

**MODIFICATION OF LUBE OIL PROPERTIES BY ADDITION
OF ORGANIC POLYMERIC ADDITIVES**

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By
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June, 2018

*Dedicated to my beloved
parents...*

DECLARATION

I declare that the thesis entitled "**MODIFICATION OF LUBE OIL PROPERTIES BY ADDITION OF ORGANIC POLYMERIC ADDITIVES**" has been prepared by me under the guidance of Prof. Pranab Ghosh, Department of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

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PREFACE

This thesis is one of the fruits of my labour under the supervision of Prof. Pranab Ghosh in the Department of Chemistry, University of North Bengal, during the period of December 2013 to May 2018. The basis for this research originally stemmed from my passion for developing multifunctional lube oil additives. As the world moves into the age of engines performing under stringent working conditions, there will be a greater need to develop additives that can support such operations. Therefore, it was my passion to develop additives that can work under severe conditions also keeping in mind the growing environmental concerns related to the additives.

Although nobody can become an expert in such a short period of time, it is no exaggeration to state that my personal learning curve, which grew like a logarithmic function, has reached a considerable level after the research. I am grateful to all those people who have contributed in this study.

Thank you all for your unwavering support.

ACKNOWLEDGEMENTS

Firstly I would like to express my sincere respect and heartfelt gratitude to my supervisor and Head, Prof. Pranab Ghosh, Department of Chemistry, University of North Bengal, Darjeeling, for giving me the wonderful opportunity to complete my Ph.D. thesis under his supervision. His friendly guidance, constant encouragement, expert advice and healthy criticism have been invaluable throughout all stages of the work. Without his continual inspiration, it would not have been possible to complete this study.

I am very much grateful to GOD and pay my obeisance to the almighty to have bestowed upon me good health, courage, inspiration, zeal and the strength to remain positive in every situation.

I sincerely express my gratitude to my beloved parents for their enormous support, sincere encouragement, inspiration and believe in myself.

I take this opportunity to sincerely acknowledge the other faculty members of this department for their imperative support.

I am also grateful to Prof. Malay Kumar Das, Department of Physics, University of North Bengal, Darjeeling, for allowing me to take the photomicrographic images from his research laboratory.

It's my fortune to gratefully acknowledge the support of all the academic staffs and the research scholars of this department for extending their unstinted support, timely motivation, sympathetic attitude and unfailing help during the course of entire study.

I sincerely admire the contribution of all my lab mates, the exciting discussions and the unforgettable moments which I enjoyed during this journey.

I would also like to extend special thanks to Indian Oil Corporation Limited for providing the base oils.

Last, but not the least, I would like to thank University of North Bengal for providing the infrastructural facilities to carry out my research work.

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ABSTRACT

Lubricants are materials that are largely used to reduce friction and wear between interacting surfaces and to assist their relative motion. Lubricants usually contain a base oil and package of additives. The additives either enhance the already existing property of the base oil or introduce some new property into it.

The present work is concerned with the synthesis, characterization and performance evaluation of some multifunctional organic polymeric additives for lube oil. The additives explored in this study are typically based on acrylate and methacrylate moiety. Other molecules used in this study are α -pinene and 1-octene. Some biodegradable multifunctional lube oil additives based on vegetable oils (almond oil, olive oil and castor oil) have also been investigated. The additives (polymeric in nature) were synthesized either thermally or by microwave irradiation in presence of initiators like azobisisobutyronitrile (AIBN) or benzoyl peroxide (BZP). The additives were characterized by spectral techniques ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and FT-IR), followed by molecular weight determination with gel permeation chromatography (GPC) and finally assessment of their thermal stability was done by thermo gravimetric analysis (TGA). The additives were investigated for their performances in different lube oils as pour point depressant (PPD) and viscosity index improver (VII) as per the standard ASTM (American society for testing and materials) methods. Biodegradability analyses were also conducted for the vegetable oil based additives by soil burial method and disc diffusion method to test their biocompatible nature.

The detailed research work here has been divided in two parts: Part I and Part II. The Part I, "Acrylate and methacrylate based polymers as multifunctional lube oil

additives” is then divided into four chapters, chapter I, chapter II, chapter III and chapter IV.

The chapter I, of part I, portrays the progresses and developments made on acrylate and methacrylate based additives for lubricating oils. Chapter II describes the synthesis, characterization and performance evaluation of the homopolymer of myristyl methacrylate and a series of copolymers of myristyl methacrylate and 1-octene. All the polymers were characterized by spectral studies, their molecular weights were determined by GPC and they were assessed for their performances as cold flow improvers and viscosity modifiers in the base oil. The results showed that the copolymers have better viscosity modification properties while the homopolymer showed better flow improving efficiency. Chapter III discusses the application of homopolymers of undecyl methacrylate and behenyl acrylate and their corresponding copolymers as multifunctional additives for lubricant formulation. Four copolymers of undecyl methacrylate with behenyl acrylate at different molar ratios were synthesized by free radical polymerization method. Detailed comparative investigation on the homo and copolymers blended base oils confirmed better additive performance of homo behenyl acrylate as viscosity index improver while the copolymers were superior as pour point depressant among all the polymers. The copolymers were also found to be thermally more stable than the homopolymers. Chapter IV comprises the study of additive performances of polymers of mixed acrylate. Four terpolymers were synthesized by using different ratios of three acrylate monomers (octyl, decyl and dodecyl). Additive performances of each of the prepared terpolymers as viscosity modifiers and pour point depressants were evaluated by standard ASTM methods. Terpolymer prepared by using a higher ratio of dodecyl acrylate was found to be more effective as pour point depressant and also as a better viscosity modifier.

The part II, “Biodegradable multifunctional lube oil additives” is again divided into four parts, chapter I, chapter II, chapter III and chapter IV.

The chapter I, of part II, contains a brief review of the works done so far on biodegradable multifunctional lube oil additives. Chapter II deals with biodegradable lube oil additives obtained from the homopolymer of almond oil and its copolymers with decyl acrylate. The polymers were characterized by spectroscopy, their molecular weights were measured by GPC and their thermal stability was determined by TGA. All the investigated polymer samples showed excellent additive performances but the copolymer with highest acrylate content showed better viscosity modification and pour point depressant property along with significant biodegradability. Chapter III explores the potential of polymers synthesized from dodecylmethacrylate and olive oil to act as an environmentally benign multifunctional lubricant additive. Different copolymers of dodecyl methacrylate with olive oil were synthesized in a focused microwave oven using a radical initiator. The copolymer samples were found to be biodegradable viscosity index improver and pour point depressant additive for lube oil. Chapter IV explores the performance of homopolymer of castor oil and three of its copolymers with α -pinene as biodegradable multifunctional mineral lube oil additive. Copolymers of castor oil with different percentages (w/w) of α -pinene along with its homopolymer were prepared via radical polymerization taking AIBN as polymerization initiator. It was found that the most important viscosity increment was exhibited by the copolymer with highest α -pinene percentage while the homopolymer showed the superior performance as PPD for the lube oils under study.

All the additives synthesized in this research illustrated excellent additive performances and, therefore, the outcome of this study can give a new dimension in the field of multifunctional additive research.

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Appendix A

List of papers published/accepted/communicated

1. Acrylate terpolymers as potential pour point depressant and viscosity modifiers for lube oil. Pranab Ghosh and **Debasish Kumar Saha**, **Petroleum Science and Technology**, 2015, 33, 1126–1132.
2. Almond oil as potential biodegradable lube oil additive: A green alternative. **Debasish Kumar Saha** and Pranab Ghosh, **Journal of Polymers and the Environment**, 2018, 26, 2392–2400.
3. Dodecylmethacrylate–olive oil copolymers as potential biodegradable pour point depressant for lubricating oil. **Debasish Kumar Saha**, Mahua Upadhyay and Pranab Ghosh. **Petroleum Science and Technology**, 2018, 36, 215–221.
4. Naturally derived green bio-additives. **Debasish Kumar Saha** and Pranab Ghosh, **Journal of Macromolecular Science, Part A: Pure and Applied Chemistry**, 2018, 55, 384–392.
5. Undecylmethacrylate–behenyl acrylate copolymers as potential multifunctional additive for lubricating oil. **Debasish Kumar Saha**, Mahua Upadhyay and Pranab Ghosh. Communicated to **Journal of Scientific and Industrial Research**. MS ID: 9108.
6. Synthesis, characterization and performance evaluation of long chain methacrylate–octene copolymer for lubricant formulation. **Debasish Kumar Saha** and Pranab Ghosh. Communicated to **Polymer Bulletin**. MS ID: POBU-D-18-00083.

Appendix B

List of seminars/symposiums/conferences attended

1. **19th CRSI NATIONAL SYMPOSIUM IN CHEMISTRY (CRSI NSC-19) - 2016.**
Organized by Department of Chemistry, University of North Bengal on July 14th to 16th, 2016. **(Poster Presentation).**
2. **NATIONAL SEMINAR ON “FRONTIERS IN CHEMISTRY 2017-18”.** Organized by Department of Chemistry, University of North Bengal on September 14th, 2017. **(Oral presentation).**

Appendix C

Abbreviations

1. AIBN – Azobisisobutyronitrile
2. AO – Almond oil
3. ASTM – American Society for Testing and Materials
4. BO1 – Base oil 1
5. BO2 – Base oil 2
6. BZP – Benzoyl peroxide
7. CO – Castor oil
8. CFI – Cold flow improvers
9. DA – Decyl acrylate
10. DDA – Dodecyl acrylate
11. DDMA – Dodecyl methacrylate
12. GPC – Gel Permeation Chromatography
13. HPLC – High Performance Liquid Chromatography
14. IOCL – Indian Oil Corporation Limited
15. IR – Infra red
16. KV – Kinematic viscosity
17. M_n – Number average molecular weight
18. M_w – Weight average molecular weight
19. NMR – Nuclear magnetic resonance
20. OA – Octyl acrylate

21. OCP – Olefin copolymers
22. OEM – Original equipment manufacturer
23. PIB – Polyisobutylene
24. PMA – Polymethacrylate
25. PPD – Pour point depressant
26. SBDT – Soil burial degradation test
27. TMS – Tetramethylsilane
28. TGA – Thermo gravimetric analysis
29. UDMA – Undecyl methacrylate
30. VI – Viscosity index
31. VII – Viscosity index improver
32. VM – Viscosity modifier
33. ZDDP – Zinc dialkyl dithiophosphate

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*General introduction of the present
investigation*

A lubricant is a substance that is introduced to reduce friction and to facilitate the relative motion between any surfaces which are in mutual contact to each other.¹ This property of reducing friction by a lubricant is known as lubricity. The history of the use of lubricants dates back thousands of years.² During the time of the pyramids, building stones were slid on oil-impregnated lumber. Calcium soaps have been identified on the axles of chariots dated to 1400 BC. Lubricants based on plant oils and animal fats were used in the Roman era. But with the development of vacuum distillation of petroleum in the early 1900s, the focus shifted toward petroleum-based materials.³ Again, with the increasing complexities of modern engines, the demands placed upon the lubricant also became proportionally more exacting.

In order to assist the relative motion and to prevent damages, lubricants in the form of solid, liquid or gases are interposed between the two surfaces. A gaseous film is usually favoured for low contact stress while liquid films are generally used where it is required to maintain the lubrication over a period of time. The solid films are usually practical for contacts with slow sliding speed.^{4,5} The chief ingredient of lubricating oil is the base oil, and depending upon the nature, it might be classified as mineral base oil, synthetic oil or as a bio-oil.

The mineral base oil is currently the most commonly used commercial lubricant around the world and is derived directly or indirectly from petroleum refining. It is composed of a complex mixture of hydrocarbons and generally these includes aromatic, olefinic, paraffinic (linear/branch) and naphthenic hydrocarbons with molecular weights ranging from C₂₀-C₇₀.⁶ The synthetic oil includes polyalpha-olefins, synthetic esters, silicones, etc., while the bio-oil includes the oil derived from plants and animals.

The lubricating oil provides a fluid layer for the separation of moving surfaces and thereby, controls the heat generated by the engines. It also has a huge number of

different purposes like reducing the viscosity variation of oil with temperature, increasing the flow ability at low temperature, corrosion prevention, inhibiting the formation of rust, protecting the engines against wear etc.^{7,8}

Engine lubricating oil makes up nearly one half of the world lubricant market but unfortunately they do not meet all the needs of lubricants used in modern engines. Engine oil is, therefore, formulated with a mixture of base oil and a specific designed additive package for specific operating conditions. Additives are materials that are specifically devised for enhancement of the physical and chemical properties of the base oils, which as a consequence results in augmenting the equipment life and boosting the lubricant performance.⁹⁻¹⁴ Without additives, even the best base oils are devoid in some features. The type and quantity of additives are chosen depending upon the lubricant in which it is to be used (hydraulic oils, engine oils, gear oils etc.) and also on the precise operating environments (machine parts materials, loads, temperature etc.).

The performance of a lubricant depends collectively on the base oil, the additive used and its formulation. Usually only one type of base stock serves the purpose of a particular lubricant but sometimes a mixtures of base oils are also used together with a variety of additives. Besides, no single additive can meet the desirable performance necessary for the efficient operation of a machine. Thus, several additives are needed to serve the original equipment manufacturer (OEM) needs and the consumer requirements. Additives are used at different concentrations ranging from 0.005 % to more than 10% by weight of the lubricant. The amount of additives may even reach 30%.¹⁵ A lubricant without the proper additive is bound to get contaminated by subsequent breakdown of the oil and, therefore, frequent oil changes would be required.

Lubricants are ubiquitous and today practically all types of lubricating oil contain at least one additive, and some may even contain additives of several different types. Although some are multifunctional i.e. they satisfy more than one function, the more commonly used additives are discussed in the following sections in term of their primary functions.

1. *Metal surface protecting additives*: They are also known as film forming agents. This type of additives includes extreme pressure additives,^{11,12} anti-wear,^{16,17} rust and corrosion inhibitors.¹⁸ These additives protect the metal surface by making a protective film through adsorption or chemical reaction and thereby prevent the formation of rust and check the wear.
2. *Performance enhancing additives*: These additives improve the performances of the lubricants and include viscosity index improver,^{6,19} pour point depressants,²⁰ detergent and dispersant.²¹
3. *Lubricant protective additives*: Out of the many causes of engine malfunction, the major cause is poor lubricant quality arising out of lubricant contamination, deposit formation, oil thickening, ring sticking, etc. The additives which are used to control these actions are known as lubricant protective additives. These additives protect the lubricant instead of the machinery equipment. These types of additives include antioxidants,²² anti foaming agents.²³

The present study includes the synthesis of some polymeric additives and evaluation of their performance in the base oil as pour point depressant and viscosity index improver. A brief background of these types of additives is described below.

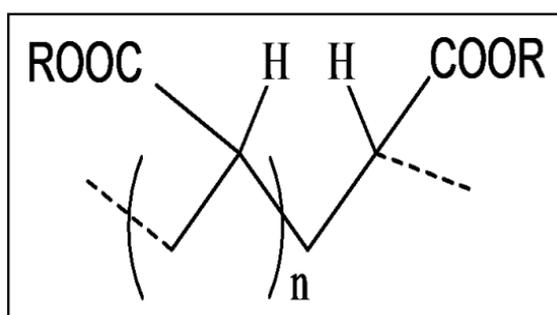
Pour point depressant: The low temperature properties are an important part of any lubricating system. The natural paraffinic mineral base oils are always associated with some waxy materials (linear high molecular weight hydrocarbon). At higher temperature, all the high molecular weight paraffins remain in a dissolved state in the base oil. But, with decreasing temperature of the oil, some of these waxy hydrocarbons tend to separate as tiny crystals entrapping a substantial amount of oil, and thus inhibit the oil flow. The oil at this point (temperature) appears hazy to the naked eye and this particular temperature is defined as cloud point. At the cloud point (i.e. the crystallisation point), the oil no longer remains a Newtonian fluid, but becomes a two-phase system. With further decrease of temperature, more and more wax precipitates as crystals and when sufficiently large number of crystals appears, they develop into plates. The plates finally grow together to form a three-dimensional network structure and immobilizes the oil. This process of the formation of grease like matrix is referred to as gelation and the lowest temperature at which the oil loses its flow ability is termed as the pour point (PP) of the oil.^{24,25}

The higher the wax content in the oil, the greater the flow problems are. Generally, the pour point is proportional to the amount of wax present in the oil and a high pour point means high paraffin content in the oil. During the refining process, most of the wax present in the crude oil is removed to obtain the base oil but some wax is still desirable for achieving the proper viscosity. The complete removal of paraffinic wax from lube oil is expensive and is very difficult. Extensive dewaxing of the base oil also

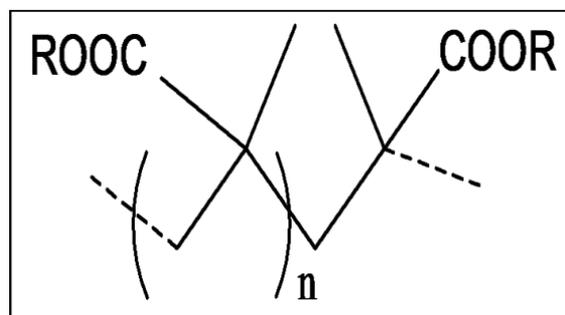
increases the formation of carbon deposits and decreases the oxidation stability of base oils.

A variety of solutions are suggested to overcome these problems associated with the base oils. Preheating of the oil to modify the wax crystal structure, application of ultrasound and microwave irradiation, application of magnetic field, addition of the light distillate to the oil are some of the techniques applied to control the low temperature properties of the oil, but each one has its own drawback and hence is not broadly accepted.^{26,27} Therefore, some speciality chemicals are added to the base oil to make them function efficiently at low temperatures and these are known as pour point depressants (PPD) or otherwise known as cold flow improvers (CFI), wax crystal modifiers and paraffin inhibitors.²⁸⁻³⁰ These CFI provides an economical way of facilitating the flow property of oil at low temperature without compromising the viscosity benefits of the wax at higher temperatures.

Polyalkyl acrylates and methacrylates,^{31,32} fumarate copolymers,³³ ethylene-vinyl acetate copolymers,³⁴ alkyl esters of styrene–maleic anhydride copolymers³⁵ and few recently used vegetable oil polymers are some of the important additives used as PPD in lubricants.³⁶



Polyalkyl acrylate



Polyalkyl methacrylate

Figure 1. Structure of some commonly used pour point depressants

The mechanism of action of PPDs has been a matter of much discussion. Early indications were that the alkyl aromatic compounds form a coating over the surface of the wax crystals through surface adsorption preventing their further growth and thus their capacity to adsorb oil and form gels. Although the exact mode of operation of PPDs is not clear, but it is believed that they all alter the crystal morphology by various means involving adsorption, nucleation or co-crystallization.^{37,38}

As shown by Light microscopy results, wax crystals formed are generally in the shape of a thin plates or blades. The PPD compounds, which generally have long hydrocarbon chains, are similar to the wax structure and, therefore, undergo co-crystallization with the wax developed in the base oil. The other polar part (in the form of acrylate, methacrylate, acetate, etc) present in the PPD molecule inhibits the lateral crystal growth by coming between the wax crystals and keeping them apart from each other thereby limiting their degree of co-crystallization.³⁹⁻⁴¹ The wax crystals are, therefore, no longer able to agglomerate and solidify to form a three-dimensional structures and inhibit the flow of the oil at low temperatures. The PPDs do not entirely prevent the wax crystal growth, but rather lowers the temperature at which the rigid crystal structure is formed.

Although the PP of most oils is related to the crystallization of wax, but the oils which are essentially wax free, have viscosity-limited PP dependence. As the temperature is lowered in such oils, their viscosity becomes progressively higher and finally reaches a point at some temperature where no flow can be observed. Since PPDs act by interfering with the growth and interlocking of the wax crystal structure, the PP of such oils cannot be altered with PPDs.

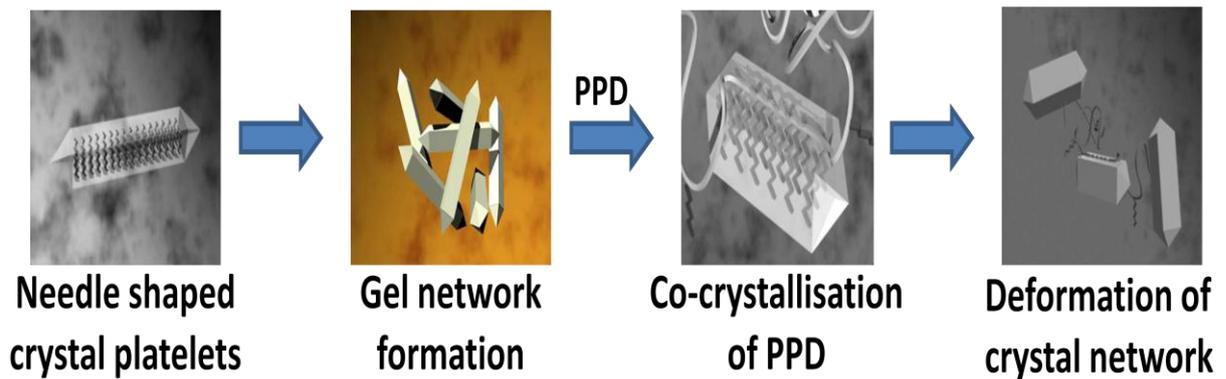


Figure 2. Schematic representation of the action mechanism of additives on wax crystals

Lubricating oils without PPDs can have a serious negative impact on engine performances. The extra workload on the engine, to overcome the increased viscosity due to wax formation, can cause cold start up problems and decrease its lifetime. PPDs are, hence, used in all types of lubricants including crankcase engine oils, hydraulic fluids, automotive gear oils, etc.

Viscosity modifier: The viscosity of a fluid is the measure of its resistance to steady deformation by tensile stress or shear stress. For liquids, it generally refers to the informal concept of thickness. The viscosity of oil is significant for its cooling and lubricity properties. The effectiveness of lubricating oil in minimising friction and wear is to a great extent influenced by its viscosity. For an oil of high viscosity, the solid surfaces in contact are fully separated by a thin film of the oil. This condition is known as hydrodynamic lubrication. For low viscous oil, the hydrodynamic pressure generated is insufficient to fully separate the surfaces and, therefore, the two opposing surfaces come into contact with each other. This condition is known as boundary lubrication. The optimum viscosity required for any lubricated system depends on the load to be supported and also on the relative velocities of the surfaces.

If the hydrodynamic lubricant film becomes too thicker, a large amount of energy is wasted in shearing the film and the heat so generated accelerates the unwanted decomposition of the lubricant. In the boundary lubrication condition, a large amount of energy is wasted in overcoming the frictional forces. Also, the wear of the machines arising from friction reduces the equipment life span. Since different machines differ in loads and velocities, a wide range of lubricant viscosities are required.

The dynamic viscosity of a fluid is its resistance to shearing flows where adjacent layers with different speeds move parallel to each other. It is expressed in the unit Pa. S (Pascal-second). On the other hand, the kinematic viscosity of a fluid is the ratio of its dynamic viscosity to the density, both measured at the same temperature. It is commonly expressed in the unit centistokes (cSt; 1 cSt = 0.01 St), or in SI units, millimetres square per second (mm^2/s ; $1 \text{ mm}^2/\text{s} = 1 \text{ cSt}$).

Viscosity of lubricating oil is also a function of temperature and it should vary as little as possible with the increase or decrease of temperature. It is, therefore, necessary to have some method of determining the viscosities of oils at temperatures other than those at which they are measured. Hence, two different temperatures are selected (usually 40°C and 100°C) for measuring the viscosities and then plotting these points on special viscosity-temperature charts developed by ASTM (American Society of Testing and Materials).⁴² Viscosity index (VI) is an arbitrary measure to express the change of viscosity with variations in temperature.⁴³ A low VI indicates a relatively high rate of change of viscosity with temperature i.e. it will thin out more at higher temperature. On the other hand, a higher VI value signifies a lesser effect of temperature on viscosity i.e. the oil will thin out less with increasing temperature.⁴⁴ It has been found that the addition of certain oil-soluble polymeric materials to base oil can greatly improve its viscosity properties and thereby the viscosity index. The additives that improve the

viscosity index of the oil are known as viscosity index improvers (VII) or alternatively known as viscosity modifiers (VM).^{45,46} VIIs keep the viscosity of the oil at a satisfactory level which provides stable oil film even at increased temperature.

Acrylate and methacrylate based polymers are the most commonly used VIIs in lubricants.⁴⁷ Some of the other reported VIIs are poly isobutylenes (PIB), olefin copolymer (OCP),⁴⁸ ethylene α -olefin copolymers, styrene isoprene copolymer (SIP), poly butadiene rubber (PBR), poly alkylstyrene,⁴⁹ maleic anhydride based polymers, and even some vegetable oil based polymers etc.³⁶

The performance of an additive as VII depends on its molecular weight, chemical behaviour, shear stability and also on its solubility in the base oil.⁵⁰ The mode of action of VII was first established by Selby in 1958.⁵¹ However, the report presented lacked any physical data supporting the proposed mechanism. Later, in a work of Flory it was stated that the radius of gyration, R_g , of additive molecules depends on the interactions between the solvent molecules and the polymer chains. The affinity among the polymer chains, in a "poor" solvent, results in the collapse of the polymer chains into compact polymer globules. However, in case of a "good" solvent, where repulsive forces act between the polymer chains, there occurs an expansion of the globule into random coils.⁵² With the rise of temperature, an enhancement in the power of solvation is observed for the solvent and consequently, there occurs an increase in the polymer-solvent interaction. As a result, the polymer molecules further changes its shape from tight coil to expanded random coil and thus offset the normal viscosity reduction with increasing temperature. The process of expansion of coil is totally reversible as with decreasing temperature the coil contraction occurs.⁵³⁻⁵⁵ Again, the increasing polymer content in the solvent increases the total amount of polymer globules in the solution bringing about a higher viscosity index for the oil.

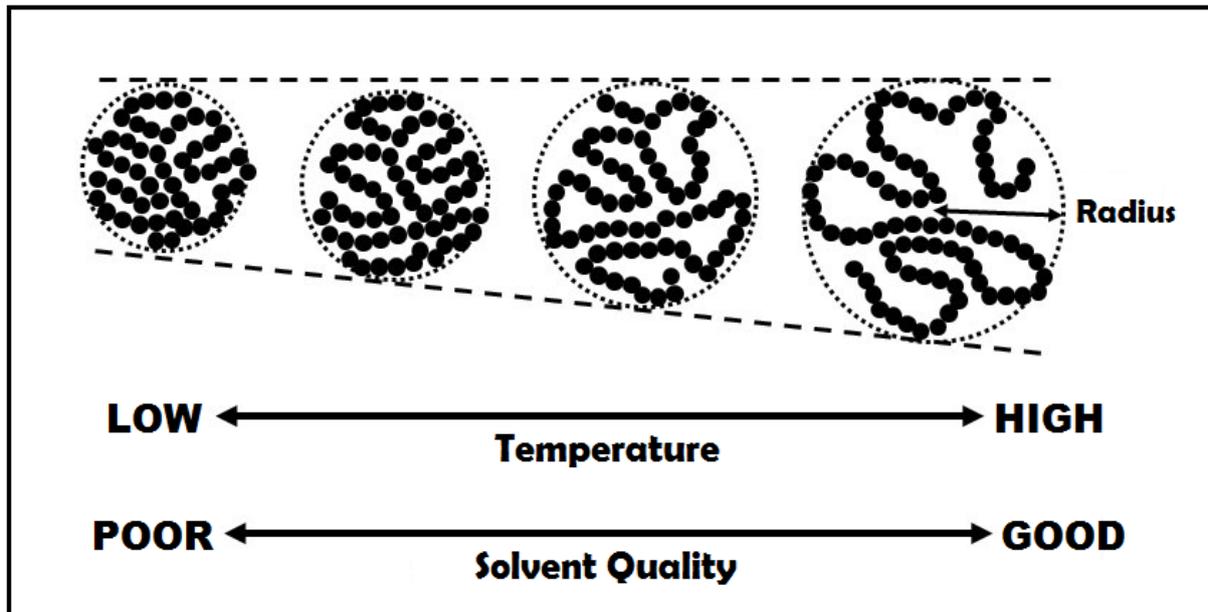


Figure 3. Coil expansion model of viscosity index improvers

The long molecules of the VIIs are also prone to degradation due to mechanical shearing in operating conditions. Under such conditions, the long chains of the VII change from a spherical coil orientation and align them in the direction of the stress thereby reducing the resistance to flow. But the chains return to their usual random arrangement once the stress is removed and, therefore, the viscosity loss is recovered. This condition is known as temporary shear breakdown. But sometimes under the service conditions, due to extreme polymer coil distortion the long chains undergo rupture to form small chains. The total viscosity contribution by the smaller ruptured molecules becomes less than that of the single parent molecule and they become less effective as VII. This condition is called permanent shear breakdown. Polymers of high molecular weight are more vulnerable to distortion while the polymers of sufficiently low molecular weight may not even undergo shearing. Therefore, a right combination of molecular weight and chain length is necessary to exhibit the optimum stability.

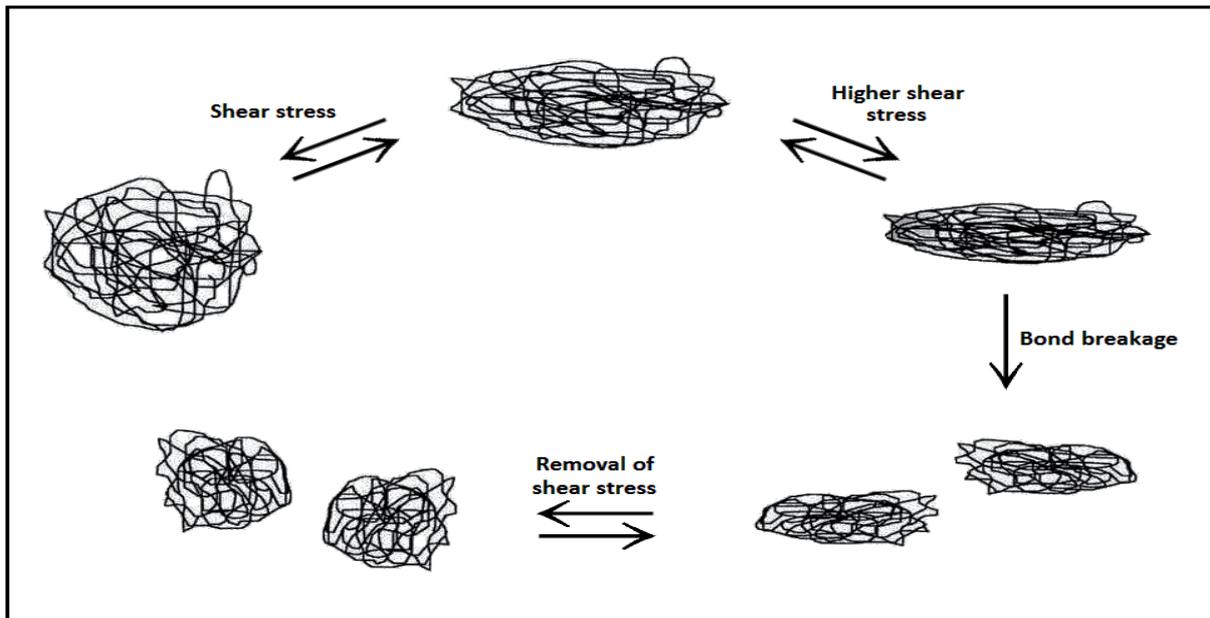


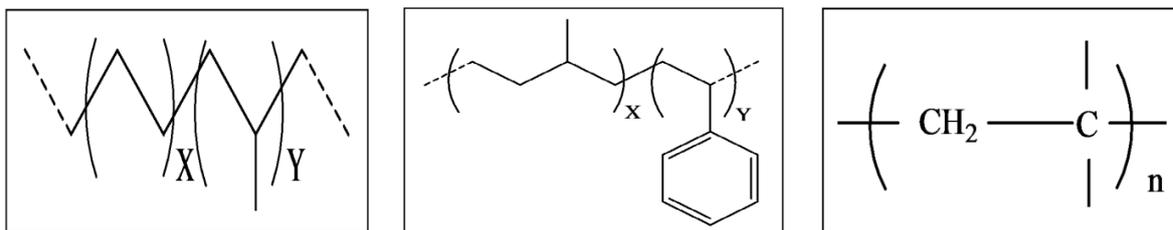
Figure 4. Temporary and permanent shearing of viscosity index improvers

Recently, a comprehensive report was presented by Michael J. Covitch *et al.*, about an improved model to correlate the polymer structures in solution with the rheological properties of a fluid. The experiment involves measurement of the polymer coil dimensions by Small Angle Neutron Scattering test and by intrinsic viscosity measurement. The critical assessment of the results indicated that the polymers which expand with temperature have greater viscosity index contributions than those that do not.⁵²

The viscosity of the solution also depends on the polymer and solvent chosen. At a very low concentration of the polymer, there is no strong interaction between polymer molecules. But as their concentration is increased, the increment in viscosity increases at a much faster rate. The following equation describes the dependence of concentration upon the viscosity.

$$\eta = \eta_c \exp(\beta C)$$

where η is the dynamic viscosity, C is the concentration of the polymer, η_c and β are constants.



Ethylene-propylene copolymer (OCP)

Styrene-isoprene copolymer (SIP)

Polyisobutylene (PIB)

Figure 5. Structure of some commonly used viscosity index improvers

Most of the additives that are in use today work either as PPD or VII or reports regarding their multifunctional additive behaviour are very little. But, with the advent of innovative technologies and to satisfy the growing OEM requirements and consumer needs, more is required out of an additive. This requires modification of the existing chemistry or manipulating the structure and architecture of the traditional additives. These variations not only improve their performance as PPD and VII but also boost their thermal stability.

In the present investigation, some acrylate based additives were synthesised for evaluation of their performance as a multifunctional additive. In addition, the growing concerns about environment were also addressed by incorporating some green natural units like almond oil, olive oil, castor oil and α -pinene. The thesis reports the synthesis characterization, and performance evaluation of some organic polymeric additives for modification of the lube oil properties. The polymers were characterised spectroscopically by FT-IR and NMR followed by determination of their thermal stability by Thermo gravimetric Analysis (TGA). Gel Permeation Chromatography (GPC) was employed to analyse the molecular weight of the polymers. Their performances as

PPD and VII were evaluated by standard methods in different base stocks. Biodegradability study was also carried out for some of the additives to get an idea about their biocompatible nature. The outcome of the present investigation has yielded some overwhelmingly satisfactory results regarding their use as potential additives which can be processed for commercial application. Additionally, the work will also enrich the little known lubricant technology and will open up new avenue and research interest among the young scientists in the field of lubricating oil additive chemistry.

References

References are given in BIBLIOGRAPHY under “General introduction of the present investigation” (Page No. 183-188).

PART-I

*Acrylate and methacrylate based
polymers as multifunctional lube oil
additives*

Chapter-I

*Background of the present
investigation*

The lube oil or base oil is the basic building unit of a lubricant and is generally produced by refining crude oils. Crude oil consists mostly of carbon (81-85%) and hydrogen (10-12%) and has a complex mixture of hydrocarbon like paraffins, naphthenes, aromatic and gaseous hydrocarbons. Crude oil also contains small amount of non hydrocarbons like sulphur, nitrogen and oxygen compounds. Depending on predominance of hydrocarbons, petroleum is classified as paraffin base, intermediate base or naphthenic base.

Although the primary function of a base oil is to reduce friction and wear between surfaces which are in contact with each other, they are also associated with a large number of secondary functions such as cooling, cleaning, suspending the impurities, maintaining low temperature flow ability etc. However, in most of the cases the base oils do not meet the current technical requirements of the original equipment manufacturers (OEM) because of their limited performance. The base oils are, therefore, blended with different additives in an expectation to improve their lubrication properties.¹ The additives cover a wide range of chemicals starting from simple molecules (organic or inorganic) to large polymeric compounds. They are selected according to the property to be introduced in the base oil and can be blended as single compound or even as a mixture of compounds to formulate the finished lubricants. Thus, the formulation of a high-performance, user friendly and cost effective lubricant largely depends on the quality of the base oil, the selection of suitable additives and their proportions. The selection of the additives, thus, requires skill and experience which will exploit the various dimensions of synergism and will relieve the known weaknesses of the base oil. The base oils with distinct properties hence acts as a carrier of additives. According to the specific functions an additive can perform, they can be classified into the following types.



Figure 6. Different types of lube oil additives

The success of a lubricant in delivering the highest level of performance depends upon understanding the interactions of the additives with the base oil and matching those to the requirements of equipments and the operating conditions to which they are exposed. Without the additives, the oil may not shield the engine properly at all operating conditions and this might lead to contamination, break down, overheating and permanent damage to the engine.

Additives have to perform a number of functions, but usually only one additive cannot satisfy all the requirements of the advanced engines. Thus, proper mixtures of different types of additives are mixed to the base oil. But, keeping in mind the cost effectiveness and the hazardous nature of the chemicals used in this field, the demand for multifunctional additive is on the rise.²⁻⁷ Multifunctional additives not only increase the life span of lubricating oils but can also increase the lifetime of engine at a cheaper cost. Therefore, research all over the world is increasingly focussed toward producing

multifunctional additives.⁸⁻¹⁰ Acknowledging this fact, the present study comprises the incorporation of two major additives (VII and PPD) in single additive system. Also, the numerous studies on high molecular weight polymeric compounds used as lube oil additives and the experienced gathered from that has serve as a opportunity in the development of multifunctional polymeric additives that have both VII and PPD properties.

Since our present investigation is on “acrylate and methacrylate based polymers as multifunctional lube oil additives”, it will be very relevant to include a brief review on VII and PPD additives of lubricating oil.

As already discussed in the general introduction section, viscosity is a very important property of a lubricant and is a measure of a fluid’s resistance to flow. At higher temperatures, the oil tends to thin out resulting in reduction in viscosity and this affect its flow ability. The parameter chosen to express the change in the viscous nature of the lube oil with temperature is called viscosity index (VI). A higher VI indicates a small change in viscosity with rise in temperature and vice-versa.^{11,12} Viscosity index improvers (VIIs) or viscosity modifiers (VMs) are additives that are added to lubricating oils to make them behave as ideal lubricant which possess almost the same viscosity at all temperatures.¹³⁻¹⁸ Long chain high molecular weight polymeric compounds are generally used as VIIs and their efficiency depends on the type and concentration of the additive.¹⁹ They generally work by changing their arrangement from tight coils to an open configuration with increasing temperature. This open configuration results in greater association with the base oil and thus a greater thickening and which offsets the normal reduction of viscosity with increasing temperature.²⁰⁻²³

Again, base oils contain substantial amounts of oil waxes called paraffins in them. Paraffins are complex mixtures of hydrocarbons containing linear chain predominantly

of 20 to 40 carbon atoms and alkanes with branched and cyclic chains. As the temperature decreases, the paraffin crystals grow generating a crystalline net which entraps the molecules of liquid hydrocarbon until the oil cannot flow.²⁴⁻²⁶ The temperature at which this happens is called the pour point (PP). Pour point depressants (PPDs) are designed to prevent the agglomeration of wax particle present in lubricating oils.²⁷⁻³⁰ If lube oils are not appropriately blended with PPDs, the flow characteristic of lube oils are highly affected which in turn affect the engine performances. The mechanism of function of PPD also grabbed much interest. It was initially believed that the PPD additives coat the paraffinic wax crystals preventing their further growth. More recently, it is believed that PPD functions by co-crystallization, nucleation or adsorption and disrupting the formation of three dimensional wax crystals network.³¹⁻³⁴ An efficient PPD should be a linear polymer with pendant hydrocarbon chain groups and also with an appropriate distance between the pendant chains in the polymeric backbone. Suitable ratios between the co-monomers, nature (amorphous or crystalline) of the additive and suitable molar mass are also the determining factors for an additive to work as effective PPD.³⁵⁻³⁸

The alkylacrylate and alkylmethacrylate are one of the most popular VII and PPD for lube oils. Due to the presence of ester linkage, they are more polar than ethylene/propylene or styrene polymers and the presence of long chain alkyl group in them imparts solubility into the lube oil. Methacrylate monomers with different alkyl chains can be copolymerized in an identical copolymerization reactivity ratio and in a statistically random distribution irrespective of the size of the alkyl groups. Various studies of previous researchers in accordance with the present line of investigation regarding VII and PPD are being discussed in the following paragraphs.

In the year 1937, Rohm and Haas patented the first polymeric PPD, poly alkyl methacrylates (PAMAs) based on waxy alkyl groups. Few years later, Ruehrwein reported the action of n-alkyl poly methacrylate as PPD in the series of methacrylate containing 12 to 18 carbon chains. It was reported that the longer alkyl chain polymers were effective as PPD in case of high temperature pour oils, while the shorter alkyl chain polymers were efficient on lower temperature pour oils.³⁹ Gavlin *et al.* analysed some acrylates and methacrylates for their PPD properties. Dodecyl methacrylate was chosen by the authors for their work and it was their first acrylic polymer to have excellent PPD properties.⁴⁰ A number of copolymers based on alkyl fumarate and vinyl acetate were synthesised by Borthakur *et al.* and their effectiveness as PPD was tested on Indian crude oils.⁴¹ El-Gamel *et al.* in the year 1997 reported the synthesis of α -olefin-alkyl methacrylate as PPD for waxy residue fuel. Their study suggested that the polymer containing alkyl group consisting of 21 carbon chain are superior as PPD.⁴²

Jian *et al.* prepared some esterified copolymers made from different fractions of maleic anhydride and α -olefin and termed them as EsMAOC polymers. The PPD performance of the polymers was tested in crude oil and heavy diesel oil.²⁸ The same group reported the synthesis of MOVAS copolymer obtained from α -olefin, maleic anhydride and a mixture of vinyl acetate and styrene and evaluated the additive for their PPD performance.⁴³ The group also prepared a viscous semi solid MOAS copolymer from maleic anhydride, acrylic alkyl ester, styrene and mixed α -olefins (the average carbon number is 15) and analysed the synthesised polymer for their PP and cold filter plugging point (CFPP) values in diesel fuel.⁴⁴

Abdel-Azim *et al.* in the year 2006 reported additives based on different esters of acrylic acid and different ratios of styrene to be used as PPD. They reported that the effectiveness of the prepared additives as PPD decreases by increasing the styrene

content in the feed.⁴⁵ Khidr, in the year 2007 prepared four copolymers made from 1-octene or 1-tetradecene and maleic anhydride and esterified them with dodecyl or NAFOL 1822B alcohol. The effectiveness of the copolymers as PPD was tested for crude oil and it was found that the alkyl chains of the copolymers are a crucial factor for a proper interaction of the additives with the crude oil.⁴⁶ In 2008, Farag prepared different copolymers by varying the molar concentration of cinnamoyloxy ethyl methacrylate and octadecyl acrylate and the PPD performance and rheological characteristics were studied using different concentrations of the prepared additives for two different waxy crude oils.⁴⁷

El-Ghazawy *et al.*, in the year 2010 reported a novel PPD for waxy crude oil based on alkyl acrylate terpolymers.⁴⁸ In another work, Khidr reported the preparation of some copolymeric and terpolymeric additives of maleic anhydride and alkyl acrylates of different chain length. The polymers were tested for both PPD and wax dispersants for paraffin gas oils and satisfactory results were obtained for the additives.⁴⁹ Jung *et al.* in the year 2011, synthesized six terpolymers and twelve copolymers based on different methacrylates to be used as flow improver in lube oil. They reported that the additives made from dodecyl methacrylate, hexadecyl methacrylate and methyl methacrylate at a molar ratio of 3.5:3.5:3 exhibited the best performance as PPD.⁵⁰ In the year 2014, polymeric additives based on decyl acrylate and styrene were synthesized by Ghosh *et al.* and they found some excellent PPD results with the polymers.⁵¹

The effectiveness of the polymers like polyvinyl palmitate, polyvinyl caprylate and copolymers of vinyl palmitate with vinyl acetate as VII were analysed by Port *et al.* and found that the additives are efficient viscosity modifiers for lubricating oils.⁵² In an experiment of Yorulmaz, the effect of degree of alkylation, the molecular weight and the size of the alkyl groups of different alkylated polystyrenes were analysed for viscosity

index improving performance.⁵³ Coutinho *et al.* synthesized copolymers based on ethylene-propylene and hydrogenated styrene-diene and carried out a comparative study between them considering their application as viscosity index improvers in multigrade engine oils.⁵⁴ Copolymers made of α -olefins (ethylene and propylene) were prepared by Reza *et al.* and were found to be a good VII at low concentration in motor oil formulation.⁵⁵

Nassar *et al.* made a comparative study of some polymeric additives prepared by copolymerization of different moles of styrene with different acrylates (decyl, 1-dodecyl, 1-tetradecyl, and hexadecyl) as VIIs. The viscosity modification properties of the additives were found to increase with increasing molecular weight of the prepared copolymers.⁵⁶ Jukic *et al.* reported dodecyl methacrylate, octadecyl methacrylate and styrene based terpolymers as VII for lubricating oil. The amount of styrene in the additive was restricted to 25% by weight. The group reported that the viscosity index increased with increasing molar mass of the additive but opposite effect was obtained by increasing the styrene percentage.⁵⁷

Additives made of dialkyl maleates with two different monomers (vinyl acetate and styrene) were synthesized by N. S. Ahmed *et al.* and their efficiency as VII (by improving the viscosity index) was studied in the base oil. The viscosity index was found to increase with increasing the concentration of the polymers in base oil and also with increasing alkyl chain length and molecular weight of the additives.⁵⁸ In 2012, Mohammed *et al.* reported additive for Iraqi lubricating oils based on poly methylmethacrylate and evaluation their performance was viscosity modifier.⁵⁹

There are also some examples where acrylates and methacrylates are found to act as both VIIs and PPDs.

Ahmed *et al.* prepared some additives through polymerisation of vinyl acetate and maleic anhydride with different acrylates and studied the effect of concentration, molecular weight and alkyl chain length on the viscosity index and pour point values of the additives.⁶⁰ In a similar work on Mexican crude oils, different additives were synthesized from vinyl acetate, *n*-butyl acrylate and styrene. The additives were evaluated for PPD efficiency and VM tendency with satisfactory results.⁶¹ Ghosh *et al.* reported copolymers of styrene and decyl acrylate and their compatibility as PPD and VM.⁶² In other work, polymers of myristyl acrylate were synthesized by two different methods viz. thermal method and microwave assisted method and their potential to act as PPD and VII were evaluated and compared.⁶³

There also has been a significant amount patent activity concerning the acrylate, methacrylate and olefinic compositions as pour point depressants and viscosity modifiers. Some of them are being presented in a selective manner, in the following paragraphs.

The U. S. Patent No. 2655479 A of Munday *et al.* reports the use of equal proportions of a copolymer of decyl acrylate and an acrylic acid ester of a mixture of alcohols derived from coconut oil to improve the PPD property. U. S. Patent No. 3598736 A describes the addition of oil soluble copolymers (containing 10 to 20 carbon atoms) of polymethacrylates to lubricating oils to improve the pour point property. A similar disclosure is also reported in U. S. Patent No. 3679644 A. The U. S. Patent No. 3598737 A reported a lubricant compositions consisting of methacrylic acid, acrylic acid and mixtures thereof which are said to improve various characteristics including pour point. The PPD ability of the group consisting of copolymers of alkyl methacrylates, alkyl acrylates and nitrogen containing esters of the acrylic acid series has been disclosed by U. S. Patent No. 3772196 A.

The U.S. Patent No. 3897353 described lubricating oil composition consisting n-alkyl methacrylate containing 12 to 18 carbon atoms as a PPD while the use of alkyl acrylate or alkyl methacrylate made from monomers with 8 to 22 carbon atoms has been disclosed by U.S. Patent No. 4073738. The use of copolymers of alkyl methacrylates containing 16 to 30 carbon atoms and with an average molecular weight ranging from 50,000 to 500,000 as PPD in petroleum oil has been reported by U. S. Patent No. 4867894 A. The use of ester of unsaturated carboxylic acid as PPD for lube oil selected from the group consisting of acrylic and methacrylic acid has been described in U. S. Patent No. 4906702 A. The preparation and evaluation of acrylate copolymers as PPD in lube oils has been reported by U. S. Patent No. 5834408 A.

The Patent No. 5955405 describes some copolymers containing 5-10 wt % of C₁₆-C₃₀ alkyl methacrylate, 5-15 wt % of butyl methacrylate and 70-90 wt % of C₁₀-C₁₅ alkyl methacrylate as excellent low temperature performance enhancer in lubricating oils. The use of a mixture of low molecular weight and selected high molecular weight alkyl methacrylate made of 16-24 carbon containing alcohols has been disclosed by U. S. Patent No. 6458749 B2. The patent describes effective low temperature fluid properties for a broad range of base oils. The use of copolymer as PPD prepared by polymerization of three α -olefin monomers (decene, tetradecene and hexadecane) with molecular weight ranging from 150,000 to 450,000 has been described in Patent No. CA 2059825 C. The Patent No. EP 0140274 discloses the use of additives for lubricating oil containing n-paraffin based poly alkylmethacrylate and acrylate. Similarly, Patent No. EP 0498549 B1 claims the preparation of a PPD terpolymer wherein the average alkyl side chain length is 10.5 to 12.0 and made from 10, 14 and 16 carbon atoms. The U. S. Patent No. 4514314 reported the application of alkyl ester copolymers as a PPD for

lubricating oils. These copolymers have a number average molecular weight optimally from 2,000 to 8,000 and preferably between 2,000 to 15,000.

The U. S. Patent No. 3607749 claimed the use of poly alkyl methacrylates preferably of molecular weight above 100,000 and more preferably above 350,000 as VIIs while the use of a lubricant composition with molecular weight in the range of about 100,000 to about 750,000 and containing about 0.60 to about 1.75 percent of an oil soluble poly methacrylate has been disclosed by U. S. Patent No. 4203854 A. The U. S. Patent No. WO2012076676 A1 disclosed a VII comprising poly alkyl methacrylate additive containing 10 to 15 carbon atoms in the alkyl residue. The use of olefinic copolymers, such as copolymers of ethylene, propylene, diolefin etc for viscosity modification of lubricating oils is disclosed in U. S. Patent No. 4517104 A. The use of copolymers derived from ethylene and one or more C₃-C₂₈ α-olefins and grafted with an ethylenically unsaturated dicarboxylic acid and subsequently reacted with a polyamine with at least two primary amine groups have been described in U. S. Patent No. 4137185 A. The most effective viscosity modification was found for the polymers with molecular weight ranging from 10,000 to 500,000.

Some multifunctional additive composition comprising of copolymer of ethylene and at least one C₃-C₁₀ α-olefin and optionally a polyene selected from nonconjugated dienes and trienes have been reported in the U. S. Patent No. 4863623. The additive is also claimed to have antioxidant and dispersant property. The use of ethylene-α-olefin polymer for improving the viscosity index was reported in U. S. Patent No. 5151204 A. The α-olefin contained 1 to 18 carbon atoms in the alkyl chain with a number average molecular weight from 20,000 to 500,000 and with terminal ethylidene unsaturation in at least about 30 % of the polymer chains.

The U. S. Patent No. 5356551 disclosed the synthesis of multifunctional additive for lubricating oil exhibiting dispersant, low temperature and viscosity modification properties. The additive with number average molecule weight from about 5,000 to 500,000 consist of at least one C₃-C₂₈ α-olefin monomer grafted with ethylenically unsaturated carboxylic acid having 1 or 2 acid or anhydride moieties such as succinic acid or anhydride. Additive based on vinyl aromatic/conjugated diene and ethylene/C₃-C₁₈ α-olefin of specific structure and composition has been described in U. S. Patent No. 4194057 A. The additive composition also contains a polybutene of defined molecular weight and is reported as excellent viscosity index improver. A lubricating oil composition of an oil soluble copolymer of ethylene and C₃-C₁₈ higher α-olefins have been disclosed in U. S. Patent No. 4088589 A with significant viscosity index improving properties. The additive is also reported to improve the low temperature performance when the copolymer contains a minor weight proportion of C₁₀-C₁₈ alkyl acrylate or methacrylate.

The U. S. Patent No. 3897353 A described additive compositions of ethylene-propylene copolymers working as VIIs and alkyl methacrylates working as PPDs. The favourable carbon number of the alkyl portion of the ester is reported between 12 to 18 carbon atoms. Another class of poly methacrylate additive have been reported in U. S. Patent No. 4956111 A with molecular weight from 10,000 to 300,000 and with an average alkyl group chain length from 12.6 to 13.8 capable of reducing the pour point to -35°C along with detergent and viscosity modification properties. The U. S. Patent No. 4668412 described the synthesis of additives containing terpolymer of stearyl methacrylate, maleic anhydride and lauryl methacrylate which has been formulated with dimethyl amino propyl amine and mannich base of amino ethyl pyrazine,

paraformaldehyde and 2, 6-ditertiarybutyl phenol. The additives are reported to act as dispersant VII and PPD.

