

**SYNTHESIS AND PERFORMANCE EVALUATION OF
CHEMICAL ADDITIVES FOR LUBE OIL**

THESIS

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By

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November, 2017

.....*Dedicated to my*

parents,

brother

&

sister

DECLARATION

I declare that the thesis entitled “**SYNTHESIS AND PERFORMANCE EVALUATION OF CHEMICAL ADDITIVES FOR LUBE OIL**” 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

I certify that **Mr. Koushik Dey** has prepared the thesis entitled “**SYNTHESIS AND PERFORMANCE EVALUATION OF CHEMICAL ADDITIVES FOR LUBE OIL**” for the award of Ph.D Degree of the University of North Bengal, under my guidance. He has carried out the research work at the Department of Chemistry, University of North Bengal. No part of the thesis has formed the basis for the award of any degree or fellowship previously.


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ABSTRACT

Lubricant is a material introduced to reduce friction between metal surfaces in mutual contact, which eventually reduces the heat generated when the surfaces are in motion. It also has the function of transmitting forces, cooling the surfaces, transporting foreign particles, safeguard against wear and prevent corrosion.

The lubricant contains base oil and an additive package. The function of additives is either to improve an already-existing property of the base fluid or to introduce some novel property.

Present work includes synthesis, characterization and performance evaluation of multifunctional additives for lube oil. The synthesized additives were acrylate based homo and copolymers of different types. In case of copolymers, the monomers used were 1-Decene and different vegetable oils. The polymers were synthesized thermally in presence of BZP/AIBN as initiator. The prepared polymer were characterized by spectral analysis (FT-IR, ^1H NMR and ^{13}C NMR), followed by molecular weight determination (viscometric / GPC) and finally thermal stability was studied by Thermo gravimetric analysis (TGA). The polymers were evaluated as viscosity modifier (VM), pour point depressant (PPD) and anti-wear (AW) additive in different paraffinic base oils according to standard ASTM methods. The oil thickening property of the polymers has also been investigated in some cases. In case of biodegradable polymeric additives, biodegradability was studied by Disc diffusion method against some fungal pathogens and by Soil burial degradation test as per ISO 846:1997. As the additives were multifunctional in nature (PPD, VM and/ or AW), attention of research on this area gives a new scope in the lubrication technology.

The thesis begins with a general introduction of present investigation. The comprehensive research work has been divided in three parts: Part I, Part II and Part III. Part I entitled, “**Liquid crystal blended polyacrylate as potential multifunctional lube oil additives**” is divided into three chapters, Chapter I, Chapter II and Chapter III. Chapter I comprises background of relevant work. Chapter II describes synthesis, characterization and performance evaluation of multifunctional additive derived from cholesteryl benzoate (CB) blended polydecyl acrylate. CB is known to have liquid crystalline properties, which can lead to provoke effective anti-wear performance of them. Yet again poly acrylates are well known as VM and PPD additives for lubricating oil. With this background 100 ppm of cholesterol benzoate was blended with poly decyl acrylate in anticipation of getting VM, PPD and AW performance in resultant blended composite. Poly decyl acrylate was synthesized from decyl acrylate, followed by spectral characterization (FT-IR, ^1H NMR and ^{13}C NMR) and viscometric molecular weight determination. The polymer was then mixed with CB to make a 100 ppm blend and the additive performance of both the homo polymer and the blended composite was carried out in two base oils. The blended composite showed better VM, PPD and AW additive performance compared to homo polymer. Chapter III comprises synergistic effect of liquid crystals on the additive properties of long chain alkyl acrylate in lube oil. The polymer was blended with LC of different ppm level and the multifunctional performance of all blended composites (100, 200, 300, 400 and 500 ppm) were studied to investigate which composite was more effective as multifunctional additive in lube oil.

Part II, “**Biodegradable multifunctional additives for lube oil**” is splitted into three chapters, Chapter I, Chapter II and Chapter III. Chapter I is a concise review on background of the topic. Chapter II describes biodegradable lube oil additives derived from copolymer of citral and

dodecyl acrylate. The copolymers were characterized by spectroscopy, TGA and molecular weight. Biodegradability was studied by i) Disc diffusion method and ii) Soil burial test. The polymer samples were recuperated after the tests and were checked to determine effective weight loss. GPC analysis and FT-IR spectra of recuperated samples were compared with respective results before the tests to verify the biodegradable nature of the copolymers. The copolymer samples found to be biodegradable VM and PPD additive for lube oil. Chapter III comprises similar kind of investigation on two systems *viz.* i) Rice bran oil + poly decyl acrylate, ii) Rice bran oil + poly 1-Decene iii). 10%, 20% and 30% copolymers were synthesized for each of them, followed by characterization and performance evaluation. Biodegradability study was also performed for the samples. The copolymers were found to exhibit excellent biodegradability and efficient VM, PPD properties for lube oil.

Part III, “**Nano blended polyacrylate as lube oil additives**” is divided into three chapters, Chapter I, Chapter II and Chapter III. The first Chapter deals with background of respective work. Chapter II comprises “Polyacrylate-nano magnetite composite as a potential multifunctional lube oil additive”. Homo poly dodecyl acrylate and magnetite nanoparticle were synthesized, characterized and some blended composites were prepared with acrylate and nanoparticle. The performance evaluation of blended composites was done as viscosity modifier, pour point depressant and anti-wear agent. Molecular weights of the polymers were determined by GPC analysis. Chapter III, “Multifunctional additive properties of acrylate based ZnO nano composite for lubricating oil” deals with anti-wear activity, Viscosity modifier and pour point depressant property of Nano-ZnO/polyacrylate composites. Homo poly dodecyl acrylate and magnetite nanoparticle were synthesized, characterized and some blended composites were prepared with acrylate and nanoparticle. The performance evaluation of blended composites was

done as viscosity modifier, pour point depressant and anti-wear agent. Molecular weights of the polymers were determined by GPC analysis.

Preface

The primary functions of a lubricant are reduction the friction and wear between two moving surfaces in relative motion, heat removal and contaminant suspension etc. Apart from these, there are additional functions for automotive and industrial purposes. Lubricant is generally a combination of lubricating oil and an additive package (up to 30%). Additives either improve the existing properties of lubricating oil or bring in some new properties. They are composed of large variety of chemicals depending on specific properties required to introduce. From last few years demands for multifunctional additives have increased noticeably. In the present work the author has synthesised some multifunctional additives for lube oil and has evaluated their additive performance in different base oils. In Part I, the polymeric additives has been synthesized from poly acrylate and are blended with liquid crystals. Their additive performance has been evaluated in different base oils. In Part II, Synthesis, characterization and performance evaluation of vegetable oil based polymeric additives has been reported. Synthesis, characterization and performance evaluation of some nanoparticles blended polyacrylate additives has been reported in Part III of the thesis.

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List of publications

1. Liquid crystal blended polyacrylate as a potential multifunctional additive for lube oil, Pranab Ghosh, **Koushik Dey**, Mahua Upadhyay, **Petroleum Science & Technology**, 2014, 32(17), 2049-2058.
2. Multifunctional additive performance of liquid crystal blended dodecylacrylate in lube oil, Mahua Upadhyay, **Koushik Dey**, Pranab Ghosh, **Indian Journal of Chemical Technology**, 2014, 21, 244-248.
3. Multifunctional biodegradable lube oil additives: Synthesis, characterization and performance evaluation, Pranab Ghosh, **Koushik Dey**, Mahua Upadhyay, Tapan Das, **Petroleum Science & Technology**, 2017, 35(1), 66-71.
4. Biodegradable multifunctional additives for lube oil: Synthesis and characterization, Mahua Upadhyay, **Koushik Dey**, Pranab Ghosh, **Petroleum Science & Technology**, 2016, 34(14), 1255-1262.
5. Potential eco-friendly multifunctional lube oil additives, **Koushik Dey**, Pranab Ghosh, Communicated to **Canadian Journal of Chemical Engineering**, MSID-CJCE-17-0406
6. Synergistic effect of liquid crystal on the additive properties of long chain alkyl acrylates in lube oil, **Koushik Dey**, Pranab Ghosh, **Communicated to International Journal of Industrial Chemistry**, 03.09.2017, MSID- IJIC-D-17-0131
7. Polyacrylate-nano magnetite composite as a potential multifunctional lube oil additive. **Koushik Dey**, Pranab Ghosh, Communicated to **Journal of Tribology International**, dated-24.10.2017

8. Multifunctional additive properties of acrylate based-ZnO nano composite for lubricating oil, **Koushik Dey**, Pranab Ghosh, Communicated to **Journal of Chemical and Engineering Data**, Dated- 25.10.2017

List of oral and poster presentation

1. Shear stability and thickening properties of homo and copolymer of methyl methacrylate, T Das, D Nandi, M Upadhyay, **K Dey** and P Ghosh, 13th annual symposium of CRSI-2011, Feb 2-4, KIIT, Bhubaneswar.
2. Polyacrylate-LC blended as a potential lube oil additive, **Koushik Dey**, Mahua Upadhyay, and Pranab Ghosh, Regional chemistry seminar-2011, May 7-8, Biratnagar, Nepal.
3. Anti-wear performance of LC blended polyacrylate in lube oil, Mahua Upadhyay, **Koushik Dey**, Tapan Das, Gobinda Karmakar, Debobrata Nandi, Pranab ghosh, CRSI Eastern zonal meeting- 2011, july 22-24, Department of chemistry, University of north Bengal.
4. Potential eco-friendly multifunctional lube oil additives, **Koushik Dey**, Mahua Upadhyay, Mahammed Golam rasul and Pranab Ghosh, 19th annual symposium of CRSI -2016, July 13-16, University of North Bengal, Darjeeling.

Abbreviations

1. ASTM- American Society for Testing and Materials
2. AW- Anti-wear
3. BO1- Base Oil Type 1
4. BO2- Base Oil Type 2
5. BPCL- Bharat Petroleum Corporation Limited
6. BZP- Benzoyl peroxide
7. CB- Cholesterol benzoate
8. CTAB- N-Cetyl-N,N,N-trimethylammonium bromide
9. FBWT- Four ball wear test
10. GPC- Gel permeation chromatography
11. HPLC- High Performance Liquid Chromatography
12. IOCL- Indian Oil Corporation Limited
13. IR- Infra red
14. KV- Kinematic Viscosity
15. LC- Liquid crystal
16. LOA- Lube oil additive
17. MMO- Mixed metal oxide
18. M_n - Number average molecular weight
19. M_w - Weight average molecular weight
20. MHS- Mark-Houwink-Sakurada
21. NMR- Nuclear magnetic resonance
22. OCP - Olefin copolymers
23. OEM- Original equipment manufacturer
24. PDA - Poly Decyl Acrylate
25. PDDA- Poly Dodecyl Acrylate
26. PIB- Polyisobutylene
27. PMA- Poly methacrylate
28. PMI- Photo micrographic image

29. PPD- Pour point depressant
30. RBO- Rice bran oil
31. SB- Schulz-Blaschke
32. SBT- Soil Burial Test
33. SC- Solomon- Ciute
34. SEM- Scanning Electron Microscope
35. SIP- Styrene isoprene polymer
36. S1- Source 1
37. S2- Source 2
38. TEM- Transmission Electron Microscope
39. TGA- Thermo gravimetric analysis
40. THK- Thickening
41. TMS- Tetra Methyl Silane
42. VI- Viscosity index
43. VII- Viscosity index improvers
44. VM- Viscosity modifier
45. WSD- Wear scar diameter
46. XRD- X-ray diffraction
47. ZDDP- Zinc di alkyl dithiophosphate

General Introduction of Present Investigation

Lubricating oil is the basic building block of a lubricant. Lubricating oil is also known as base oil or lube oil. They are intricate mixture of paraffinic, naphthenic and aromatic hydrocarbon with a broad range of molecular weight, varying viscosity, density etc. The principal application of the lube oils is to reduce friction between metal surfaces which are on continual movement in an engine. In addition to friction reduction, lube oil plays a few varieties of functions in an engine e.g. resistance of oil viscosity with variation of temperature, improve flow properties at low temperature, less fuel consumption, corrosion inhibition and so on. Such massive work load led to lack of quality performance and eventually repeated oil change is required. With the advancement of technology and different kinds of modern engines, demands for technically better lube oil are mounting which embrace multifunctional performance, cost effectivity along with biodiversity protection. Natural petroleum based lube oils are incompetent to meet all the requirement of modern engine. Therefore to improve the performance of base oil, a huge number of functional additives¹⁻⁶ is added in lube oil. They not only improve the performance of base oil that already present on it but also introduce some new additional properties. These species are called lubricating oil additives and the additive incorporated lube oil is termed as commercial lubricant. The additives are generally chemical compound which are used as single chemical or blend of two or more compounds in base oil in varying range of concentration according to their requirement and field service performance. Most of the additives generally have long chain hydrocarbon unit in their structure to make them soluble in base oil.

Lubricant additives mainly fall into three general categories:

a) **Protect the lubricated surface:** These additives protect the lubricated metal surface from rust or wear by forming a protective film on them. Extreme pressure,¹ friction modifier, corrosion inhibitors,² anti-wear³ (AW) etc are examples of this kind.

b) **Protect the base oil:** These kinds of additives protect the base oil as well as the additives from oxidation, high temperature cracking etc. Antioxidant ⁴ and foam inhibitors ⁵ are of this type.

c) **Improve the base oil performance:** These additives are used to introduce some new and useful performance to the lubricant or to enhance the already existing properties of base oil. Viscosity modifier (VM),⁶ pour point depressant (PPD),⁷ detergent, dispersant, demulsifier⁸ etc. are common of these kinds of additives.

The present investigation includes the syntheses of some polymeric VM, PPD and AW additives, followed by their characterization and performance evaluation in base oils.

Concise backgrounds of these three types of additives are represented below.

◆ **Viscosity modifiers:** Viscosity is the most important single property of lubricating oil. For satisfactory performance of any kind of equipment, the first essential condition is to use an oil of suitable viscosity to meet the operating conditions. In selecting the proper lubricating oil for a particular application, viscosity is a primary concern. The viscosity of any fluid varies with temperature, decreasing as the temperature is increased, and increasing as the temperature is decreased. Viscosity index improvers (VII) or viscosity modifier (VM) are substances that oppose the variation of viscosity with temperature. They increase the viscosity of lube oil at higher temperature and minimize the increase of viscosity of oil at low temperature, thus maintaining a favourable relation between temperature and viscosity. The change of viscosity with variations in temperature is quantitatively express by an arbitrary number called Viscosity index ⁹ (VI). The higher value of viscosity index indicates the low rate of viscosity change of the oil with temperature variation and vice versa. The performance of viscosity improvers depends on their solubility in base oils, molecular weight, chemical behaviour and shear stability.¹⁰ VIIs

are long chain, high molecular weight polymers which perform by causing the relative viscosity of an oil to raise more at high temperature than at low temperatures. Usually this result is owing to an alteration in the polymer's physical configuration with rising temperature. It is postulated that at low temperature the polymer molecules remain in a coiled form so that their consequence on viscosity is minimized in base oil. As temperature increases the polymer molecules tend to straighten out, and the interaction among these long molecules and the oil results a proportionally greater thickening effect and thus effective volume is also increases.¹¹ This expansion of polymer coils with rise in temperature donate more and more viscosity to the oil. The coil expansion process is completely reversible as coil contraction occurs with falling temperature.

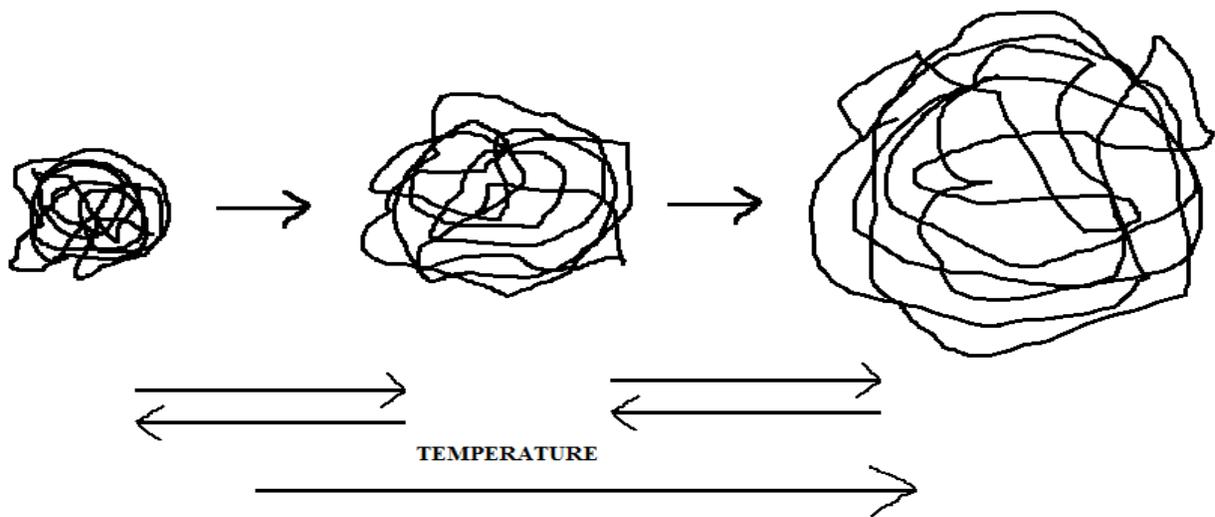


Figure 1: Polymer coil expansion with temperature

This increase in volume of polymer molecules (VM) causes increase of base oil viscosity which counterbalances the normal reduction of base oil viscosity with rise in temperature.¹² The VM of higher molecular weight also increases effective volume in oil solution and shows higher viscosity index value. A good VM should be more effectual in increasing the viscosity of oils of low viscosity and low effectual as the viscosity of base oil increases. By proper lubricant

formulation it is possible to create an engine lubricant which fulfils both the low and high temperature demand of the SAE viscosity classification system.

The most commonly reported VM's are methacrylate polymers and copolymers, acrylate polymers, polyisobutylene (PIB),¹³ olefin copolymer (OCP), styrene butadiene copolymers, hydrogenated styrene isoprene copolymer (SIP), polybutadiene rubber (PBR) etc.

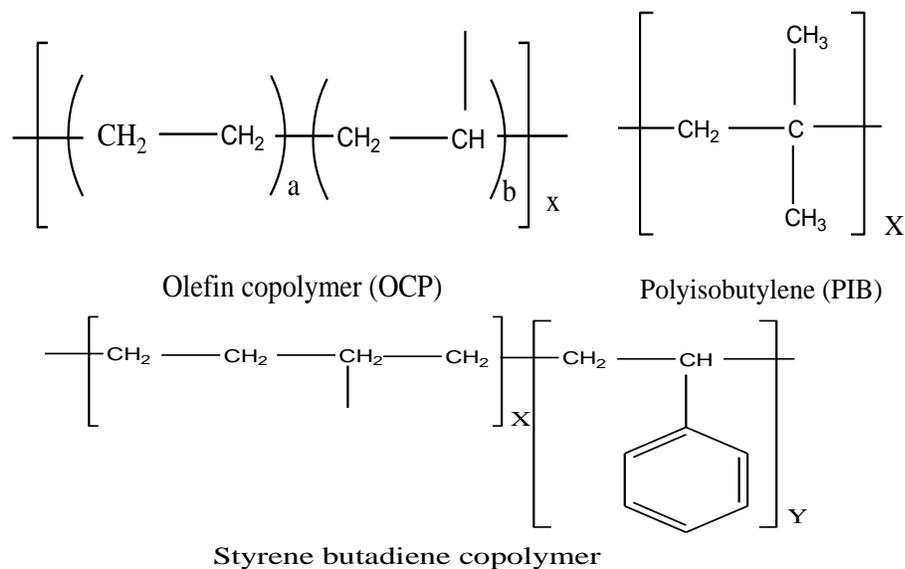


Figure 2: Structure of commonly used viscosity modifiers

Pour point depressant: Crude oil contains paraffin waxes (linear high molecular weight hydrocarbon), which tend to be separated from oil at a definite temperature (the cloud point). Paraffin wax deposition at low temperature is one of the serious and long-standing troubles in petroleum industry. At low temperatures, wax crystals easily form solid cakes, which can block filters and in the end lead to engine malfunction. As the temperature decreases the process of crystal growth increases and at a particular temperature the oil stops flowing. The lowest temperature at which oil can flow freely under its own weight is called pour point. To improve

the fluidity at low temperature, pour point depressant (PPD) or lube oil flow improver's additives are used. It has been found that, by the addition of additives the shape of wax crystal modified. Various postulates have been suggested to explain this phenomenon and to steer the PPD product design. Among the various mechanisms nucleation, adsorption co-crystallisation and improved wax solubility are extensively accepted by mechanism researchers.^{14, 15} A low pour point is mostly important for suitable performance of lubricants in cold climates. Most common PPD's are fumarate/ vinyl acetate copolymers,¹⁶ polymethacrylates,¹⁷ polyacrylates¹⁸ etc.

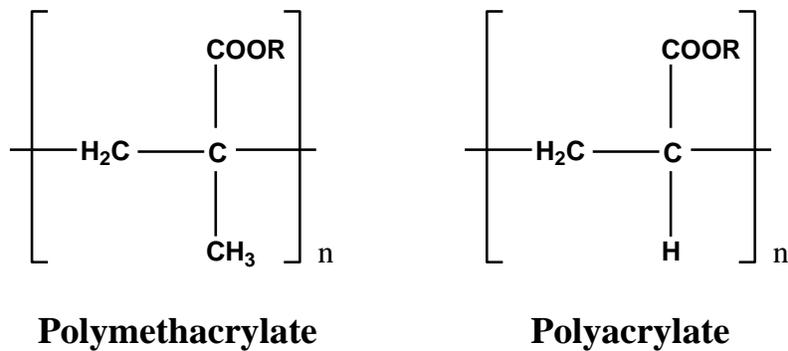


Figure 3: Commonly used pour point depressants

This wax crystal networks also increase the oil viscosity and the consequence is usually momentary as a normal combustion engine can create sufficient shear to disrupt the wax. But this increases the workload on the engine and reduces its lifetime. Pour point depressants are polymeric compounds that constitute a long hydrocarbon chain with a polar part. The long hydrocarbon chain provides interaction between paraffin and the additive. The polar part is accountable for wax crystal morphology modification, inhibiting the crystal growth stage.

Anti-wear additive: Anti-wear additives formulated for lubricating oil to prevent direct metal-to-metal contact between parts of gears. These are act as boundary lubrication additives. Continuous friction between metal parts produces wear on metal surfaces which trim down the engine performance for long period of application. These wear and surface damage induced by

the friction in moving parts in an engine can be decreased by anti-wear additives. Anti-wear additives form a surface film by tribochemical reaction to reduce wear between metal surfaces. Potent AW additives adsorb strongly or chemisorbs onto metal surfaces. In case of chemisorptions sometimes electron transfer occurs between absorbed molecule and metal surface¹⁹ (Figure 4).

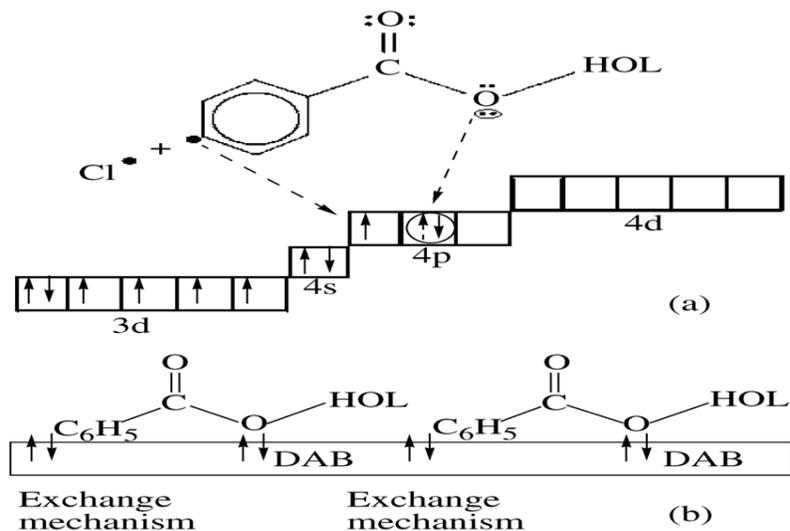


Figure 4: Schematic representation of (a) donor-accepter bond and (b) chemisorptions between AW additive (cholesteryl based) and metal (Fe) surface

Among a range of compound organic phosphates, polysulfide, dithiocarbamates are extensively used AW and extreme pressure additive.²⁰ However, the most important progress in anti-wear chemistry was happened with the discovery (during the 1930s and 1940s) of zinc dialkyldithiophosphate (ZDDP), which is rapidly became the most extensive AW additive in formulated engine oils.²¹ This also functions as a corrosion inhibitor and antioxidant. Researchers revealed that ZDDP breaks down and turns into a “tribofilm,” a thin, solid layer that sticks to the surfaces in contact and protects them from wear. Stearic acid is an effective AW additive under milder condition (under 150°C). Tricresyl phosphate (TCP) is also used for high-temperature

operation as AW and EP additive in turbine engine lubricants, and also in some crankcase oils and hydraulic fluids. Dithiocarbamates and dithiophosphate are complex organic molecules having sulfur and phosphorous elements. These two elements are well-known poisonous for catalytic converters. Moreover, only at high temperature these compounds are active. This means a critical phase in cold starts of engines. Because of hazardous nature of the above compounds in recent times liquid crystals ³ and nano particles ²² are used as AW additive. Both of them have suitable structural characteristics which facilitates them to cover metal surfaces by absorption or even chemisorptions.

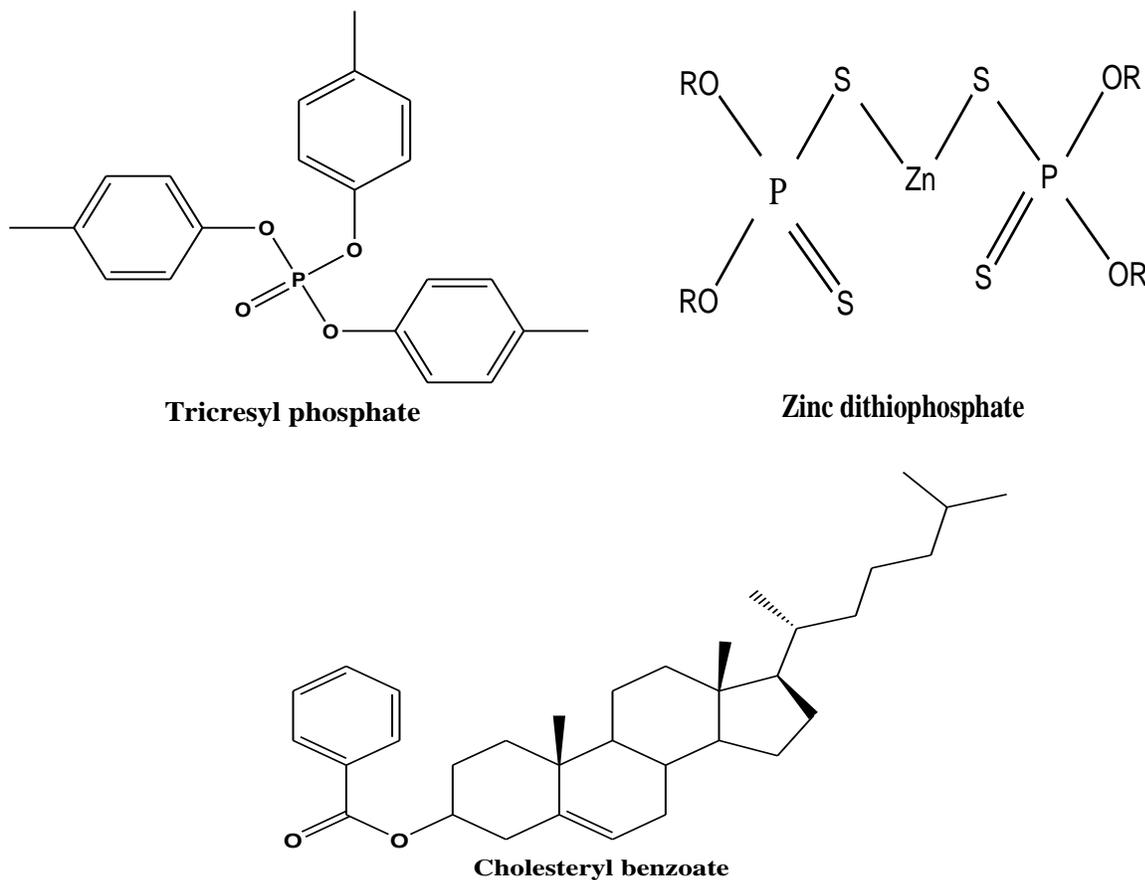


Figure 5: Some anti-wear additives

A lot of exciting studies have been accepted to elucidate the mechanism of anti-wear additives. Extreme pressure additives form stable protective films by thermo chemical reaction with the

metal surfaces. This film can combat extreme temperature and mechanical pressure, thereby protecting metal surface.

A number of additives have been studied and reported to perform either only as a VM²³ or PPD²⁴ or AW²⁵ additive or little more based on offering bi-functional performance like VM-PPD²⁶ or VM-AW²⁷ etc, but literature concerning multifunctional performance of additives system are very meager till date. With the development of modern engines and technologies, cost effective and eco-friendly additives²⁸⁻³⁰ imparting multifunctional performance is in great demand. In this connection for the development of lubricating oil additives attempts were made to insert multifunctional performance in a single additive system to meet the above demands. Liquid crystal blended polyacrylate systems were synthesised and evaluated as potential multifunctional additive. Noticeably very little amount of liquid crystal compound was used to ensure cost benefit. Looking into the concept of greener technology, the present study also includes synthesis and performance evaluation of vegetable oil based multifunctional additives. Vegetable oils used in the study are citral oil and rice bran oil. The nanoparticles used in the study are zinc oxide (ZnO) and magnetite (Fe₃O₄). The formulated lubricating oil additives showed excellent multifunctional performance in addition to very significant biodegradability.

In brief the thesis comprises synthesis, characterization and performance evaluation of a broad variety of different chemical additives for lube oils. The characterization was carried out spectroscopically (by FT-IR and NMR) followed by determination of thermal stability through thermo gravimetric analysis (TGA). Molecular weight of the polymers was determined by viscometric analysis or by gel permeation chromatographic method (GPC method). Finally performances of the additives chiefly as viscosity modifier (VM), pour point depressant (PPD) and anti-wear (AW) were assessed by standard ASTM methods in different base stocks.

Thickening property of some of the prepared additives were also determined and reported. Biodegradability study was performed by disc diffusion method using different fungal pathogens and by soil burial test as per ISO 846: 1997 rules. The outcome of the present study has yielded some potential additives which can be processed for commercial application and will be the carry on by our group in near future. Additionally, the study has also contributed a lot to the little known lube oil additive chemistry and will unquestionably help to cultivate research interest among the young scientists in the area of lubrication technology.

References

References are given in BIBLIOGRAPHY under General introduction of present investigation (PP 148-151).

Part-I

Liquid Crystal Blended Polyacrylate as
Multifunctional Additives for Lube Oil

Chapter-I

Background of the Present Investigation

A lubricant is a materials introduced to improve the smoothness of moving surfaces in mutual contact. Lubricants can be liquids, semi-liquids, solid or gas in nature. The lubricant is composed of base oil and an additive package. The base oil contains a complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with varying molecular weights ranging from high value to medium. They are found in nature with varying viscosities, densities and distillation curves. Although the primary function of base oil is to minimize friction between metal surfaces by forming a film between them, still a number of secondary functions are also needed from base oils such as temperature resistance towards viscosity, low temperature flow ability, cost effectiveness, fuel economy, enhancement of engine lifetime etc to meet the upcoming demand of modern technology. But classical base oil in most of the cases does not satisfy the current technical necessities because of their limits in enhancement of their properties. Thus base fluids generally cannot satisfy the necessities of high performance lubricants without taking the advantage of modern additive technology. In the view of improvement of the lubricating properties of base oils, different kinds of additives are doped into them. Lube oil additives¹ are substances which either impart some new and useful properties or enhance the already existing properties of base oils. Lubricating oil additives are chemical compounds added to base oils to impart specific properties to the oils. The physical and chemical natures of compounds play an important role in their additive performance. Additives generally cover a broad range of chemicals; those are may be simple organic molecules, polymers, or inorganic compounds. The lubricating oil additives are mostly polymeric materials. This is because of the fact that polymer shows good solubility characteristics in base oil. They can be used as single compound or blend of compounds in base oil. By means of performance, different types of additives are there. Few of the most important additives in this field are depicted in the next page.

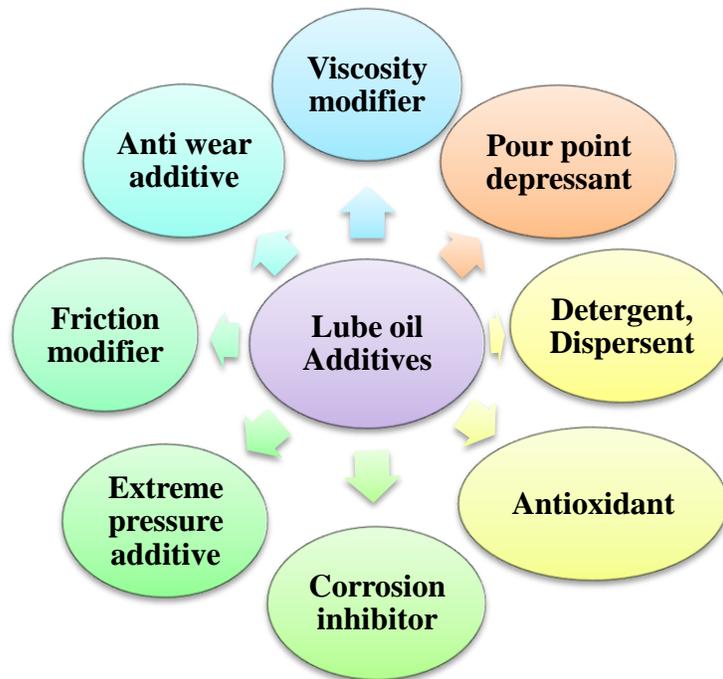


Figure 1a: Different kinds of lube oil additives

These additives when added in base oil impart their natural properties and field performances in existing applications are also improved. Due to the cost and the harmful nature of the chemical additives used in this field, there is an increasing demand for multifunctional additives. In current context multifunctional additives play the key role in the engine oil technology. Hence research to produce multifunctional additives is increases throughout the world.²⁻⁶ Again, according to the literature survey, more than one kind of additive performance can be obtained in a single system in case of multifunctional additive.⁷⁻¹⁰ Thus introduction of multifunctional property in single system have become very significant nowadays. With this background the present investigation comprises the inclusion of three major additive performances (VM, PPD and AW) in single additive system. In accordance with the present investigation, it will be very relevant to include a brief review on VM, PPD and AW additives of lubricating oil. Polymers are generally high

molecular weight compound and the numerous investigation and experience in the use of these polymers as additives are now opening the possibility of development of polymeric multifunctional additives that shows both PPD and VII properties.

As described in the general introduction, the most important single property of lubricating oil is viscosity and the additive used to maintain this viscosity change with temperature is called viscosity modifier. The viscosity index (VI) is an arbitrary number¹¹ describes the performance of a viscosity modifier. VI indicates the resistance of a lubricant to change in viscosity with variation of temperature. Viscosity modifiers (VM) or viscosity index improvers (VII) are compounds which modify the rate of change of viscosity of oil with temperature. Addition of appropriate VM increases the VI of base oil in particular temperature range. Higher the VI value higher is the resistance of oil to change viscosity with temperature. Again efficiency of a VM depends on concentration and on the type of the additive being used. In the application of multigrade motor oils, this quality is most perceptible. Generally, an efficient VM is a long chain high molecular weight polymeric compounds.¹² Performance of the VM depends on the behaviour of the polymer molecules in the oil in terms of molecular weight, solubility and resistance to shear degradation.¹³ The solubility of a polymer generally increases with increasing temperature as the tight coils form of the polymer molecules change to an open configuration, which has a higher volume. With the increase of volume the viscosity of the oil also increases, which actually compensate the normal reduction of viscosity with increasing temperature.^{14, 15} A high molecular weight polymer also increase the effective volume in an oil solution¹⁶ and as a result, a higher molecular weight polymer shows higher viscosity index value compared to a lower molecular weight polymer of the same type.¹⁷

The pour point of oil is considered to be the temperature at which the oil begins to lose its fluidity under the effect of gravity under prescribed conditions.¹⁸ For an engine to work smoothly at cold condition, low pour point of base oil is crucial. The use of chemicals to depress the pour points of lubricating oil is common, and such chemicals make possible the production of low pour point oil without extensive dewaxing. Generally most mineral oils contain some dissolved wax, and as the oils are cooled, this wax crystals are begins to separate from the oil which inturn form a rigid structure and traps the oil in small pockets.¹⁹ When this wax crystal structure becomes adequately strong; the oil completely lost its ability to flow under the experimental conditions. Low pour points of base oil can be achieved by exclusive removal of waxy components of the oil during refining. But this technique makes the oil lower susceptible towards oxidation and increases the formation of carbon deposits. Another way to get lower pour point is to hinder the formation of wax crystal structure at low temperature in the base oil. This can be achieved by incorporating certain high molecular weight polymeric compounds in the base oils. These polymers avert the wax crystallization and thus improve the flow property of oil. These compounds are known as pour point depressant or flow improver. The efficiency of a pour point depressant depends on structural properties, chemical composition and alkyl chain length. The action mechanism of PPD is of much interest. It was assumed that PPD additives coat the wax crystals preventing further growth. Later more accepted mechanism involves co-crystallisation of polymer with wax particle. This process inhibits the formation of three dimensional networks and preserves the wax as tiny particle in the oil and ensures fluidity.²⁰⁻²²



Crystal network without
pour point depressant



Crystal network with
pour point depressant

Figure 1b: Mechanism of PPD action

Light microscopy analysis suggests that wax crystals are basically thin plates. The crystal network structure of wax gels with and without pour point depressant has been extensively studied by researchers using XRD.²³ It was argued that in isolated base oil the paraffin crystallizes predominantly in orthorhombic structure. During the formation of gel in base oil, the crystal structure of wax altered to hexagonal form. The pour point depressant (PPD) additive hastened the formation of hexagonal planes. The PPD additives offer an economical means of facilitating the low temperature flow ability of oil in an engine with ease.

The study of the earlier researchers regarding VM and PPD additives are being presented in the following paragraphs.

U.S. Patent No. 5834408 disclosed preparation and evaluation of acrylate based copolymers as a PPD in lube oil. U.S. Patent No. 4867894 showed excellent pour point properties of petroleum

oil containing copolymers of methyl methacrylate having an average molecular weight from 50,000 to 500,000.

U.S. Patent No. 4956111 described the application of polymer of poly methacrylate having an alkyl group with an average chain length ranging from 12.6 – 13.8 can decrease the pour point to -35° C and is compatible with other kind of additives e.g. VM and detergents.

U.S. Patent No. 4906702 described the PPD performance of olefin copolymer of unsaturated carboxylic acid ester for lube oil.

U.S. Patent No. 4668412 has claimed the synthesis of a dispersant VII and pour point depressant of a terpolymer of maleic anhydride and lauryl methacrylate and stearyl methacrylate which has been formulated with dimethyl amino propyl amine and manich base of amino ethyl pyrazine, paraformaldehyde and 2, 6-ditertiarybutyl phenol.

U.S. Patent No. 4032459 also disclosed the novel lubricating composition containing a copolymer of hydrogenated butadiene and isoprene with PPD and superior VII properties.

U.S. Patent No. 4073738 disclosed acrylate and methacrylate based copolymers and copolymers of styrene and conjugated dienes exhibit high stability to shear and may be useful for lubricating gearbox or I. C. Engines and the composition may be useful as a VII.

U.S. Patent No. 5955405 disclosed a poly (meth) acrylate copolymers comprising from 5 to 15 wt% butyl methacrylate, 70-90 wt% C-10 to C-15 alkyl (meth) acrylate, from 5-10 wt% C16 – C30 alkyl (meth) acrylate having excellent low temperature fluidity to lubricating oils.

U.S. Patent No. 4886520 described an oil composition comprising mineral oils and synthetic oil which showed enhance viscosity index and pour point properties by the addition of a terpolymer

comprising an alkyl ester of an unsaturated monocarboxylic acid, and olefinically unsaturated homo and heterocyclic nitrogen compound and then a perfluoro alkyl ethyl acrylate or methacrylate or an allyl acrylate or methacrylate.

U.S. Patent No. 6458749 described the polymerization of a mixed methacrylate made of alcohols containing C16 – C24 carbon are particularly effective by satisfying different aspects of low temperature fluidity properties over a wide range of base oils.

In 2005 Azim et al reported octadecene – methacrylate based copolymer as multifunctional additive (VM, PPD, Dispersancy - detergent).²⁴ It was found that with increasing alkyl chain length and concentration of additive the efficiency of compounds as VM increases where as their efficiency as PPD decreases with increasing the concentration of prepared polymeric additive . In 2009 Azim et al again reported a new kind of copolymer system based on methyl methacrylate-styrene as multifunctional (VM, PPD and detergent- dispersant) lubricating oil additive.²⁵ Another similar kind of work described a method to prepare a series of copolymer and terpolymer of alkyl acrylate and maleic anhydride and they investigated the structural influence of the copolymer and terpolymers on PPD properties.²⁶ Acrylate based viscosity modifier and pour point depressant additives are most common. A number of reports are available on competency of poly alkyl methacrylate and poly alkyl acrylate as PPD and VM .^{27- 29} The initial article on pour point depressants additive was reported in 1930s.³⁰ Almost two decades later a report by Ruehrwein which showed the action of n- alkyl poly methacrylate as PPD in the series of alkyl group like dodecyl, tetradecyl, hexadecyl and octadecyl.³¹ It was proposed that the polymers having longer alkyl groups were effective in depressing the pour point of high temperature pour oils, while shorter alkyl group containing polymers were effective on lower temperature pour oil. The literature survey on VM and PPD additives showed widespread

application of homo as well as copolymer of acrylate and methacrylate. But tribological activity of such system is very rare.³²

All metal surfaces irrespective of their finish contain valleys, asperities, ridges and depressions. So when two moving metal surfaces come in contact, because of friction there arise wear on the metal surfaces, which ultimately lead to the poor performance of engine. Thus with increasing friction the wear is also increases. To avoid this friction some additives are incorporated in lube oil which can minimize friction and improve lubricity. The lubricity is a measure of the reduction of friction and wear by lubricant. So it is not a property of matter and direct measurement cannot be possible. Tests are there which are often done by performed to quantify a lubricant's performance for a specific system. Between two fluids of same viscosity, the one that is considered to have higher lubricity property which results smaller wear scar. Anti-wear additives are used to reduce wear and surface damage caused by the friction between moving parts of gears by making a protective film in between them. All anti-wear additives form a protective layer or film at the bearing surface at start up periods and in the boundary lubrication regime. This is the fundamental mechanism of anti-wear additives. In the parts of engine the major cause of wear is because of asperities in metal surfaces.³³ Tribological performance of lubricants depends on their structure. Solid compounds such as graphite, titanium disulfide (TiS_2) or tungsten disulfide (WS_2) are usually used as lubricants due to their layered structure. A layered arrangement of atoms in the crystal lattice enables the formation of a slip plane of protector function. It has been accepted from long time that the presence of a close-packed molecular monolayer can prevent direct contact between the metal surfaces and minimizes the friction dramatically, while wear behavior is controlled by surface chemistry. Liquid crystalline compounds, which are known to have the fluidity characteristics of a liquid and the elasticity

characteristics of a crystalline solid and have layered structure.³⁴ The presence of layered structure with the properties mentioned above on contacting body surfaces, would allow providing simultaneously both a low friction coefficient and a high wear resistance. They can be even more useful because of the presence of polar groups in mesogenic compounds; this causes a better adsorption on the steel surface. This effect makes the slip plane formation even easier and this plane known to have a protective role.³⁵ The use of thermotropic and lyotropic liquid crystals having smectic, nematic and cholesteric mesophases derived from Schiff bases, cyanoaryls, azoxys and esters was extensively studied as lube oil additive. MLCs were used in pure form or as a blended composite and as lubricant additives.³⁶⁻⁴⁰ The molecular orientation of nematic liquid crystal 4-pentyl-4' cyanobiphenyl (5CB) in a shear flow between parallel plates was studied by Nakano⁴¹. Molecular orientation depends on the product of the film thickness the sliding velocity. MLCs of cholesteryl types have also received great attention, as they are found naturally to act as biological lubricants. Waters *et al.*⁴² found that lubricant containing liquid crystal of cholesterol palmitate significantly reduces wear and atomic force microscopy (AFM) studies showed that the liquid crystal compound formed a protective layers on the high-nitrogen stainless-steel femoral heads, counterface surfaces and ultra-high molecular weight polyethylene. It was concluded that a remarkable reduction of wear could be achieved by inclusion of liquid crystal based lubricant in hip-replacement elements. Kupchinov *et al.*⁴³ reported the results of investigations performed on the anti-wear property of liquid crystals and their solutions in synthetic oils and in petroleum as a function of MLC concentration. The lubricant containing MLCs decreases friction coefficient and thus reduces wear. Several studies have been committed to set up a relationship between molecular structure and tribological properties and molecular structure of MLCs.⁴⁴⁻⁴⁸ Among the various MLCs cyanophenyls and cyanobiphenyls are the most

commonly studied as lubricants, due to their accessibility and their electrooptical applications. Mori and Iwata⁴⁹ investigated the tribological behaviour of smectic and nematic liquid crystals like alkyl cyanobiphenyl (CB), alkylcyanophenyl cyclohexane (CPC), alkoxy cyanobiphenyl (ECB) using a two-roller friction tester. Numerous families of MLCs (thermotropic) have been studied to use as commercial oil additives.⁵⁰ The study implies variations in bulk viscosity and temperatures have no significant effect on friction values. A 1 wt% addition of cholesteryl based liquid crystals to two different base oils lowers friction coefficients of steel was studied.

