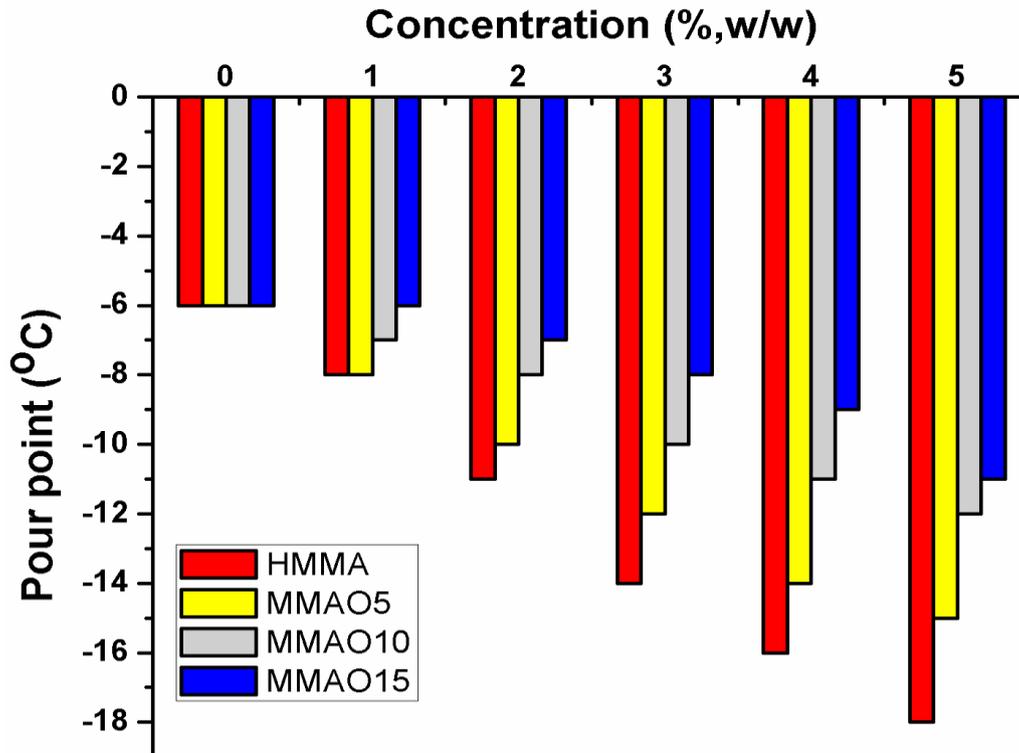


Figure 1.2.9: Variation of viscosity index of the base fluid doped with additives at different concentrations

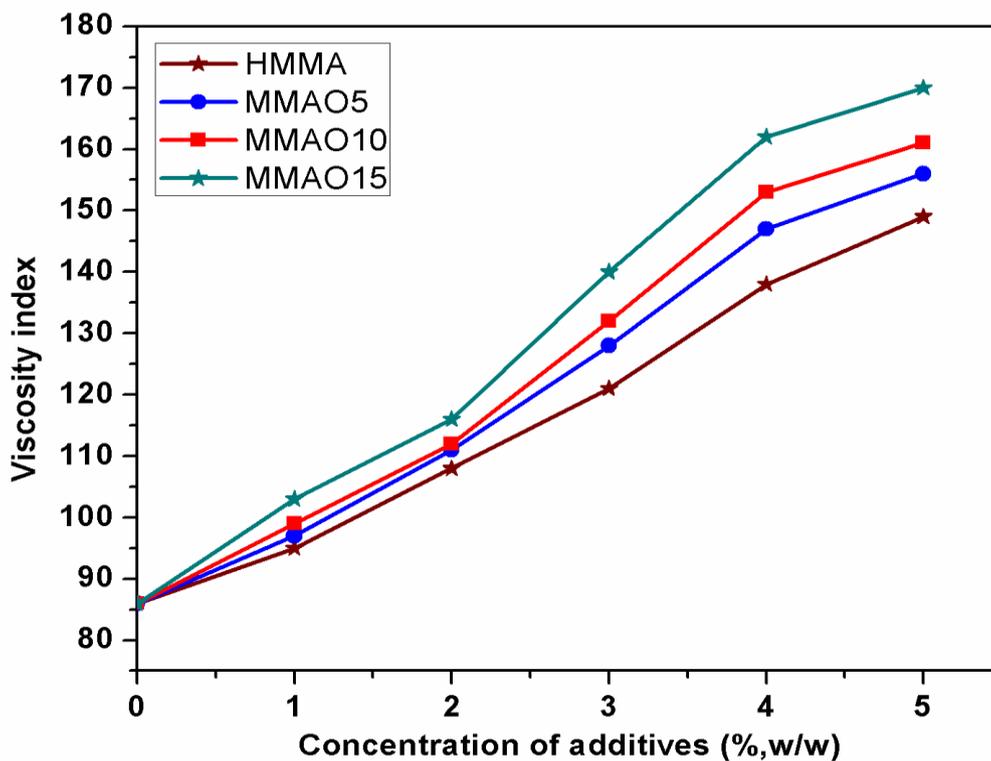


Figure 1.2.10: Photomicrograph of: (a). pure base fluid (b). base fluid + additive HMMA (4%, w/w) (c). base fluid + additive MMA05 (4%, w/w) (d). base fluid + additive MMA010 (4%, w/w) (e). base fluid + additive MMA015 (4%, w/w)