The use of a lubricating oil composition containing mineral oils is reported in U. S. Patent No. 4886520 A which showed more enhanced VII and PPD properties by the addition of a terpolymer containing an olefinically unsaturated homo or heterocyclic nitrogen compound, alkyl ester of an unsaturated monocarboxylic acid and an allyl acrylate or methacrylate or a perfluoro alkyl ethyl acrylate or methacrylate.

From the above literature study, it was found that a lot of work has already been done on acrylate, methacrylate and olefin polymers with varying structure and morphology for improving the pour point and viscosity index of lubricating oils. However, the reports regarding their multifunctional performance are very scanty. Also, the acrylate and methacrylate based polymeric additives are among the most widely used commercial additives for lubricating oils. Moreover, with the new standards regarding the emissions of gases and with the associated changes in the engine designs, it was felt necessary to further explore this area of chemistry and develop multifunctional additives with superior performance, reduced cost and better fuel economy. Keeping this in mind, the author has synthesized homopolymers and copolymers of acrylates and methacrylate of different alcohols and evaluated their performance as VII and PPD in different types of base oils. The different acrylates and methacrylate used are octyl acrylate, decyl acrylate, dodecyl acrylate, behenyl acrylate, undecyl methacrylate and myristyl methacrylate while the other monomer unit used for synthesizing copolymers is 1-octene. The results of the present investigation would undeniably facilitate the development of some superior and efficient multifunctional additives having both PPD and VII properties for lube oils.

References

References are given in BIBLIOGRAPHY under Chapter-I of Part-I (Page No. 188-194).

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

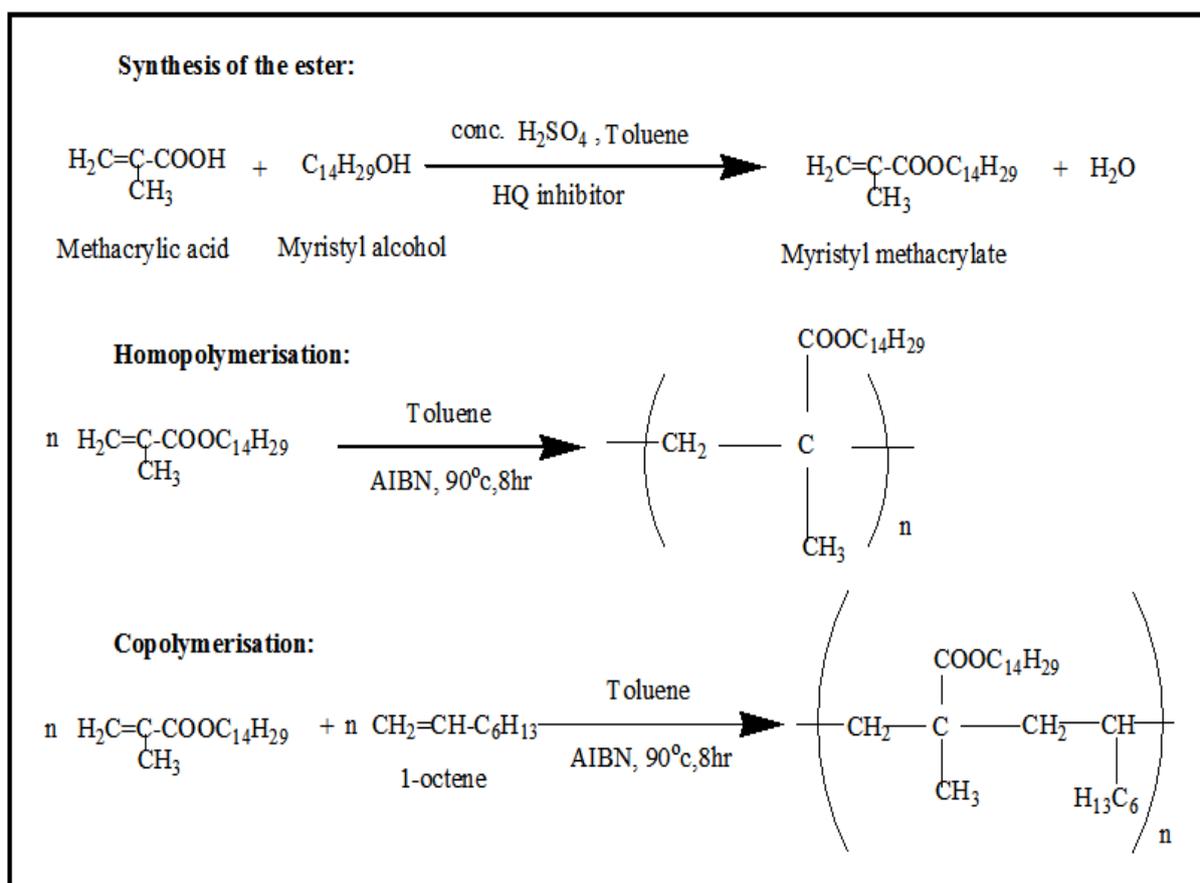
1.2.2.3 Purification of the prepared methacrylate ester

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.

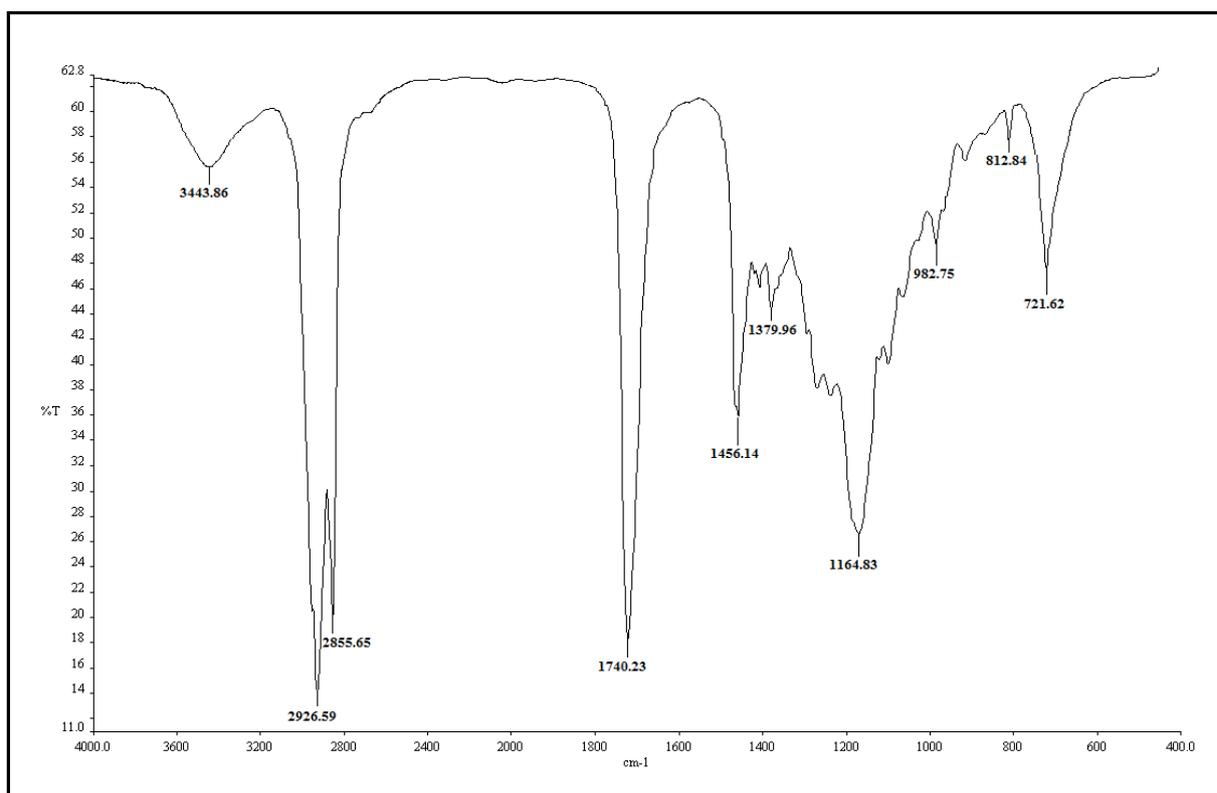
Figure 1.2.1: FT-IR spectra of the additive HMMA

Figure 1.2.2: FT-IR spectra of the additive MMA05

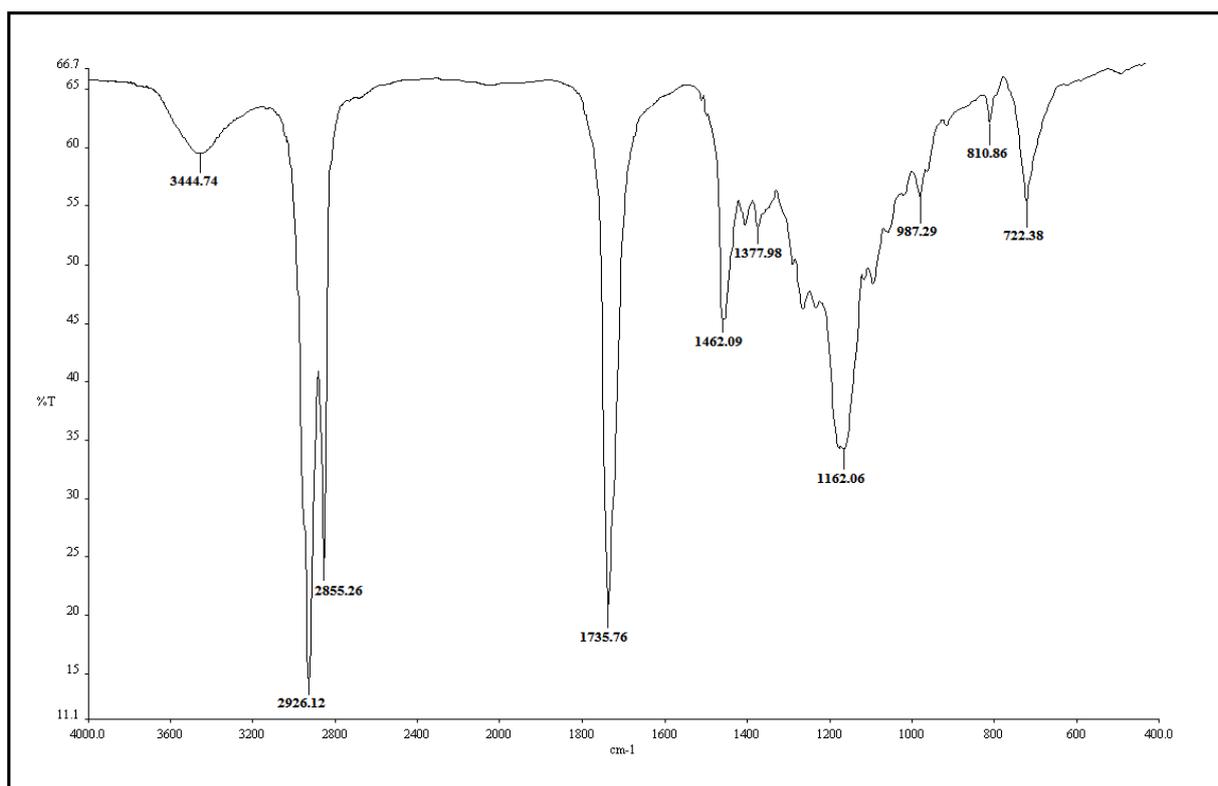
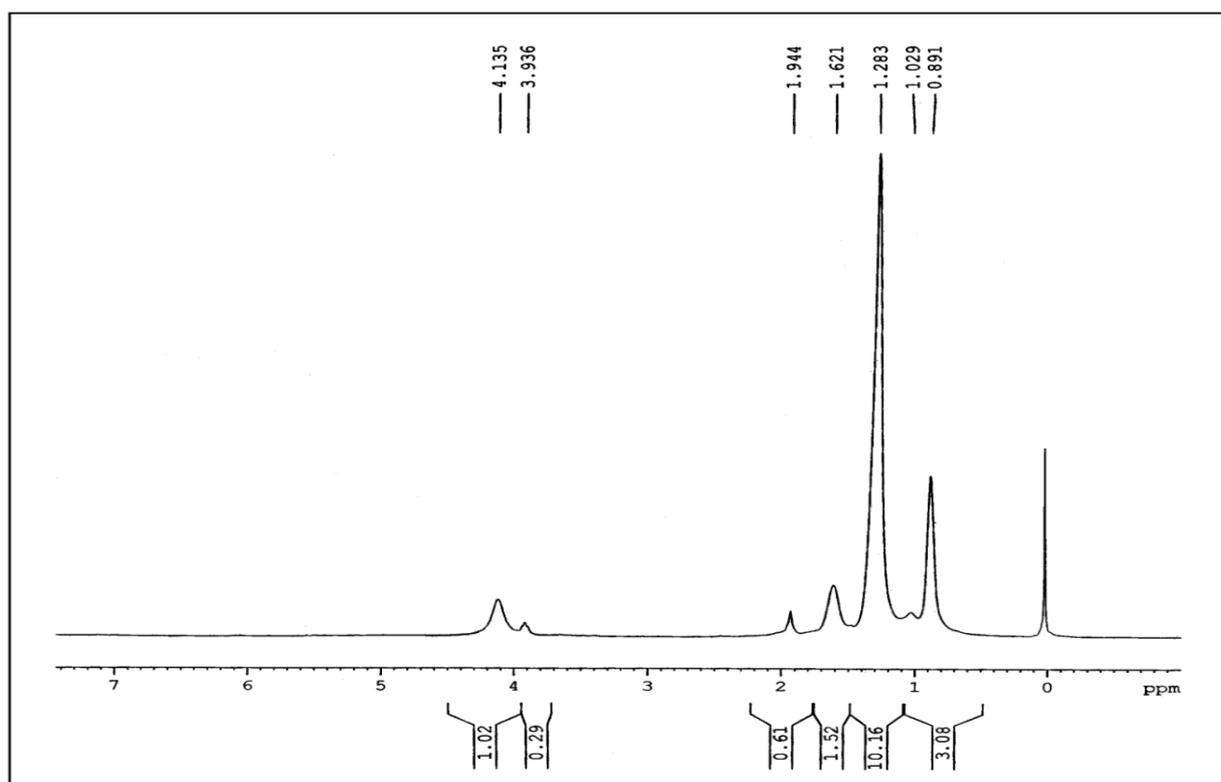
Figure 1.2.3: ¹H-NMR spectra of the additive HMMA

Figure 1.2.4: $^1\text{H-NMR}$ spectra of the additive MMA05

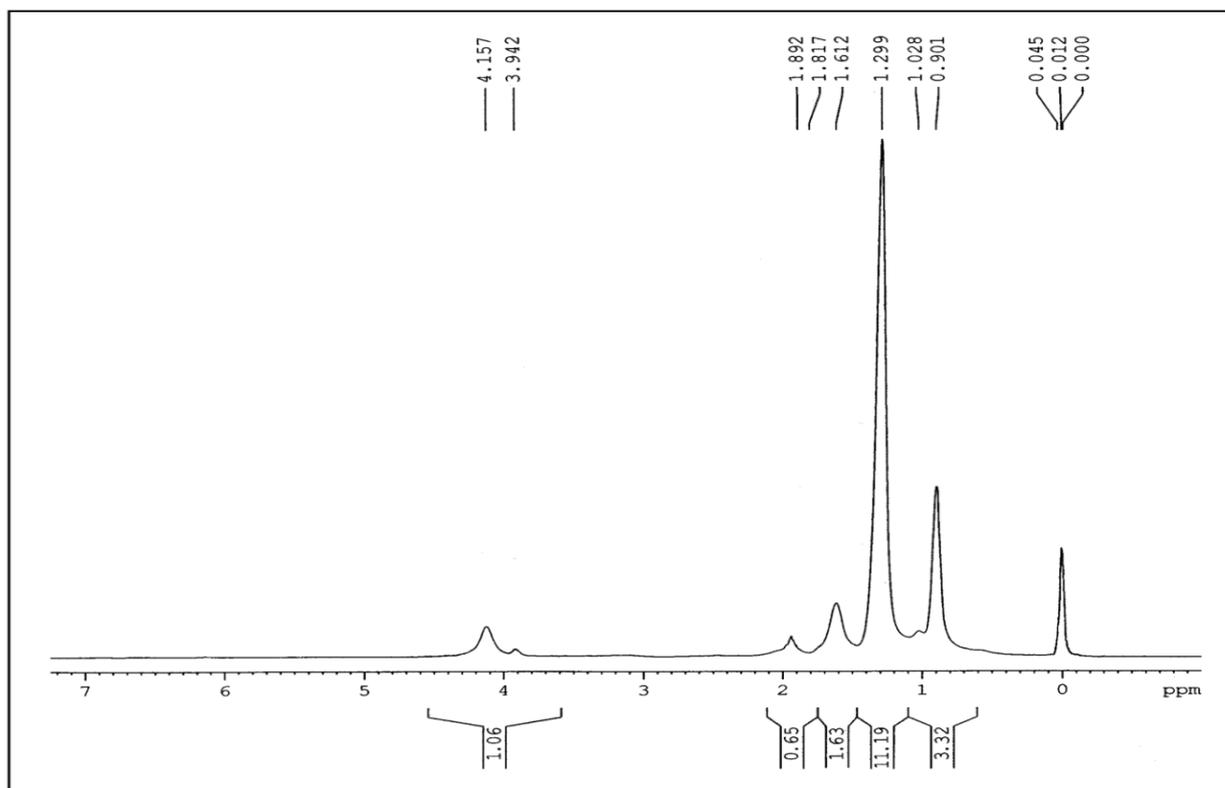


Figure 1.2.5: $^{13}\text{C-NMR}$ spectra of the additive HMMA

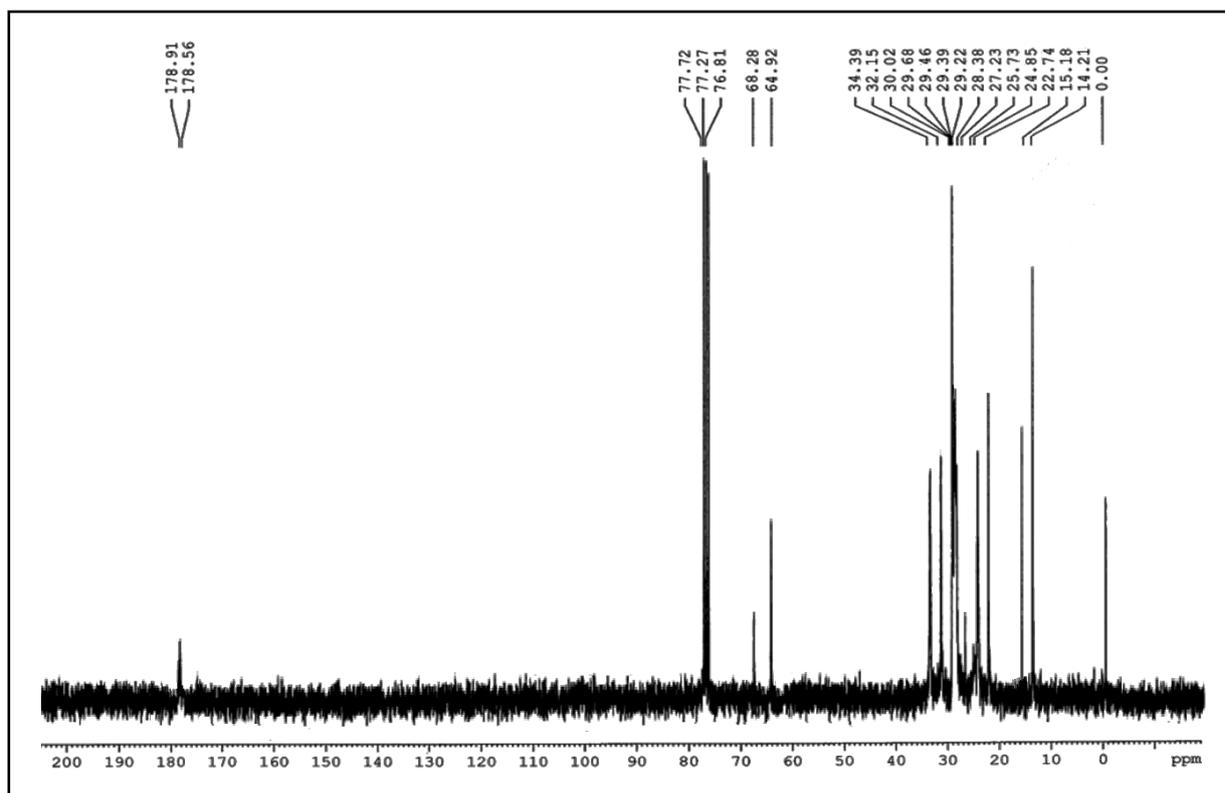


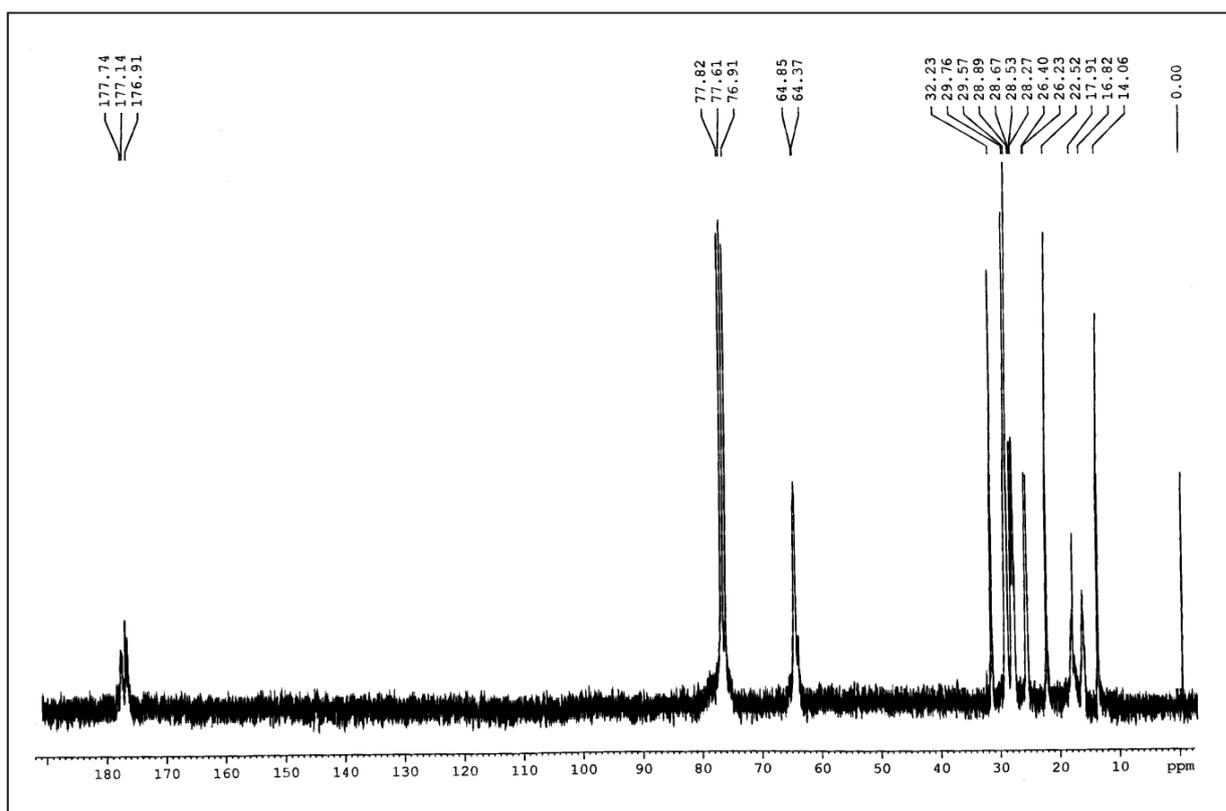
Figure 1.2.6: ^{13}C -NMR spectra of the additive MMAO5

Figure 1.2.7: Thermo gravimetric analysis of the additives

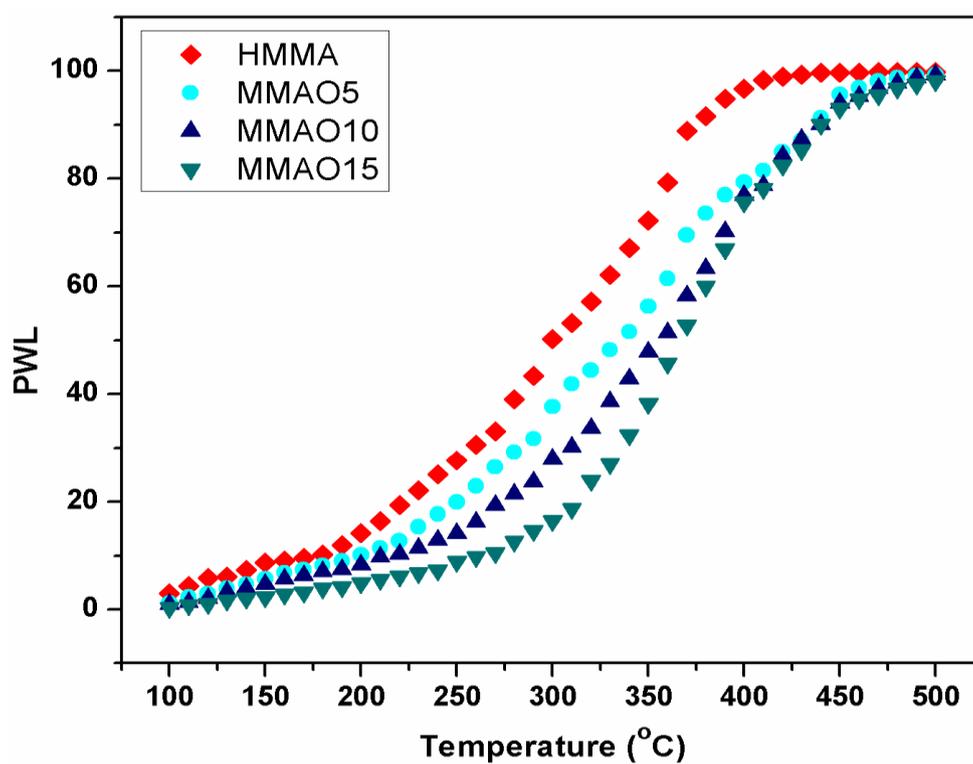


Figure 1.2.8: Variation of pour points of the base fluid doped with additives at different concentrations

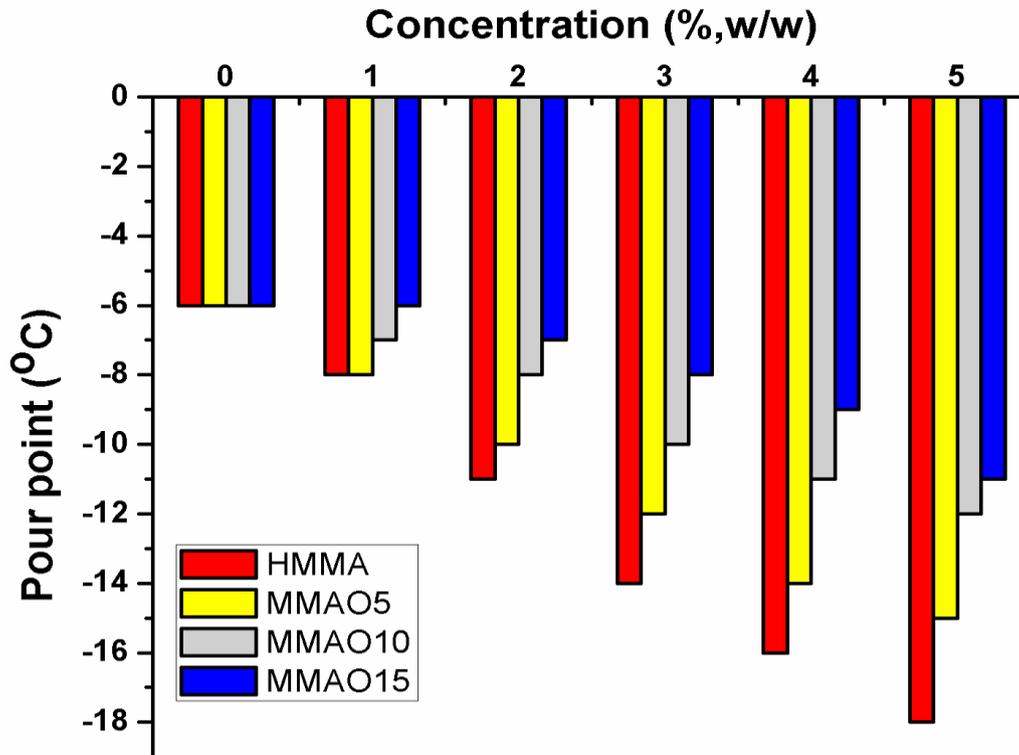


Figure 1.2.9: Variation of viscosity index of the base fluid doped with additives at different concentrations

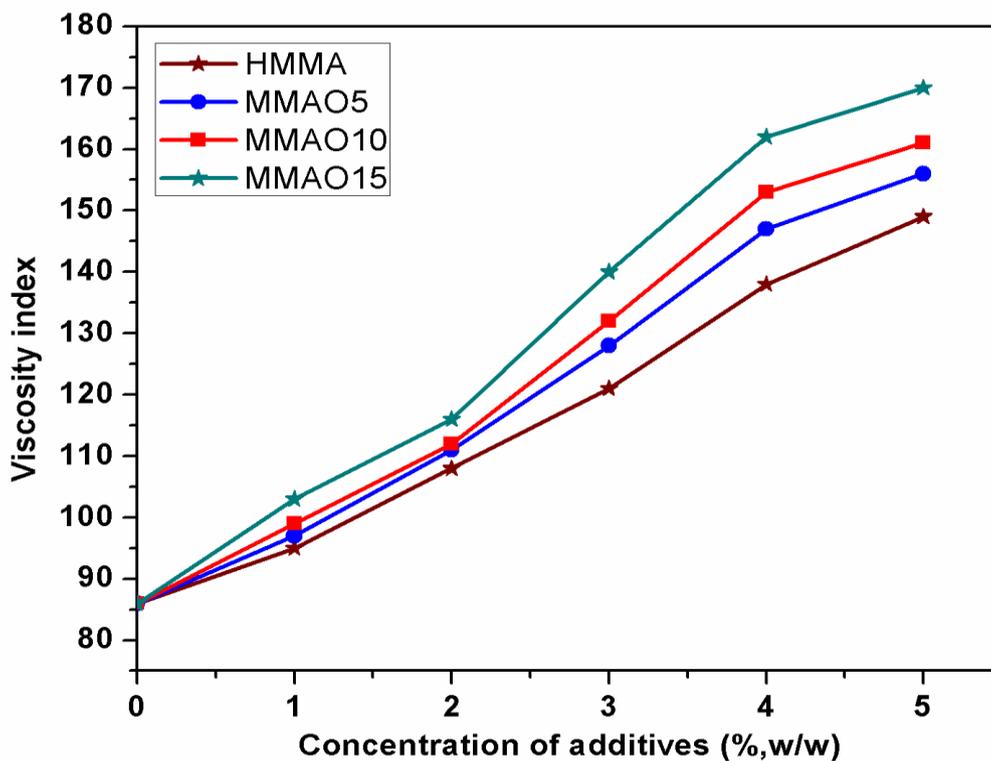
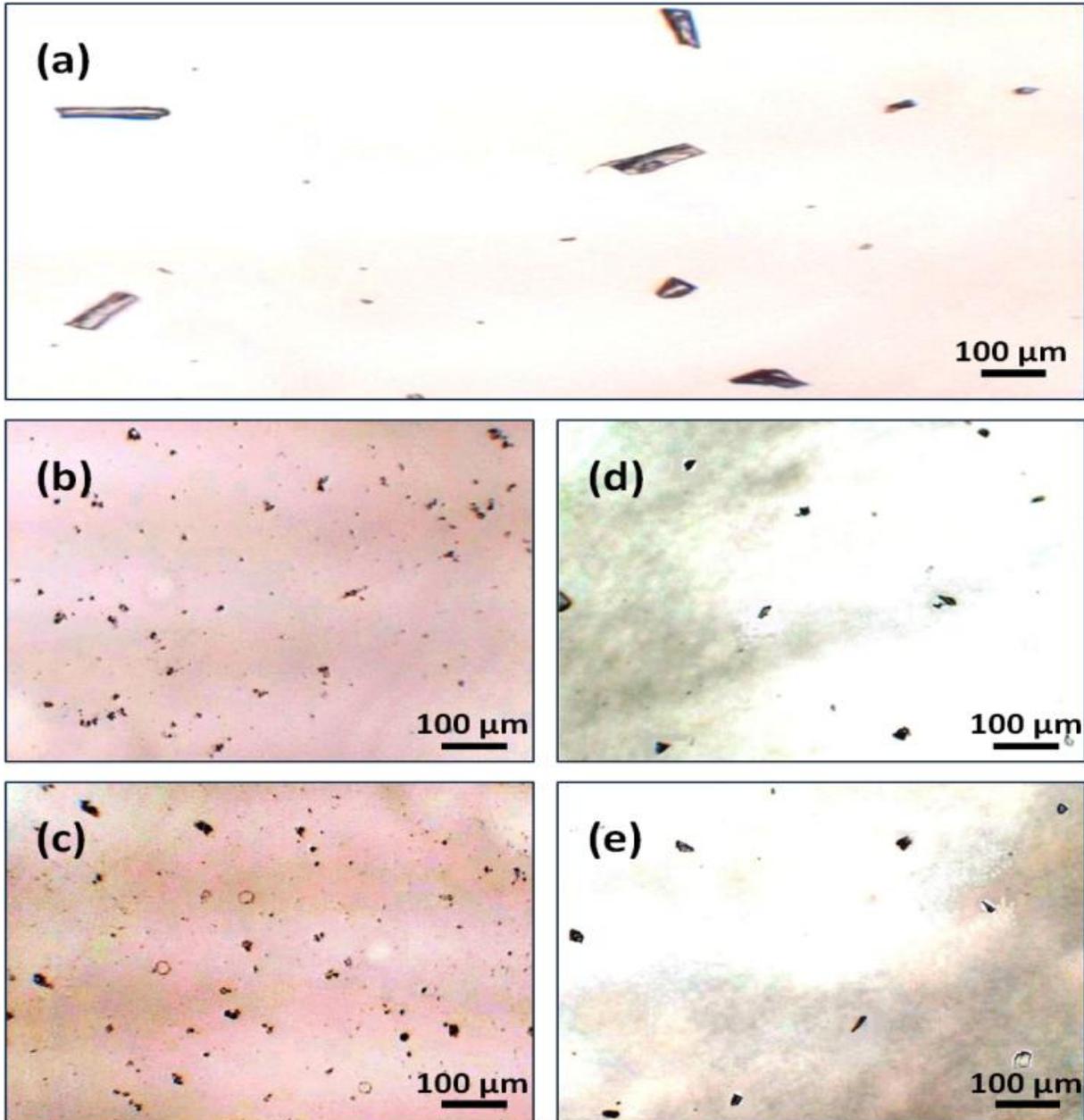


Figure 1.2.10: Photomicrograph of: (a). pure base fluid (b). base fluid + additive HMMA (4%, w/w) (c). base fluid + additive MMA05 (4%, w/w) (d). base fluid + additive MMA010 (4%, w/w) (e). base fluid + additive MMA015 (4%, w/w)



Chapter-III

*Undecyl methacrylate based polymers
as multifunctional additives for lube oil*

1.3.1 Introduction

The use of poly acrylates and poly methacrylates in lubricating oils as useful additives have been documented for a few years now.¹ The methacrylates are recognized as an efficient pour point depressant (PPD) and the acrylates as an effective viscosity index improver (VII) for the lube oil.^{2,3} PPDs are the additives added for maintaining the flow of oil and its transportation at low temperature. This is because of the fact that the oil's flow ability is completely ceased below a certain temperature called the pour point of that oil.⁴ At this temperature, the oil develops wax crystal network and interferes with the flow of the oil. When added to the oil, the hydrocarbon chain of the PPDs gets inserted into the wax lattice and inhibits or modifies the wax crystal formation. The PPDs are, therefore, also called wax crystal modifiers. The VIIs are the additives added to resist the change in viscosity of the oil with temperature variation. Their performance is denoted by a number called viscosity index that indicates the resistance of a lubricant to viscosity change.⁵ A high viscosity index indicates that the temperature does not influence the viscosity to any large degree and vice versa.

Although the conventional acrylate and methacrylate additives with C₁₀-C₁₄ alkyl groups enhance the viscosity index and C₁₆-C₁₈ alkyl groups contribute mainly towards lowering of pour point of the base oils, but with the new standards regarding the emissions of gases and with the associated changes in the engine designs, it became necessary to bring about a modification in lubricant composition and formulation.⁶ This directed all lubricant technologists toward the development of novel polymeric additives with multifunctional activity and ability to maintain clean engine operations. Lubricant manufacturers are, therefore, trying out copolymerization with different

monomers to induce additional viscometric and rheological benefits into the additives. Again, copolymerization with suitable monomer may also increase the molecular weight and crosslink density of the additives. In addition, with the emerging trend of getting better fuel economy, people have started producing cost effective lubricant additives with multifunctional performances to be added to the lube oil.

Long chain behenyl acrylate (BA, prepared from behenyl alcohol and acrylic acid) was chosen here as a potential candidate for copolymerization with undecyl methacrylate (UDMA) and an extensive analysis of their additive performance along with that of polybehenyl acrylate and polyundecyl methacrylate has been carried out. FT-IR and NMR were used for the structural characterization of the polymers, thermo gravimetric analysis (TGA) was performed to assess their thermal response at high temperature and their molecular weight was determined with gel permeation chromatography (GPC). The results evaluated for the polymers are encouraging and comprises the subject matter of the report.

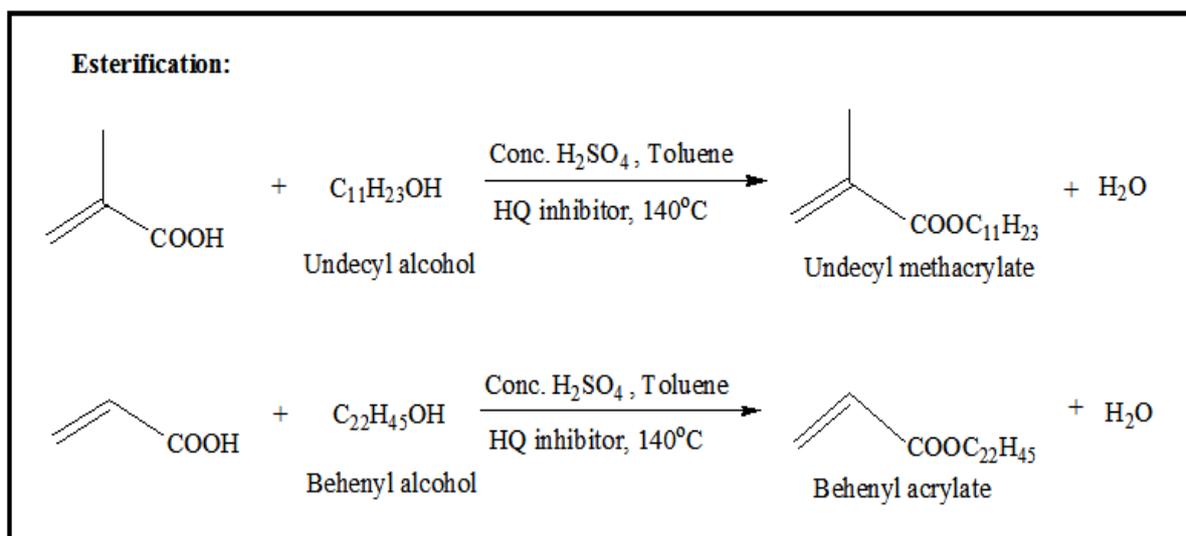
1.3.2 Experimental section

1.3.2.1 Materials

Undecyl alcohol was purchased from Sigma-aldrich. Methacrylic acid, acrylic acid, behenyl alcohol, hydroquinone, H₂SO₄ and BZP were purchased from Merck specialities Pvt., Ltd. Hexane and methanol were obtained from Nice chemicals Pvt., Ltd. The CHCl₃-CH₃OH 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 1.3.1).

1.3.2.2 Esterification

The esters, UDMA and BA were prepared from the corresponding acids and alcohols in a 1:1 ratio. The esterification was performed under nitrogenous atmosphere in toluene using a reaction kettle and taking catalytic quantity of conc. 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 $140\text{ }^\circ\text{C}$ with the help of a thermostat. The measure of the amount of water liberated during the reaction helped in monitoring the extent of reaction.



Scheme 2: Preparation of undecyl methacrylate and behenyl acrylate

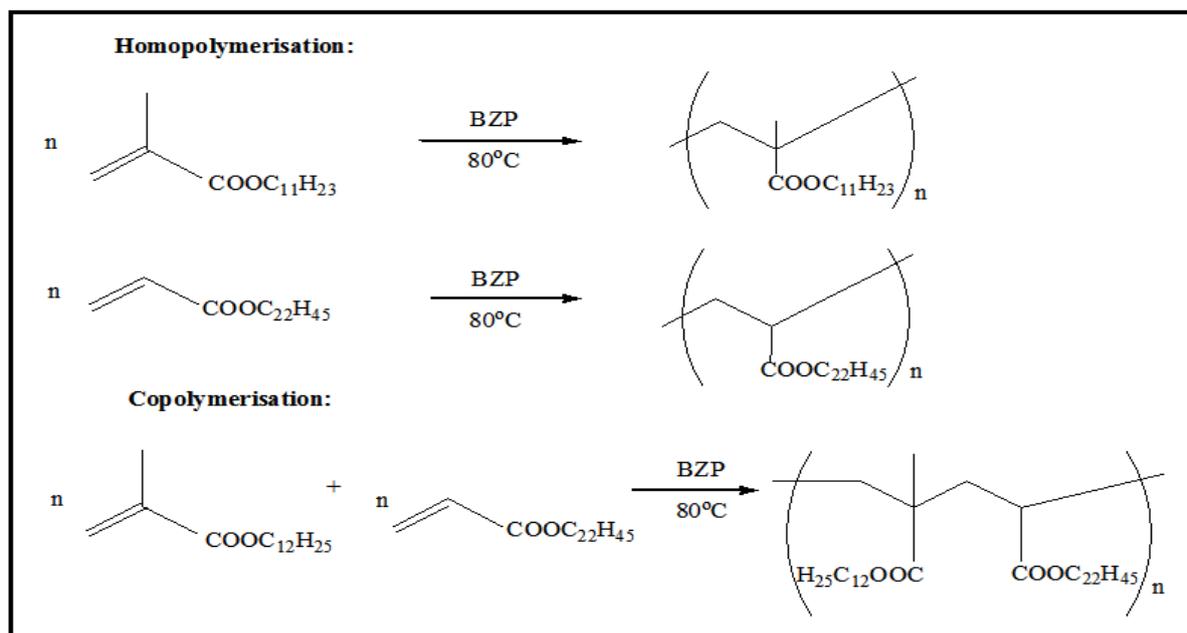
1.3.2.3 Purification of the prepared esters

1 g of charcoal was first added to each of the esters and was refluxed for 3 hours. After the fixed 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 present in small amount) until it became neutral to pH paper. The esters UDMA and BA were finally left over night on anhydrous CaCl_2 . For further use, CaCl_2 was separated by filtration and toluene was recovered by distillation under reduced pressure and the ester was used in the polymerization reaction.⁷

1.3.2.4 Preparation of homopolymers and copolymers

The copolymers were prepared through free radical polymerization method in four different percentage of BA (10, 20, 30 and 40, w/w) in the compositional mixture of UDMA and BA using BZP as initiator.



Scheme 3: Preparation of homopolymers and copolymers

A three necked round bottom flask connected with a condenser, thermometer and fitted with a magnetic stirrer was used in the polymerization process. The flask was also connected with an inlet for the introduction of nitrogen. In the flask, mixture of exact

percentage of the monomers was heated to 80 °C and maintained at that temperature for half an hour. The initiator BZP (1% w/w, with respect to the total monomers) was then added and heated for 6 hour keeping the temperature constant at 80 °C. The detailed procedure is also mentioned in our other publication.⁸

The two homopolymers, poly-UDMA and poly-BA were also prepared following the same procedure. By FT-IR and NMR analysis 85-90% incorporation of BA was estimated in the polymer backbone (Table 1.3.2).⁹

1.3.3 Measurements

1.3.3.1 Spectroscopic measurements

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

1.3.3.2 Evaluation of thermal stability

A Mettler TA – 3000 apparatus was used to record the thermal stability of the polymers having a heating rate of 10 °C min^{-1} .

1.3.3.3 Measurement of average molecular weight

A GPC instrument (Waters Corporation, USA) was used to calculate the average

molecular weights of the polymers having calibrated polystyrene standards in THF. The PDI was also calculated using the instrument. The values are presented in Table 1.3.3. A gradual increase in the molecular weight was observed for the polymers with the increase in the percentage of BA in the feed.

1.3.3.4 Evaluation of viscosity index

The VI of the two different base oils blended with the polymers was calculated to verify the potential of the synthesized polymers as viscosity index improver. The VI was calculated using an Ubbelohde viscometer which was calibrated at 40 °C and 100 °C with purified methanol and triply distilled water prior to the experiment.¹⁰ The time taken by the polymer 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 sample solutions from the following equation,¹¹

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

where t and ρ are the flow time and density of the polymer solution respectively.

A DMA 4500M vibrating-tube density meter (Anton paar, Austria) was used to compute the densities of the polymer solutions. The VI was evaluated from the given empirical equation,¹²

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

where n is a constant characteristic for each oil and is calculated by the following equation,¹³

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

where ν_1 and ν_2 are the kinematic viscosities of the polymer doped oil at lower and higher temperature respectively and k is a function dependent solely on temperature.

1.3.3.5 Evaluation of pour point

The pour points of the base oils blended with different percentages of the prepared polymers were tested according to the ASTM D97 method on a cloud and pour point tester (Wadegati labequip Pvt., Ltd., India) in the temperature range of 0 to -71 °C.

1.3.3.6 Photo micrograph and wax modification

The photomicrographs showing wax crystallization behaviour of the base oils blended with different percentages of the prepared polymers were recorded in a Banbros polarizing microscope (BPL-400B, India). The temperature was set at 273 K and it was suitably controlled on the microscope slide by an attached cooling thermostat. The magnification used here was 200X.

1.3.4 Results and discussion

1.3.4.1 Spectroscopic data analysis

FT-IR spectra: The recorded spectra (Fig. 1.3.1) of poly undecyl methacrylate showed signal for the stretching vibration of ester carbonyl (C=O) at 1732.6 cm^{-1} while the ester C–O–C stretching vibration peak appeared at 1164.6 cm^{-1} . The band for the C–H bending vibrations of CH_2 and CH_3 groups appeared at 1464.7 and 722.2 cm^{-1} while the band for the stretching vibrations of the paraffinic C–H bonds appeared at 2879.3 and 2951.1 cm^{-1} . The disappearance of the characteristics peaks of olefins in the product indicates the formation of the polymer.

¹H-NMR spectra: The polymer P-1, in its ¹H-NMR spectra (Fig. 1.3.2), displayed the presence of the protons of -COOCH₂ group by appearing as a broad peak centred at 4.01 ppm; other peaks around 0.86 ppm were due to the methyl protons of undecyl and methacrylate chain. The peaks in the range of 1.1–1.6 ppm were for the methylene protons of the acrylate chain.

¹³C-NMR spectra: The ¹³C-NMR spectra (Fig. 1.3.3) of P-1 showed peaks between 14.2 and 41.4 ppm for all the methyl and methylene carbon atoms. The -OCH₂ carbons of the polymer appeared between 58.3 and 65.1 ppm while the peak around 177.6 ppm is attributed to the carbonyl carbons of the ester groups. Similar absorption bands (both in NMR and FT-IR, Figs. 1.3.4, 1.3.5 and 1.3.6) were also obtained for the BA homopolymer (P-6).

The structural characterization of the copolymers (P-2 to P-5) was also accomplished by their ¹H-NMR, ¹³C-NMR and FT-IR study. Due to similarity in composition, all the copolymers exhibited resembling spectral outline. Selecting the polymer P-5 as a standard copolymer, its FT-IR spectra displayed a strong signal for the stretching vibration of ester carbonyl (C=O) at 1735.4 cm⁻¹ in addition to the signal at 1166.6 cm⁻¹ for the ester C-O-C stretching vibration. The band for the C-H bending vibrations of CH₂ and CH₃ groups appeared near 1456.8 and 712.3 cm⁻¹ while the band at 2872.3 and 2927.2 cm⁻¹ were for the stretching vibrations of the paraffinic C-H bonds (Fig. 1.3.7). In its ¹H-NMR spectra (Fig. 1.3.8), the protons of -COOCH₂ group of UDMA and BA appeared as a broad signal centered at 4.08 ppm while the other peaks between 0.73 and 0.87 ppm were due to the methyl protons of undecyl, behenyl and methacrylate chain. The peaks in the range of 1.2–1.6 ppm were for the methylene protons of the acrylate chains. The ¹³C-NMR spectra (Fig. 1.3.9) of the copolymer showed signals for the methyl and methylene carbon atoms between 14.2 and 45.5

ppm. The $-OCH_2$ carbons of the polymer appeared around 65 ppm while the peak for the carbonyl carbons of the ester groups of UDMA and BA appeared around 176.6 ppm. Moreover, no peaks for unsaturation were present in any of the copolymers.

1.3.4.2 Thermo gravimetric analysis

The thermo gravimetric results of all the polymers (homo and copolymers) are depicted in Table 1.3.4. The results demonstrate that the thermal stability of most of the copolymers is greater than the homopolymers. Moreover, with the increasing percentage of BA in the copolymers, an increase in their thermo oxidative stability is also observed. The proportionate increase in the molecular mass of the copolymers along with their narrower molecular weight distribution must be the reason for their increased stability.

1.3.4.3 Performance as viscosity index improver

The effectiveness of the synthesized polymers as VII was ascertained by evaluating the VI of the polymer doped base solutions. Different percentages of the prepared polymer solutions ranging between 1 and 5 wt% were used to study their performance and the computed VI data are showed in Figs. 1.3.10 and 1.3.11.

From the outcome it is obvious that for all the instances the VI values improved with increasing polymer percentage in the base oils. This is in agreement with our earlier findings.¹⁴ This outcome is because of the increased solubility of polymer with increasing temperature of the base oil. With increased solubility and effective interaction between the polymer chains and the solvent molecules, the polymer

molecules change from a tight coiled micelle to an expanded one.¹⁵ This increased magnitude of polymer micelle volume compensates the reduction of viscosity of the base fluid and, hence, decreases the changes of viscosity of the mixture with temperature alteration. Besides, the overall size and volume of the micelles also gets enlarged with the rise of polymer mass in the base fluid. This increase in micelle volume imparts a higher VI for the polymer solution in contrast to that of the small percentage of the same polymer.¹⁶

Interestingly, the homopolymer of BA (P-6) acted as a better viscosity modifier than the rest of the polymers. The result indicated that the efficiency to act as VII increases with increasing the alkyl chain length of the alcohol moiety. Also, the BA homopolymer is associated with the highest molecular weight among all the polymers. Thus, the outcome is because of the combined effect of the molecular weight and the chain length of the polymer.¹⁷

1.3.4.4 Performance as pour point depressant and wax modification analysis

The synthesized additive compositions were evaluated for their pour points and the data are plotted in Figs. 1.3.12 and 1.3.13. The results showed that all the polymers are excellent as PPD but the efficiency increased with increasing their concentration only up to a certain limit. This can be explained by considering the solvation power of the oil. With decreasing temperature, any solvent gradually becomes less effective in solvation and when the concentration of the solute and its molecular weight increases, the solvation capability becomes even lesser.¹⁸ Again, the interaction between the alkyl chain moieties of the polymer and the paraffin wax constituent in the lube oil is essential in controlling the wax crystal size. Higher the interaction, higher will be the

pour point depression. Long alkyl chain length of the polymer are usually efficient in controlling wax growth but sometimes too long polymer chain becomes ineffective and wax crystal formation is not successfully inhibited. The interaction depends upon various factors like the similarity in structure and chain length of the polymer with that of the waxes, matching crystalline packing of the polymers and the waxes, similarity in the melting point of waxes with the polymers and the molecular weight of the polymers.¹⁹ Here, the polymer P-5 has greater efficiency as PPD among all the polymers. The proper ratio of two different types of polymer chain length must have provided the polymer with the right kind of structure, appropriate melting point and effective molecular weight for the most effective interaction with waxes among all the additives.