From the literature survey about anti-wear additive it was found that liquid crystals of different morphology and structure have excellent tribological properties, but they are not effectual for every other kind of additive performance. By taking into account of the above point we got the idea of blending liquid crystals with poly acrylate together to get multifunctional (VM, PPD, AW) performance. Again by kept in mind the minimum cost of production the author has used very low quantity of liquid crystal in a blend. Again to correlate the amount of liquid crystal and effectivity, different blended composite having varying amount of liquid crystal in same polyacrylate was prepared and the performance of the samples was compared. The poly acrylates used in this section is homo poly decyl acrylate, Thus in view of the current need and the importance as given by the original equipment manufacturers (OEMs), it was felt to carry out the present investigation towards the improvement of an efficient multifunctional additive having PPD, VM and AW properties for lube oil.

References:

References are given in BIBLIOGRAPHY under Chapter I of Part I (PP 151-156).

Chapter II

**Liquid Crystal Blended Polyacrylate
As a Potential Multifunctional Additive for
Lube Oil**

1.1.1. Introduction:

Lubricants are substances those add performance to base oil in terms of fuel economy, cost effectiveness, increased engine lifetime and so on. Minerals oils (e.g., paraffin oil) can be used as lubricants. But modern devices need the quality increase of used lubricants. Classical lubricants do not meet contemporary technical requirement because of their limits in improvement of their properties. In the aim of the improvement of their lubricants properties, the various substances are doped in the base oil. Recent trend indicate toward using compounds with layered structure (e.g., graphite, WS_2 , MoS_2) as performance additives. The liquid crystal compound can also be used for same reason. Presence of layered structure in between metal surfaces prevents direct contact between them and thus acts as anti-wear additive.¹⁻² Poly acrylates and poly methacrylates are well known as viscosity modifier and pour point depressant from years.³ But a very few attempts has been made so far to study the influence of incorporation of liquid crystal structure to an acrylate based additive on their additive performance in lube oil.

Keeping this view in mind and in continuation of our efforts toward the synthesis of performance additives for lube and crude oils, acrylate based polymer was synthesized and blended with liquid crystal of cholesteryl benzoate to evaluate their performance in lube oil in comparison to the pure polymer. Oil thickening property of the polymer and LC-polymer blend in lube oil, which is a direct measure of percent increase in the viscosity of the base stocks for addition of its unit amount of weight, has also been investigated and reported here. This property can also be taken as the measure of extent of interaction of the polymer with the base stock, greater the thickening property; greater is the extent of interaction.⁴ Fuel economy may also be predicted by the thickening power of a lube oil additive. The results of our above investigations have been presented in this article.

1.1.2. Experimental Procedure

1.1.2.1. Material and Methods

Toluene, hydroquinone and H₂SO₄, decyl alcohol, and acrylic acid (stabilized with 0.02% hydroquinone monomethylether) were purchased from Merck Specialties Pvt. Ltd. Hexane and methanol were obtained from Thomas Baker (Chemicals) Pvt. Ltd. Benzoyl peroxide (BZP), purchased from LOBA chemicals was recrystallized from CHCl₃-MeOH before use. The rest of the materials were used as they were obtained without further purification. The base oils were collected from IOCL, Dhakuria, Kolkata and BPCL, Siliguri and their properties are depicted in **table 1.1**.

1.1.2.2. Preparation of decyl acrylate

Esterification was carried out by conventional method using 1.1 mol of acrylic acid and 1 mol of decyl alcohol, using a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid, and toluene as a solvent in nitrogenous atmosphere as reported earlier.⁵

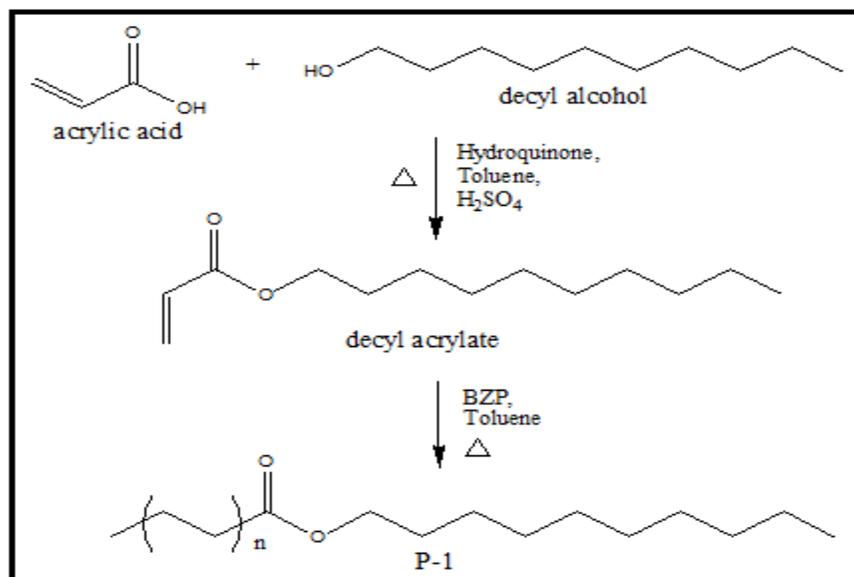
1.1.2.3. Purification of decyl acrylate

The prepared ester (decyl acrylate) was purified according to the following method: appropriate amount of charcoal was added to the ester. It was allowed to reflux for 3 hrs. and then filtered off. The filtrate was taken in a separating funnel and washed with 0.5N sodium hydroxide solution by thorough shaking. The whole process was repeated several times to ensure complete exclusion of unreacted acid and alcohol. Then the purified ester was washed several times with distilled water to remove any traces of sodium hydroxide; the ester was then left overnight on

calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

1.1.2.4. Preparation of homo polymer of decyl acrylate (P-1)

The polymerization was carried out thermally in a four-necked round bottomed flask equipped with a magnetic stirrer, thermometer, condenser and an inlet for nitrogen insertion. Taking appropriate amount of DA and radical initiator (BZP) in toluene as a solvent in the flask, the polymerization was started. The temperature of the reaction was maintained at 353 K for 6 hrs. After the completion of reaction time, the reaction mixture was poured into methanol with continuous stirring to terminate the polymerization and precipitate of homo polymer was appeared. The polymer (P-1) obtained was then purified by repeated precipitation of its hexane solution using methanol followed by drying under vacuum at 313 K.



Scheme: Preparation of decyl acrylate and poly decyl acrylate (P-1)

1.1.2.5. Preparation of poly decyl acrylate-LC blend

Required amount of polymer was taken in toluene; liquid crystal of cholesteryl benzoate (100 ppm with respect to polymer) was added to make a 100 ppm blend. The mixture was heated at 40°C with stirring for 1 hour to prepare a homogeneous blend. The blended composite was designated as P-2. Five different concentrations (1–5%, w/w) of additive samples (P-1 and P-2) solutions were prepared by the addition of required amount additive to the base oils, namely BO1(two different sources, S1 and S2) and BO2 (two different sources, S1 and S2) followed by heating at 60°C with constant stirring for 30 min.

1.1.3. Measurements

1.1.3.1. Molecular weight determination

The molecular weight (by viscometric method) of the polymer was determined by Mark-Houwink- Sukurda relation, by measuring the intrinsic viscosity of the polymer solution in toluene ⁶ as shown below:

$$[\eta]=KM^a \quad (1)$$

where $[\eta]$, the intrinsic viscosity can be calculated from different equations⁷⁻¹⁰ e.g. Huggins,

Kraemer, Martin, Schulz-Blaschke as follows

$$\text{Huggin (H)} \quad \eta_{sp}/C = [\eta]_h + k_h [\eta]_h^2 \quad (2)$$

$$\text{Kraemer (K)} \quad \ln \eta_r/C = [\eta]_k - k_k [\eta]_k^2 C \quad (3)$$

$$\text{Martin (M)} \quad \ln \eta_{sp}/C = \ln [\eta]_m + k_m [\eta]_m C \quad (4)$$

$$\text{Schulz-Blaschke (SB)} \quad \eta_{sp}/C = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad (5)$$

Where, C= concentration of the polymer solution (g.cm⁻³)

Where $\eta_r = t/t_0$, relative viscosity or viscosity ratio (where t is time flow of additive doped base oil solution and t_0 is time flow of pure base oil),

$\eta_{sp} = \eta_r - 1$, specific viscosity,

$[\eta]_h$ = intrinsic viscosity, respective to Huggins equation,

$[\eta]_k$ = intrinsic viscosity, respective to Kraemer equation,

$[\eta]_m$ = intrinsic viscosity, respective to Martin equation,

$[\eta]_{sb}$ = intrinsic viscosity, respective to Schulz–Blaschke equation;

k_h , k_k , k_m and k_{sb} are Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively.

M is the viscosity average molecular weight (equation 1) and K and a are the Mark-Houwink constants. Parameters K and a depend on the type of polymer, solvent and temperature. There are a specific set of Mark-Houwink constants for every polymer-solvent combination. So, these constant values are to be known for appropriate polymer-solvent combination in order to get an accurate measure of molecular weight.

1.1.3.2. Spectroscopic analysis

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

1.1.3.3. Thermo gravimetric Analysis (TGA)

A Mettler TA – 3000 system was used to obtain TGA data, at a heating rate of 10°C/min. 0.2 g of polymer sample was taken in a platinum crucible and heated gradually from room temperature to 700K.

1.1.3.4. Evaluation of viscosity improver property

An Ubbelohde OB viscometer was used for viscometric study of the prepared samples (in two base oils BO1 and BO2) which was thoroughly cleaned, dried and calibrated at the experimental temperatures (313K and 373K) with triply distilled, degassed water and purified methanol.^{11,12} It was then filled with experimental sample solution and positioned vertically in a glass sided thermostat. After attainment of thermal equilibrium, the time required to flow of sample solution was recorded with a digital stopwatch. In all experiments an average of three measurements was taken into account and safety measures were taken to diminish losses due to evaporation. The kinematic viscosity (ν) of the sample solutions was determined at 313 K and 373 K, using the following equation.¹³ These values of kinematic viscosity is useful to calculate viscosity index (VI).

$$\nu = (Kt - L/t) \rho \quad (6)$$

Where K and L are the viscometric constants and ρ and t are density of experimental solution and time of flow respectively.

The densities were measured using a vibrating - tube density meter (Anton paar, DMA 4500M). The density meter was calibrated prior to measurements with distilled and degassed water and dry air at experimental temperature and atmospheric pressure. VI was determined from the following empirical equation.¹³

$$VI = 3.63 (60 - 10^n) \quad (7)$$

Where n is given by,

$$n = (\ln v_1 - \ln k) / \ln v_2 \quad (8)$$

where v_1 is the kinematic viscosity (cSt) at lower temperature (313 K), v_2 is the kinematic viscosity (cSt) at higher temperature (373 K), k is a function of temperature only and n is a constant characteristic for each oil.¹³

Five different concentrations ranging from 1 wt% to 5% wt% of the sample solutions were used to examine the effect of concentration on VI.

1.1.3.5. Evaluation of pour point depressant (PPD) properties

Evaluation of the prepared samples as pour point depressants (PPDs) additives were done using two different base oils (BO1 and BO2) by the pour point test according to the ASTM D97-09 on a Cloud and Pour Point Tester model WIL-471 (India).

1.1.3.6. Evaluation of anti-wear (AW) properties

Anti-wear properties of the base stocks as well as polymer samples (P-1 and P-2) in base stocks were studied in sliding contact by means of a four-ball wear test machine as per ASTM D 4172 method by employing a 20 kg and 40 kg load condition.

1.1.3.7. Evaluation of thickening properties

A thickening agents or thickeners are the substances which can increase the viscosity of a solution or liquid/solid mixture. Thickening power of the polymer samples was determined by evaluating the percent increase in kinematic viscosity of the base stocks by the addition of unit amount of additive, which may be expressed as follows

$$\% \text{ Thickening} = [(v \text{ of additive doped base oil} - v \text{ of base oil}) / v \text{ of base oil} \times mf] \times 100 \quad (4)$$

Where, ν = kinematic viscosity of individual solution. mf= mass fraction

Thickening also determines the extent of base oil-polymer interaction, which is directly proportional with thickening.⁴ The five different concentrations (1 to 5% wt/wt) of additive doped base oils were used in the measurements.

1.1.4. Results and Discussion

1.1.4.1. Spectroscopic analysis

The homo poly decyl acrylate (P-1) exhibited IR absorption band at 1733 cm^{-1} for the ester carbonyl stretching vibration along with other peaks at 1457, 1378, 1265, and 1167 cm^{-1} . ^1H NMR spectra of P-1 (**Figure 1.2**) showed the presence of $-\text{OCH}_2$ protons as a broad singlet centered at 4.02 ppm, methyl protons between 0.81 to 0.86 ppm corresponds to that of the P-1 chain. The absence of singlet between 5 ppm and 6 ppm indicate the nonexistence of any vinylic protons in the polymer. ^{13}C NMR spectrum (**Figure 1.3**) of the polymer (P-1) confirms the presence of carbonyl carbon at 174.47 ppm and also the sp^3 carbons in the region 65.99 to 13.95 ppm.

1.1.4.2. Molecular weight determination

Viscometric analysis was carried out by using the six equations as mentioned above. A plot of $\log \eta_{sp}$ versus $\log c[\eta]$ for all samples (P-1 and P-2) gave a linear relation which signifies that the measurements were performed in Newtonian flow.¹⁴ Comparison among the polymer solution and the LC blended polymer solution indicated that, the latter has greater intrinsic viscosity $[\eta]$ values than the pure polymer. The viscosity average molecular weight of P-1 as determined from the intrinsic viscosity data using Huggins (M_h), Kraemer (M_k), Martin (M_m) and Schulz-Blaschke (M_{sb}) equations was presented in **table 1.3**.

1.1.4.3. Thermo gravimetric analysis

TGA data showed better thermal stability of the LC-blended polymer (P-2) in comparison to the pure polymer (P-1). P-1 had 19% loss in its weight at 518K and 92% loss at 608K, whereas for P-2 the weight loss was 12% at 538K and 82% at 638K.

1.1.4.4. Efficiency as Viscosity index improver

Figure 1.4 represents the viscosity index values of the additive doped base oils. From the figure, it is observed that the viscosity index (VI) values of the LC-polymer blend (P-2) doped base oil are always better than the pure polymer (P-1) doped oils at every concentration irrespective of the base oils. Again with both kinds of additives and up to a certain limit (4%) there is always a steady increase of VI values with the increase in additive concentration. Increase of concentration of the polymeric additive may lead to increase in total volume of polymer micelles in the oil solutions, which ultimately results a high viscosity index values.¹⁵

1.1.4.5. Efficiency as pour point depressants

Different level of concentrations ranging from 1 wt% to 5 wt% of the polymer solution in base oils were tested as PPD and the experimental results are shown in **figure 1.5**. The results showed that the prepared additives (P-1 and P-2) were efficient as pour point depressant and the efficiency increases by increasing the additive concentration in case of P-1, but in case of P-2 it was up to a certain limits (4%). This fact may be explained by taking into consideration the hydrodynamic volume of the polymer doped in oil. The hydrodynamic volume increases with increase in polymer concentration in base oil and thus the interaction increases. Again further depression in the pour point was observed in the case of P-2 doped base oils. The extended conformation of the polymer chain of the LC blended composite may be responsible for showing its better efficiency in comparison to the pure polymer.

1.1.4.6. Efficiency as anti-wear additive

Anti-wear properties of the pure polymer (P-1) and its blended composite (P-2) in comparison to that of the base oils were evaluated by using a four ball wear test machine as per ASTM test conditions. The wear scar diameter (WSD) measured in all these cases employing a 20 kg and 40 kg load condition are showed in **figure 1.6 and figure 1.7** respectively. In the case of pure base stocks, WSD decreased with the decrease in base stock viscosity. In case of pure polymer (P-1) doped base oil marginal decrease with increasing VM concentration was found in both base stocks (BO1 and BO2). Considerable decrease in WSD is observed in the case of the LC blended composite at every concentration. It was also observed that using a 20 kg load the decrease in WSD were much better than the higher load condition (40 kg).

1.1.4.7. Efficiency as thickening agents

A continuing decrease of the thickening power with the increase in concentration of both the polymer and LC-polymer blend was observed in both the base oils (BO1 and BO2) and it is depicted in **table 1.4**. Development of a coiled like aggregation with increase in concentration in the base stock may be responsible for such kind of thickening power of the additives. The result also showed that the thickening power of the LC-polymer blend (P-2) was slightly higher in comparison to the pure polymer (P-1). Thus it seems that the use of LC blended polymer in base oil may reduce the fuel consumption to some extent.

1.1.5. Conclusion

Liquid crystal of cholesteryl benzoate (CB) induces excellent anti-wear performance in comparison to the pure polymer along with the improvement of existing PPD, VI, and thickening properties of the PDA. However, both of them were found equally effective as thickeners for the base oils studied. In general, it was observed that, the values of viscosity index and pour point

properties increases with increasing concentration of the additives while the thickening power decreases. Hence, it can be concluded that the LC blended composite is effective as multifunctional additive for lube oil.

1.1.6. References

References are given in BIBLIOGRAPHY under Chapter II of Part I (PP 156-158).

1.1.7. Tables and Figures

Table 1.1: Properties of base oils

<i>Properties</i>	<i>Base oils</i>			
	BO1		BO2	
	S1	S2	S1	S2
Density, kg.m ⁻³ at 313K	840	880	940	950
Viscosity × 10 ⁻⁶ , m ² .s ⁻¹ at 313K	6.70	7.46	24.22	25.28
Viscosity × 10 ⁻⁶ , m ² .s ⁻¹ at 373K	2.00	2.15	4.39	4.49
Cloud point, °C	-10	-10	-8	-8
Pour point, °C	-3	-3	-6	-6

Where, BO1: Base oil of type 1, BO2: Base oil of type 2, S1: source 1, S2: source 2.

Table 1.2: Intrinsic viscosity values of prepared samples in toluene as solvent

<i>Sample</i>	<i>Intrinsic viscosity × 10⁻⁶, m².s⁻¹</i>			
	[η] _h	[η] _k	[η] _m	[η] _{sb}
P-1	2.411	2.418	2.431	2.452
P-2	2.523	2.528	2.541	2.552

P-1: Homo poly decyl acrylate, P-2: LC (100 ppm cholesterol benzoate) blended with P-1, η- Intrinsic viscosity, Subscripts h, k, m and sb denote values obtained using Huggins, Kraemer, Martin and Schulz-Blaschke equation respectively.

Table 1.3: Viscometric molecular weight

<i>Sample</i>	$[M]_h$	$[M]_k$	$[M]_m$	$[M]_{sb}$
P-1	7152	7277	7234	7320
P-2	7614	7635	7689	7735

P-1: Homo poly decyl acrylate, P-2: LC blended P-1, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$, Subscripts h, k, m and sb denote values obtained using Huggins, Kraemer, Martin and Schulz-Blaschke equation respectively.

Table 1.4: Thickening property of additives in base oils at 313 K

<i>Sample</i>	<i>Base oils</i>	<i>% Thickening of additive doped base oils at different conc.</i>					
		1%	2%	3%	4%	5%	
P-1	BO1	S1	49.003	26.342	17.879	15.219	13.447
		S2	38.995	20.612	14.788	11.991	10.676
	BO2	S1	41.884	21.989	16.343	13.909	10.935
		S2	36.005	18.914	15.786	11.569	10.095
P-2	BO1	S1	55.342	33.453	23.895	20.334	17.876
		S2	41.434	31.987	20.654	17.878	13.543
	BO2	S1	39.909	23.789	16.776	13.434	11.112
		S2	33.352	21.132	14.656	12.667	11.556

P-1: Homo poly decyl acrylate, P-2: LC (100 ppm. cholesterol benzoate) blended with P-1, BO1— Base oil of type 1, BO2 — base oil of type 2, S1 — source 1, S2 — source 2. 1 to 5% is concentrations of additive.

Figure 1.1: FT-IR spectra of homo poly decyl acrylate

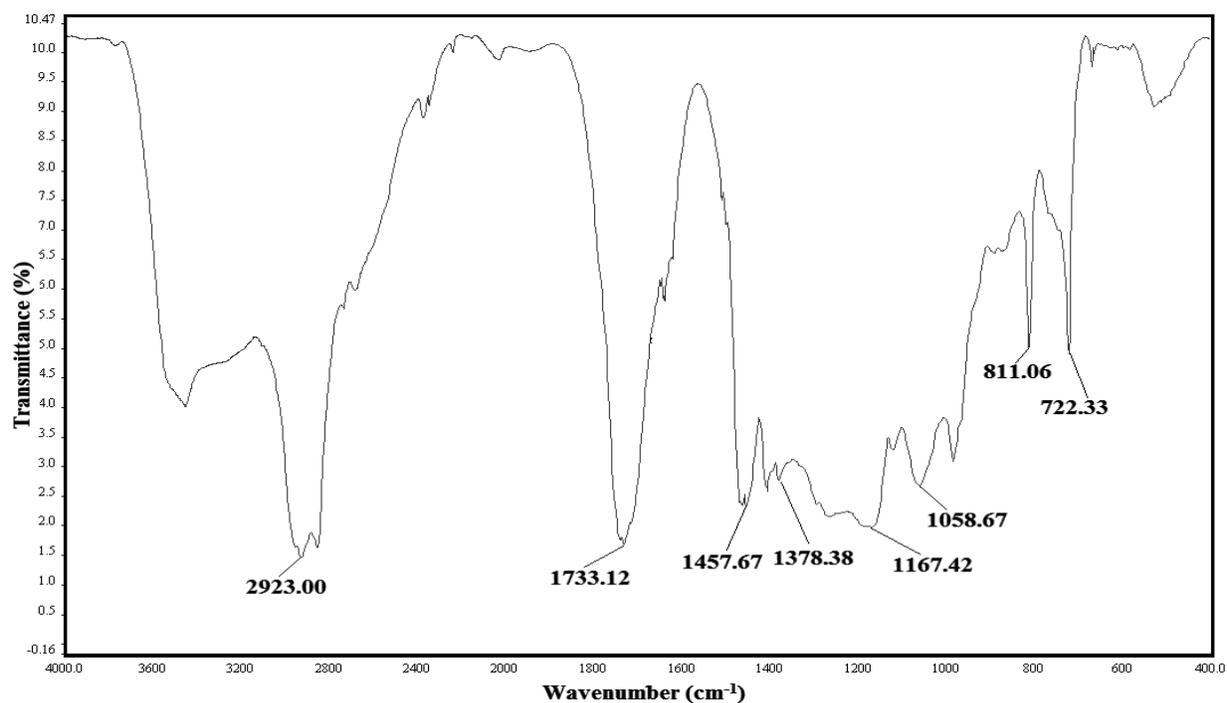


Figure 1.2: ¹H NMR spectra of homo poly decyl acrylate

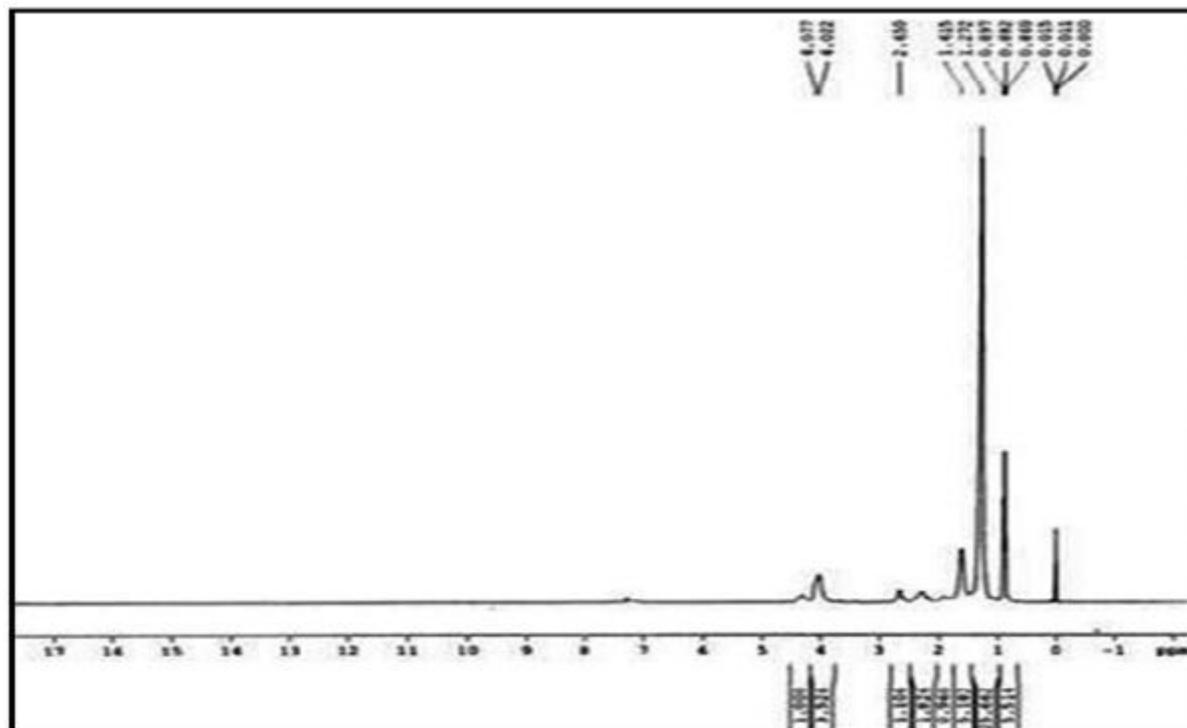


Figure 1.3: ^{13}C NMR spectra of homo poly decyl acrylate

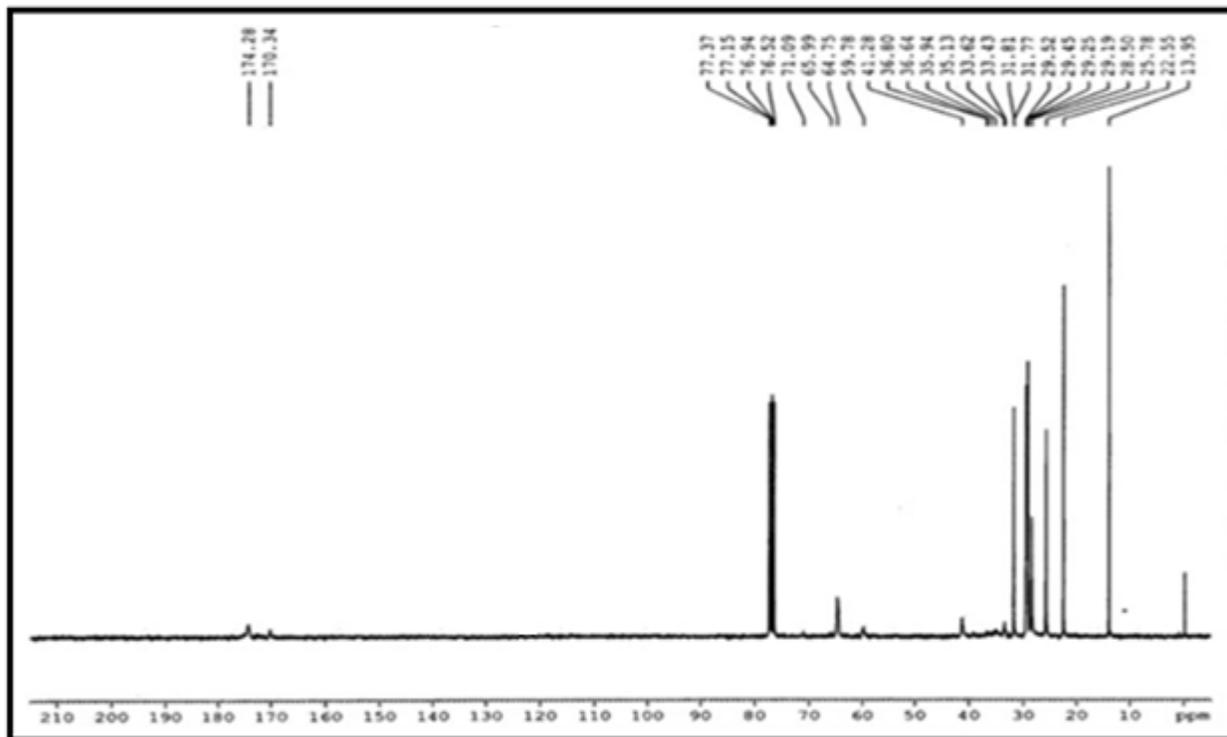


Figure 1.4 (a): Plot of viscosity index vs. additive concentration in BO1 from S1 and S2 respectively

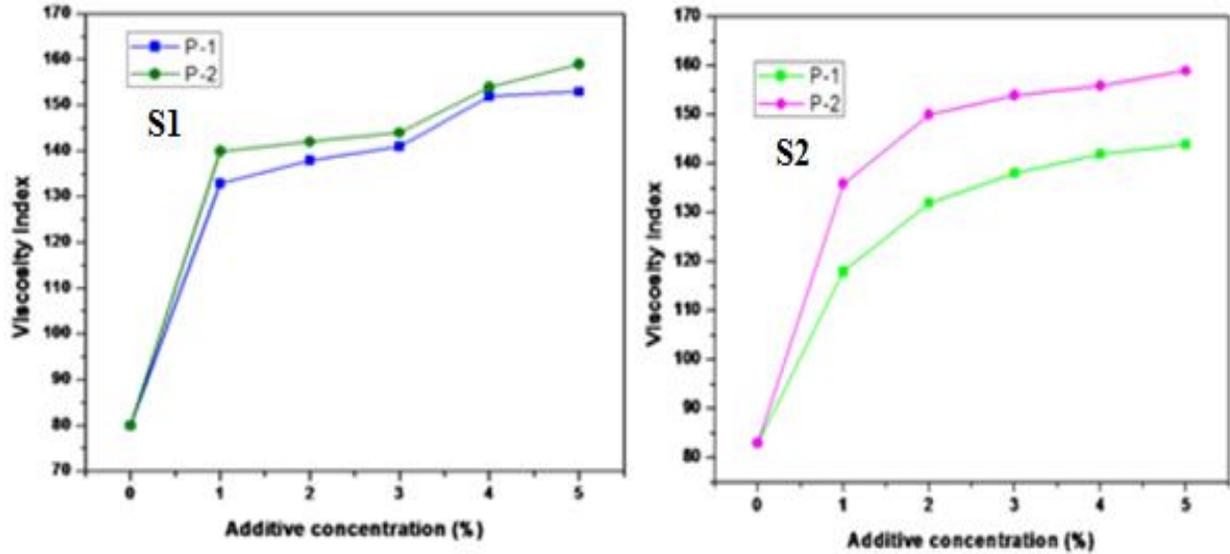


Figure 1.4 (b): Plot of viscosity index vs. additive concentration in BO2 from S1 and S2 respectively

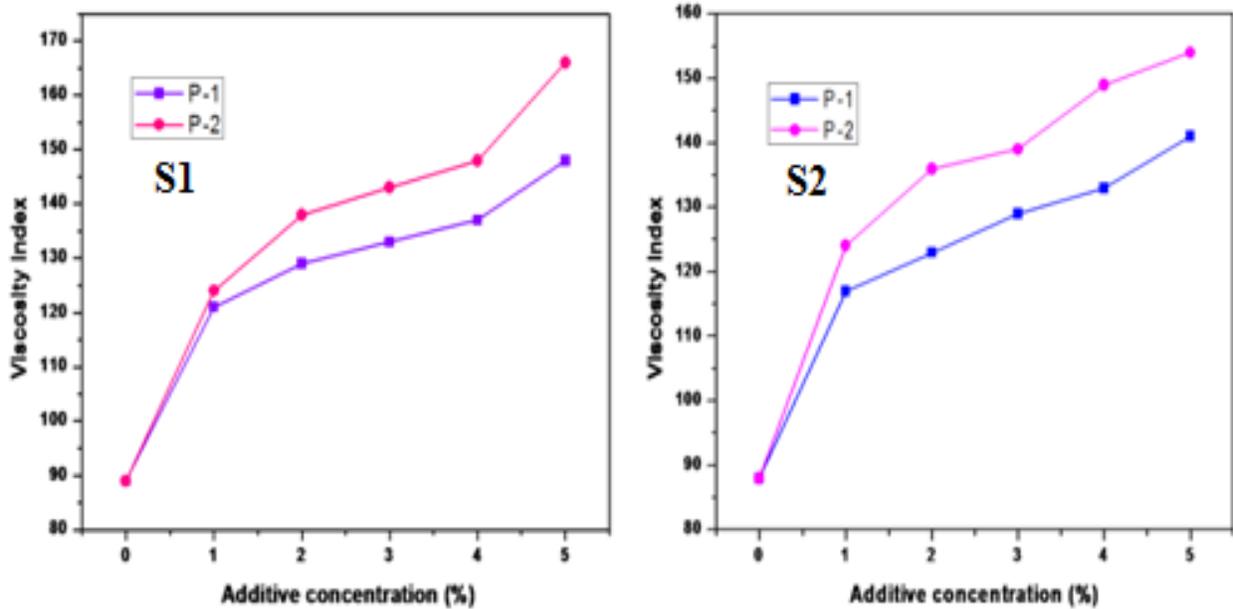


Figure 1.5(a): Plot of pour point vs. additive concentration in BO1 from S1 and S2 respectively

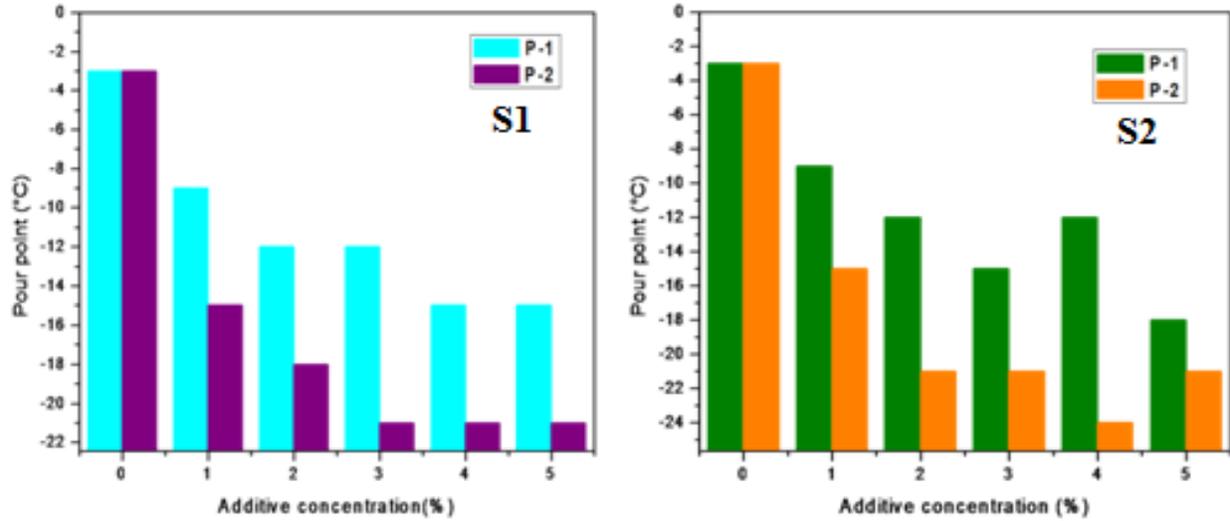


Figure 1.5(b): Plot of pour point vs. additive concentration in BO2 from S1 and S2 respectively

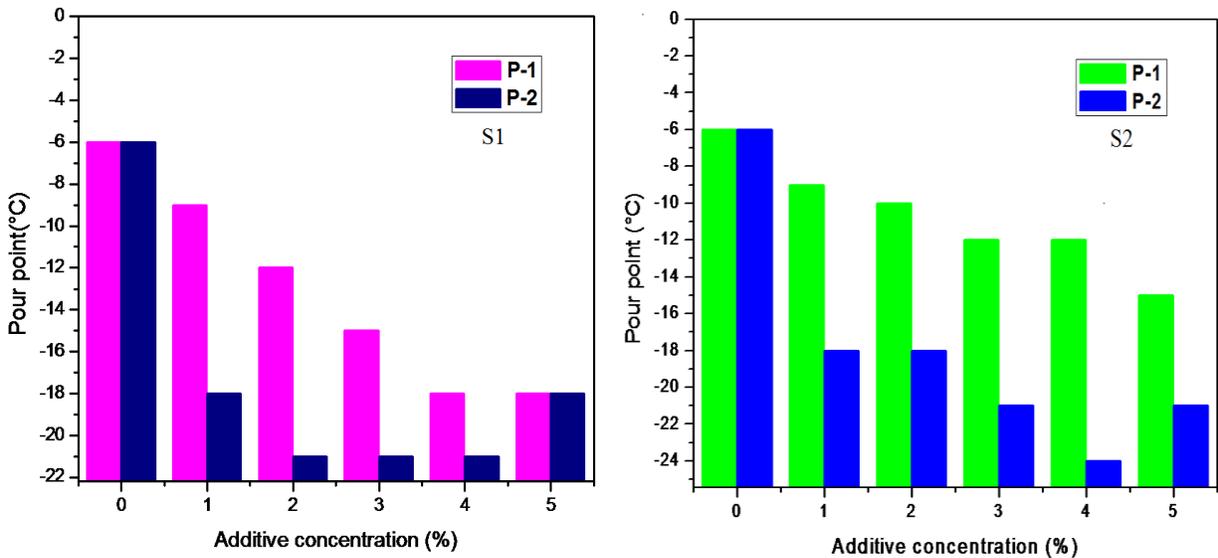


Figure 1.6: Plot of wear scar diameter (WSD) vs. additive concentration in base oils from S1 and S2 respectively at 20 kg load

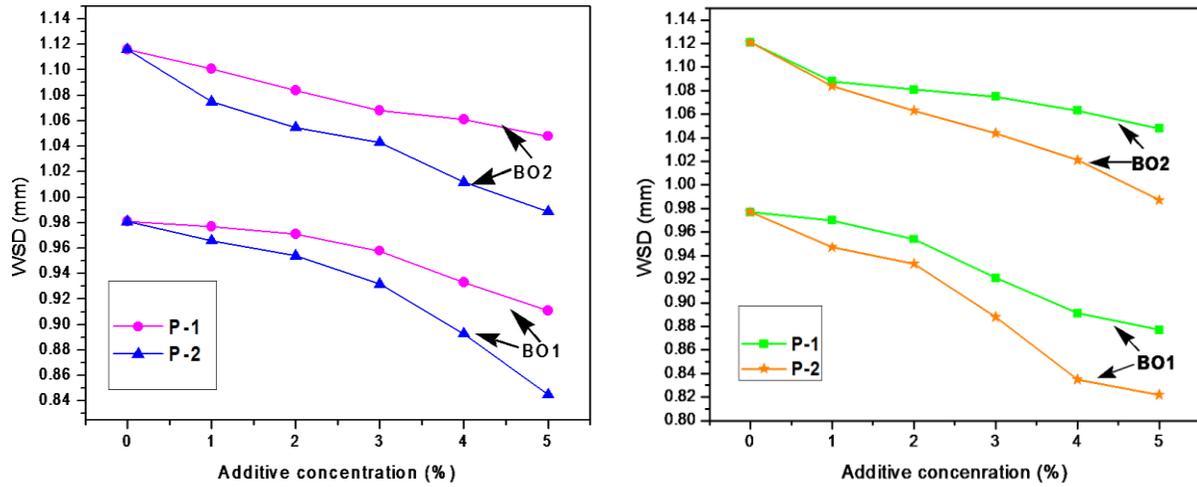
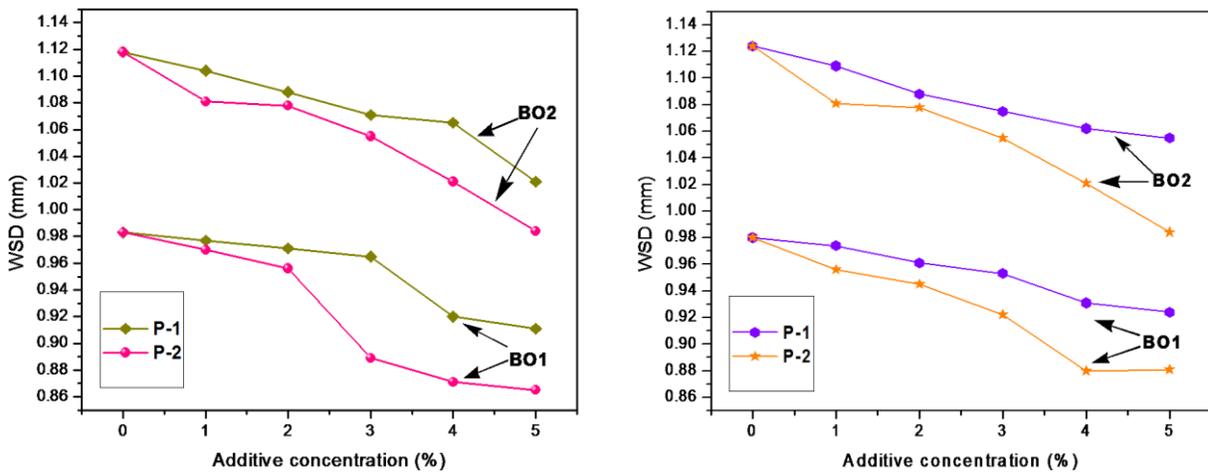


Figure 1.7: Plot of wear scar diameter (WSD) vs. additive concentration in base oils from S1 and S2 respectively at 40 kg load



Chapter III

Synergistic effect of liquid crystal on the
additive properties of long chain alkyl
acrylates in lube oil

1.2.1. Introduction

After the successful application of cholesteryl benzoate-polymer composite (which contain 100 ppm. of CB in polymer) as multifunctional additive the author has continued the search towards different kind of blended composites of CB with acrylate polymer of varying ppm level liquid crystal in polymer matrix. As we know mineral oils are commonly used as a lubricating medium. The possibility of enhancement in their lubricating properties is restricted and that is why one must use additives for the existing minerals oils to improve them. Nowadays, the used additives for lubricating oils are among others graphite and molybdenum disulfide. A mechanism of lubricant acting with these additives is based on formation of the surface-active film filling irregularities of a material surface. These additives increase lubricity of the oil base because they possess the stronger ability of adsorbing oil than metal, and their layered structure enables formation of a slip plane. Liquid crystalline compounds, which are characterized by an oriented arrangement of molecules as well as a sort of positional ordering, can play the same role. Applications of liquid crystals, being in a pure state and additives for mineral oils, as lubricants have been reported in the literature in the last few years.¹⁻⁴

It is well reported that cholesteryl based liquid-crystal additives to lubricating oils improve their anti-wear and antiscoring properties.⁵⁻⁸ Among the different kind of cholesteryl based compound like cholestery acetate, cholesteryl pelargonate, cholesteryl acrylate, cholesteryl benzoate; cholesteryl benzoate (CB) showed good film thickening property.⁹ This is because of higher polarity of CB. Despite of the anti-wear property, these compounds are not so effective as every kind of additive performance. Again poly acrylates are known to act as pour point depressants and viscosity modifier additives¹⁰ but as anti-wear additive these are not so effective.

¹¹ In this connection of developing multifunctional additives having VII, PPD and AW property,

we have already studied the additive performance of CB-poly acrylate blended composite.¹²⁻¹³ The study indicated that the additives improved VI, PPD and AW property. In the continuation of this study the authors were made an attempt to investigate the additive performance of CB-homo poly decylacrylate composite having different ppm level of CB in the blended composites.

1.2.2. Experimental procedure

1.2.2.1. Material and methods

Decyl alcohol, and acrylic acid (stabilized with 0.02% hydroquinone monomethylether), toluene, hydroquinone and H₂SO₄ were purchased from Merck Specialties Pvt. Ltd. Methanol and hexane were purchased from Thomas Baker (Chemicals) Pvt. Ltd. Benzoyl peroxide (BZP) was purchased from LOBA chemicals. The paraffinic base oil obtained from Indian oil corporation limited, Dhakuria, Kolkata, West Bengal, India which has a density of 0.94 g.cm⁻³ at 40°C, kinematic viscosity of 24.229 cSt (40°C) and 4.39 cSt (100°C) and a VI of 89, was used as received for all lubricant formulations. The properties of base oil are also depicted in **table 1.5**.

1.2.2.2. Preparation of monomer (via esterification)

Esterification reaction was carried out by usual method taking acrylic acid and decyl alcohol with mole ratio of 1.1:1, using a Dean Stark apparatus in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone as a polymerization inhibitor for acrylic acid and toluene as a solvent in nitrogenous atmosphere as reported in a earlier publication.¹⁴

1.2.2.3. Purification of prepared monomer

The decyl acrylate was purified according to the method reported in earlier publication.¹⁴

1.2.2.4. Preparation of homo polymer

The polymerization of decyl acrylate was carried out by taking required amount of DA and radical initiator (BZP) and toluene as a solvent in a four-neck round bottom flask and according to the process as reported earlier.¹⁴ The polymer obtained was then purified by frequent precipitation of its hexane solution using methanol followed by drying under vacuum at 313 K.

1.2.2.5. Preparation of LC-polymer blend

Required amount of polymer was taken in toluene; liquid crystal of cholesteryl benzoate was added to make a 100, 200, 300, 400, 500 ppm blend. They were heated at 40°C with stirring for 1 hour for homogeneous blending. The designation and composition of all the blended composites are given in **table 1.7**.

1.2.3. Measurements

1.2.3.1. Molecular weight determination

Ubbelohde OB viscometer was used to study the viscometric properties of polymer at 313 K temperature. Toluene was used as solvent. The time flow of at least five different concentrations of the polymer solution was observed for experimental determination. The lowest value of solution concentration was selected for calculation in the single point measurement. For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl/g}$ and $a = 0.725$ were employed in Mark Houwink–Sukurda relation.¹⁴ The intrinsic viscosity was calculated from different equations as described in chapter II.

1.2.3.2. Spectroscopic analysis

IR spectra were recorded using 0.1 mm KBr cells on a Shimadzu FT-IR 8300 spectrometer at room temperature within the wave number range of $400\text{--}4000 \text{ cm}^{-1}$. ^1H and ^{13}C NMR spectra

were recorded in Bruker Advance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl_3 was used as solvent and TMS (tetramethylsilane) was used as reference material.

1.2.3.3. Thermo gravimetric analysis (TGA)

The thermograms in air were determined on a Mettler TA-3000 system, at a heating rate of 10K/min. For D and the liquid crystal blended composites (L-1, L-2, L-3, L-4, L-5), 1g each was placed in the platinum crucible and heated gradually from room temperature to 850K.

1.2.3.4. Evaluation of additives as viscosity index improver

The prepared lubricant formulations were evaluated as viscosity modifiers or viscosity index improvers in base oils according to the ASTM D2270 method and by following the equations as reported in a publication.¹⁵ The kinematic viscosity of the additives doped base oil was determined at 40°C and 100°C. Different concentration ranging from 1 wt% to 5 wt% was used to verify the effect of additive concentration on VI.

1.2.3.5. Evaluation of additive as pour point depressant

The evaluation of the lubricant formulations as pour point depressants (PPD) in base oil were performed according to the ASTM D97 method on a Cloud and Pour Point Tester model WIL-471 (India). Here also concentration varying from 1 wt% to 5 wt% was used.

1.2.3.6. Evaluation of additive as anti-wear agent

The anti-wear properties of the homo polymer and LC blended polymer in base oil were examined in sliding contact by means of a four-ball wear test machine as per ASTM D 4172 method employing 20 kg and 40 kg load.

1.2.4. Results and discussion

1.2.4.1. Spectroscopic analysis

The main objective of this study is to investigate the lubricating performance of CB-polymer blended composites having different concentration (ppm) of CB. The homo poly decyl acrylate (D) was already characterized by spectroscopic method and same polymer was taken for this investigation.

1.2.4.2. Molecular weight determination

The molecular weight of homo polymer (D) was already determined by viscometric method as described in chapter II.

1.2.4.3. Thermo gravimetric analysis

The TGA data of homopolymer (D) and five different blended composites are represented in **figure 1.8**. From the figure, it is found that all the blended composites (L-1, L-2, L-3, L-4 and L-5) are comparatively more thermally stable than homopolymer (D) and the thermal stability is increases with increasing the concentration of CB in the polymer matrix. But this effect of CB in the polymer matrix is not so effective after L-3 composite. At 290°C temperature the percent of decomposition of the polymers from D to L-5 are 38.86, 31.23, 30.97, 29.12, 28.92, 28.86 respectively, whereas at 390°C temperature the percent weight loss of the polymers are 86.34, 78.23, 77.12, 76.17 and 76.13 respectively. That means beyond 300ppm level, the incorporation of CB in polymer matrix did not influence the thermal stability further.

1.2.4.4. Efficiency of additive as viscosity index improver

VI values were determined by dissolving the additives (D, L-1, L-2, L-3, L-4 and L-5) to the base oils at different concentrations ranging from 1 wt% to 5% wt%. The experimental results are reflected in **figure 1.10**. From the figure it is established that, VI values gradually increases with increasing the concentration of additives in base oil which is in accord with the earlier

study.¹⁶ It is also observed that the VI values of the LC blended polymers doped base oil are comparatively better than the pure polymer (D) doped base oil. The long range order of CB molecules results the additional viscosity increase of blended composites. The VI values increases from L-1 to L-3 significantly, but after that there is no significance improvement of VI (L-4, L-5) values. This may be due to saturation effect of CB molecules in polymer matrix.

1.2.4.5. Efficiency of additives as pour point depressant

The pour point values of all the lubricant compositions prepared by dissolving the additives in base oil at different level of concentration varying from 1 to 5% (w/w) are represented in **figure 1.9**. All the compositions were exhibited good pour point depressant property and the efficiency increases with increasing the concentration of additives up to a certain limit (3% concentration). This indicates that at lower temperature the lubricant compositions interacts with the paraffinic wax in base oil and decreases their crystal size.¹⁷ The L-1 composite has comparatively better efficiency as PPD among the six polymer compositions. The higher polarity effect of CB may influence the PPD properties. LC blended composites (L-1, L-2, L-3, L-4 and L-5) have lower pour point compared to D in every concentration level.

1.2.4.6. Efficiency of additive as anti-wear agent

The tribological properties (anti-wear) of the formulated lubricant compositions were determined by measuring wear scar diameter (WSD) by four ball wear test apparatus applying 20 kg and 40 kg load and the values are depicted in **Figure 1.11** and **1.12** respectively. For all additives doped base oil WSD increases with increasing load. That means at milder condition formulated additives working as better AW additives. Again, with increasing concentration of additives WSD decreases at both load condition which is in agreement with our earlier study.¹² The anti-wear performance of the base oil is significantly enhanced when the polymer (D) is blended with

CB and is reflected in lower WSD values of the formulated lubricants and the effect is more significant up to L-3, after this i.e, for L-4 and L-5 no significant lowering of WSD was observed compared to L-1, L-2 and D. The better performance of LC blended composites may be due to the highly polar character and layer structure of CB. With increasing concentration, more CB molecules are absorbed by solid metal surfaces and thicker film is formed. But no significant improvement of WSD at higher concentration may be due to over saturation at metal surfaces by CB molecules.

1.2.5. Conclusion

From this study it was found that all the lubricant composition formulated with CB blended polymers (L-1, L-2, L-3, L-4 and L-5) showed excellent performance as PPD, VI and AW additives compared to homo polymer (D). It was also found that L-3 composites showed comparatively better performance than other blended composites. It implies that, there is a certain limit of significant performance of blended composites. This may be due to the over saturation of CB after certain concentration.

1.2.6. References

References are given in BIBLIOGRAPHY under Chapter III of Part I (PP 158-159).

1.2.7. Tables and figures

Table 1.5: Properties of base oil

<i>Properties</i>	<i>Base oil</i>
Density (g.cm ⁻³) at 40°C	0.94
Viscosity at 40°C in cSt	24.229
Viscosity at 100°C in cSt	4.390
Cloud point (°C)	-8
Pour point (°C)	-6

Table 1.6: Molecular weight of homo poly decyl acrylate (D) used in this investigation

<i>Intrinsic viscosity</i>				<i>Viscosity average molecular weight</i>			
η_h	η_k	η_m	η_{sb}	M_h	M_k	M_m	M_{sb}
2.411	2.418	2.431	2.452	7152.53	7277.79	7234.55	7320.89

Table 1.7: Designation and composition of LC-blended composites

<i>Designation</i>	<i>Composition</i>	
	Polymer in g	LC (CB) in mg
D	4	0
L-1	4	0.4
L-2	4	0.8
L-3	4	1.2
L-4	4	1.6
L-5	4	2.0

Figure 1.8: TGA data of polymer (D) and blended composites (L-1, L-2, L-3, L-4 and L-5)

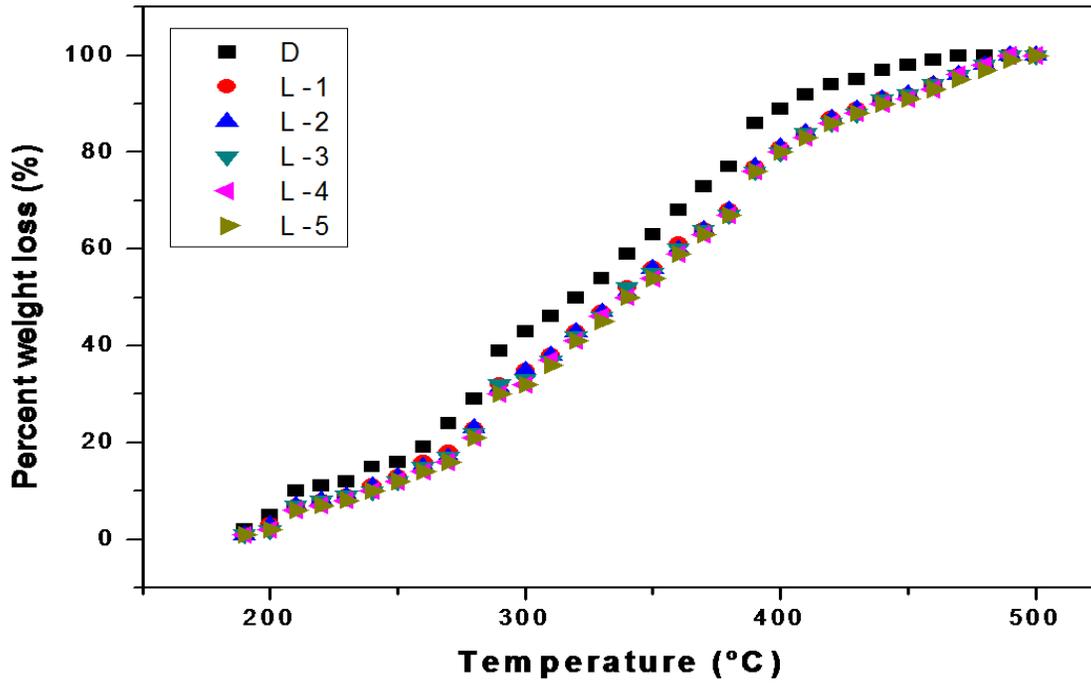


Figure 1.9: Plot of pour point of formulated lubricants as a function of additives concentration (w/w)

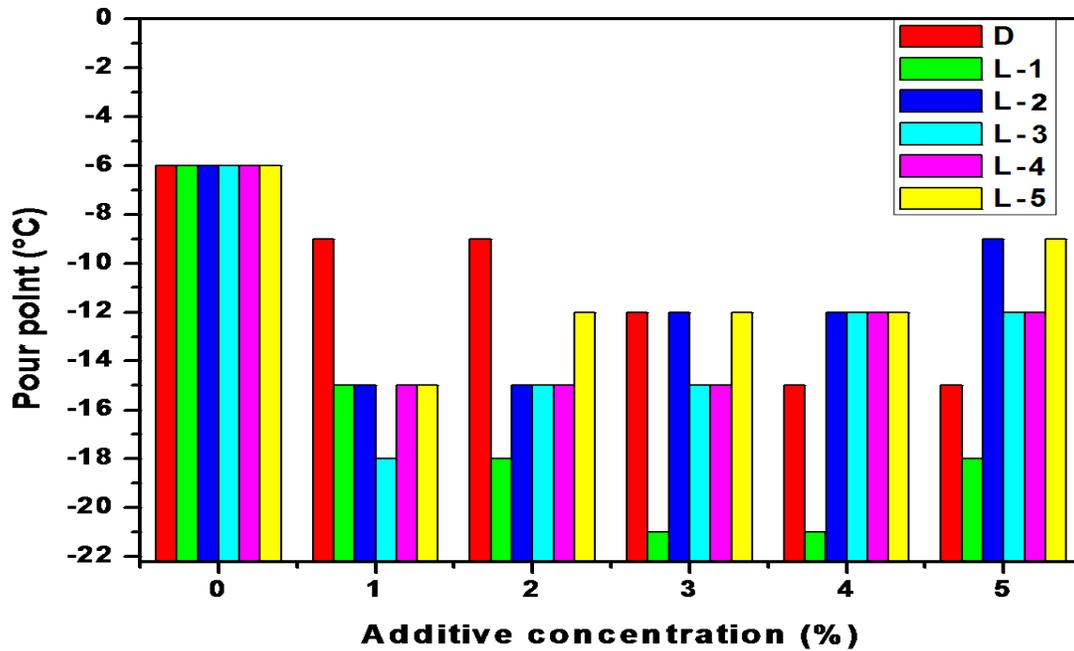


Figure 1.10: Plot of viscosity index of formulated lubricants as a function of additives concentration (w/w)

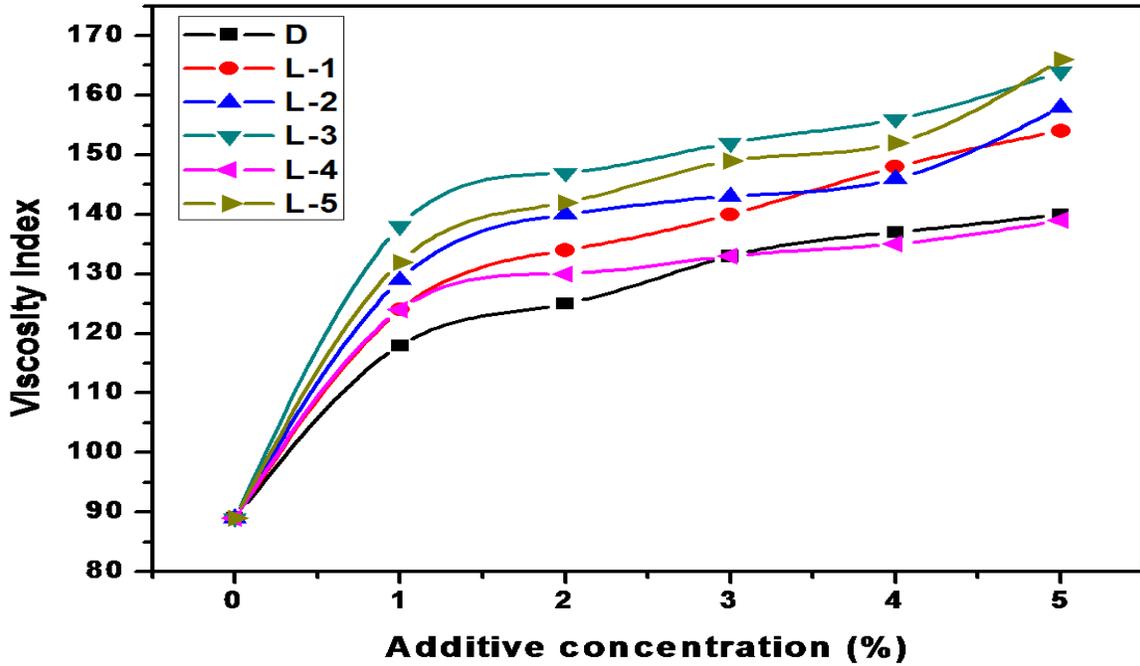


Figure 1.11: Wear scar diameter (mm) of formulated lubricants as a function of additives concentration (w/w) at 20 kg load condition

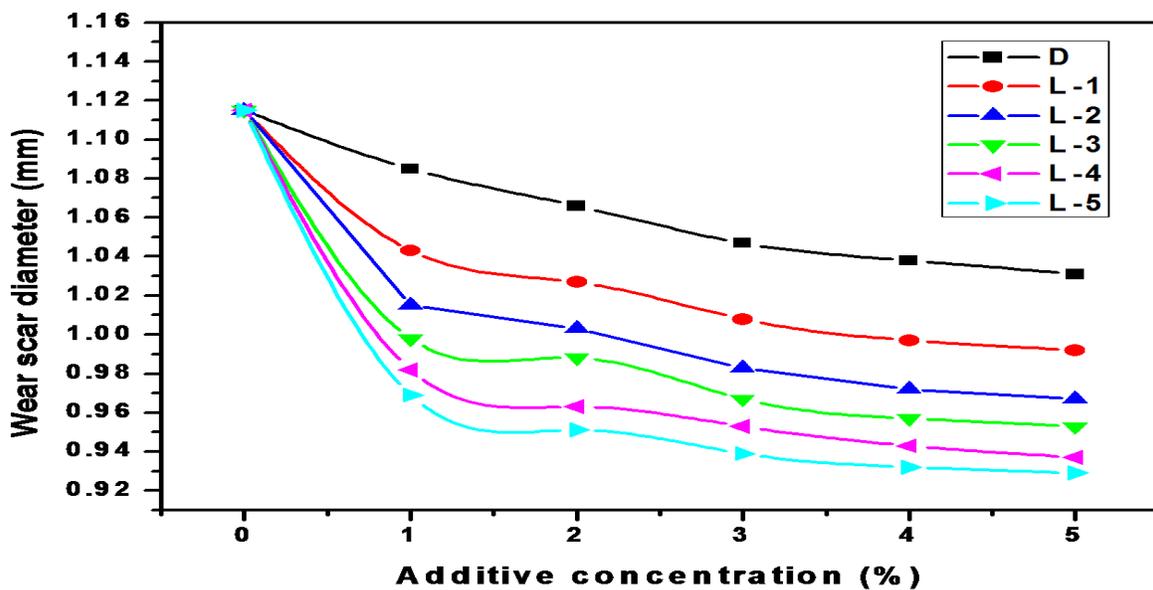
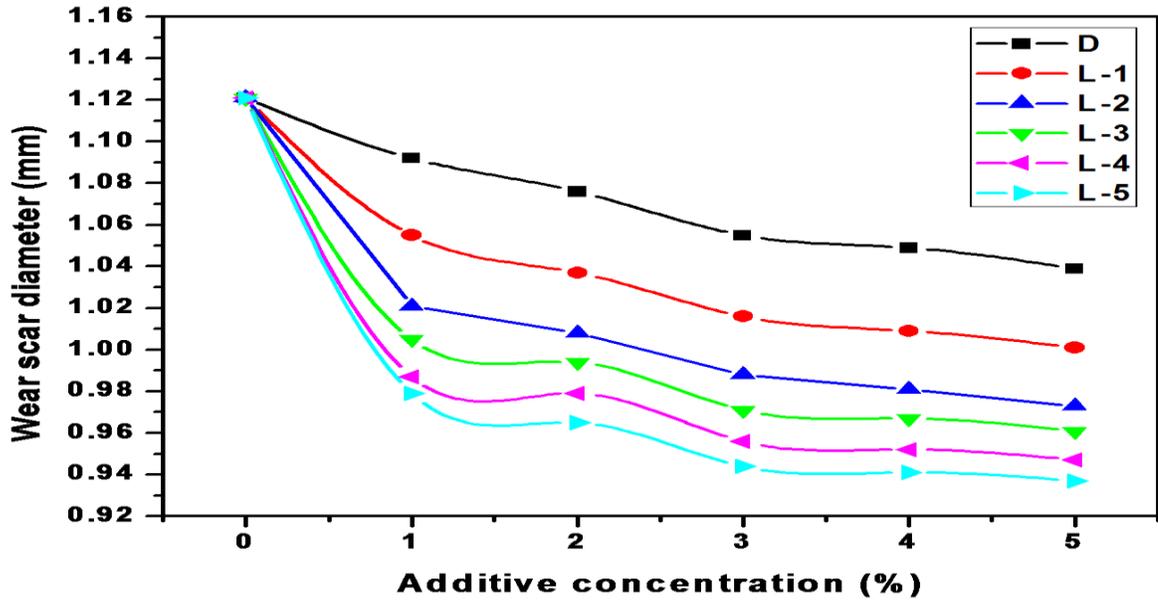


Figure 1.12: Wear scar diameter (mm) of formulated lubricants as a function of additives concentration (w/w) at 40 kg load condition



Part II

Biodegradable Multifunctional Additives For Lube Oil

Chapter I

Background of the Present Investigation

Today conservation of energy and materials is becoming a very importance issue. The main reason of energy loss in a mechanical system is the friction but this can be minimized by lubrication. Thus, it is very essential to develop the lubrication performance. A good combination of base oil and additives is the key to develop this process. Again the natural reservoir of petroleum crude oil decreases day by day and thus price of oil is increases rapidly.¹For most lubricated applications, the conventional choice is a mineral oil based lubricant, because of its well known properties. However due to their natural toxicity and non-biodegradable nature,^{2, 3} they pose a constant warning to ecology and immense ground water reserves. These oils pollute the air, soil, and drinking water and influence human and plant life to a great extent. Therefore, strict specifications on various environmental issues such as biodegradability, toxicity, safety, health and emissions are required in certain specific areas.⁴ Thus the requirement of environmentally suitable lubricants is increasing along with the public concerns for a pollution-free environment.^{2, 3} Due to an increasing concern over the environmental issues, the lubricant companies have been trying to prepare biodegradable lubricants with quality better to those based on petroleum oil.⁵ The use of renewable raw materials can appreciably contribute to a sustainable development,⁶ typically interpreted as 'acting responsibly to meet the requirements of the present without compromising the capability of future generations to meet their own needs'.⁷ In ages of exhausting fossil oil stocks and an increasing emission of green house gases it is apparent that the consumption of renewable raw materials is one crucial step towards a sustainable development. In particular, this can perennially provide a raw material basis for daily life products and avoid extra contribution to green house effects because of CO₂ emission minimization. Furthermore, the use of renewable raw materials, taking advantage of the synthetic potential of nature, can (in some cases) meet

other principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity of the resulting products.⁶

Some of the most commonly applied renewable raw materials such as polysaccharides (mostly cellulose and starch), plant oil, wood, sugars and others used in the chemical industry for nonfuel applications. Products obtained from these renewable sources have diverse applications in pharmaceuticals, packaging materials, coatings or fine chemicals etc. Nowadays plant oils are the most essential renewable raw material for the chemical industry and are extensively used as raw materials for cosmetic products, surfactants, and lubricants.⁸

The vegetable oils are a potential source of environmentally benign (eco-friendly) lubricants⁹⁻¹⁴ because of its biodegradability, renewability, and excellent lubrication performance. A majority of vegetable oils consist of mainly two broad chemical categories: monoesters and triesters. The main constituents of most vegetable oils are triglycerides, which are produced by three fatty acid chains connected to glycerol by ester groups. A small portion of vegetable oils are monoesters of long-chain fatty acid and fatty alcohols of diverse chemistry.^{13,14} The vegetable oil triglycerides containing fatty acids are all of similar in length (14–22 carbons chain) with varying levels of unsaturation.^{13,15,16} The majority of vegetable oils have separate regions of non-polar and polar groups in the same molecule. Due to the presence of polar groups in vegetable oil, they are amphiphilic in nature and therefore they can be used as both boundary and hydrodynamic lubricant.^{11, 17} There are many advantages of using vegetable oils such as low volatility caused by high molecular weight triglyceride molecule, fine boundary lubrication characteristics because of the polar ester group and high viscosity index value, high solubilising power for polar contaminants and additive molecules, and cheaper than synthetic oils.^{4, 10, 12, 18-24}

About 90% to 95% of the total weight of triglycerides (**figure. 2a.**) accounts for fatty acids and their composition is characteristic of the plant, the crop, the season and the growing conditions.²⁵ The word ‘oil’ hereby refers to triglycerides that are liquid at room temperature. The physical and chemical properties of vegetable oils are mostly affected by the stereochemistry of the double bonds present in the fatty acid chains, their degree of unsaturation and the length of the carbon chain of the fatty acids.

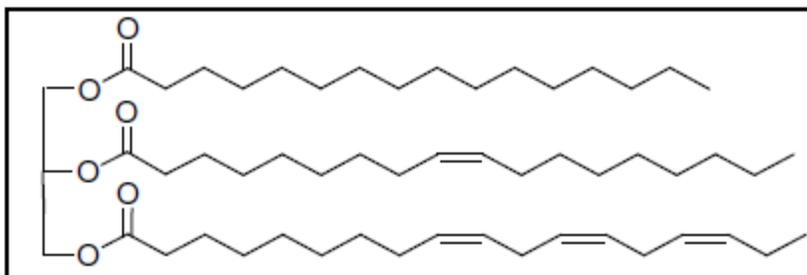


Figure 2a: General structure of triglyceride ester present in vegetable oil

The structure of triglyceride is also accountable for the inherent disabilities of vegetable oils as lubricant. For a lot of reactions, the fatty acids containing unsaturated double bonds act as active sites. There are two major problems associated with vegetable oils as functional fluids offer low resistance to thermal oxidative stability^{12, 26-34} and poor low-temperature properties,^{28, 29, 33, 35-38} which results quick degradation, deposit formation and thickening in use. The poor thermal and oxidative instability of plant oils is due to the presence of unsaturation (double bond) in the fatty acid chain and the “-CH group” of the alcoholic part.^{10,38} The susceptibility towards oxidation of a vegetable oil is due to the quick reactions at the double-bonded functional groups.³⁹ Hence higher the level of unsaturation, higher the sensitivity of oil towards oxidation.^{23,24} Oxidative degradation results to an increased viscosity that restricts the useful life time of vegetable oil based fluids.³⁰ It is also noticed that vegetable oils show poor corrosion protection.⁴² Cloudiness and solidification become apparent in vegetable oil at low temperatures upon prolonged exposure

to low temperature (-10 to 0°C).^{40,41} Another problem is the susceptibility of the ester functionality present in the triacylglycerol structure to hydrolytic breakdown.⁴³ As a result, contamination with water in the form of emulsions must be prohibited. Poor thermal and oxidation stability along with poor low-temperature flow properties bound their potential application as lubricants in industry.⁴⁴ Vegetable oils exhibit particularly effective boundary lubricity additives. A boundary lubricity additive functions by its ability to adhere to the metal surface. This property is because of the high polarity of the entire vegetable oil which allows strong interactions with the lubricated surfaces. Polar compounds, for example synthetically prepared esters or naturally occurring triglycerides are especially efficient at this function due to their capability to orient a polar head group of the molecule onto a metal surface. This polarity produces a strong affinity to the metal by one end of the molecule and allows a non-polar hydrocarbon to extend out and provide a barrier between metal surfaces. Boundary lubricity is affected by affinity of the lubricant molecules to the surface and also by possible reaction with the surface.

Conversion of alkene groups of the aliphatic chains of fatty acid of vegetable oil to other functional groups that can provide a better oxidative stability, while reducing structural homogeneity of the oil by attaching alkyl side chains would improve temperature performance.⁴⁵ Numerous modern technologies have been accepted to solve the issues concerning the application of plant oils in lubricants. Some of them are additive treatment, genetic and chemical modification.¹⁹

Vinci et al.⁴⁶ have suggested a thermo-oxidatively stable base lubricant based on methyl-12-hydroxystearate, a derivative of the castor oil with 70% renewable carbon content. Joseph and Sharma⁴⁷ studies shows that the thermo-oxidative stability of vegetable oils (when used as

lubricant base oils at temperatures around 120°C) can be enhanced by the mixture of aminic and phenolic type antioxidants. Mendoza et al.⁴⁸ developed a formulated some additives based on sunflower oil for hydraulic systems of agricultural tractors, they can be considered with a biodegradability of 89%, substantial improvement of pour point up to -29°C (considering the pour point of sunflower base oil of -3°C). Again, the additive considerably improved the oxidation stability of the sunflower base oil. The microweldings formation has not been observed with this formulated oil and satisfies the requirements of the reference mineral fluids for extreme pressure tribological tests. Regueira et al.⁴⁹ has investigated the compressibility and viscosity properties of vegetable oils for their application as hydrolytic fluid and lubricants. From their study, it is manifest that chemically modified vegetable oils have prominent scope for use as base oils.

The lubricant characteristic has been trying to develop biodegradable lubricants with improved technical characteristics than usual lube oil additives and research in this direction is opening up a new opportunities. Franco et al has reported a new biolubricant formulation having high oleic sunflower oil which was blended with polymeric additives e.g. Sunflower oil bio fuels, polymeric additives e.g. ethylene vinyl acetate (EVA) and styrene-butadiene-styrene copolymers.⁵⁰ This lubricant formulations improved the kinematic viscosity values and viscosity thermal susceptibility. In recent times, the application of triglycerides molecules in polymer science was reviewed with a focus on cross-linked systems for resin and coating applications with the conclusion that triglycerides molecules are anticipated to play a major role during the 21st century to produce polymers from renewable sources.⁵¹ Other than these cross-linked polymers, linear polymers can also be obtained from plant oils.

US patent no. 4873008 has presented a lubricating compositions based on jojoba oil. The compositions provide better-quality lubrication performance as antifriction, anti-wear and load-carrying properties. US patent no. 5229023 disclosed synthesis and evaluation of a group of lubricant additives comprises telomerized vegetable oils that have high viscosity and improved oxidative stability. US patent no. 4152278 discussed about tribological performance of some vegetable wax ester. Again US patent no. 4970010 has disclosed a group of sulfurized, phosphite derivatives of vegetable oils with superior lubricating properties. US patent no. 4925581 disclosed a procedure for sulfurizing meadowfoam oil which is soluble in a mineral oil and claimed the application of such meadowfoam oil derivatives as lubricant additives. US patent no. 6534454 B1 discussed regarding biodegradable vegetable oil compositions for lubricant. The compositions consist of at least one triglyceride component, an antioxidant comprising an amine or phenol derivatives.

Erhan et al.¹² has described superior oxidation and low temperature stability of vegetable oil based lubricants by means of different kind of sunflower oil and soybean oil. Biresaw et al.¹¹ has reported frictional properties of some triglyceride vegetable oils. Boshui et al.⁵² studied the effects of two fatty acidic diethanolamide borates as additives on biodegradability and lubricity of an unready biodegradable paraffinic lubricating oil. Ghosh et al.⁵³ studied the multifunctional (VM, PPD and AW) greener additives performance for lubricating oil which contains copolymers of rice bran oil, peanut oil and β -pinene with isodecyl acrylate.

Generally, vegetable oils have been used to improve the tribological performance of base oils. Except that application of them as viscosity modifier (VM) and pour point depressant (PPD) is not so well known. That means the additive performances of only vegetable oils are not very hopeful in lubricant industry. So to use of them as LOA the author has polymerized citral oil

with alkyl poly acrylate, rice bran oil with 1-decene and poly acrylate which combined high viscosity properties of vegetable oil with excellent low temperature flow property of poly alkyl acrylate and good anti-wear property in a single entity, in addition to considerable biodegradability.

In an era of mounting oil prices, global warming and other environmental issues (e.g. waste) the change from fossil feedstock to renewable resources can significantly contribute to a sustainable development in the future. The synthesis of monomers as well as polymers from plant oils has already got some industrial application and current developments in this area offer promising new opportunities.

References

References are given in BIBLIOGRAPHY under Chapter I of Part II (PP 160-165).

Chapter II

Citral-Polyacrylate Based Biodegradable Lube Oil Additives

2.1.1. Introduction

The commercial synthetic acrylate –based additives are non-biodegradable and their widespread use has raised many environmental concerns. Due to increasing environmental pollution the direction towards the development of environmentally benign polymeric additives in the lubricant chemistry is increasing day by day. A recent demand for eco-friendly technology promoted the researchers to develop environmentally benign additives for the lubricant formulation. The use of biodegradable vegetable oils was known from a long time.¹⁻⁴ They not only offers such biodegradable property along with this they can offer significant performances as a pour point depressant, viscosity index modifier and anti-wear additives.

Keeping these mind and in continuation of our studies towards the development of chemical additives for lubricating oil, in the present investigation an attempt has been made to synthesize some copolymer of citral with acrylate ester through the process of copolymerization to getting an ideal blend of performance as well as eco-friendly chemistry. Our present investigation comprises the synthesis of homopolymer of dodecyl acrylate and copolymer of dodecyl acrylate with citral, their characterization, biodegradability test and their evaluation as a pour point depressant, viscosity modifier and anti-wear additives.

2.1.2. Experimental procedure

2.1.2.1. Materials and methods

Toluene, Hydroquinone and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd. Acrylic Acid (stabilised with 0.02% Hydriquinone monomethylether) and dodecyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Hexane was purchased from S D Fine Chem. Ltd. Methanol was purchased from Thomas Baker (Chemicals) Pvt. Ltd. Benzoyl Peroxide (BZP)

obtained from LOBA chemicals was recrystallised from CHCl_3 -MeOH before use. Citral was collected from local grocery shop. The base oils were collected from IOCL, Dhakuria, Kolkata, India. Rest of the materials was used as they were obtained without further purification. All samples were tested before their expiry dates.

2.1.2.2. Preparation of monomer: Esterification

Dodecyl acrylate was prepared by esterification reaction of acrylic acid and dodecyl alcohol with mole ratio of 1.1:1. The reaction was performed in a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone with respect to the reactants as polymerization inhibitor, and toluene as a solvent. The reaction was carried out under nitrogen atmosphere. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of water liberated during reaction to give the ester, dodecyl acrylate (DDA).

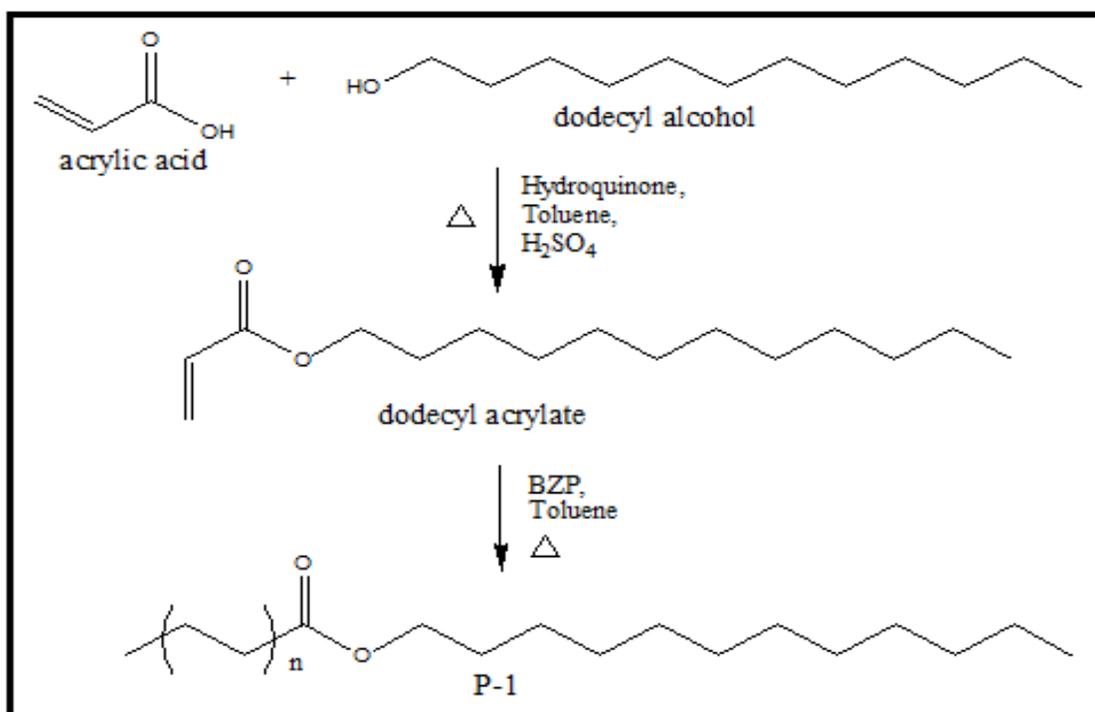
2.1.2.3. Purification of the monomer

In the purification process at first, desired amount of charcoal was added to the ester, followed by reflux for 3 h and then filtered. The filtrate was then washed repetitively with 0.5N sodium hydroxide solution to ensure complete removal of unreacted acid. Then to remove traces of sodium hydroxide, purified ester was washed several times with distilled water. The ester was then left on calcium chloride overnight and recollected by distillation under reduced pressure. This purified ester was then used in the polymerization process.

2.1.2.4. Preparation of homopolymer and copolymer

The polymerization was carried out in a four-necked round bottom flask furnished with a condenser, stirrer, thermometer and an inlet for the nitrogen insertion. Required amounts of dodecyl acrylate and initiator (BZP) were taken in the flask and toluene was also added as

solvent. The reaction temperature was controlled at 353 K for 6 hours. Then the reaction mixture was poured into methanol solvent with stirring to cease the polymerization and a precipitate was appeared. The precipitated homopolymer (P-1) was further purified by frequent precipitation of its hexane solution with methanol followed by drying under vacuum at 313 K. For the synthesis of copolymer a dropping funnel was used for the drop wise addition of required mass of citral in the R.B flask containing DDA, BZP and toluene. The addition was continued under homogeneous stirring for 2 hours. The copolymer of DDA and different percent composition of citral was designated as sample P-2, P-3 and P-4 respectively containing 5%, 10% and 15% citral with respect to DDA. The structures of the prepared polymers are shown in **scheme 1**.



Scheme 1: Preparation of dodecyl acrylate and poly dodecyl acrylate (P-1)

2.1.3. Measurements

2.1.3.1. Thermo gravimetric analysis

The thermal stability of the polymer samples was also determined on a Mettler TA- 3000 systems, at a heating rate of 10 K min⁻¹. All the samples were heated gradually from room temperature to 690 K in a platinum crucible.

2.1.3.2. Determination of molecular weight by GPC method

In GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were measured. The poly dispersity index was also calculated. In this method HPLC grade THF (0.4%, w/v) was used as mobile phase in the water 2414 GPC system (polystyrene calibration) at 35°C with a flow rate of 1 ml/min.

2.1.3.3. Biodegradability analysis

The degree of biodegradability of the polymeric additives was tested by (i) disk diffusion method against fungal pathogens and by (ii) soil burial test as per ISO 846:1997. Polymeric samples recovered after the tests were verified by measuring weight loss and IR spectra was taken to observe any considerable shift of IR frequencies.⁵⁻⁷

2.1.3.3.1. Disc diffusion method

Culture media for fungal pathogens were prepared in Petri dishes by taking suitable amount of dextrose, agar agar and potato extract. All glass apparatus were autoclaved prior to use. Five fungal pathogens were used in this analysis namely *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA), *Colletotrichum gloeosporioides* (CG), and *Curvularia eragrostidis* (CE). The growth of fungal pathogens was confirmed by change in colour of the culture media from yellow to blackish. Specific amount of polymer samples (1g) were added in Petri dishes and incubated for 30 days at 310K in an incubated chamber. After 30 days, polymer

samples were recovered from culture media by chloroform, purified and dried in an open vessel.⁸ The weights of dried samples were taken and FT-IR were taken. The microbial degradation was verified by measuring the shift of IR frequency of the ester carbonyl after biodegradability test.

2.1.3.3.2. Soil burial test

The soil burial test was carried out as per ISO 846:1997 method. Specific amount (1g) of polymer samples were buried in soil collected from University campus (University of north Bengal) in a tray. Prior to use the relative humidity of the soil was adjusted to 50% - 60% and temperature was kept at 303K with a thermostat in a humidity chamber. The buried films were recovered after 60 days, washed with chloroform, purified and dried.⁹ The dried samples were weighed and their FT-IR spectra were recorded.

2.1.3.4. Performance evaluation as viscosity modifier

Viscosity index (VI) of the polymeric additives was determined in two paraffinic base oils (BO1 and BO2) to evaluate the efficiency of the prepared polymeric additives as viscosity modifier (VM). An Ubbelohde OB viscometer was used in this experiment at the temperatures 313K and 373K. The detailed process is previously described in Chapter II of Part I.

Five different concentrations ranging from 1 wt % to 5 wt % of the polymeric sample solutions were used to study the effect of additive concentration on VI.

2.1.3.5. Performance evaluation as PPD

The pour point depressant property of the prepared polymeric additives was determined in two base oils (BO1 and BO2) by the pour point test on a Cloud and Pour Point Tester model WIL-471(India) according to ASTM D97 method. In this case also five different concentrations of the additives were used for each sample.

2.1.3.6. Performance evaluation as AW additives

The AW properties were assessed by Four-ball wear test apparatus according to ASTM D 4172-94 method ¹⁰ applying two different weight loads, 147 N and 392 N at 75°C for 30 min. with the rotational speed of the ring was 1200 rpm.

The physical properties of the base oils are depicted in **table 3.3**.

2.1.4. Results and discussion

2.1.4.1. Spectroscopic analysis

FT-IR spectrum (**figure 2.1(a)**) of homopoly dodecyl acrylate (P-1) showed absorption band at 1732 cm⁻¹ for the ester carbonyl stretching vibration along with other peaks at 1467, 1271, 1190, 1060 cm⁻¹. In the ¹H NMR spectra of P-1 showed broad singlet centred at 4.02 ppm due to the protons of -OCH₂ group. Methyl protons of dodecyl chain appeared between 0.81 ppm and 0.86 ppm and the absence of singlet between 5 ppm and 6 ppm implies the absence of any vinylic proton in the polymer and it is depicted in **figure 2.1 (b)**. In the ¹³C NMR spectrum of P-1, the carbonyl carbon appeared at 174.4 ppm along with other SP³ carbons appeared in the range of 65.03 to 10.66 ppm and it is showed in **figure 2.1 (c)**.

In the FT-IR spectrum of copolymers, the ester carbonyl appeared at 1731.71 cm⁻¹ along with a peak appeared at 1714.30 cm⁻¹ for aldehyde group of citral. Peak at 1165 cm⁻¹ is due to ester C-O stretching vibration and peak at 2854 cm⁻¹ is due to the aldehydic C-H. In the ¹H NMR of the copolymers, a multiplet in the range of 4.119- 4.402 ppm indicates the -OCH₂ protons. All the SP³ protons appear in the range of 1.259- 1.989 ppm. Two peaks at 5.343 ppm and 5.360 ppm are due to the ethylinic double bond in the citral part of the copolymer. A peak around 10 ppm is due to the aldehydic proton of citral in the copolymer. In the ¹³C NMR of copolymer, the peaks in the range of 167.70- 173.36 ppm indicates the presence of ester carbon and the peaks at 190.81 ppm due to the aldehydic group of citral in the copolymer. The -OCH₂ carbon peak appeared at 68.93

ppm and peaks in the range of 14.09- 34.05 ppm indicate all the SP³ carbons of copolymer and spectra are showed in **figure 2.2**.

2.1.4.2. Thermo gravimetric analysis

TGA data is represented in **table 2.4** for homo and copolymer of dodecyl acrylate. From the data it is found that, the copolymers (P-2, P-3 and P-4) are thermally more stable than the homopolymer (P-1). It was also found that, with increasing citral concentration in the feed, the thermal stability increases.

2.1.4.3. Analysis of biodegradability test

Table 2.3 represents the biodegradability test results obtained by using disk diffusion method and soil burial test. All the copolymers were found to be significantly biodegradable against the fungal pathogen, *alterneria alernata* but the homopolymer was not found to be biodegradable at all. It was further confirmed by the shift of IR frequency of the ester carbonyl from 1731 cm⁻¹ to 1712 cm⁻¹, 1716 cm⁻¹ after the biodegradability test. It was also found that extent of weight loss in disc diffusion method was higher than soil burial test.

FT-IR spectra of the polymer samples, before and after disc diffusion test, were also compared (**figure 2.3, 2.4, 2.5 and 2.6**) to confirm the biodegradable nature of the prepared copolymers. IR peaks of sample P-2 (**figure 2.4**) at 1454, 1161cm⁻¹ has shifted considerably after disc diffusion test. The other copolymer samples (P-3 and P-4) also showed similar pattern of IR shift (**figure 2.5and figure 2.6**).

2.1.4.4. Efficiency of additives as viscosity modifier

The Viscosity index values of the additives doped base oils of all the polymers (P-1, P-2, P-3 and P-4) are presented in the **table 2.5**. Table showed that with increase in the concentration of polymer in the base oils (type BO1 and type BO2) there is a gradual increase of VI values (up to 4%). The increase of concentration of the polymer also leads to an increase in total volume of polymer micelles in the oil solutions. Consequently, a high concentration of polymer will impart a high viscosity index rather than a low concentration of the same polymer.

2.1.4.5. Efficiency of additives as pour point depressant

The experimental data for the PPD values of samples containing different additive concentrations ranging from 1 wt% to 5 wt% are grouped in **figure 2.7(a)** (in the base oil type BO1) and in **figure 2.7(b)** (in the base oil type BO2) which indicates that the prepared additives are efficient as pour point depressant and the pour point values of all the polymer decreases with increase in concentration of the additive. The pour point values of all the copolymers (P-2, P-3 and P-4) are more or less same but lower than the homopolymer (P-1). Hence all the copolymers were excellent pour point depressant additives.