The photomicrograph was also used to study the action mechanism of pour point depressant in the lube oil and the results are displayed in Fig. 1.3.14 (a-g). Fig. 1.3.14a is the photomicrograph of pure lube oil where there is large number of rod shaped wax crystals. The photomicrographs of lube oil blended with different polymers (P-1 to P-6) at 3% (w/w) concentration are shown in the Fig. 1.3.14b-g respectively and the images suggests a decrease in the size of wax crystals. The images are thus in good agreement with the pour point values reported earlier (Figs. 1.3.12 and 1.3.13). Thus, an important modification in the wax crystals is observed because of the addition of all the polymers but, polymer P-5 showed the greatest improvement.

1.3.5 Conclusions

All the polymers of undecylmethacrylate and behenylacrylate showed better performances both as viscosity index improver and pour point depressant additive for lube oil. Polymer P-6 acted as a superior viscosity modifier compared to others while

the pour point depressant property of P-5 was much better among all the polymers. BA has a significant role in enhancing the performances of the additives. The long hydrocarbon chain of BA molecule is the key reasons for exhibiting better PPD performance of the copolymeric additives. On the other hand, higher molecular weights of the polymers are responsible for showing superior viscosity index values. In addition, the polymers exhibited remarkable thermal stability and the copolymer with highest BA content showed the maximum thermal stability amongst the other five polymers. Comparative study thus suggests that the polymer P-5 with 40% BA was the most effective multifunctional additive among all the polymers. Therefore, the above study is definitely a constructive approach to formulate a multifunctional and hence cost effective lubricant composition.

1.3.6 References

References are given in BIBLIOGRAPHY section under Chapter-III of Part-I (Page No. 199-201).

1.3.7 Tables and figures

Table 1.3.1: Physical properties of base oils

Properties	Base oils	
	B01	B02
Density (g cm ⁻³) at 313 K	0.83498	0.89653
Viscosity (cSt) at 313 K	6.921	23.837
Viscosity (cSt) at 373 K	1.656	3.993
Viscosity index	80	85
Pour point (°C)	-3	-6

B01: base oil type 1, B02: base oil type 2.

Table 1.3.2: Percentage composition of the copolymers as obtained by spectroscopic method

Polymers	Mass fraction of the polymers		NMR estimation of the mass fraction of BA	FT-IR estimation of the mass fraction of BA
	UDMA	BA		
P-1	1.00	0.0	-	-
P-2	0.90	0.10	0.09	0.08
P-3	0.80	0.20	0.16	0.17
P-4	0.70	0.30	0.25	0.26
P-5	0.60	0.40	0.37	0.36
P-6	0.0	1.00	-	-

P-1: homopolymer of undecyl methacrylate, P-2: 10% BA + UDMA, P-3: 20% BA + UDMA, P-4: 30% BA + UDMA, P-5: 40% BA + UDMA, P-6: homopolymer of behenylacrylate.

Table 1.3.3: GPC results of the polymers

Polymers	GPC values of the polymers		
	M_n	M_w	PDI
P-1	19174	35854	1.87
P-2	23577	39138	1.66
P-3	23703	40532	1.71
P-4	24055	42816	1.78
P-5	25989	43661	1.68
P-6	21365	44864	2.09

Table 1.3.4: TGA results of the polymers

Polymers	TGA values	
	Decomposition temperature (°C)	PWL
P-1	325/458	46/92
P-2	327/468	43/90
P-3	351/487	45/92
P-4	358/495	44/93
P-5	370/524	45/92
P-6	311/462	44/90

PWL: percent weight loss.

Figure 1.3.1: FT-IR spectra of poly undecyl methacrylate (P-1)

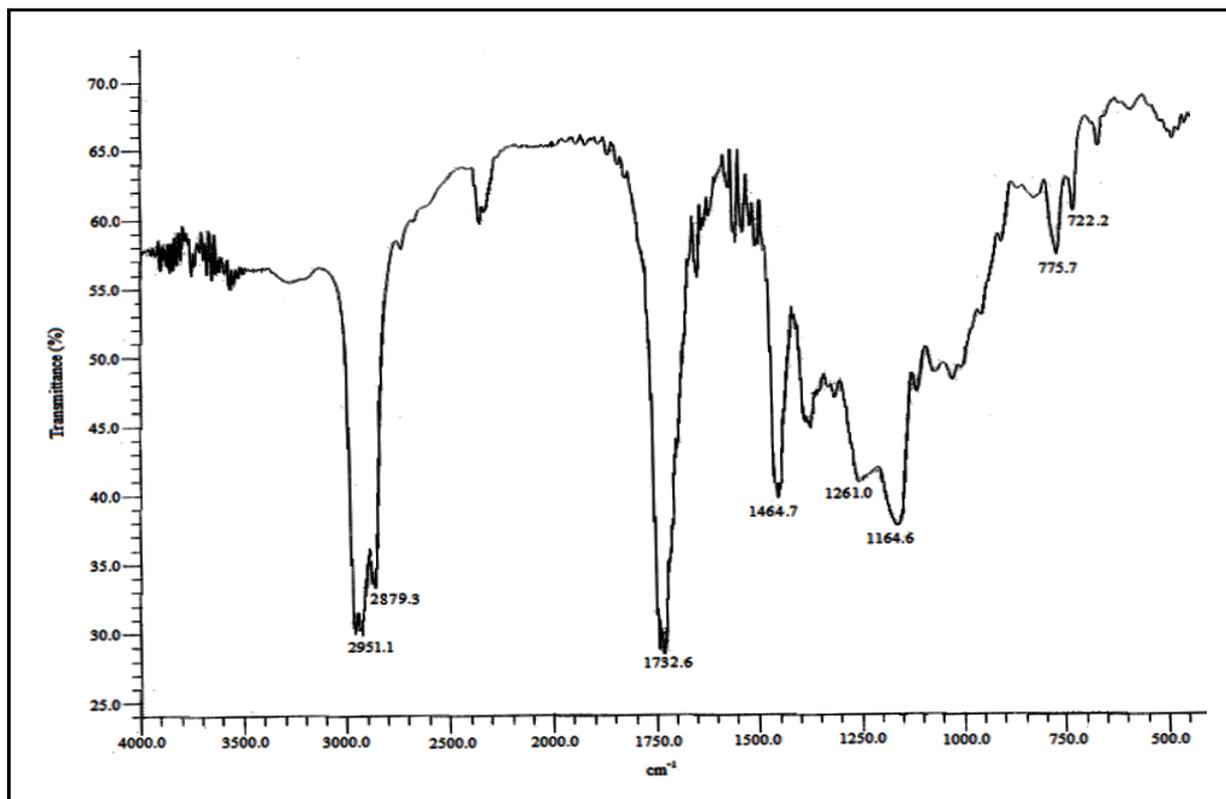
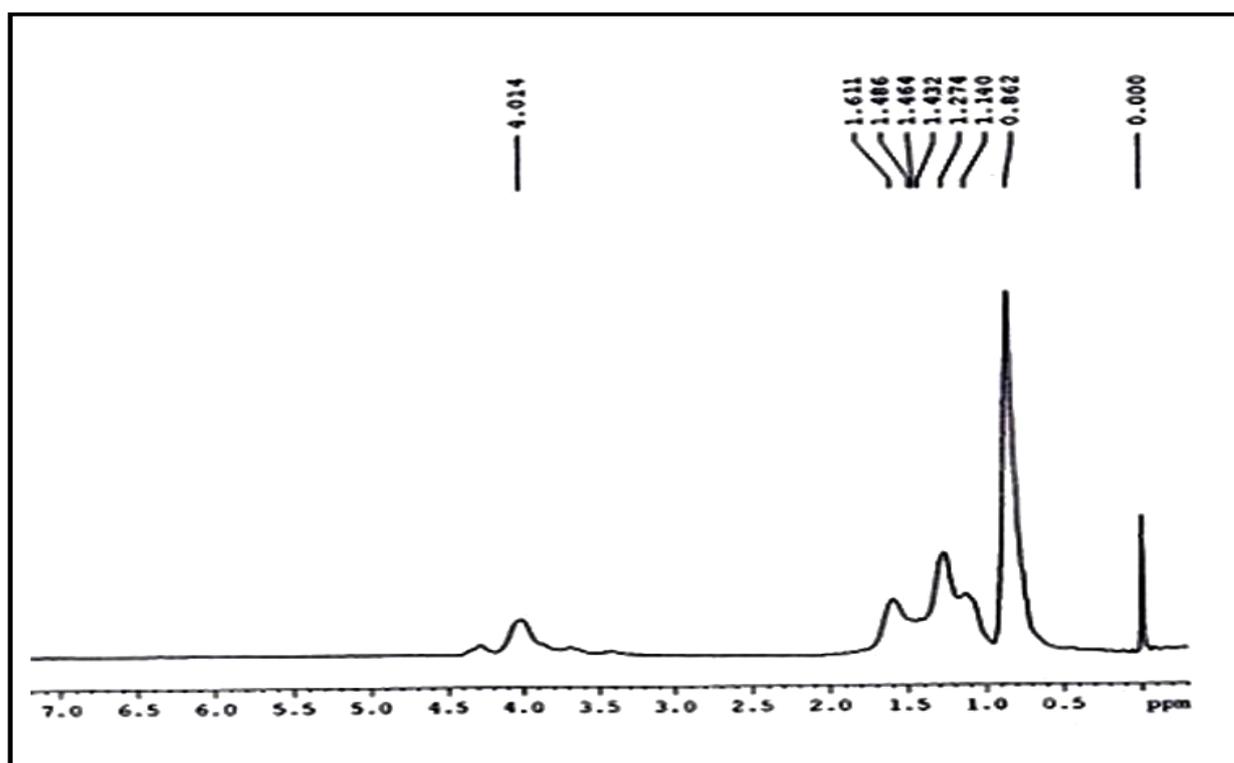
Figure 1.3.2: NMR spectra (^1H) of poly undecyl methacrylate (P-1)

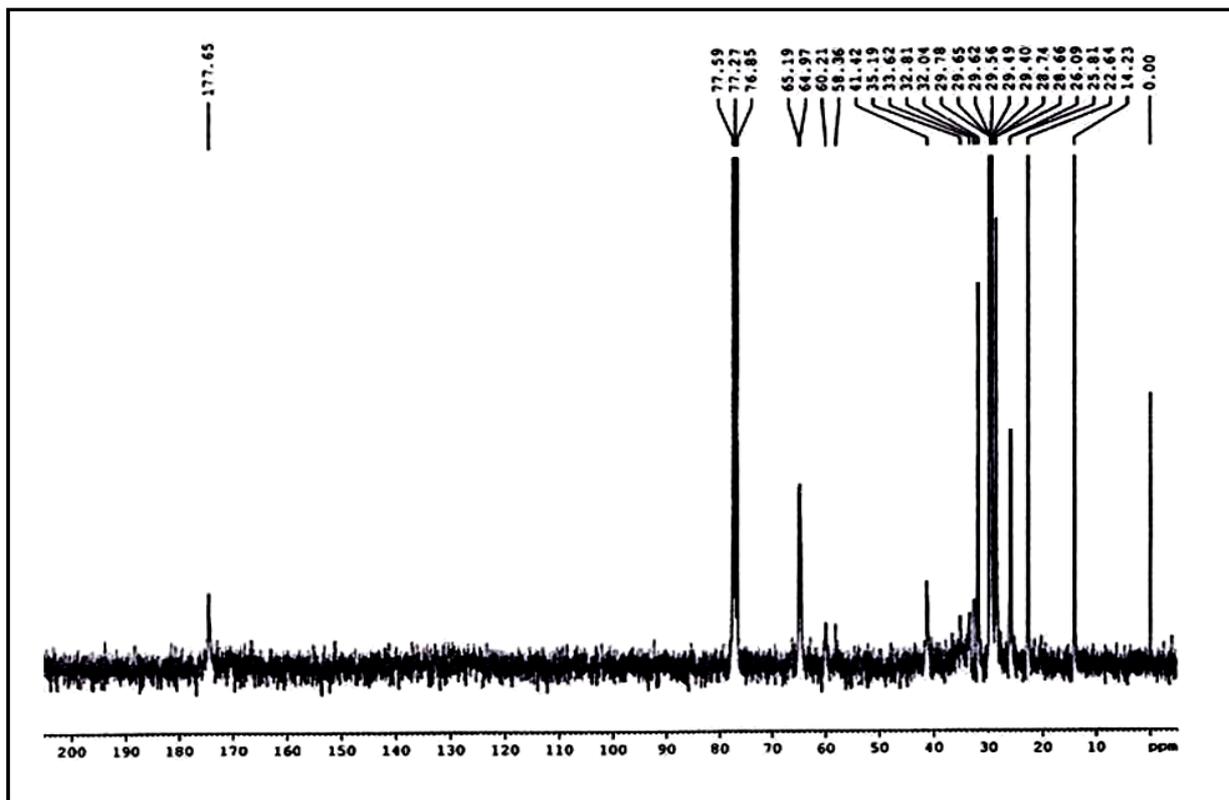
Figure 1.3.3: NMR spectra (^{13}C) of poly undecyl methacrylate (P-1)

Figure 1.3.4: FT-IR spectra of poly behenyl acrylate (P-6)

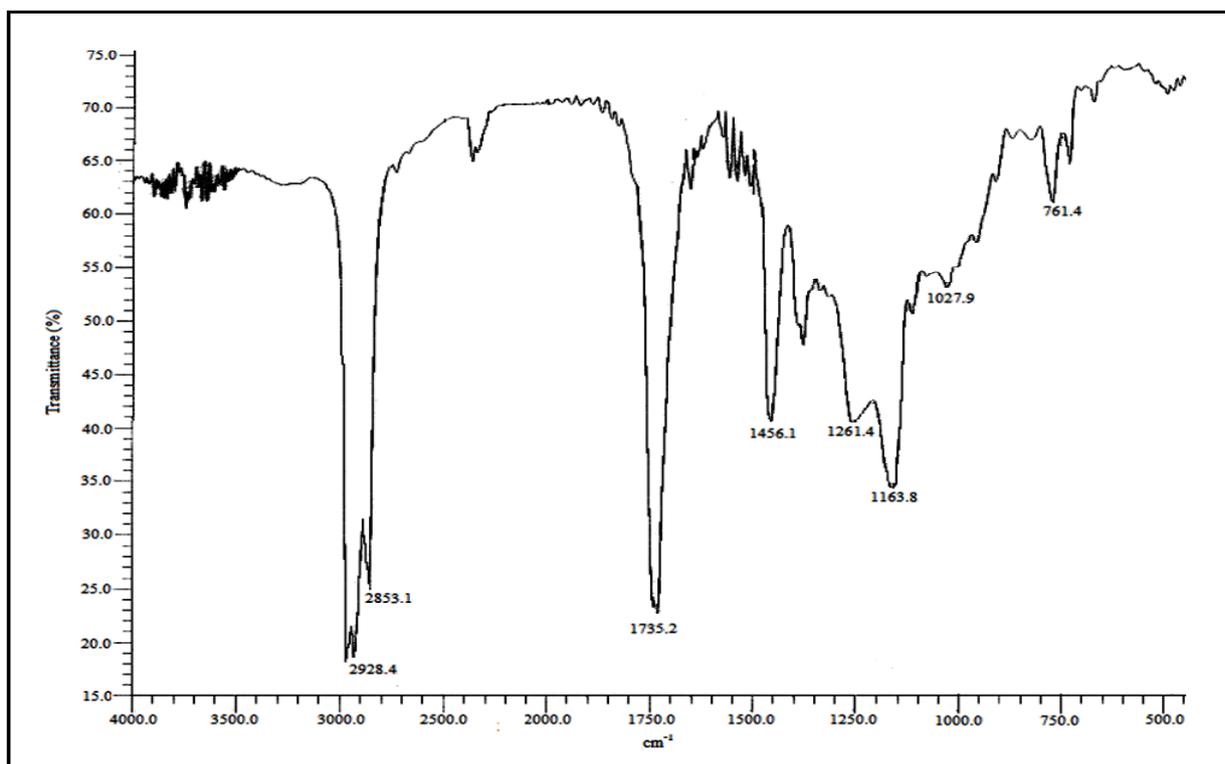


Figure 1.3.5: NMR spectra (^1H) of poly behenyl acrylate (P-6)

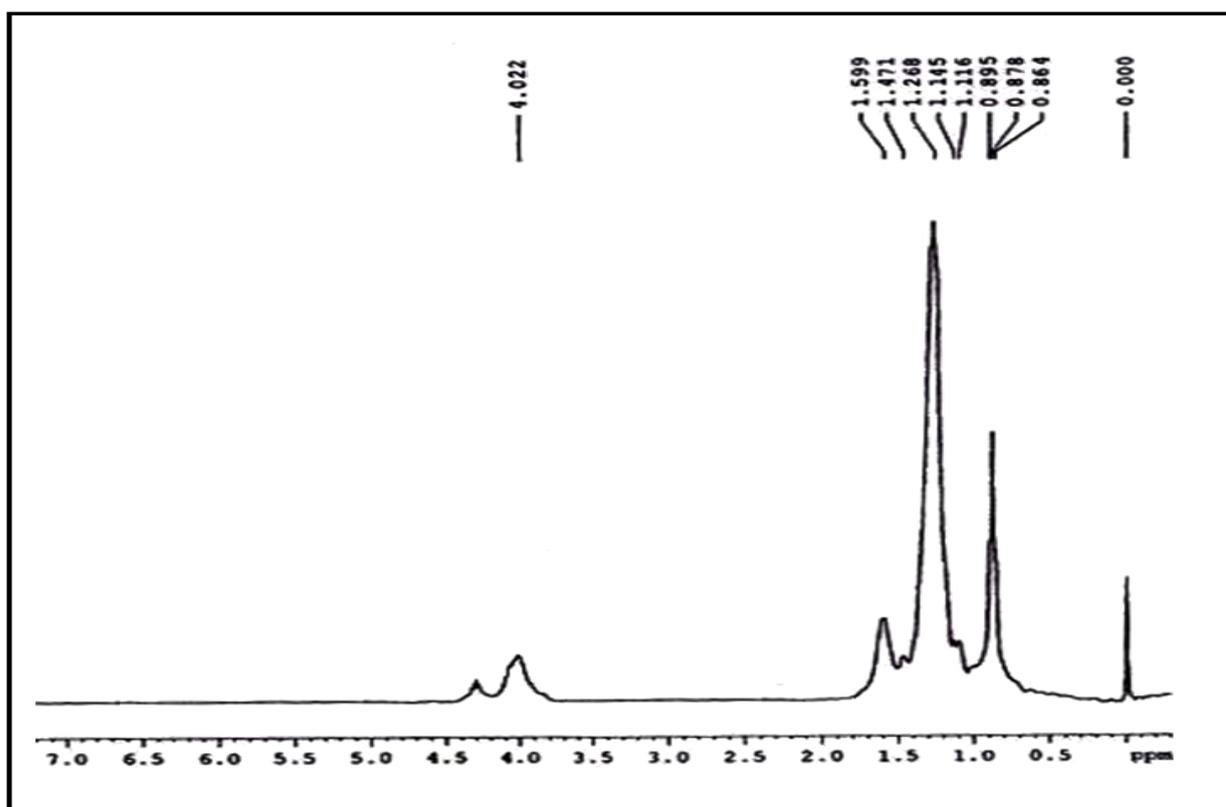


Figure 1.3.6: NMR spectra (^{13}C) of poly behenyl acrylate (P-6)

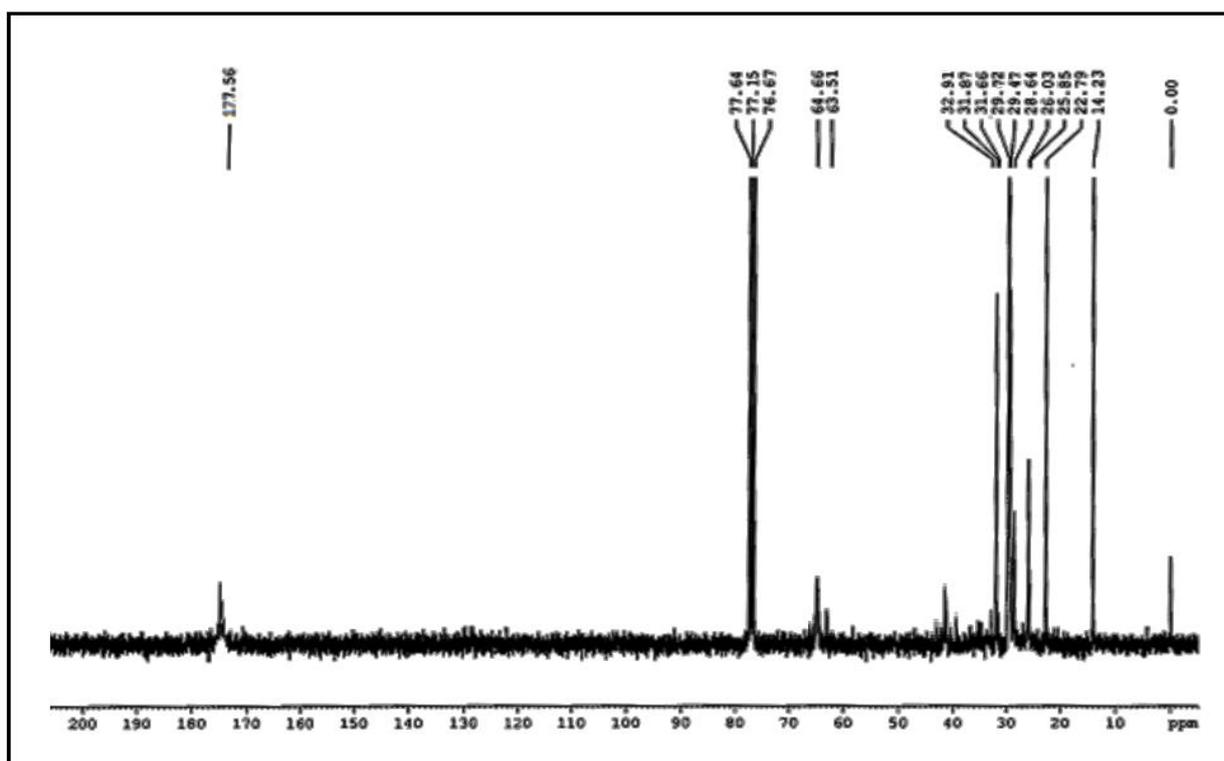


Figure 1.3.7: FT-IR spectra of the copolymer P-5 (selecting as a standard copolymer)

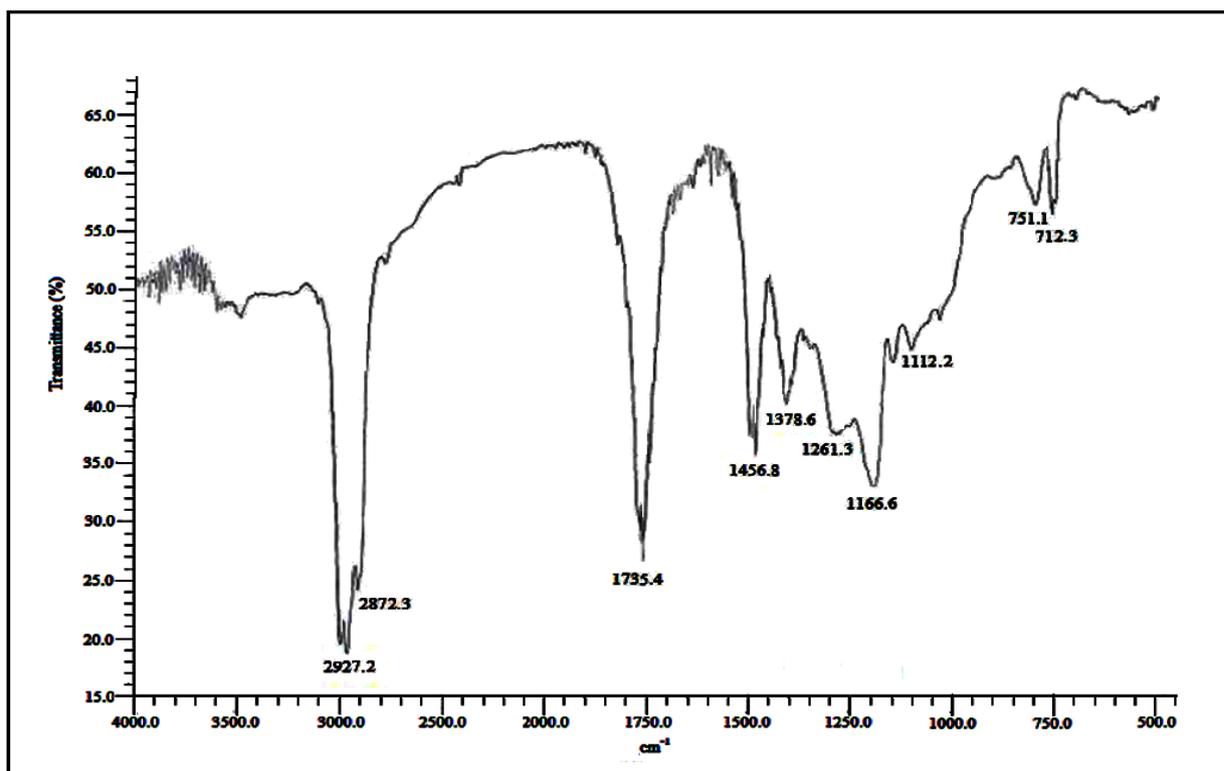
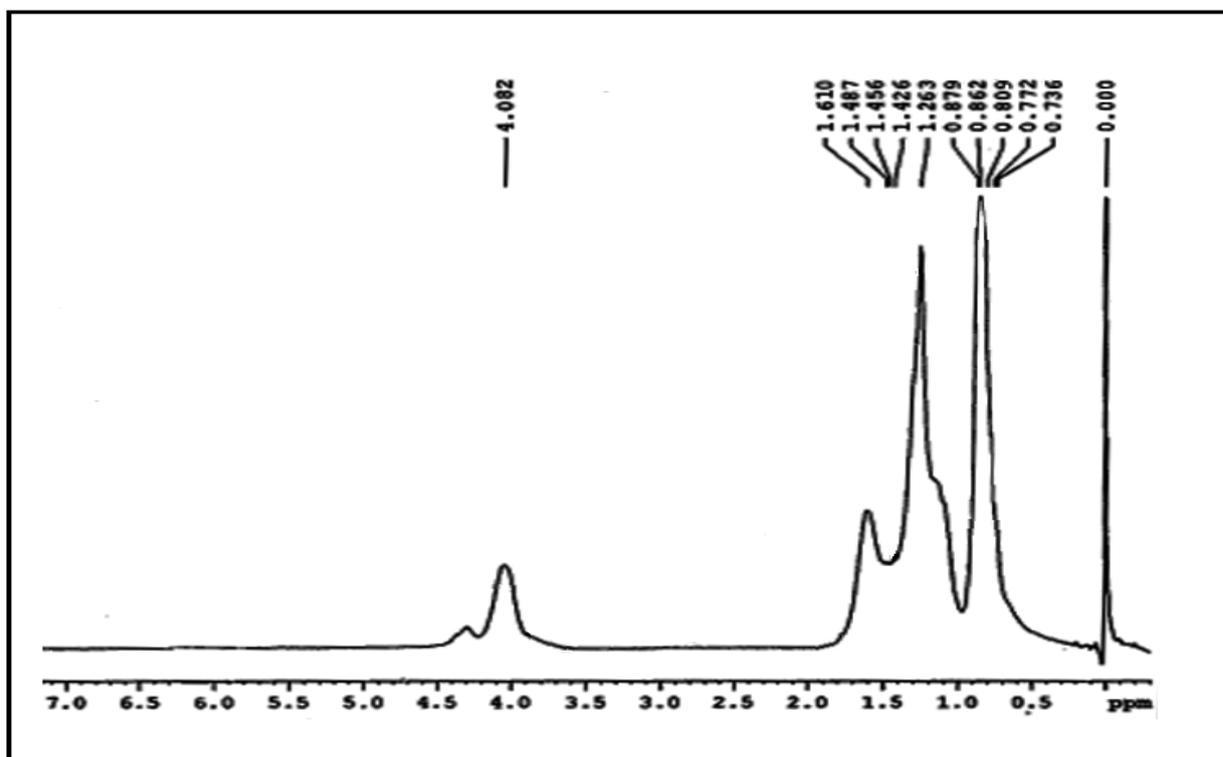
Figure 1.3.8: NMR spectra (¹H) of the copolymer P-5 (selecting as a standard copolymer)

Figure 1.3.9: NMR spectra (^{13}C) of the copolymer P-5 (selecting as a standard copolymer)

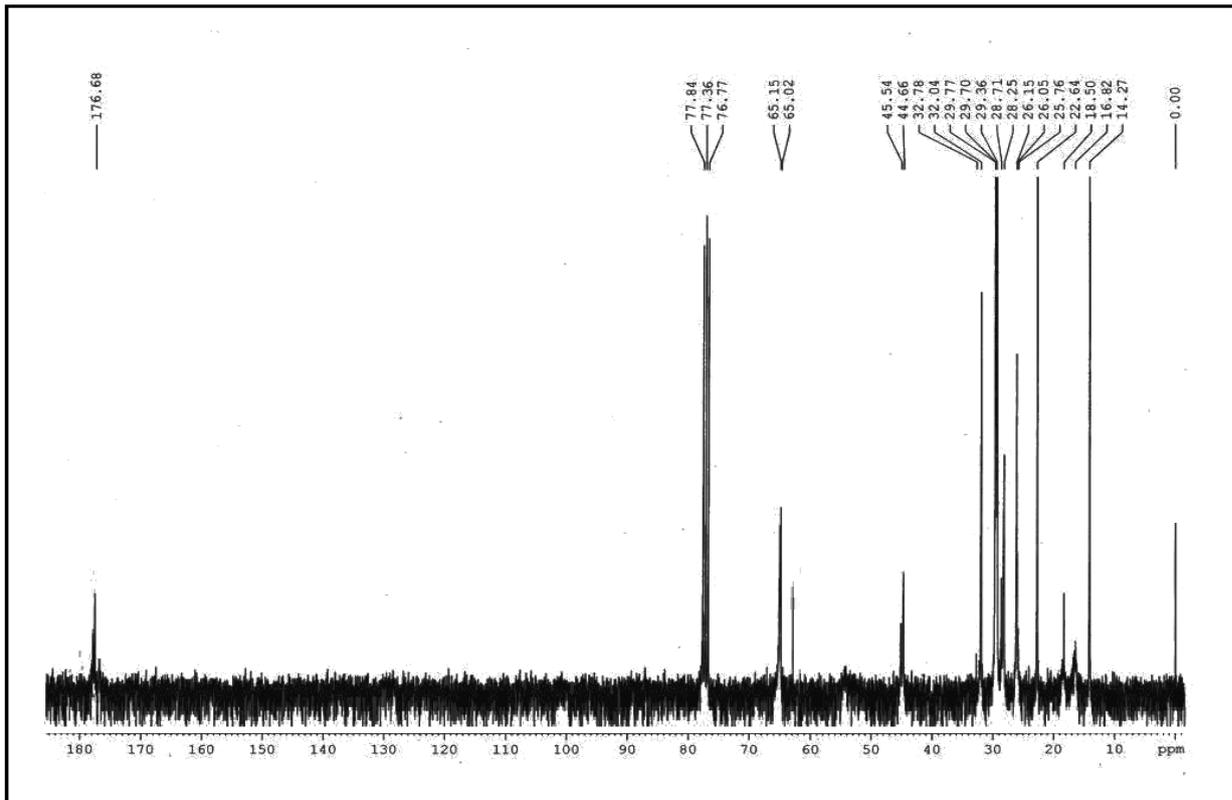


Figure 1.3.10: Viscosity index (VI) values of polymers P-1 to P-6 doped in base oil B01

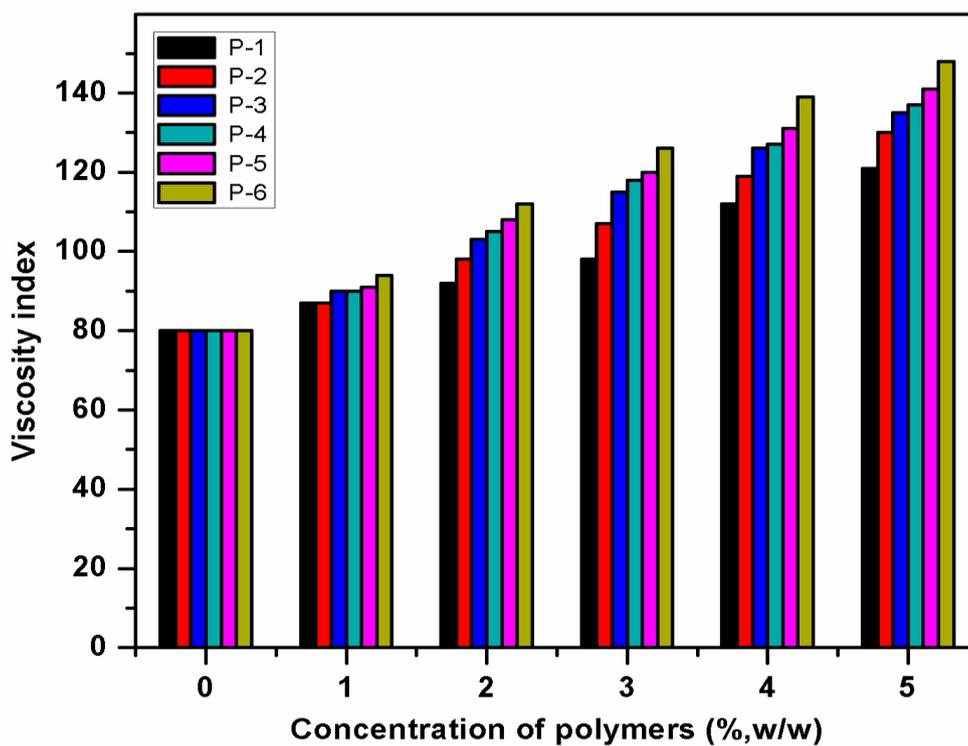


Figure 1.3.11: Viscosity index (VI) values of polymers P-1 to P-6 doped in base oil B02

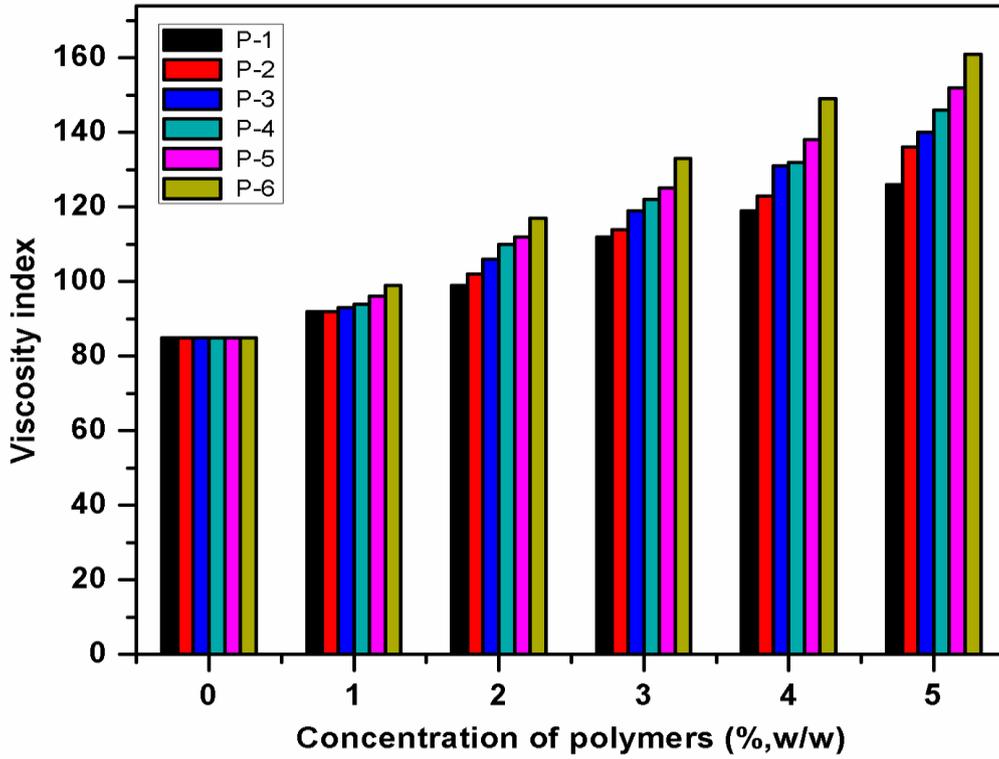


Figure 1.3.12: Pour point (PP) of the polymers P-1 to P-6 doped in base oil B01

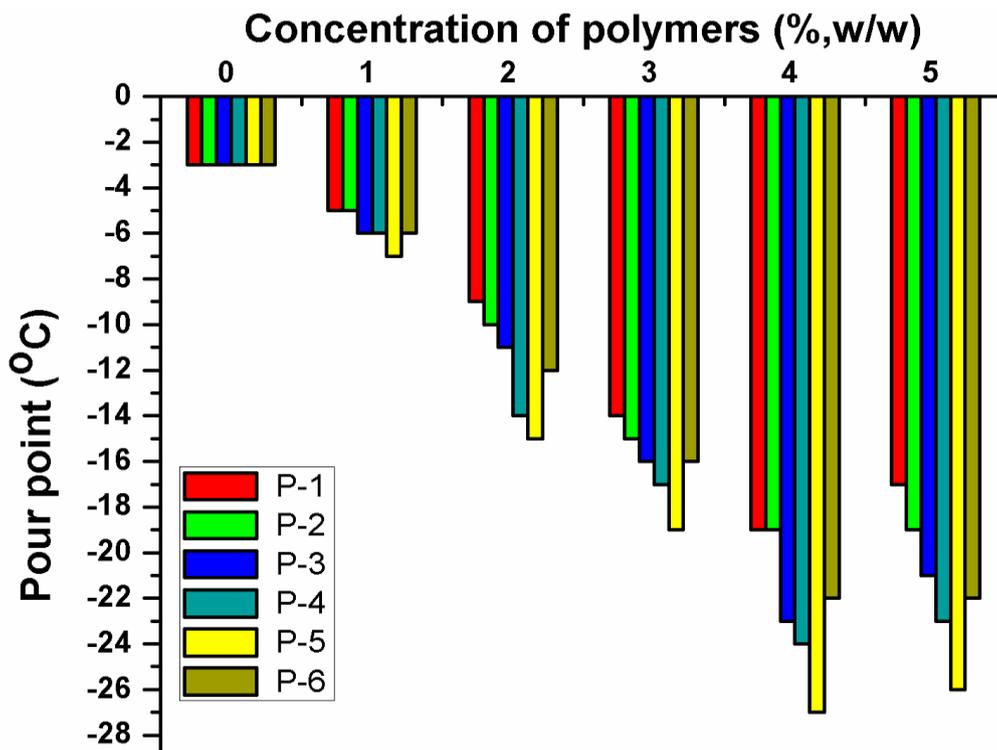


Figure 1.3.13: Pour point (PP) of the polymers P-1 to P-6 doped in base oil B02

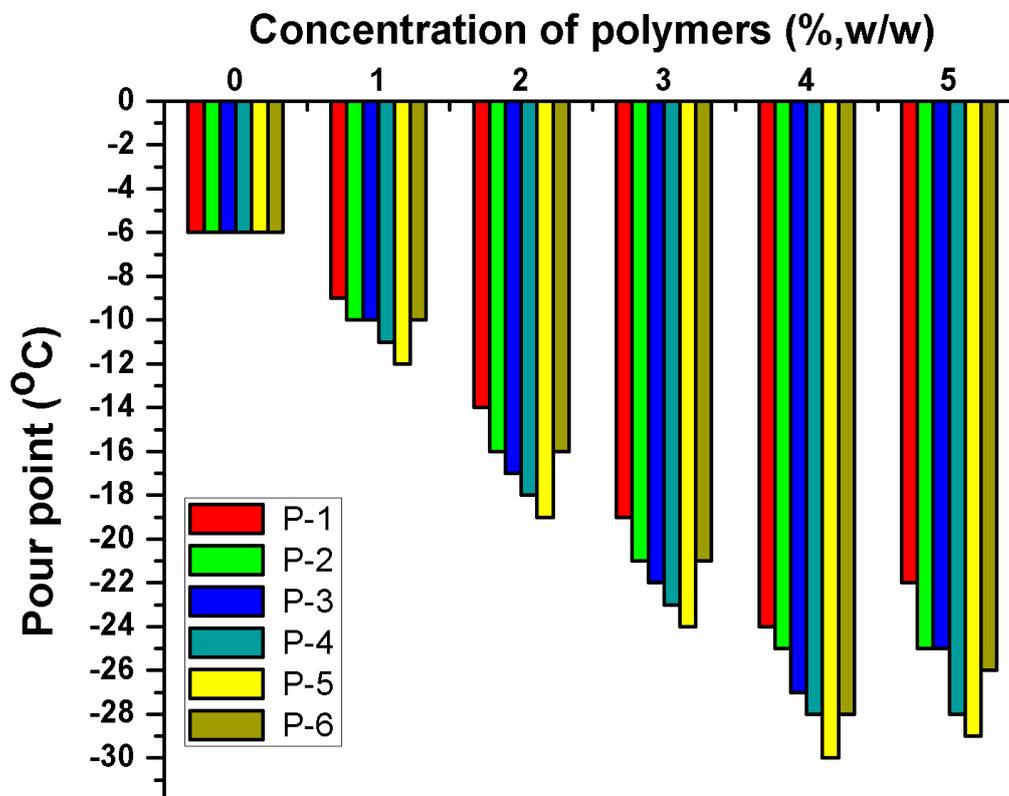
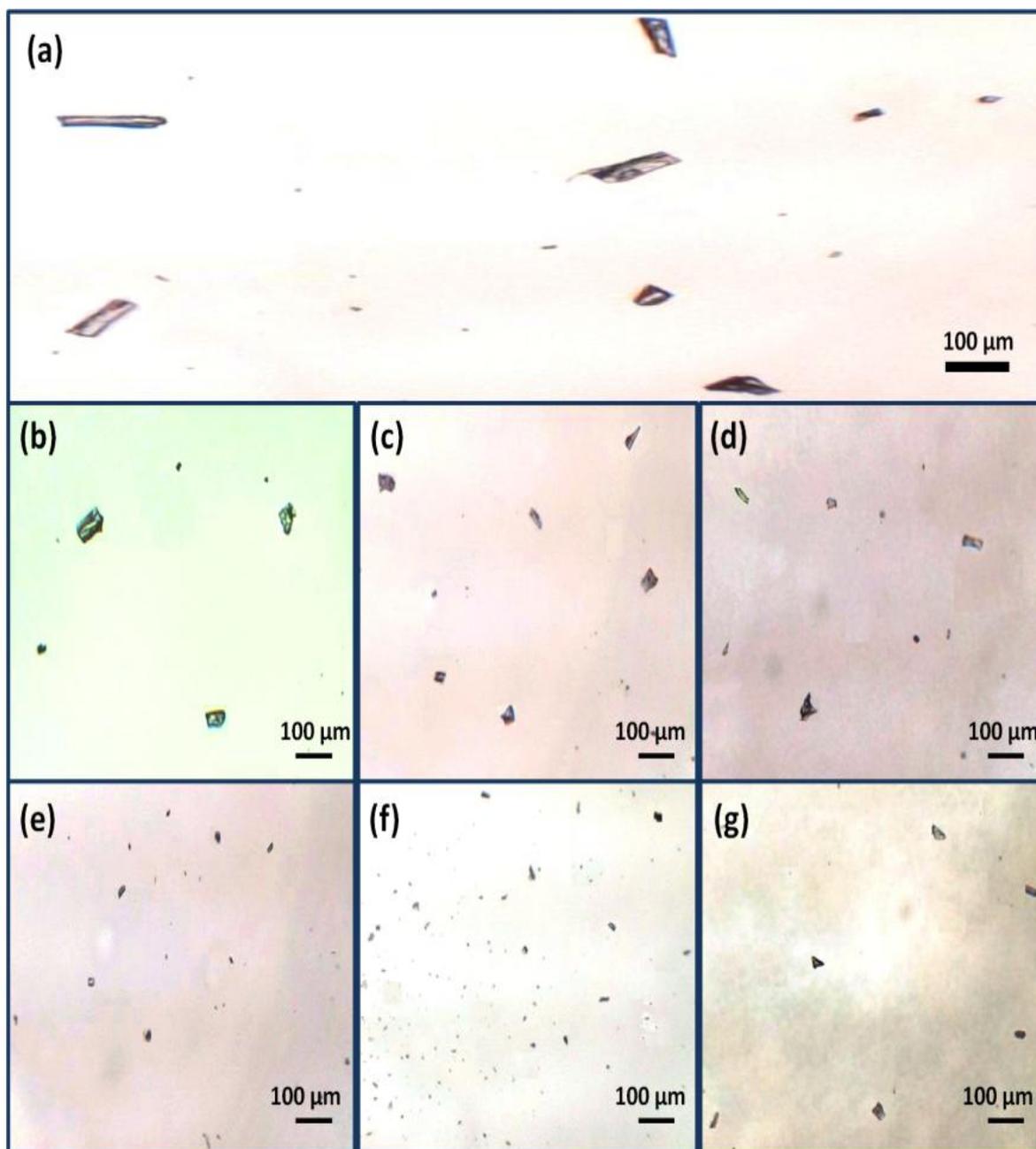


Figure 1.3.14: Photomicrograph of: (a). pure base oil B01 (b). B01 blended with polymer P-1 (3%, w/w) (c). B01 blended with polymer P-2 (3%, w/w) (d). B01 blended with polymer P-3 (3%, w/w) (e). B01 blended with polymer P-4 (3%, w/w) (f). B01 blended with polymer P-5 (3%, w/w) (g). B01 blended with polymer P-6 (3%, w/w)



Chapter-IV

*Acrylate terpolymer based polymeric
additives as a pour point depressant
and viscosity modifier for lube oil*

1.4.1 Introduction

The materials that are largely used to reduce friction and wear between interacting surfaces and to assist the relative motion of solid bodies are called lubricants. Important advancements in lubricant industry have consequently led to tremendous revolution in the field of engines, high speed machinery and manufacturing industries. These developments have also created enormous potential for modern engines and equipments that are operating under more harsh and challenging environments. But, to achieve such a high level of performance, lubricating oils are always formulated with diverse class of additives.¹ These oils are thus a combination of a base oil and various additives. Removal of heat, reducing the thermal or oxidative degradation of oils, suspension and removal of wear particles, minimizing rust and corrosion are some of the key roles that can be played by an additive.²

Also, low viscosity of oil creates a potential problem as it causes a drop in the oil's lubricating ability at high temperature. Better oils by maintaining an ample viscosity at high temperature allows smooth interaction of interacting surfaces. Viscosity modifiers or viscosity index improvers (VII) are polymers that are usually added to the base oils to serve this particular purpose.³ They allow the lubricants to meet certain high-temperature viscosity targets while preserving acceptable low-temperature fluidity. The polymer chains of VII adopt a coiled aggregation at low temperature in order to minimize their effect on viscosity. This means that they have a small hydrodynamic volume and a minimum association with the bulk oil and the effect is a very little viscosity increase. But, when the temperature is increased, the situation is reversed and the chains have a tendency to straighten out with increased polymer chain entanglements causing an increase in the oil's viscosity.⁴ In other words, the polymers

become more soluble at higher temperatures and, consequently cause an increase in viscosity. Viscosity Index or VI is an arbitrary parameter that indicates this effect of change of temperature on the kinematic viscosity of oil.⁵ Oils with higher VI ratings are more useful, as they are more stable under changing temperature conditions and suggest a narrower change in viscosity over a standard temperature range of operation.

Again, in low temperature, where the solubility of dissolved waxy hydrocarbons of mineral oils is sufficiently low, they tend to separate from the oil forming a rigid network of crystals.⁶ While doing so, they capture the remaining oil in cage-like structures and stop the oil from flowing or pouring. This lowest temperature at which the oil will still pour or flow is defined as the pour point of the oil. In order to improve the pour point, wax crystal modifiers alternatively known as pour point depressants (PPD) are mixed to the oil.⁷ Generally the pour point improves with the increasing PPD concentration in the base stock. However, there also exist an optimum concentration for almost every PPD where after the pour point deteriorates with the increasing PPD concentration. Various theories have been put forward by different group of researchers about the mechanism of action of PPDs among which nucleation, adsorption, co-crystallization and improved wax solubility are widely accepted.^{8,9} The deterioration in the pour point depression property of the additives with the increasing PPD fraction is sometimes because of the strong linkage of the PPD molecules with the waxy hydrocarbons present in the oil. Due to such a strong association, the PPD molecules become more bulky and less soluble ultimately making it less effective.¹⁰

Acrylates and methacrylates are some of the well documented viscosity modifier and pour point depressant from years.¹¹ A lot of work has been carried out considering the polymerisation of two acrylate or methacrylate monomers but reports regarding terpolymerization are very few. The introduction of a third monomer into the polymer

moiety can sometime initiate new properties and features to the polymer and offer additional parameters to control the copolymer properties. With this view in mind, the present work comprises the synthesis of acrylate based terpolymers using octyl, decyl and dodecyl alcohol. The prepared terpolymers were evaluated for their performance as PPD and VII under identical condition.

1.4.2 Experimental Section

1.4.2.1 Materials

1-Octanol (GC 98%) and 1-decanol (GC 98%) were purchased from Loba Chemie Pvt., Ltd. 1-Dodecanol (GC 98%) and acrylic acid (GC 99%, stabilized with 0.02 % hydroquinone mono methylether) were obtained from Sisco Research Laboratories Pvt., Ltd. Toluene was refluxed for 2 h in presence of sodium and purified by distillation to be used as a solvent. H₂SO₄ and hydroquinone were obtained from Merck Specialities Pvt., Ltd. AIBN was purchased from Spectrochem Pvt., Ltd., and methanol (GC 98%) was obtained from Thomas Baker (Chemicals) Pvt., Ltd. The two base oils (BO1 and BO2) were collected from Indian Oil Corporation Limited, India (Table 1.4.1).

1.4.2.2 Esterification

The ester, dodecyl acrylate (DDA) was synthesised by reacting 1.1 mol of acrylic acid with 1 mol of dodecyl alcohol. The reaction was performed in a three necked reaction kettle in the presence of 0.25 % hydroquinone (with respect to the reactants) as inhibitor for the polymerization of acrylic acid, conc. H₂SO₄ as catalyst and under a slow stream of deoxygenated nitrogen. The alcohol and the acid were mixed with an

equal weight of toluene (as a solvent), the mixture was steadily heated and the temperature was increased up to 403 K with the help of a thermostat. Assessment of the completeness of the reaction was done by monitoring the quantity of water collected in the Dean-Stark apparatus connected with the reaction kettle. The other two esters, decyl acrylate (DA) and octyl acrylate (OA) were also prepared using acrylic acid, decyl alcohol and octyl alcohol respectively following the same procedure.

1.4.2.3 Purification of the prepared esters

The prepared esters were purified by adding 1 g of charcoal to it and refluxing it for 3 hour. The charcoal was then filtered off and the filtrate was rinsed in a separating funnel with 0.5N NaOH solution. The process was repeated several times to make sure the total elimination of any unreacted acids. The ester was then 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 was finally left over night on anhydrous CaCl₂ for drying. The CaCl₂ was removed by filtration and the toluene was recovered by distillation under reduced pressure. The ester left was ready to be used in the polymerization process.¹²

1.4.2.4 Synthesis of the terpolymers

The terpolymerization reaction was performed in a four necked round bottom flask fitted with a heating jacket system, a thermometer, a reflux condenser, and equipped with a magnetic stirrer. The flask was also connected with an inlet for the introduction of nitrogen gas. The prepared esters, OA, DA and DDA were placed in the flask in a 1:1:1 (w/w) ratio and toluene was added to it (as a solvent). The initiator

AIBN (0.4% of the monomers) was then added to the reaction mixture and it was heated and kept for 6 h at 353 K to prepare the terpolymer. After the stipulated time, the reaction 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. Further, for purification of the polymer, it was precipitated by methanol from its hexane solutions repetitively and then dried under vacuum at 313 K. Similar polymerizations using different ratios of OA, DA and DDA (2:1:1, 1:2:1, and 1:1:2 respectively) were also carried out and the polymers were purified under the same conditions (Table 1.4.2).