The efficiency of the polymers as effective pour point depressant was also assessed through photo micrographic analysis. The wax crystal size is significantly decreased from large crystal structure (base oil) to very small dots dispersed in the oil phase of the lube oil in case of all the polymeric additives.¹¹ The photo micrographic images (PMI) of all the samples and base oil were depicted in **figure 2.8**

2.1.4.6. Efficiency of additives as AW agents

Decrease in WSD (mm) with increasing concentration of the additives was found in both the base stocks and under both load condition but the decrease was generally greater under 40 kg

load condition (**figure 2.9**), that implies that additives were not so effective at higher load condition. However, beyond 5% additive concentration no significant AW performance was observed. All the copolymers showed better AW property than homopolymer (P-1), this is because of the presence of aldehydic functionality additional to ester functionality of the copolymers.^{5, 6} Hence, the copolymer (P-4), which contain larger proportion citral unit into the polymer matrix showed better performance as AW additives.

2.1.5. Conclusion

The homopolymer (P-1) as well as copolymers (P-2, P-3 and P-4) were showed excellent PPD and AW property. The copolymer showed excellent biodegradable property. Thus it can be concluded that the copolymers can be used as biodegradable PPD and AW additives for lubricating oil.

2.1.6. References

References are given in BIBLIOGRAPHY under Chapter II of Part II (PP 165-166).

2.1.7. Tables and figures

Table 2.1: Properties of base oils

<i>Properties</i>	<i>BO1</i>	<i>BO2</i>
Density(kg.m ⁻³) at 313K	839.98	918.68
Viscosity at 313K	5.97×10 ⁻⁶	20.31×10 ⁻⁶
Viscosity at 373K	1.48×10 ⁻⁶	3.25×10 ⁻⁶
Viscosity index	80.05	89.02
Cloud point (°C)	-10	-8
Pour point (°C)	-3	-6

Table 2.2: Molecular weight characteristics of the samples

<i>Polymer sample</i>	<i>M_n</i>	<i>M_w</i>	<i>PDI</i>
P-1	33789	38412	1.14
P-2	31854	37407	1.17
P-3	25118	30574	1.22
P-4	24272	29872	1.23

Where P-1: Homo poly dodecyl acrylate, P-2: copolymer of dodecyl acrylate+ 5% citral, P-3: copolymer of dodecyl acrylate + 10% citral, P-4: copolymer of dodecyl acrylate + 15% citral

Table 2.3: Results of biodegradability test by disc diffusion method and soil burial test for polymeric additives

<i>Polymers</i>	<i>Disc diffusion method</i>	<i>Soil burial test</i>
	<i>Alternaria alternata</i> Wt. loss (%)	Microorganism Wt. loss (%)
P-1	00	00
P-2	31.60	16.30
P-3	37.70	23.20
P-4	40.30	25.70

Table 2.4: TGA data of polymer samples

<i>Polymer Samples</i>	<i>TGA data</i>	
	Decomposition Temperature (K)	Percent weight loss (PWL)
P-1	513/606	16/96
P-2	523/616	14/95
P-3	533/616	15/92
P-4	543/626	15/95

Table 2.5: Viscosity index value of additive doped Base oil

<i>Sample</i>	<i>VI in BO1</i> <i>Concentration of the additives, % in w/w</i>						<i>VI in BO2</i> <i>Concentration of the additives, % in w/w</i>					
	0	1	2	3	4	5	0	1	2	3	4	5
P-1	80	121	122	123	125	132	89	107	112	117	116	120
P-2	80	113	114	115	119	127	89	101	112	112	119	121
P-3	80	112	113	118	120	125	89	107	106	113	115	117
P-4	80	111	113	119	123	124	89	106	105	112	116	118

Where, P-1: Homo poly dodecyl acrylate, P-2: copolymer of dodecyl acrylate+ 5% citral, P-3: copolymer of dodecyl acrylate + 10% citral, P-4: copolymer of dodecyl acrylate + 15% citral

Figure 2.1(a): FT-IR spectra of homo poly dodecyl acrylate

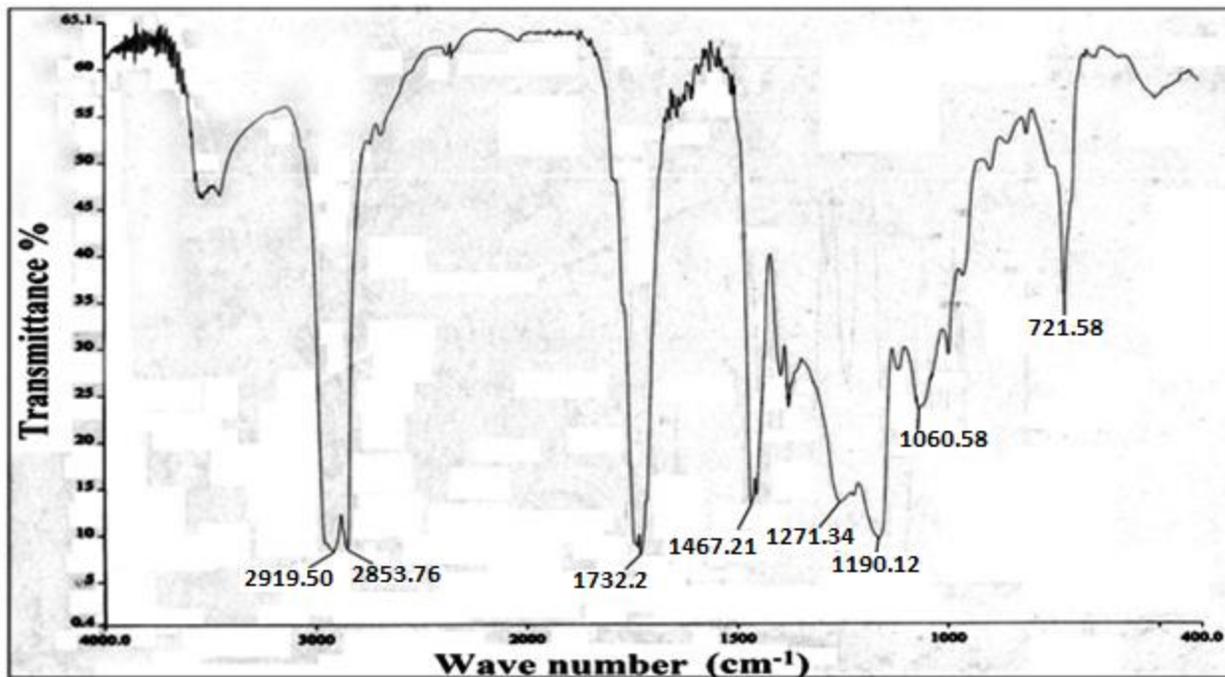


Figure 2.1(b): ¹H NMR spectra of homo poly dodecyl acrylate

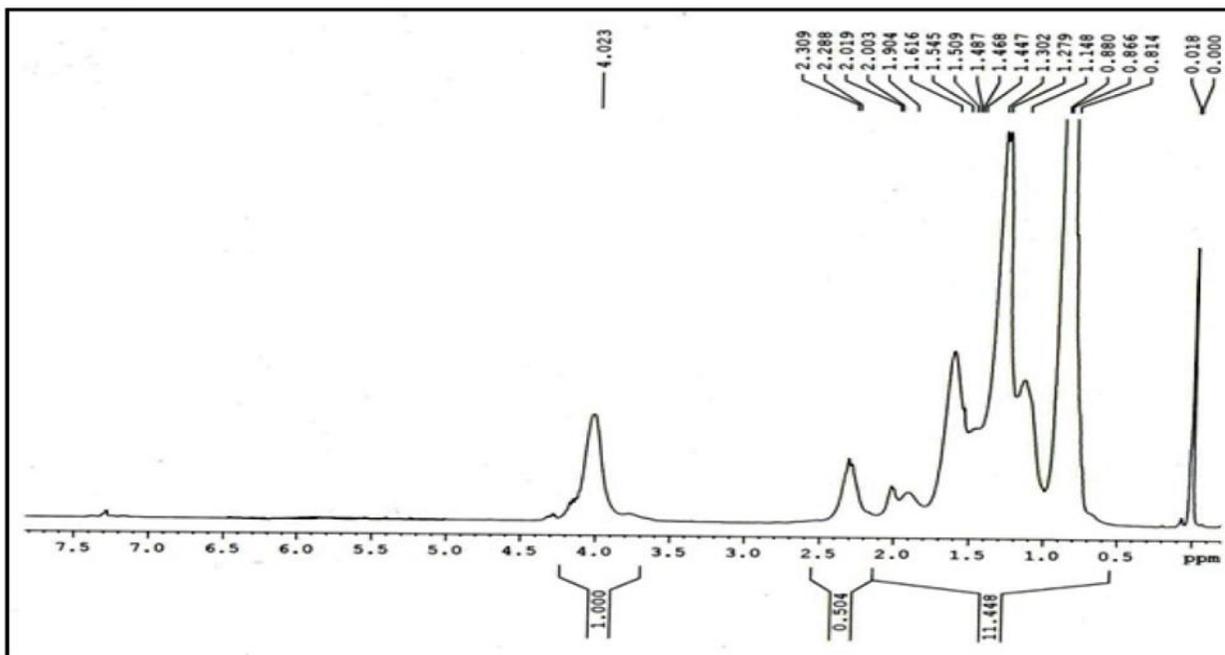


Figure 2.1(c): ^{13}C NMR spectra of homo poly dodecyl acrylate

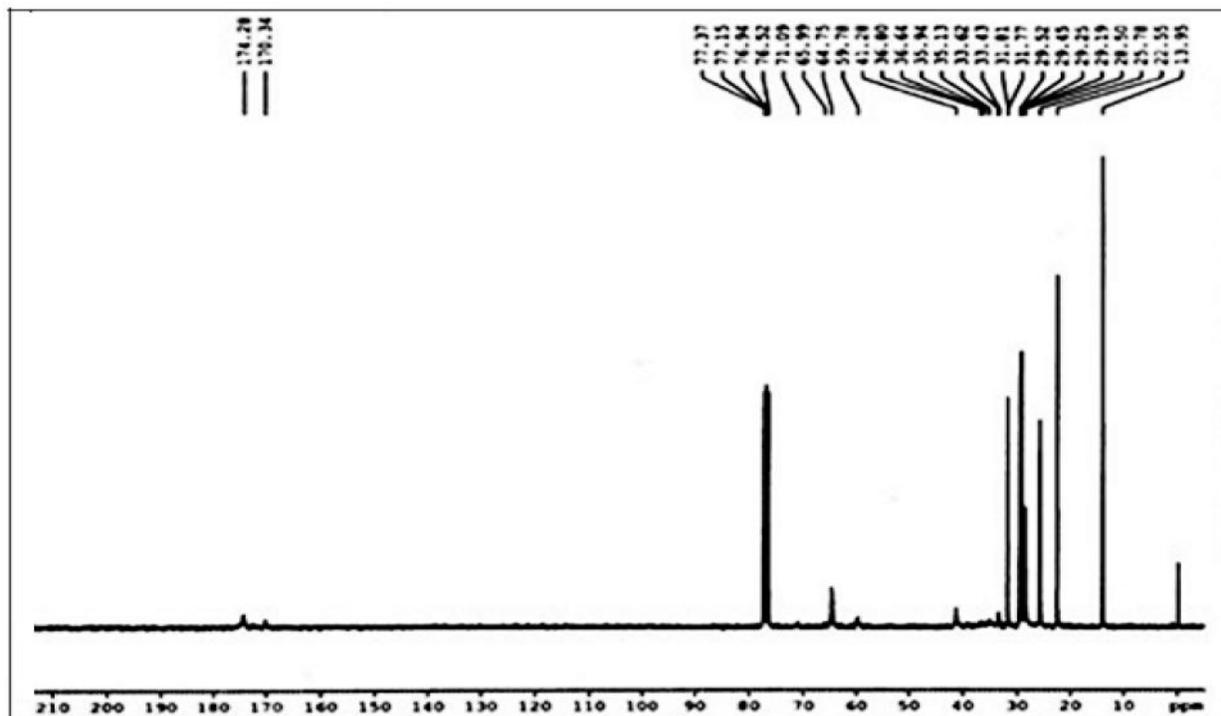


Figure 2.2(a): FT-IR spectra of copolymer of dodecyl acrylate with citral

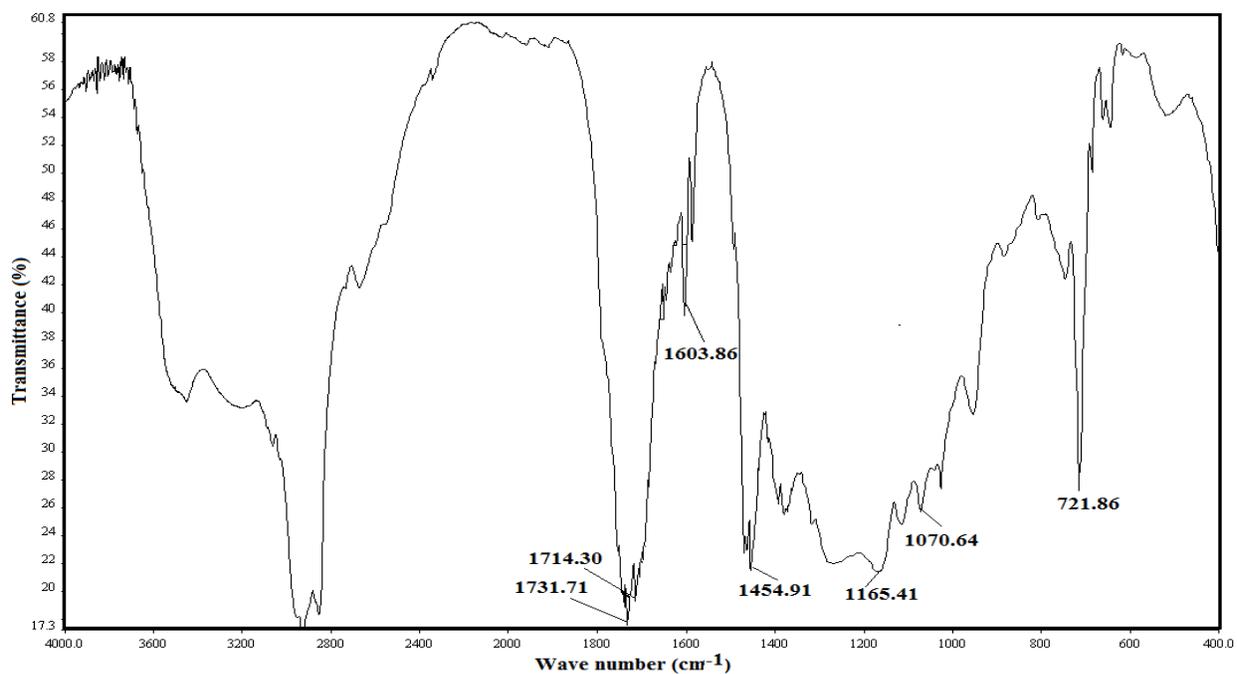


Figure 2.2(b): ^1H NMR spectra of copolymer of dodecyl acrylate with citral

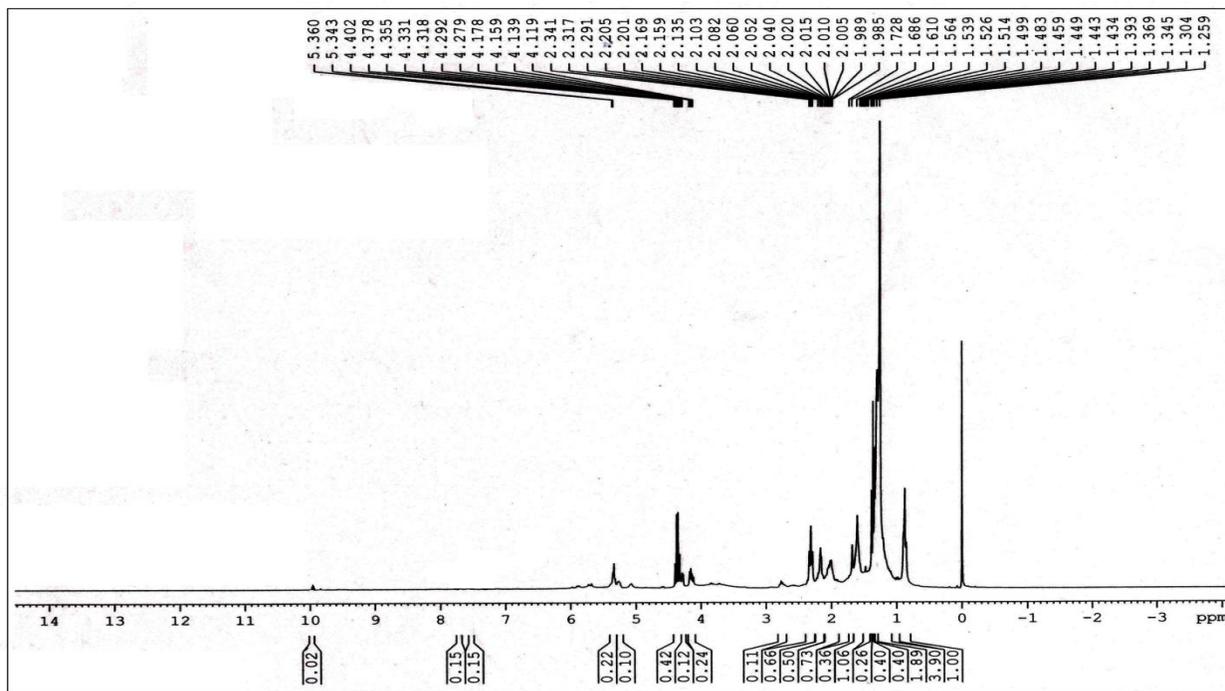


Figure 2.2(c): ^{13}C NMR spectra of copolymer of dodecyl acrylate with citral

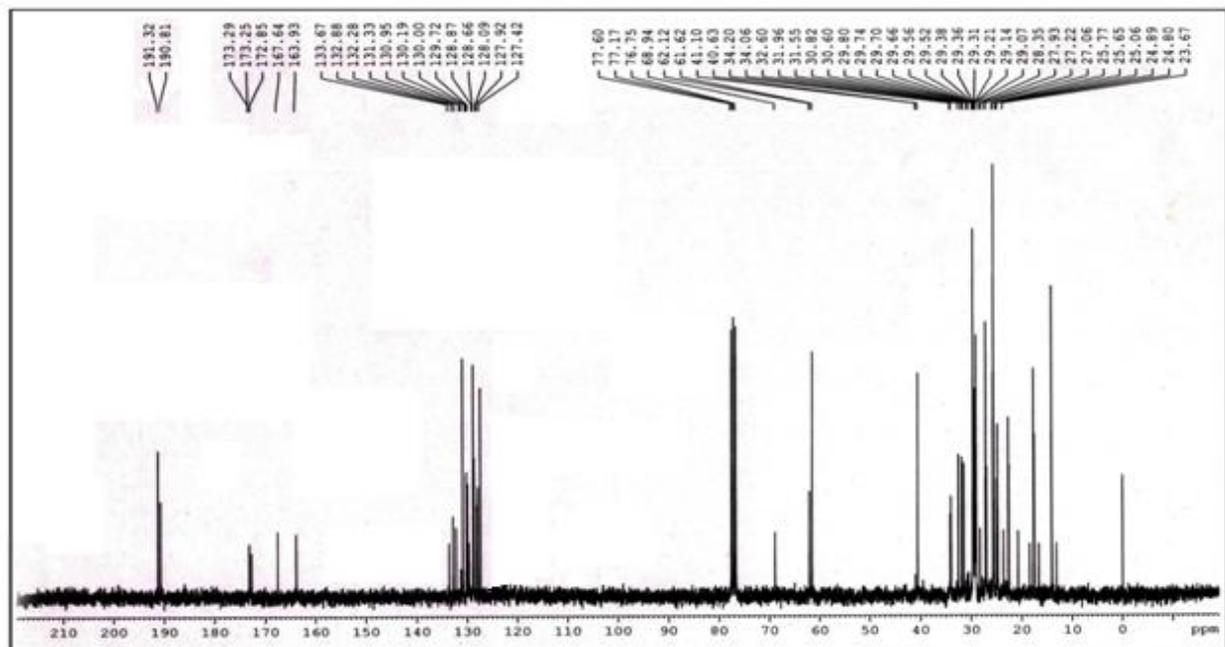


Figure 2.3: Comparative FT-IR spectra of P-1 before and after disc diffusion test

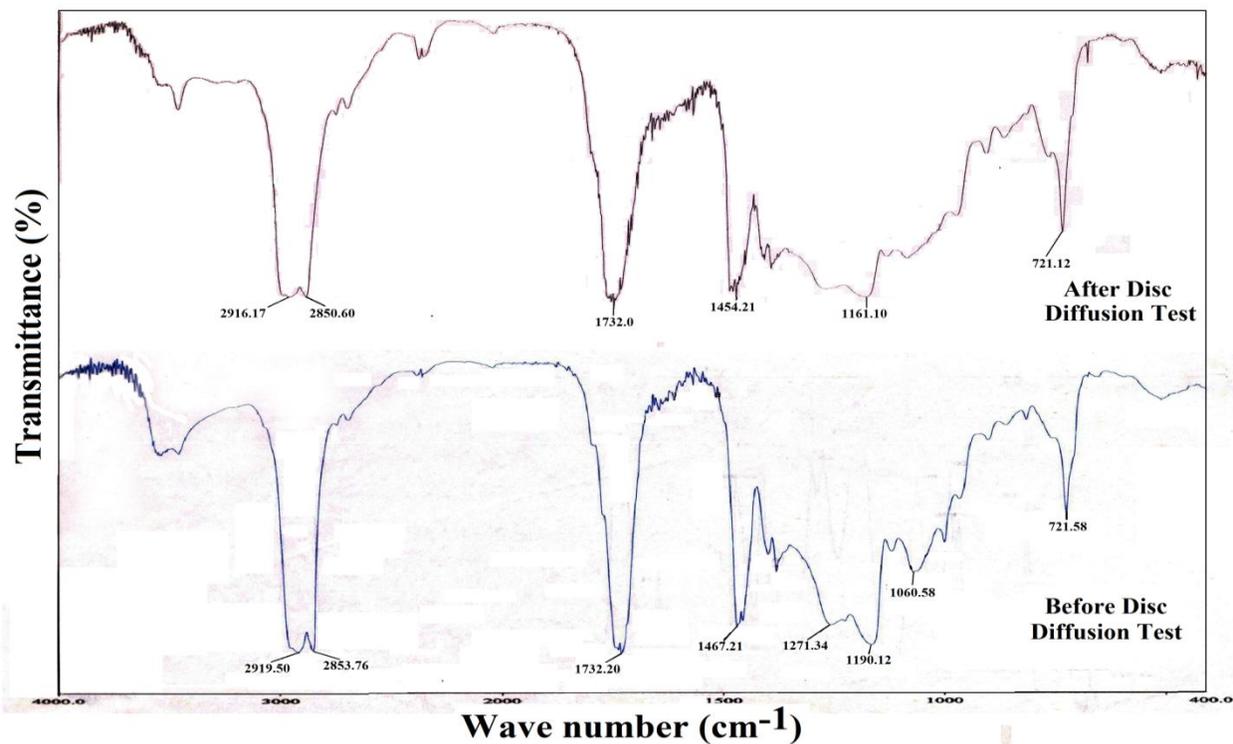


Figure 2.4: Comparative FT-IR spectra of P-2 before and after disc diffusion test

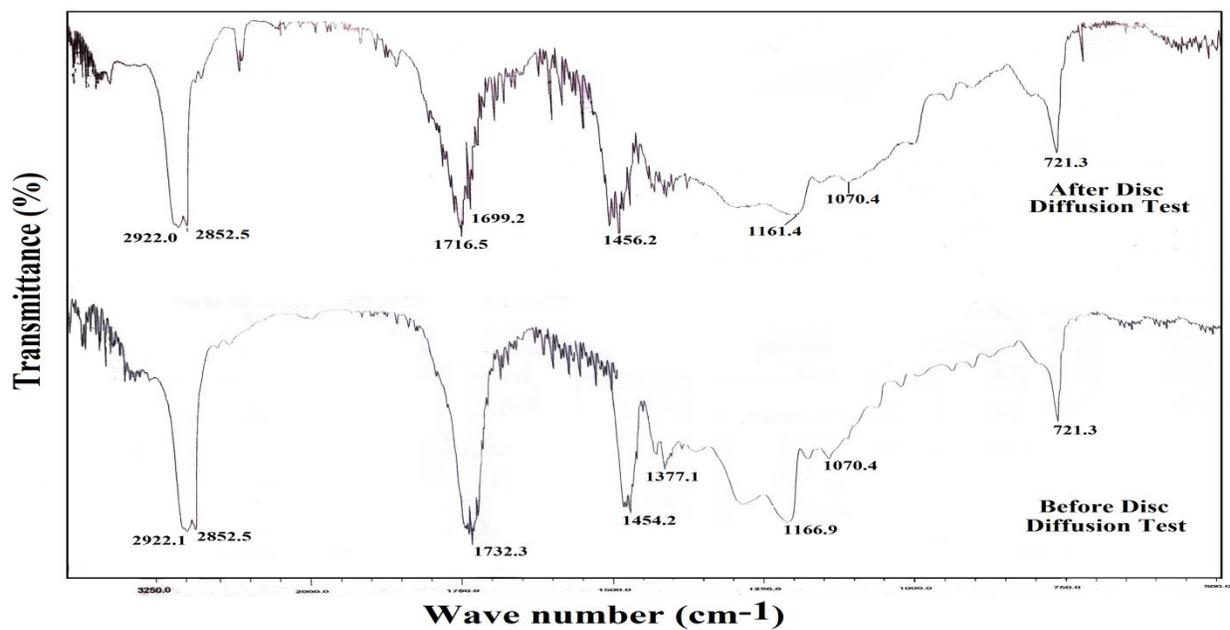


Figure 2.5: Comparative FT-IR spectra of P-3 before and after disc diffusion test

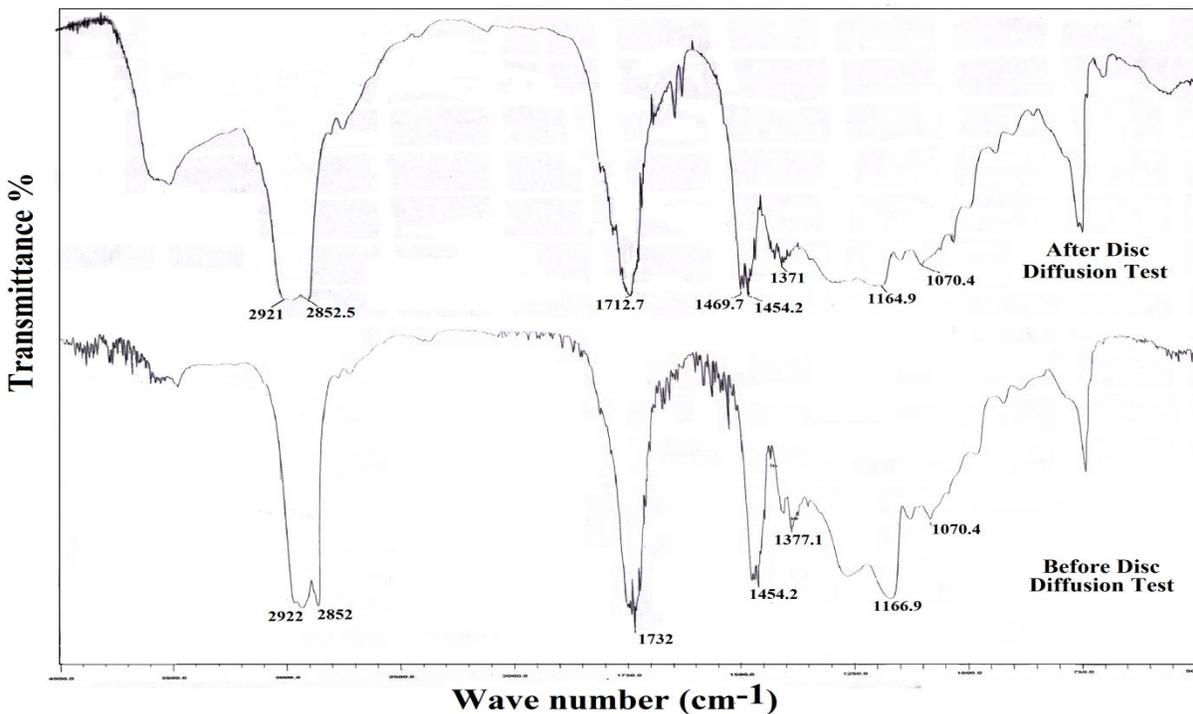


Figure 2.6: Comparative FT-IR spectra of P-4 before and after disc diffusion test

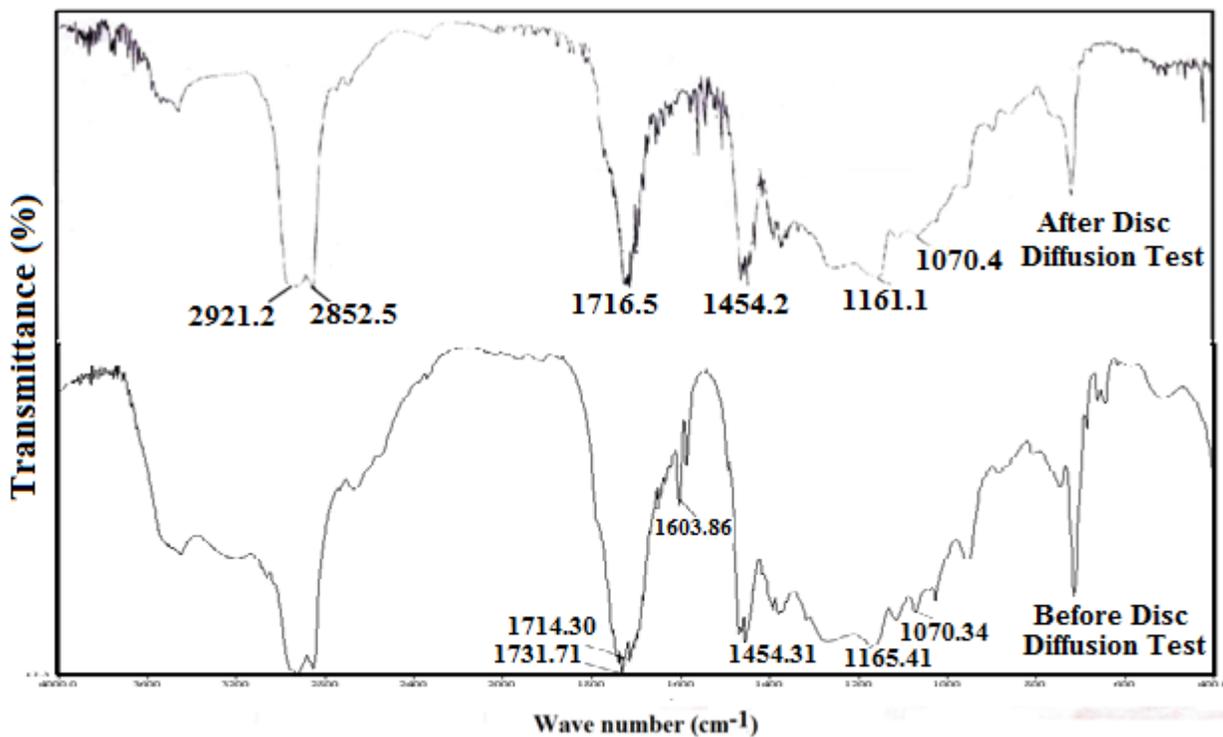


Figure 2.7(a): Plot of pour point of formulated lubricants as a function of additives concentration (w/w) in base oil BO1

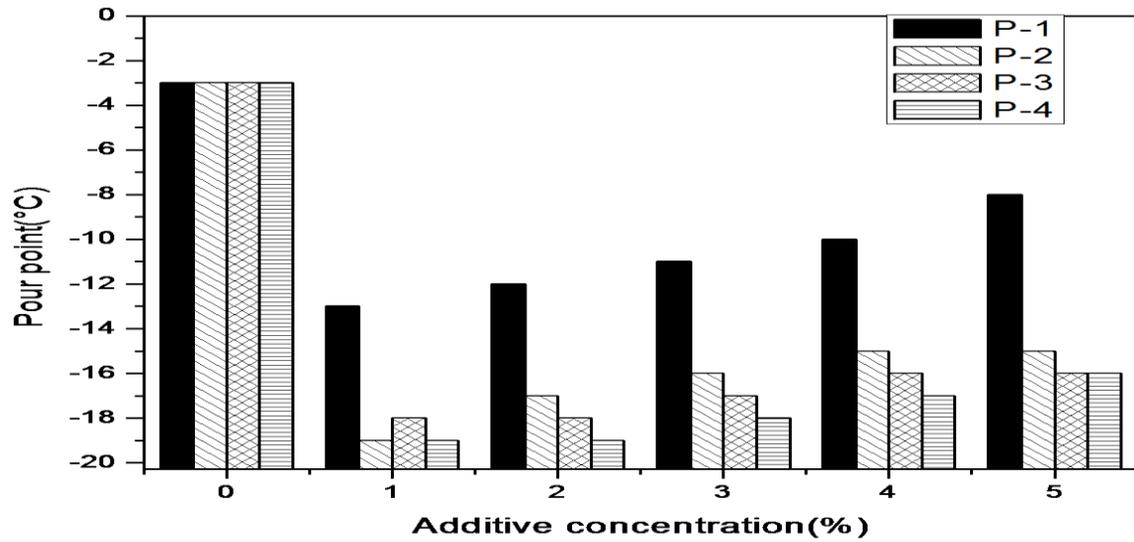


Figure 2.7(b): Plot of pour point of formulated lubricants as a function of additives concentration (w/w) in base oil BO2

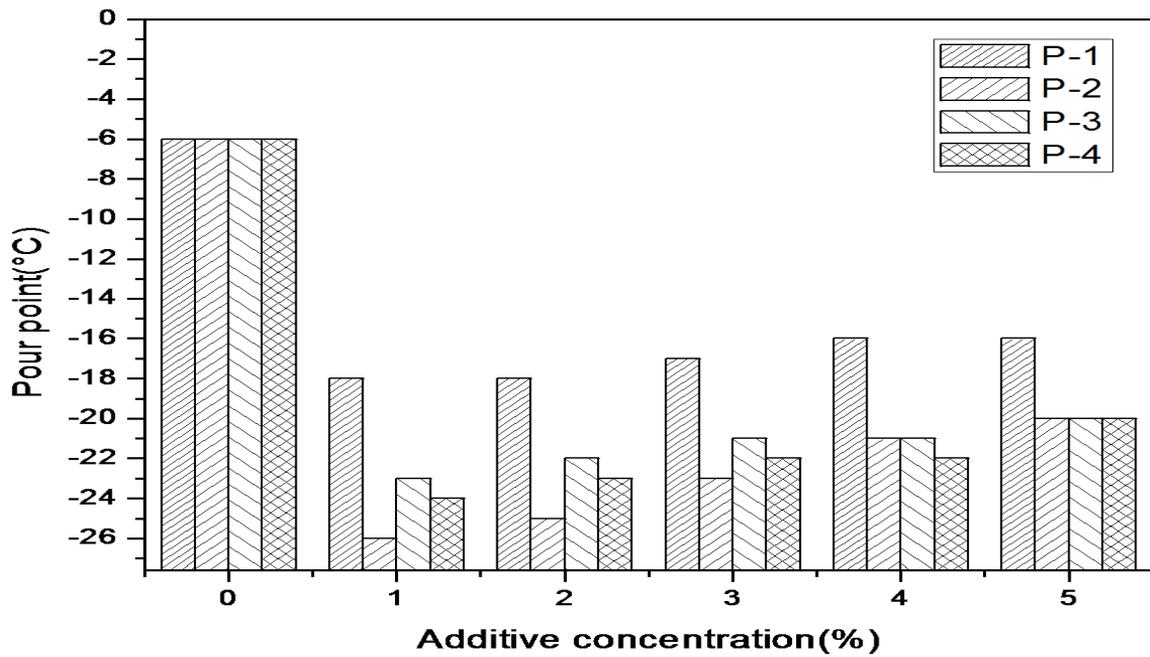


Figure 2.8: Photomicrographic images of base oil (left side) and additive (P-1, P-2, P-3 and P-4) doped base oil (right side)

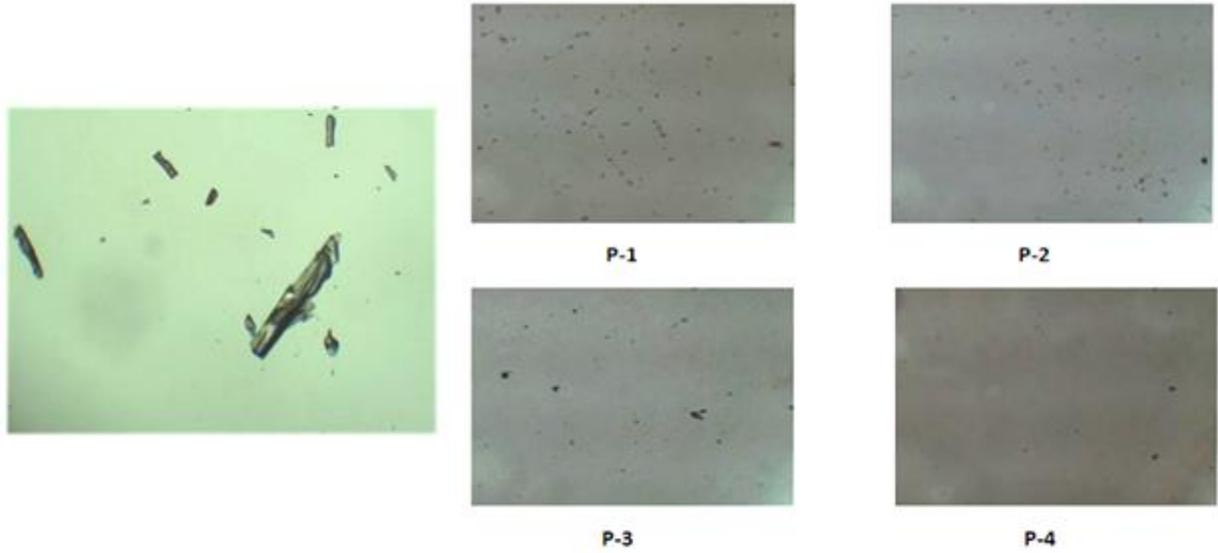


Figure 2.9(a): Plot of wear scar diameter vs. additive concentration in base oil BO1 at 20 kg load condition

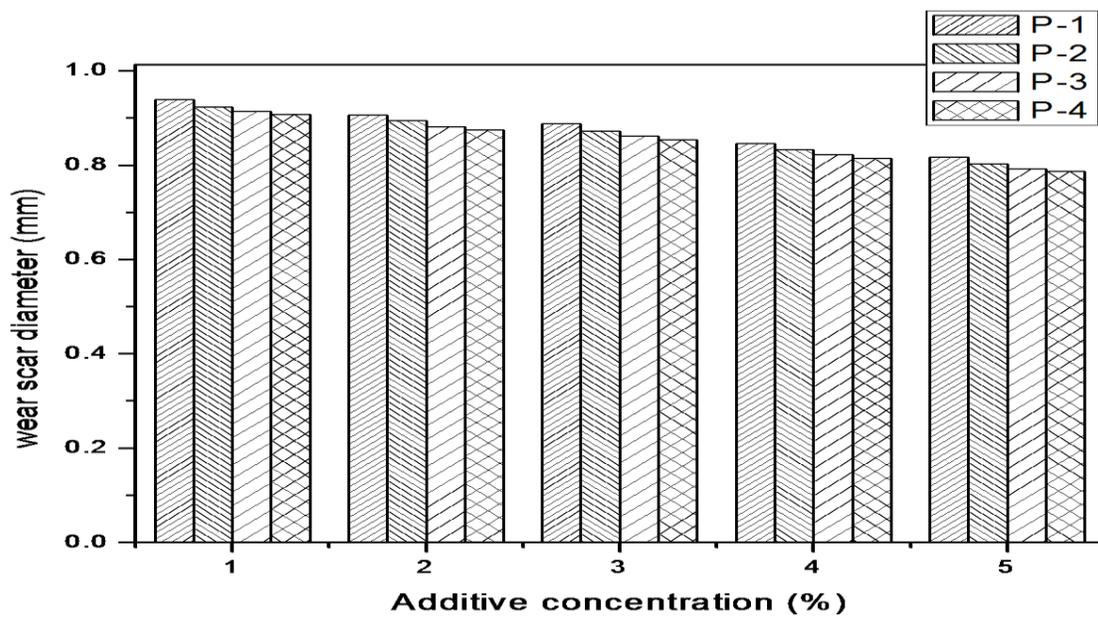


Figure 2.9(b): Plot of wear scar diameter vs. additive concentration in base oil BO1 at 40 kg load condition

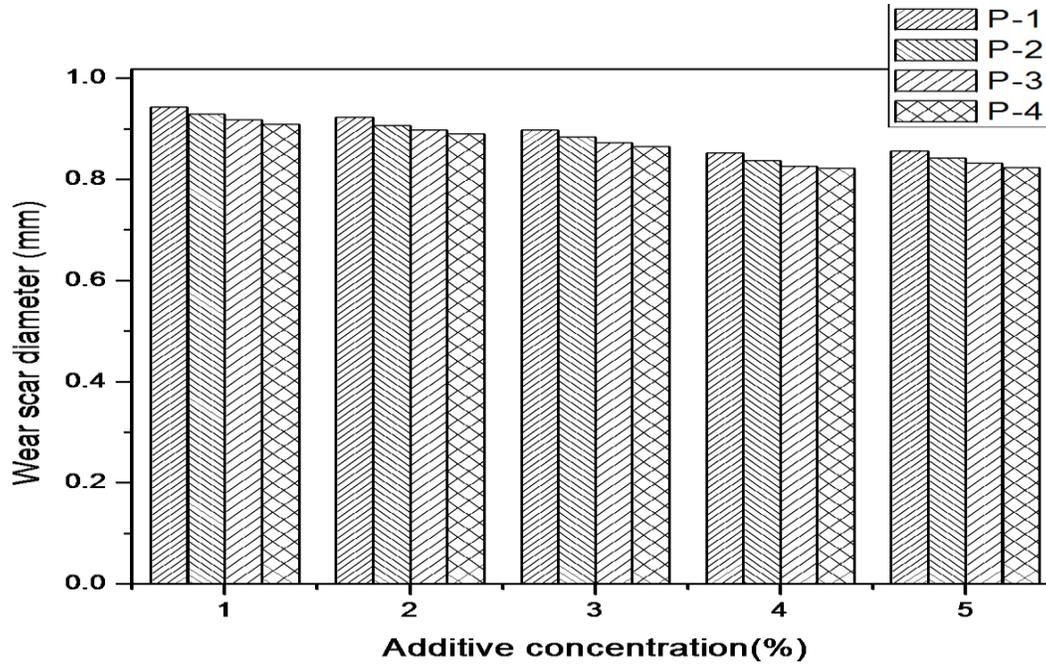


Figure 2.9(c): Plot of wear scar diameter vs. additive concentration in base oil BO2 at 20 kg load condition

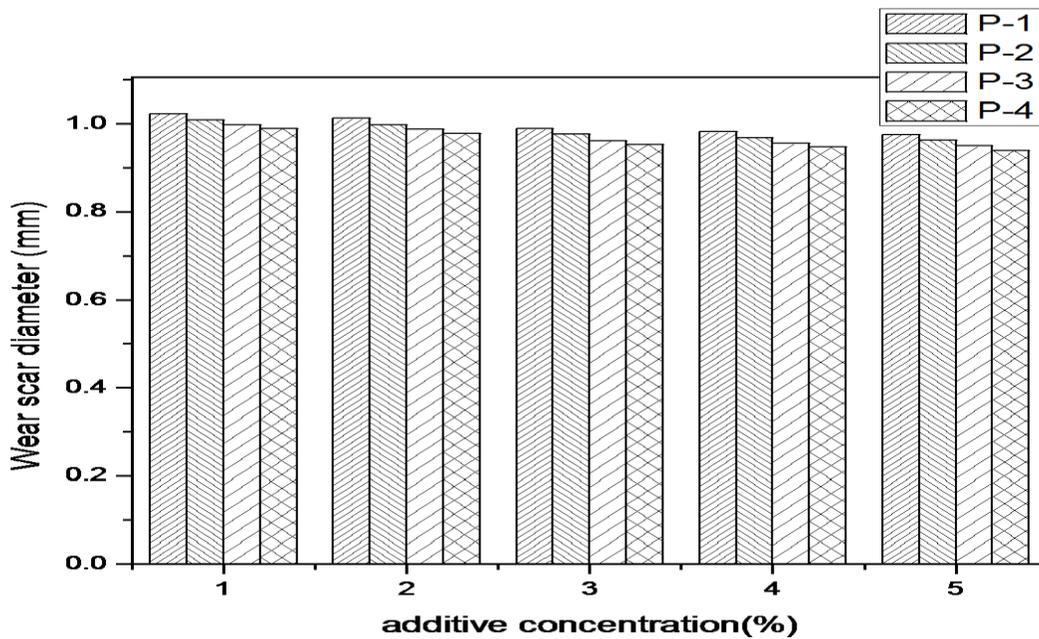
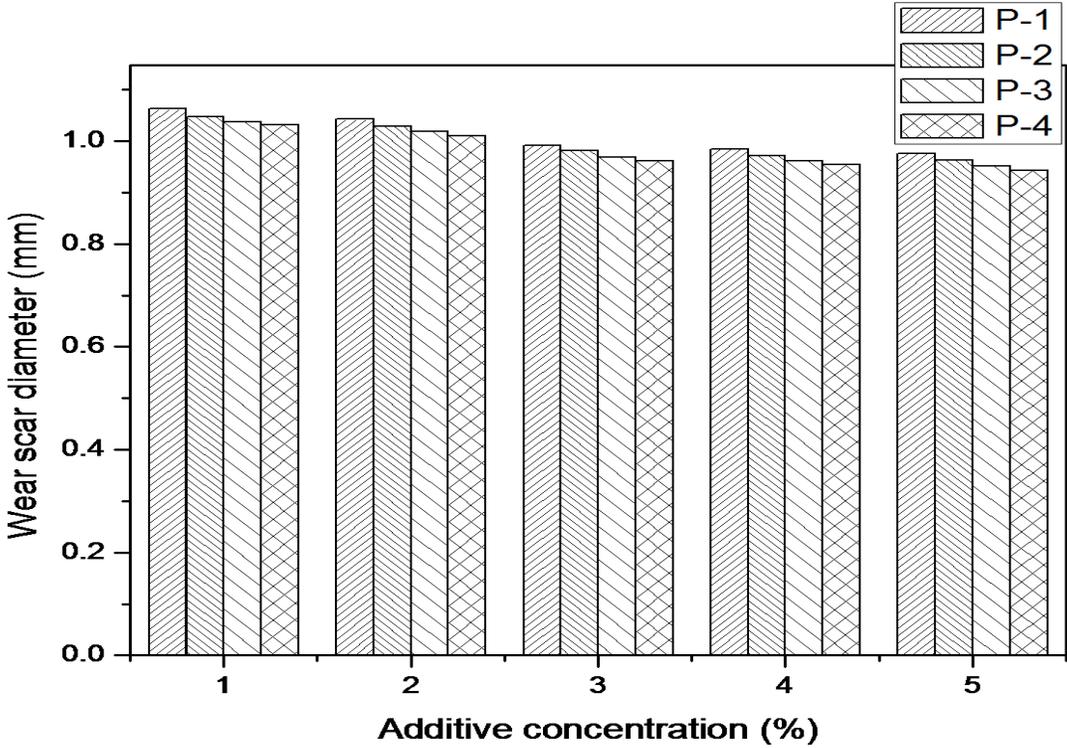


Figure 2.9(d): Plot of wear scar diameter vs. additive concentration in base oil BO2 at 40 kg load condition



Chapter III

**Copolymer of Rice bran oil with
Decyl acrylate and 1-decene as
Lube Oil Additives**

2.2.1. Introduction

Lubricant oil is well known to reduce the friction between two sliding bodies in contact and thus reducing possible wear and damage to the surface of the moving bodies. In addition to base fluid or base oils they contains about 10–20% of additive package. Viscosity index improver (VII), pour point depressants (PPDs), detergents, dispersants, anti-wear, extreme pressure, antioxidant and corrosion inhibitors are the examples of generally used lubricant additives. Among them most important are PPDs¹ and VMs.²

Although lots of additives are in use as PPDs^{1, 3, 4} and VMs.^{2, 5} But due to potent toxicity most of them are not environmentally benign. Consequently, the development of eco-friendly lubricants has become the major concern of the present decade. Plant oils are known to act as promising base fluid for biolubricants because of their excellent lubricity, biodegradability, and viscosity-temperature characteristics. On the other hand, poor thermal stability has rendered restricted application of them in the lubricant formulations. In consideration of that, their copolymerization with acrylate monomers may be undertaken for the development of some novel polymeric additives in anticipation that they may be used as environmental friendly additives for lubricant formulation.