1.4.3 Measurements

1.4.3.1 Spectroscopic measurements

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

1.4.3.2 Determination of molecular weight of the prepared terpolymers

The molecular weights of the prepared terpolymers were determined by using gel permeation chromatography (GPC) system (Waters Corporation; USA) equipped with a 2414 refractive index detector (polystyrene calibration), Waters 515 HPLC pump in HPLC grade THF (0.4% w/v) as an eluent at 40°C.

1.4.3.3 Evaluation of the prepared polymers as PPDs in base oils

The prepared polymers were tested for their pour point (PP) depression ability according to the ASTM D97-09 method on a Cloud and Pour Point Tester (WIL-471, India) in two base oils (BO1 and BO2). The effect of polymer concentration on the PP was investigated by using different percentages of the polymer.

1.4.3.4 Evaluation of the prepared polymers as VIIs in base oils

The alteration of kinematic viscosity (KV) of oil with the variation of temperature is denoted by an arbitrary dimensionless number called VI. The VI was evaluated according to the ASTM D2270 method for the two base oils blended with different percentages of the additive at 40°C and 100°C.¹³ The effectiveness of an additive as VII is assessed by the increase in the VI value of the base oils after addition of the additive. The KV was determined by the equation,

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

where K and L are viscometric constants; t is the time of flow of the lube oil blended with different mass fraction of the additive to pass through the two calibrated marks in the Ubbelohde viscometer and ρ is density of the additive doped lube oil.¹⁴

The densities of the additive doped oils were determined with the help of a DMA 4500 M vibrating-tube density meter (Anton paar, Austria) and the time of flow of the oils were recorded with a digital stopwatch. All the measurements per batch were made in duplicate. The VI value was determined from the following standard empirical equation,

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

where n is a constant depending upon the temperature range chosen for the oil. The value of n was calculated by the equation,

$$n = (\ln v_1 - \ln k) / \ln v_2 \quad \text{Eq. (4)}$$

where v_1 and v_2 are the kinematic viscosities of the oil blended with the additive at lower and higher temperature respectively. The value of k is independent of the nature of the oil and is a function of temperature alone. The value of k was found to be 2.715 for the given temperature range.¹⁵

1.4.4 Results and discussion

1.4.4.1 Spectroscopic analysis

The FT-IR spectra of the polymer P-1 (Fig. 1.4.1) showed signal for the stretching vibration of ester carbonyl (C=O) at 1735.8 cm^{-1} while the broad signals in the regions of 1465.8 cm^{-1} and at 1164.9 cm^{-1} were due to the stretching vibrations of ester C–O–C group. The signals observed in the regions of 1072.3 cm^{-1} and 717.5 cm^{-1} were for the C–H bending vibrations of CH_2 and CH_3 groups while the peaks observed in the regions of 2923.9 cm^{-1} and 2854.5 cm^{-1} were for the stretching vibrations of paraffinic C–H bonds.

In the $^1\text{H-NMR}$ spectra (Fig. 1.4.2), the polymer P-1 displayed the presence of the proton of $-\text{COOCH}_2$ group by appearing as a broad peak centred at 4.01 ppm. Signals also appeared in the range of 0.861 to 0.903 ppm and 1.268 to 1.602 ppm for all the methyl and methylene protons respectively.

The proton decoupled $^{13}\text{C-NMR}$ spectra (Fig. 1.4.3) displayed peak at 174.6 ppm for the carbonyl carbons of the ester groups. The absence of unsaturation in the polymer was indicated by the nonappearance of any olefinic peaks in the spectra. All the

other synthesised polymers (P-2, P-3 and P-4) showed similar peaks in their FT-IR and NMR (^1H and ^{13}C) spectrum indicating that the prepared polymers are in good agreement with the expected structures.

1.4.4.2 Performance of the prepared polymers as PPD

Evaluation of the synthesised polymers for their PPD performances showed good results (Figs. 1.4.4 and 1.4.5) in the base oils under investigation. The results pointed out that the prepared polymer P-4 is more efficient as PPD than the other polymer samples in both the base oils. Also, it is clearly noticeable that the effectiveness of all the polymers as PPD increased with its decreasing concentration in the base oils. This outcome can be explained by the fact that the solvation power of any solvent decreases with decreasing temperature. So, when the temperature is lowered during pour point analysis, but the concentration as well as the molecular weight of the polymer is increased in the oil, there occurs a substantial reduction in the solvation power and the polymers become less soluble in the oil. This reduction in the solvation capability reduces the PP efficiency of the polymers in the oil.¹⁶

1.4.4.3 Performance of the prepared polymers as VII

Assessment of the results (Table 1.4.3), as obtained, showed that the VI values increased with the increase in polymer percentage irrespective of the base oil and the polymer used. A critical analysis of the VI values also showed that polymer P-4 has the most superior performance as VII followed by polymer P-3, P-1 and P-2. The results suggested that the performance of the prepared polymers as VII is directly proportional

to the alkyl chain length of the acrylate used. Also, the increase in the alkyl chain length has a direct effect on increasing the molecular mass of the polymers (Table 1.4.2). Thus, the increased effective radius of polymer micelle with the increased molecular weight of the polymer can be the cause of this direct relationship of VI with the chain length of the acrylate.¹⁷ Besides, the increase in the VI values with increasing polymer percentage in the base oil can be the result of increased hydrodynamic volume of the polymer. Hydrodynamic volume is the volume of the polymer and the associated oil. At higher temperature there occurs an increase in the power of solvation of the oil and, therefore, an expansion of polymer molecules and increase in the size of the micelle takes place.¹⁸ Thus, higher the percentage of polymer in the oil, higher is the volume of the micelle and subsequently higher will be its association with the oil leading to higher VI.³

1.4.5 Conclusions

The systematic analysis of the synthesised polymers revealed that all the polymers performed as efficient PPDs and VIIs. The VI values, as obtained, increased with an enhancement in polymer percentage in the oil and terpolymer P-4 with the highest ratio of DDA acted as a superior VI improver compared to the other polymers. Also, it was established that the terpolymer P-4 is more efficient as PPD for the given lube oils under consideration. Thus, a significant modification of base oil properties has been achieved by addition of these polymers to the given lube oils.

1.4.6 References

References are given in BIBLIOGRAPHY section under Chapter-IV of Part-I (Page No. 201-203).

1.4.7 Tables and figures

Table 1.4.1: Physical properties of base oils

Properties	Method	B01	B02
Viscosity at 40 °C (cSt)	ASTM D445	7.132	23.387
Viscosity at 100 °C (cSt)	ASTM D445	1.849	3.911
Density (g.cm ⁻³) at 40 °C	ASTM D4052	0.83645	0.85492
Viscosity index	ASTM D2270	80	85
Pour point, °C	ASTM D97	-3	-6

Table 1.4.2: Terpolymer designation and molecular weight

Terpolymer designation	Monomer feed ratio (w/w)			Molecular weight	
	Octyl acrylate	Decyl acrylate	Dodecyl acrylate	M_n	M_w
P-1	1	1	1	17633	22395
P-2	2	1	1	16200	19926
P-3	1	2	1	18734	27351
P-4	1	1	2	20986	28752

Table 1.4.3: Viscosity index (VI) values of polymers (P-1 to P-4) doped in base oils

Polymer	Base oil	Concentration of polymer doped base oils (w/w)					
		VI					
		0%	1%	2%	3%	4%	5%
P-1	BO1	80	86.21	93.31	98.69	106.2	113.6
	BO2	85	90.25	97.37	102.9	109.2	118.3
P-2	BO1	80	85.73	91.19	97.55	104.6	110.1
	BO2	85	89.3	94.21	99.41	106.3	113.4
P-3	BO1	80	86.49	94.62	101.5	109.7	116.4
	BO2	85	90.12	98.04	106.3	114.3	122.6
P-4	BO1	80	90.56	97.14	105.5	112.6	121.8
	BO2	85	94.64	102.9	108.2	118.8	127.1

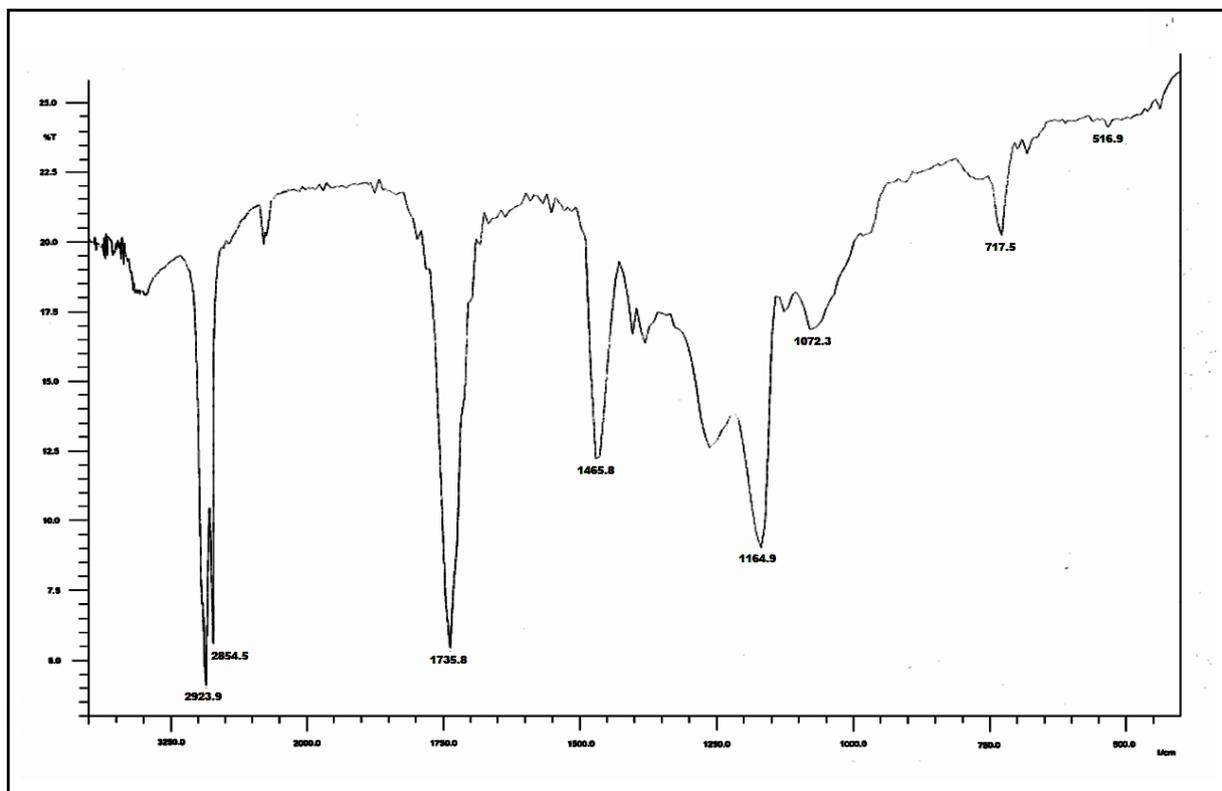
Figure 1.4.1: IR spectra of polymer P-1

Figure 1.4.2: $^1\text{H-NMR}$ spectra of polymer P-1

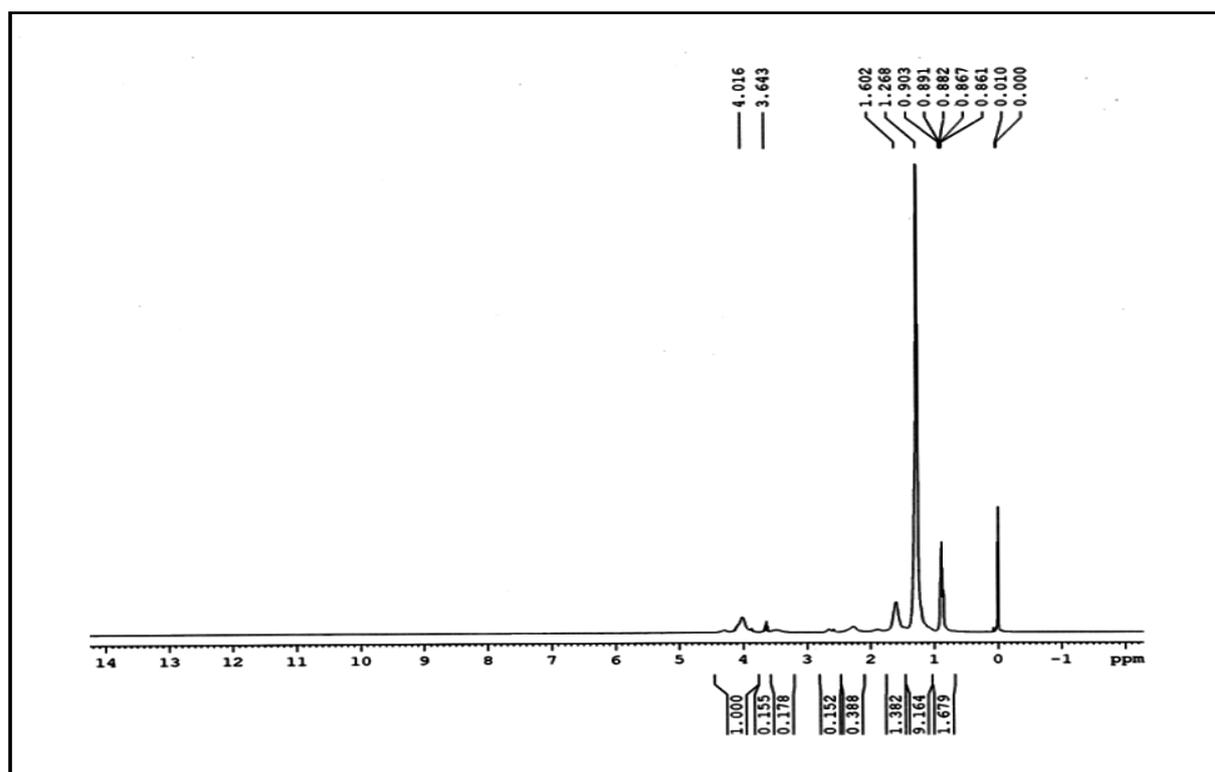


Figure 1.4.3: $^{13}\text{C-NMR}$ spectra of polymer P-1

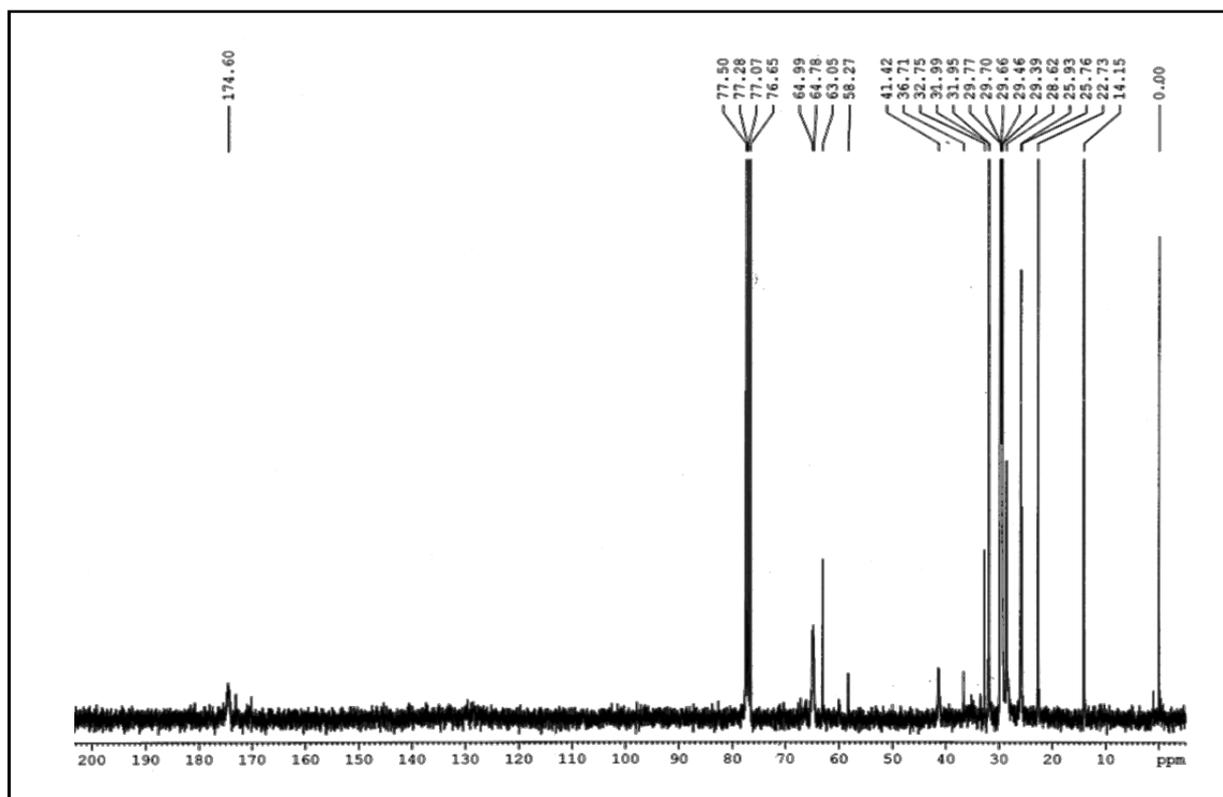


Figure 1.4.4: Comparison of pour point values of the polymers in BO1

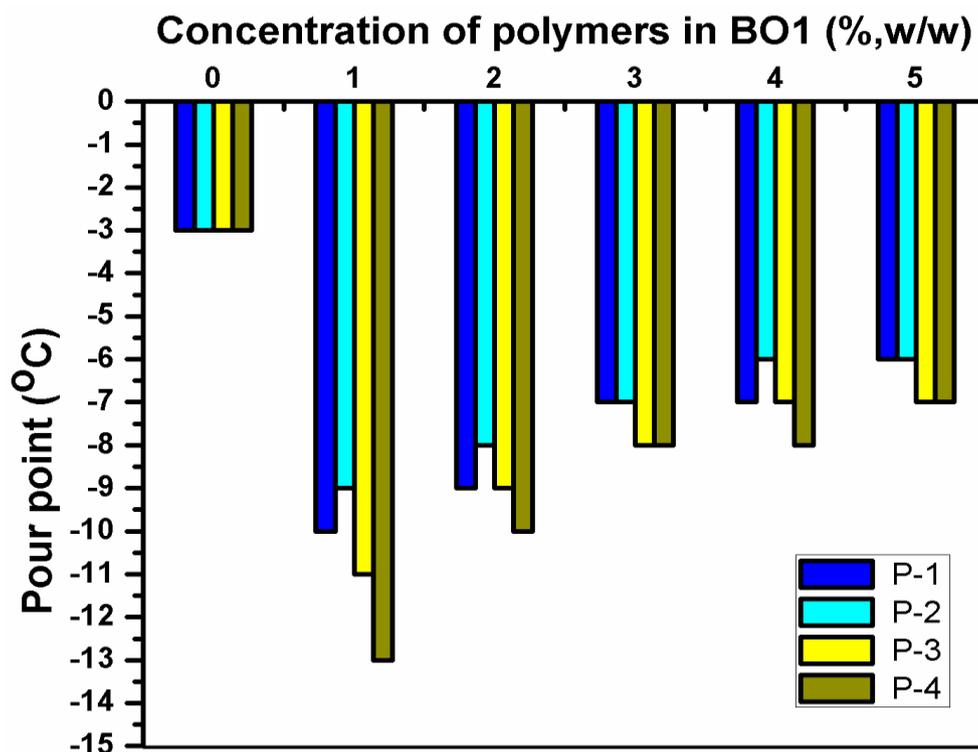
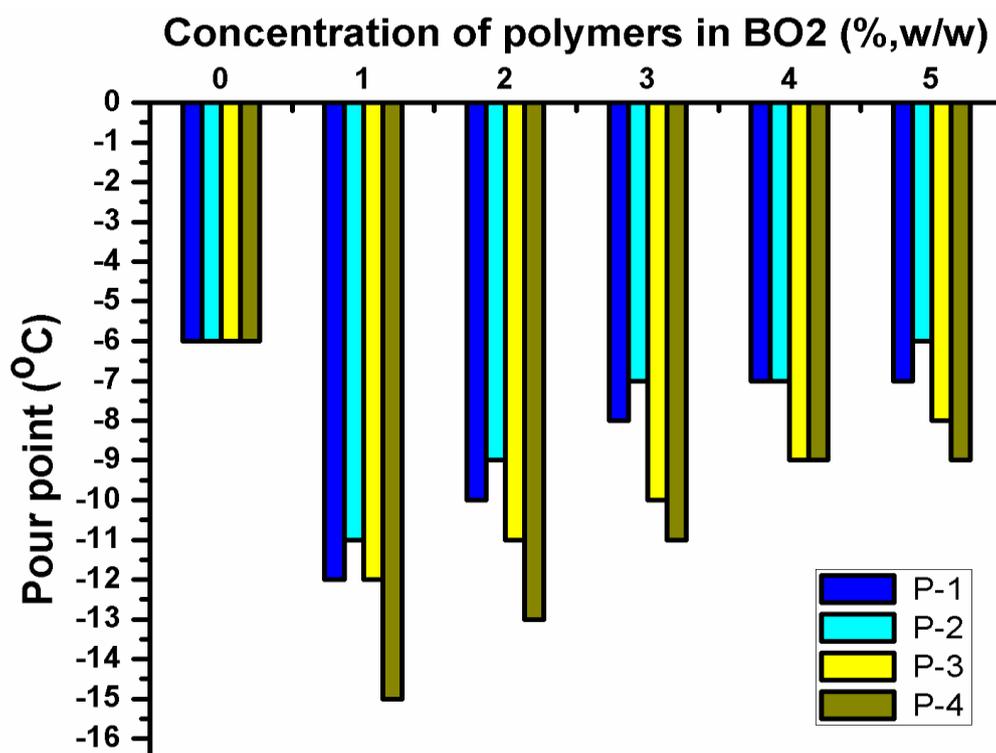


Figure 1.4.5: Comparison of pour point values of the polymers in BO2



PART-II

Biodegradable multifunctional lube oil additives

Chapter-I

*Background of the present
investigation*

Petroleum is a naturally occurring liquid found beneath the earth's surface. It consists of hydrocarbons of different molecular weights and is refined into various types of fuels. Petroleum is an important raw material and is crucial to many industries like pharmaceuticals, pesticides, fertilizers, solvents and plastics. But, being a fossil fuel, the world is increasingly concerned about the depletion of the earth's finite reserves of crude oil and the negative impact it has on the earth's biosphere. Moreover, these crude oils are considered as potential soil and water pollutants due to their widespread toxicity and carcinogenicity. They even pose a potential danger to the environment as they are not readily biodegradable and thus tend to persist in the biosphere with a negative impact on the ecosystem.^{1,2} It is also argued that about 40% of these crude oil-based lubricants sold globally are reintroduced into the atmosphere every year via non-recoverable usages like industrial waste, engine exhaust and various refinery processes.^{3,4} Even the disastrous effect of events like oil spills on the ecosystem can't be ignored.

The toxic effects of crude oil based oleochemicals have been explained by several groups of researchers.⁵⁻⁷ Tang *et al.* highlighted the toxic effect of petroleum soil contamination on earthworm, bacteria and plants. Soil contaminated with more than 3% of oil caused complete death of earthworms. Similarly, inhibition rate of bacteria was almost about 100% at petroleum content of 1%. The rate of germination of plants also showed similar trends.⁵ Ramadass *et al.* also showed entire mortality of earthworms when the concentration of used motor oil was greater than 3.8 g/kg of soil.⁶ These oleochemicals can also affect human beings to a large extent by contaminating the groundwater and marine life used for human consumption.

The lubricants that we use today mostly come from crude oil, and with the increasing demand of energy, the increase in the annual global production of oils and

lubricants has also gone up. But, the eventual disposal of this very large volume of lubricants has obviously become an environmental burden. Moreover, stringent government directives and several regulations are currently being enacted on these lubricants.⁸⁻¹⁰ The introduction of product ecolabelling is such a government initiative to meet high environmental and performance standards for group of products and services.¹¹ In EU ecolabel scheme, special consideration is being given to the protection of the environment against pollution caused by mineral oils based lubricants (Commission Decision 05/360/EC). Waste oil disposal in the EU is regulated according to Directive 75/439/EEC. This directive specifies a hierarchy of waste oils management which gives preference to regeneration or refining, but accepts burning under environmentally acceptable conditions.¹² But, the burning of these oils has a pivotal role in global warming along with some other problems. Besides the hydrocarbons, these crude oils remain associated with some nitrogen and sulphur compounds along with small quantity of metal atoms and, therefore, a range of pollutants like sulphur dioxide, ground level ozone, toxic metal oxides etc is released into the atmosphere. Recently a report called “Lubricating Oils and Greases - Global Strategic Business Report 2015” suggested for eco friendly products due to tight environment regulations. The surge in crude oil prices in many parts of the world and increased public awareness for a pollution-free environment has also stimulated keen interest for environment friendly lubricant.

Renewable raw supplies like vegetable oils, polysaccharides (mainly cellulose and starch) have gained prominence as an alternative to petroleum-derived product and can play a significant role in the development of sustainable green chemistry. Other factor that initiated and fuelled this trend is the necessity of releasing the oleochemical industry from its dependence on depleting resources and pushing them towards

industrially applicable renewable alternatives. The use of renewable raw materials can immensely contribute to a goal of sustainable development i.e. to act responsibly to meet the needs of the present without compromising the ability of future generations to meet their own needs.^{13, 14}

Again, a bio lubricant is a renewable lubricant that is biodegradable, nontoxic and environmentally benign. Vegetable oils, which otherwise is one of the most important renewable raw material for the chemical industry have now emerged as a sustainable and economical bio alternative to conventional petro-based lubricants.¹⁵⁻²⁴ Vegetable oils are basically a mixture of triglycerides or triesters of long chain fatty acids combined with glycerol.²⁵⁻²⁷ Generally, the fatty acid chains in most vegetable oils are similar in length with 14 to 24 carbon atoms (both saturated and unsaturated), and sometimes with the presence of a hydroxyl group (Fig. 2.1). The fatty acid composition also depends upon the plant type, the season and the growing conditions.

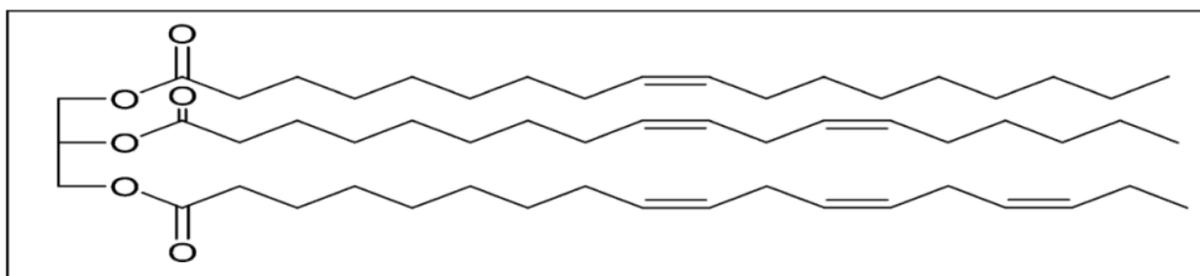


Figure 2.1: General structure of triglyceride esters present in vegetable oils

The most common vegetable oils are castor oil, sunflower oil, soybean oil, rapeseed oil, linseed oil, karanja oil, rice bran oil, jatropha oil etc. The different properties of vegetable oil are largely dependent on the composition and nature of fatty acids present in the vegetable oils. Vegetable oils are frequently used as plasticizers, inks, stabilizers, surface coating materials, starting materials to produce polyols etc.²⁸⁻³⁴ The application of these plant oils as toughening agents was also reported.^{35, 36}

They are considered a viable and versatile lubricant because of their ingrained biodegradability, low toxicity, aromatic free composition, wide accessibility, future-availability and low cost.³⁷⁻⁴⁰ Due to the large molecular weight of triglycerides molecules, vegetable oils have low evaporative losses.⁴¹ They also have separate regions of polar and non-polar groups in the same molecule. The polar ester group stick fast to metal surfaces and provides good boundary lubrication characteristics to the veg-oil.^{23,42} They are also associated with high solubilizing power for polar contaminants.^{18,19,22,43-50} Because of the high flash point of these oils, they require less maintenance on storage and disposal leading to higher safety.^{33, 51-53} The high viscosity index, high lubricity and high load-carrying capacity provide options for designing lubricants for use over a wide temperature range.^{18-20,41} Better skin compatibility, less dermatological problems are also among the other useful aspects that make vegetable oil an industrially attractive raw material.⁵⁴

However, their widespread application is restricted by certain limitations, particularly related to the thermo-oxidative stability that should be technologically improved.⁵⁵⁻⁵⁹ Narrow viscosity range as compared to the mineral oil, crystallization at relatively high temperatures and poor cold flow properties also block their path for a universal acceptability.⁶⁰⁻⁶⁴ The unsaturations present in the fatty acid portion of these plant oils are the active sites for oxidation leading to decreased thermal and oxidation stability. The bisallylic protons are very prone to radical attack and, therefore, undergo oxidative cleavage to form polar oxy compounds.⁶⁵⁻⁶⁹ This leads in insoluble deposit and enhances the viscosity of the oil and reduces their life span. On the other hand, a higher percentage of saturated fatty acids in the triglycerides moiety favour triglycerides crystallization.^{25,62} The ester functionality present in the triglycerides structure renders these oils vulnerable to hydrolytic breakdown.^{70,71} Upon prolonged exposure to low

temperatures, these oils also suffer from cloudiness and undergo solidification causing poor flow properties.^{72,73} Besides, vegetable oils show poor corrosion protection.⁷⁴ Because of these performance limitations the mineral oil base lubricants still dominate the world market.

Thus, to succour the known weaknesses of the vegetable oil, several techniques were adopted among which genetic alteration, additive treatment and chemical modification are the most effective ones.⁷⁵⁻⁷⁹ Chemical modification is an attractive way to improve the performance restrictions with the focus on eliminating the bisallylic proton functionalities in methylene interrupted poly unsaturation. The presence of stable moiety improves their oxidative stability and thus one of their prime limitations. The low temperature performance can be improved by reducing the structural uniformity present in the oil by attaching alkyl side chains.⁸⁰

There exist several references that depict the use of chemically modified vegetables oils as potential lubricants.

Regueira *et al.* calculated the viscosities and compressibility of vegetable oil based lubricants for their potential application as hydrolytic fluid and found some excellent results.⁸¹ Joseph *et al.* found that around 120 °C, the thermo-oxidative stability of vegetable oils is significantly improved by adding a mixture of amine and phenolic antioxidant and these oils can be effectively used as base oils.⁸² Lathi and Mattiasson reported the production of biodegradable lubricant base stocks from epoxidized vegetable oil via cationic ion-exchange resins as catalysts.⁷⁹ Gast *et al.* prepared products by a ring-opening reaction of epoxidized fatty acid esters with superior pour points values.⁸³ Sharma *et al.* reported that the hydroxyl thioether derivatives of vegetable oils can significantly improve the surface adsorption on metals leading to a reduction in wear and friction coefficient.⁸⁴ A survey report was brought forward by

Sony *et al.* on the use of bio-lubricant based on plant oil for their excellent biodegradability, low volatility and other useful tribological properties.⁸⁵

Vinci *et al.* reported a lubricant based on a derivative of castor oil (methyl-12-hydroxy stearate) with enhanced thermo-oxidative stability and 70% renewable carbon content.⁸⁶ Suhane *et al.* found that castor and mahua oil when mixed in a certain ratio can act as a valuable lubricant for many automotive application and found improved performances than many commercial gear oil.⁸⁷ The transesterification method was employed for the synthesis of base oil from castor seed to use as bio lubricant in an experiment carried out by Amdebrhan *et al.*⁸⁸

Mendoza *et al.* formulated a base oil based on sunflower oil with biodegradability of 89% and pour point of -27 °C for hydraulic system of agricultural tractors. They also reported enhanced oxidation stability for the base oil.⁸⁹ Quinchia *et al.* proposed the blending of additives like ethylene-vinyl acetate and styrene-butadiene-styrene copolymers with high-oleic sunflower oil for lubricant application and reported improved kinematic viscosity and viscosity index.⁹⁰ Ghosh *et al.* studied the performance of the copolymer of sunflower oil with alkyl acrylates as VII additive and reported some useful results.⁹¹ The same research group prepared the biodegradable homopolymer of sunflower oil by thermal and microwave irradiation and studied the performance as VII and PPD for lubricating oils.⁹² Asadauskas *et al.* reported that addition of a small percentage of PPD depressed the pour points of canola and high-oleic sunflower oils to a sufficiently low value.⁹³

Bisht *et al.* reported the use of jojoba oil as a lubricant base stock and found enhanced tribological properties like higher viscosity index, improved antiwear and antifoam properties and also increased friction reduction properties.⁹⁴ Recently, Nasser

et al. reported the performance of polymers of jojoba oil and different alkyl acrylate and α -olefins as additive in lubricating oil with suitable results.⁹⁵

Karmakar *et al.* formulated additives based on the homopolymer of soybean oil and its copolymers with styrene, 1-decene and methyl acrylate. The additive performance of these polymers as VII and PPD in different lube oils was evaluated and reported.⁹⁶ Adhvaryu and Erhan proposed epoxidized soybean oil as a potential lubricant for high temperature applications.¹⁸ Hwang *et al.* reported that lubricants produced by reacting epoxidized soybean oil with various alcohols improved the low temperature property and oxidative stability of soybean oil based lubricants.⁶⁸ Campanella *et al.* proposed a way for the production of lubricants from vegetable oils obtained from temperate climate crops (soybean and sunflower seeds).⁴¹ The research group of Suarez *et al.* demonstrated that the lubricity of diesel oils can be significantly improved by adding soybean oil methyl esters and diesel-like pyrolytic fuel (produced through pyrolysis of soybean oil) in it.⁹⁷ Alves *et al.* reported that the presence of ZnO and CuO nanoparticles in modified vegetable oils such as epoxidised soybean and sunflower oils resulted in higher friction coefficient than the mineral oils.⁹⁸ Quinchia *et al.* studied the lubricating properties of sunflower oil, castor oil and soybean oil based lubricants using 4 wt% of ethylene-vinyl acetate copolymer and 1 wt% of ethyl cellulose as additives and found excellent results of friction and wear behaviour.⁹⁹

Sulek *et al.* reported that the addition of fatty acid methyl ester derived from rapeseed oil resulted in 20 % decrease in friction in diesel fuel.¹⁰⁰ Sukjit and Dearn found that addition of fatty acid methyl ester obtained from rapeseed could result in reduction in the wear scar diameter by 40 % in diesel fuel.¹⁰¹ Wu *et al.* demonstrated the application of epoxidized rapeseed oil as a biodegradable lubricant with higher

oxidative stability.¹⁰² Gong *et al.* investigated the wear characteristics of synthetic thiophosphate as additives in rapeseed oil in sliding of steel.¹⁰³

Maleque *et al.* worked on palm oil and had shown that palm oil methyl ester additives improved the performance of the diesel base oil as a lubricant.¹⁰⁴ Masjuki and Maleque found that adding 5 vol% of palm oil methyl ester resulted in low wear rate of EN31 steel ball bearing in the base oil lubricant.¹⁰⁵

Govindapillai *et al.* showed that the chemical modification of coconut oil have a significant effect in improving its pour point values.¹⁰⁶ Jayadas and Prabhakaran reported that addition of 2 wt% of ZDDP in coconut oil resulted in significant wear reduction in the four-ball test.¹⁰⁷

Durak and Karaosmanoglu disclosed the application of cottonseed oil as a friction modifier additive.¹⁰⁸ Another work by Xu *et al.* demonstrated that the lubrication capacity of diesel oils doped with bio-oil (produced through fast pyrolyzing rice husk) was superior to those of the conventional diesel fuels.¹⁰⁹ As reported by Panchal *et al.*, the base stock produced from transesterified tobacco oil methyl esters was successfully used to formulate lubricating grease with improved performances.¹¹⁰

The usefulness of these plant based lubricants can also be estimated by the fact that several patent exists regarding their use as base oil or as an additive.

The synthesis and assessment of vegetable oil based lube oil additive as a potential viscosity improver and thermal stability enhancer was explained by US patent no. 5229023. The use of biodegradable vegetable oil composition for lubricants was illustrated by U. S. Patent No. 6534454 B1. The U. S. Patent No. 4152278 described the performance of vegetable wax esters as an anti wear, extreme pressure and friction modifier. The application of sulfurized vegetable oils containing antioxidants for use as base fluids was disclosed by U. S. Patent No. 5703022 A. The US patent no. 4873008

explained the synthesis and utilization of jojoba oil and sulfurized jojoba oil based additive. The use of Meadowfoam oil and meadowfoam oil derivatives as lubricant additives was suggested by U. S. Patent No. 5023312 A. The U. S. Patent No. 5888947 A claims the application of biodegradable lubricants largely derived from castor or lesquerella and the vegetable wax from meadowfoam oil or jojoba oil for operating in internal combustion engines.

Various conferences held around the globe also discussed the application of vegetable oils and the pivotal role they play in the advancement of sustainable green chemistry. In the National Conference on Advanced Trends in Mechanical Engineering, held in the year 2002, in India, the application of non-edible vegetable oil for improving the performance in diesel engine was discussed. The IEEE EIC Climate Change Conference (EIC CCC) in Canada, held in the year 2006, discussed at length about the biodiesel productions from vegetable oils using heterogeneous catalysts. The biodiesel obtained from transesterification of canola oil with methanol reduced the wear scan diameter by 16% and increased the lubricity of base stock by 20%. The performance of vegetable oil based nano fluids as lubricants in turning of AISI1040 steel was reviewed at the International Conference on Emerging Trends in Mechanical Engineering (ICETME 2013), held in India. The second International Conference on Sustainable Materials (ICoSM), held in Malaysia in the year 2013, exchanged views about the wear resistance and anti-friction ability characteristic of Jatropha oil and palm fatty acid distillate.

Again, microwave irradiation technique is a well known method for drying and heating common household items. It is also successfully utilised for carrying out a variety of organic and inorganic chemical reactions. Chemical transformations under microwave irradiation undergo a significant enhancement in reaction speed compared

to the conventional heating. The microwave assisted reactions were also found to have immense success regarding their selectivity, higher yields and higher product purities because of the fast, direct and selective heating of the target molecules.¹¹¹ Moreover, the use of high pressure synthesis performed in closed vessels and under solvent free conditions paves the way for environmentally benign reaction conditions following the green protocols. The author, therefore, also choose to synthesise vegetable oil-based lube oil additive under microwave condition.

From the above discussion it is quite evident that plant oils are an essential component to bring about renewability and non-toxicity in the lubricating oil formulation. But the literature survey reveals that most of the bio-additives serve only one particular rheological purpose. Also, the additive performances of sole vegetable oils are not very encouraging. The author, therefore, firmly believe that there is an ample scope for development of bio-additives with multifunctional properties that will guarantee performance, longevity and eco-friendliness and can be used as both viscosity modifiers and pour point depressants for lube oil. Hence, the author has polymerised different vegetable oils with alkyl acrylate, alkyl methacrylate or other useful components which combines high viscometric performance of vegetable oil and excellent low temperature flow ability of acrylate moiety in a single system along with considerable biodegradability. Besides, with the continuous improvement of engines, as brought about by the original equipment manufacturers (OEM), there exists abundant possibility for further investigation in this area of multifunctional additives research and develop bio-additives that is both efficient in its performance as well as environmental benign as compared to the chemically synthetic additives.

References

References are given in BIBLIOGRAPHY under Chapter-I of Part-II (Page No. 203-214).

Chapter-II

*Almond oil based multifunctional
greener additives for lubricating oil*

2.2.1 Introduction

Lubricating oils are principally a blend of a base oil and an additive, mixed in different ratios according to the requirements for various purposes.¹ The additives normally boost the rheological properties of the lubricant base oils,² such as variation of its viscosity with temperature (viscosity index, VI),³ low temperature flow ability (pour point, PP),⁴ together with optimising other parameters to a satisfactory level. Although additives of numerous types have been devised to optimize the modern lubricants, acrylate based polymers are in use as an additive for quite a long time.⁵

The base oil of the lubricating oils is typically derived from petroleum and principally consists of a mixture of paraffinic hydrocarbons of different chain lengths. However, these crude oil wells are exhausting very fast and, thus, so are the main reserves of lubricating oils.⁶ These oils and additives also pose a potential risk to the ecology due to their inherent non-biodegradability and their role in water and soil contamination, caused by spillage during application or improper disposal of the used oil. Stringent regulations are, therefore, currently being imposed in a number of countries on mineral oil-based lubricants together with their non-biocompatible toxic wastes supplies.^{7,8} This increasing ecological consciousness, together with the challenge to develop lubricants with characteristics superior to those based on mineral oil only has provided researchers with the momentum to search for some novel, environmentally benign, multifunctional additives. In this search, vegetable oils have been considered as a potential candidate. Vegetable oils are oils that have been extracted from various plants. They are largely triglycerides of long chain fatty acids. Multidisciplinary research efforts have yielded a high level of technical and commercial success with respect to these bio-based materials.

These plant oils are currently in the focus of the chemical and polymer industry, as they have many useful properties including natural biodegradability,^{9,10} good lubricity, non toxicity, high viscosity index,¹¹ low cost and various other excellent tribological properties.¹²⁻¹⁴ They also present the largest renewable platform due to their universal wide availability and sustainability. Different vegetable oils, such as sunflower oil, soybean oil, garlic oil, etc. are currently being looked as a potential replacement for petroleum based lubricating oils and synthetic esters (modified petroleum based components for specific uses).^{15,16} However, extensive application of these bio-oils is still challenged by one or more of their possible inherent limitations. The fatty acid chains of almost every vegetable oil have a high degree of C-C unsaturations, resulting in poor thermal and oxidative stability and limiting their use as lubricants to a narrow range of temperature.¹⁷ These oils also experience poor low temperature fluidity which leads to degradation, rapid thickening and deposit formation of the oil at low temperature.^{18,19} Hence, plant oils must be genetically or chemically customized to improve their desired properties. This can be attained by homopolymerisation of the oil or its copolymerisation with an appropriate monomer.¹⁵ The introduction of a second type of monomer unit in the polymer moiety of the oil may introduce some additional properties and features to the copolymer.

Hence, with a view of developing novel, environmentally benign, polymeric additives for lubricating oil and with features better than petroleum oils, the author chose almond oil (AO). Almond oil, being a good source of naturally derived unsaturated fatty acids,²⁰ is a suitable candidate to incorporate biodegradability in its acrylate copolymer.

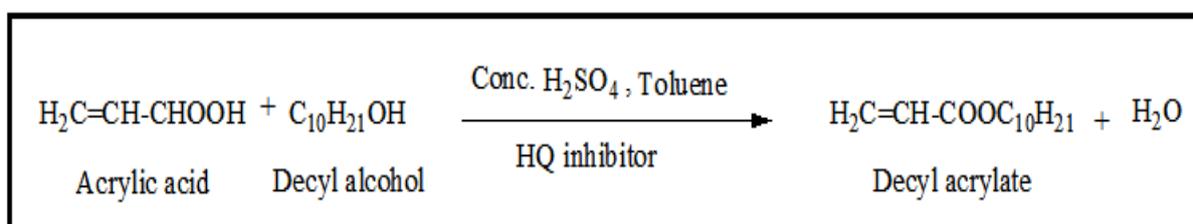
2.2.2 Experimental section

2.2.2.1 Materials

Almond oil (AO) was collected from a local grocer's shop. Acrylic acid (stabilized with 0.02% hydroquinone mono methylether) was obtained from Sisco Research Laboratories Pvt. Ltd., (India). Toluene was from Merck Specialties Pvt. Ltd., (India). Methanol (Thomas Baker Chemicals Pvt. Ltd., India) and decanol (Loba Chemie Pvt. Ltd., India) were used as-received. Before use, AIBN (Azobisisobutyronitrile, Spectrochem Pvt. Ltd., India) was recrystallized from CHCl_3 - CH_3OH . Mineral base oils (BO1 and BO2) were received from Indian Oil Corporation Ltd. (IOCL), India. The physical properties of the base oils are tabulated in Table 2.2.1. Fungal specimens for testing the biodegradability of the polymers were obtained from the Department of Microbiology, North Bengal University, West Bengal, India.

2.2.2.2 Esterification of acrylic acid with decyl alcohol

The ester, decyl acrylate (DA), was prepared by reacting 1 mol of decyl alcohol with 1.1 mol of acrylic acid. The reaction was carried out in a three necked round bottom flask in 100 mL of toluene and 0.25% of hydroquinone with respect to the reactants as polymerization inhibitor and under a slow stream of deoxygenated nitrogen. Conc. H_2SO_4 was used here as a catalyst.



Scheme 4: Preparation of the ester decyl acrylate

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 amount of water liberated helped in monitoring the extent of reaction.

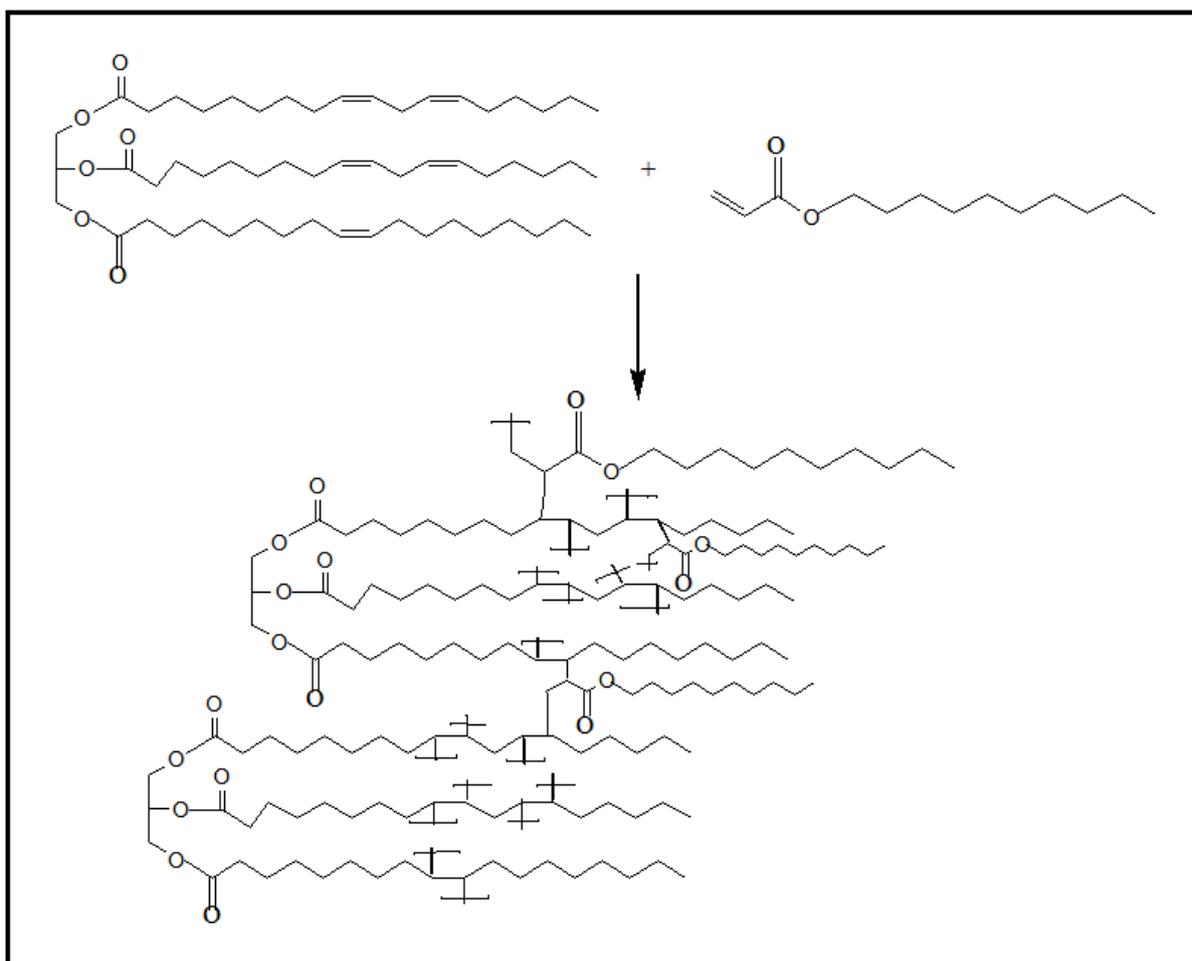
2.2.2.3 Purification of the decyl acrylate ester

For the purification of decyl acrylate ester, 1 g of charcoal was added to it and refluxed for 3 hours. After the stipulated time, the charcoal was filtered off and the filtrate was washed 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 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 DA was finally left over night on anhydrous CaCl₂ for drying. The CaCl₂ was then removed by filtration and toluene was recovered by distillation under reduced pressure.⁵ The ester left behind was ready for further use.

2.2.2.4 Synthesis of the polymer

The homopolymerization of AO and its copolymerization with decyl acrylate were carried out in a four necked, round-bottom flask. The homopolymer of AO (HAO) was prepared by taking 10 g of AO in the round-bottom flask equipped with a thermometer, mechanical stirrer, condenser and an inlet for the introduction of nitrogen. AIBN (0.4% of the monomers) was used as an initiator and was added in five different lots during the reaction. The reaction was carried out for 7 h and the temperature was maintained at 363 K to prepare the homopolymer. The reaction mixture was poured into methanol,

at the end of the reaction time, with stirring, to terminate the polymerization and precipitate the polymer. Additional purification of HAO was carried out by repeated precipitation of its hexane solutions by methanol followed by drying under vacuum at 313 K. Similar synthesis was carried out for preparation of the copolymers by taking 10 g total of AO with 5 or 10% of DA, keeping the other components the same. The mass fraction of the monomers in the copolymers is given in Table 2.2.2.



Scheme 5: Preparation of copolymer of almond oil with decyl acrylate

2.2.3 Measurements

2.2.3.1 Spectroscopic measurements

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

2.2.3.2 Thermo gravimetric measurements

The thermal stabilities of all the prepared polymers (additives) were determined by a TGA-50 thermogravimetric analyzer (Shimadzu Corporation, Japan), at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ using an alumina crucible. The thermo-oxidative stability of the additives was determined in terms of percent of weight loss (PWL) with increase in temperature. A higher decomposition temperature for the polymer for a given PWL indicates a superior thermo-oxidative stability. The PWL was determined by the equation,

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

where M_0 is the initial mass and M_1 is the left over mass of the polymer until constant weight, after the test.

2.2.3.3 Determination of molecular weight of the prepared polymers

The molecular weights of the prepared polymers were determined using a GPC system (Waters Corporation, USA) equipped with a 2414 refractive index detector (polystyrene calibration), a 717 plus autosampler and a Waters 515 HPLC pump (Table 2.2.3). HPLC grade THF was used as an eluent at a flow rate of 1.0 mL/min at 30 $^{\circ}\text{C}$. The

polydispersity index (PDI, M_w/M_n) of the prepared polymers (which indicates the nature of distribution of the molecular weights in the prepared polymers) was calculated by determining the weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymers.

2.2.3.4 Evaluation of viscosity index (VI)

The viscosity index (VI) is a parameter that indicates the effect of alteration of temperature on the kinematic viscosity (KV) of the oil. A higher value of VI denotes a lower rate of change of viscosity with the variation in temperature. The viscosity index was calculated as per the ASTM D2270 method for the two base oils (BO1 and BO2) [21]. The KV of the base oils blended with the additives was evaluated at 313 and 373 K, at different concentrations of the additive, to analyse the effect of concentration on VI of the additive mixed lube oil. KV was calculated by the equation,

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

where K and L are viscometric constants; ρ is the density of the additive mixed oil and t is the time of flow of the additive mixed base oil to pass through the two calibrated marks in the Ubbelohde viscometer.

2.2.3.5 Evaluation of the pour point (PP)

The pour points of the two lube oils (BO1 and BO2) with added synthesised additives were evaluated according to the ASTM D97-09 method on a cloud and pour point tester (Wadegati Labequip Pvt. Ltd., India). The result of additive concentration on the PP was analysed by using different concentrations of the additives.

2.2.3.6 Biodegradability test

Numerous tests have been devised for assessing the biodegradability of plant oil based additives, as they have an innate biodegradability compared to the synthetic acrylate ones. Here the biodegradability was evaluated by (a) the soil burial degradation test of films of the additives as per ISO 846:1997^{22,23} and (b) the disc diffusion method against fungal pathogens.²⁴ The degree of degradation of the additives in the experiments was assessed by calculating the percent weight loss (PWL) of the samples. The degradation of the additives was also affirmed by examining the shift in the IR frequency of the ester carbonyls along with the change in their molecular mass after the biodegradability test.