With this background the present work is intended for the synthesis of copolymer of rice bran oil–1-decene and rice bran oil–decyl acrylate (DA) followed by characterization of them (by thermo gravimetric, gel permeation chromatography [GPC], and spectral analysis) and finally evaluation of their additive performance (as PPDs and VMs) in lubricating oil.

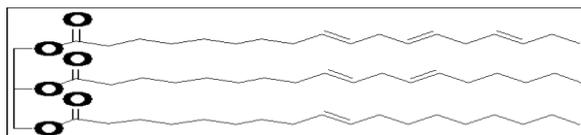


Figure 2b: General structure of triglyceride ester present in Rice bran oil

2.2.2. Experimental procedure

2.2.2.1. Materials and methods

Hydroquinone, Toluene, and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (stabilized with 0.02% hydroquinone monomethyl ether) and decyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Hexane and 1-decene was purchased from S D Fine Chem. Ltd. Rice bran oil was collected from local market and methanol was purchased from Thomas baker Pvt. Ltd. and were used as received. Benzoyl peroxide (BZP) was obtained from LOBA chemicals, which was recrystallized from CHCl₃- MeOH before use. Specifications of the chemicals are depicted in Table 1. Two different kinds of base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in Table 2.

2.2.2.2. Esterification: Preparation of monomer

The preparation of decyl acrylate ester from acrylic acid and decyl alcohol was performed by following the procedure described in chapter II of part I and this was also reported in our previous publication.⁶

2.2.2.3. Purification of prepared monomer

The prepared ester was purified according to the procedure described in chapter II of part I.

2.2.2.4. Preparation of copolymers

The rice bran oil–DA and rice bran oil-1-decene copolymers were prepared by using different concentrations of DA and 1-decene (10%, 20%, and 30% [w/w]) with rice bran oil, P-1 to P-3, and P-4 to P-6, respectively. The radical polymerization was carried out following the method as described in chapter II of part II and this was also reported in our previous publication.⁷

2.2.3. Measurements

2.2.3.1. Spectroscopic measurements

The IR spectra of the samples were recorded on a Perkin Elmer FT-IR 8300 spectrophotometer using 0.1 mm KBr cells at room temperature. The NMR (^{13}C and ^1H) spectra were recorded in a 300 MHz Bruker Avance FT-NMR spectrometer using 5mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) was used as reference material.

2.2.3.2. Thermo gravimetric analysis

The thermo grams of the polymer samples in air were obtained on a Mettler TA – 3000 system, at a heating rate of 10K min^{-1} . The samples were heated continuously in a platinum crucible from room temperature to 620 K.

2.2.3.3. Determination of molecular weight by GPC

In GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were measured and the poly dispersity index was also calculated. In this method HPLC grade THF (0.4%, w/v) was used as mobile phase in the water 2414 GPC system (polystyrene calibration) at 35°C with a flow rate of 1 ml/min .⁷ The results are represented in table . The whole process was also reported earlier from our laboratory.

2.2.3.4. Biodegradability analysis

The biodegradability of the polymers was tested by (i) disk diffusion method against five different fungal pathogens and by (ii) soil burial test as per ISO 846:1997 method. The samples were recovered after the test for determination of any weight loss. FT IR spectra of the recovered samples were recorded to examine change in IR frequency before and after biodegradability test. Again GPC analysis of the recovered polymers was carried out in an anticipation to see any change of M_n and M_w after biodegradation.

2.2.3.4.1. Disc diffusion method

Disc diffusion test was performed in presence of five fungal pathogens namely *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA), *Colletotrichum gloeosporioides* (CG), and *Curvularia eragrostidis* (CE) as described in Chapter II of Part II and the process was also reported earlier from our laboratory.⁵

2.2.3.4.2. Soil burial test

The soil burial degradation test of polymer sample films was performed as per ISO 846:1997 method according to the procedure described in chapter II of part II and the process was also reported earlier from our laboratory.⁵

2.2.3.5. Evaluation of viscosity index of the prepared additives in lube oil

The viscosity index of the polymer samples was evaluated in two base oils (BO1 and BO2) according to the ASTM D2270 method. The whole procedure is already described in Chapter II of Part I and it was also reported earlier from our laboratory.⁸

Five different concentrations (1 wt% to 5 wt %) of the sample solutions were used to examine the consequence of additive concentration on VI.

2.2.3.6. Evaluation of pour point of the additives in lube oil

The pour point depressant properties of the prepared polymers were tested in two base oils (BO1 and BO2) on a Cloud and Pour Point Tester model WIL-471(India) according to ASTM D 97 method.

Five different concentrations (1 wt% to 5 wt %) of the polymer samples were employed to compare additive concentration with pour point effectiveness.

2.2.4. Results and discussion

2.2.4.1. Spectroscopic analysis

FT-IR spectra of copolymer of rice bran oil–DA showed absorption at 1733cm^{-1} for the ester C-O stretching vibration along with other peaks at 1457, 1244, and 1171 cm^{-1} and a peak at 723.3 cm^{-1} was due to C-H bending. In its ^1H NMR spectra, the polymer exhibited a broad singlet ranging between 4.11 and 4.31 ppm due to the $-\text{OCH}_2$ protons of rice bran oil and DA along with the $-\text{CH}_3$ protons ranging between 0.86 and 0.88 ppm and $-\text{CH}_2$ protons ranging between (1.25 and 1.61) ppm. The synthesis of the copolymer was further confirmed by the nonappearance of sp^2 hydrogen in its ^1H NMR and sp^2 carbon in ^{13}C NMR spectrum, respectively and spectra are showed in **figure 2.10**

FT-IR spectra of copolymer of rice bran oil–1-decene exhibited absorption at 1732 cm^{-1} for the ester C-O stretching vibration along with other peaks at 1456, 1378, 1244, 1174, and 724 cm^{-1} . In its ^1H NMR spectra, the polymer exhibited a broad singlet ranging between 4.11 and 4.3 ppm owing to the proton of $-\text{OCH}_2$ group of RBO along with the $-\text{CH}_3$ protons at 0.88 ppm and $-\text{CH}_2$ protons spanning between 1.26 and 1.62 ppm. The synthesis of the copolymer was further verified by the nonappearance of sp^2 hydrogen and sp^2 carbon in its ^1H and ^{13}C NMR, respectively and spectra are showed in **figure 2.11**

2.2.4.2. Thermo gravimetric analysis (TGA)

Figure 2.14 represents a plot of TGA data which shows a comparison between the thermal stability of rice bran oil–DA and rice bran oil–1-decene copolymers. The analysis discloses that for both set of polymers, thermal stability increases with increasing concentration of 1-decene and DA in the feed and the copolymers of rice bran oil + DA are more stable than the corresponding copolymers of rice bran oil +1-decene.

2.2.4.3. Analysis of biodegradability test

Both sets of copolymers showed significant weight loss against fungal pathogens, *Calletotricheme camellia* and *Alternaria alternata* after Disc diffusion test (**table 2.8a**). Even though the extent of weight loss was less in Soil burial test (**table 2.8b**), the results are still considerable. Again the degradation result was better for Rice bran oil-DA copolymers. The copolymer of 10% Rice bran oil and DA (P-1) found to endure highest weight loss in both the biodegradability tests. Moreover there was considerable shift in molecular weight of the copolymer samples after Disc diffusion test. The result of GPC analysis of the polymer samples before and after biodegradability test is depicted in **table 2.9**. FT-IR spectra of copolymer samples recovered after disc diffusion test were compared with respective spectra before the test and the results are compiled in **figure 2.12 and 2.13**

2.2.4.4. Efficiency of copolymers as viscosity index improver (VII)

The VI values of copolymers in two base oils (determined in six different concentrations) tabulated in **table 2.11** reveals that in both the base oils the values are greater for rice bran oil-DA copolymers than that for respective rice bran oil-1-decene copolymers and for DA copolymers, the VI value increases with increasing RBO concentration in the feed, and similar tendency is also observed for copolymers of RBO-1-decene. This consequence may be explained on the basis of the molecular weight of the polymers. Again, VI increases with increase in concentration of the polymers in solution. The reason may be that although the viscosity of the lube oil gets decreased at higher temperature, the polymer molecules may effectively counterbalance this reduction in viscosity by thickening the oil changing its shape from tight coil to expanded one due to increased polymer-solvent interaction. This in turn increases viscosity of the solution. Again, a higher polymer concentration means increase in total

volume of polymer coils in the solution which imparts a higher VI compared to a low concentrated polymer solution.^{2,5}

2.2.4.5. Efficiency of copolymers as pour point depressant

The pour point (PP) values of the polymers in both the base oils are tabulated in **table 2.10**, which indicates that, their PPD efficiency increases (up to a certain limit) with increasing concentration of the polymer in base oils. Comparison among the PP values indicates that the efficiency of the polymers as PPD is better for DA copolymers than the 1-decene copolymers. Again, the efficiency in base oil, BO1 is better than that of in BO2.

2.2.5. Conclusion

The rice bran oil + DA copolymers are thermally more stable than the rice bran oil + 1-decene copolymers and thermal stability increases with increasing concentration of 1-decene and DA in the copolymers. Performance evaluation of the additives indicates that the rice bran oil + DA copolymers act as better PPD and viscosity modifiers compared to the RBO + 1-decene copolymers. All the studied polymers showed biodegradable property in addition to the multifunctional additive performance (PPD and VM), and so are considered as being more useful in field applications compared to the existing additives.

2.2.6. References

References are given in BIBLIOGRAPHY under Chapter III of Part II (PP 167).

2.2.7. Tables and figures

Table 2.6: Properties base oils

<i>Properties</i>	<i>Base oils</i>	
	BO1	BO2
Density, kg.m ⁻³ at 313K	836.98	868.03
Viscosity × 10 ⁻⁶ , m ² .s ⁻¹ at 313K	6.70	24.22
Viscosity × 10 ⁻⁶ , m ² .s ⁻¹ at 373K	2.00	4.39
Cloud point, °C	-10	-8
Pour point, °C	-3	-6

Where BO1: base oil type 1, BO2: base oil type 2

Table 2.7: GPC analysis data of the polymer samples (P-1 to P-6)

<i>Polymer samples</i>	M_n	M_w	<i>PDI</i>
P-1	35709	43837	1.22
P-2	23332	31234	1.33
P-3	18965	27654	1.45
P-4	16392	23597	1.43
P-5	14815	21230	1.43
P-6	12112	17659	1.45

Where, Mn: Number average molecular weight, Mw: Weight average molecular weight, PDI: Poly dispersity index

Table 2.8 (a): Results of biodegradability test by the disc diffusion method

Sample	Incubation period (days)	Percent weight loss in presence pathogens				
		CC	FE	AA	CG	CE
	P-1	30	33	00	48	00
P-2	30	25	00	44	00	00
P-3	30	27	00	37	00	00
P-4	30	23	00	31	00	00
P-5	30	17	00	27	00	00
P-6	30	11	00	28	00	00

Incubated for 30 days at 310K, CC, FE, AA, CG, and CE are the pathogens used. CC= *Colletotrichum camelliae*, FE= *Fusarium equiseti*, AA= *Alternaria alternata*, CG= *Colletotrichum gloeosporioides* and CE= *Curvularia eragrostidis*

Table 2.8 (b): Result of biodegradability test by soil burial method

Weight loss in soil burial test						
Polymer sample	P-1	P-2	P-3	P-4	P-5	P-6
Weight loss (%)	32	28	22	18	15	12

Incubated for 60 days at 303 K and humidity 50-60%

Table 2.9: Comparative GPC data of polymer samples in biodegradability test

<i>Polymer samples</i>	<i>Before biodegradability test</i>		<i>After biodegradability test</i>	
	M_n	M_w	M_n	M_w
P-1	35709	43837	31421	41238
P-2	23332	31234	19816	28764
P-3	18965	27654	17657	24569
P-4	16392	23597	14710	21056
P-5	14815	21230	12348	19379
P-6	12112	17659	10528	14592

Table 2.10: Dependence of PP (in °C) on the concentration of Additives in BO1 and BO2

<i>Base oil (PP)</i>	<i>Conc., %</i>	<i>Sample</i>					
		P-1	P-2	P-3	P-4	P-5	P-6
BO1 (-3)	1	-9	-15	-15	-9	-9	-12
	2	-12	-18	-21	-9	-12	-12
	3	-15	-21	-24	-12	-15	-15
BO2 (-6)	1	-12	-15	-18	-15	-21	-18
	2	-15	-18	-21	-18	-24	-24
	3	-15	-24	-27	-21	-18	-24

Table 2.11: Dependence of VI on the concentration of Additives in BO1 and BO2

<i>Base oil(VI)</i>	<i>Conc.,%</i>	<i>Sample</i>					
		P-1	P-2	P-3	P-4	P-5	P-6
BO1 (85)	1	112	116	119	100	110	118
	2	112	118	125	104	112	122
	3	125	130	132	106	114	128
	4	125	135	138	118	126	135
	5	128	136	145	121	128	138
	6	134	136	146	125	129	137
BO2 (80)	1	95	98	101	98	100	104
	2	97	100	110	109	104	110
	3	102	115	115	115	118	119
	4	105	115	123	118	122	125
	5	115	123	132	131	130	132
	6	116	128	138	137	129	138

Figure 2.10 (a): FT-IR spectra of copolymer of Rice bran oil-DA

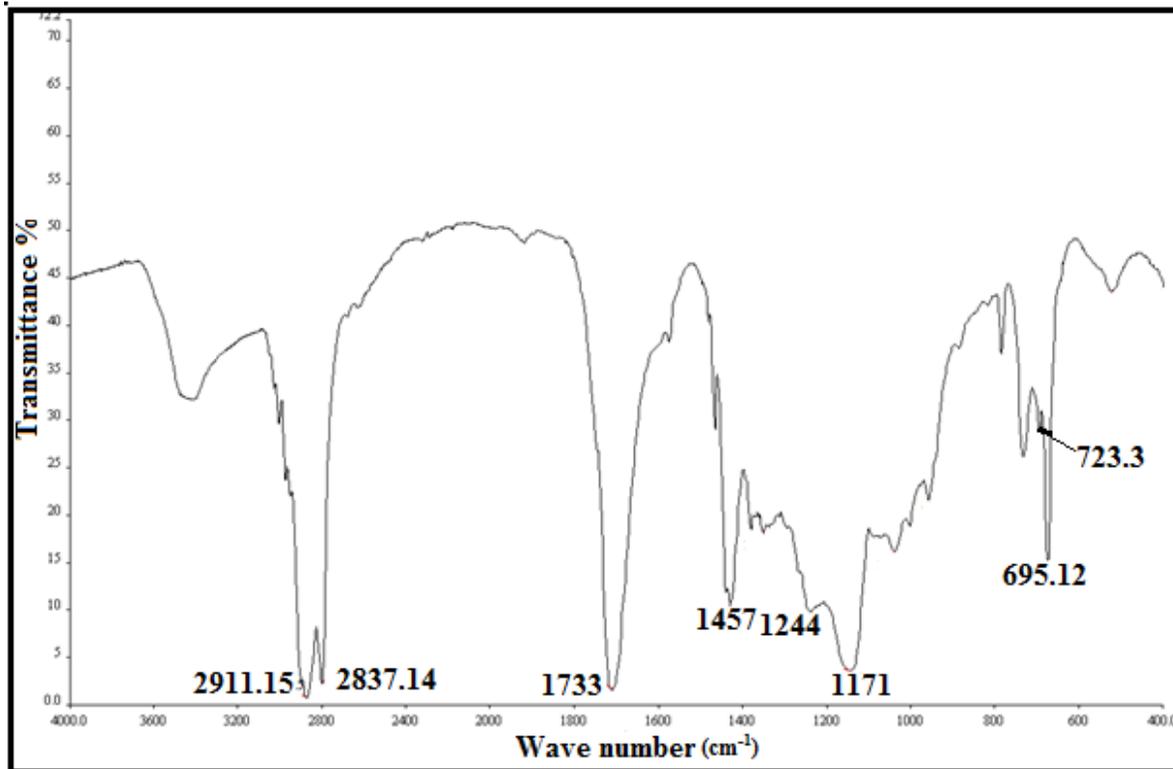


Figure 2.10 (b): ¹H NMR spectra of copolymer of Rice bran oil-DA

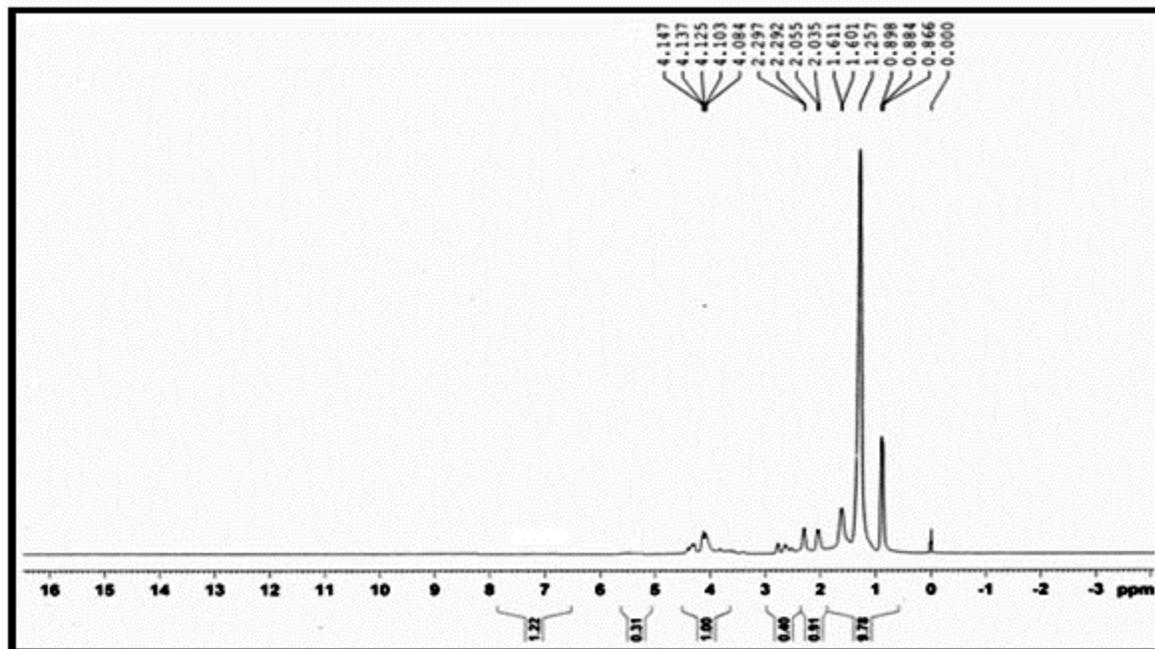


Figure 2.10 (c): ^{13}C NMR spectra of copolymer of Rice bran oil-DA

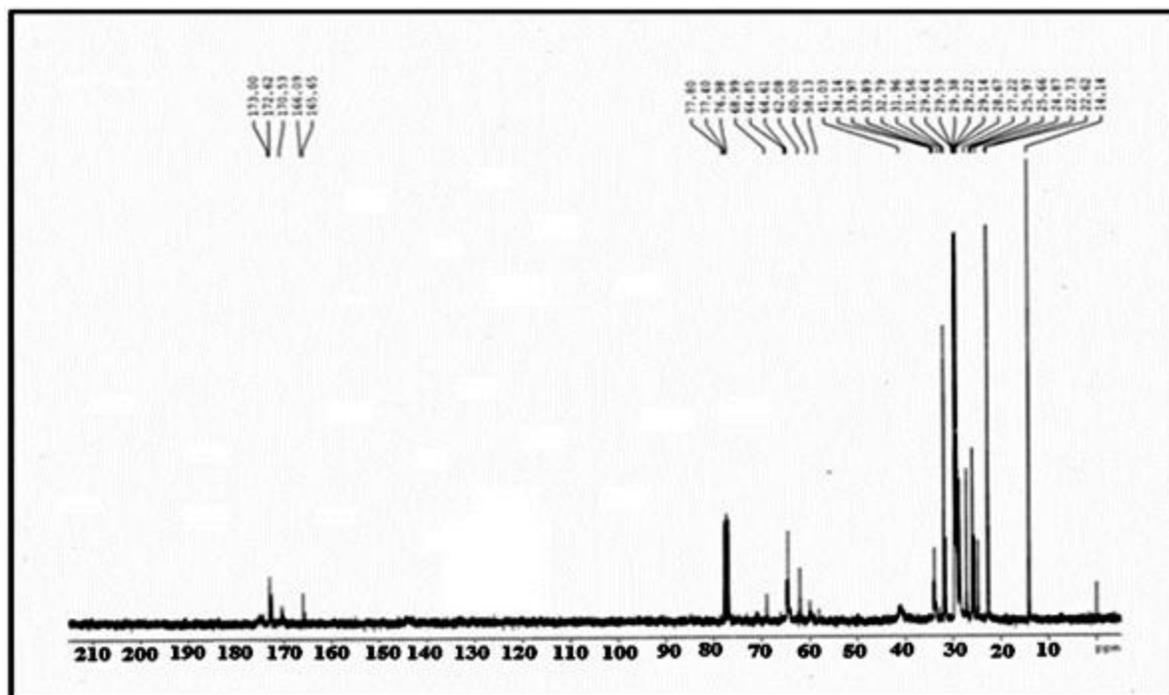


Figure 2.11 (a): FT-IR spectra of copolymer of Rice bran oil-1-Decene

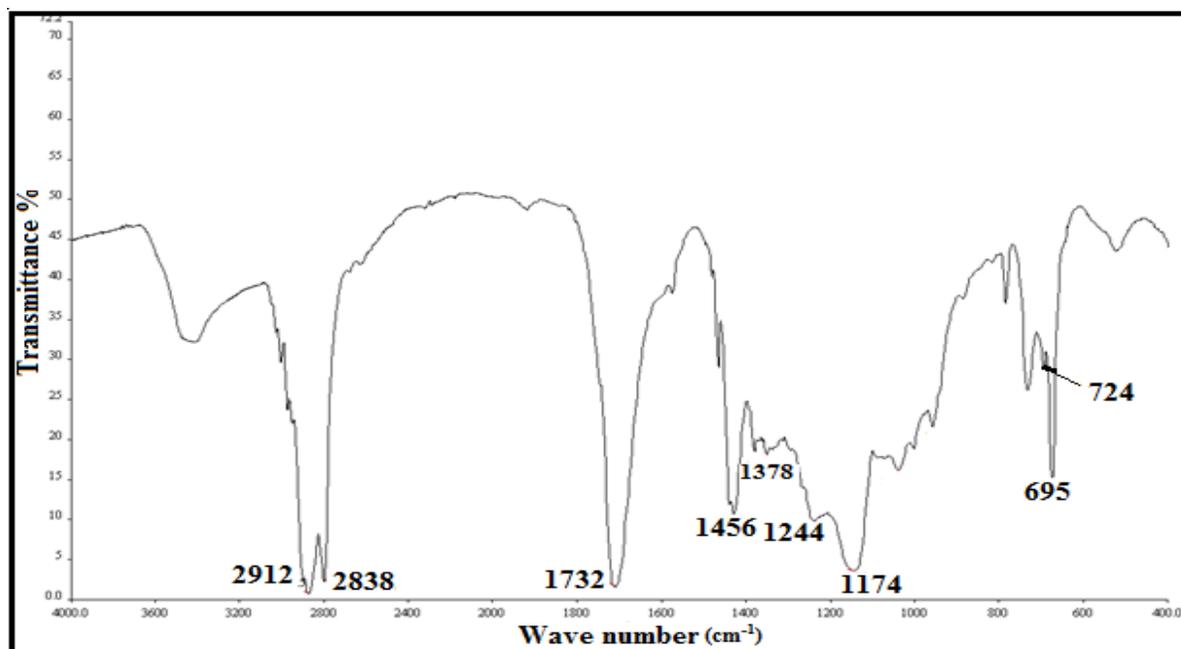


Figure 2.11 (b): ^1H NMR spectra of copolymer of Rice bran oil-1-Decene

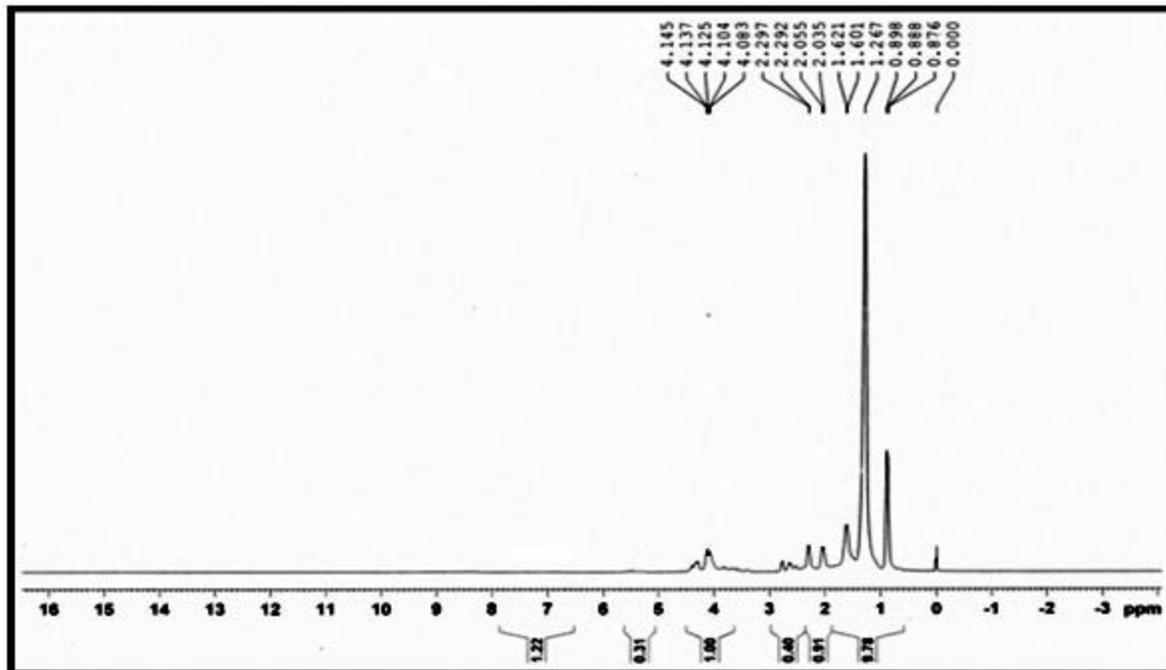


Figure 2.11 (c): ^{13}C NMR spectra of copolymer of Rice bran oil-1-Decene

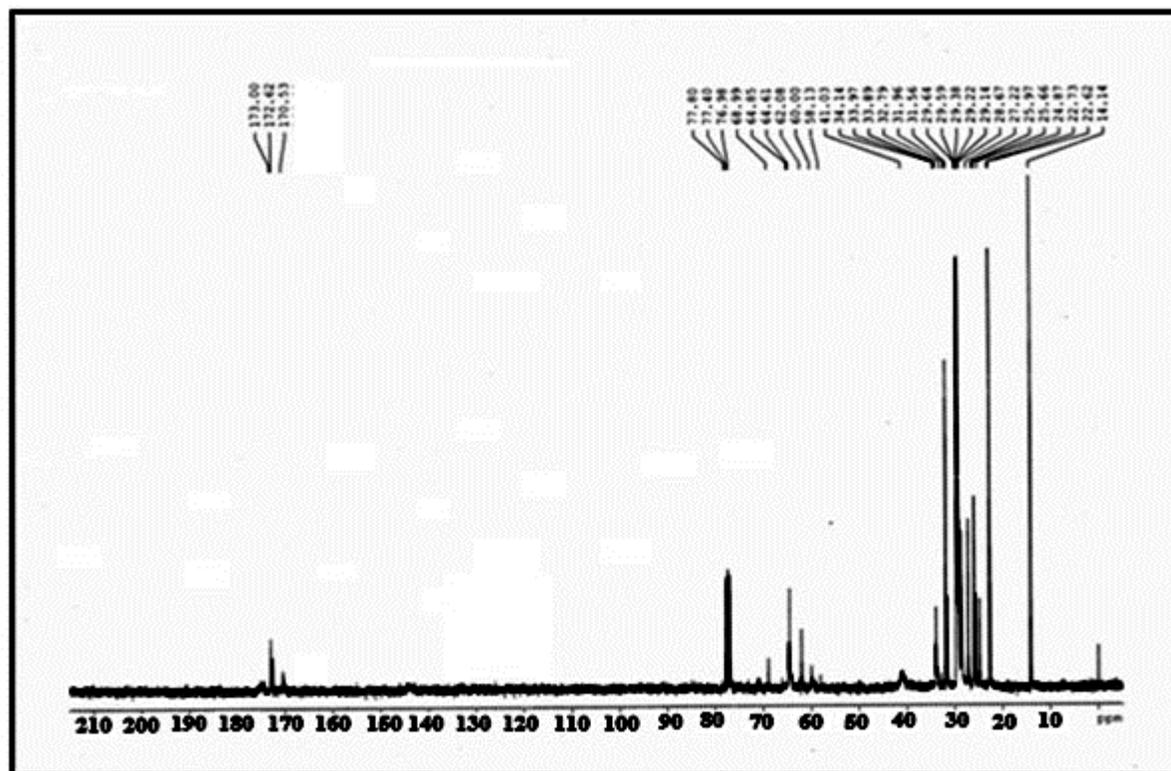


Figure 2.12: Comparative FT-IR spectra of copolymer of Rice bran oil-DA

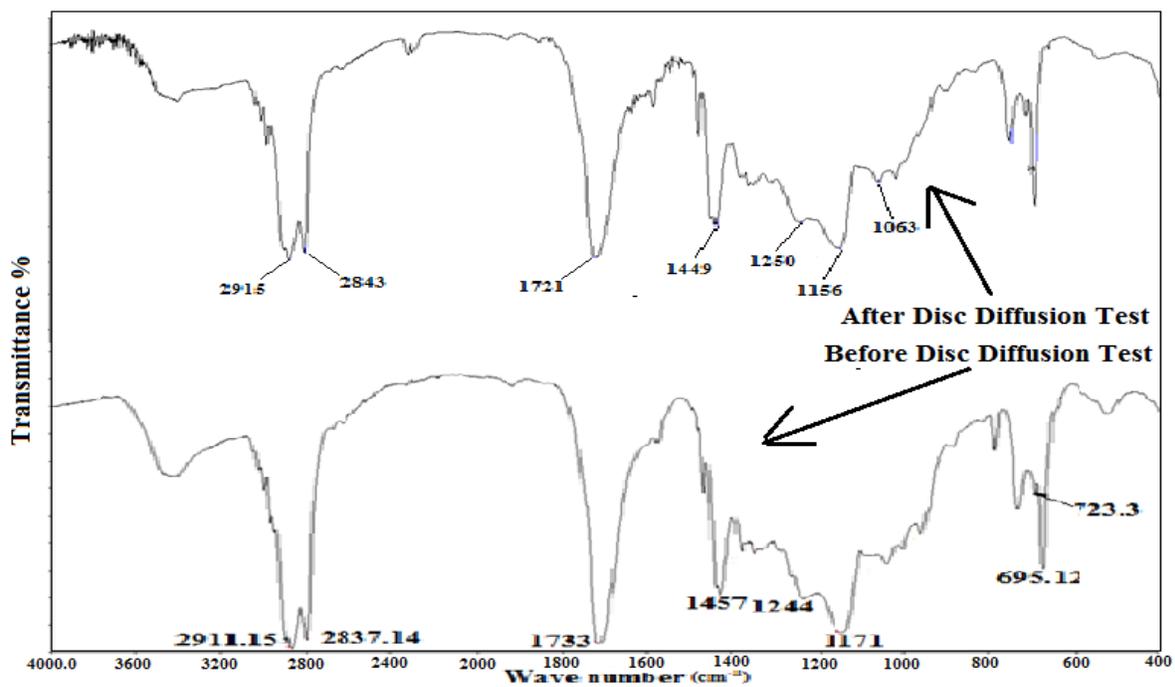


Figure 2.13: Comparative FT-IR spectra of copolymer of Rice bran oil-1-Decene

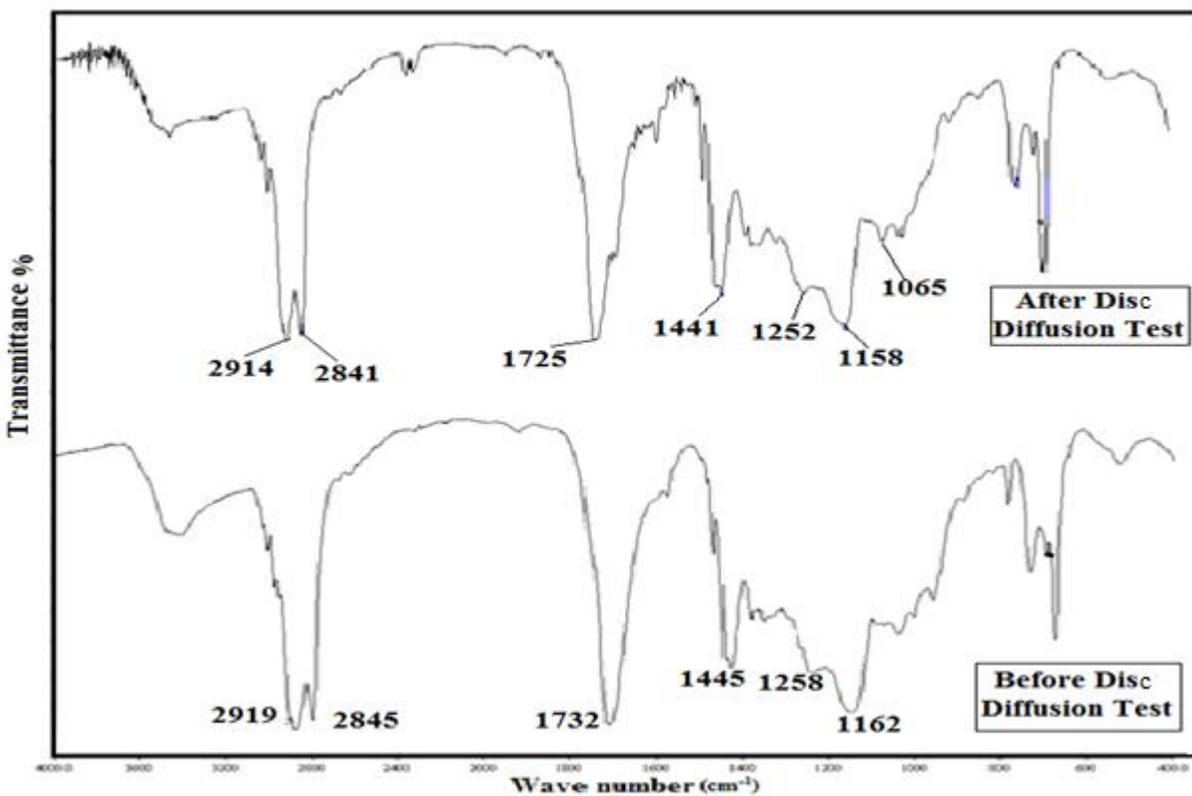
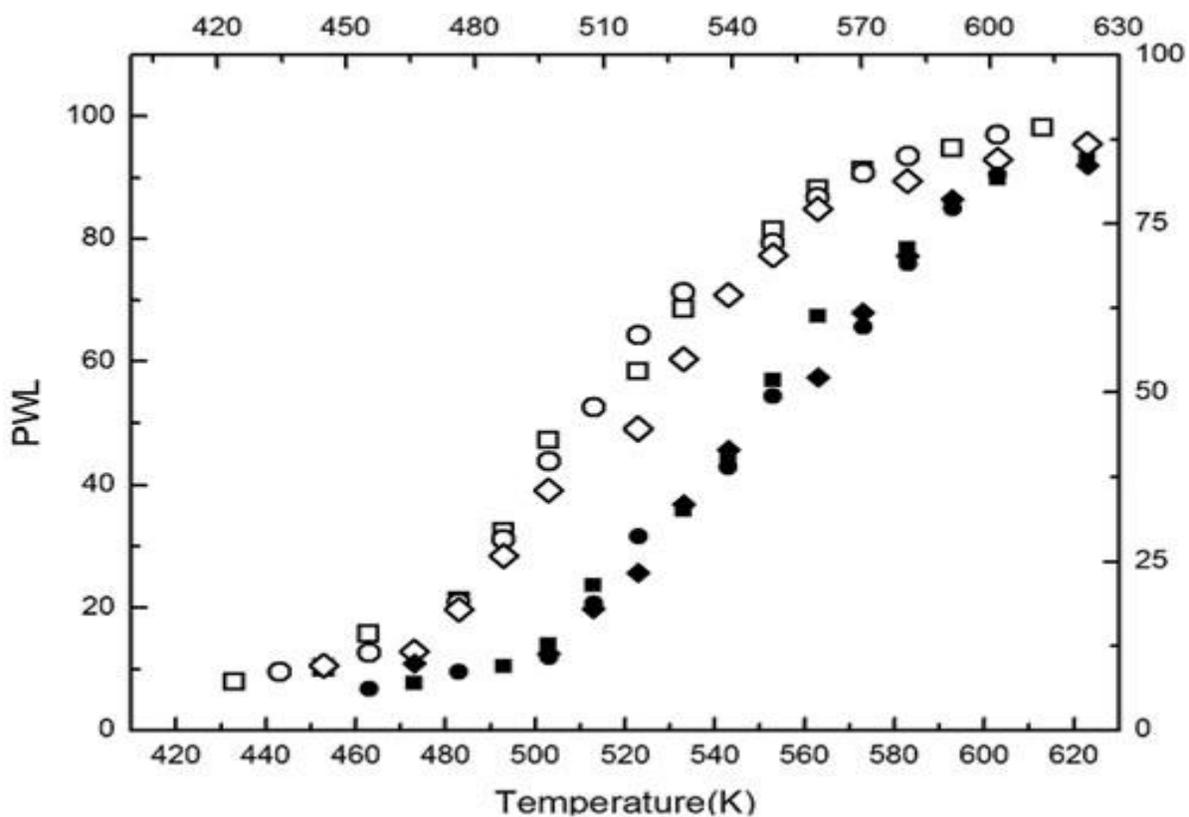


Figure 2.14: Comparative TGA data of copolymer of Rice bran oil-DA (P-1, P-2, and P-3) and Rice bran oil- 1-Decene (P-4, P-5 and P-6)



Where, PWL= percent weight loss. Temperature is in K. ■, P-1; ●, P-2; ◆, P-3; □, P-4; ○, P-5; ◇, P-6.

Figure 2.15 (a): Dependence of viscosity index on additive concentration in base oil BO1

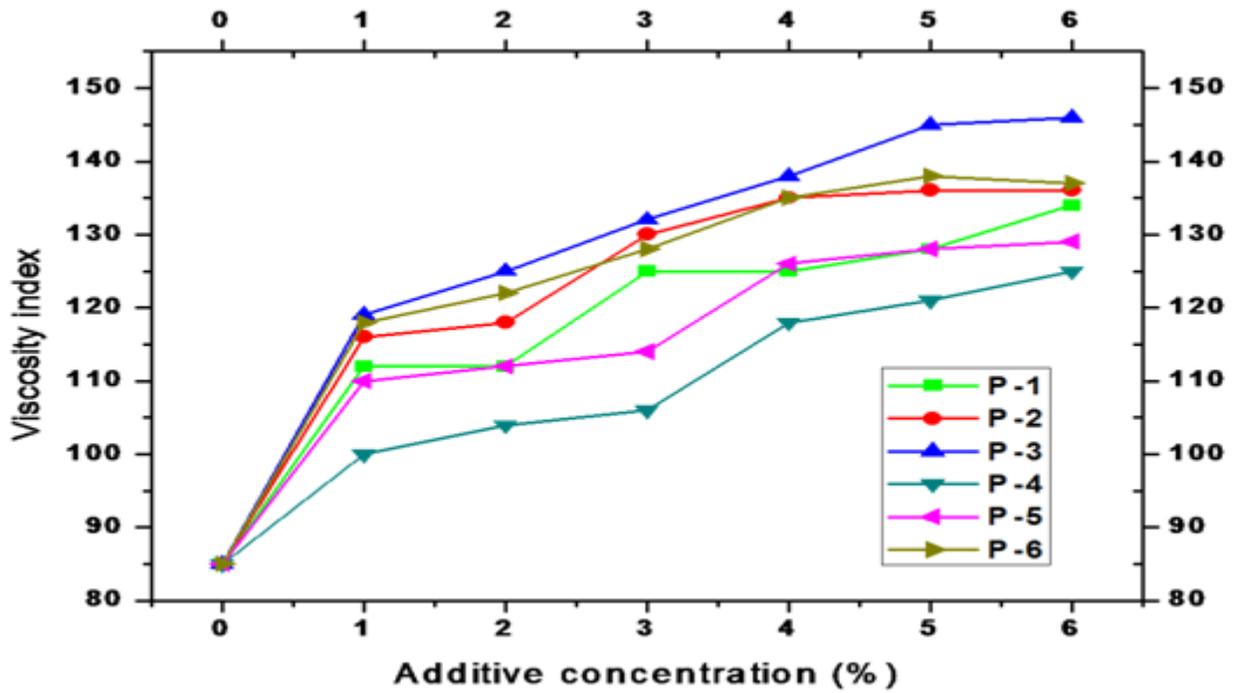


Figure 2.15 (b): Dependence of viscosity index on additive concentration in base oil BO2

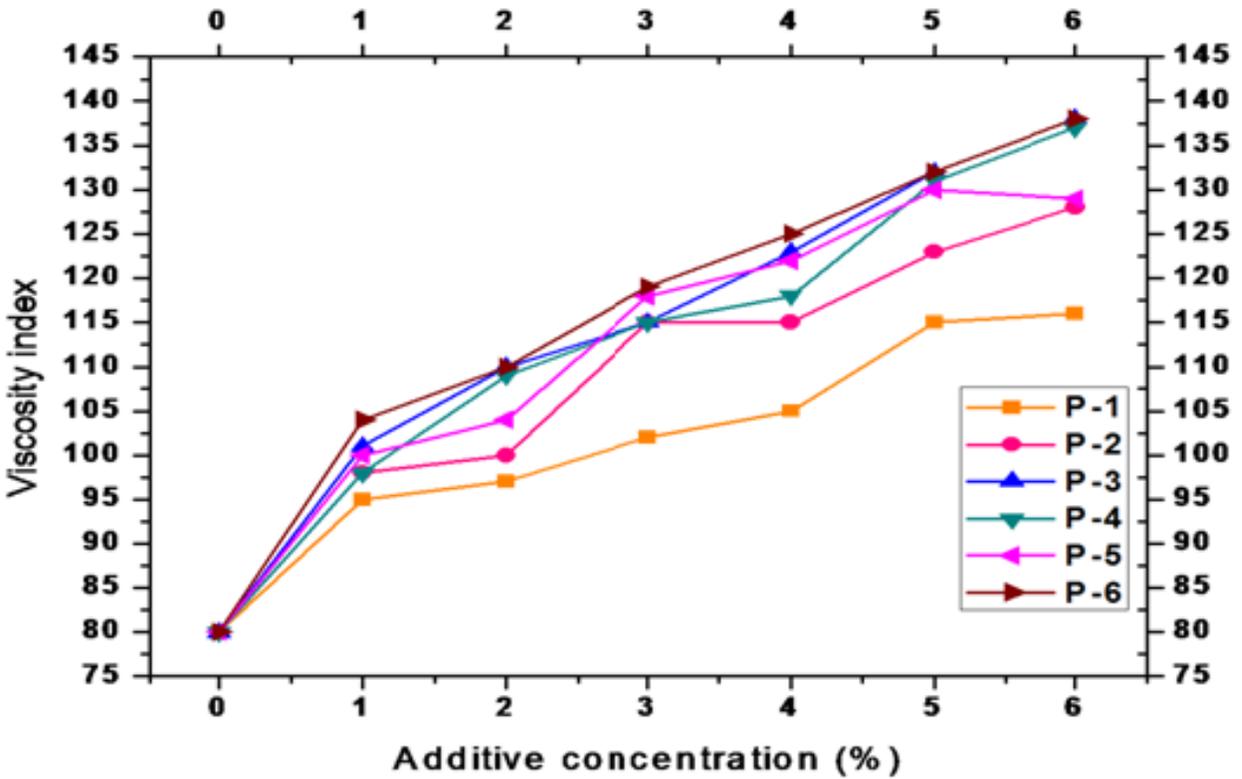


Figure 2.16 (a): Dependence of pour point on additive concentration in base oil BO1

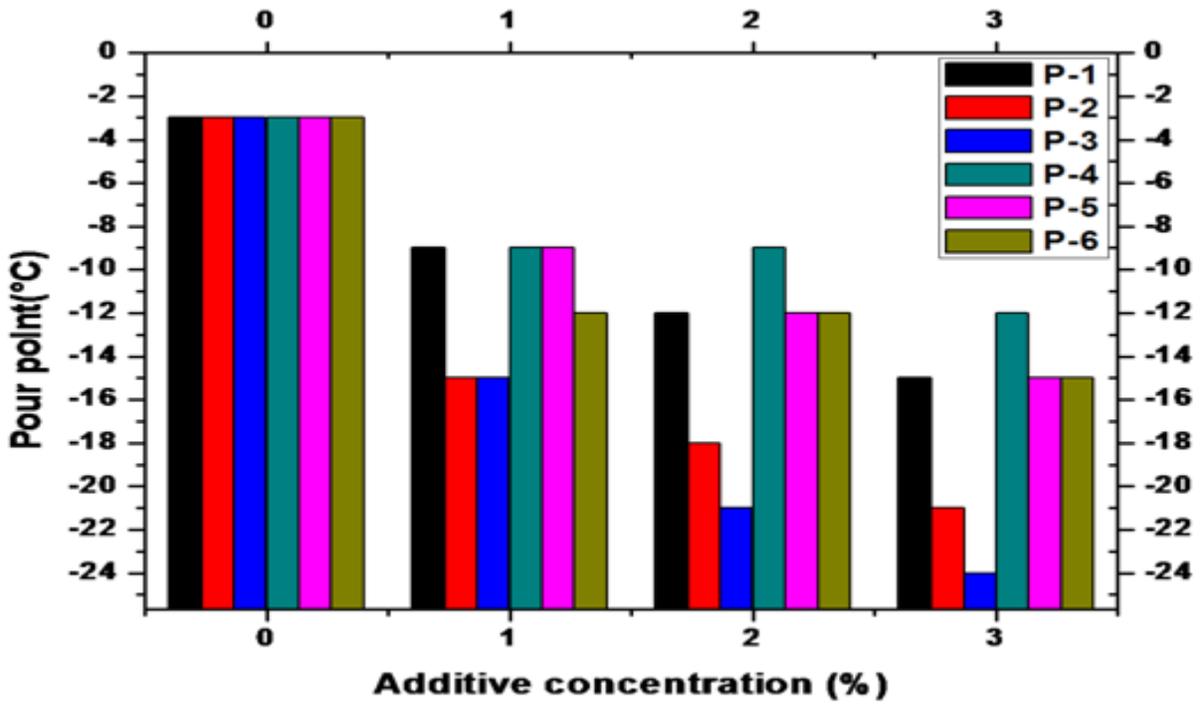
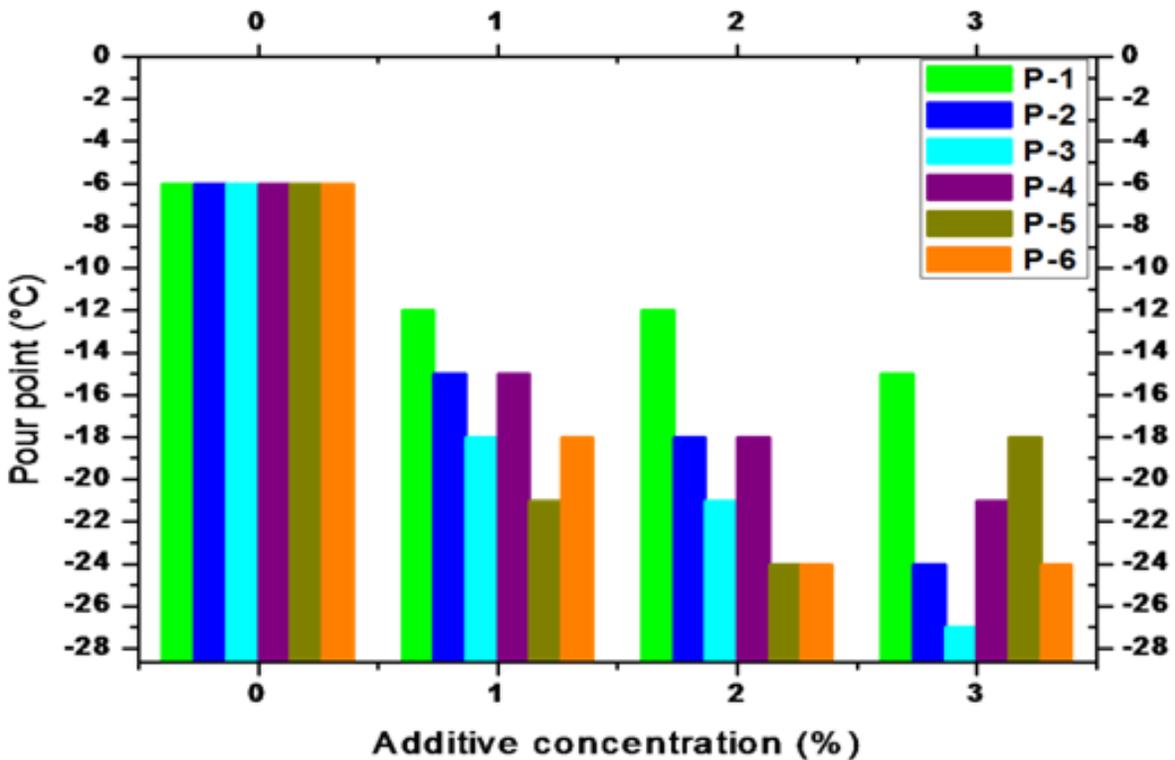


Figure 2.16 (b): Dependence of pour point on additive concentration in base oil BO2



Part III

Nano Blended Polyacrylate as Lube Oil Additive

Chapter-I

Background of the Present Investigation

The most revolutionary technology of the 21st century is nanotechnology. It has versatile application in many fields and ushers material science into a new era. Usually particles size between 1 and 100 nanometers are referred as nanoparticles. The term 'nanoparticle' is not generally applied to individual molecules. The exciting panorama of nanotechnology has potential application in almost every area of life. Synthesis and processing of nano materials and exploring their probable applications are essential aspects of nanotechnology. Research and development in this field helps in understanding, emerging and creating superior, as well as revised forms of devices, materials and systems for upcoming applications. Every field from electronics and medicine to apparels and manufacturing flourish from the advances in nanotechnology, which is versatile in its application. This technology has engrossed strong interest from the researchers across the world. Nanotechnology exercises breakthrough in fields such as- medicines, agriculture, catalysts, healthcare and energy. For instance, the understanding of cost effective power harvest by means of solar and fuel cells with better competency is a contemporary challenge. It can be used to undertake environmental troubles and may be used to develop proficient drug delivery processes. Genetic development enhances agricultural productivity and can facilitate to make crops resistant to heat and water logging. Nanotechnology has lots of future applications and potential that will become well-known with further development. Nanomaterials with desired morphology, size and chemical composition are necessary in order to learn their physical properties and application. Usually nanoparticles are defined as particles of less than 100 nm in size, which as a small object behaves as a whole unit in terms of its physical properties. The materials are more effective at nanoscale dimensions than their larger sized counterparts for two reasons: first, their small size results a very high surface area to volume ratio; second, when such materials are fabricated on the nanoscale, they attain

interesting surface properties owing to their active surface atoms that are not found inside their large-sized counterparts. Nanomaterials including nanowires, carbon nanotubes, semiconductor quantum dots, metal, and other inorganic nanoparticles (such as copper, silver and gold) are formed through different methods and are being tested for their potential applications.

Nanoparticles can be classified into two classes:

1. Organic nanoparticles

2. Inorganic nanoparticles

Carbon nanostructures such as graphene, fullerenes and nanotubes are organic nanoparticles, while inorganic nanoparticles may consist of noble metal nanoparticles (like silver and gold), metal oxide nanostructure, semiconducting nanoparticles (like titanium dioxide and zinc oxide) and magnetic nanoparticles. There is an emerging interest on inorganic nanoparticles, which show advanced material properties with processing and efficient flexibility. Inorganic nanomaterials have been extensively used in diverse fields; in medicine field owing to their versatile biocompatibility (for example, hydroxyapatite based artificial bones, titanium based dental implants) and their possibility to get functionalize helps in targeted drug delivery and controlled release of drugs. Glass and paint industries take advantage of the interesting properties of inorganic nanoparticles.

The inorganic nanoparticles are being added into lubricant formulations by oil companies exclusively to improve the extreme pressure (EP), anti-wear (AW) and anti-friction properties, in that way improving the efficiency and service life of machinery.¹

With advanced machinery and equipment of the speed, load, temperature and other parameters of increasing the lubricating oil's anti-wear agent has not entirely meet their antifrication and anti-

wear performance requirements. Due to this, oil-soluble additives with anti-wear and anti-friction capabilities have been studied widely in recent years.²⁻⁴

The widespread studies on tribological characteristics of nanoparticles as lubricating oil additives have been carried out.⁵⁻⁷ Unfortunately, insolubility and the obscurity of stable dispersion of inorganic material hold down their application in lubricating oil. The dispersion stability of nanoparticles is superior to micron particles in base oil. Therefore, it is essential to study lubricating oil additives based on nanoparticles.

The main benefit of using nanolubricants is that they are comparatively insensitive to temperature and that tribochemical reactions are limited, compared to traditional additives. One more advantage of the addition of nanoparticles in lubricating oil is that they cannot be retained by the filters. Furthermore, roughness of sliding surfaces is often a several micrometers so that nanoparticles can deposit in troughs on the rubbing surface.⁸⁻¹²

Numerous papers have reported that the incorporation of nanoparticles to lubricant is effective in dropping wear and friction. The friction-reduction and anti-wear behaviors are reliant on the characteristics of nanoparticles, such as size, shape, and concentration. One important property that makes nanoparticles different from other materials is the fact that they have a massive surface area. Due to their very high surface area, nanoparticles are exceptionally reactive compared to its larger form. The first key step in experimental studies with nanofluids is their preparation. Nanofluids are not merely liquid-solid mixtures. Some special requirements are vital, e.g., stable and durable suspension, negligible agglomeration of particles, no chemical change of the fluid, etc. Now a days, generally used nanoparticles are Oxide Ceramics- Al_2O_3 , CuO , Metal Carbides – SiC , Nitrides – AlN , SiN , Metals – Al , Cu , Nonmetals – Graphite, Carbon nanotubes, Layered – $\text{Al}+\text{Al}_2\text{O}_3$, $\text{Cu}+\text{C}$, PCM-S/S, functionalized nanoparticles.

Agglomeration is become a major problem during synthesis of nanofluids. Generally, ultrasonic equipment is used to intensively disperse the particles and reduce the agglomeration of particles. Numerous nanoparticles have recently been investigated for use as oil additives. Nano-powders of some metals and their compounds exert an especially effective influence on the characteristics of lubricants. The application of nanoparticles that include Cu, CuO, Fe, Ni, TiO₂ and other metallic nanoparticle additives in lubricating oils provides good friction reduction and anti-wear behavior.^{9, 10, 13-17}

Juozas Padgurskas, Raimundas Rukuiza et. al. Investigated the tribological behaviour of mineral oil having Fe, Cu and Co nanoparticles and their combinations. The tribological tests revealed that each set of nanoparticles significantly decreased the friction coefficient and wear of friction pairs. The use of Cu nanoparticles showed the most effectual reduction of friction and wear in each combination of nanoparticles. Surface analysis shows that the constituent elements of nanoparticles precipitated on the contact surface during the use of the oils with nano-additives.¹⁸

The friction reduction and anti-wear mechanism (**figure: 3a**) of nanoparticles in lubricant have been reported as protective film, rolling effect and third body.

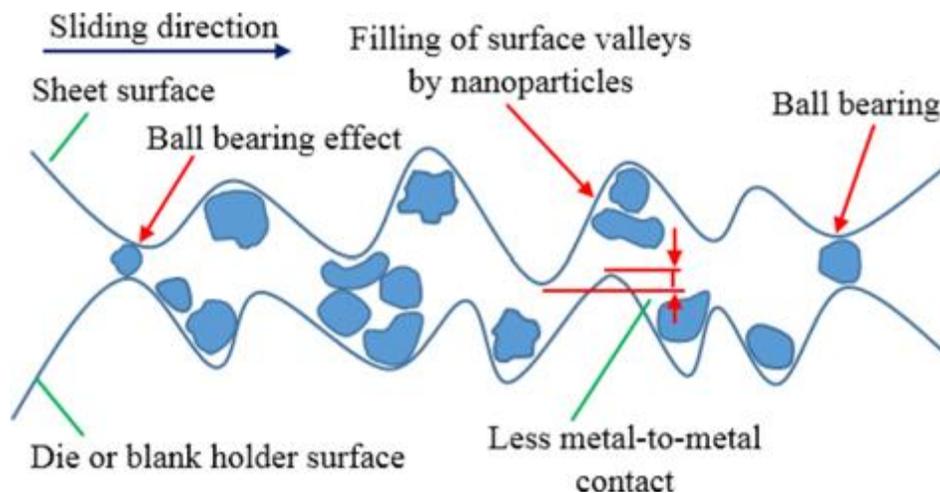


Figure 3a: Action mechanism of nanoparticles between lubrication surfaces

A variety of mechanisms (**figure:3b**) have been proposed to explain the lubrication enhancement of the nanoparticles suspended lubricating oil (i.e., nano-oil), including the ball bearing effect,¹⁹⁻²¹ protective film,^{12,14, 22-24} mending effect,²⁵ polishing effect.²⁶ The nanoparticles hovering in lube oil play the role of ball bearings between the frictional surfaces. In addition to that, they also create a protective film to some extent by covering the rough friction surfaces. The nanoparticles deposit on the friction surface and compensate for the loss of mass which is known as mending effect. Again the roughness of the lubricating surface is reduced by nanoparticle-assisted abrasion which is known as polishing effect. Among the above mentioned lubrication mechanism ball bearing and protective film are the direct effect of nanoparticles on lubrication enhancement and the other two are the secondary effect of the nanoparticles on surface enhancement.

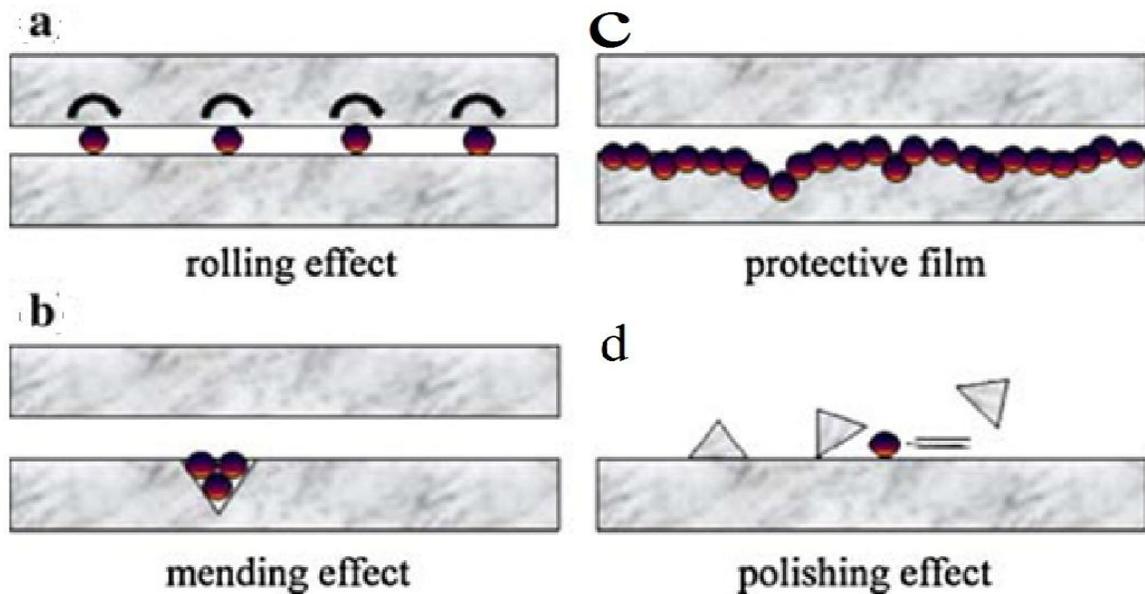


Figure 3b: Possible lubrication mechanisms between the frictional surfaces by the application of nanoparticle added lube oil.

J.L. Viesca , A. Herna´ ndez Battez investigated the influence of the incorporation of carbon-coated copper nanoparticles (25 nm) on the tribological behavior of a polyalphaolefin (PAO6)

and compared this behavior with the case of non-coated copper nanoparticles, determining the influence of coating. The study concludes that the addition of carbon-coated copper nanoparticles decreases wear and increases the load-carrying capacity of PAO6. This tribological improvement is due to the deposition of nanoparticles on the rubbing surfaces and probably by their action as tiny bearings. The copper nanoparticles coated with carbon did not perform better than non-coated ones.²⁷

R. Chou, A. Hernandez Battez examined the influence of addition of 20 nm diameter nickel nanoparticles on the tribological behavior of synthetic oil (polyalphaolefin, PAO6). A TE53SLIM tribometer for testing at medium loads and a four-ball machine (ASTM D2783) were used in this research. The study leads to the conclusion that the addition of nickel nanoparticles to PAO6 results in a decrease in friction and wear and an increase in the load-carrying capacity of base oil. This tribological activity is strongly related to the deposition of nanoparticles on the rubbing surfaces.²⁸

Sudeep Ingole, Archana Charanpahari studied the effects of titanium dioxide nanoparticle additives on the lubricated friction and wear performance of self-mated E52100 bearing steel were investigated by a reciprocating pin-on-disk apparatus. The additives were (a) nano-sized titanium dioxide (TiO_2) and (b) commercially available TiO_2 (P25). The friction and wear characteristics were tested at a constant applied load and rate of reciprocation. At all concentrations, P25 increased the coefficient of friction, but the addition of TiO_2 nanoparticles reduced the variability and stabilized the frictional performance.²⁹

Y.Y. Wu, W.C. Tsui study investigated the tribological properties of two lubricating oils, a Base oil and API-SF engine oil, with TiO_2 , CuO, and Nano-Diamond nanoparticles used as additives. The friction and wear experiments were carried out using a reciprocating sliding tribotester. The

experimental outcome showed that nanoparticles, mainly CuO, exhibit good friction-reduction and anti-wear properties in oil. The addition of CuO nanoparticles in the Base oil and in the API-SF engine oil decreased the friction coefficient by 18.4 and 5.8%, respectively, and reduced the worn scar depth by 16.7 and 78.8%, respectively, as compared to the standard oils devoid of CuO nanoparticles.²⁰

D.X. Peng Y. Kang investigates the tribological properties of liquid paraffin to which diamond and SiO₂ nanoparticles had been added, which prepared by the surface modification method using oleic acid and observed by scanning electron microscopy (SEM) and infrared (IR) spectroscopy. Also, the dispersion capacity and stability dispersivity of both modified nanoparticles in liquid paraffin were studied using a spectrophotometer. The study shows the dispersion capability and the dispersing stability of oleic acid-modified diamond and SiO₂ nanoparticles in liquid paraffin. The tribological properties are evaluated using a ball-on-ring wear tester. The results show that both nanoparticles have better anti-wear and antifriction properties at a tiny concentration in liquid paraffin.³⁰

Jingfang Zhou, Zhishen Wu studied the LaF₃ nanoparticle surface coated by organic compounds containing S and P were synthesized by the chemical surface modification method. The particle size and structure were characterized and tribological behaviors were evaluated on a four-ball machine. The results showed that LaF₃ nanoparticles as an oil additive can strikingly improve the load-carrying capacity and anti-wear property of the base oil and had better friction-reduction when compared to that of ZDDP. It can be found that the boundary film on the worn surface was composed of LaF₃ nanoparticles depositing film and tribochemical reaction film of the elements of S and P, which contributed to excellent tribological properties of LaF₃ nanoparticle modified by compound containing S and P as an additive in liquid paraffin.³¹

Z.S. Hu, J.X. Dong studies the Nanoparticle amorphous lanthanum borate with a particle size of 20–40 nm was prepared with a Replacing Solvent Dry technique and characterized using TEM and XRD. Its tribological properties as a wear resistance additive of lubricating oil were evaluated with a four-ball tribotester. The wear scar was characterized with XPS. The wear resistance and load carrying capacity of 500SN base oil was improved by the lanthanum borate. The Diboron trioxide and FeB were formed on the wear scar surface. These tribochemical reaction products as well as some depositions formed a wear resistance film on the rubbing surface, which provided the oil with an excellent load carrying capacity.³²

Cai-xiang et al. Investigated the tribological properties of lubricating oil (500SN Base Oil) containing TiO₂ and CeO₂ nanoparticles with appropriate surfactants such as Span-20, Tween-20, Tween-60, and Sodium sodecylbenzenesulfonate. In the study 40 kinds of lubricating oils were prepared, according to different weight fractions (0.2%, 0.4%, 0.6%, 0.8%, 1.0%, respectively) and different weight proportions of CeO₂ and TiO₂ nanoparticles (0:1, 1:1, 1:2, 1:3, 1:4, 3:1, 2:1, 1:0, respectively). The morphology and size of CeO₂ and TiO₂ nanoparticles were tested with a transmission electron microscope (TEM). The tribological properties of the oils were examined with an MRS-1J four-ball tribotester. The research results showed that when the amount by weight of CeO₂ nanoparticles to TiO₂ nanoparticles is 1:3, and the total weight portion is 0.6%, the lubricating oil showed the best anti-wear and friction reducing properties. The incorporation of CeO₂ nanoparticles reduces the requisite amount of TiO₂ nanoparticles.³³

Kalakada et al.³⁴ developed the mathematical model for relationship between viscosity and temperature for the lubricant SAE 15W40 multi grade engine oil having Al₂O₃ and ZnO nanoparticles. The incorporation of nanoparticles on commercially accessible lubricant noticeably enhances the viscosity of lubricant and also changes the performance characteristics.

Peng et al.³⁵ studied the antifriction and anti-wear properties of lubricating oil containing nano-ZnO and nano-TiO₂. The study reveals that both the nanoparticles as additive in lubricating oil exhibit good anti-wear property. Veerandra et al.³⁶ discloses the synthesis of mixed metal oxide (MMO) nanoparticle of CuO-ZnO by co-precipitation method and friction and wear properties were studied by using pin on disc tester in SAE 20W50 oil which contain dispersed nanoparticle at different level of concentrations (0.5%, 1.0% and 2.0% wt). The study showed that the wear scar diameter (WSD) decreases with increasing the concentration of nanoparticles in SAE 20W50.

Nano scale ZnO has been attracting significant interest because of its unique structure and performance.³⁷⁻³⁹ This is due to the fact that nano ZnO has large surface area, high surface energy, strong adsorption, high diffusion, easy sintering, low melting point and other outstanding characteristics. When the nano ZnO is used as the additive in base oil, there will be different friction reduction and wear resistant effects on lube oils. In this investigation another nanoparticle was chosen namely magnetic nanoparticle. Magnetic nanoparticles have been extensively studied because of their attractive properties, and ample scope of potential applications in ferrofluids, information storage, medicine, pigment, biomedical and bioengineering etc.⁴⁰

From the above literature survey regarding the application of nanoparticles as lubricating oil additives, it is found that they are mainly used as anti-wear and anti friction agents. But they are not reported to use as other kind of additive. Moreover, polyacrylates were known to perform as effective viscosity modifier additive and pour point depressant additive. Hence to develop multifunctional performance additives for lube oil, authors were interested to develop

multifunctional additives by blending suitable proportion of different oxide based nanoparticles with acrylate based polymers and their performance as lube oil additives were studied.

References

References are given in BIBLIOGRAPHY under Chapter I of Part III (PP 168-172).

Chapter II

Polyacrylate-Nano Magnetite Composite as a Potential Multifunctional Lube Oil Additive

3.1.1. Introduction

In industry, mainly in machine industry widely utilized materials are lubricants. The proper application of lubricants can improve the efficiency of the engine, prolong the machine life as well as economize on energy. In the last few decades, use of oil-soluble additives in lubricant as effective friction reduction and anti-wear property have been extensively studied in lubrication engineering.¹⁻³ Though, the use of these additives has arisen some troubles, for example pollution, toxicity, waste disposal etc. With the advent of nanomaterials, nanoparticles were incorporated into lubricating oil to improve the tribological properties. In recent years, a great number of studies have been carried out on the effects of a range of inorganic nanoparticles as lubricating oil additives on friction and wear.⁴⁻⁷ Owing to the wonderful tribological properties of nanoparticles and good environmentally benign property, they have been preferred as an exceptional candidate for traditional lubricating oil additives, particularly at high load, high sliding speed and high frictional conditions.⁸⁻¹⁰

Use of graphite nanosheets as lubricating oil additives improves tribological properties of paraffin oil.¹¹ The anti-wear property of paraffin oil was significantly improved by the incorporation of MoS₂ nanoparticles.¹²⁻¹³ Oxide based nanoparticles such as CuO nanoparticles exhibit good anti-wear and friction reduction properties.¹⁴ Cai-Xiang et. al reported the anti-wear and friction reducing properties of CeO₂ and TiO₂ nanoparticles in lubricating oil.¹⁵ All the nanoparticles mentioned above are nonmagnetite and there are few reports on tribological properties of magnetic nanoparticles as lube oil additives.¹⁶ Huang et. al reported the effect of magnetite nanoparticle on tribological property of paraffin oil which disclosed the improvement of load carrying capacity and anti-wear property compared to pure paraffin oil.¹⁶ From the above discussion it is revealed that magnetite nanoparticle and other oxide based nanoparticles are used

only as anti-wear and friction reducing additives in lubricating oil. Furthermore, acrylate based polymers are known to perform as good viscosity index improver (VII),¹⁷⁻¹⁹ pour point depressant (PPD).²⁰ They were not known to act as good anti-wear and friction reducing additives. Hence to impose the multifunctional performance (VII, PPD, anti-wear) into the additives, authors are attempting to prepare those kinds of additives. Keeping this view in mind, we are blending homopoly dodecylacrylate with magnetite nanoparticle to develop multifunctional additives for lubricating oil.

3.1.2. Experimental procedure

3.1.2.1. Materials and methods

Acrylic acid, dodecyl alcohol, BZP and hydroquinone were purchased from Merck specialities Pvt. Ltd. Methanol, hexane and conc. H₂SO₄ were purchased from Thomas baker Pvt. Ltd. BZP was recrystallized from CHCl₃-MeOH. Iron(II)sulphate heptahydrate, potassium nitrate and potassium hydroxide were purchased from Merck specialities Pvt. Ltd. The base oil was collected from IOCL, Dhakuria, Kolkata, India.

3.1.2.2. Preparation of dodecyl acrylate by Esterification

Dodecyl acrylate (DDA) was prepared by esterification of acrylic acid with dodecyl alcohol in the mole ratio of 1.1:1. The detailed process was already described in chapter II of part II.

3.1.2.3. Purification of the prepared ester (DDA)

The prepared ester (DDA) was purified according to the process as described in chapter II of part II.

3.1.2.4. Synthesis of homo polymer of DDA

The homo poly dodecyl acrylate was synthesized and purified according to the procedure described in chapter II of part II.

3.1.2.5. Preparation of magnetite (Fe₃O₄) nanoparticles

Magnetite nanoparticles were synthesized with modification of the method reported by Bruce et al. Solutions of iron(II) sulphate heptahydrate (1.67 g, 6×10^{-3} mol) in 50 ml deionized water, potassium nitrate (1.01 g, 1×10^{-2} mol) in 10 ml of deionized water, and 2.5 M potassium hydroxide were prepared. 1% (w/w) stabilizer (CTAB) was mixed with the iron salt solution under vigorous stirring for two hours. To this solution, potassium nitrate was added and stirring was continued for another half an hour. Then, 10 ml of 2.5 M potassium hydroxide (2.5×10^{-2} mol) was slowly added to the above solution. The reaction mixture was heated to 100°C under nitrogen and maintained at this temperature for two hours. The nitrogen flow was then turned off and the mixture was cooled down to room temperature. After cooling, the black precipitate was repeatedly washed with deionized water, centrifuged and allowed to dry under vacuum at 50°C overnight.²¹

3.1.2.6. Preparation of poly dodecyl acrylate- Fe₃O₄ nanocomposites

PDDA- Fe₃O₄ nanocomposites were prepared by mixing the PDDA/toluene solution and nano-Fe₃O₄ particles. The PDDA- Fe₃O₄ suspension was prepared as follows: 5g of PDDA were dissolved in toluene and required amount (0.5, 1 and 1.5mg) of nano- Fe₃O₄ particles were added into the PDDA/toluene solution under ultrasonic wave and vigorous stirring to prepare 100, 200 and 300 ppm blend. The suspension was then poured into a glass plate and allows the toluene to evaporate naturally and a semi solid mass of polymer-nanocomposites was obtained.

3.1.3. Measurements

3.1.3.1. Spectroscopic measurements

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

3.1.3.2. Thermo gravimetric analysis (TGA)

The thermal stabilities of the prepared homo polymer and polymer/nano composite were determined by a thermo gravimetric analyzer (Shimadzu TGA-50) using an alumina crucible in air. The system was run at a heating rate of 10°C/min. The percentage of weight loss (PWL) of the samples with rise in temperature was calculated.

3.1.3.3. Determination of molecular weight by GPC

By GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were determined. The poly dispersity index was also calculated. In this method HPLC grade THF (0.4%, w/v) was used as mobile phase in the water 2414 GPC system (polystyrene calibration) at 35°C with a flow rate of 1 ml/min.

3.1.3.4(a). Characterization of nano- Fe_3O_4 by SEM and X-RD

The synthesized Fe_3O_4 -nanoparticles were characterized by Field Emission Scanning Microscope (FE-SEM, INSPECT F50, FEI) and X-ray diffraction (X-RD, Advance D8, Bruker).

3.1.3.5. Performance evaluation as viscosity modifier

Viscosity index (VI) of the polymeric additives was determined in paraffinic base oil to evaluate the efficiency of the prepared polymeric additives as viscosity modifier (VM). An Ubbelohde OB viscometer was used in this experiment at the temperatures 313K and 373K. The detailed process is previously described in Chapter II of Part I.

Five different concentrations ranging from 1 wt % to 5 wt % of the polymeric sample solutions were used to study the effect of additive concentration on VI.

3.1.3.6. Performance evaluation as pour point depressant

The pour point depressant property of the prepared polymeric additives was determined in base oil by the pour point test on a Cloud and Pour Point Tester model WIL-471(India) according to ASTM D97 method. In this case also five different concentrations of the additives were used for each sample.

3.1.3.7. Evaluation of tribological performance of prepared additives

The anti-wear performance of the lubricant compositions were evaluated in terms of wear scar diameter (WSD) by Four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method.²² In this experiment 392 N (40 kg) load at 75°C for 30 min. was employed to measure the wear scar diameter (WSD). The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm, respectively. The details procedure is described in our publication elsewhere.²³

3.1.4. Results and discussion

3.1.4.1. Spectroscopic analysis

FT-IR spectrum of homopoly dodecyl acrylate (A) showed absorption band at 1734.56 cm^{-1} for the ester carbonyl stretching vibration along with other peaks at 1458.40, 1370.18, 1169.67,

1070.96 cm^{-1} . In the ^1H NMR spectra of A showed broad singlet centred at 4.013 to 4.293 ppm due to the protons of $-\text{OCH}_2$ group. Methyl protons of dodecyl chain appeared between 0.866 ppm and 0.878 ppm and the absence of singlet between 5 ppm and 6 ppm implies the absence of any vinylic proton in the polymer. In the ^{13}C NMR spectrum of P-1, the carbonyl carbon appeared at 174.3 ppm along with other SP^3 carbons appeared in the range of 64.72 to 13.94 ppm and it is showed in **figure 3.1**. The FT-IR spectra (**figure 3.2**) of polymer/ Fe_3O_4 nanocomposite showed absorption band at 1726.12 cm^{-1} . This shifting of carbonyl stretching frequency may be due to some association of nano magnetite and poly dodecyl acrylate.

3.1.4.2. Thermo gravimetric analysis

The TGA data of the polymer (A) and polymer/ Fe_3O_4 nanocomposite (F-1, F-2 and F-3) are depicted in **figure 3.5**. It was seen from the figure that, thermal stability of nano blended composites is higher than that of A. Hence, by incorporation of nano- Fe_3O_4 into A increases the thermal stability. At 380°C, the percentage of decomposition of A, F-1, F-2 and F-3 were 32.42% and 21.35% respectively, whereas at 490°C, the percent of weight loss of A, F-1, F-2 and F-3 were 93.71% and 70.56% respectively. The addition of nano- Fe_3O_4 affects the degradation mechanism and as a result improves thermal stability of polymer (A). The decrease of mobility of polymer chain and the tendency of magnetite nanoparticle to eliminate free radicals may be the key effects accountable for this enhancements.²⁴

3.1.4.3. Characterization of nano- Fe_3O_4

Figure 3.3 shows the X-ray diffraction pattern of the prepared magnetite nanoparticle. The six most intense peaks at 30.3°, 35.6°, 43.2°, 53.6°, 57.1° and 62.8° respectively were markedly observed, which was found very similar in a research article.²¹ The purity of the magnetite

nanoparticle was also confirmed by X-RD due to absence of other peaks of iron oxide like maghematite or hematite in samples. Hematite nanoparticles shows nine intense peak in the diffraction angle from 6° to 70° .²⁵

Figure 3.4 shows the scanning electron micrograph of the prepared magnetite nanoparticle and the shape of the particle were also marked in the figure which shows that the particles were nearly spherical. It can be seen from the **figure 3.4** that the particles have an average size of about 29 ± 2 nm.

3.1.4.4. Efficiency of additive as viscosity modifier

Figure 3.6 represents the viscosity index values of the additive doped base oil. It is observed that, the viscosity index (VI) values of the polymer/nano- Fe_3O_4 composites (F-1, F-2 and F-3) doped base oil are better than the pure polymer (A) doped oil at every concentration. Again with both type of additives, there is always a steady increase of VI values with the increase in additive concentration. Increase of concentration of the additives leads to increase in total volume of polymer micelles in the solutions. The additional increase of volume compared to pure polymer may be due to the fact that, the nanoparticles present in the polymer matrix leads to the polymer chain separated from each other.

3.1.4.5. Efficiency of additive as pour point depressant

Different level of percentage concentration varying from 1 wt% to 5 wt% of the additives in the base oil was tested as PPD and the results are depicted in **figure 3.7**. The results showed that the additives (A, F-1, F-2 and F-3) are efficient as PPD and the efficiency decreases with increasing additive concentration. The PPD property of all the blended composites is very similar with that

of A. That means incorporation of nanoparticles into the polymer matrix does not affect the PPD property appreciably compared to polymer (A).

3.1.4.6. Tribological performance

The tribological properties of all the lubricant compositions (A, F-1, F-2 and F-3) were determined by measuring WSD by FBWT apparatus employing 40 kg load and the results were depicted in **figure 3.8**. The AW performance of the base oil is significantly enhanced when the additives are blended with it and is indicated by the lower WSD values of the lubricant compositions. The nano-magnetite blended composites exhibited better anti-wear performance compared to only polymer (A) and the performance becomes increasingly better with increasing the amount of nanoparticles in the polymer matrix as is shown in the **figure 3.8**.

3.1.5. Conclusion

In this study nano-Fe₃O₄ was synthesized with better size distribution which was established by SEM and XRD study. The interaction of nano-Fe₃O₄ with PDDA was studied by FT-IR spectral analysis and it suggests that there is definite interaction between them. From the above study it was found that all the nano blended composites showed performance as viscosity modifier and anti-wear additives for lube oil. Moreover the thermal stability of polymer was also improved by the incorporation of nano magnetite into the polymer matrix. This change of properties of polymer is also a proved of nano-polymer interaction. Therefore, the above study is definitely a potential approach to design multifunctional additives for lubricating oil.

3.1.6. References

References are given in BIBLIOGRAPHY under Chapter II of Part III (PP 172-174).