2.2.3.6.1 Soil burial degradation test (SBD Test)

The effect of microorganisms on the surface of polymer film is studied in the SBD test.²⁵ Here, 2 g of every polymeric additive was taken to produce the polymer films. The films so created were then buried in soil in a bacteriological incubator. The soil (containing the microorganisms) was first placed in a tray, its relative humidity was set to 50–60% by adjusting the humidity chamber and the temperature was selected at 303 K. The soil for this work had been gathered from the North Bengal University campus (West Bengal, India) with pH 7.3 and moisture of 25%. The buried polymer films were taken out for study up to a period of 3 months at regular intervals of 15 days. For each work (time interval), a different film was used. Recovered films after the biodegradation test were washed with chloroform, filtered with Whatman grade 41 filtration paper and dried in a vacuum oven at 323 K. They were then again decontaminated by precipitation

of their hexane solution by methanol and then dried in a vacuum oven until a constant weight was reached at 323 K. The weights of the sample, before and after drying, were recorded to determine the PWL.

2.2.3.6.2 Disc diffusion (DD) method

In this test method, four fungal pathogens, viz. *Colletotrichum gloeosporioides* (CG), *Fusarium equiseti* (FE), *Colletotrichum camelliae* (CC) and *Alternaria alternate* (AA) were selected to check the biodegradation of the prepared samples in a bacteriological incubator (Sigma Scientific Instruments Pvt. Ltd., India). Culture media for the fungal strains were first prepared by mixing potato extract, agar powder and dextrose in a 10:1:1 proportion by mass. 3 g of the culture media was taken in Petri dishes with 2 g of each of the additives and incubated for 30 days at 310 K with the selected fungal pathogens. A change in colour from yellow to blackish was indicative of the fungal growth. After 30 days, the polymeric additives were recovered from the fungal strains and washed with chloroform, purified and then dried. The PWL [Eq. (1)] for each of the samples was recorded and their molecular weights were determined by GPC method.

2.2.4 Results and discussion

2.2.4.1 Spectroscopic analysis

The FT-IR absorption indicated the presence of ester carbonyl groups of HAO at 1744.4 cm^{-1} . The broad peak in the region of 1165.7 cm^{-1} was due to the ester C-O stretching vibration. The peaks emerging in the regions of 723.9, 1377.8 and 1463.8 cm^{-1} corresponds to the C-H bending vibrations of CH_2 and CH_3 groups. Absorptions

appearing in the regions of 2855.1 cm^{-1} and at 2926.1 cm^{-1} were due to the stretching vibrations of the paraffinic C-H bonds. The nonexistence of olefinic peaks in the range of $1550\text{--}1680\text{ cm}^{-1}$ in the polymer and their appearance in the monomers supports the polymer formation (Fig. 2.2.1).

In the $^1\text{H-NMR}$ spectra of HAO (Fig. 2.2.3), the triglyceride group protons ($-\text{COOCH}_2$) showed broad peaks in the range of $4.1\text{--}4.3\text{ ppm}$. Peaks also emerged for the methylene protons in the range of $1.3\text{--}2.2\text{ ppm}$ while the peaks in the range of $0.86\text{--}0.88\text{ ppm}$ were for the methyl protons. The shift between 2.3 and 2.4 ppm occurred due to the protons of $-\text{OCOCH}_2-$ groups present in HAO. The nonappearance of any peaks in the range of $5.5\text{--}6.5\text{ ppm}$ also supports the formation of the polymer.

In the proton decoupled $^{13}\text{C-NMR}$ spectra of HAO (Fig. 2.2.5), the methyl and methylene carbon atoms of AO showed signals between 14.1 and 33.9 ppm . The signals appearing between 172.9 and 178.5 ppm is attributed to the carbonyl carbons of the ester groups whereas the $-\text{OCH}_2$ carbons of the triester appeared between 62.1 and 68.9 ppm . The absence of unsaturation in the polymers was indicated by the lack of any peaks in the range $130\text{--}150\text{ ppm}$.

Polymers S-2 and S-3 showed related peaks in their NMR (^1H and ^{13}C) and FT-IR spectrum suggesting that the prepared polymers are in good agreement with the expected structures.

2.2.4.2 Thermogravimetric analysis (TGA) study

The studies of the thermogravimetric analysis of the polymers are shown in Table 2.2.4. Here, two different decomposition temperatures of the polymers are reported for a better comparison. The polymer S-1 at $300\text{ }^\circ\text{C}$ showed a PWL value of 52 while at 425

°C it had a PWL of 94. The polymer S-2 for a similar PWL (values of 49 and 93) has a higher decomposition temperature of 325 and 465 °C respectively. As indicated by the percentage of degradation (measured in terms of PWL) of the polymers, it is quite clear that the thermal stability of the copolymers was moderately superior to that of the homopolymer. Additionally, it was also learned that the copolymer S-3 is more stable at higher temperatures compared to the other polymers with the highest decomposition temperature of 360 and 490 °C for the PWL values of 48 and 95 respectively. This increased stability is may be due to a lower level of branching in the copolymer S-3 as suggested by the respective PDI values in Table 2.2.3.²⁶

2.2.4.3 Performance of the prepared additives as viscosity index improvers

The VI values of the lube oils blended with the additives are shown in Figs. 2.2.8 and 2.2.9. Detailed study of the data as obtained showed that the VI values of the base oils were significantly augmented by the addition of the additives. Besides, the result improved with the increase in additive concentration regardless of the additive and the base oil used. A critical examination of the VI values also explained that the copolymers acted as a better VI enhancer in contrast to the homopolymer. The inclusion of DA in the almond oil backbone improved the VI values and the improvement was highest for the copolymer S-3 with a greater proportion of DA, followed by copolymer S-2, and then the polymer S-1. Here, the increase in the VI results with growing additive concentration in the lube oil can be the outcome of increased hydrodynamic volume of the additive. Hydrodynamic volume is the volume of the polymer and the associated base oil. The potential of a polymer to operate as a VII is directly associated with the hydrodynamic volume occupied by the randomly coiled polymer chain.²⁷ It is claimed that in cold

conditions the polymers have a small hydrodynamic volume i.e., the molecules of the polymer take up a coiled form so that their influence on viscosity is minimized. At elevated temperature, when the viscosity of the lube oil is likely to decrease, an expansion or uncoiling of the polymer molecules takes place ensuring an increase in the size of the polymer micelle. This inflated micelle, simultaneously with the increase in the power of solvation at higher temperature, nullifies the drop in viscosity of the base oil with increase in temperature.²⁸ Hence, higher the proportion of polymer in the base oil, bigger is the volume of the micelle and subsequently higher will be the viscosity index.²⁹

2.2.4.4 Performance of the prepared additives as pour point depressants

Assessment of the synthesised additives for their PPD properties showed good results (Figs. 2.2.10 and 2.2.11). It is clearly noticeable that the effectiveness of the prepared polymers as PPDs steadily improved with their increasing concentration in the base oils studied. Also the results suggested that the prepared additive sample S-3 was more effective as a PPD than the homopolymer (S-1) and the other copolymer (S-2) with different acrylate ratio in the base oils. The dissolved wax like paraffinic hydrocarbons present in mineral oils have a tendency to separate from the oil at low temperatures appearing as a stiff network of crystals which checks the oil from flowing.³⁰ With the purpose of improving its pour point (the lowest temperature at which the oil stays flowing), pour point depressants are suitably blended to the oil. The blending of additives disrupts these stiff networks of wax crystals preventing their formation. Different theories have been proposed for the mode of action of PPDs, among which nucleation, co-crystallization, adsorption and improved wax solubility are

generally accepted.^{31,32} The PPD molecules usually consists of a wax like paraffinic part that works by offering nucleation sites and co-crystallizes with the mineral oil's wax like hydrocarbons and gradually become a part of them while the polar segments associated with the PPDs, dissimilar to the wax crystals, prevents the expansion of the rigid network of wax matrices.³³ The almond-acrylate copolymers, owing to their more polar behaviour,³³ are more valuable against the creation of wax crystals, thereby claiming superior pour point results compared to that for the homopolymer.

2.2.4.5 Photo micrographic analysis

A BPL-400B polarizing microscope (Banbros Engineering Pvt. Ltd., India) was selected to study the photomicrographs of the additive blended base oils (Fig. 2.2.12). The photomicrographs depicted the wax crystallization response of the synthesised polymers dissolved in the base oils. The temperature of the oils for analysing the photomicrographs was controlled on the microscope slide by an attached cooling thermostat. The magnification of the microscope was adjusted at $\times 200$ and all photos were taken at 273 K. The photomicrographs explained that the wax morphology changed in accordance with the nature of additives added. Fig. 2.2.12a, which is for the pure lube oil, has large wax crystals of estimated 100 μm size; on doping with the additives there was a substantial reduction of wax crystal dimension along with the formation of several highly dispersed small crystals. The polymer S-3 (Fig. 2.2.12d) has the smallest dispersed wax crystals compared to the others. These results are in conformity with the pour point values obtained earlier.

2.2.4.6 Analysis of biodegradability test

Weight losses of the additive samples after the SBD and DD biodegradability tests are reported in Fig. 2.2.13 and Table 2.2.5 respectively. The analysis of the investigations showed considerable biodegradation for all the additives. The results of the SBD tests pointed out that the biodegradation of the additives under study increased continuously with the increasing number of days. Additionally, all the polymers of almond oil had notable weight losses against the fungal pathogens, especially against *Alternaria alternata* (AA), in the DD test. The GPC of the polymers after the DD method was also carried out and the results were compared with the respective polymers before biodegradation. The results indicated considerable change in the M_n and M_w of the polymers and thus revealed the biodegradability of the prepared polymers. Furthermore, as expected for zero acrylate percentage and owing to the presence of the bio-based monomer unit, the additive S-1 displayed the highest biodegradability in comparison to all the additives in both of the tests. The FT-IR spectra of the HAO additive, before and after the DD test (Fig. 2.2.7), were also compared. The IR peaks of the additive S-1 at 1744, 1464, 1378, 1166 and 724 cm^{-1} diminished noticeably in peak height and intensity after the DD test. This decrease in the IR peak intensities is possibly due to the scission of the polymer chains during biodegradation of the polymer units.³⁴ The other additives also displayed shift in their IR peaks but to a much smaller extent. The drop and the shift in the IR peak intensities of the additives after the biodegradation tests along with the results of PWL of the additives confirmed the biodegradable nature of the synthesised additives.

2.2.5 Conclusions

The above findings pointed out that all the prepared additives worked as excellent multifunctional additives augmenting the lubricant property of the base oils. Some key improvement in pour point and viscosity index values were obtained by the inclusion of acrylate monomers in the triglyceride backbone of the almond oil. The thermal stability of almond oil increased significantly with polymerization. Again, the thermo-oxidative stability of the copolymer with highest DA content was the maximum and had the best performance. The VI values, as obtained, improved with the increase in the proportion of the additives, and polymer S-3, with a higher fraction of DA, worked as a superior VI improver compared to the others. Furthermore, it was also found that the copolymer S-3 operated more efficiently as a PPD than the homopolymer for the given lube oils under investigation. The biocompatible natures of the additives were also recognized and HAO displayed the highest biodegradability among the prepared additives. Hence, we suggest that the prepared additives may be used for the formulation of a biodegradable, multifunctional additive for lube oils for a greener future.

2.2.6 References

References are given in BIBLIOGRAPHY under Chapter-II of Part-II (Page No. 214-218).

2.2.7 Tables and figures

Table 2.2.1: Physical properties of base oils

<i>Properties</i>	<i>Method</i>	<i>B01</i>	<i>B02</i>
Viscosity at 40 °C in cSt	ASTM D445	7.132	23.387
Viscosity at 100 °C in cSt	ASTM D445	1.849	3.911
Viscosity Index	ASTM D2270	80	85
Pour Point, °C	ASTM D97	-3	-6
Density (g.cm ⁻³) at 40 °C	ASTM D4052	0.83645	0.85492

Table 2.2.2: Percentage composition of the copolymers as estimated by spectroscopic method

<i>Polymers</i>	<i>Mass fraction in the polymers</i>		<i>NMR estimation of the mass fraction of decyl acrylate</i>	<i>IR estimation of the mass fraction of decyl acrylate</i>
	<i>Almond oil</i>	<i>Decyl acrylate</i>		
S-1	1	0	-	-
S-2	0.95	0.05	0.020	0.023
S-3	0.90	0.10	0.041	0.048

S-1: Homopolymer of almond oil, S-2: almond oil + 5% decyl acrylate, S-3: almond oil + 10% decyl acrylate.

Table 2.2.3: Average molecular weight and PDI values determined by GPC

Polymers	$M_n \times 10^4$	$M_w \times 10^4$	PDI
S-1	2.157	3.301	1.53
S-2	1.989	2.766	1.39
S-3	1.782	2.458	1.37

Table 2.2.4: TGA data of the polymer samples

Polymers	Decomposition temperature (°C)	PWL
S-1	300/425	52/94
S-2	325/465	49/93
S-3	360/490	48/95

Table 2.2.5: Result of biodegradability test by DD method and comparative average molecular weight values

<i>Polymers</i>	<i>Incubation period (days)</i>	<i>Pathogen</i>	<i>PWL</i>	<i>Molecular weight</i>			
				<i>Before biodegradation</i>		<i>After biodegradation</i>	
				<i>M_w</i>	<i>M_n</i>	<i>M_w</i>	<i>M_n</i>
S-1	30	CC	0.35	33018	21575	29249	20312
		FE	0.73				
		AA	26.28				
		CG	0.79				
S-2	30	CC	0.21	27669	19897	25308	18756
		FE	0.51				
		AA	16.72				
		CG	0.48				
S-3	30	CC	0.11	24588	17824	22286	16772
		FE	0.34				
		AA	12.09				
		CG	0.36				

Figure 2.2.1: IR spectra of polymer S-1

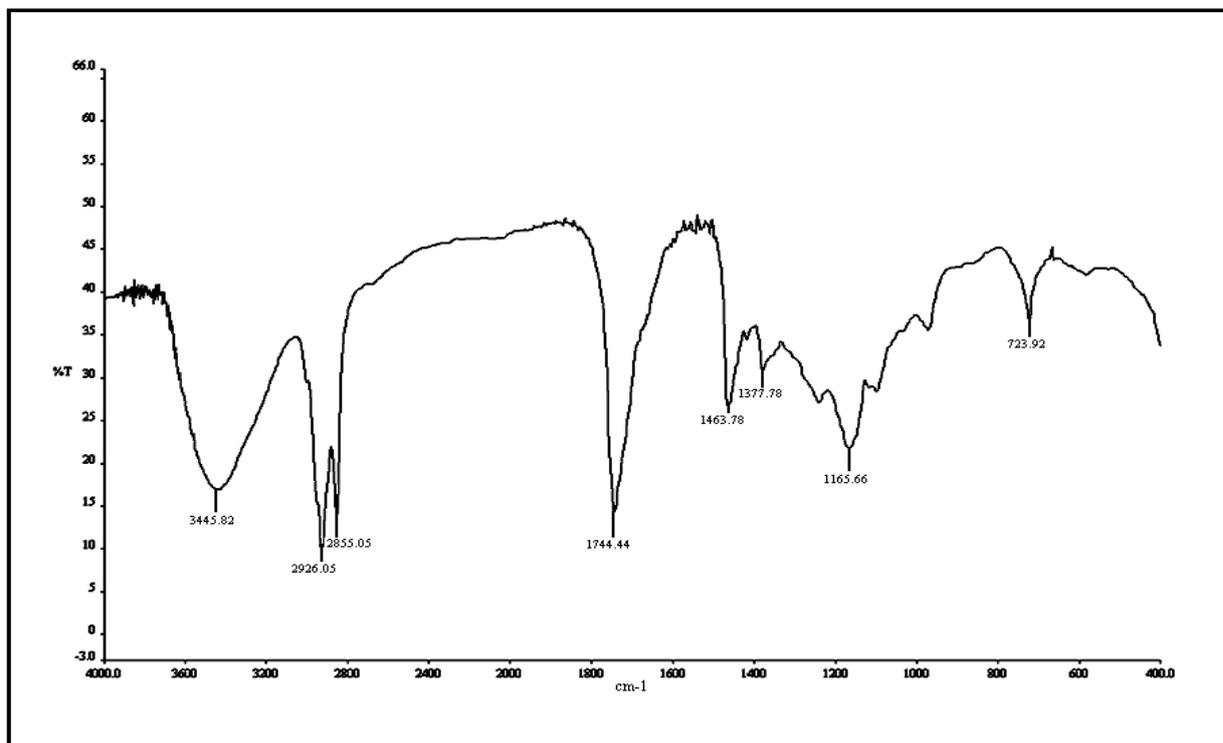


Figure 2.2.2: IR spectra of polymer S-2

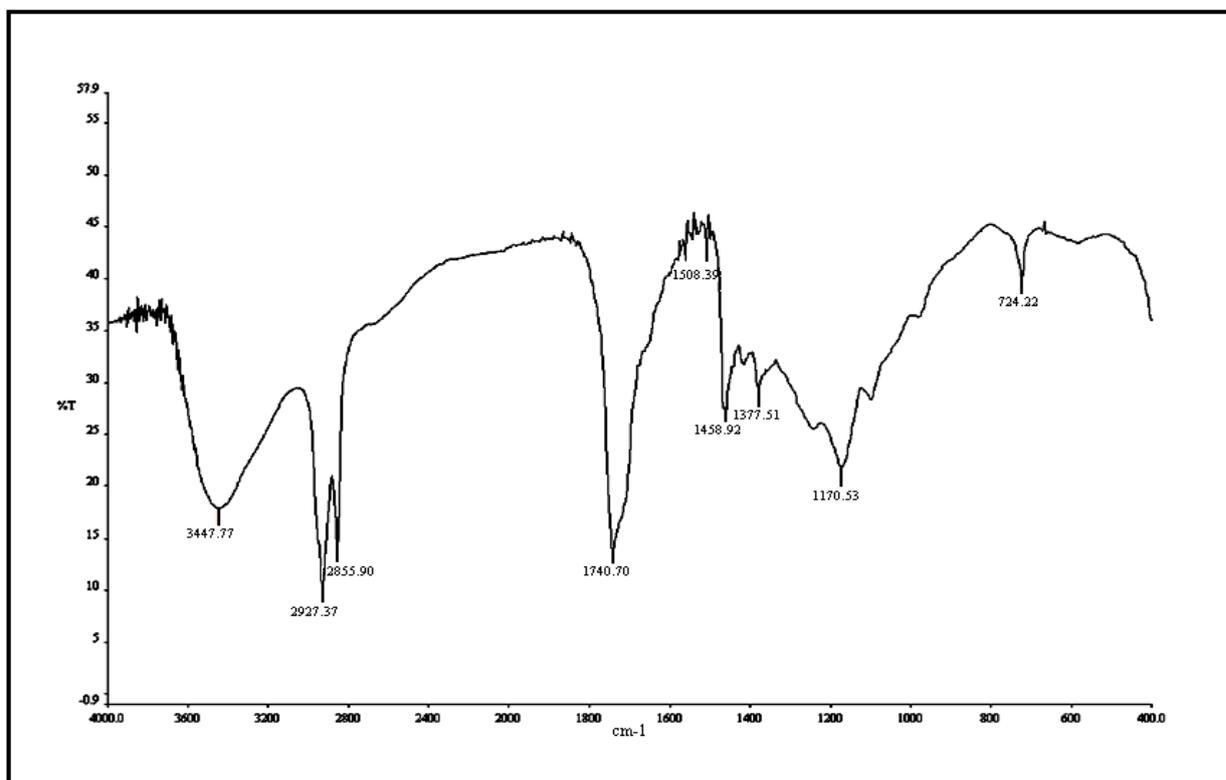


Figure 2.2.3: $^1\text{H-NMR}$ spectra of polymer S-1

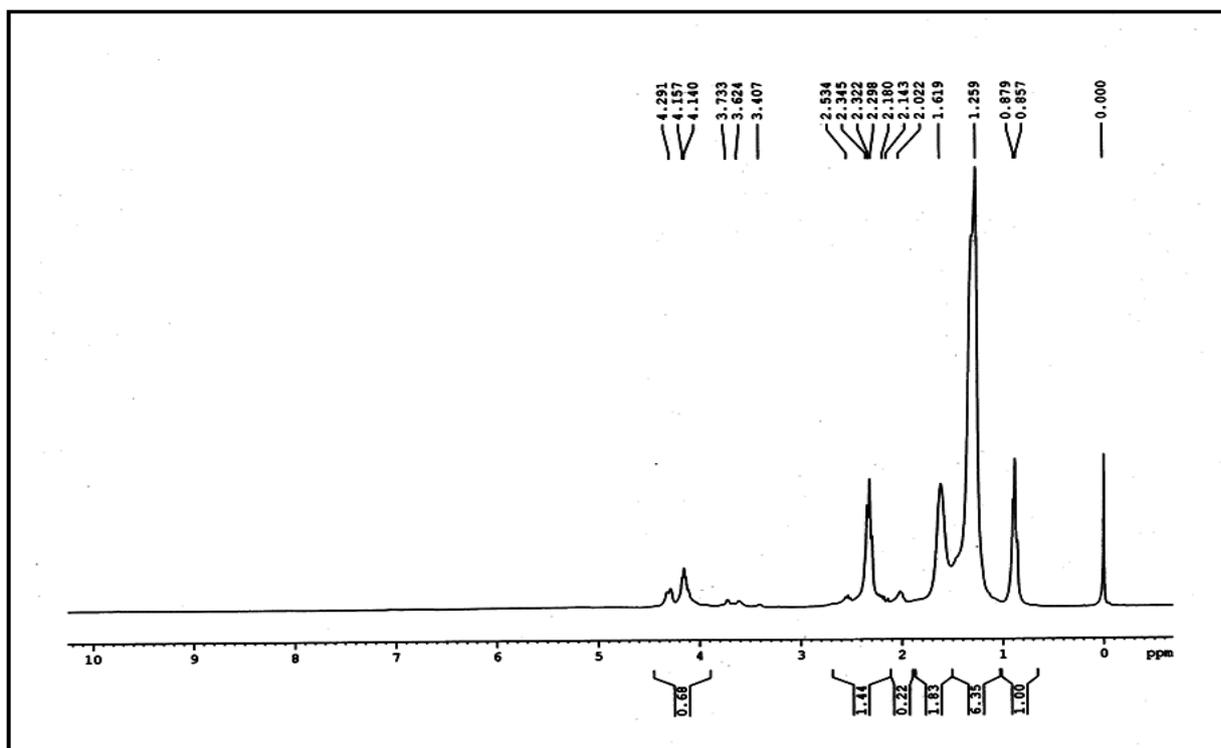


Figure 2.2.4: $^1\text{H-NMR}$ spectra of polymer S-2

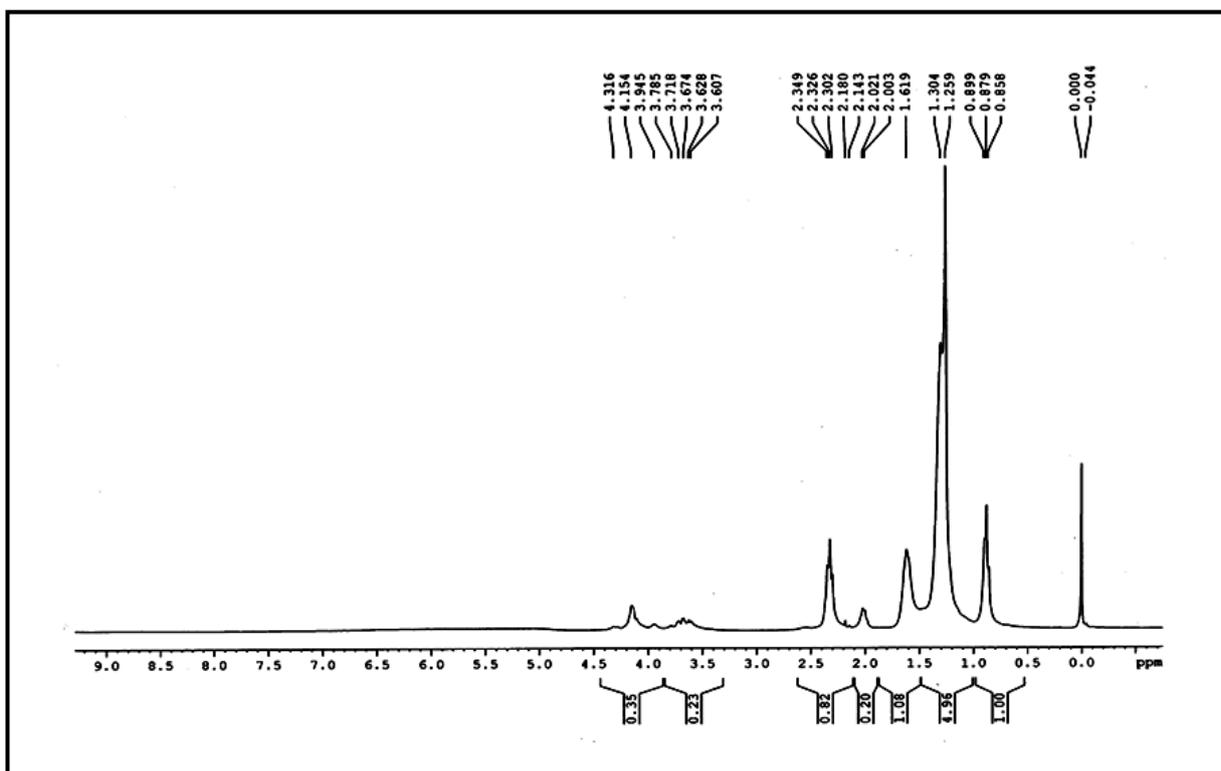


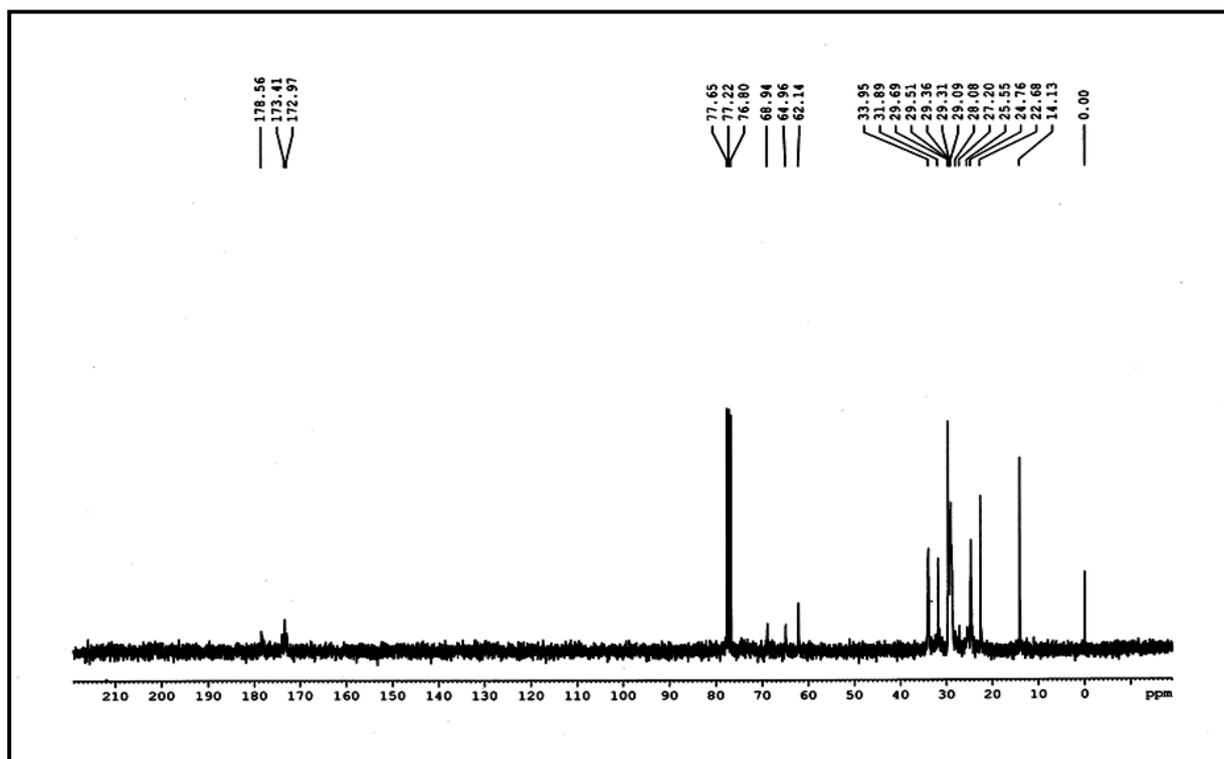
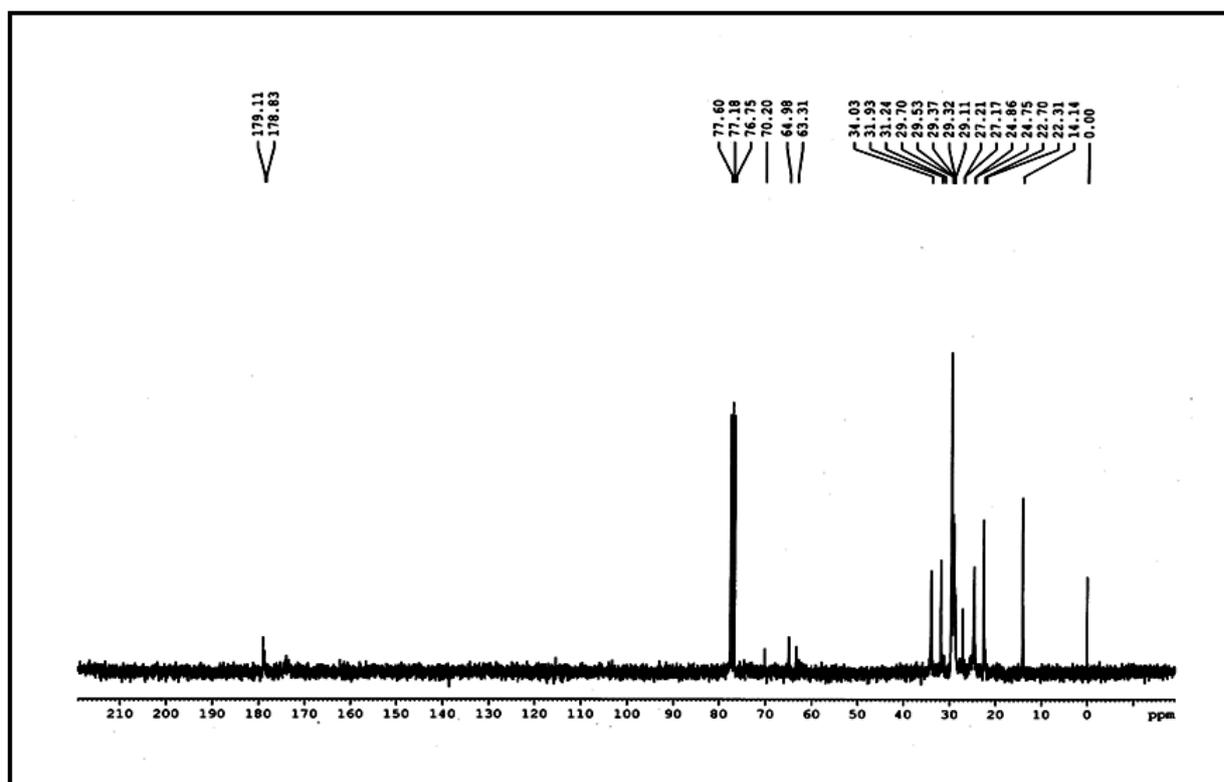
Figure 2.2.5: ^{13}C -NMR spectra of polymer S-1Figure 2.2.6: ^{13}C -NMR spectra of polymer S-2

Figure 2.2.7: Comparative FT-IR spectra of polymer S-1 (a) before and (b) after the DD test

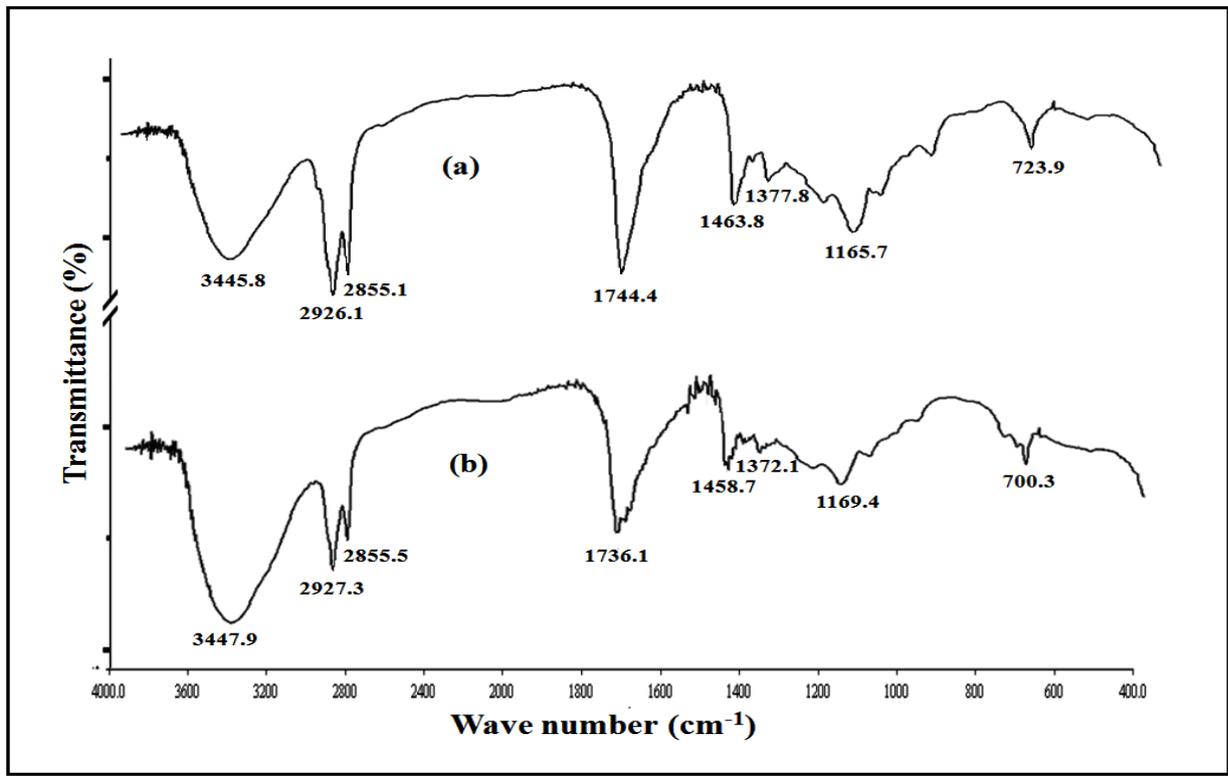


Figure 2.2.8: Viscosity index values of additives S-1 to S-3 doped in base oil B01

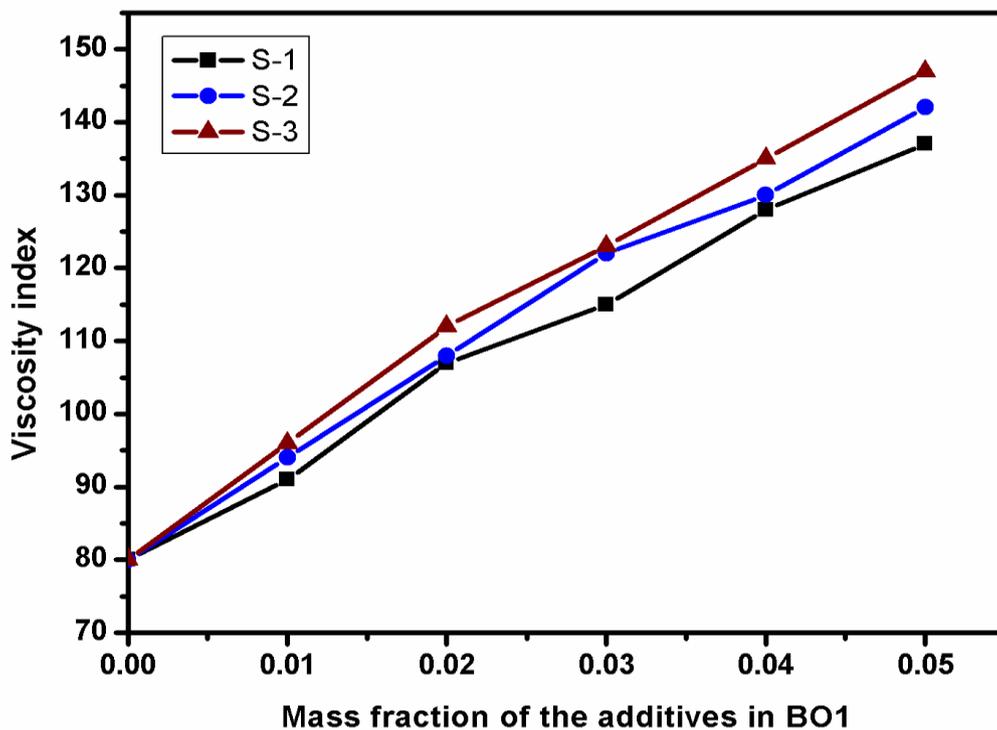


Figure 2.2.9: Viscosity index values of additives S-1 to S-3 doped in base oil B02

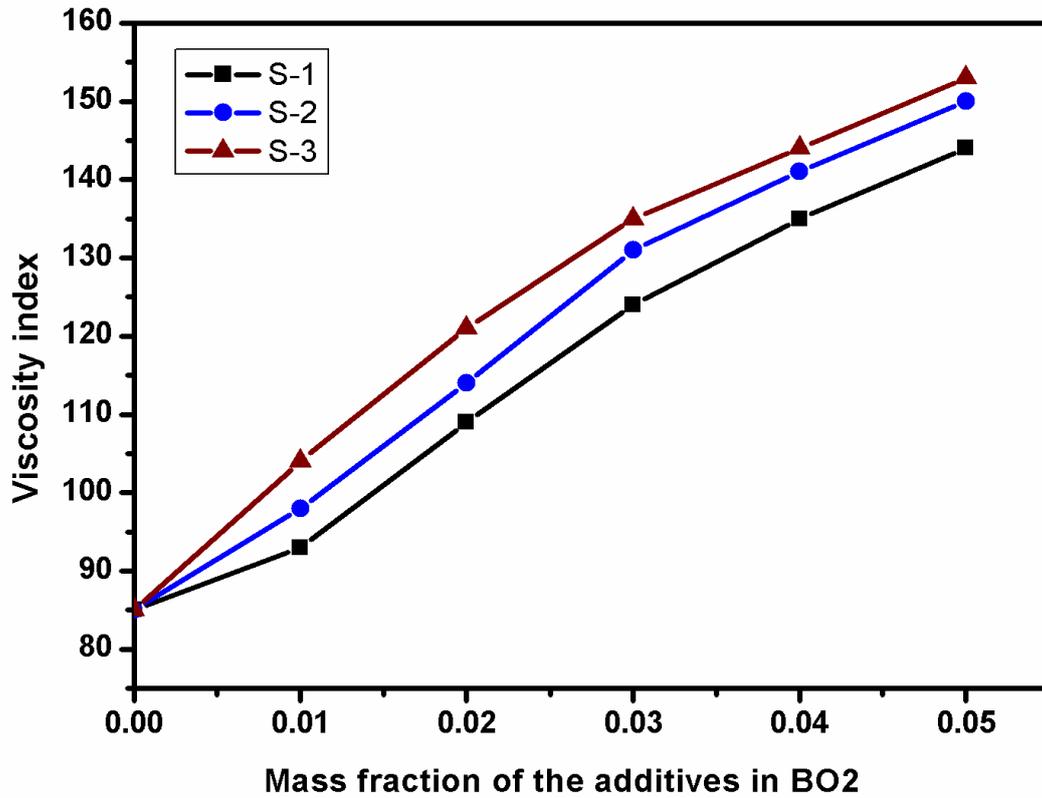


Figure 2.2.10: Pour point of the additives S-1 to S-3 doped in base oil B01

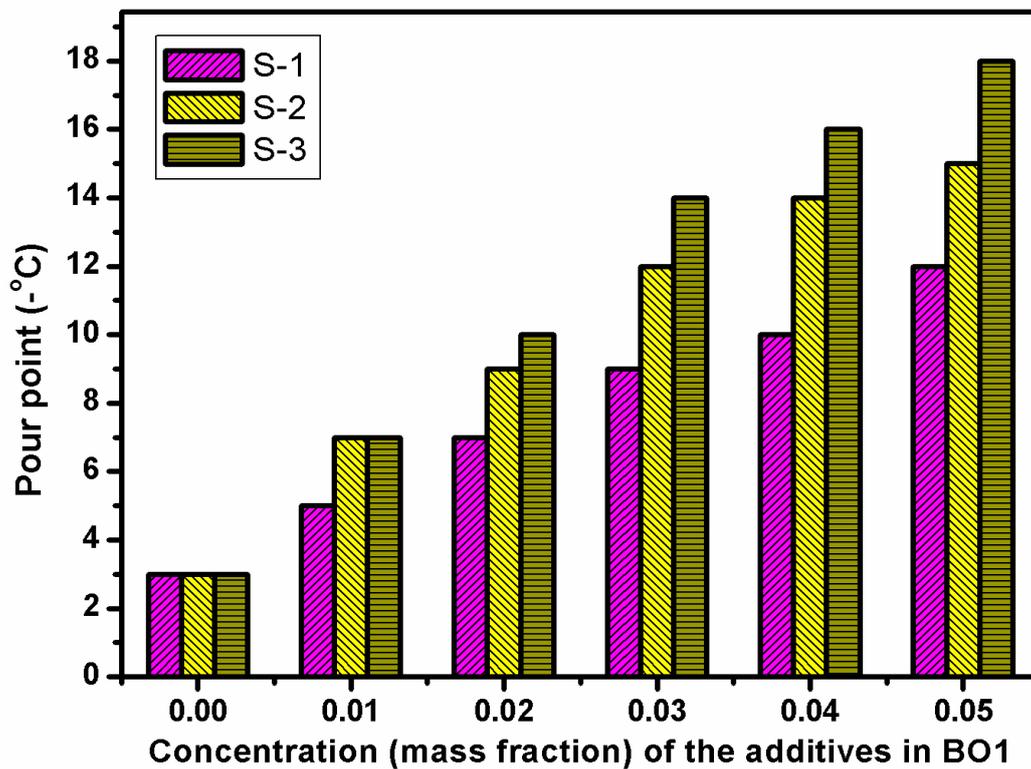


Figure 2.2.11: Pour point of the additives S-1 to S-3 doped in base oil B02

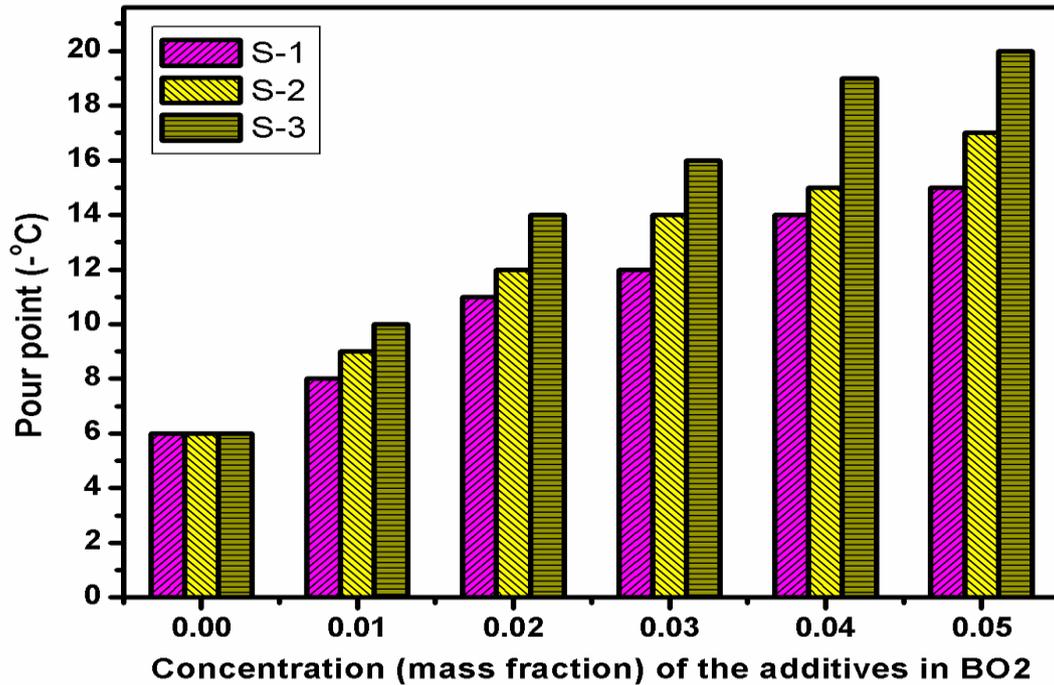


Figure 2.2.12: Photomicrographs of base oil B01: (a) without additives (b) blended with additive S-1 at 0.03 mass fraction (c) blended with additive S-2 at 0.03 mass fraction (d) blended with additive S-3 at 0.03 mass fraction

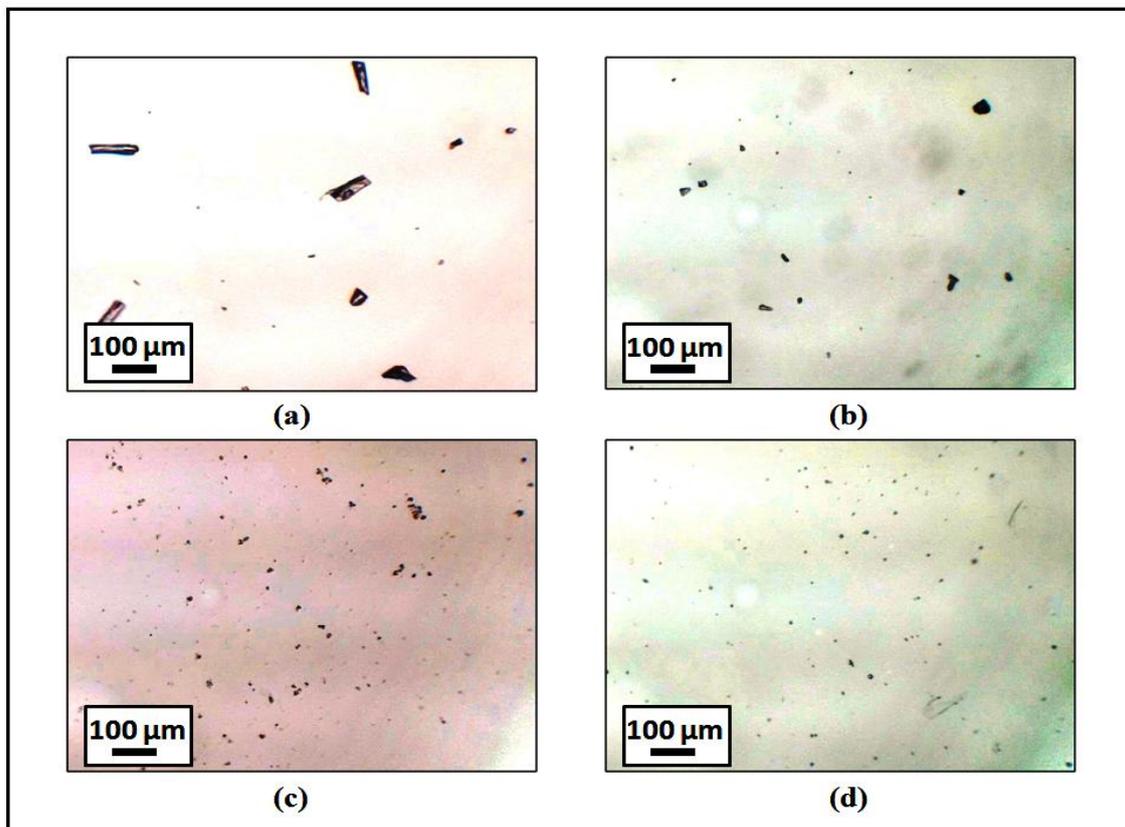
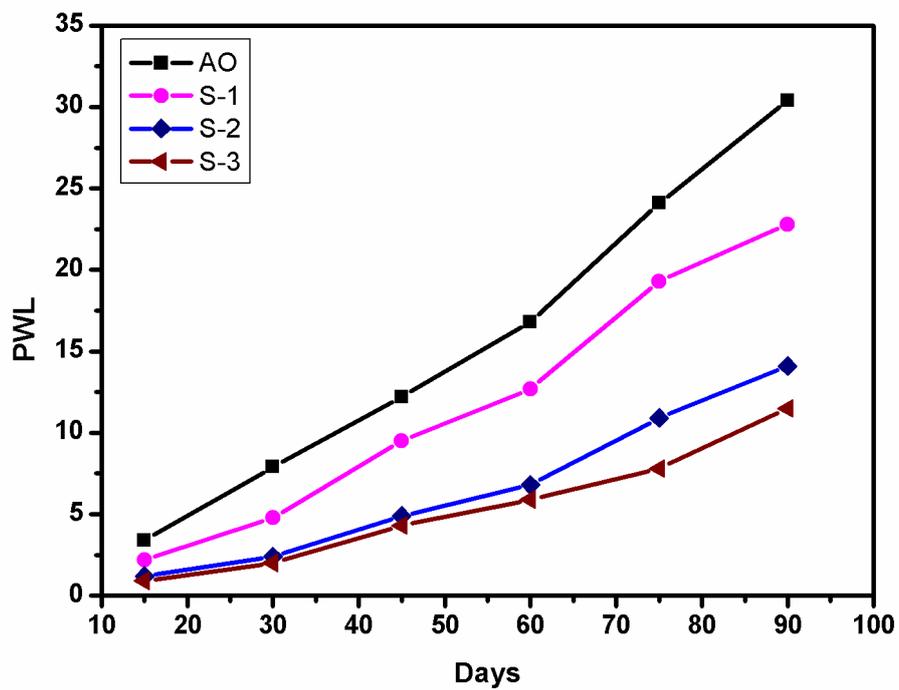


Figure 2.2.13: Degradation of almond oil (AO) and the additives measured in the SBD test



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 index¹ 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, H₂SO₄, BZP and hydroquinone were purchased from Merck Specialties Pvt. Ltd., (India). Hexane and methanol were obtained from Nice chemicals Pvt., Ltd. The CHCl₃-CH₃OH 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 H₂SO₄. 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 CaCl₂ for drying. The CaCl₂ 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. CDCl₃ was used as solvent and TMS as reference material. IR spectra were recorded on a Shimadzu 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 alternata* (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 B01 and B02 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,

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

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,

$$n = (\ln v_1 - \ln k) / \ln v_2 \quad \text{Eq. (3)}$$

Here, v_1 and v_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.

$^1\text{H-NMR}$ spectra: In its $^1\text{H-NMR}$ spectra (Figure 2.3.2), P-1 exhibited the presence of the protons of $-\text{COOCH}_2$ 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.