3.1.7. Tables and figures

Table 3.1: Properties of base oil

<i>Properties</i>	<i>Base oil</i>
Density(kg.m ⁻³) at 313K	918.68
Viscosity at 313K	20.31×10 ⁻⁶
Viscosity at 373K	3.25×10 ⁻⁶
Viscosity index	89.02
Cloud point (°C)	-8
Pour point (°C)	-6

Table 3.2: Designation and Composition of poly dodecyl acrylate-nano magnetite composites

<i>Designation</i>	<i>Composition</i>	
	Polymer in g	Nano (Fe ₃ O ₄) in mg
A	5	0
F-1	5	0.5
F-2	5	1.0
F-3	5	1.5

Figure 3.1(a): FT-IR spectra of polymer (A)

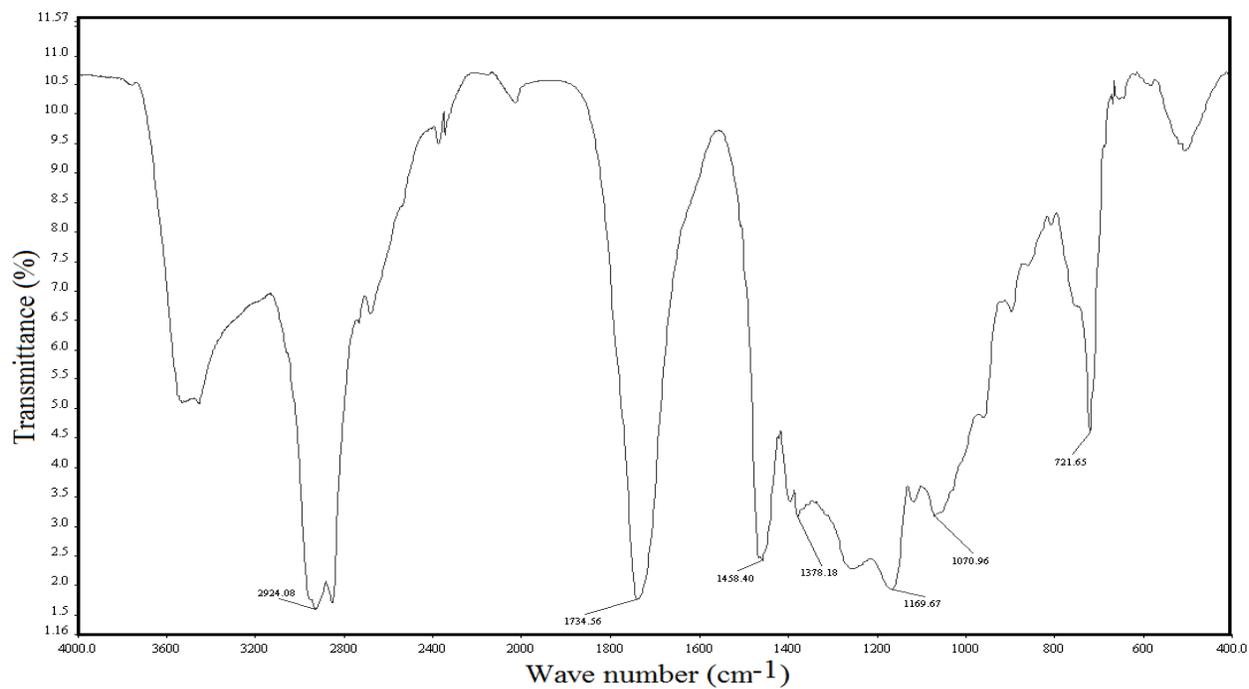


Figure 3.1(b): ¹H NMR spectra of polymer (A)

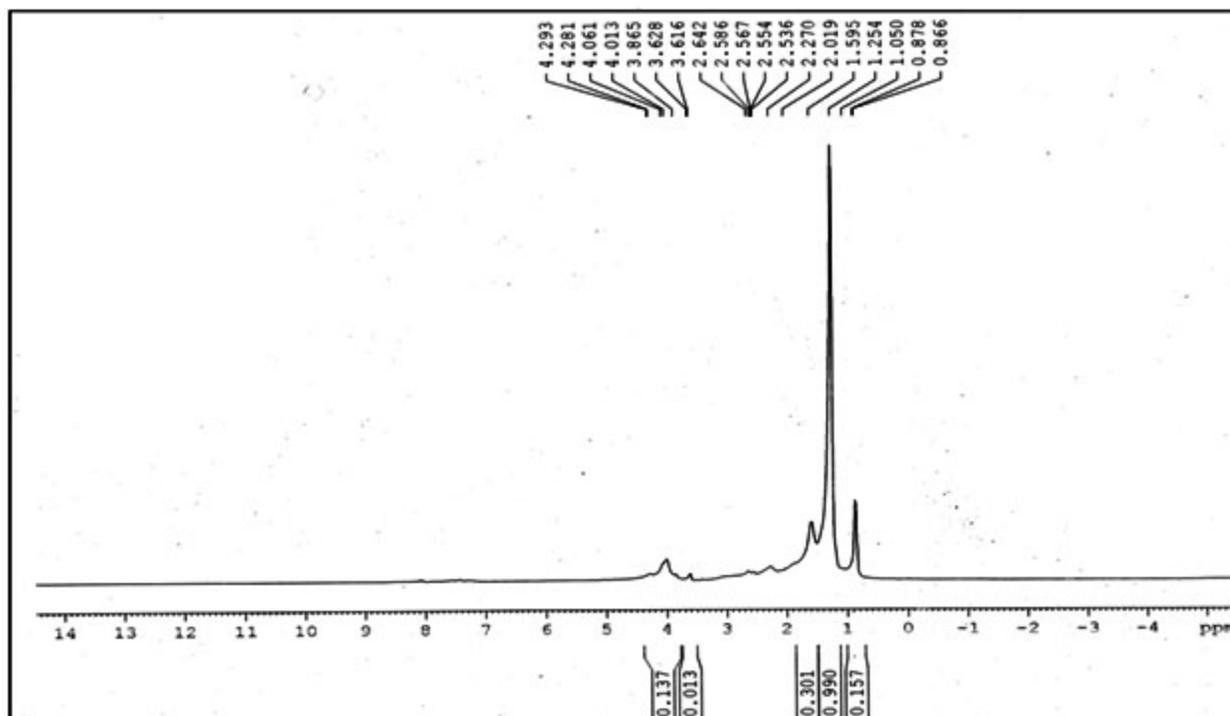


Figure 3.1(c): ^{13}C NMR spectra of polymer (A)

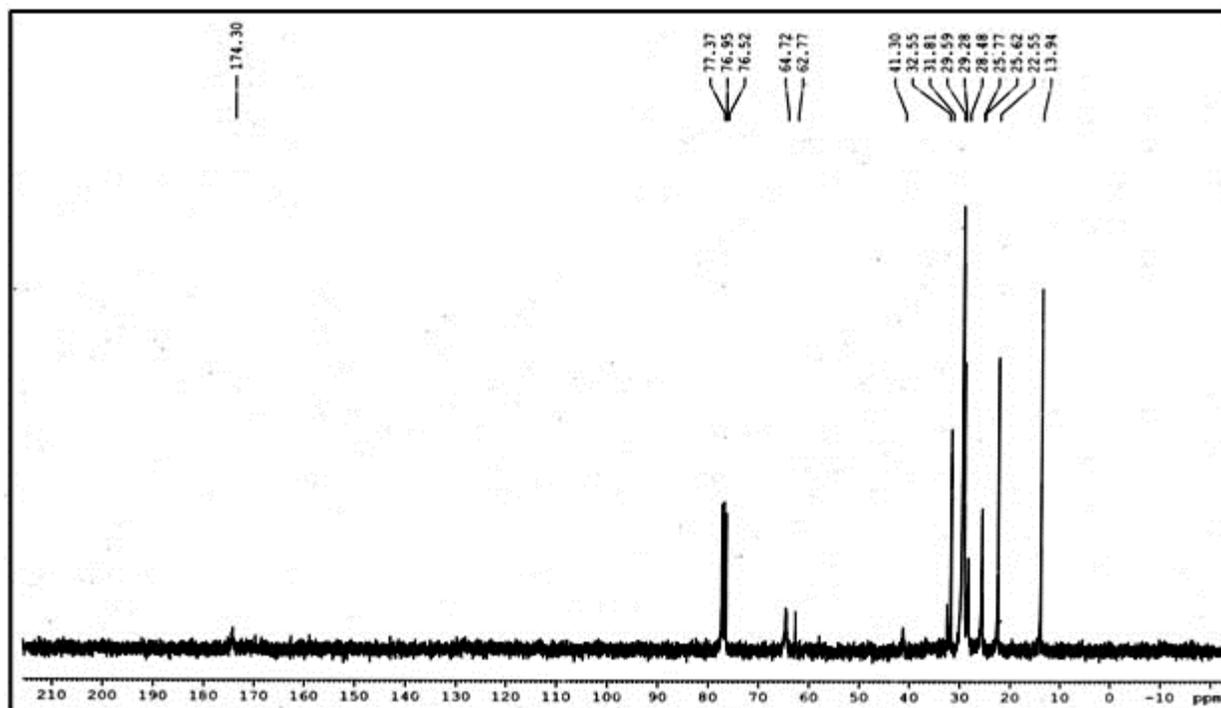


Figure 3.2: Comparative FT-IR spectra of polymer (a), polymer/ Fe_3O_4 nanocomposite (b)

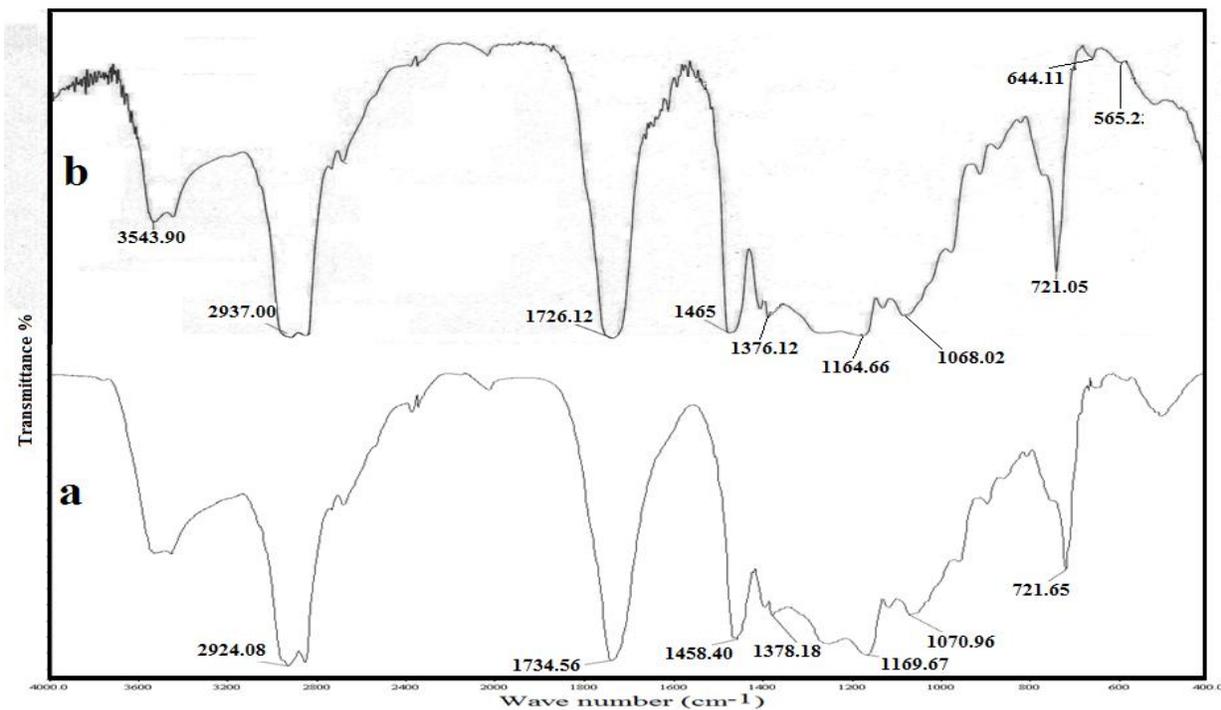


Figure 3.3: X-RD pattern of prepared nano-Fe₃O₄

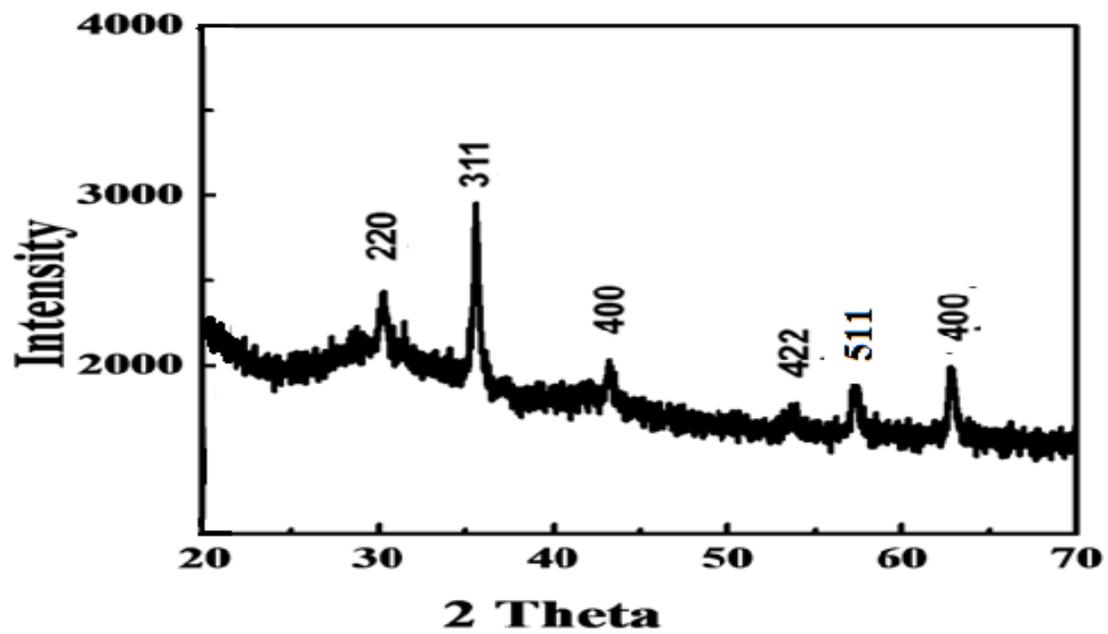


Figure 3.4: SEM images of prepared nano-Fe₃O₄ at different magnifications

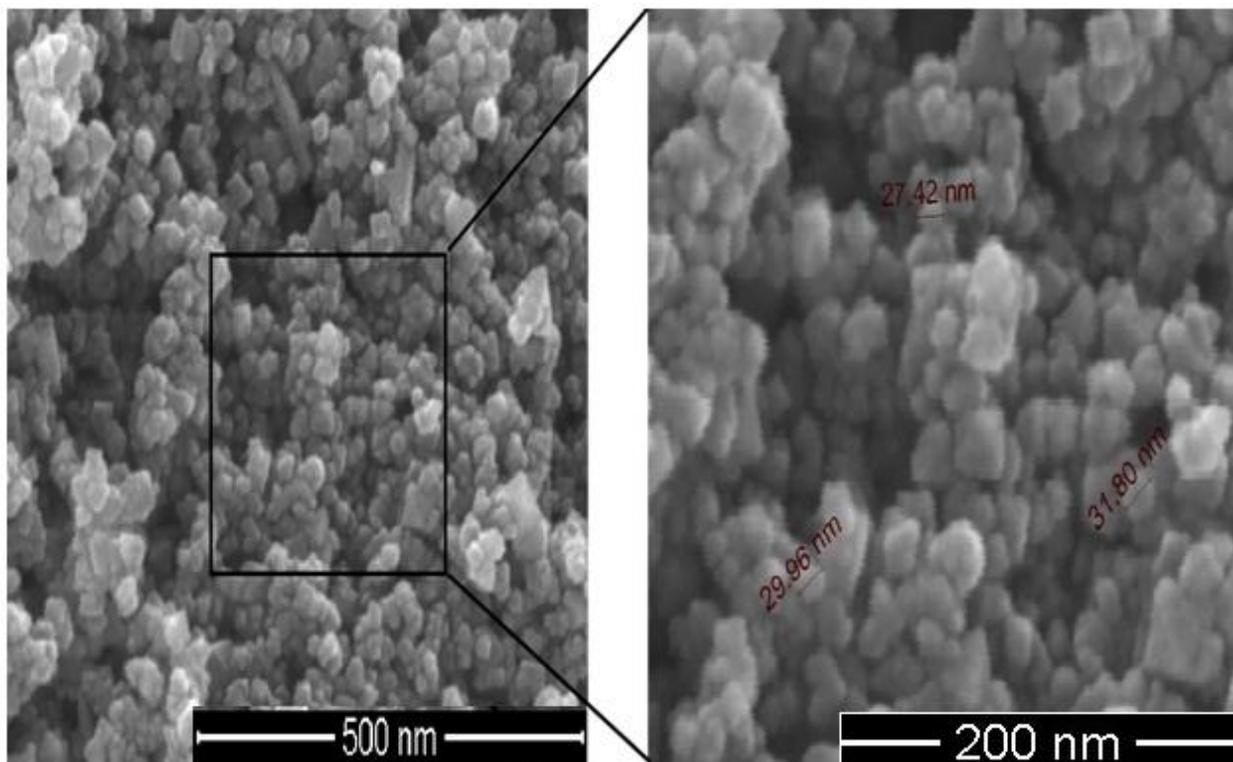


Figure 3.5: TGA data of polymer (A) and polymer/Fe₃O₄ nanocomposite (F-1, F-2 and F-3)

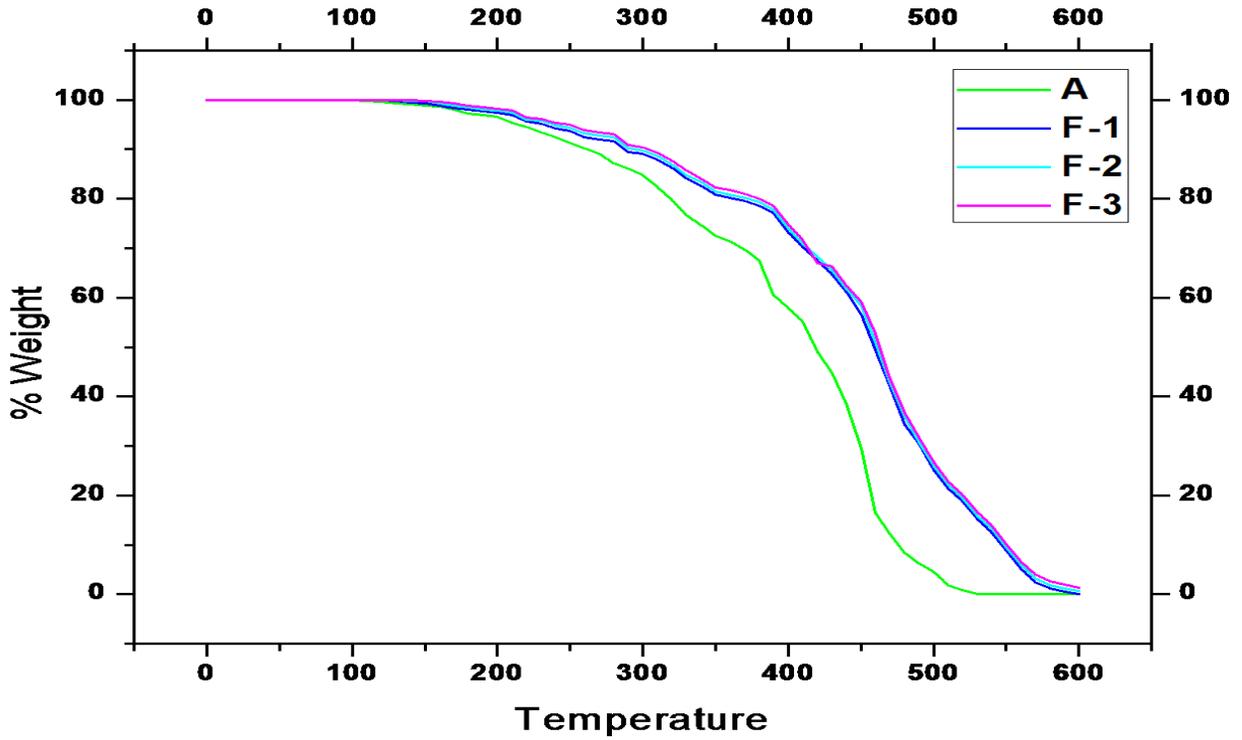


Figure 3.6: Plot of Viscosity index of the additives doped base oil with additive concentration

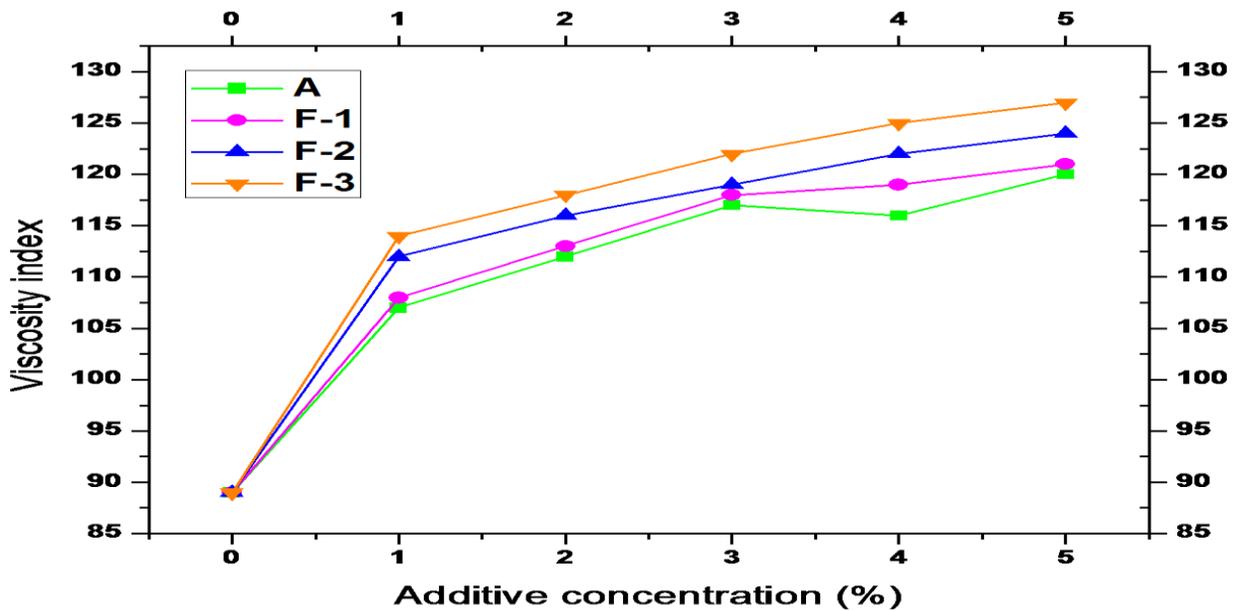


Figure 3.7: Plot of pour point of the additives doped base oil with additive concentration

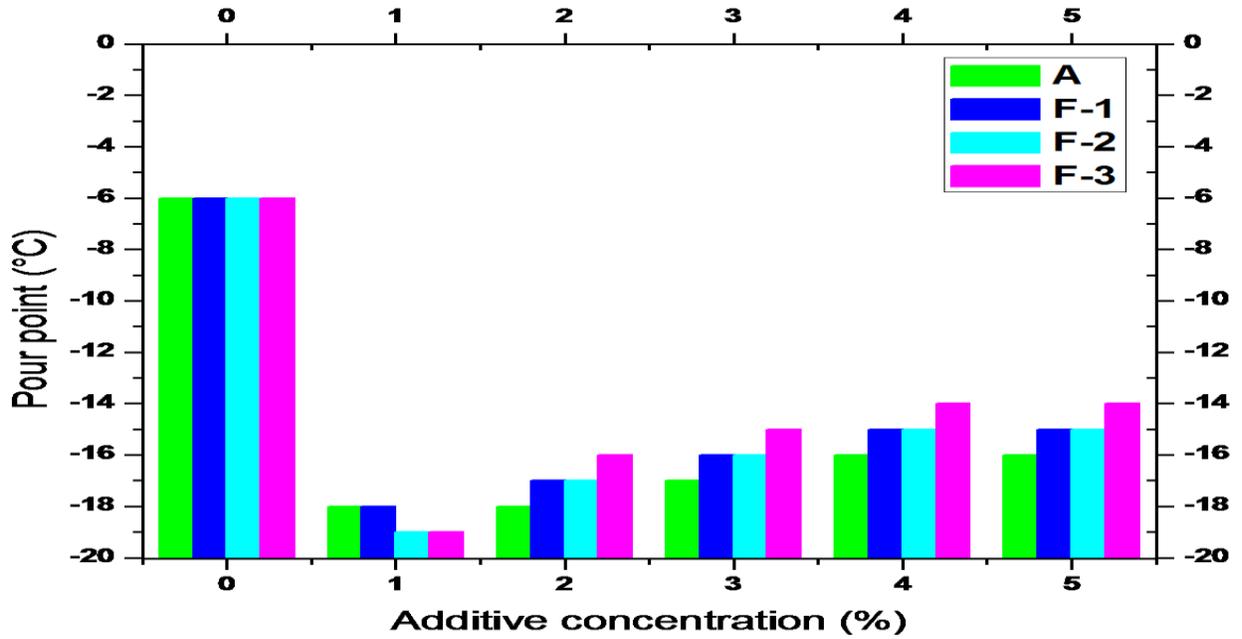
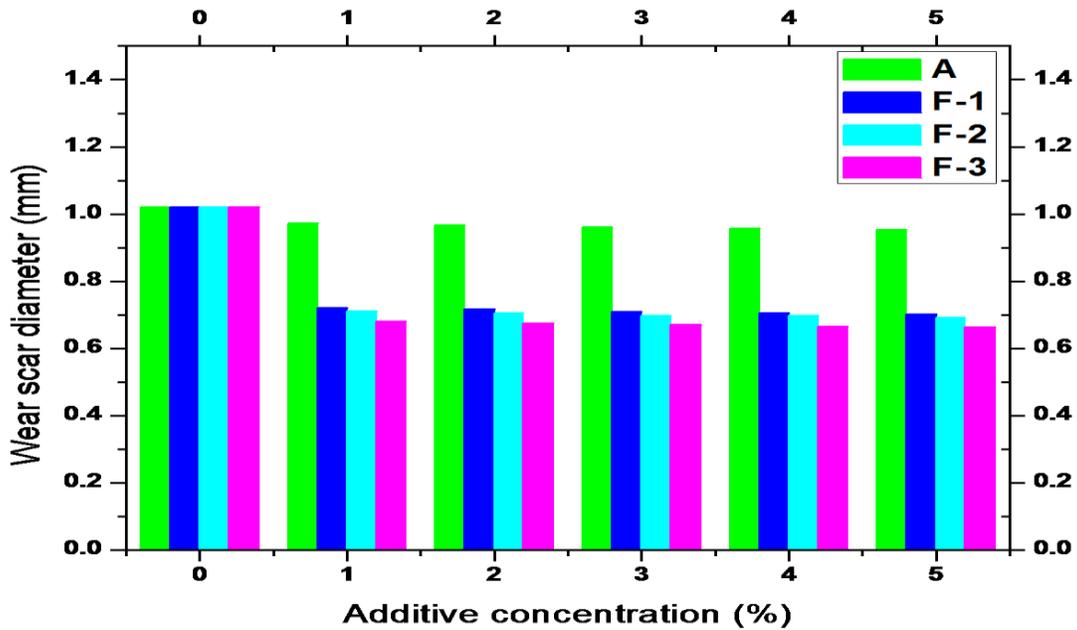


Figure 3.8: Wear scar diameter (WSD) of the lube oil blended with additives at different percentage (w/w)



Chapter III

Multifunctional Additive Properties of Acrylate Based ZnO Nano Composite for Lubricating Oil

3.2.1. Introduction

The lubricating oil is the blood of the machine's service life and operation and economic efficiency of the machine are relative to the quality, performance and sensible use of the oils.¹⁻² The two major constituents of tribology are friction and wear. Thus when these are controlled and reduced, automatically increase the service life of machine. This ultimately saves money. The awareness of the subject, i.e. detection of tribological problems and their solution can give rise to considerable saving. According to some estimation, losses due to unawareness of tribology amount to about 6% of its gross national product in the United States. Thus the significance of friction reduction and wear manage cannot be overemphasized for economic reasons and long term dependability. In these regard peoples are focused on the application of nanoparticles in lubricating oil. Nanoparticles brought into lubricating oils can boost the properties of anti-wear, extreme pressure and friction reducing competency and service life of the machine were also improved.³ The friction reduction and anti-wear action are relying on the characteristics of nanoparticles, for example size, shape and concentration. One important property that makes nanoparticles dissimilar from other materials is the fact that they have a very large surface area. Due to their very large surface area, nanoparticles are exceptionally reactive compared to its bulk form. Now a day, generally used nanoparticles are oxides based- Al_2O_3 , CuO , ZnO , metals- Al , Cu , nonmetals- graphite, carbon nanotubes, layered composites- $\text{Al}-\text{Al}_2\text{O}_3$, $\text{Cu}+\text{C}$, functional nanoparticles etc. Out of the many kinds of nanoparticles, oxides based nanoparticles such as ZnO has been attracting considerable interest because of its unique structure and performance.⁴⁻⁷ Nano ZnO has huge surface area, high surface energy, high diffusion, strong adsorption, and other wonderful characteristics. Base oil additives of nano sized, which are suitable for the high temperature work, heavy load, low speed, have excellent

anti-wear resistance, extreme pressure resistance performance and better lubrication properties. In addition, nano- ZnO is a widely used nano oxides and its preparation scheme is simple. Nano- ZnO used as lube oil additive will not only enhance the tribological properties of base oils, in addition also potentially reduce the cost of lube oil. On the other hand, nano-ZnO is hydrophilic-oleophobic with poor oil solubility. It needs to depend on the role of dispersant, ultrasonic dispersion or strong agitation to disperse nano-ZnO particles in the base oils.⁸⁻¹² Again, nano-ZnO particles were not known to show other kind of additive performance other than anti-wear, friction reduction and extreme pressure additive performance. So to disperse nano-ZnO nanoparticle and to meet the purpose of developing multifunctional performance additive, nano-ZnO was dispersed in polymer matrix (acrylate based) by sonication. Since acrylate based polymer were known to perform as good viscosity index improver¹³⁻¹⁵ and pour point depressant.¹⁶ The multifunctional performance (tribological performance, viscosity index improver, pour point depressant) of this nano-ZnO/polymer blend was studied.

3.2.2. Experimental details

3.2.2.1. Materials and methods

Acrylic acid, dodecyl alcohol, BZP and hydroquinone were purchased from Merck specialities Pvt. Ltd. Methanol, hexane and conc. H₂SO₄ were purchased from Thomas baker Pvt. Ltd. BZP was recrystallized from CHCl₃-MeOH. Zinc chloride and sodium hydroxide were purchased from Merck specialities Pvt. Ltd. The base oil was collected from IOCL, Dhakuria, Kolkata, India.

3.2.2.2. Preparation of monomer

Dodecyl acrylate (DDA) was prepared by esterification of acrylic acid with dodecyl alcohol in the mole ratio of 1.1:1. The detailed process was already described in chapter II of part II.

3.2.2.3. Purification of the prepared monomer

The prepared ester (DDA) was purified according to the process as described in chapter II of part II.

3.2.2.4. Preparation of homo polymer

The homo poly dodecyl acrylate was synthesized and purified according to the procedure described in chapter II of part II.

3.2.2.5. Preparation of ZnO nanoparticle

5.5 g of the zinc chloride was dissolved in 100ml of distilled water in a beaker. This solution was kept under constant magnetic stirring till zinc chloride totally dissolved in the distilled water. The temperature of the solution was raised to 90°C by electric hot plate heating. Meanwhile 20 g of sodium hydroxide was dissolved in 100ml of distilled water in a separate vessel. From the prepared sodium hydroxide solution, 16 ml of sodium hydroxide is added to the beaker with constant stirring, drop by drop touching the walls of the beaker. The aqueous solution turned into a milky white colloid without any precipitation. The reaction was allowed to proceed for 2 hrs after complete addition of sodium hydroxide. After the complete reaction, the solution was allowed to settle and the supernatant solution was removed by washing with distilled water for 5 times. After complete washing, the nano-ZnO was dried at 100°C for 30 min. and then it changed into powder form.¹⁷ The reaction involved is given below



Scheme: Reaction involved during synthesis of nano-ZnO

3.2.2.6. Preparation of poly dodecyl acrylate- ZnO nanocomposites

PDDA- ZnO nanocomposites were prepared by mixing the PDDA/toluene solution and nano-ZnO particles. The PDDA- ZnO suspension was prepared as follows: 5g of PDDA were dissolved in toluene and required amount (0.5, 1 and 1.5mg) of nano-ZnO particles were added into the PDDA/toluene solution under ultrasonic wave and vigorous stirring to prepare 100, 200 and 300 ppm blend. The suspension was then poured into a glass plate and allows the toluene to evaporate naturally and a semi solid mass of polymer-nanocomposites was obtained.

3.2.3. Measurements

3.2.3.1. Spectroscopic measurements

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

3.2.3.2. Thermo gravimetric analysis (TGA)

The thermal stabilities of the prepared homo polymer and polymer/nano composite were determined by a thermo gravimetric analyzer (Shimadzu TGA-50) using an alumina crucible in

air. The system was run at a heating rate of 10 °C/min. The percentage of weight loss (PWL) of the samples with rise in temperature was calculated.

3.2.3.3. Determination of molecular weight by GPC

By GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were determined. The poly dispersity index was also calculated. In this method HPLC grade THF (0.4%, w/v) was used as mobile phase in the water 2414 GPC system (polystyrene calibration) at 35°C with a flow rate of 1 ml/min.

3.2.3.4. Characterization of nano- ZnO by SEM and X-RD

The synthesized ZnO-nanoparticles were characterized by Field Emission Scanning Microscope (FE-SEM, INSPECT F50, FEI) and X-ray diffraction (X-RD, Advance D8, Bruker).

3.2.3.5. Performance evaluation as viscosity modifier

Viscosity index (VI) of the polymeric additives was determined in paraffinic base oil to evaluate the efficiency of the prepared polymeric additives as viscosity modifier (VM). An Ubbelohde OB viscometer was used in this experiment at the temperatures 313K and 373K. The detailed process is previously described in Chapter II of Part I.

Five different concentrations ranging from 1 wt % to 5 wt % of the polymeric sample solutions were used to study the effect of additive concentration on VI.

3.2.3.6. Performance evaluation as pour point depressant

The pour point depressant property of the prepared polymeric additives was determined in base oil by the pour point test on a Cloud and Pour Point Tester model WIL-471(India) according to ASTM D97 method. In this case also five different concentrations of the additives were used for each sample.

3.2.3.7. Evaluation of tribological performance of prepared additives

The anti-wear performance of the lubricant compositions were evaluated in terms of wear scar diameter (WSD) by Four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method.¹⁸ In this experiment 392 N (40 kg) load was applied at 75°C for 30 min. to measure the wear scar diameter (WSD). The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm, respectively. The details procedure is described in our publication elsewhere.¹⁹

3.2.4. Results and discussion

3.2.4.1. Spectroscopic analysis

Again in this investigation we were used poly dodecyl acrylate (A) as in the previous study (Chapter-II of Part-III). Here also we observed shifting of IR stretching frequency (**figure 3.9**) of carbonyl group from 1734.56 cm⁻¹ (ester carbonyl) to 1728 cm⁻¹. Hence it can be concluded that, ZnO nanoparticles formed a coordinate type of bond with ester group of A.

3.2.4.2. Thermo gravimetric analysis

The TGA data of the polymer (A) and polymer/ZnO nanocomposites (Z-1, Z-2 and Z-3) are represented in **figure 3.12**. It was seen from the figure that, thermal stability of all nano blended composites is higher than that of A. At 380°C, the percentage of decomposition of the polymer (A) and nanocomposites from Z-1 to Z-3 were 32.42%, 22.88%, 22.09% and 21.29% respectively, whereas at 490°C, the percent of weight loss of A, Z-1, Z-2 and Z-3 were 93.71%, 74.86%, 74.08% and 73.27% respectively. Hence thermal stability of the polymer/ZnO nanocomposites (Z-1, Z-2 and Z-3) was improved by dispersion of the nano-ZnO into the A. This enhancement of thermal stability may be due to the reduction of mobility of polymer chain and the tendency of nanoparticles to remove free radicals.²⁰

3.2.4.3. Characterization of nano- ZnO

Figure 3.10 shows the X-ray diffraction pattern of ZnO nanoparticle. The nanoscale range of particles in the prepared materials was indicated by a definite line broadening of the X-RD peaks. The eight most intense diffraction peaks located at 31.84° , 34.52° , 36.33° , 47.63° , 56.71° , 62.96° , 68.13° and 69.18° have been clearly observed which is in good agreement with a research work published elsewhere.²¹ Moreover it also suggests that the synthesized nanoparticles was free of impurities as it does not shows any characteristics X-RD peaks other than nano-ZnO peaks.

Figure 3.11 represents the scanning electron micrograph (SEM) of the ZnO nanoparticles at different magnifications. These SEM pictures substantiate the formation of ZnO nanoparticles. These pictures confirm the approximate spherical shape to the ZnO nanoparticles. It also can be seen from the pictures that the size of the nano-ZnO is in the range of 16-18 nm.

3.2.4.4. Efficiency of additive as viscosity modifier

Figure 3.13 represents the viscosity index values of the lubricants blended with the additives. It is observed that, the viscosity index (VI) values of the polymer/nano-ZnO composites of different composition (Z-1, Z-2 and Z-3) at different concentration level are better than the pure polymer (A). Again with both type of additives, there is always a steady increase of VI values with the increase in additive concentration. Increase of concentration of the additives leads to increase in total volume of polymer micelles in the solutions. The additional increase of volume compared to pure polymer may be due to the fact that, the nanoparticles present in the polymer matrix leads to the polymer chain separated from each other.

3.2.4.5. Efficiency of additive as pour point depressant

Different level of percentage concentration varying from 1 wt% to 5 wt% of the additives in the base oil was tested as PPD and the results are depicted in **figure 3.14**. The results showed that the additives (A, Z-1, Z-2 and Z-3) are efficient as PPD and the efficiency decreases with increasing additive concentration. The PPD property of all the blended composites is very similar with that of A. That means, incorporation of nanoparticles into the polymer matrix does not affect the PPD property compared to polymer (A).

3.2.4.6. Tribological performance

The tribological properties of all the lubricant compositions (A, Z-1, Z-2 and Z-3) were determined by measuring WSD by FBWT apparatus employing 40 kg load and the results were depicted in **figure 3.15**. The AW performance of the base oil is significantly enhanced when the additives are blended with it and is indicated by the lower WSD values of the lubricant compositions. The nano-ZnO blended composites exhibited better anti-wear performance compared to only polymer (A) and the performance becomes increasingly better with increasing the amount of nanoparticles in the polymer matrix as is shown in the **figure 3.15**.

3.2.5. Conclusion

In this study nano-ZnO was synthesized with better size distribution which was established and characterized by SEM and XRD study. The interaction of nano-ZnO with PDDA was studied by FT-IR analysis and it suggests that there is definite interaction between them. All the nano blended composites showed excellent performance as viscosity modifier and anti-wear additives for lube oil but they did not improve the pour point performance compared to polyacrylate. Moreover the thermal stability of polymer was also improved by the incorporation of nano ZnO into the polymer matrix. This change of properties of polymer is also evidence of nano-polymer

interaction in the blended composites. Therefore, the above study is definitely a potential approach to design multifunctional additives for lubricating oil.

3.2.6. References

References are given in BIBLIOGRAPHY under Chapter III of Part III (PP 174-177).

3.2.7. Tables and Figures

Table 3.3: Properties of base oil

<i>Properties</i>	<i>Base oil</i>
Density(kg.m ⁻³) at 313K	918.68
Viscosity at 313K	20.31×10 ⁻⁶
Viscosity at 373K	3.25×10 ⁻⁶
Viscosity index	89.02
Cloud point (°C)	-8
Pour point (°C)	-6

Table 3.4: Designation and Composition of poly dodecylacrylate-nano ZnO composites

<i>Designation</i>	<i>Composition</i>	
	Polymer in g	Nano (ZnO) in mg
A	5	0
Z-1	5	0.5
Z-2	5	1.0
Z-3	5	1.5

Figure 3.9: Comparative FT-IR spectra of polymer (a), polymer/ZnO nanocomposite (b)

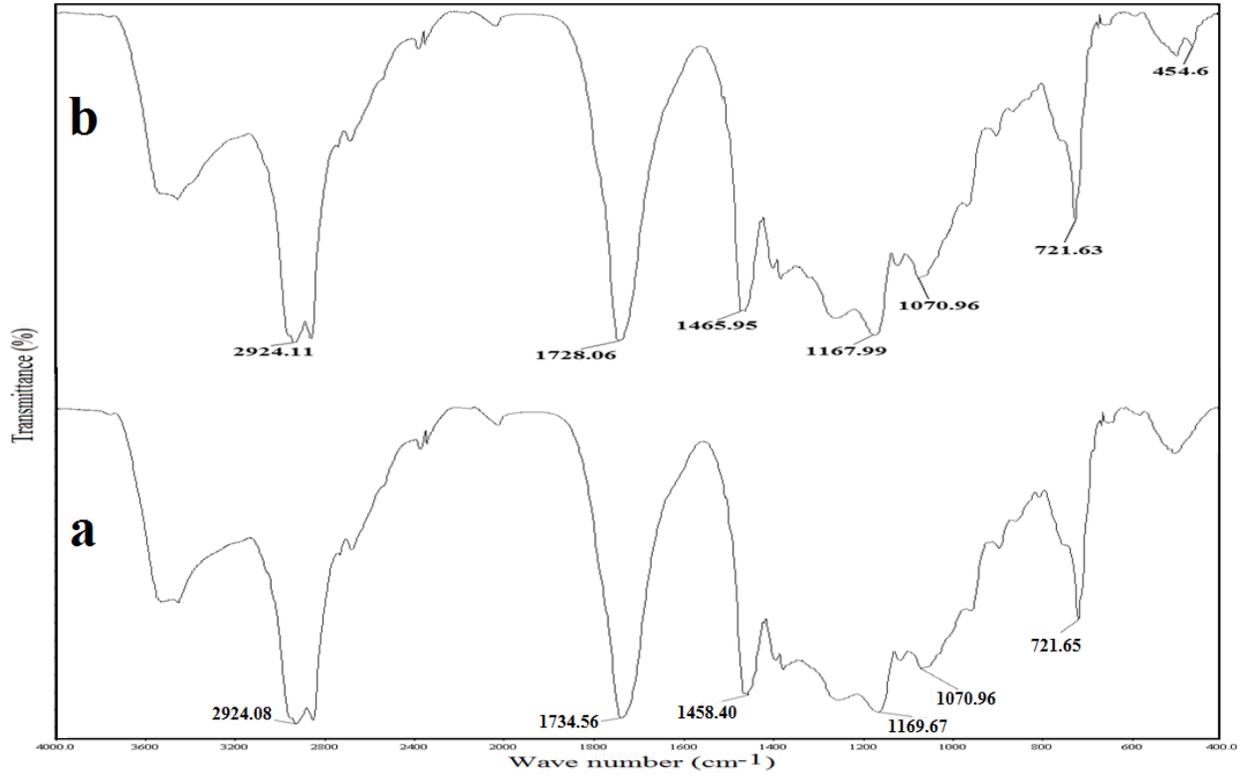


Figure 3.10: X-RD spectra of prepared ZnO nanoparticle

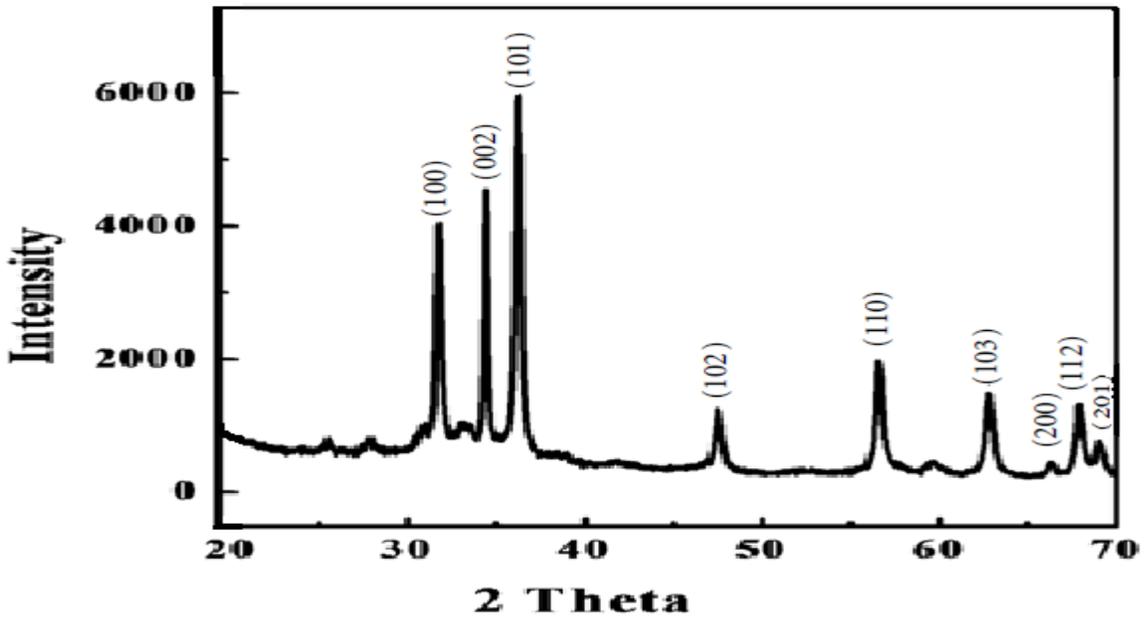


Figure 3.11: SEM pictures (a, b, c and d) of prepared ZnO nanoparticle at different magnifications

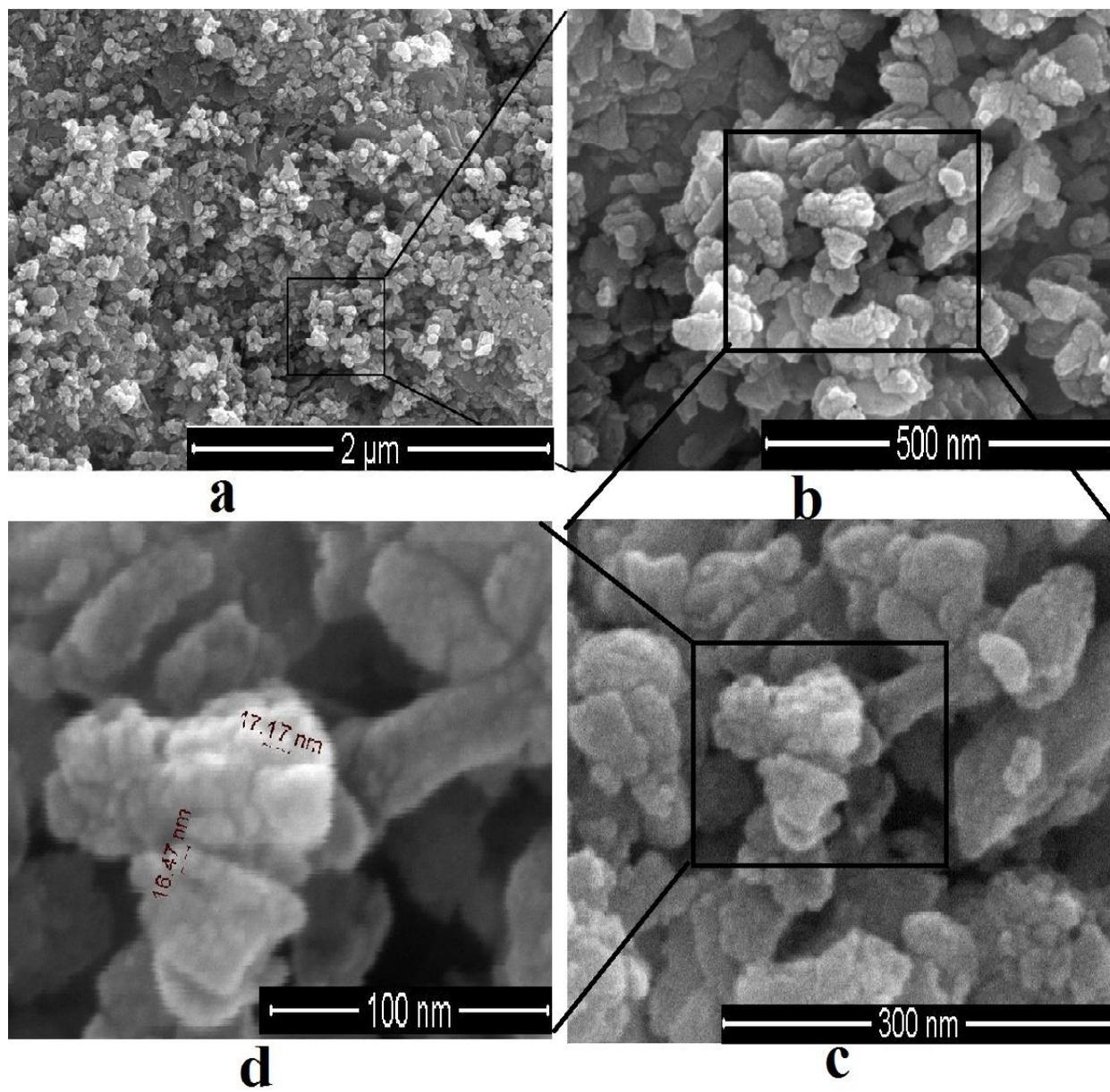


Figure 3.12: TGA data of polymer (A) and polymer/ZnO nanocomposite (Z-1, Z-2 and Z-3)