¹³C-NMR spectra: The proton decoupled ¹³C-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 -OCH₂ 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 ¹H-NMR, ¹³C-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 ¹H-NMR spectra of P-5 (Fig. 2.3.5), the protons of -COOCH₂ 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 -OCOCH₂- 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 ¹³C-NMR spectrum of P-5 (Fig. 2.3.6) showed peaks for the -OCH₂ 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 led 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

<i>Properties</i>	<i>Base oils</i>	
	<i>B01</i>	<i>B02</i>
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

<i>Polymers</i>	<i>Mass fraction of the polymers</i>		<i>NMR estimation of the mass fraction of olive oil</i>	<i>FT-IR estimation of the mass fraction of olive oil</i>
	<i>DDMA</i>	<i>Olive oil</i>		
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

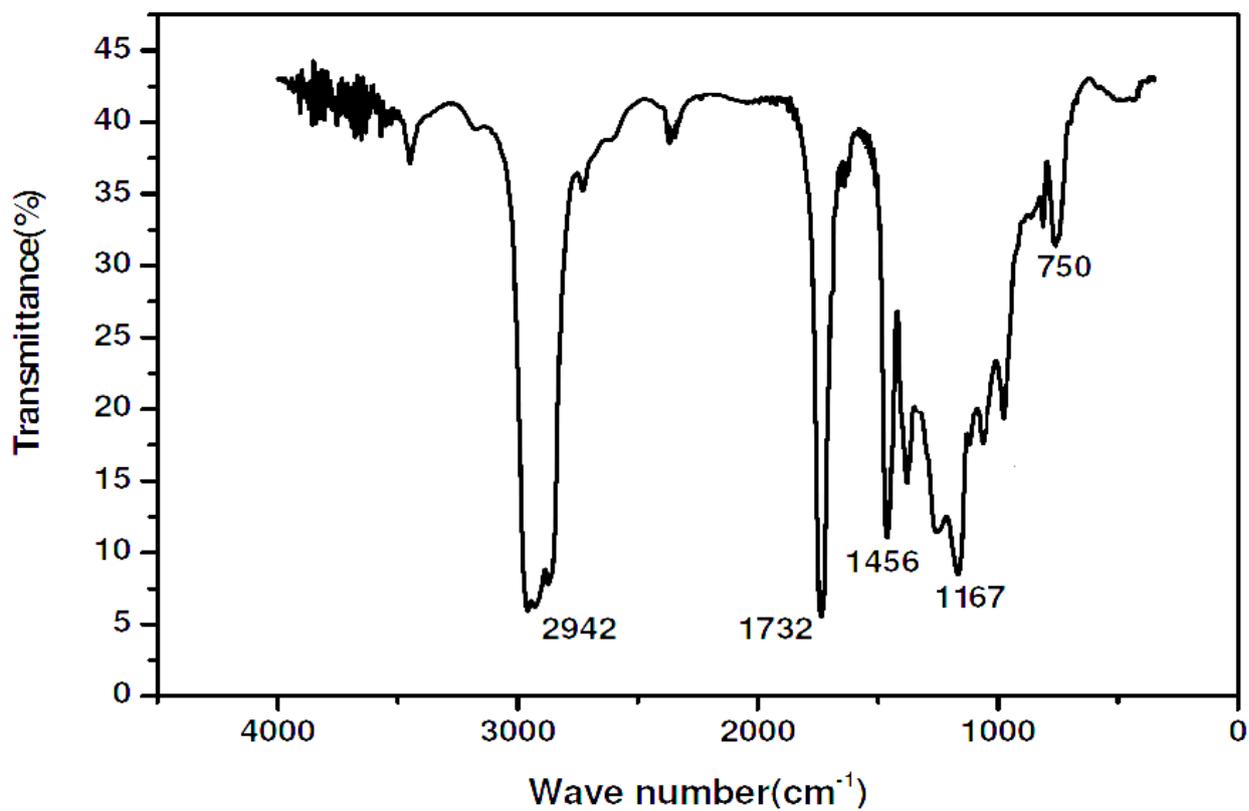
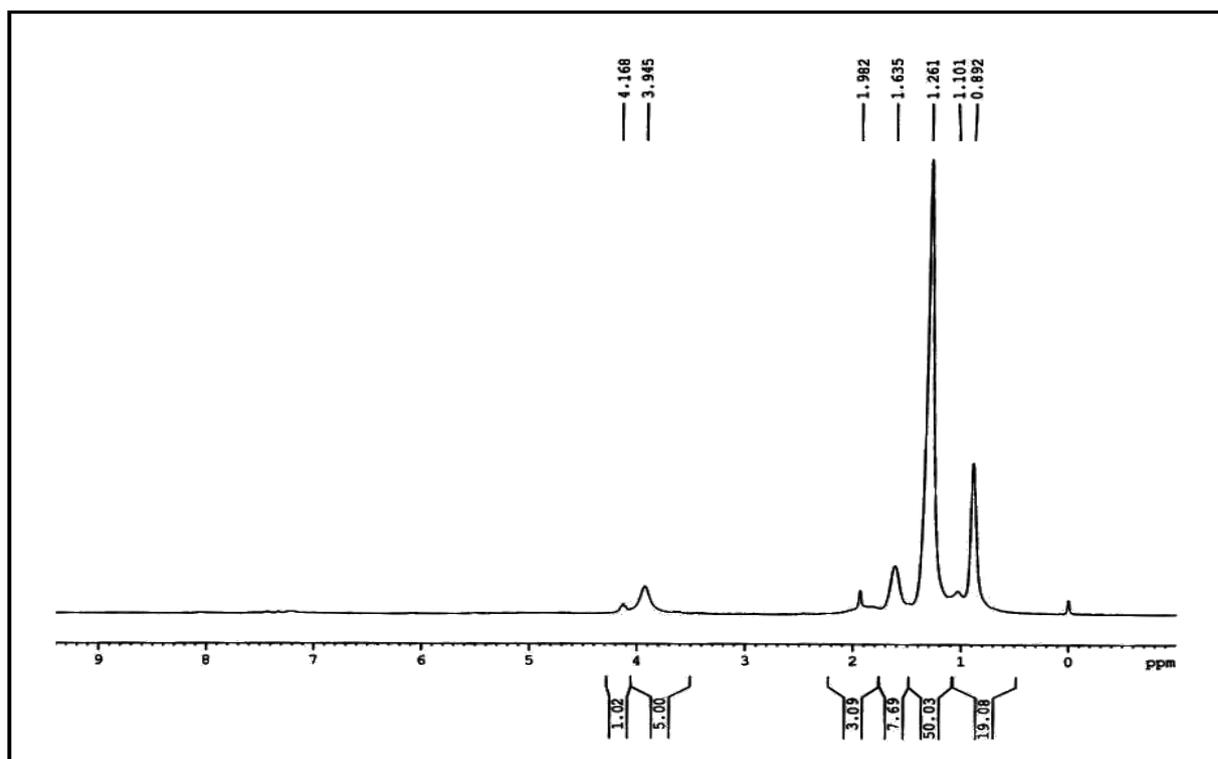
Figure 2.3.2: ^1H -NMR spectra of polymer P-1

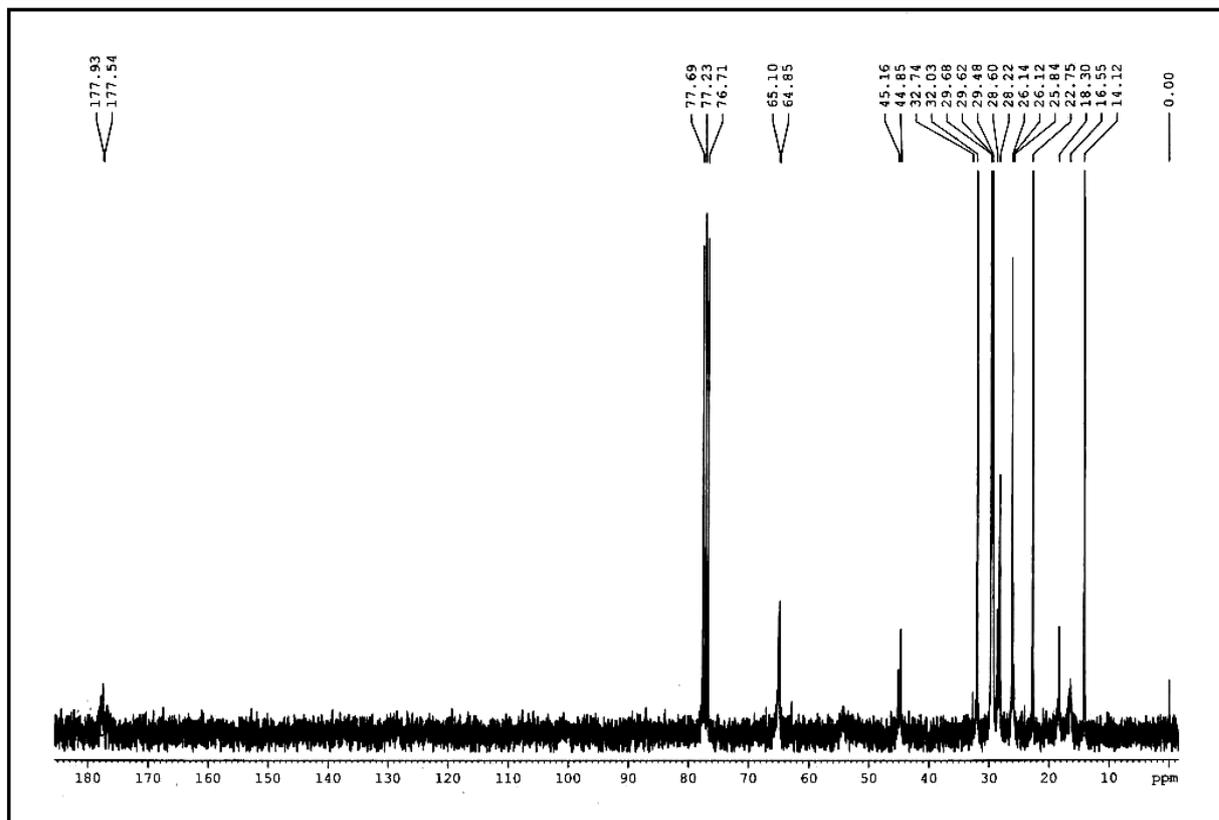
Figure 2.3.3: ^{13}C -NMR spectra of polymer P-1

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

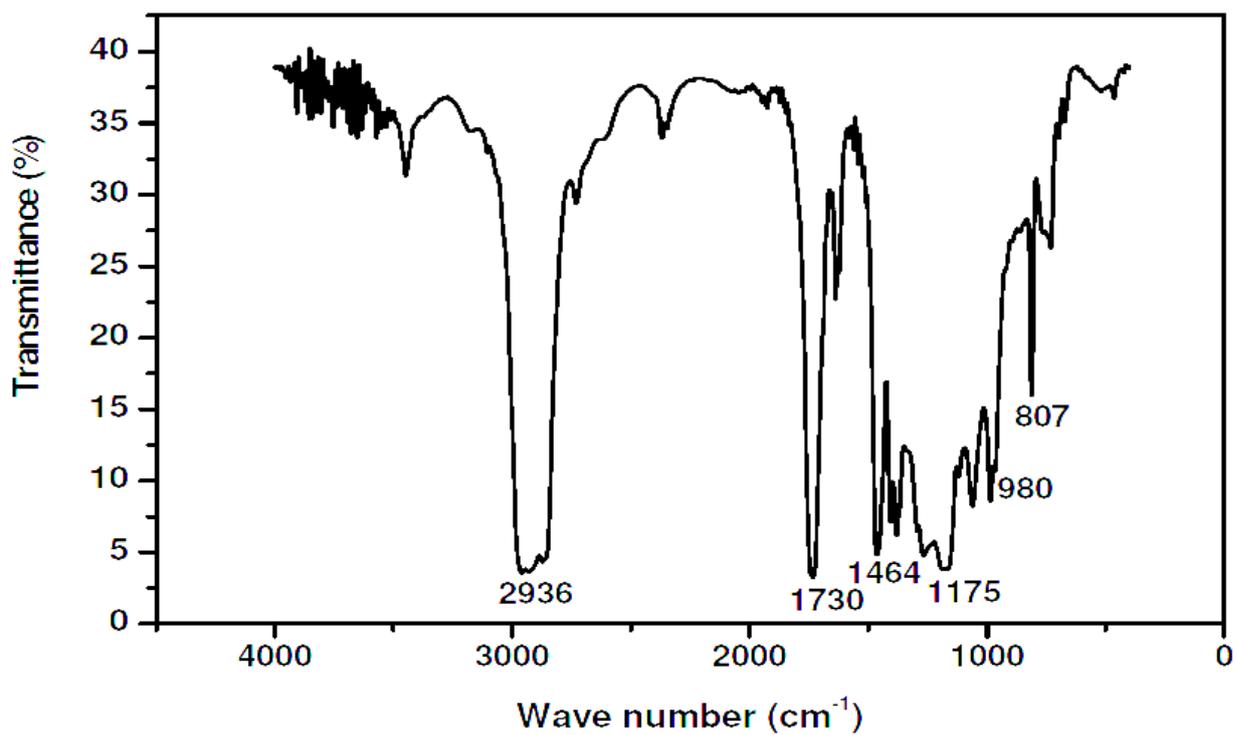


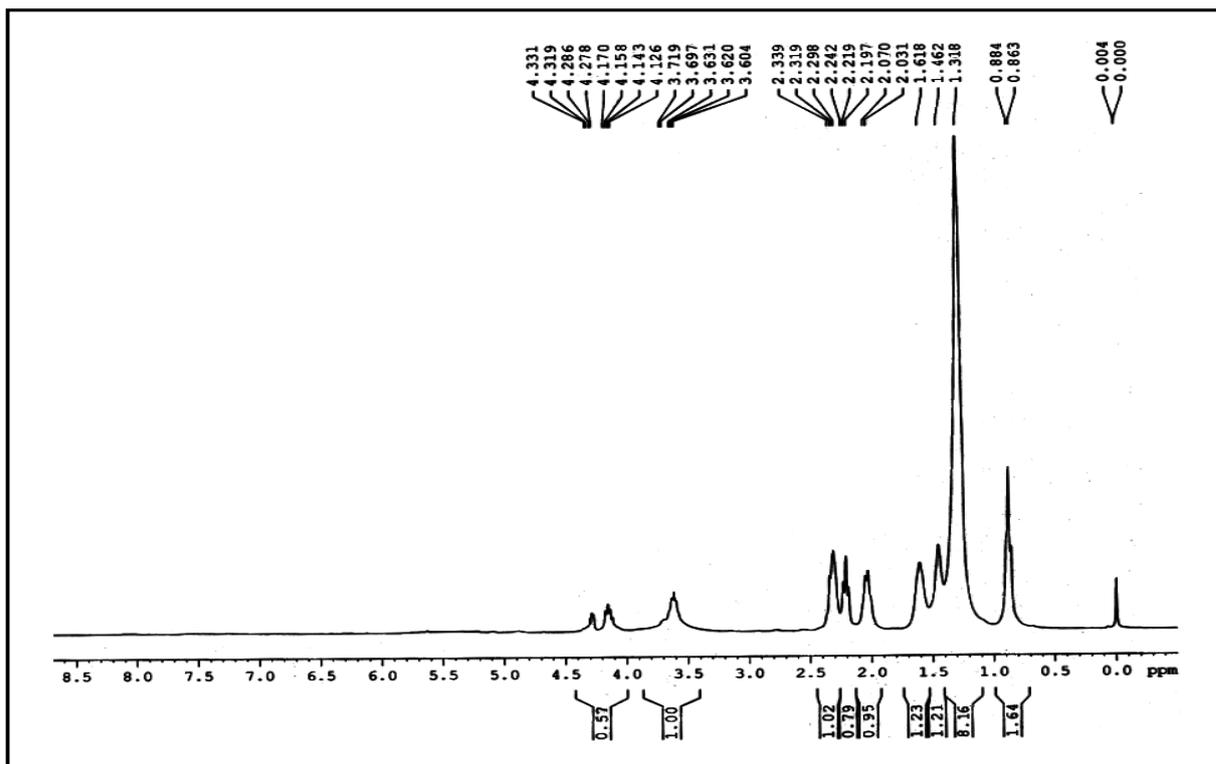
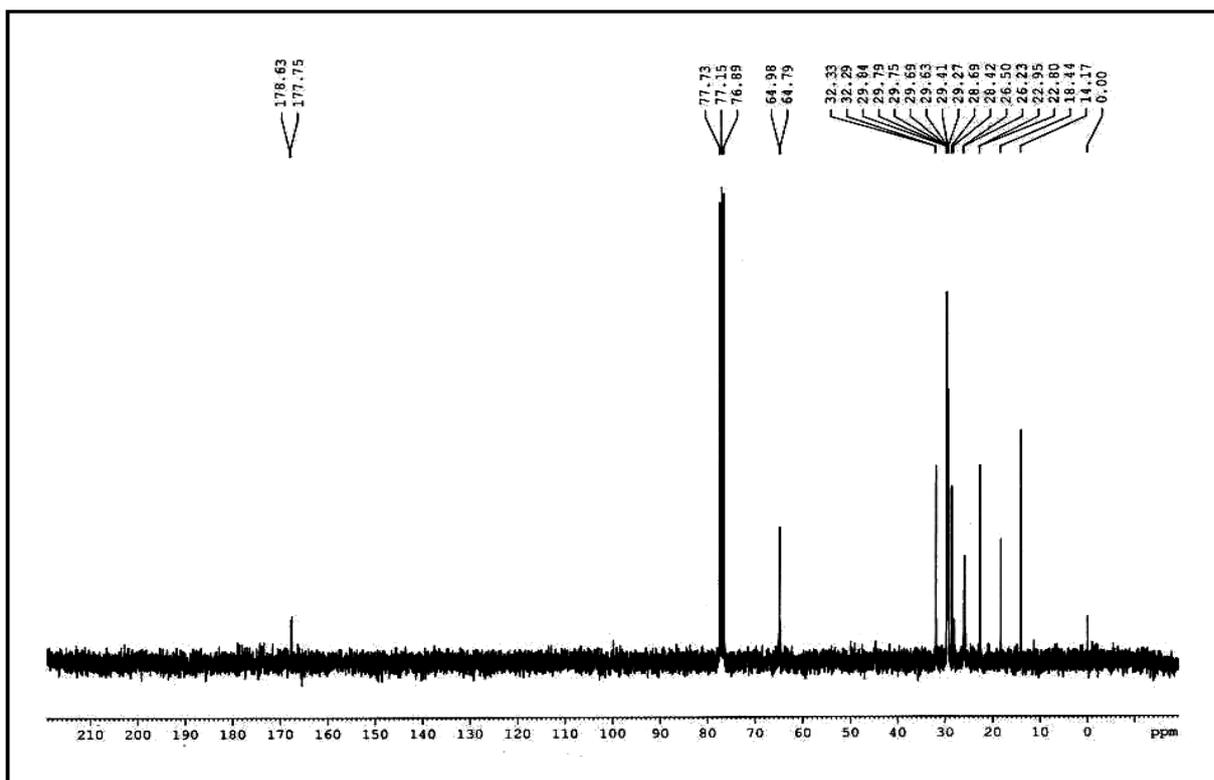
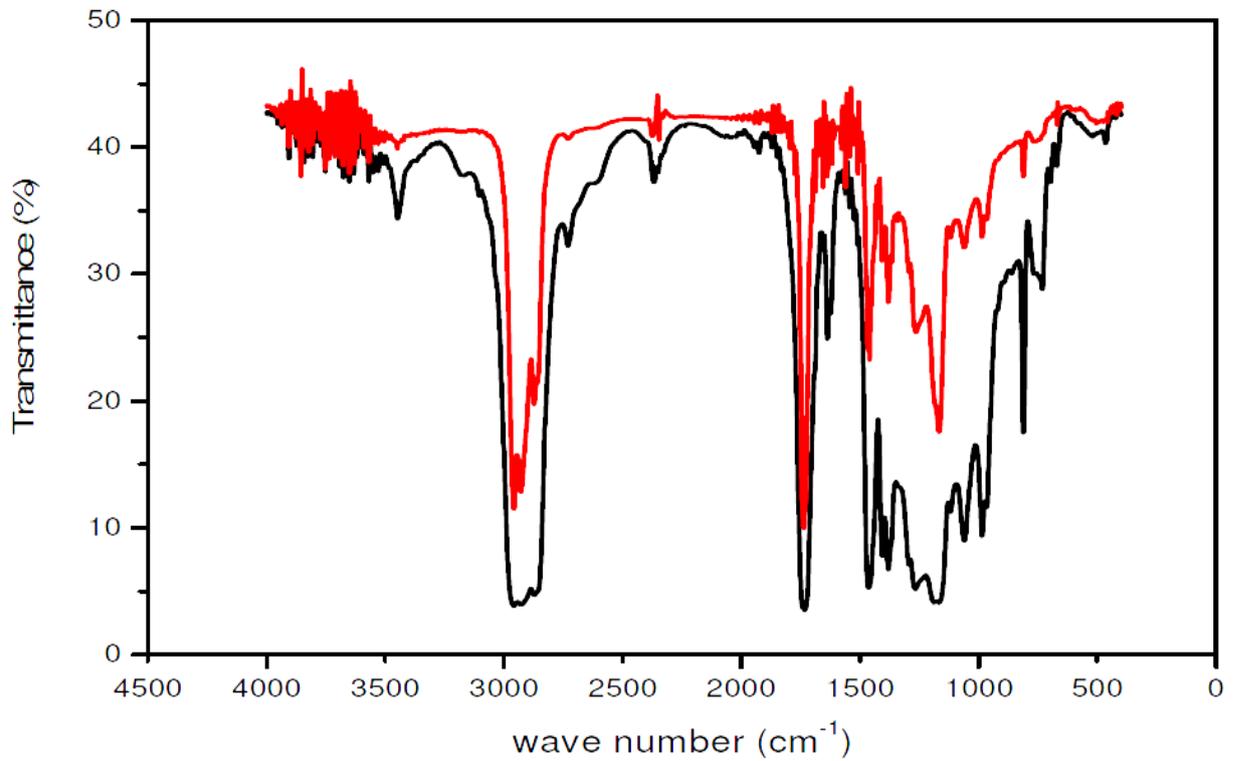
Figure 2.3.5: $^1\text{H-NMR}$ spectra of polymer P-5Figure 2.3.6: $^{13}\text{C-NMR}$ spectra of polymer P-5

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 B01 in various percentages

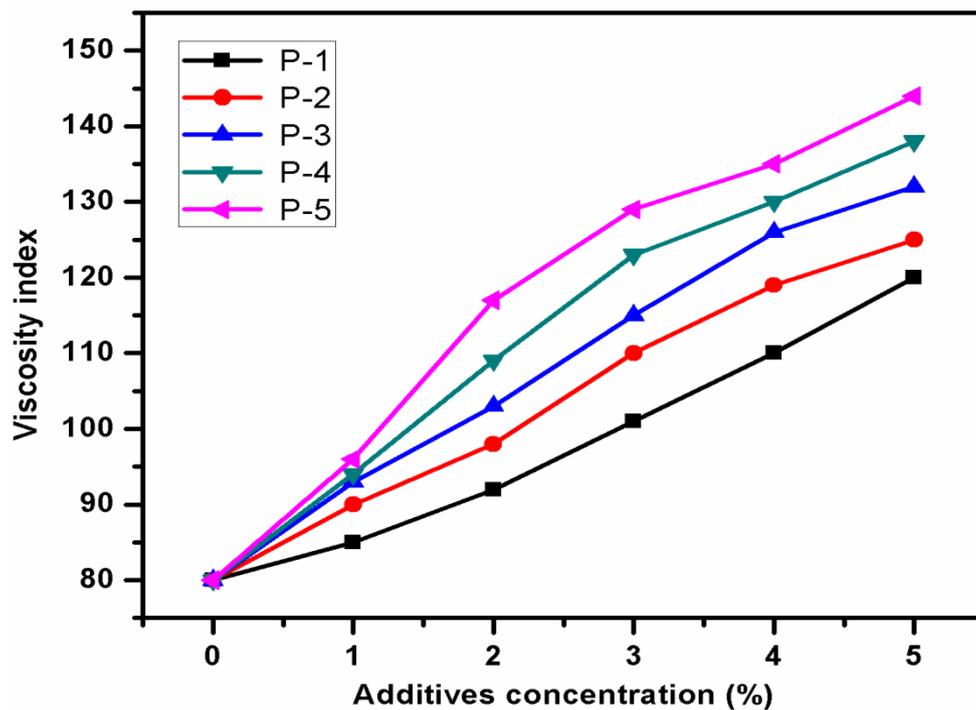


Figure 2.3.9: Viscosity index of the polymer blended B02 in various percentages

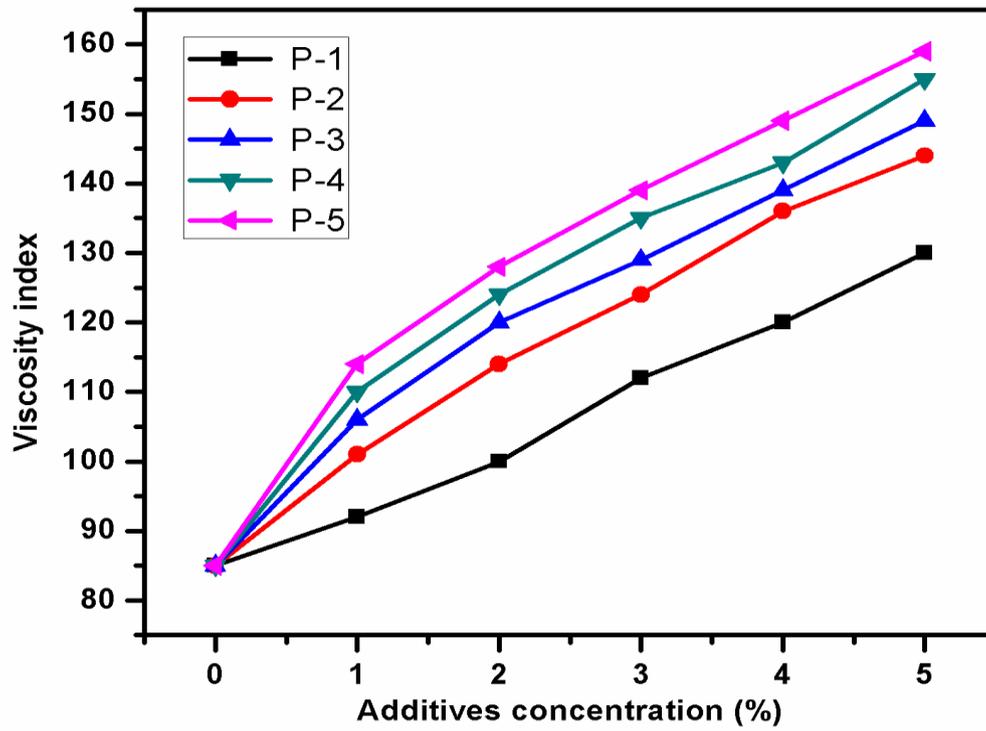


Figure 2.3.10: Pour point of the polymer blended B01 in various concentrations

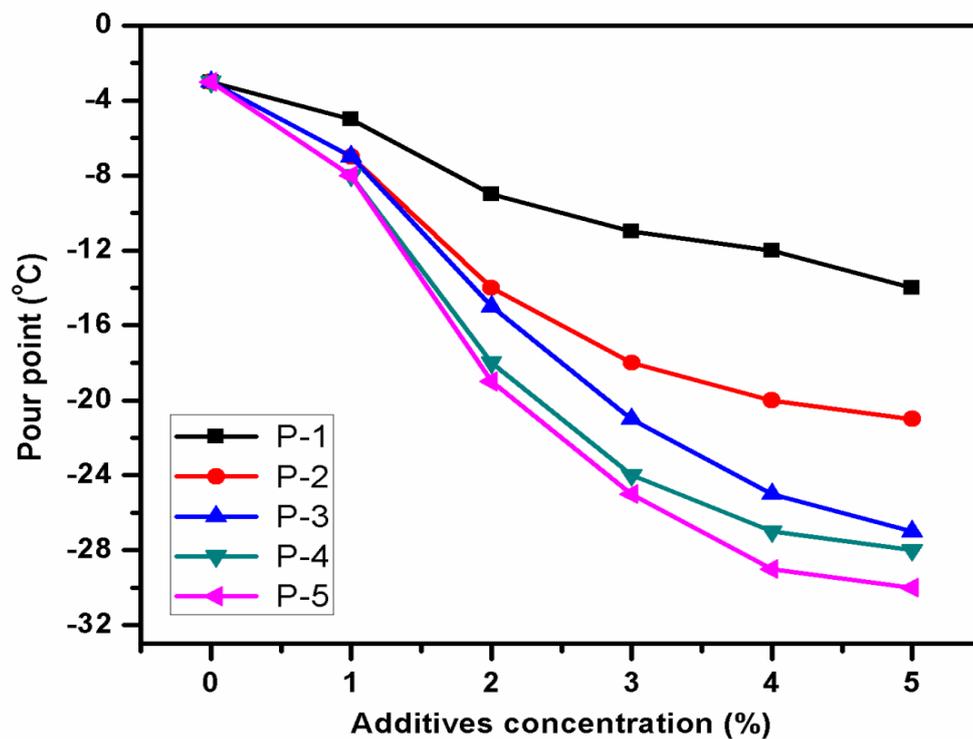
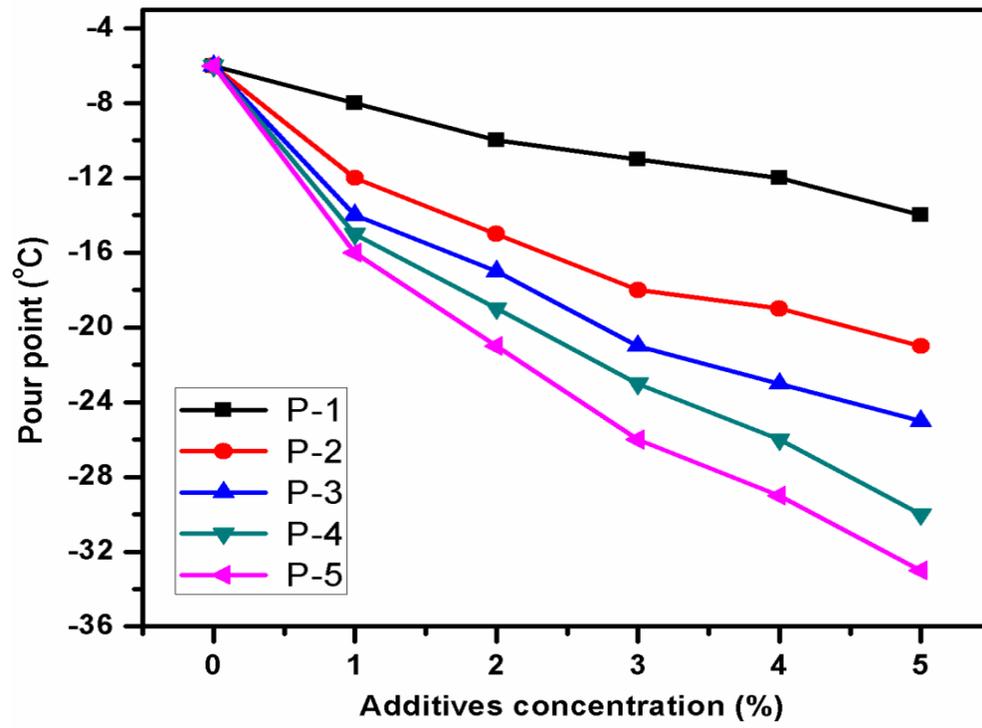


Figure 2.3.11: Pour point of the polymer blended B02 in various concentrations



Chapter-IV

*Sustainable lubricant additives based
on castor oil and α -pinene*

2.4.1 Introduction

The last few decades were the era for rapid progresses in science and technology. Their fast progresses have also augmented the production of synthetic materials globally every year. Among these materials, lubricants constitute a very large fraction. They are largely a mixture of a base oil and an additive.¹ The additives blended in the base oil have a wide variety of functions to deliver. They commonly are merged together as viscosity index improvers (VII) to bring about a variation in the viscosity index, to alter the low temperature fluidity as pour point depressants (PPD) and to keep many other parameters of the base stock to a satisfactory level.^{2,3}

Though quite a large number of additives have been formulated to specialize the new age lubricants, the poly acrylate and poly methacrylate based additives are still in use in massive amount.⁴ As a matter of fact, improvements of new age equipments are now indispensable without modern lubricant technology. Millions of tons of lubricants are produced every year to satisfy the mounting pressure from equipment manufacturers. It is estimated that about 40 million tons of lubricants are consumed globally every year.⁵

The present day lubricants are derived predominantly from petroleum base stocks and given their extensive carcinogenicity and toxicity, they are considered as potential soil and water pollutants. The problem even becomes graver when these petroleum-based products somehow enter the biosphere. It is argued that approximately 40% of these lubricants produced globally are reintroduced to the atmosphere annually through various non recoverable usages like refinery processes, urban runoff, industrial and municipal waste, accidental spillage etc.⁶ This can have severe biological effects

with the potential to destroy the biota locally. Several research groups reported the pernicious effects of mineral oils on the atmosphere.^{7,8}

Besides, with the rising demand of energy and the stock of fossil fuels declining all over the globe, there is an imperative need to explore some alternative biocompatible lubricants. In this investigation, lubricants derived from plant oils and their derivatives have gathered keen attention as an alternative to petroleum-based product and as a next generation lubrication solution. Even the escalating prices of mineral oils as compared to the plant oil in different parts of the world have forced to identify plant oils as a potential candidate for environment compatible lubricants. In addition to biocompatibility, these oils also have several other technical features that are ideal for their use in industrial application. With the high molecular mass of the triglyceride present in plant oils, they have a very little volatility and a nominal alteration in viscosity with temperature. The additive molecules and polar contaminants are also highly soluble in these plant oils.⁹

Unfortunately, plant oils also experience some of their inherent shortcomings. The bisallylic protons of the triglycerides are very prone to radical attack and therefore undergo oxidative cleavage to form polar oxy compounds.¹⁰ The compounds so formed eventually results in insoluble deposit and enhance the viscosity of the oil. These shortcomings have, therefore, limited their market share globally to about only about 1%.¹¹ Thus, to compete with petroleum based oils and to bring resurgence in their market share, the disadvantages that are present in these vegetable oils must be removed without compromising their excellent tribological and environmentally relevant properties. One possible answer to this is to provide more stability by reducing or eliminating the unsaturation present in the triglyceride structures of vegetable oils with polymerisation or to blend it with some more stable alternatives.

Moreover, in order to retain the biocompatibility of the final lubricant formulation, the additive in the lubricants must also be biodegradable. The lubricant and the additive industries have been working together in this direction to develop environmentally friendly green products. Some research groups have reported the use of plant oil derivatives as a base fluid and, therefore, a combination of plant oil based additives and a base fluid derived from plant oil can act as a valuable alternative to petroleum based products and incur biodegradability to it.^{6,12} Bio lubricants are considered as the lubricants of future and with over 100 species of tree born oil seeds available in India, it possess a great potential for production of bio lubricants from this seeds.¹³ As reported by the Food and Agriculture Organization of the United Nations (FAO), India is among the world's largest producer of castor beans. Castor oil or its derivatives have been exploited broadly in the formulation of several products like feedstock for fuels, various functional fluids, reactive components of paints, coatings, polymers, process oils and base oil for lubricants.¹⁴ Hence, due to its unique oleo chemical properties and in view of synthesizing new eco-friendly bio-additives, castor oil was chosen here. Again, α -pinene is a commonly seen terpenoid found in nature. It is a compound of the oils and resins of many species of coniferous trees especially the pine. It is also found in the oil of rosemary. In this study, homopolymer of castor oil and its copolymers with different proportion of α -pinene were produced. Their additive performances as VII and PPD were investigated through standard ASTM techniques for the base oils under examination. Besides, biodegradability of the synthesized polymers was also examined to assess their environmentally benign nature.

2.4.2 Experimental section

2.4.2.1 Materials

Castor oil (CO) was collected from a local grocer's shop and α -Pinene (GC 98 %) was purchased from Acros Organics (India). The solvent, toluene (GC 99.5%), was obtained from Merck Specialties Pvt., Ltd., (India). Methanol (GC 99.8%) was obtained from Thomas Baker Chemicals Pvt., Ltd., (India). Azobisisobutyronitrile (AIBN, GC 98%, to be used as an initiator) was purchased from Spectrochem Pvt., Ltd., (India) and was recrystallized from CHCl_3 - CH_3OH before use. The rest of the chemicals were used as obtained without further purification. The fungal specimen was collected from the Department of Microbiology, North Bengal University, West Bengal, India. The two mineral base oils (BO1 and BO2) were kindly supplied by Indian Oil Corporation Ltd. (IOCL), India. The physical properties of the base oils are shown in Table 2.4.1 and the fatty acid composition of castor oil is shown in Table 2.4.2.

2.4.2.2 Preparation of the homopolymer and copolymers

Preparation of the homopolymer of castor oil (HCO) and its copolymer with α -pinene in three different concentrations [5%, 7.5% and 10%, (w/w)] were carried out in a reaction kettle. To carry out the homopolymerization reaction, 20 gram of CO was placed in a reaction kettle fitted with a thermometer, condenser and an inlet for the introduction of nitrogen. 10mL of toluene was then added to the kettle and mixed thoroughly with CO. AIBN (0.2 gram) was subsequently added to the mixture for acting as an initiator for the polymerization reaction. Finally, the kettle was placed on a magnetic stirrer and the mixture was maintained at 363 K for 8 hour to prepare the homopolymer. After the fixed time, the reaction mixture was poured into methanol with continuous stirring to terminate the polymerization and precipitate the polymer. For

further purification, the polymers were dissolved in hexane and were repeatedly precipitated by methanol followed by drying under vacuum at 313 K.

For the copolymerization reaction, 20 gram total of CO was taken with 5%, 7.5% or 10% of α -pinene. The copolymerization was similarly carried out in a reaction kettle additionally attached with a dropping funnel to add α -pinene drop wise. The required mass of CO and initiator AIBN (1% by weight with respect to the monomers) was placed in the flask, followed by the drop wise addition of the required mass of α -pinene for 2 hours. The reaction temperature was maintained at 363 K for 48 hour until the polymerisations were complete. The polymers were then purified as reported for the homopolymer. The polymer designations and the composition of the monomers in the copolymers are given in Table 2.4.3.

2.4.2.3 Preparation of bio-additive based lubricating oil formulations

The prepared bio-additives (polymers) were mixed with the two types of base oils (BO1 and BO2) in different percentage ratios (1% to 5%, w/w). The blends were stirred in batches of 200cm³ at 323 K for 4 hour, at a rotational speed of 300 rpm, to obtain uniform additive dispersion in the lubricants. The blends were then cooled down to room temperature for further study.

2.4.3 Measurements

2.4.3.1 Spectroscopic measurements

For recording the NMR spectra, the selected instrument was a Bruker Avance (Germany) 300 MHz FT-NMR using a 5 mm BBO probe. Here CDCl₃ was used as solvent

and tetramethylsilane (TMS) as a reference material. The infrared spectra were recorded on a Shimadzu (Japan) FT-IR 8300 spectrometer, within the wavenumber range of 400 to 4000 cm^{-1} using 0.1 mm KBr cells at room temperature.

2.4.3.2 Thermo-oxidative stability measurements

A thermogravimetric analyzer (Shimadzu TGA-50, Japan) was used to establish the thermo-oxidative stabilities of all the prepared additives. The additives were heated in air using an alumina crucible at a rate of 10 $^{\circ}\text{C}$ per min. Their thermal stability can be measured in terms of percentage of weight loss (PWL) or percentage of residual weight with rise in temperature. The PWL was determined by the equation,

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

where M_0 is the initial mass and M_1 is the remaining mass after the test until constant weight.

2.4.3.3 Determination of average molecular weight

A GPC device (Waters Corporation, USA) was used to establish the average molecular weight (M_w and M_n) and PDI (M_w/M_n) of the prepared additives. The GPC arrangement (polystyrene calibration) was connected with a 2414 refractive index detector, Waters 515 HPLC pump and a 717 plus autosampler. HPLC grade THF was used as an eluent for the instrument at a flow rate of 1.0 mL/min at 30 $^{\circ}\text{C}$. Table 2.4.4 shows the average molecular weight values as calculated by GPC.

2.4.3.4 Evaluation of pour point (PP)

The pour points of the base oils mixed with different amount of the prepared additives were tested in the temperature range of 0 to -71 °C according to ASTM D97 method on a cloud and pour point tester (Wadegati labequip Pvt., Ltd., India).

2.4.3.5 Evaluation of viscosity index (VI)

The alteration of kinematic viscosity (KV) of oil with the variation of temperature is denoted by an arbitrary dimensionless number called viscosity index (VI). A higher value of VI signifies a relatively small change in viscosity with the temperature variation.

The VI was evaluated according to the ASTM D2270 method for the two base oils blended with different percentages of the additive at 313 K and 373 K (ASTM 2004). The effectiveness of an additive as VII is assessed by the increase in the VI value of the base oils after addition of the additive. The KV was determined by the equation,

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

where K and L are viscometric constants; t is the time of flow of the lube oil blended with different mass fraction of the additive to pass through the two calibrated marks in the Ubbelohde viscometer and ρ is density of the additive doped lube oil.¹⁵

The densities of the additive doped oils were determined with the help of a DMA 4500 M vibrating-tube density meter (Anton paar, Austria) and the time of flow of the oils was recorded with a digital stopwatch. All the measurements per batch were made in duplicate. The VI value was determined from the following standard empirical equation,

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

where n is a constant depending upon the temperature range chosen for the oil. The value of n was calculated by the equation,

$$n = (\ln v_1 - \ln k) / \ln v_2 \quad \text{Eq. (4)}$$

where v_1 and v_2 are the kinematic viscosities of the oil blended with the additive at lower and higher temperature respectively. The value of k is independent of the nature of the oil and is a function of temperature alone. For the given temperature range, the value of k was found to be 2.715.¹⁶

2.4.3.6 Photo micrograph and wax modification

The photomicrographs presenting wax crystallization behaviour of the base oils mixed with different ratios of the prepared additive were recorded in a Banbros polarizing microscope (BPL-400B, India). The temperature was set at 273 K and it was suitably controlled on the microscope slide by an attached cooling thermostat. The magnification used here was 200X.

2.4.3.7 Biodegradability test

Biodegradation can be defined as the mineralisation or breakdown of an organic matter due to microbial activity, leading to a significant change in its chemical structure. If complete biodegradation takes place under aerobic conditions the material will be converted to carbon dioxide and water, while under anaerobic conditions the organic carbon of the material will be converted to biogas. In both cases, the organic carbon is also partly converted to new biomass.

Out of the several techniques of examining the chemicals for biodegradation, the soil burial degradation test as per ISO 846:1997 and the disc diffusion test against fungal pathogen were chosen here.^{17,18} PWL [Eq. (1)] of the additives was analysed to examine the magnitude of degradation in the burial test. The shift in the IR frequency of the ester carbonyls after the biodegradability test along with the change in their molecular mass was also a parameter to judge the degradation of the additives.

2.4.3.7.1 Soil burial degradation test (SBD test)

The soil used for this test had been obtained from the campus of North Bengal University (West Bengal, India) with a measured value of pH 7.2 and moisture content of 26%. The soil was first taken in a humidity chamber, set at 303 K, to adjust the relative humidity to around 60%. Separate polymeric films were produced from all the additives by taking 2 gram of the additives in each case.¹⁹ The films were then buried in the soil (containing the microorganisms) in a bacteriological incubator (Sigma Scientific Instruments Pvt., Ltd., India). After every 15 days, the buried additive films were taken out for analysis and the process was repeated for a period of 90 days with a different film used for each time period. The recovered polymeric films were cleaned with chloroform, filtered with Whatman grade 41 filtration paper and then dried in a vacuum oven at 323 K. They were again purified by dissolution in hexane and reprecipitation with methanol followed by drying under vacuum at 323 K to constant weight. For each of the films, the weights after drying were recorded to verify the percentage of weight loss.

2.4.3.7.2 Disc diffusion (DD) test

The disc diffusion test includes the arrangement of culture media for the fungal strains and assessing the biodegradation of the additives against fungal pathogens. Here the biodegradation was tested for the fungal pathogen, *Alternaria alternate* (AA). For creating the culture media, dextrose, agar powder and potato extract were mixed in a ratio of 1:1:10 by weight. For this test, 2 gram of the synthesised additive was taken in a sterilized Petri dish and inoculated by spraying the fungal pathogen. To keep away from any further contamination, the sterilized Petri dish was sealed by wax and incubated at 310 K in a bacteriological incubator. The whole procedure was implemented for all the additives separately with the fungal pathogen. During incubation, the spores (colonies) emerging as black spots were observed to grow suggesting the fungal growth on the additives. After a stretch of 30 days, the additives were recovered from the culture and rinsed with chloroform, filtered with Whatman grade 41 filtration paper and dried in a vacuum oven at 323 K. PWL was computed for all the additives and their molecular weights were calculated by GPC analysis.

2.4.4 Results and discussion

2.4.4.1 Spectroscopic data analysis

FT-IR Spectroscopy: The FT-IR spectra of HCO (P-1, homopolymer of castor oil) showed signal for the stretching vibration of ester carbonyl group (C=O) at 1741 cm^{-1} while the peak (broad) for ester C–O stretching vibration appeared at 1174 cm^{-1} . Peaks in the region of 1460 cm^{-1} , 1375 cm^{-1} and 724 cm^{-1} were for the bending vibrations of the C–H bonds. The intense absorptions at 2855 cm^{-1} and at 2927 cm^{-1} are attributed to the stretching vibrations of the paraffinic C–H bonds. The broad IR transmission at 3438 cm^{-1} indicated the presence of O–H stretching of the alcoholic moiety of ricinoleic acid

present in castor oil (Fig. 2.4.2). Additives P-2, P-3 and P-4 have almost similar IR peaks (Figs. 2.4.3, 2.4.4 and 2.4.5). In their spectra, the peaks at 1746, 1744 and at 1745 cm^{-1} pointed out the existence of ester carbonyl groups. The ester C–O proved their presence by vibrating (stretching vibrations) at 1168, 1172 and 1168 cm^{-1} respectively. Their IR spectrum also had characteristic peaks at 721 to 724 cm^{-1} , 1373 to 1375 cm^{-1} and 1451 to 1461 cm^{-1} representing the bending vibrations of the C–H bonds for the methylene and methyl groups of castor oil and α -pinene. The observed transmissions at 2852 to 2855 cm^{-1} and 2919 to 2926 cm^{-1} were caused by the stretching of C–H bonds. The characteristics O–H stretching peaks were present in all the additives at 3414, 3406 and at 3417 cm^{-1} respectively. The lack of any peaks in the range of 1600 cm^{-1} to 1680 cm^{-1} pointed out the nonexistence of any olefinic carbon in the additives and therefore the formation of the desired product.

¹H-NMR: The proton NMR spectroscopy showed multiple peaks in the spectra of the additives. HCO showed signal for the methyl protons at δ 0.82 ppm while the signals in the range of δ 1.24 to 2.16 ppm appeared for the methylene protons of alkyl groups. The presence of $-\text{OCOCH}_2-$ moiety in castor oil is showed by the chemical shift between δ 2.25 and 2.27 ppm while the hydrogens of the $-\text{OH}$ group of ricinoleic acid appeared as broad peak centered at δ 3.57 ppm. The signals in the spectra between δ 4.09 and 4.25 ppm appeared due to the protons of $-\text{COOCH}_2$ groups of the triglyceride of castor oil. Any useful proton peaks were found to be missing between δ 5.5 and 6.5 ppm signifying complete utilisation of olefinic groups in the polymerisation process (Fig. 2.4.6). The other copolymer (P-2 to P-4) showed nearly similar chemical shifts between δ 0.81 and 0.82 ppm for the methyl protons. The peaks between δ 1.24 and 2.19 ppm appeared because of the methylene protons of castor oil and α -pinene, while the signals between δ 2.22 and 2.69 ppm is attributed to the protons of $-\text{OCOCH}_2-$ groups. The peaks

between δ 3.54 to 3.66 ppm are credited to the -OH group of castor oil while the protons of -COOCH₂ groups showed signals in the range of δ 4.04 to 4.26 ppm. Also the nonappearance of any signals between δ 5.5 and 6.5 ppm in the proton NMR spectra point towards the absence of sp² carbons in the copolymers (Figs. 2.4.7, 2.4.8 and 2.4.9).

¹³C-NMR: All the sp³ (-CH₃ and -CH₂) carbon atoms of the alkyl chain of castor oil, present in HCO, appeared between δ 12 and 36 ppm in the ¹³C NMR spectra. The -COOCH₂ groups in the triglyceride backbone of castor oil indicated their presence by the signals between δ 61 and 68 ppm. Peak appearing at δ 70 ppm indicated the carbon joined to the -OH group of the ricinoleic acid present in castor oil and the signals between δ 172 and 173 ppm is credited to the carbonyl carbon of the ester group. HCO displayed no peaks between δ 120 and 150 ppm, signifying the successful conversion of olefinic carbons to saturated carbons during polymerisation (Fig. 2.4.10). The other polymers (P-2, P-3 and P-4) displayed similar ¹³C spectra with observed transmissions between δ 14 and 37 ppm indicating the sp³ carbons of castor oil and α -pinene. The signals between δ 62 to 69 ppm are attributed to the presence of -COOCH₂ groups of the triglyceride moiety. The peaks ranging from δ 70 to 72 ppm appeared because of the carbon joined to the -OH group in castor oil while the carbonyl carbons showed their presence between δ 170 and 178 ppm. Also, no signals were present between δ 120 and 150 ppm in any of the copolymers (Figs. 2.4.11, 2.4.12 and 2.4.13).

2.4.4.2 Thermogravimetric analysis (TGA)

Fig. 2.4.16 presents a comparative data of the thermogravimetric analysis of the synthesised additives. After thermal degradation, at 300 °C, the percentages of residual weight of the additives P-1, P-2, P-3 and P-4 were found to be 50.35, 79.53, 75.19 and

73.23 respectively. At 400 °C the amount (percentages of residual weight) left were 2.28, 52.65, 46.36 and 43.84 respectively. The results showed that the copolymers were better in thermo-oxidative stability than the homopolymers. Moreover, as suggested by the percentage of residual weight values, the thermal strength of copolymers increased with decreasing α -pinene fraction in the additives. Also, the thermal degradation of additive P-2 was found to be the least. This increased thermal stability of the additive P-2 is probably due to its comparatively narrower molecular weight distribution (as suggested by the PDI value) and the highest molecular weight among the additives.²⁰

2.4.4.3 Analysis of pour point data

The pour points of the additive-doped lube oils were tested by mixing the additives at different fractions (1% to 5%, w/w) with the base oils (B01 and B02) and the investigational results are plotted in Figs. 2.4.17 and 2.4.18. It is clearly noticed that the effectiveness of the additives as PPD gradually became better with increase in their concentration in the base oils. Moreover, with the increment of α -pinene fraction in the additive their effectiveness as PPD gradually decreased. PPDs typically have no impact on the crystallization temperature. Though, the improvement in the PPD properties of an additive is as a consequence of disruption of the rigid network of wax crystals that are formed at lower temperatures from the dissolved waxy hydrocarbons present in mineral oils. The size and growth of wax crystals can be suitably controlled by PPDs and thereby the ability of these crystals to flocculate and interlock among themselves.²¹

These depressants control the crystal growth either by adsorption on the precipitating wax or by cocrystalization. PPDs typically have a paraffinic part that resembles the wax structure and, hence, cocrystallizes with the oil's wax forming

components and becomes associated with them while the polar section present in the PPDs confines their extent of cocrystallization.²² Improved wax solubility and nucleation are also among the other theories suggested for the mechanism of action of PPDs.²³ The PPD property of the additive P-1 was better here as compared to the other additives with different concentrations of α -pinene. The reason for this is possibly the better interaction of additive P-1 with the wax crystals when compare to the others. The extent of interaction varies with the polarity of additive molecules and a more polar additive can form stronger H-bond with the polar groups of resin and asphaltene present in the base oil.²⁴ The high percentage of ricinoleic acid (with polar hydroxyl group) in castor oil (Fig. 2.4.1) makes them highly polar and the incorporation of α -pinene in the castor oil moiety diminishes the polarity of the overall additive molecule. This reduction in their polarity decreases their effectiveness to act as an efficient PPD.

2.4.4.4 Analysis of viscosity index data

The result, as presented in Fig. 2.4.19, explains that the VI of the base stocks mixed with the additives were significantly superior compared to the base stocks lacking the additives. The investigation also revealed that irrespective of the nature of the base stock and the additive, the VI improved with enhancement in the additive concentration. All the additives (P-1 to P-4) showed excellent results but the incorporation of α -pinene to CO enhanced the VI to a much greater extent. Among all the additives, at a 5 wt % of additive concentration, additive P-4 showed the highest increase of VI for both the base stocks (VI value 167 for B01 and 174 for B02). At the same concentration, additive P-1 (HCO) produced a VI of only 144 and 150 for B01 and B02 respectively. The VI values as plotted in Fig. 2.4.19, increased in the order P-1 < P-2

< P-3 < P-4. The ability to act as a viscosity index improver, by any polymer, is governed by its chain topology, temperature dependent solubility, molecular weight and structure of polymeric macromolecules.²⁵ These factors decide the hydrodynamic volume of the haphazardly curled polymer chain which in turn compensates the reduction of the viscosity of the base oil with increasing temperature. It is believed that in the base oil, the polymer molecules remain in a coiled shape. With increasing temperature, the polymer coils expands ensuing an enhancement in polymer chain entanglements. Besides, with increase in polymer percentage, the interaction between the base oil and these macromolecules also increases ensuring a greater thickening and a higher VI for the oil.²⁶ The VI obtained for the copolymers here are higher than P-1 and the results may be attributed to their greater molecular weight and narrower molecular weight distributions. Polymers with hyper-branched structure and with the compact chain arrangement have a reduced hydrodynamic volume compared to the polymers of linear chain topology of similar molecular weight. Additionally, as a result of their restricted hydrodynamic volume, these hyper-branched polymers hinder the spreading out of polymer coil dimension resulting in reduced chain entanglements among themselves.²⁷ Hence, additive P-4 with high molecular weight and the most linear chain topology produced a greater thickening of the oil and in doing so generated the highest VI.

2.4.4.5 Analysis of photo micrographic image

The study of photo micrographic image of the lube oil helps to understand the effect of additives on their pour point values. The photomicrographs depicted in Fig. 2.4.20 gave a picture of the variation of wax morphology according to the nature of additives added. Fig. 2.4.20a, which represents the pure base oil, showed large cyclic

and needle shaped wax crystals of approximate size of 100 μm . The base oil when blended with 4% (w/w) of the additives, showed a substantial reduction in the size of wax crystals. The large crystals were converted into numerous finely dispersed crystals. A higher wax alteration was noticed for the additive P-1 (Fig. 2.4.20b) with most finely dispersed wax crystals while the additive P-4 (Fig. 2.4.20e) showed the least wax modification. Study of the photomicrographs thus revealed that additive P-1 acted as a better PPD than the other additives. So, the wax modification results, as illustrated by the photomicrographs are in good agreement with the flow parameter (pour point) of the additives determined by the ASTM method.

2.4.4.6 Analysis of biodegradability test

The additives here are all synthesised from natural monomer units and are likely to show significant amount of biodegradability. The biodegradability test results procured by analysing the disc diffusion test and the soil burial test methods are presented in Table 2.4.5 and Fig. 2.4.21 respectively and the results reflected plenteous bio-assimilation for the additives.

In the SBD test, the breakdown of all the additives by the soil microbes escalated with the increasing number of days. After 90 days, the additive P-1 exhibited the highest degradation among the other additives with a weight loss of 27.6%. After the same time period, additive P-4 exhibited a weight loss of 19.5% which is least amid all the additives.

The analysis of the DD test also displayed similar trend against the fungal pathogen. The bio-assimilation of additive P-1 was the highest in this test as well with 30.3 % weight loss after a span of 30 days. The PWL of the other additives (P-2, P-3 and

P-4) were 26.7, 22.9 and 19.7 respectively after the same stretch of 30 days. GPC of the additives after the DD test was also conducted and the numbers were compared with the respective additives before biodegradation (Table 2.4.5). The figures reflected sizeable change in the M_n and M_w of the additives and thus revealed the biodegradability of the prepared additives.²⁸

The FT-IR spectra of the additives, before and after the DD test were also studied to identify any shift in their IR peaks (Figs. 2.4.14 and 2.4.15). The signal of the ester carbonyl group at 1741 cm^{-1} , for the additive P-1, shifted noticeably to 1728 cm^{-1} with a decrease in the peak height and intensity after the test. IR transmissions of the additive at 724, 854, 1174, 1243, 1375, 1460 and 3438 cm^{-1} has also shifted markedly after the DD test. Similar shift in the IR signals were noticed for the other additives as well. This shift in the IR peaks is possibly due to the scission of the polymer units after biodegradation.²⁹ These variations in the IR peaks of the additives, the change in their weight-average molecular weight (M_w) and number-average molecular weight (M_n) along with their PWL confirmed the biocompatible property of the prepared additives.

2.4.5 Conclusions

In this work, thorough analyses of the synthesised polymers were carried out to assess their performance as a multifunctional additive. The results pointed out that mixing of these additives to the base oil improved their lubricant property greatly. A comprehensive study of the additives showed that the copolymers were superior as VII. The most significant viscosity increment was displayed by the additive P-4 while the additive blend P-1 exhibited superior performance as PPD for the lube oils under examination. The application of copolymer always yielded a significant increase in

thermal stability and the additive P-2 had the best performance. Furthermore, the study illuminated that all the additives are also environmentally benign. Therefore, the prepared bio-additives may be used for designing green bio-lubricant formulations for lube oil to satisfy the mounting environmental and performance concerns of modern lubricants.

2.4.6 References

References are given in BIBLIOGRAPHY under Chapter-IV of Part-II (Page No. 220-223).

2.4.7 Tables and figures

Table 2.4.1: Physical properties of base oils

Properties	Method	B01	B02
Viscosity at 40 °C in cSt	ASTM D445	7.229	23.472
Viscosity at 100 °C in cSt	ASTM D445	1.874	3.938
Viscosity Index	ASTM D2270	81	86
Pour Point, °C	ASTM D97	-3	-6
Density (g.cm ⁻³) at 40 °C	ASTM D4052	0.83689	0.85514

Table 2.4.2: Fatty acid composition of castor oil

<i>Fatty acid</i>	<i>Average % composition</i>
Palmitic C16:0	1.7
Stearic C18:0	1.9
Oleic C18:1	5.3
Linoleic C18:2	7.0
Linolenic C18:3	1.5
Ricinoleic C18:1:OH	82.4

Table 2.4.3: Percentage composition and designation of the polymers

<i>Polymers</i>	<i>% of monomers in the polymers</i>		<i>Solvent, Initiator</i>
	<i>Castor oil</i>	<i>α-pinene</i>	
P-1	100	0	Toluene, AIBN
P-2	95	5	Toluene, AIBN
P-3	92.5	7.5	Toluene, AIBN
P-4	90	10	Toluene, AIBN

P-1: Homopolymer of castor oil, P-2: Copolymer of castor oil + 5% α -pinene, P-3: Copolymer of castor oil + 7.5% α -pinene, P-4: Copolymer of castor oil + 10% α -pinene.

Table 2.4.4: Average molecular weight of polymers determined by GPC

Polymers	Average molecular weights		
	M_w	M_n	PDI
P-1	17882	11247	1.59
P-2	30214	21428	1.41
P-3	29636	21952	1.35
P-4	28574	23421	1.22

Table 2.4.5: Result of biodegradability test by DD method and comparative average molecular weight values determined by GPC

Polymers	Incubation period (days)	Pathogen	PWL	Molecular weight			
				Before biodegradation		After biodegradation	
				M_w	M_n	M_w	M_n
P-1	30	AA	30.3	17882	11247	15978	10902
P-2	30	AA	26.7	30214	21428	27228	20267
P-3	30	AA	22.9	29636	21952	27134	20873
P-4	30	AA	19.7	28574	23421	26965	22321

Figure 2.4.1: Triester of glycerol and ricinoleic acid (structure of the major component of castor oil)

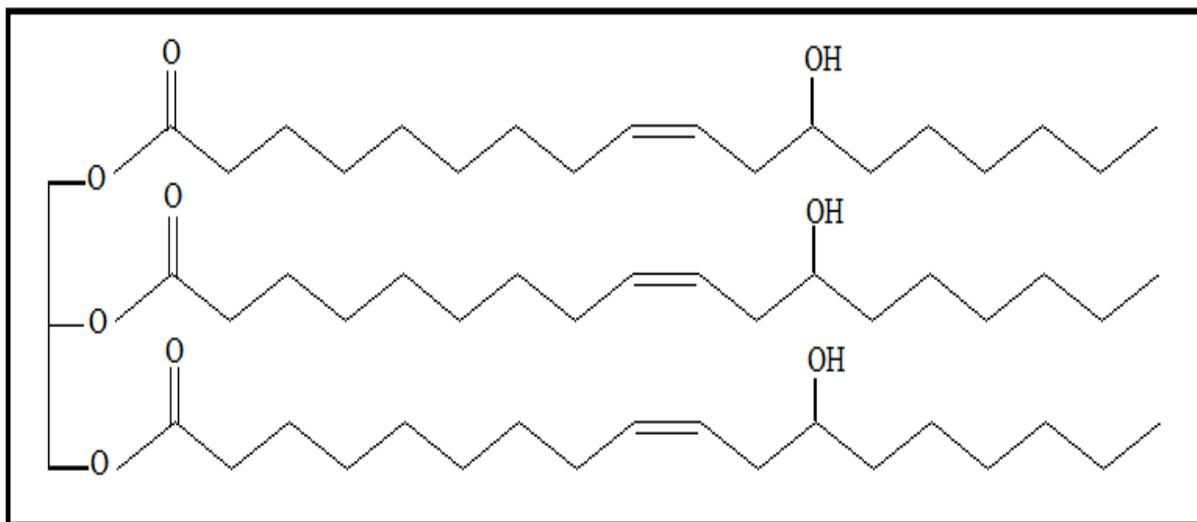


Figure 2.4.2: FT-IR spectra of homopolymer of CO (P-1)

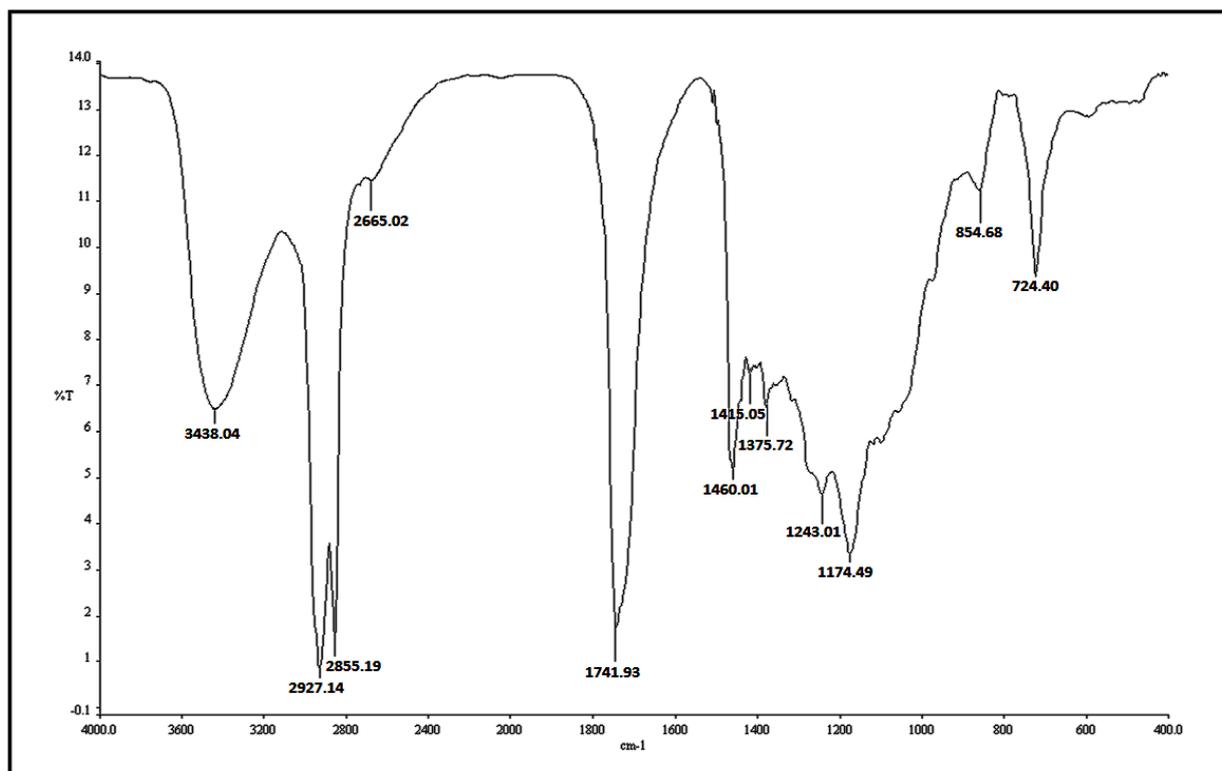


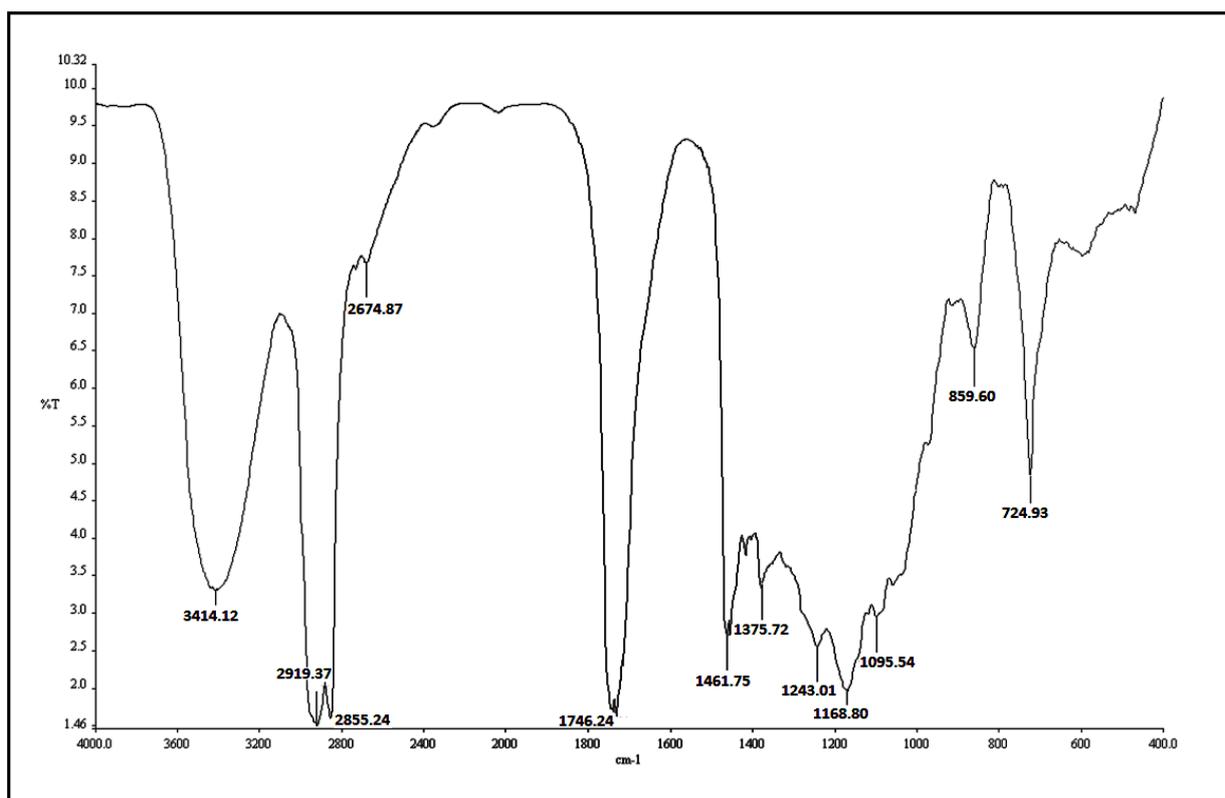
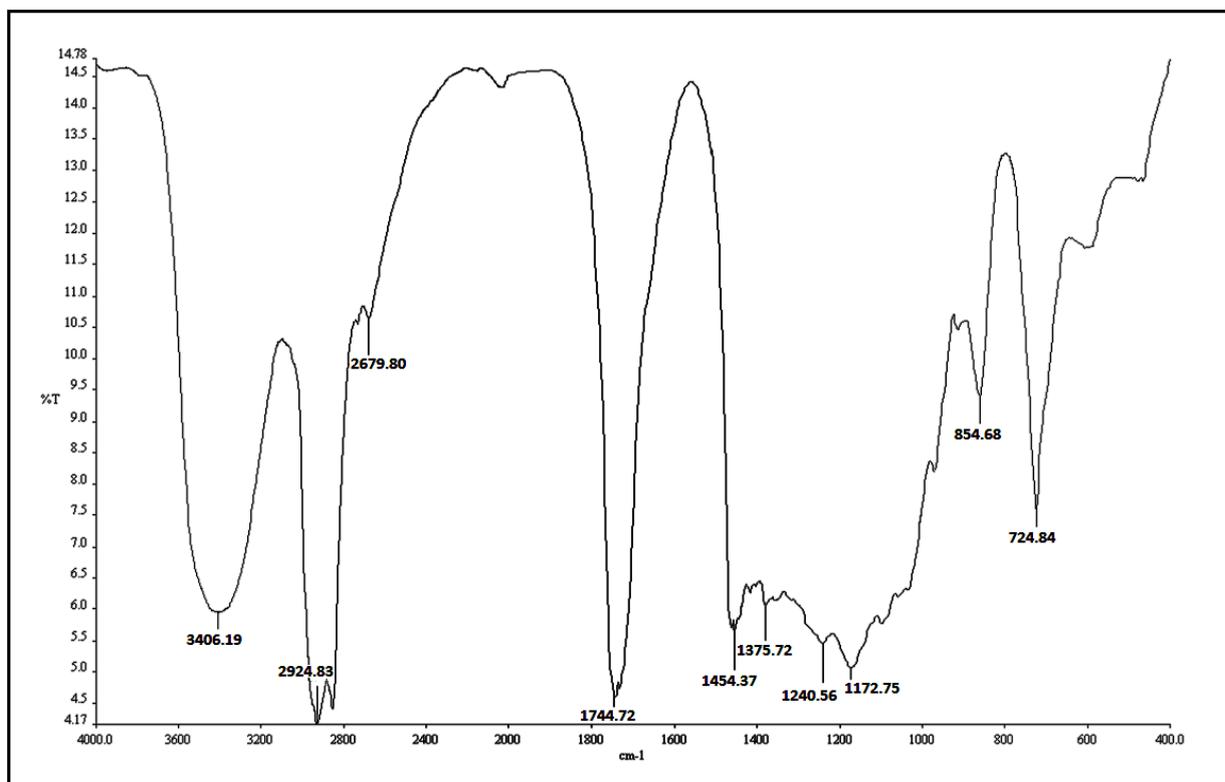
Figure 2.4.3: FT-IR spectra of copolymer of CO with 5% α -pinene (P-2)**Figure 2.4.4: FT-IR spectra of copolymer of CO with 7.5% α -pinene (P-3)**

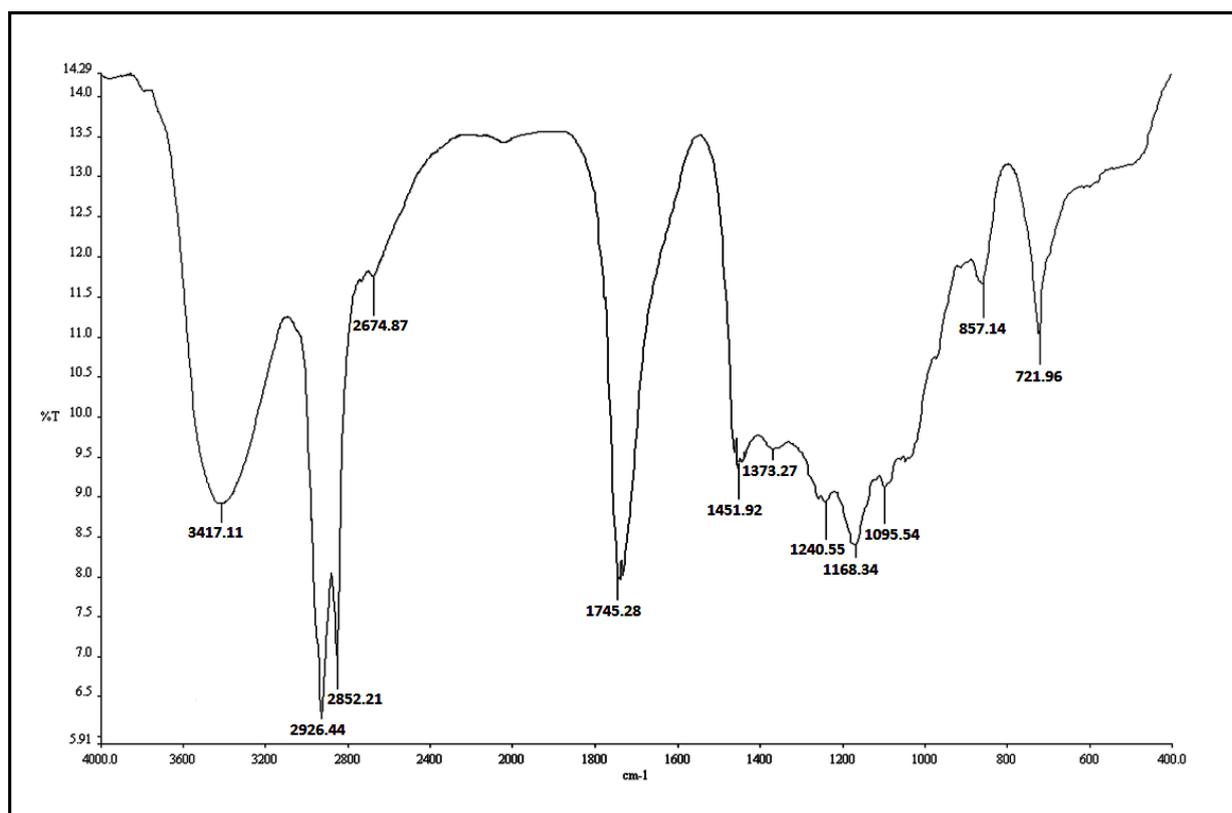
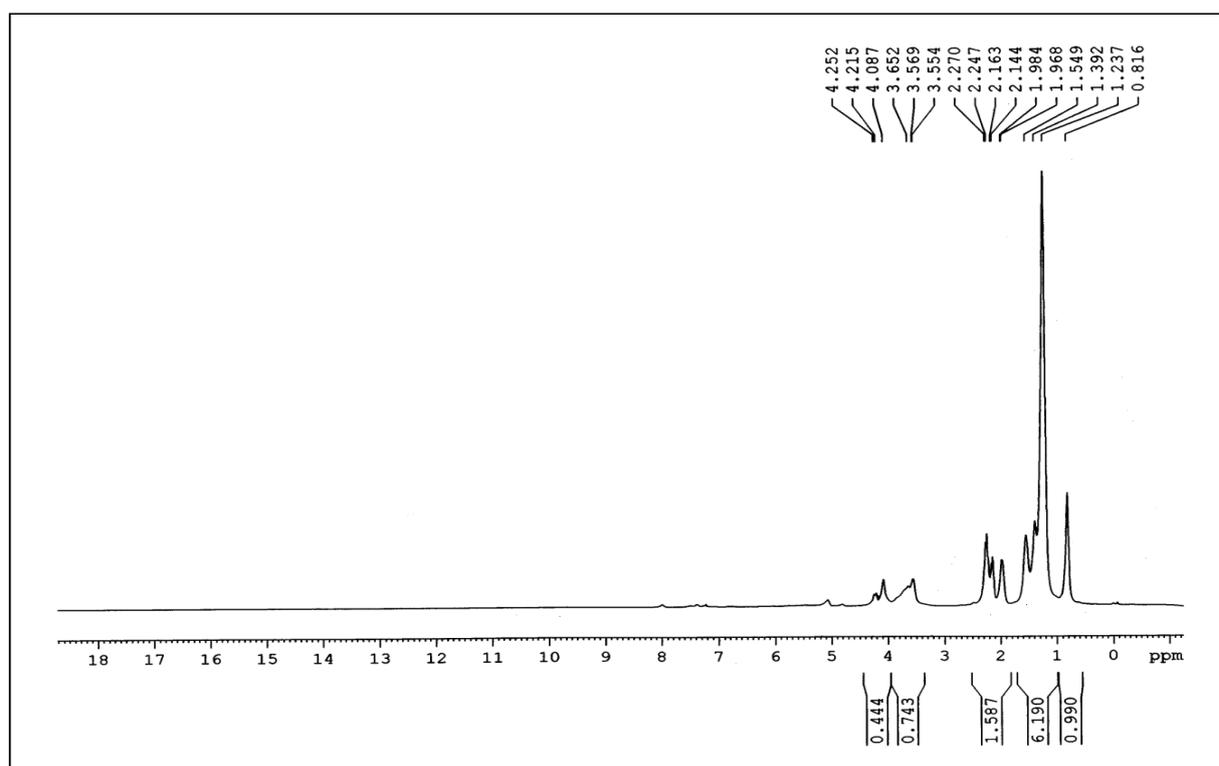
Figure 2.4.5: FT-IR spectra of copolymer of CO with 10% α -pinene (P-4)Figure 2.4.6: $^1\text{H-NMR}$ spectra of homopolymer of CO (P-1)

Figure 2.4.7: $^1\text{H-NMR}$ spectra of copolymer of CO with 5% α -pinene (P-2)

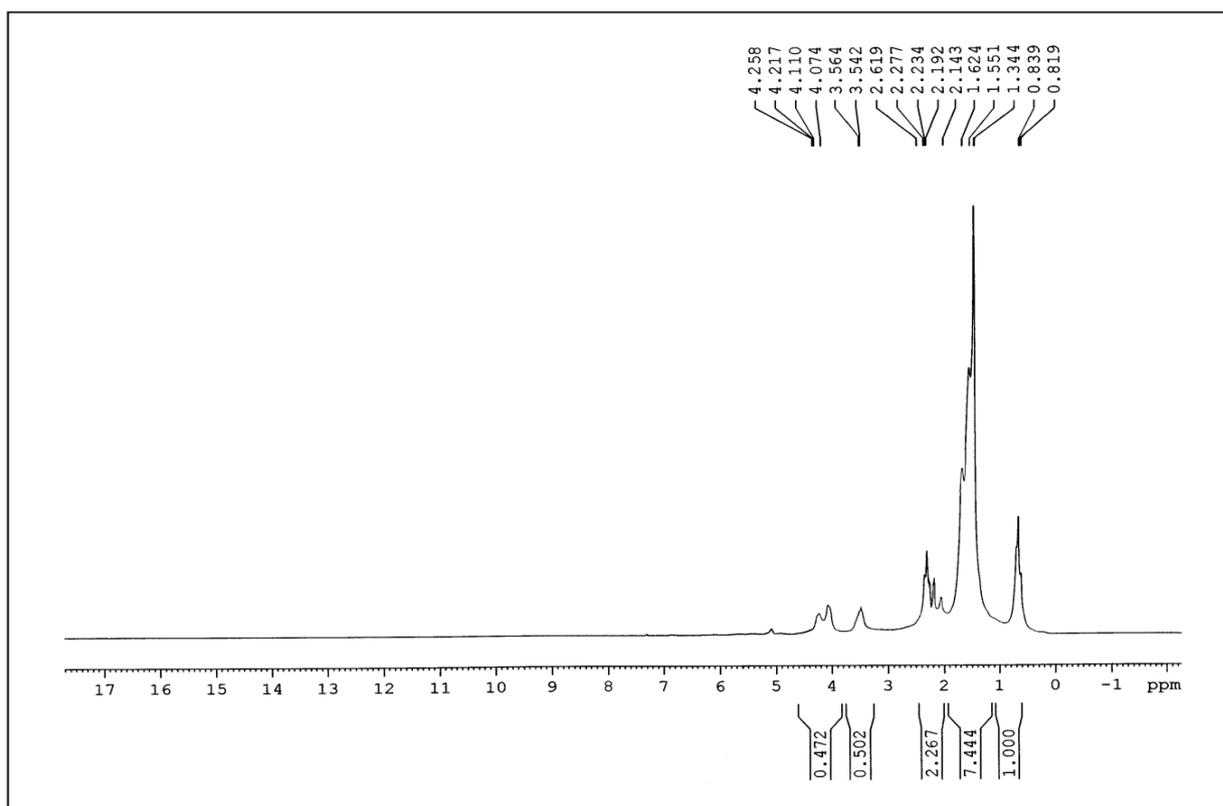


Figure 2.4.8: $^1\text{H-NMR}$ spectra of copolymer of CO with 7.5% α -pinene (P-3)

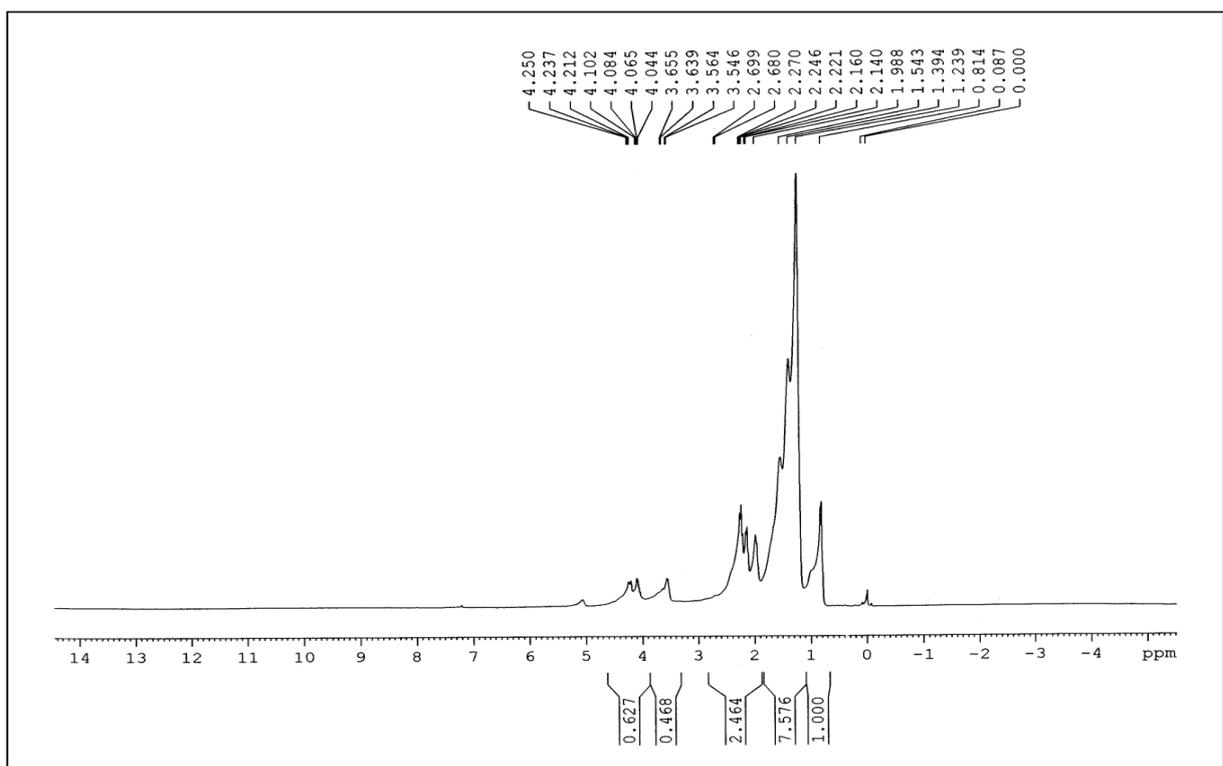


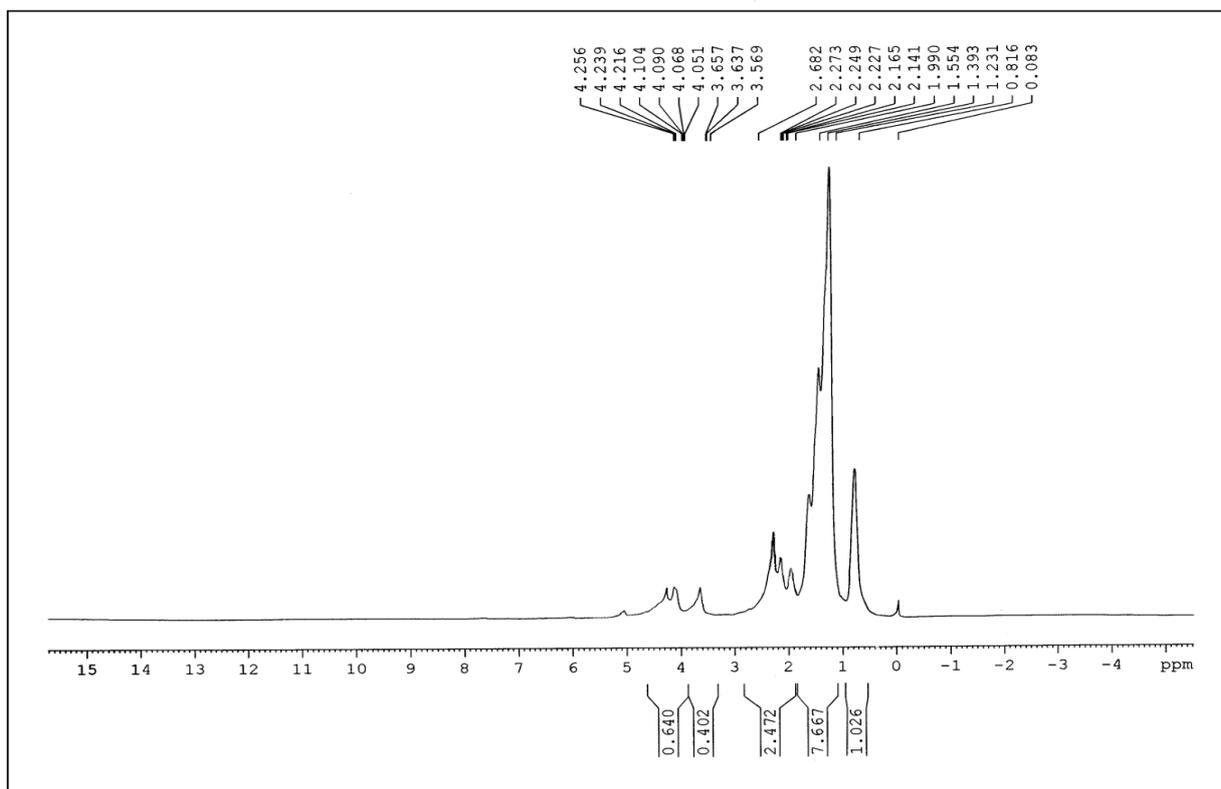
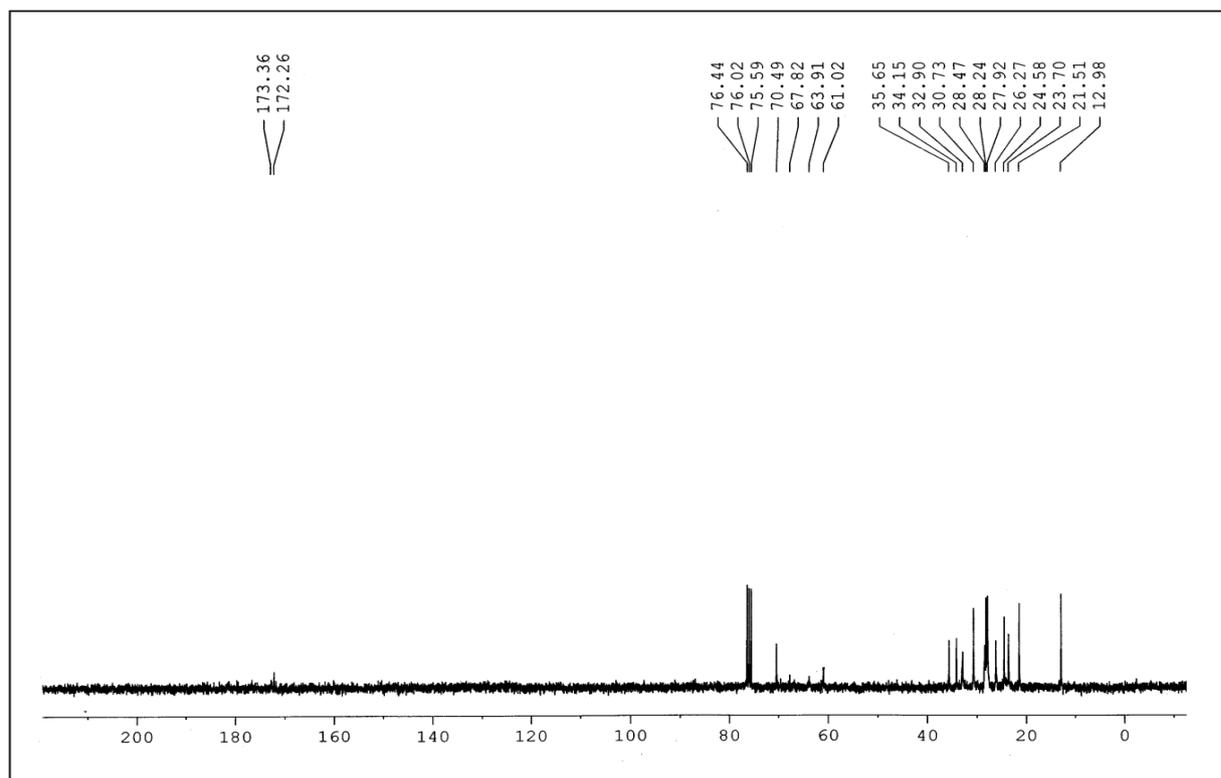
Figure 2.4.9: $^1\text{H-NMR}$ spectra of copolymer of CO with 10% α -pinene (P-4)Figure 2.4.10: $^{13}\text{C-NMR}$ spectra of homopolymer of CO (P-1)

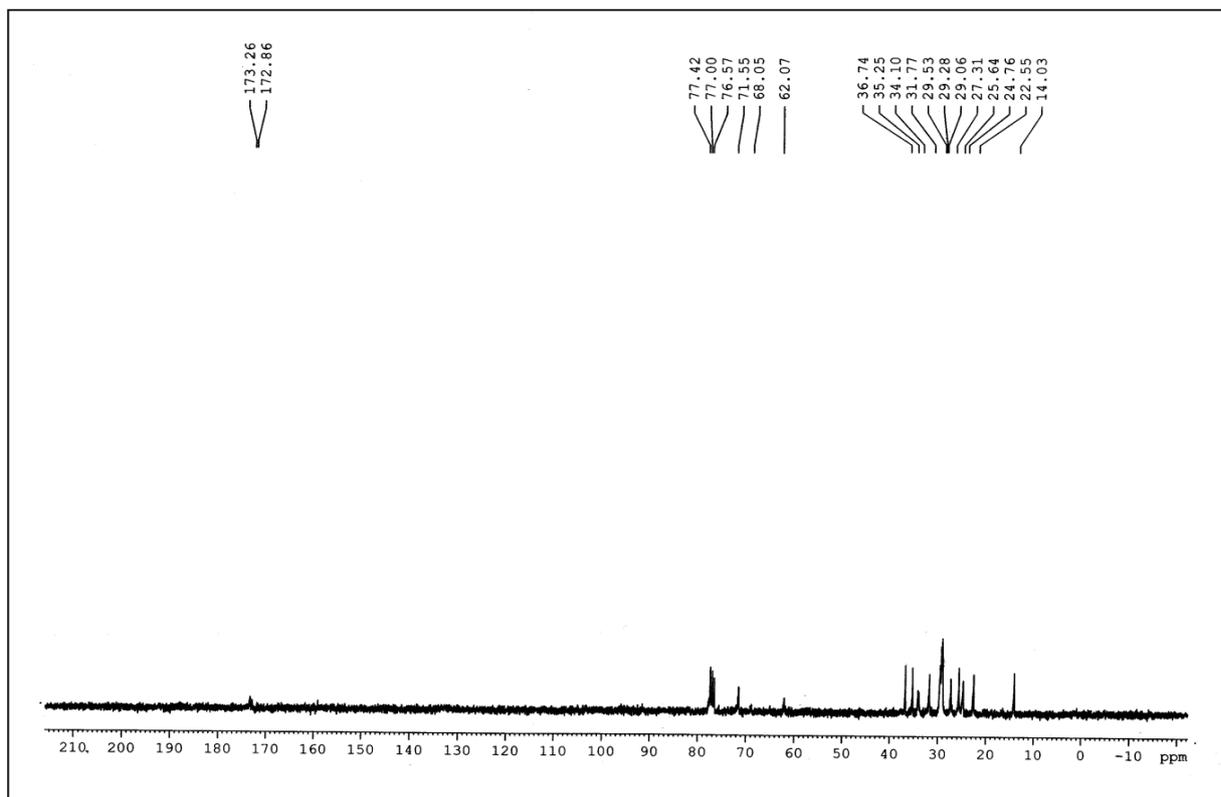
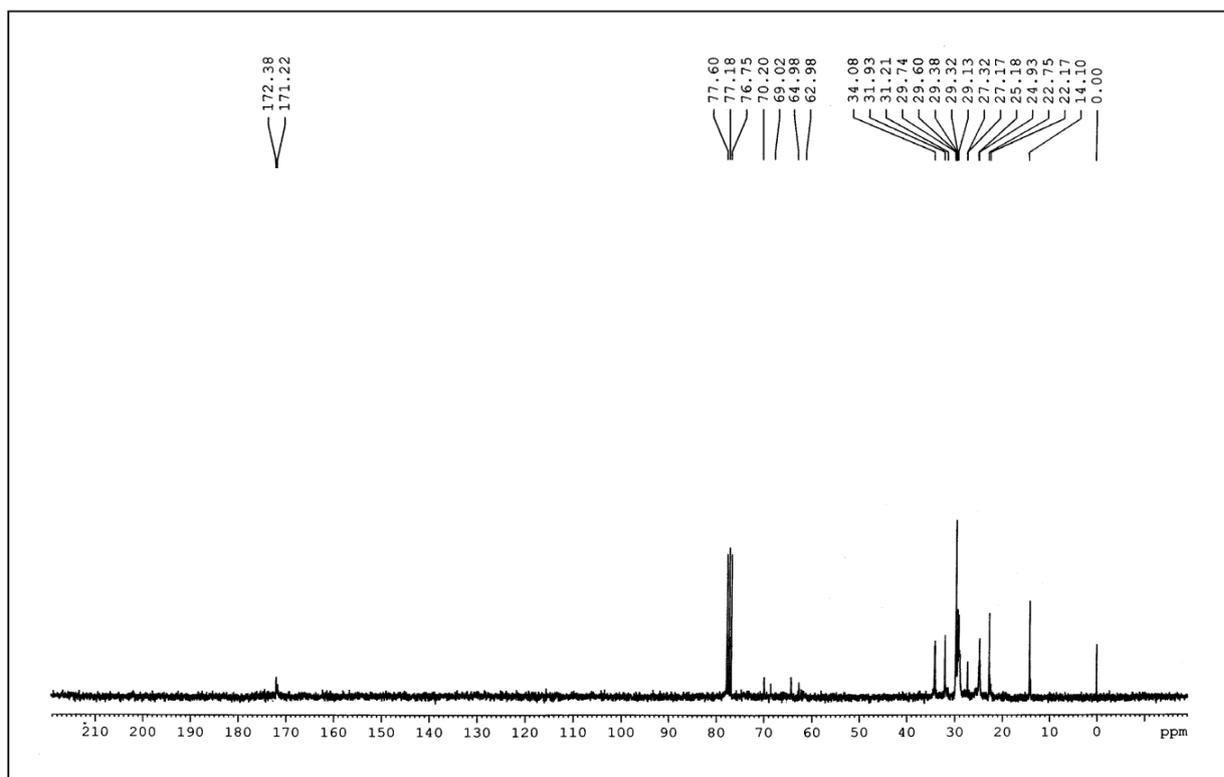
Figure 2.4.11: ^{13}C -NMR spectra of copolymer of CO with 5% α -pinene (P-2)Figure 2.4.12: ^{13}C -NMR spectra of copolymer of CO with 7.5% α -pinene (P-3)

Figure 2.4.13: ^{13}C -NMR spectra of copolymer of CO with 10% α -pinene (P-4)

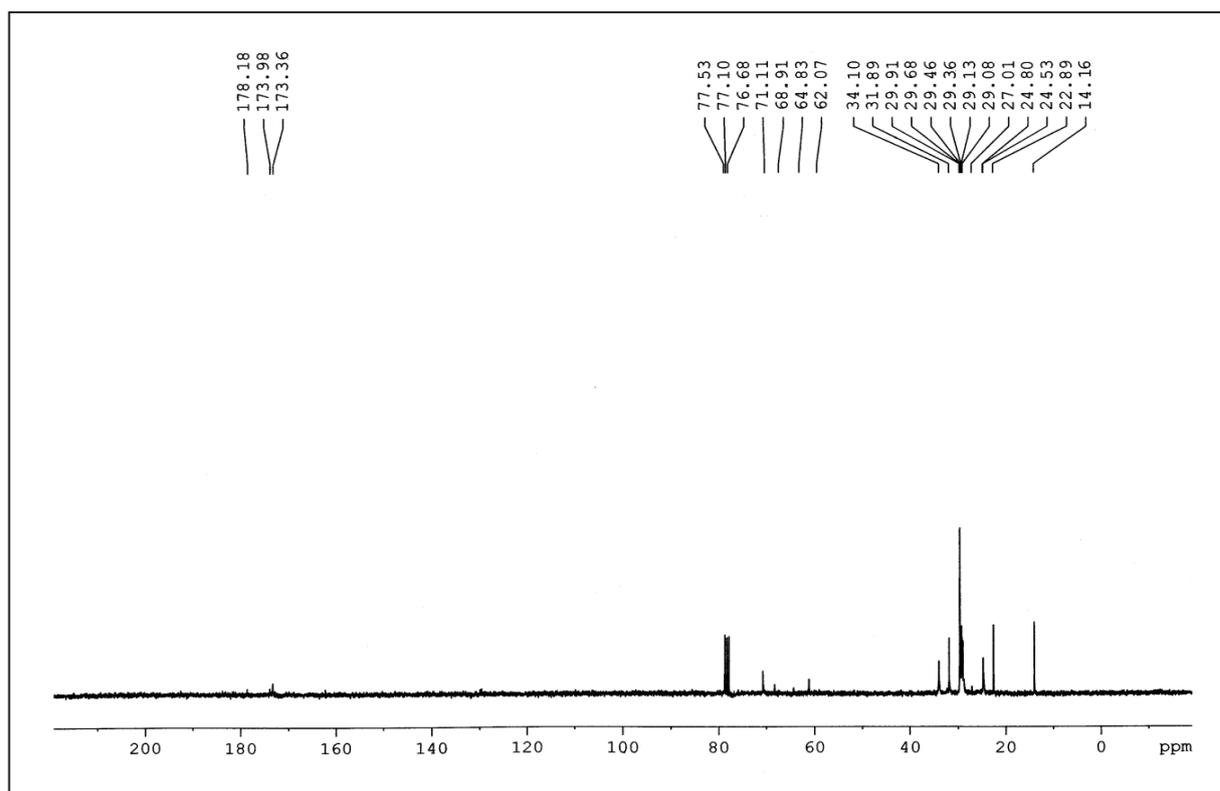


Figure 2.4.14: FT-IR spectra of homopolymer P-1 after biodegradation

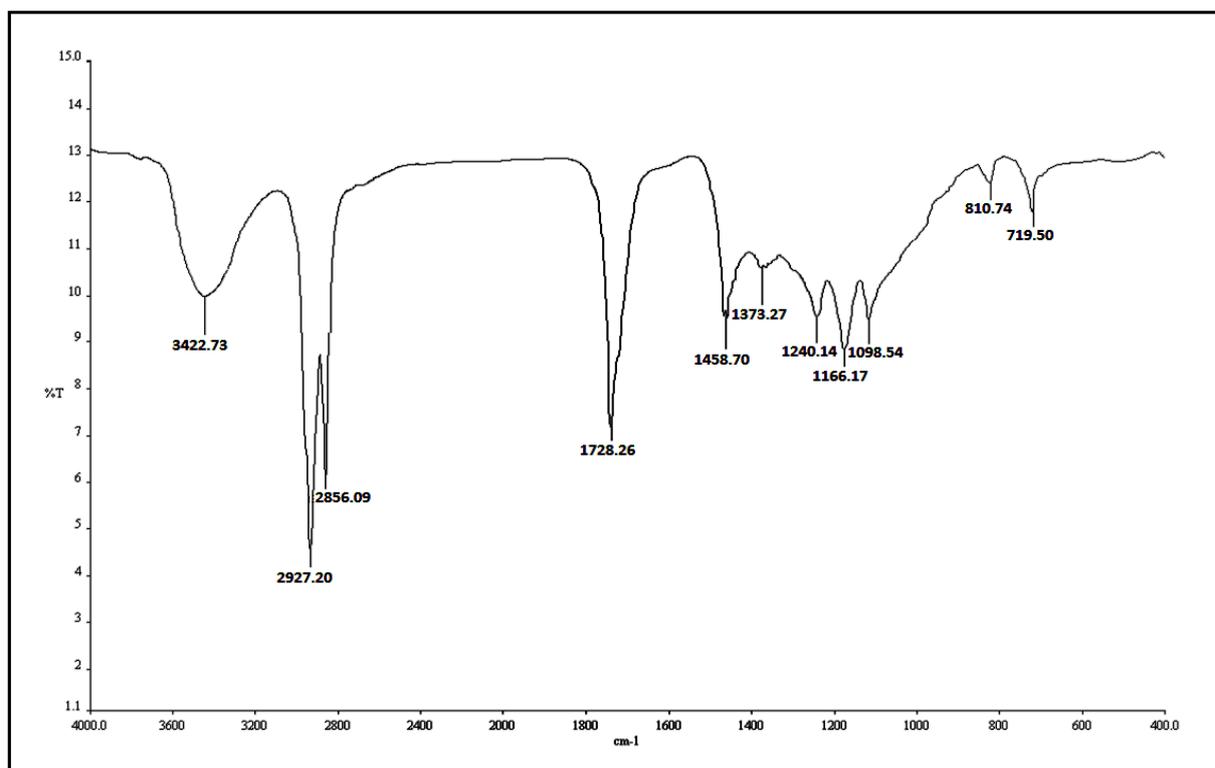


Figure 2.4.15: FT-IR spectra of copolymer P-4 after biodegradation

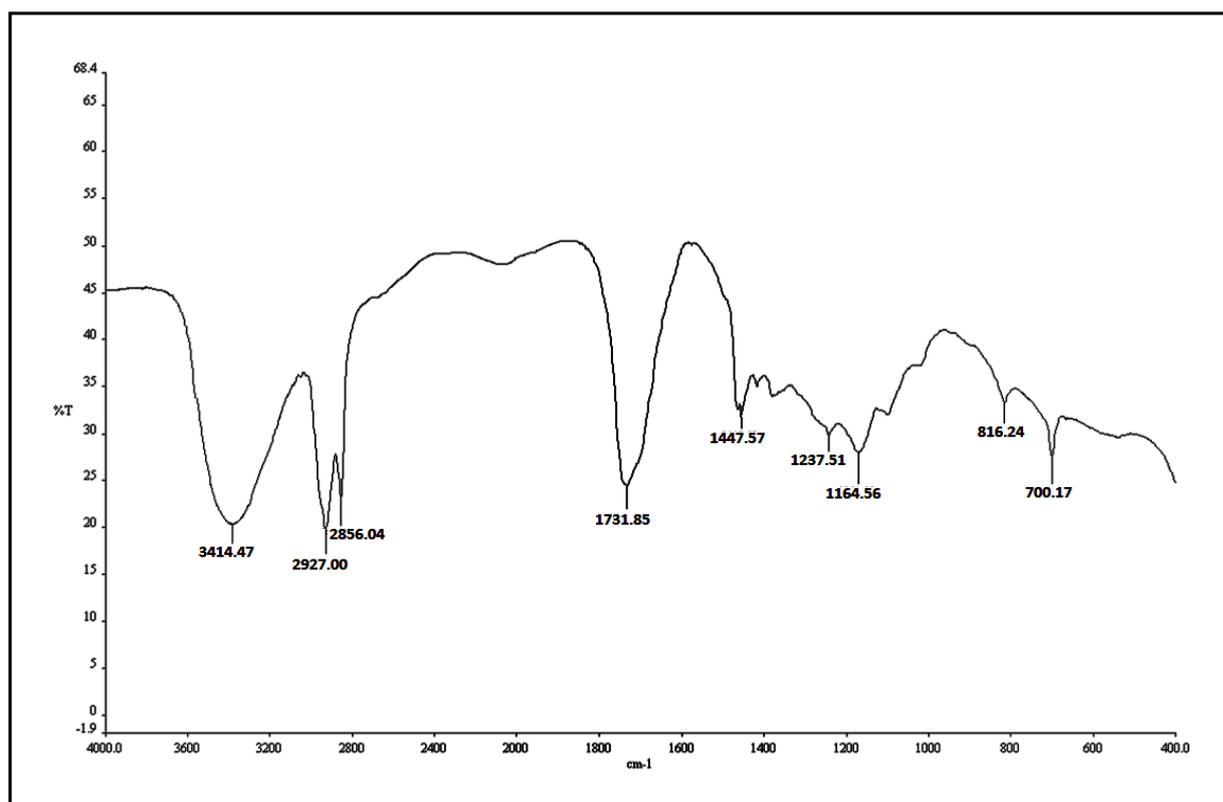


Figure 2.4.16: TGA results of the polymers

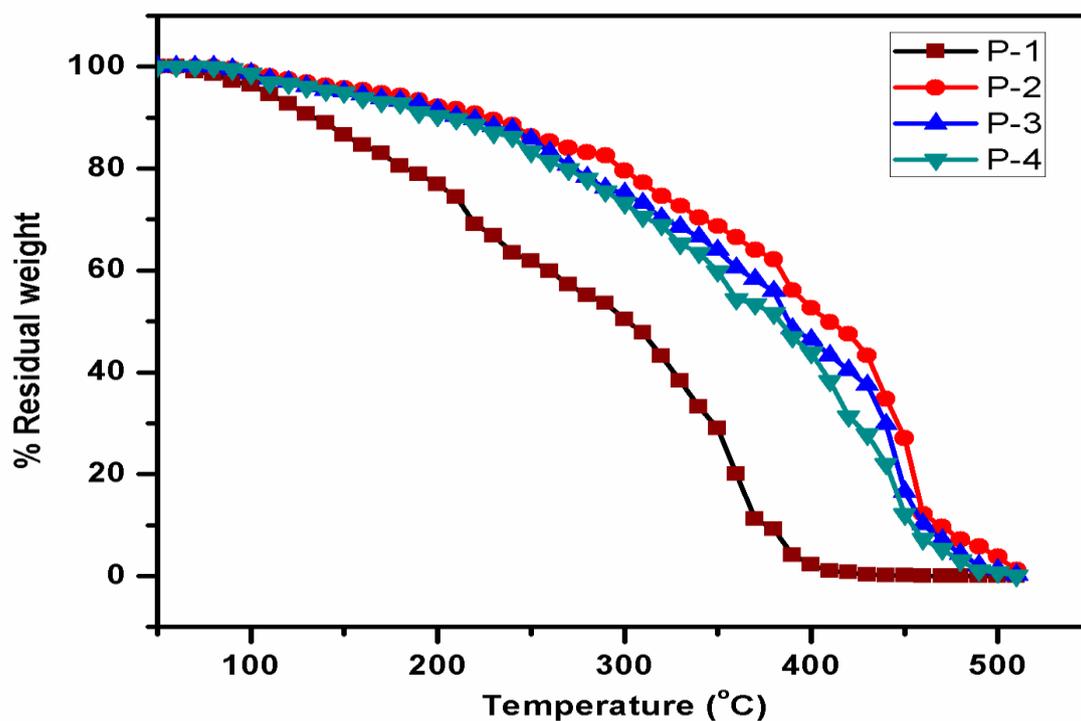


Figure 2.4.17: Pour point variation of the base oil (BO1) blended with additives at different concentrations