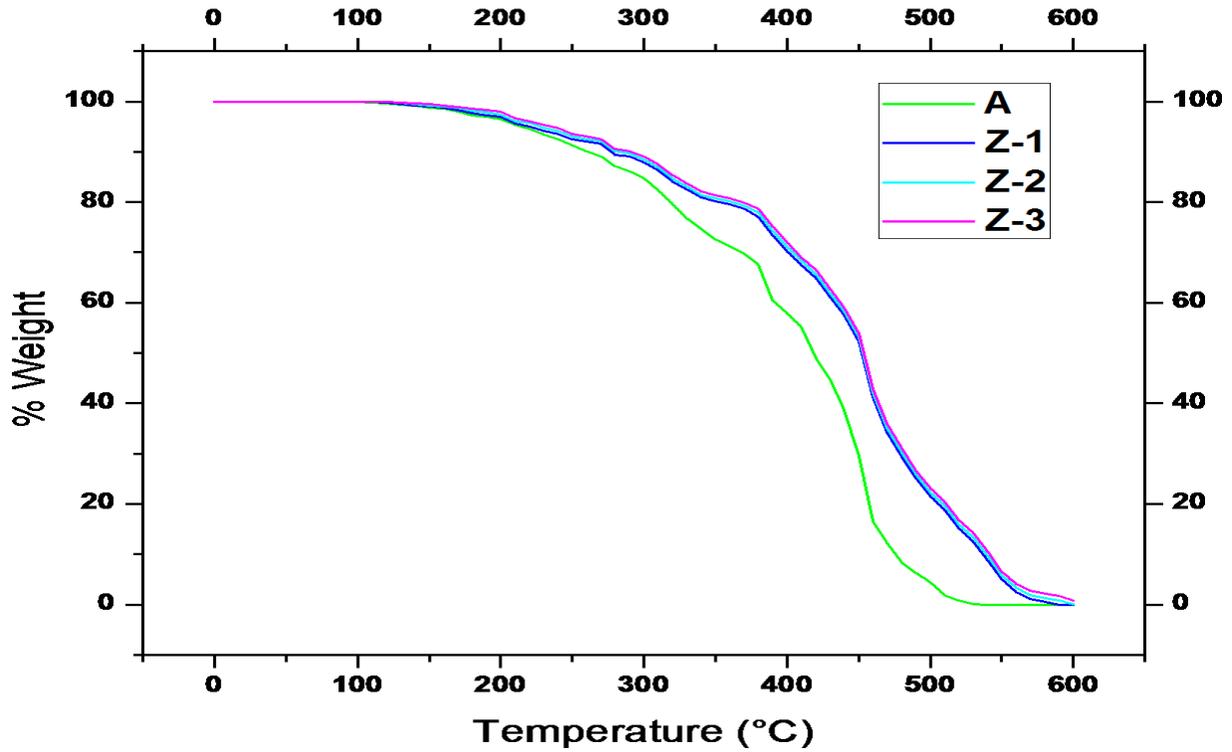


Figure 3.13: Plot of viscosity index of the additives (A, Z-1, Z-2 and Z-3) doped base oil with additive concentration

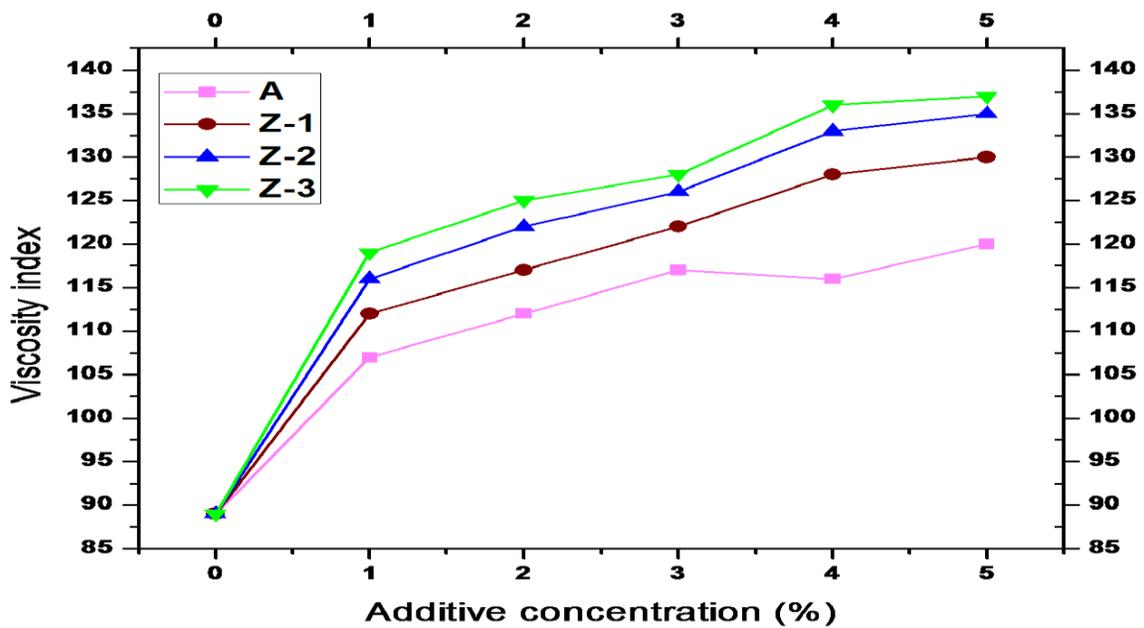


Figure 3.14: Plot of pour point of the additives (A, Z-1, Z-2 and Z-3) doped base oil with additive concentration

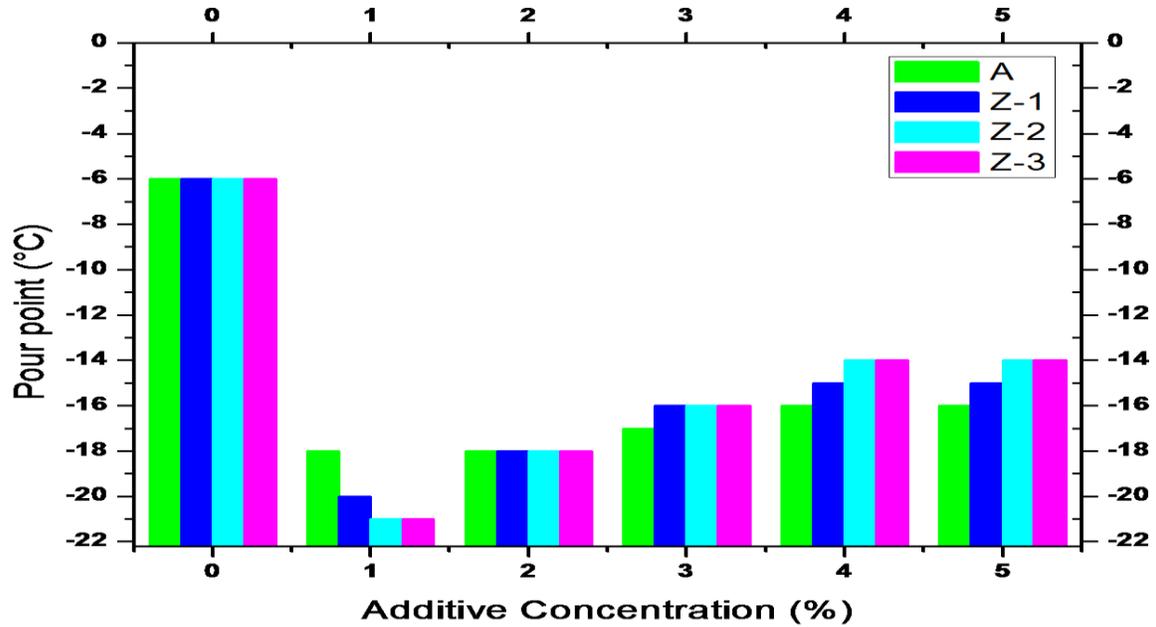
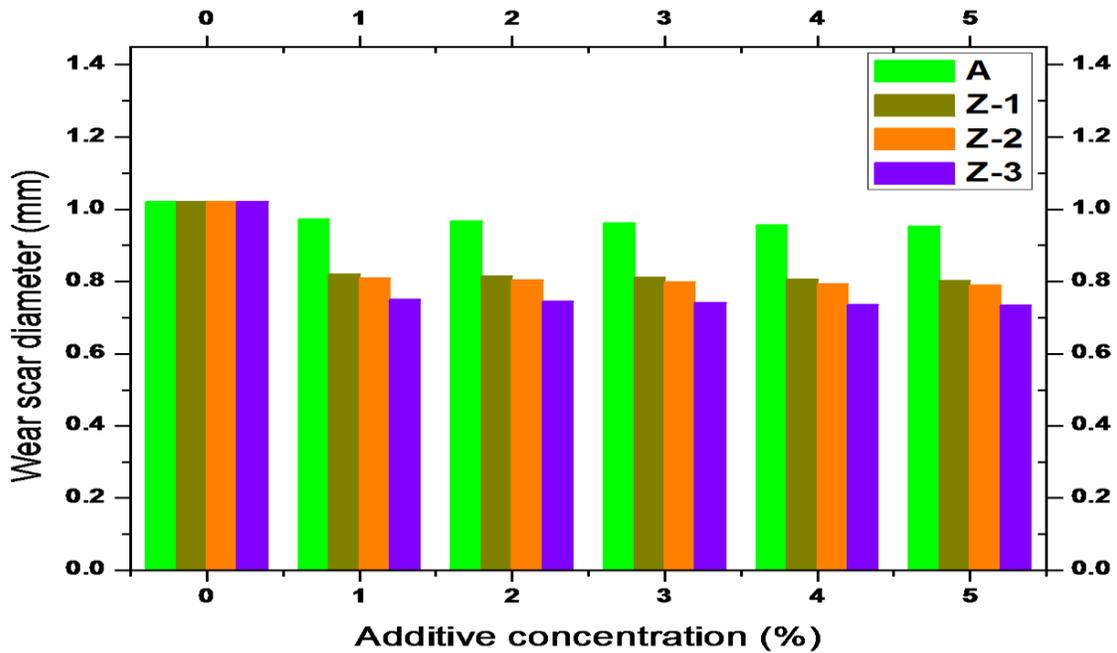


Figure 3.15: Wear scar diameter (WSD) of the lube oil blended with additives (A, Z-1, Z-2 and Z-3) at different percentage (w/w)



General Introduction of Present Investigation

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Liquid Crystal Blended Polyacrylate as a Potential Multifunctional Additive for Lube Oil

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Polydecylacrylate (PDA) is synthesized, characterized (FT-IR and NMR), and evaluated for its performance as anti wear (AW), pour point depressant (PPD), viscosity modifier (VM), and thickening agent in lube oil of different compositions. In addition physical blend of it with liquid crystal (LC) of cholesteryl benzoate (CB) is also made and evaluated, and the data is compared. Molecular weight of the prepared polymer and that of it blends was determined by viscometric analysis. The blends showed better efficiency to act as multifunctional (AW, PPD, VM) additives compare to the pure homopolymer in lubricating oil.

Keywords: anti wear, liquid crystal, oil thickening property pour point, thermo gravimetric analysis, viscosity modifier

INTRODUCTION

Lubricants are substances those add performance to base oil in terms of fuel economy, cost effectiveness, increased engine lifetime and so on. Minerals oils (e.g., paraffin oil) can be used as lubricants. But modern devices need the quality increase of used lubricants. Classical lubricants do not meet contemporary technical requirement because of their limits in improvement of their properties. In the aim of the improvement of their lubricants properties, the various substances are doped in the base oil. Recent trend indicate toward using compounds with layered structure (e.g., graphite, WS₂, MoS₂) as performance additives. The liquid crystal compound can also be used for same reason. Presence of layered structure in between metal surfaces prevents direct contact between them and thus acts as anti wear additive (Carrión et al., 2009; Eidenschink, 1988).

Acrylates and methacrylates are well known as viscosity modifier and pour point depressant from years (Ghosh et al., 1998). But a very few attempts has been made so far to study the influence of incorporation of liquid crystal structure to an acrylate based additive on their additive performance in lube oil.

With this view in mind and in continuation of our efforts toward the synthesis of performance additives for lube and crude oils, acrylate based polymer was synthesized and blended with liquid crystal of cholesteryl benzoate to evaluate their performance in lube oil in comparison to the pure polymer. Oil thickening property of the polymer and LC-polymer blend in lube oil, which is a direct measure of percent increase in the viscosity of the base stocks for addition of its unit amount of weight, has also been investigated and reported here. This property can also be taken as the measure

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of extent of interaction of the polymer with the base stock, greater the thickening property; greater is the extent of interaction (Ghosh et al., 1998). Fuel economy may also be predicted by the thickening power of a lube oil additive. The results of our above investigations have been presented in this article.

The molecular weight of the additives prepared was determined by viscometric method using Mark Houwink–Sukurda relation (Eq. [1]), by using the intrinsic viscosity values obtained from graphic extrapolation (Eqs. [2]–[5]) and single point determination method (Eqs. [6] and [7]) as reported in literature (Ghosh et al., 2011).

$$[\eta] = KM^a \quad (1)$$

Where $[\eta]$, the intrinsic viscosity, can be calculated by different equations, parameter K and a depend on the type of polymer, solvent and temperature. M is the viscosity average molecular weight and K and a are the Mark-Houwink constants.

$$\text{Huggins (H)} \quad \eta_{sp}/C = [\eta]_h + k_h [\eta]_h^2 C \quad (2)$$

$$\text{Kraemer (K)} \quad \ln \eta_r/C = [\eta]_k - k_k [\eta]_k^2 C \quad (3)$$

$$\text{Martin (M)} \quad \ln (\eta_{sp}/C) = \ln [\eta]_m + k_m [\eta]_m C \quad (4)$$

$$\text{Schulz – Blaschke (SB)} \quad \eta_{sp}/C = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad (5)$$

Where $\eta_r = t/t_0$, relative viscosity or viscosity ratio; $\eta_{sp} = \eta_r - 1$, specific viscosity; $[\eta]_h$ = intrinsic viscosity, respective to Huggins equation; $[\eta]_k$ = intrinsic viscosity, respective to Kraemer equation; $[\eta]_m$ = intrinsic viscosity, respective to Martin equation; $[\eta]_{sb}$ = intrinsic viscosity or limiting number, respective to Schulz-Blaschke equation; and k_h , k_k , k_m , and k_{sb} are Huggins, Kraemer, Martin, and Schulz-Blaschke coefficients, respectively.

The Solomon-Ciuta and Deb–Chanterjee relations are the following:

$$\text{Solomon – Ciuta (SC)} \quad [\eta] = [2 (\eta_{sp} - \ln \eta_r)]^{1/2} / C \quad (6)$$

$$\text{Deb – Chanterjee (DC)} \quad [\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp})^{1/3} / C \quad (7)$$

EXPERIMENTAL

Materials

Toluene, hydroquinone and H_2SO_4 , decyl alcohol, and acrylic acid (stabilized with 0.02% hydroquinone monomethylether) were purchased from Merck Specialties Pvt. Ltd. Hexane and methanol were obtained from Thomas Baker (Chemicals) Pvt. Ltd. Benzoyl peroxide (BZP), purchased from LOBA chemicals was recrystallized from CHCl_3 -MeOH before use. The rest of the materials were used as they were obtained without further purification.

Esterification

Esterification was carried out by conventional method using 1.1 mol of acrylic acid and 1 mol of decyl alcohol, using a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid, and toluene as a solvent in nitrogenous atmosphere as reported elsewhere (Ghosh et al., 2011).

Purification of prepared esters

The prepared esters were purified according to the procedure reported earlier (Ghosh et al., 2011).

Preparation of the homopolymer

The polymerization was carried out in a four-necked round bottomed flask, taking desired mass of DA and initiator (BZP) in toluene and by following the process as reported previously (Ghosh et al., 2011). The polymer obtained was then purified by repeated precipitation of its hexane solution using methanol followed by drying under vacuum at 313 K.

Preparation of the polymer solutions and LC-polymer blend

Required amount of polymer was taken in toluene; liquid crystal of cholesteryl benzoate was added to make a 100 ppm blend. They were heated at 40°C with stirring for 1 hour. Five different concentrations (1–5%, w/w) of polymer solutions were prepared by the addition of required amount polymer to the base oils, BO1 and BO2 followed by heating at 60°C with constant stirring for 30 min. Another five different concentrations (1–5%, w/w) of polymer-LC blend solutions were prepared in same way.

Measurements

Spectroscopic measurements

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

Viscometric measurements

Ubbelohde OB viscometer was used for determination of viscometric properties at 313 K in toluene solution. Experimental determination was carried out by counting time flow at least five different concentrations of the sample solution. The time flow of the solution was determined manually using a chronometer. The lowest value of solution concentration was chosen for calculation in the single point measurement. For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl/g}$ and $a = 0.725$ were employed in Mark Houwink–Sukurda relation (Ghosh et al., 2011).

Thermo gravimetric analysis (TGA)

A Mettler TA – 3000 system was appointed to obtain TGA data, at a heating rate of 10°C/min.

Evaluation of pour point depressant properties of the additives in lube oil

Evaluation of the prepared compounds as pour point depressants (PPDs) was done in two different base oils by the pour point test according to the ASTM D97 on a Cloud and Pour Point Tester model WIL-471 (India).

Evaluation of the prepared additives as viscosity index improver in lube oil

The prepared polymers and the blends were evaluated as viscosity modifiers in two base oils according to the ASTM D2270 method and by following the equations as reported elsewhere (Tanveer and Prasad, 2006). 1–5 wt% of polymer concentration was used to check the effect of polymer concentration on VI. The kinematic viscosity of the oil containing the different concentrations of the tested polymers was determined at 40°C and 100°C as per ASTM D 445 method.

Anti wear properties

Anti wear properties of the base stocks as well as polymer LC blend in base stocks were studied in sliding contact by means of a four-ball wear test machine as per ASTM D 4172 method using a 20 kg and 40 kg load.

Evaluation of thickening property

Thickening power of the polymer was determined by calculating the percent increase in viscosity of the base stocks by the addition of unit amount of additive.

Properties of the base oils

Physical properties of the base oils are in tabular form.

RESULTS AND DISCUSSION

Spectroscopic Analysis

The homopolymer, polydecylacrylate (PDA), exhibited IR absorption band at 1733 cm^{-1} for the ester carbonyl along with other peaks at 1457, 1378, 1265, and 1167 cm^{-1} . $^1\text{H-NMR}$ spectra of it (Figure 1) showed the presence of $-\text{OCH}_2$ protons as a broad singlet centered at 4.02 ppm, methyl protons between 0.81 to 0.86 ppm corresponds to that of the PDA chain. $^{13}\text{C-NMR}$ spectrum (Figure 2) of the polymer confirms the presence of carbonyl carbon at 174.47 ppm and also the absence of any sp^2 carbons.

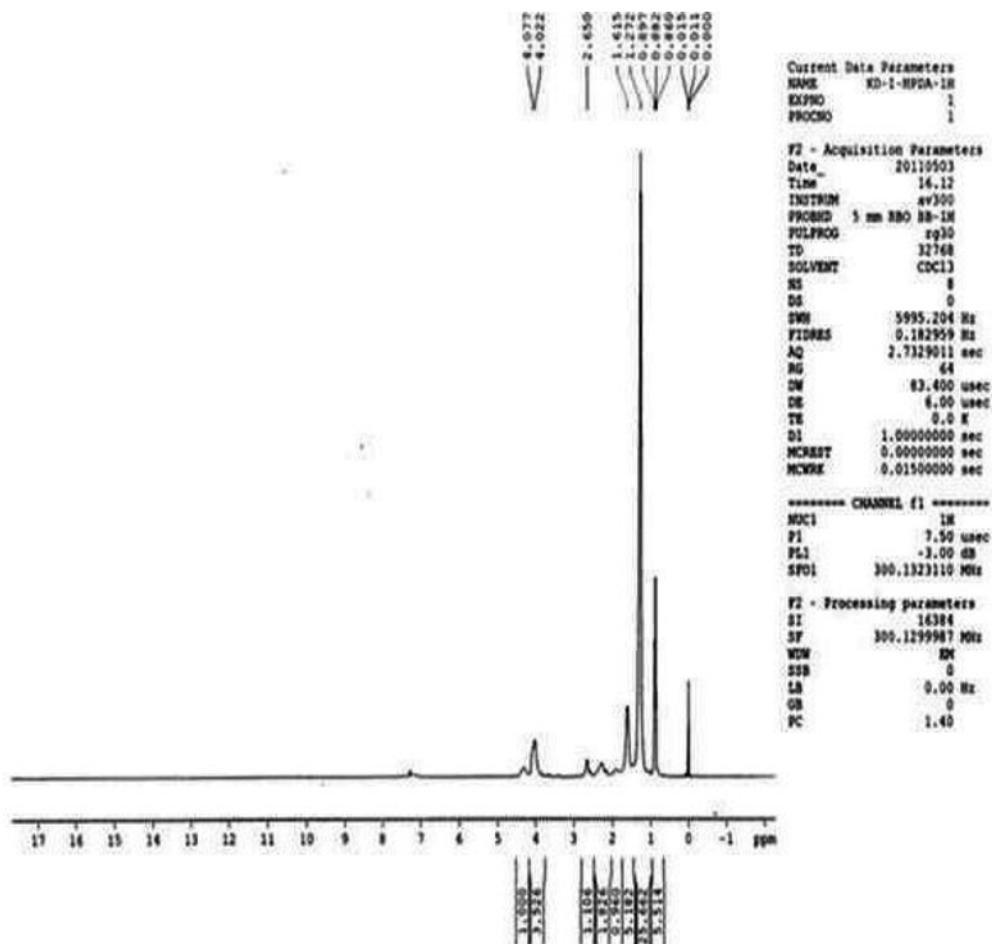


FIGURE 1 1H NMR spectra of homo polydecylacrylate.

Thermogravimetric Analysis

TGA data (Table 1) showed better thermal stability of the LC-blended polymer in comparison to the pure polymer. In Table 1, PWL represents percent weight loss and decomposition temperature values are in degrees Celsius.

Viscometric Analysis

Viscometric analysis was carried out by using the six equations as mentioned above. A plot of $\log \eta_{sp}$ versus $\log c[\eta]$ for all samples yielded a linear relation which indicate that the measurements were performed in Newtonian flow (Mello et al., 2006).

Comparison (Table 1) among the polymer solution and the LC added polymer solution indicated that, the latter has greater intrinsic viscosity $[\eta]$ values than the pure polymer.

TABLE 1
Viscosity Average Molecular Weight and TGA Property of Pure Polymer and Its LC-blended Composite

Property	Sample	
	LC blended Polymer	Pure Polymer
Intrinsic viscosity value/molecular weight		
$[\eta]^a/M_h$	2.523/7614.82	2.411/7152.53
$[\eta]^a/M_k$	2.528/7635.70	2.418/77277.79
$[\eta]^a/M_m$	2.541/7689.92	2.431/7234.55
$[\eta]^a/M_{sb}$	2.552/7735.86	2.452/7320.89
$[\eta]^b_{sb}/M_{sb}$	2.587/7882.59	2.478/7428.18
$[\eta]^b_{sc}/M_{sc}$	2.601/7941.45	2.485/7457.15
$[\eta]^b_d/M_{dc}$	2.639/8101.97	2.489/7473.70
TGA		
Decomposition temperature	265/365	245/335
PWL	12/82	19/92

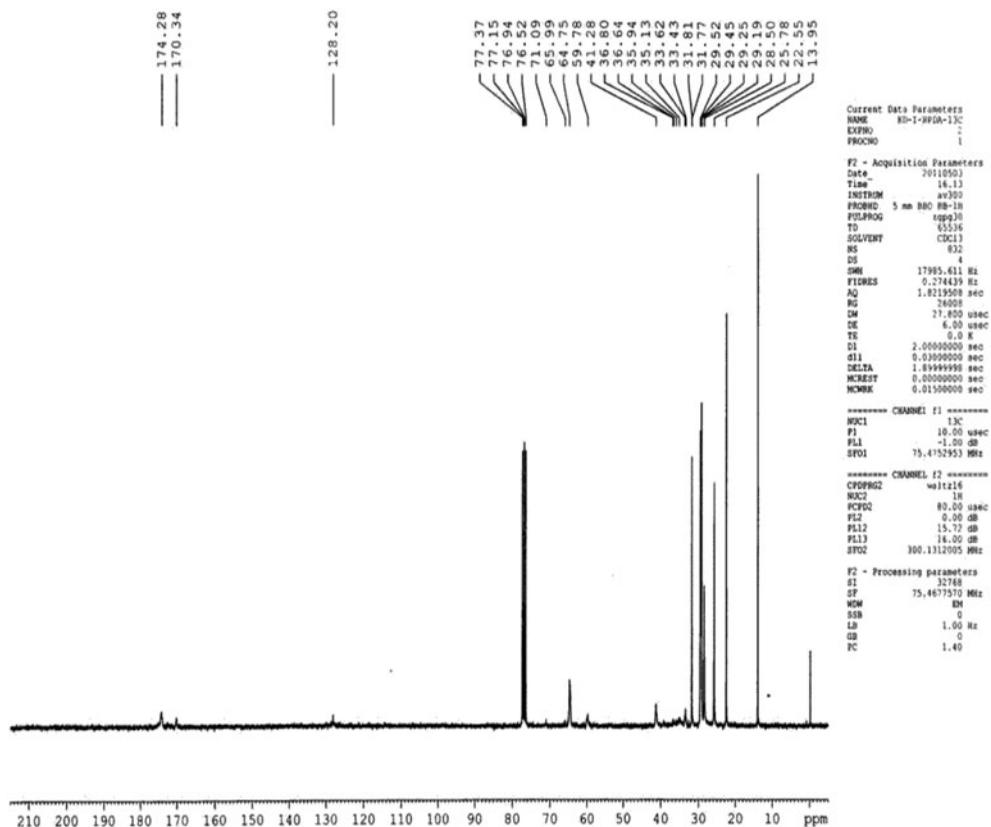


FIGURE 2 ^{13}C NMR spectra of homo polydecyl acrylate.

TABLE 2
 Viscosity Index (VI), Pour Point Depressant (PPD), and Thickening Properties (THK) of Pure Polymer and Its LC Blended Composite in Different Levels of Concentration in Base Oil

Property	Base Oil	Sample																			
		LC blended polymer					Pure polymer														
		0%	1%	2%	3%	4%	5%	0%	1%	2%	3%	4%	5%	0%	1%	2%	3%	4%	5%		
PPD	BO1	S1	-3	-15	-18	-21	-21	-21	-21	-21	-21	-21	-3	-9	-12	-12	-9	-15	-15	-15	
		S2	-3	-15	-21	-21	-24	-21	-21	-21	-21	-21	-3	-9	-12	-12	-15	-15	-12	-18	-18
	BO2	S1	-6	-18	-21	-21	-21	-21	-21	-21	-21	-21	-6	-9	-9	-9	-12	-12	-15	-18	-18
		S2	-6	-18	-18	-21	-24	-21	-21	-21	-21	-21	-6	-9	-10	-12	-12	-12	-12	-15	-15
	VI	BO1	S1	80	140	137	144	151	159	159	159	159	80	133	138	138	141	141	152	153	153
			S2	83	136	150	156	155	165	165	165	165	83	118	132	132	138	138	142	144	144
BO1		S1	89	124	138	143	148	166	166	166	166	89	121	129	129	148	148	137	133	133	
		S2	88	120	136	139	149	154	154	154	154	88	122	118	118	125	125	112	129	129	
THK (at 313K)	BO1	S1	—	55.342	33.453	23.895	20.334	17.876	17.876	17.876	17.876	—	49.003	26.342	17.879	15.219	13.447	13.447	13.447	13.447	
		S2	—	41.434	31.987	20.654	17.878	13.543	13.543	13.543	13.543	—	38.995	20.612	14.788	11.991	10.676	10.676	10.676	10.676	
	BO2	S1	—	39.909	23.789	16.776	13.434	11.112	11.112	11.112	11.112	—	41.884	21.989	16.343	13.909	10.935	10.935	10.935	10.935	
		S2	—	33.352	21.132	14.656	12.667	11.556	11.556	11.556	11.556	—	36.005	18.914	15.786	11.569	10.095	10.095	10.095	10.095	

TABLE 3
Anti Wear Performance of Additive Doped Base Oil

Sample	Base Oils, With Their WSD in mm	WSD (mm) of Polymer Base Oil Blend										
		WSD at 20 kg Load					WSD at 40 kg Load					
		1	2	3	4	5	1	2	3	4	5	
LC -polymer blend in base oil	BO1	0.966	0.954	0.932	0.893	0.845	0.970	0.956	0.889	0.871	0.865	
	S20.977	0.947	0.933	0.888	0.835	0.822	0.956	0.945	0.922	0.880		
	BO2	S11.116	1.075	1.055	1.043	1.012	0.989	1.085	1.077	1.008	0.985	
Pure polymer in base oil	BO1	S21.121	1.084	1.063	1.044	1.021	0.987	1.081	1.078	1.055	1.021	
	S10.981	0.977	0.971	0.958	0.933	0.911	0.977	0.971	0.965	0.920		
	BO2	S20.977	0.970	0.954	0.921	0.891	0.877	0.974	0.961	0.953	0.931	
		S11.116	1.101	1.084	1.068	1.061	1.048	1.104	1.088	1.071	1.065	
		S21.121	1.088	1.081	1.075	1.063	1.048	1.109	1.088	1.075	1.062	
											1.055	
												1.055

TABLE 4
Base Oil Properties

Properties	BO1		BO2	
	S1	S2	S1	S2
Density (g.cm ⁻³) at 40°C	0.84	0.88	0.94	0.95
Viscosity at 40°C in cSt	6.70	7.46	24.229	25.284
Viscosity at 100°C in cSt	2.00	2.15	4.390	4.495
Cloud point, °C	-10	-10	-8	-8
Pour point, °C	-3	-3	-6	-6

Table 1 also presents the values of molecular weight obtained by viscometric methods for the homopolymer.

Efficiency of the Prepared Compounds as Pour Point Depressant

PPD properties of the different level of polymer doped (1–5 wt%) as well as LC–polymer blend in base oils were tested and the experimental data are presented in Table 2. The extended conformation of the polymer chain of the LC added composition may be responsible for showing its better efficiency in comparison to the pure polymer.

Efficiency of the Prepared Compounds as Viscosity Index Improvers

It is observed that (Table 2) the viscosity index (VI) values of the of the LC-polymer blend doped base oil are always better than the pure polymer doped oils. Irrespective of the additive and up to a certain limit (4%) there is always a gradual increase of VI values with the increase in additive concentration. Increase of concentration of the polymer may lead to increase in total volume of polymer micelles in the oil solutions, which in turn will impart a high viscosity (Nassar, 2008).

Anti wear Properties

Anti wear properties of the pure additive and its blend in comparison to that of the base oils were evaluated by employing a four ball wear test machine as per ASTM test conditions. The wear scar diameter (WSD) measured in all these cases using a 20 kg and 40 kg load condition are depicted in Table 3. In the case of pure base stocks, WSD decreased with the decrease in base stock viscosity. In case of pure additive doped base oil marginal decrease with increasing VM concentration is found in BO1 and BO2 base stocks. Significant decrease in WSD is observed in the case of the LC blended additive at all concentrations. It is also observed that using a 20 kg load the decrease in WSD were much better than the higher load condition (40 kg).

Thickening Properties

A gradual decrease of the thickening power with the increase in concentration of both the polymer and LC-polymer blend is observed in the base oils (Table 2). Formation of a coiled like aggregation with increase in concentration in the base stock may be responsible for such kind of thickening

power of the additives. The result also showed that the thickening power of the LC-polymer blend was slightly higher in comparison to the pure polymer. Thus it appears that the use of LC blended polymer in base oil may reduce the fuel consumption to some extent.

Base oil properties are depicted in Table 4.

CONCLUSION

Liquid crystal of cholesteryl benzoate induces excellent anti wear performance in comparison to the pure polymer along with the enhancement of existing PPD, VI, and thickening properties of the PDA. However, both of them are found equally effective as thickeners for the base oils studied. In general, it is observed that, the values of viscosity index and pour point increases with increasing concentration of the additives whereas the thickening power decreases.

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Multifunctional biodegradable lube oil additives: Synthesis, characterization, and performance evaluation

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ABSTRACT

Copolymers of different concentration of decyl acrylate and 1-decene with rice bran oil were prepared and their characterization was carried out by spectral (NMR, IR), thermogravimetric, and gel permeation chromatography analysis. Performance evaluation of them in lube oil indicates that the polymers effectively act as pour point depressant and viscosity modifier. The viscosity index and pour point values depend on the nature of mineral base oils, polymer type, and also on the concentration of the additives in solution. Biodegradability test was also carried out and as anticipated, the rice bran oil-copolymers showed excellent biodegradable nature among the additives.

KEYWORDS

Additives; biodegradable polymers; multifunctional; pour point depressant; thermogravimetric analysis; viscosity modifier

1. Introduction

Lubricant oil is known to decrease the friction between two sliding bodies in contact and thus reducing possible wear and damage to the surface of the moving bodies. In addition to base fluid or base oils they consist about 10–20% of additive package. Pour point depressants (PPDs), viscosity modifiers (VMs), dispersants, detergents, antiwear and extreme pressure, and antioxidant and corrosion inhibitors are the examples of additives generally used. Among them most important are PPDs (Khidr, 2007) and VMs (Nassar, 2008).

Although many additives are in use as PPDs (Khidr, 2007; Ghosh et al., 2010; Du et al., 2012) and VMs (Nassar, 2008; Ghosh et al., 2011), because of potent toxicity most of them are environmentally not benign. Thus, the development of eco-friendly lubricants has become the major issue of the present decade. Plant oils are promising as base fluid for biolubricants because of their excellent lubricity, biodegradability, and viscosity-temperature characteristics. However, poor thermal stability has rendered limited application of them in the lubricant formulations. In view of that, their copolymerization with acrylate monomers may be undertaken for the development of some novel polymeric additives in anticipation that they may be used as environmentally accepted additives for lubricant formulation.

With this background the present work is directed towards the synthesis of copolymer of rice bran oil–1-decene and rice bran oil–decyl acrylate (DA) followed by characterization of them (by thermogravimetric, gel permeation chromatography [GPC], and spectral analysis) and evaluation of their additive performance (as PPDs and VMs) in lubricating oil.

Table 1. Specification of the chemicals used.

Chemical name	Source	Mole fraction purity
Toluene	Merck Specialities Pvt. Ltd.	0.995
Hydroquinone	Merck Specialities Pvt. Ltd.	0.990
H ₂ SO ₄	Merck Specialities Pvt. Ltd.	—
Acrylic acid	SRL Pvt. Ltd.	0.990
Decanol	S. D. Fine-Chem Ltd.	0.980
Hexane	S. D. Fine-Chem Ltd.	0.995
1-Decene	Across Organics.	0.950
Methanol	Thomas Baker Pvt. Ltd.	0.980
Benzoyl peroxide	LOBA chemicals	0.980
Rice bran oil	Local Market	—

2. Experimental

2.1. Materials

Toluene, hydroquinone, and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (stabilized with 0.02% hydroquinone monomethyl ether) and decyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Hexane and 1-decene was purchased from S D Fine Chem. Ltd. Rice bran oil was collected from local market and methanol was purchased from Thomas baker Pvt. Ltd. and were used as received. Benzoyl peroxide (BZP) obtained from LOBA chemicals was recrystallized from CHCl₃-MeOH before use. Specifications of the chemicals are depicted in Table 1. Two different base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in Table 2.

2.2. Esterification

The preparation and purification of DA from acrylic acid and decyl alcohol was carried out by following the method reported earlier from our laboratory (Ghosh et al., 2015).

2.3. Preparation of copolymers

The rice bran oil-DA and rice bran oil-1-decene copolymers were prepared by using different concentrations of DA and 1-decene (10%, 20%, and 30% [w/w]) with rice bran oil, P-1 to P-3, and P-4 to P-6, respectively. The radical polymerization was carried out following the method as reported elsewhere (Ghosh et al., 2016).

2.4. Measurements

2.4.1. Spectroscopic measurements

The IR spectra of the samples were recorded on a Perkin Elmer FT-IR 8300 spectrophotometer using 0.1 mm KBr cells at room temperature. The NMR spectra were recorded in a 300 MHz Bruker Avance FT-NMR spectrometer using 5 mm BBO probe. CDCl₃ was used as solvent and tetramethylsilane (TMS) was used as reference material.

Table 2. Base oil properties.

Properties	Base oils	
	BO1	BO2
Density at 313 K, kg.m ⁻³	836.98	868.03
Viscosity at 313 K, Pa·s	5.97×10^{-3}	20.31×10^{-3}
Viscosity at 373 K, Pa·s	1.48×10^{-3}	3.25×10^{-3}
Cloud point, °C	-10	-8
Pour point, °C	-3	-6
Viscosity index	85	80

Table 3. The weight average and number average molecular weights (M_w and M_n) and polydispersity of the polymers before and after biodegradability test.

Polymer samples [RBO: DA (P-1 to P-3) and RBO:1-deccene (P-4 to P-6), w/w]	Before biodegradability test			After biodegradability test		
	M_n	M_w	PDI	M_n	M_w	PDI
P-1 (9:1)	35709	43837	1.12	31421	41238	1.41
P-2 (8:2)	23332	31234	1.65	19816	28764	1.84
P-3 (7:3)	18965	27654	1.71	17657	24569	1.98
P-4 (9:1)	16392	23597	1.55	14710	21056	1.86
P-5 (8:2)	14815	21230	1.43	12348	19379	1.74
P-6 (7:3)	12112	17659	1.41	10528	14592	1.75

M_n = number average molecular weight; M_w = weight average molecular weight; PDI = polydispersity index.

2.4.2. Molecular weight determination by GPC

The weight average and number average molecular weights (M_w and M_n) and polydispersity indices of the polymers were measured in Waters' GPC equipment using polystyrene standards for calibration in THF phase. Details of the experimental procedure followed were mentioned in an earlier publication (Ghosh et al., 2016). The results are tabulated in Table 3.

2.4.3. Thermogravimetric analysis

The thermograms of the samples in air were obtained on a Mettler TA 3000 system, at a heating rate of 10 K min^{-1} . The samples were heated gradually from room temperature to 600°C in a platinum crucible.

2.4.4. Evaluation of pour point of the additives in lube oil

The PPD properties of different concentrations of the polymer doped base oils was tested according to the ASTM D97-09 method on a Cloud and Pour Point Tester model WIL-471 (India).

2.4.5. Evaluation of viscosity index of the prepared additives in lube oil

The viscosity index (VI) of different concentrations of the additives in the base oils was evaluated in two base oils according to the ASTM D2270 method and following the equations as reported by Tanveer and Prasad (2006).

2.4. Biodegradability test

Biodegradability of the new polymers was tested (a) by the disc diffusion method against five different fungal pathogens, namely, *Calletotricheme camellia*, *Fussarium equisetae*, *Alterneria alternata*, *Collet-richum gleosporoides*, and *Curvularia eragrostidies* following the method as reported earlier (Ghosh et al., 2011) and (b) by the soil burial degradation test of polymer sample films as per ISO 846:1997 (Chandure and Umare, 2007) as per the earlier literature report (Ghosh et al., 2011).

2.5. Properties of base oils

Physical properties of the base oils are tabulated in Table 2.

3. Results and discussion

3.1. Spectroscopic data

FT-IR spectra of rice bran oil-DA exhibited absorption at 1733 cm^{-1} for the ester CO stretching vibration along with other peaks at 1457, 1244, and 1171 cm^{-1} and a peak at 723.3 cm^{-1} was due to C-H bending. In its ^1H NMR spectra, the polymer showed a broad singlet ranging between 4.11 and 4.31 ppm due to the $-\text{OCH}_2$ protons of rice bran oil and DA along with the $-\text{CH}_3$ protons ranging between 0.86 and 0.88 ppm and $-\text{CH}_2$ protons ranging between (1.25 and 1.61) ppm. The formation of the copolymer

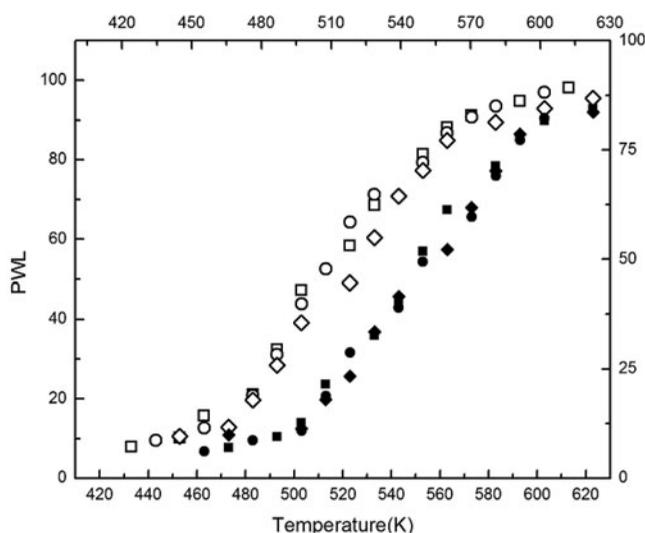


Figure 1. Plot of PWL versus temperature. PWL = percent weight loss. Temperature is in K. ■, P-1; ▲, P-2; ◆, P-3; □, P-4; ○, P-5; ◇, P-6.

was further indicated by the absence of sp^2 hydrogen in its 1H and sp^2 carbon in ^{13}C NMR spectrum, respectively.

FT-IR spectra of rice bran oil-1-decene copolymer exhibited absorption at 1732 cm^{-1} for the ester CO stretching vibration along with other peaks at 1456, 1378, 1244, 1174, and 724 cm^{-1} . In its 1H NMR spectra, the polymer showed a broad singlet ranging between 4.11 and 4.3 ppm due to the proton of $-OCH_2$ group of RBO along with the $-CH_3$ protons at 0.88 ppm and $-CH_2$ protons ranging between 1.26 and 1.62 ppm. The formation of the copolymer was further indicated by the absence of sp^2 hydrogen and sp^2 carbon in its 1H and ^{13}C NMR, respectively.

3.2. Thermogravimetric analysis

Plot of TGA data (Figure 1) presents a comparison between the thermal stability of rice bran oil-DA and rice bran oil-1-decene copolymers. The analysis reveals that for both set of polymers, thermal stability increases with increasing concentration of 1-decene and DA in the feed and the rice bran oil + DA copolymers are more stable than the corresponding rice bran oil + 1-decene copolymers.

3.3. Performance evaluation of the prepared polymers as PPD

The pour point (PP) values of the polymers in both the base oils are tabulated in Table 4, which indicates that their PPD efficiency increases (up to a certain limit) with increasing concentration of the polymer in base oils. Comparison among the PP values indicates that the efficiency of the polymers as PPD is greater for DA copolymers than the 1-decene copolymers. Again, the efficiency in base oil, BO1 is greater than that of in BO2.

3.4. Performance evaluation of the prepared polymers as VM

The VI values in two base oils (measured in six different concentrations) tabulated in Table 4 indicate that in both the base oils the values are greater for rice bran oil-DA copolymers than that for respective rice bran oil-1-decene copolymers and for DA copolymers, the VI value increases with increasing RBO concentration, and similar trend is also observed for RBO-1-decene copolymers. This result may be explained on the basis of the molecular weight of the polymers. Again, with increase in concentration of the polymers in solution, VI increases. The reason may be that although the viscosity of the lube oil gets decreased at higher temperature, the polymer molecules may effectively offset this reduction

Table 4. Dependence of PP in °C and VI on the concentration of additives in BO1 and BO2.

Property/base oil (PP/VI)	Conc., %	Sample					
		P-1	P-2	P-3	P-4	P-5	P-6
PP/BO1(-3)	1	-9	-15	-15	-9	-9	-12
	2	-12	-18	-21	-9	-12	-12
	3	-15	-21	-24	-12	-15	-15
PP/BO2(-6)	1	-12	-15	-18	-15	-21	-18
	2	-15	-18	-21	-18	-24	-24
	3	-15	-24	-27	-21	-18	-24
VI/BO1(85)	1	112	116	119	100	110	118
	2	112	118	125	104	112	122
	3	125	130	132	106	114	128
	4	125	135	138	118	126	135
	5	128	136	145	121	128	138
	6	134	136	146	125	129	137
VI/BO2(80)	1	95	98	101	98	100	104
	2	97	100	110	109	104	110
	3	102	115	115	115	118	119
	4	105	115	123	118	122	125
	5	115	123	132	131	130	132
	6	116	128	138	137	129	138

BO = base oil; PP = pour point; VI = viscosity index.

Table 5. Result of biodegradability test by the disc diffusion method and soil burial degradation.

Sample	Weight loss in disc diffusion method, g Pathogens used					Weight loss in soil burial degradation, g
	CC	FE	AA	CG	CE	
P-1	0.33	0	0.48	0	0	0.32
P-2	0.25	0	0.44	0	0	0.28
P-3	0.27	0	0.37	0	0	0.22
P-4	0.23	0	0.31	0	0	0.18
P-5	0.17	0	0.27	0	0	0.15
P-6	0.11	0	0.28	0	0	0.12

CC = *Calletotricheme camellia*; FE = *Fussarium equisetiae*; AA = *Alterneria alternata*; CG = *Colletrichum gleosproides*; CE = *Curvularia eragrostidies*.

in viscosity by thickening the oil changing its shape from tight coil to expanded one due to increased polymer-solvent interaction. The result is increase in viscosity of the solution. Again, a higher polymer concentration means increase in total volume of polymer coils in the solution which imparts a higher VI compared to a low concentrated polymer solution (Nassar, 2008; Ghosh et al., 2011).

3.5. Analysis of biodegradability test results

Biodegradability test results (Table 5) with both set of copolymers showed significant biodegradability against the fungal pathogens, *Calletotricheme camellia* and *Alterneria alternata*, though the result is better for the rice bran oil-DA copolymers. Soil burial test results also indicated similar extent of biodegradability. Change in molecular weight also supported the biodegradable nature of the polymers (Table 3).

4. Conclusions

The rice bran oil + 1-decene copolymers are thermally more stable than the rice bran oil + DA copolymers and thermal stability increases with increasing concentration of 1-decene and DA in the copolymers. Evaluation of performance of the additives indicates that the rice bran oil + DA copolymers act as better PPD and viscosity modifiers compared to the RBO + 1-decene copolymers. The investigated

polymers showed biodegradability in addition to the multifunctional additive performance (PPD and VM), and so are considered as being more useful in field applications compared to the existing additives.

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