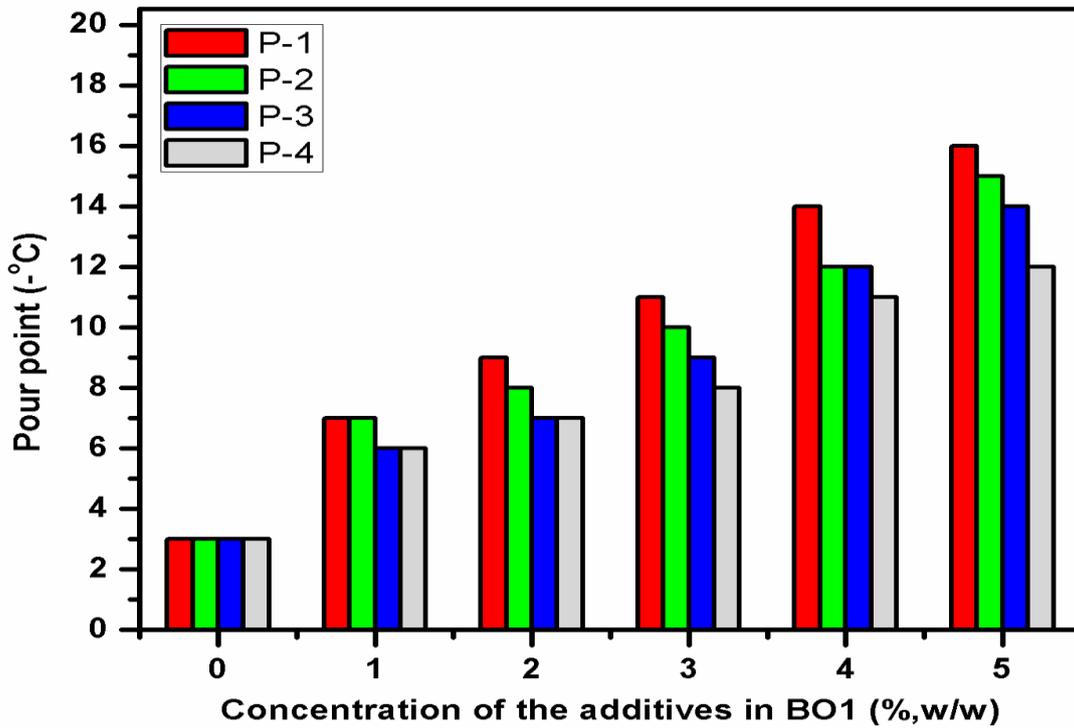


Figure 2.4.18: Pour point variation of the base oil (BO2) blended with additives at different concentrations

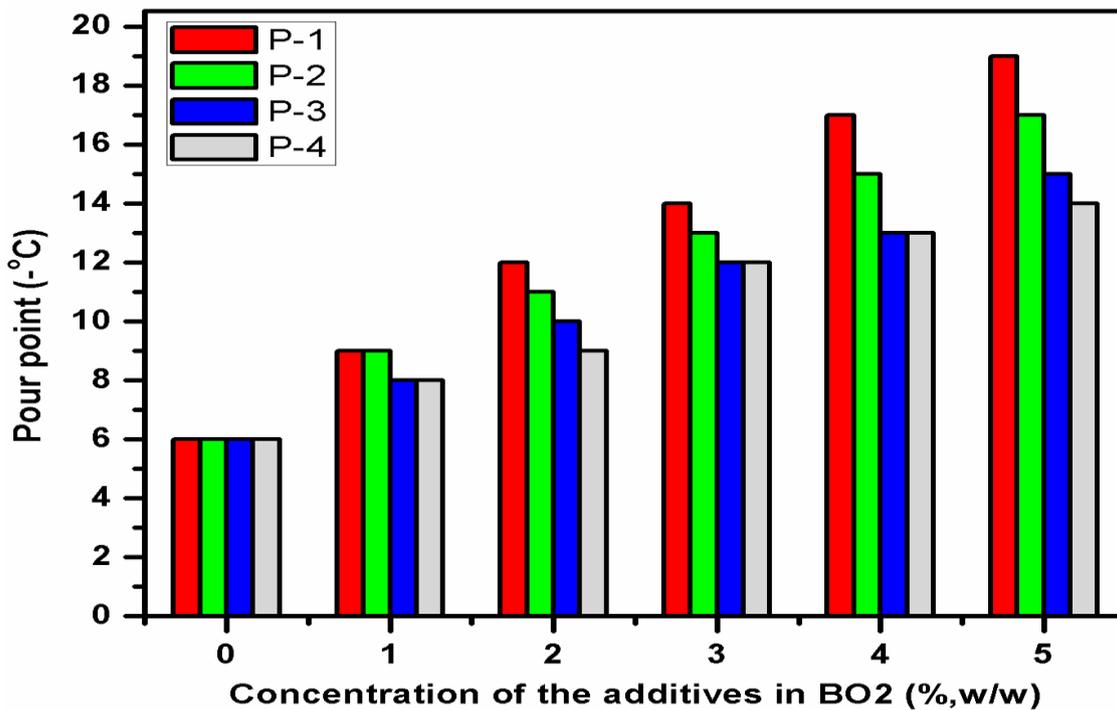


Figure 2.4.19: Viscosity index variation of the base oils (B01 and B02) blended with additives at different concentrations

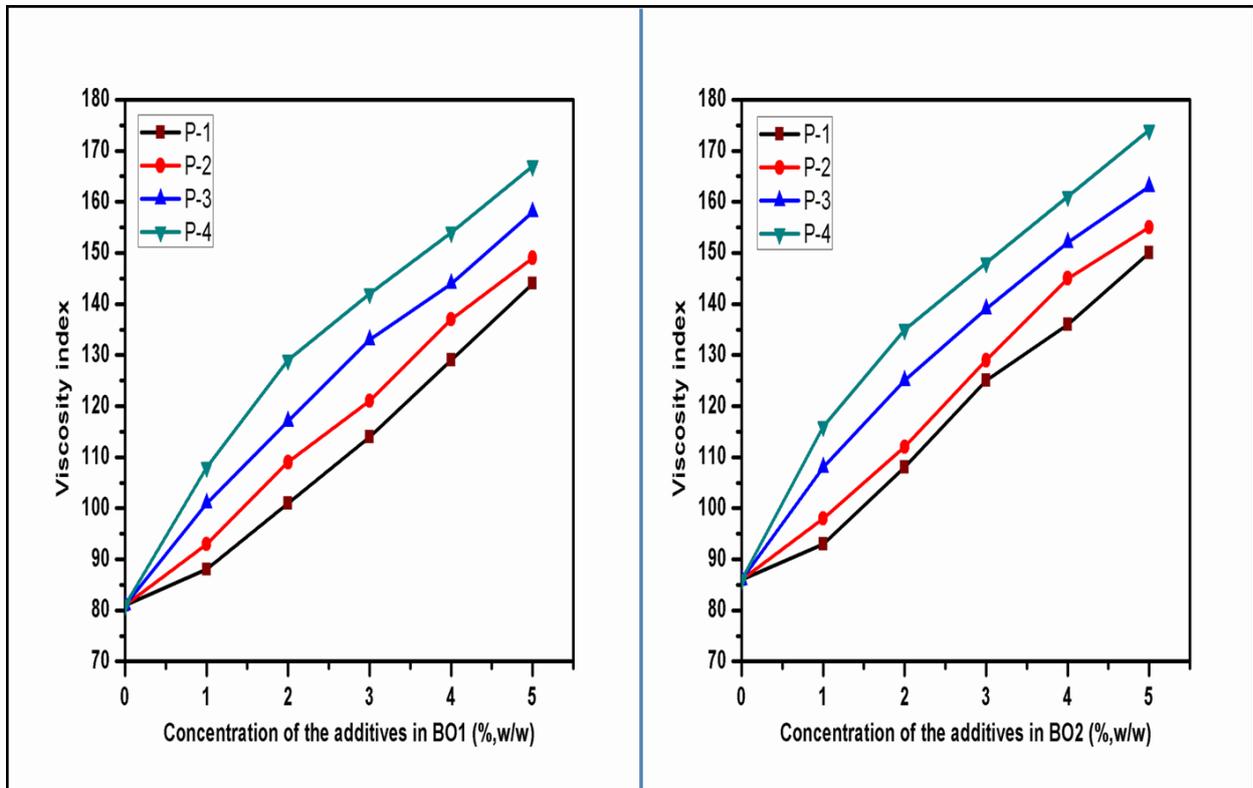


Figure 2.4.20: Photomicrograph of: (a). untreated base oil B01 (b). B01 blended with additive P-1 (4%, w/w) (c). B01 blended with additive P-2 (4%, w/w) (d). B01 blended with additive P-3 (4%, w/w) (e). B01 blended with additive P-4 (4%, w/w)

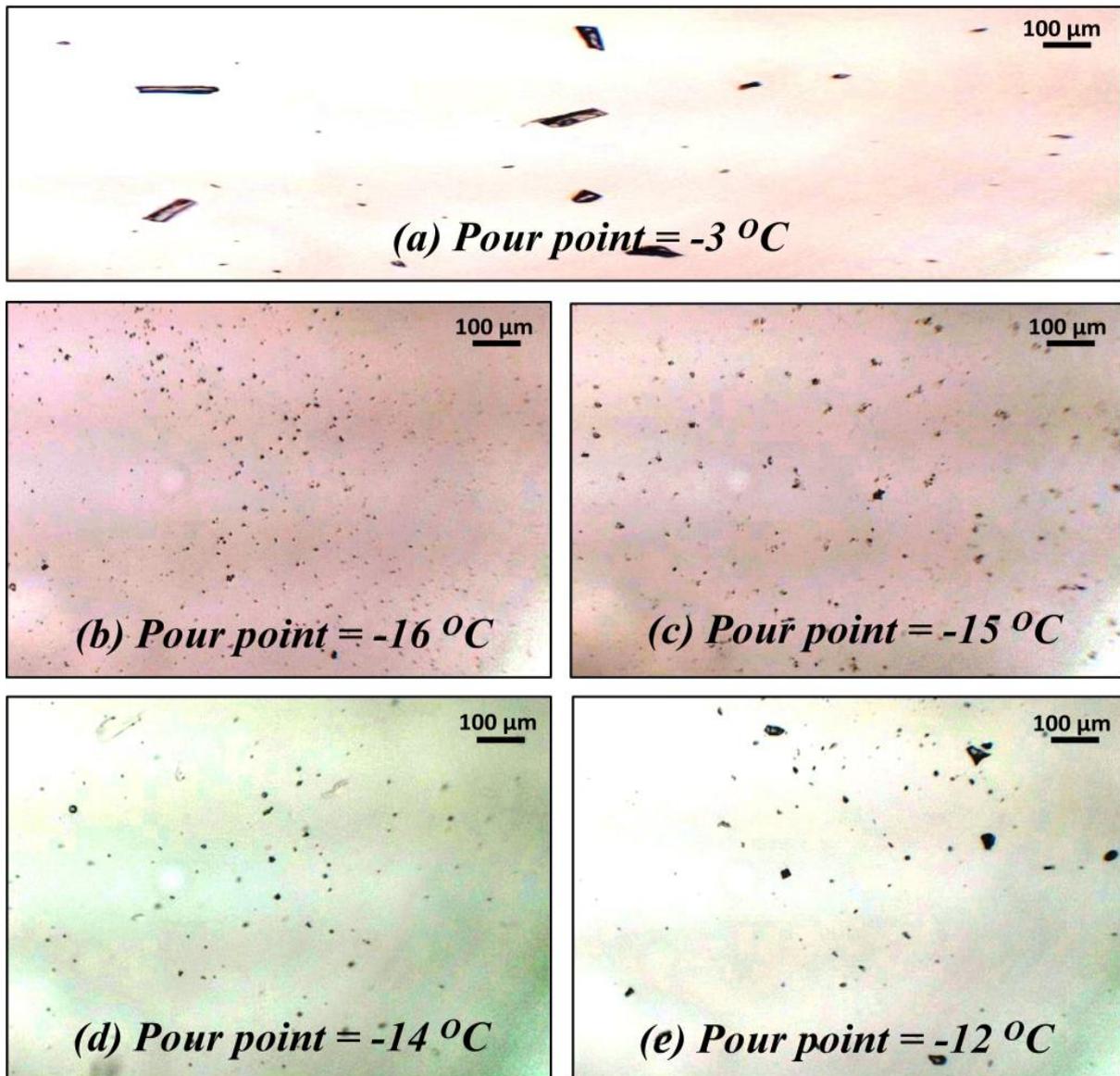
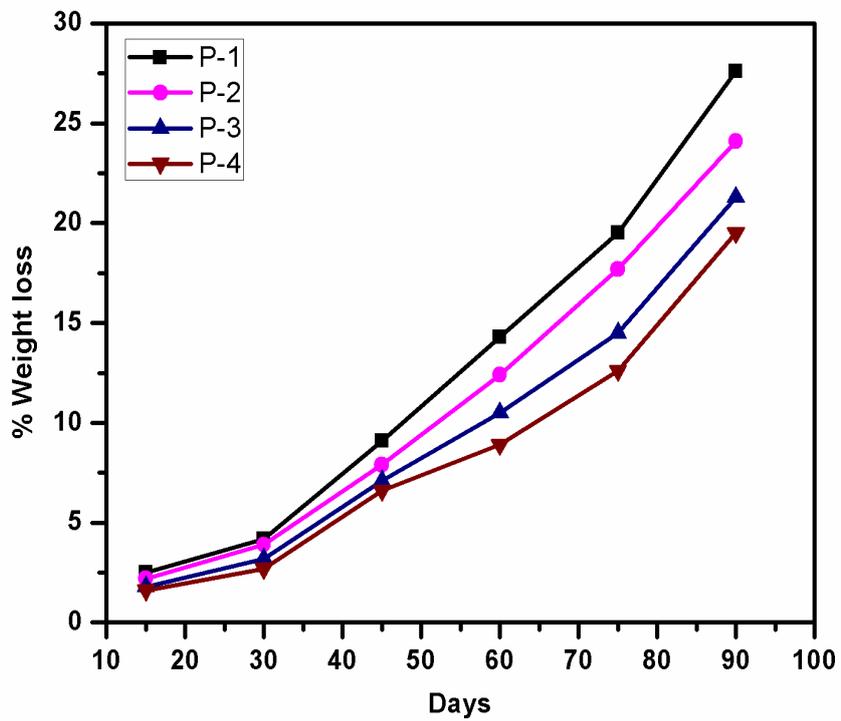


Figure 2.4.21: Degradation of the additives measured in the SBD test



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General introduction of the present investigation

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Part-I

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Naturally derived green bio-additives

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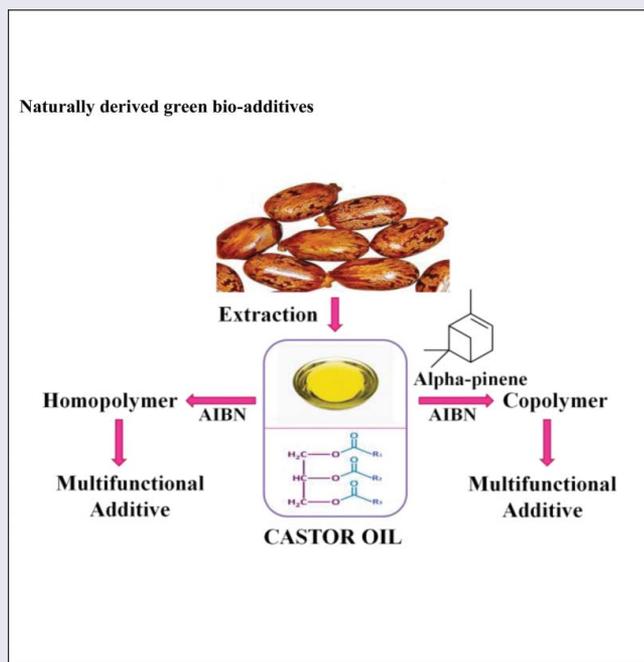
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ABSTRACT

During the last few years, special attention has been paid by the lubricant industry towards vegetable oil-based lubricants due to their biodegradability, renewability and excellent tribological properties. But to maintain the biodegradability of the final lubricants, the additive in the lubricants must also be biodegradable. Hence, in our present work, multifunctional lubricating oil additive based on castor oil has been investigated as a less toxic, feasible alternative to traditional petroleum based additives. Homopolymer of castor oil and its copolymer with α -pinene were synthesized by a thermal method using azobisisobutyronitrile as a radical initiator. Characterization of the prepared polymers was performed by spectral analysis and gel permeation chromatography (GPC). Additive performances of each of the prepared polymers as viscosity index improvers/viscosity modifiers and pour point depressants were carefully evaluated. Photo micrographic image was used to study the effectiveness of the additives as pour point depressants. Thermogravimetric analysis (TGA) was conducted to investigate the thermal response of the additives at high temperature. Finally, biodegradability of all the polymers was tested against fungal pathogen by the disc diffusion method and soil burial test. The study illuminated excellent additive performances of the polymers and thus their potential for acting as entirely naturally derived green bio-additives for lube oil.

GRAPHICAL ABSTRACT



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Lube oil additives; pour point depressant; viscosity index improver; biodegradability; castor oil

Introduction

Rapid developments in science and technology, especially over the last few decades, have increased the amount of synthetic

materials produced globally each year. Among these materials, lubricants constitute a very large fraction. They are primarily a blend of a base oil and an additive.^[14] The additive present in

the lubricants have various functions to perform. They generally are blended as pour point depressants (PPD) to alter the low temperature fluidity, bring about a variation in the viscosity index as viscosity index improvers (VII) and to keep many other parameters of the oil to an optimum level.^[17,21] It is estimated that approximately 40 million tons of lubricants are consumed worldwide every year.^[16]

The lubricants that are in use today originate mostly from petroleum base stocks and are considered as potential water and soil pollutants owing to their extensive toxicity and carcinogenicity. It is also claimed that about 40% of these petroleum-based lubricants sold worldwide are reintroduced to the biosphere every year via accidental spillage, refinery processes and various other non recoverable usages.^[23] This can have detrimental biological effects with the potential to destroy the biota locally. The toxic effects of mineral oils on the environment have been highlighted by several groups of researchers.^[9,22,27] Humans are also affected through consumption of contaminated groundwater and marine life. Moreover, with the stock of fossil fuels dwindling throughout the world and demand of energy ever increasing, there is an urgent need to investigate on some alternative biocompatible lubricants. In this exploration, lubricants derived from vegetable oils and their derivatives have stimulated keen interest as an alternative to petroleum-derived product. Even the higher prices of mineral oils as compared to the vegetable oil in many parts of the world have compelled to recognize vegetable oils as a promising candidate for environment friendly lubricants. In addition to biodegradability, these oils also have some other technical properties that are suitable for their use in industrial application. With the high molecular weight of the triglyceride present in vegetable oils, they have a very low volatility and a minimal change in viscosity with temperature. Vegetable oils also have a high solubilising power for polar contaminants and additive molecules.^[5]

Unfortunately, vegetable oils also suffer from some of their inherent disadvantages. The bisallylic protons of the triglycerides are very prone to radical attack and therefore undergo oxidative cleavage to form polar oxy compounds.^[15] This subsequently results in insoluble deposit and increases the viscosity of the oil. These disadvantages have restricted their market share to about 1% worldwide.^[24] Thus, to bring resurgence in the market share, their disadvantages must be removed and this can be done by polymerisation or blending it with some more stable alternatives.^[20]

Besides, in order to maintain the biodegradability of the final lubricant formulation, the additive in the lubricants must also be biodegradable. Vegetable oil derivatives have been reported as a base fluid by some groups and, therefore, a combination of vegetable oil base fluid and additives made of vegetable oil can act as a useful alternative to petroleum derived products and incur biodegradability to it.^[6,23] As reported by the Food and Agriculture Organization of the United Nations (FAO), India is among the world's largest producer of castor beans. Due to its unique oleo chemical properties, castor oil derivatives have been extensively used in the formulation of various functional fluids, process oils and base oil for lubricants.^[19] Hence, in view of developing new eco-friendly bio-additives, castor oil was chosen along with α -pinene which is a widely seen terpenoid found in nature. In

this investigation, homopolymer and copolymers of castor oil with different percentages of α -pinene were synthesized to evaluate their performances as additives. In addition, biodegradability of the polymers was also tested to evaluate their environmentally benign nature.

Experimental

Materials

Castor oil (CO) was collected from a local grocer's shop. Toluene (GC 99.5%) was purchased from Merck Specialties Pvt., Ltd., (India). Methanol (GC 99.8%) was obtained from Thomas Baker Chemicals Pvt., Ltd., (India). α -Pinene (GC 98%) was obtained from Acros Organics (India). Azobisisobutyronitrile (AIBN, GC 98%, Spectrochem Pvt., Ltd., India) was recrystallized from CHCl_3 – CH_3OH before use. The rest of the materials were used as received without further purification. The fungal specimen was collected from the Department of Microbiology, North Bengal University, West Bengal, India. Mineral base oils (BO1 and BO2) were kindly supplied by Indian Oil Corporation Ltd. (IOCL), India. The physical properties of the base oils are shown in Table 1 and the fatty acid composition of castor oil is shown in Table 2.

Preparation of the homopolymer and copolymers

Preparation of the homopolymer of castor oil (HCO) was carried out in a four necked, round-bottom flask. To carry out the homopolymerization reaction, 20 gram of CO was placed in a flask attached with a condenser, thermometer and an inlet for the introduction of nitrogen. 10mL of toluene was added as a solvent and azobisisobutyronitrile (AIBN, 1% by weight with respect to the monomer) was used as an initiator for the polymerization reaction. The flask was then placed on a magnetic stirrer and the reaction temperature was maintained at 363 K for 8 hours to prepare the homopolymer. After the stipulated time, the reaction mixture was poured into methanol with continuous stirring to terminate the polymerization and precipitate the polymer. For further purification, the polymers were dissolved in hexane and were repeatedly precipitated by methanol followed by drying under vacuum at 313 K. For the synthesis of the copolymers, 20 gram total of CO was taken with 5%, 7.5% or 10% of α -pinene. The copolymerization was also carried out in a four-necked round-bottom flask attached with a dropping funnel to add α -pinene drop wise. The desired mass of CO and initiator AIBN was placed in the flask, followed by the drop wise addition of the desired mass of α -pinene for 2 hours. The reaction temperature was maintained at 363 K for 48 hours until the polymerisations were complete. The polymers were

Table 1. Physical properties of base oils.

Properties	Method	BO1	BO2
Viscosity at 40°C in cSt	ASTM D445	7.229	23.472
Viscosity at 100°C in cSt	ASTM D445	1.874	3.938
Viscosity Index	ASTM D2270	81	86
Pour Point, °C	ASTM D97	–3	–6
Density ($\text{g}\cdot\text{cm}^{-3}$) at 40°C	ASTM D4052	0.83689	0.85514
Wax content in wt%		1.8	1.1

Table 2. Fatty acid composition of castor oil.

Fatty acid	Average % composition
Palmitic C16:0	1.7
Stearic C18:0	1.9
Oleic C18:1	5.3
Linoleic C18:2	7.0
Linolenic C18:3	1.5
Ricinoleic C18:1:OH	82.4

then purified as reported for the homopolymer. The composition of the monomers in the copolymers is given in Table 3.

Preparation of bio-additive based lubricating oil formulations

The prepared polymers (additives) were added to the base oils (BO1 and BO2) in different percentage concentrations (1–5% w/w). The blends were stirred in batches of 200 cm³, at a rotational speed of 300 rpm, for 4 hour at 323 K to obtain uniform polymer dispersion in the lubricants. The blends were then cooled down to room temperature.

Spectroscopic measurements

Infrared spectra (FT-IR spectra) were recorded on a Shimadzu (Japan) FT-IR 8300 spectrometer, within the wavenumber range of 400 to 4000 cm⁻¹ using 0.1 mm KBr cells at room temperature. For recording the NMR spectra, Bruker Avance (Germany) 300 MHz FT-NMR instrument was used using a 5 mm BBO probe. CDCl₃ was used here as solvent and tetramethylsilane (TMS) as reference material.

Thermo-oxidative stability measurements

A thermogravimetric analyzer (Shimadzu TGA-50, Japan) instrument was used to determine the thermo-oxidative stabilities of all the prepared additives in air, using an alumina crucible at a heating rate of 10°C per min. The thermal stability of the additives can be measured in terms of percentage of residual weight or percentage of weight loss (PWL) with rise in temperature. The PWL was determined by the equation,

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

where M₀ is the initial mass and M₁ is the remaining mass after the test until constant weight.

Table 3. Polymers designation, percentage composition and average molecular weight values determined by GPC.

Polymers	% of monomers in the polymers		Solvent, Initiator	Average molecular weights		
	Castor oil	α-pinene		M _w	M _n	PDI
P-1	100	0	Toluene, AIBN	17882	11247	1.59
P-2	95	5	Toluene, AIBN	30214	21428	1.41
P-3	92.5	7.5	Toluene, AIBN	29636	21952	1.35
P-4	90	10	Toluene, AIBN	28574	23421	1.22

P-1: Homopolymer of castor oil, P-2: Copolymer of castor oil + 5% α-pinene, P-3: Copolymer of castor oil + 7.5% α-pinene, P-4: Copolymer of castor oil + 10% α-pinene. M_n and M_w are number-average and weight-average molecular weights. PDI is polydispersity index

Determination of average molecular weight

Waters (USA) GPC instrument was used to determine the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI, M_w/M_n) of the prepared polymers. The GPC system (polystyrene calibration) was equipped with a 2414 refractive index detector, Waters 515 HPLC pump and a 717 plus autosampler. HPLC grade THF was used as an eluent for the instrument at a flow rate of 1.0 mL/min at 30°C. Table 3 shows the average molecular weight values as determined by GPC.

Performance evaluation

Evaluation of pour point (PP)

The pour point of the base oils blended with different percentages of the prepared additive was tested according to the ASTM D97 method on a cloud and pour point tester (Wadegati labequip Pvt., Ltd., India) in the temperature range of 0 to -71°C.

Evaluation of viscosity index (VI)

The variation of kinematic viscosity (KV) of oil with the change of temperature is specified by an arbitrary dimensionless number called viscosity index. A higher value of viscosity index (VI) signifies a relatively small change in viscosity with the temperature variation. The VI was evaluated according to the ASTM D2270 method at 313 K and 373 K.^[1] The effectiveness of an additive as VII is assessed by the increase in the VI value of the base oils after addition of the additive.^[28]

Photo micrograph and wax modification

The photomicrographs showing wax crystallization behaviour of the base oils blended with different percentages of the prepared additive were recorded in a Banbros polarizing microscope (BPL-400B, India). The temperature was set at 273 K and it was suitably controlled on the microscope slide by an attached cooling thermostat. The magnification used here was 200X.

Biodegradability test

Biodegradation can be defined as the breakdown or mineralisation of an organic material due to microbial activity, leading to a significant change in the chemical structure of the material.

During biodegradation, the organic carbon is partly converted to new biomass. Out of the several testing methods for testing of chemicals on biodegradation, the soil burial degradation test as per ISO 846:1997 and the disk diffusion method against fungal pathogen were chosen here.^[3,11] PWL [Eq. (1)] of the samples was studied to determine the amount of degradation of the polymers in the burial test. The shift in the IR frequency of the ester carbonyls after the biodegradability test along with the change in their molecular mass was also a parameter to judge the degradation of the polymers.

Soil burial degradation test (SBD test)

The soil used in the SBD test had been obtained from the campus of North Bengal University (West Bengal, India) having pH 7.2 and with the moisture content of 26%. The soil was first taken in a humidity chamber, set at 303 K, to adjust the relative humidity to around 60%. Two gram of an additive was taken to create a polymeric film and different films were produced from all the polymers.^[25] The films were then buried in the soil (containing the microorganisms) in a bacteriological incubator (Sigma Scientific Instruments Pvt., Ltd., India). After every 15 days, the buried polymer films were taken out and the process was continued for a period of 3 months with a different film used for each time period. The recovered films were washed with chloroform, filtered with Whatman grade 41 filtration paper and then dried in a vacuum oven at 323 K. The weights after drying were recorded for each of the films to determine the percentage of weight loss.

Disc diffusion (DD) test

The disc diffusion method consists of the preparation of culture media for the fungal strains and testing the biodegradation of the additives against fungal pathogens. Here the biodegradation was tested for the fungal pathogen, *Alternaria alternata* (AA). For preparing the culture media, potato extract, agar powder and dextrose were mixed in a ratio of 10:1:1 by weight. To carry out the test, two gram of the prepared additive was taken in a sterilized Petri dish and inoculated by spraying the fungal pathogen. To avoid any further contamination, the sterilized Petri dish was sealed by wax and incubated at 310 K in a bacteriological incubator. The process was carried out for all the additives separately with the fungal pathogen. During incubation, the spores (colonies) appearing as black spots were observed to grow indicating the fungal growth on the polymers. After a period of 30 days, the additives were recovered from the culture and washed with chloroform, filtered with Whatman grade 41 filtration paper and dried in a vacuum oven at 323 K. The PWL was calculated for all the additives and their molecular weights were determined by GPC method.

Results and discussion

Spectroscopic data analysis

FT-IR Spectroscopy: The FT-IR spectroscopy was particularly useful in determining the functional groups present in the additives. The homopolymer of castor oil (HCO) exhibited IR

absorption band at 1741 cm^{-1} for the ester carbonyl group while the broad peak around 1174 cm^{-1} was attributed to the ester C–O stretching vibration. Peaks in the region of 1460 cm^{-1} , 1375 cm^{-1} and 724 cm^{-1} were for the bending vibrations of the C–H bonds. The paraffinic C–H bonds also had intense absorptions at 2927 cm^{-1} and at 2855 cm^{-1} that corresponds to their stretching vibrations. The broad IR transmission at 3438 cm^{-1} represented the characteristics O–H stretching of the alcoholic group of ricinoleic acid present in castor oil. The other three polymers (P-2 to P-4) showed almost similar IR peaks. In their spectra, the peaks at 1746, 1744 and at 1745 cm^{-1} indicated the presence of ester carbonyl groups. The ester C–O showed their stretching vibrations at 1168, 1172 and 1168 cm^{-1} respectively. Their IR spectrum also had characteristic peaks at 1451 to 1461 cm^{-1} , 1373 to 1375 cm^{-1} and 721 to 724 cm^{-1} representing the bending vibrations of the C–H bonds for the methylene and methyl groups of castor oil and α -pinene. The observed absorption bands at 2919 to 2926 cm^{-1} and 2852 to 2855 cm^{-1} were due to the stretching of C–H bonds. The characteristics O–H stretching peaks at 3414, 3406 and at 3417 cm^{-1} were present in all the polymers. The nonappearance of any peaks in the range of 1600 cm^{-1} to 1680 cm^{-1} indicated the absence of any olefinic carbon in the polymers and therefore the formation of the desired product.

¹H NMR: The Bruker Avance FT-NMR instrument used to perform the proton NMR spectroscopy showed multiple peaks in the spectra of the additives and the peaks were used to characterise the different types of protons. HCO showed peak for the methyl protons at δ 0.82 ppm while the peaks in the range of δ 1.24 to 2.16 ppm were for the methylene protons of alkyl groups. The protons of –OCOCH₂– groups present in castor oil showed chemical shift between δ 2.25 and 2.27 ppm and the hydrogens of the –OH group of ricinoleic acid appeared as broad peak centered at δ 3.57 ppm. The chemical shift in the spectra between δ 4.09 and 4.25 ppm appeared due to the protons of –COOCH₂ groups of the triglyceride of castor oil. Any significant proton shifts were found to be absent between δ 5.5 and 6.5 ppm indicating complete utilisation of olefinic groups in the polymerisation process. The other polymer (P-2, P-3 and P-4) showed nearly similar chemical shifts between δ 0.81 and 0.82 ppm for the methyl protons. The signals between δ 1.24 and 2.19 ppm is attributed to the methylene protons of castor oil and α -pinene, while the protons of –OCOCH₂– groups showed their presence by appearing between δ 2.22 and 2.69 ppm. The peaks ranging from δ 3.54 to 3.66 ppm is credited to the –OH group of castor oil and the protons of –COOCH₂ groups showed shifts between δ 4.04 to 4.26 ppm. Also the nonappearance of any peaks in the range of δ 5.5 and 6.5 ppm in the ¹H NMR spectra point towards the absence of sp² carbons in the copolymers.

¹³C NMR: The ¹³C NMR spectra of HCO showed signal appearing between δ 12 and 36 ppm due to the existence of all sp³ (–CH₃ and –CH₂) carbon atoms of the alkyl chain of castor oil. The presence of –COOCH₂ groups in the triglyceride backbone of castor oil is indicated by the shift between δ 61 and 68 ppm. Peak appearing at δ 70 ppm indicated the carbon joined to the –OH group of the ricinoleic acid present in castor oil. Peaks between δ 172 and 173 ppm is attributed to the carbonyl carbon of the ester group. HCO exhibited no signals

between δ 120 and 150 ppm, indicating the successful conversion of olefinic carbons to saturated carbons during polymerisation. The copolymers (P-2 to P-4) showed similar ^{13}C spectra with shift between δ 14 and 37 ppm representing the sp^3 carbons of castor oil and α -pinene. The peaks ranging from δ 62 to 69 ppm showed the presence of $-\text{COOCH}_2$ groups of the triglyceride moiety. The carbon joined to the $-\text{OH}$ group in castor oil appeared between δ 70 to 72 ppm while the carbonyl carbons indicated their presence between δ 170 and 178 ppm. Peaks between δ 120 and 150 ppm were absent in all the copolymers. (All IR and NMR spectra are given in supporting information).

Thermogravimetric analysis (TGA) study

Figure 1 presents a comparison between the thermogravimetric analysis data of the prepared polymers. The results showed that the copolymers were better in thermo-oxidative stability than the homopolymers. The percentages of residual weight of the polymers P-1 to P-4 after thermal degradation were found to be 50.35, 79.53, 75.19 and 73.23 respectively at 300°C . At 400°C the amount (percentages of residual weight) left were 2.28, 52.65, 46.36 and 43.84 respectively. As indicated by the percentage of residual weight values, the thermal stability of copolymers increased with decreasing α -pinene concentration in the polymers and thermal degradation of polymer P-2 was the least. Hence, polymer P-2 is thermally most stable among the prepared additives. This increase in the thermal stability of the polymer is probably due to its highest molecular weight and comparatively narrower molecular weight distribution as indicated by the PDI value.^[8]

Analysis of pour point data

Pour points of the additive-doped lube oils were tested by blending the additives with the base oils (BO1 and BO2) at different concentrations (1% to 5%, w/w) and the experimental results are shown in Figures 2 and 3. It is clearly seen that the efficiency as PPD gradually improved with the increase in the concentration of the additive in the base oils. Moreover, with

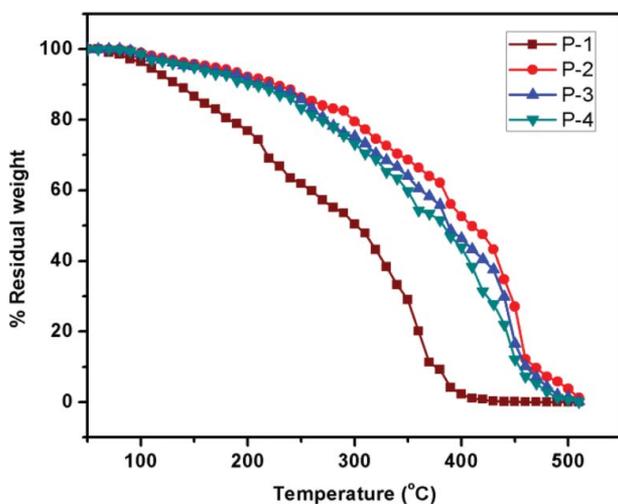


Figure 1. TGA results of the polymers.

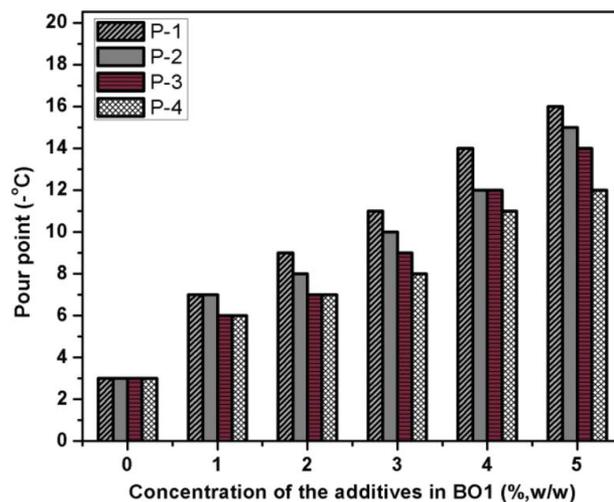


Figure 2. Pour point variation of the base oil (BO1) blended with additives at different concentrations.

the increase in the α -pinene concentration in the additive their efficiency as PPD gradually decreased. PPDs usually have no effect on the crystallization temperature. However, the improvement in the PPD properties is due to disruption of the rigid network of wax crystals that are formed at lower temperatures from the dissolved waxy hydrocarbons present in mineral oils. PPDs can reduce the size and growth of wax crystals and thereby the ability of these crystals to flocculate and interlock among themselves.^[2] PPDs usually have a wax like paraffinic part that cocrystallizes with the oil's wax forming components and essentially becomes a part of them and the polar component present in the PPDs limits their degree of cocrystallization.^[12] Nucleation and improved wax solubility are among the other theories suggested for the mechanism of action of PPDs (Chen et al.^[4]). Here the homopolymer P-1 was better as a PPD compared to the other polymers with different concentrations of α -pinene. This may be due to the better interaction of polymer P-1 with the wax crystals compared to the others. The degree of interaction depends upon the polarity of additive molecules, where a more polar additive can form stronger H-bond with the polar groups of resin and

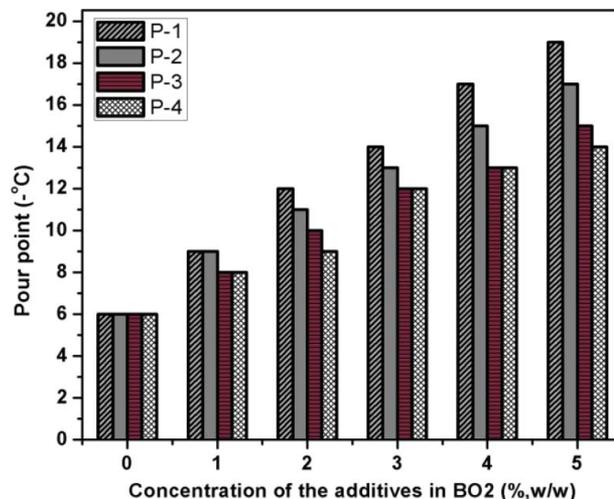


Figure 3. Pour point variation of the base oil (BO2) blended with additives at different concentrations.

asphaltene present in the base oil.^[26] Castor oil has a very high percentage of ricinoleic acid (containing polar hydroxyl group) in them and the introduction of α -pinene in the castor oil moiety decreases the polarity of the overall additive molecule. This decrease in their polarity reduces their effectiveness to act as an efficient PPD.

Analysis of viscosity index data

The data, as presented in Figure 4, shows that the VI values of the base oils blended with the additives were significantly increased compared to those of the base oils without the additives. The investigation also revealed that irrespective of the additive and the nature of the base oil, the VI value increased with increase in the additive concentration. All the polymers (homopolymer and copolymers) showed excellent results but the introduction of α -pinene to CO enhanced the VI to a much greater extent. At a 5 wt % of additive concentration, among the other polymers, polymer P-4 showed the highest increase of VI for both the base oils (VI value 167 for BO1 and 174 for BO2). At the same concentration, HCO showed a VI value of only 144 and 150 for BO1 and BO2 respectively. As shown in Figure 4, the VI index value increased in the order P-1 < P-2 < P-3 < P-4. For a polymer, the ability to act as a VI improver is governed by its molecular weight, temperature dependent solubility, chain topology and structure of polymeric macromolecules.^[10] These parameters determine the hydrodynamic volume of the randomly coiled polymer chain which in turn counterbalances the reduction of the viscosity of the base oil with increasing temperature. It is assumed that the polymer molecules in the base oil remain in a coiled shape. With increasing temperature, the polymer coils expands resulting in an increase in polymer chain entanglements. Moreover, with increase in polymer concentration, the interaction between these macromolecules and the base oil also increases ensuring a greater thickening and a higher viscosity index for the oil.^[18] The higher values of VI as obtained for the copolymers here is

attributed to their greater molecular weight and narrower molecular weight distributions. Due to the compact chain structure, polymers with hyper-branched arrangement have a reduced hydrodynamic volume compared to the polymers of linear chain topology of similar molecular weight. In addition, due to their restricted hydrodynamic volume, these hyper-branched polymers inhibit the expansion of polymer coil dimension resulting in reduced chain entanglements among themselves.^[29] Thus, polymer P-4 with higher molecular weight and the most linear chain topology produced a greater thickening of the oil and thereby the highest viscosity index.

Analysis of photo micrographic image

The photo micrographic image of the base oil with and without the additives helps to study the effect of additives on their pour point values. The photomicrographs illustrated in Figure 5 showed the variation of wax morphology according to the nature of additives added. The base oil without the additive (Figure 5a) showed large cyclic and needle shaped wax crystals of approximate size of 100 μm . When treated with 4% (w/w) of the additives, there occurred a substantial reduction in the size of wax crystals. The large crystals were converted into numerous finely dispersed crystals. A higher wax modification was observed for the polymer P-1 (Figure 5b) with most finely dispersed wax crystals while the polymer P-4 (Figure 5e) showed the least wax modification. Analysis of the photo micrographic images thus revealed that polymer P-1 acted as a better PPD than the other polymers. Therefore, the wax modification results, as obtained by the photo micrographic images are in good agreement with the flow parameter (pour point) of the polymers determined by the ASTM method.

Analysis of biodegradability test

The polymers here are all made of natural monomer units and therefore they are likely to show significant amount of

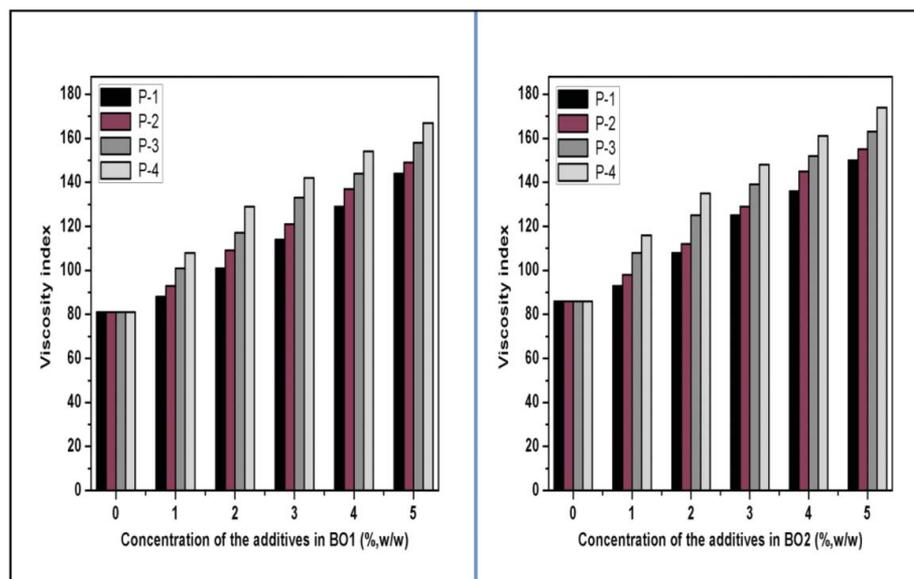


Figure 4. Viscosity index variation of the base oils (BO1 and BO2) blended with additives at different concentrations.

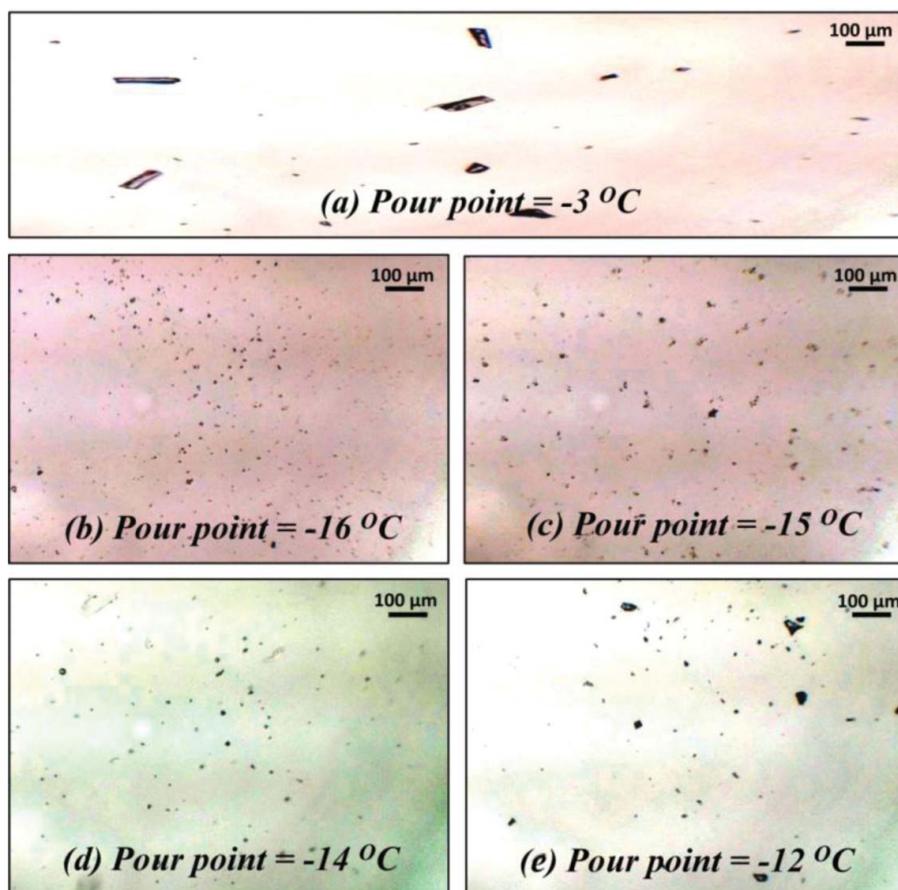


Figure 5. Photomicrograph of: (a). untreated base oil BO1 (b). BO1 blended with additive P-1 (4%, w/w) (c). BO1 blended with additive P-2 (4%, w/w) (d). BO1 blended with additive P-3 (4%, w/w) (e). BO1 blended with additive P-4 (4%, w/w).

biodegradability. The biodegradability test results obtained by using the soil burial test and the disk diffusion test methods are presented in Figure 6 and Table 4 respectively and the results indicated considerable bio-assimilation for the polymers. In the SBD test, the degradation of all the polymers by the microbes in the soil increased with the increasing time period (number of days). After 90 days, the homopolymer of CO showed the

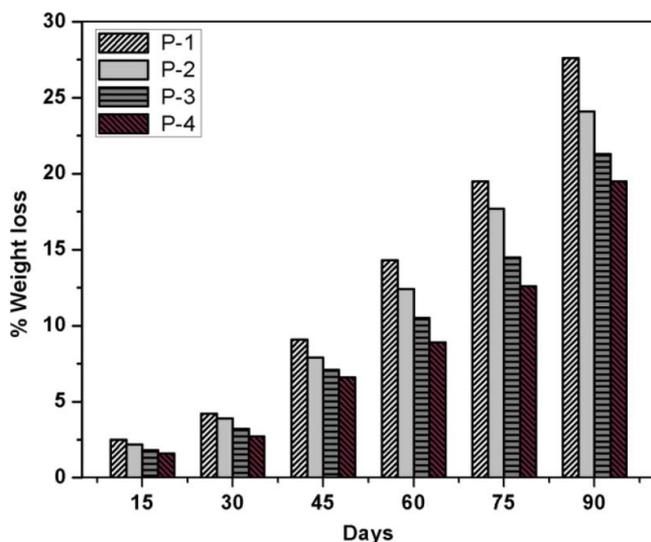


Figure 6. Degradation of the additives measured in the SBD test.

highest degradation among other polymers with a weight loss of 27.6%. After the same time period, copolymer P-4 showed a weight loss of 19.5% which is least among all the polymers. The test results of the DD method also showed similar trend against the fungal pathogen. The biodegradation of polymer P-1 was the highest in this test as well with 30.3% weight loss after a span of 30 days. The percentage weight losses of the other polymers (P-2 to P-4) were 26.7, 22.9 and 19.7 respectively after the same number of days. GPC of the polymers after the DD method was also performed and the results were compared with the respective polymers before biodegradation (Table 4). The results indicated considerable change in the M_n and M_w of the polymers and thus revealed the biodegradability of the prepared polymers.^[7] FT-IR spectra of the polymers, before and after the DD test were also studied to identify any shift in their IR peaks. For the polymer P-1, the IR peak of the ester carbonyl group at 1741 cm^{-1} has shifted markedly to 1728 cm^{-1} with a decrease in the peak height and intensity after the test. IR peaks of the sample at 724, 854, 1174, 1243, 1375, 1460 and 3438 cm^{-1} has also shifted noticeably after the DD test. Similar shift in the IR peaks were observed for the other polymers as well. This shift in the IR peaks is possibly due to the scission of the polymer units after biodegradation.^[13] These changes in the IR peaks of the polymers, their decrease in the number-average molecular weight (M_n) and weight-average molecular weight (M_w) along with their PWL confirmed the biodegradable property of the prepared polymers.

Table 4. Result of biodegradability test by disc diffusion method and comparative average molecular weight values determined by GPC.

Polymers	Incubation period (days)	Pathogen	PWL	Molecular weight			
				Before biodegradation		After biodegradation	
				M _w	M _n	M _w	M _n
P-1	30	AA	30.3	17882	11247	15978	10902
P-2	30	AA	26.7	30214	21428	27228	20267
P-3	30	AA	22.9	29636	21952	27134	20873
P-4	30	AA	19.7	28574	23421	26965	22321

Conclusions

In this research, detailed analyses of the prepared polymers were carried out to evaluate their performance as a multi-functional additive. The results indicated that the addition of these additives to the base oil enhanced their lubricant property considerably. A comprehensive study of the polymers revealed that the copolymers were superior as VII. The most important viscosity increment was exhibited by the copolymer P-4 while the homopolymer blend P-1 showed the superior performance as PPD for the lube oils under study. The use of copolymer always yielded an important increase in thermal stability and the polymer P-2 had the best performance. Furthermore, it was observed that all the additives are also environmentally benign. Therefore, the prepared bio-additives may be used for designing green bio-lubricant formulations for lube oil to satisfy the mounting environmental and performance concerns of modern lubricants.

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