

***MODIFICATION OF VEGETABLE OILS AS
A POTENTIAL BASE OIL AND A
MULTIFUNCTIONAL LUBE OIL
ADDITIVE.***

A Thesis Submitted to the
UNIVERSITY OF NORTH BENGAL

For the Award of
DOCTOR OF PHILOSOPHY (Ph.D.)

in

Chemistry

By

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June-2021

*Dedicated to my
Parents*

DECLARATION

I, DIBAKAR ROY declare that the thesis entitled "***MODIFICATION OF VEGETABLE OILS AS A POTENTIAL BASE OIL AND A MULTIFUNCTIONAL LUBE OIL ADDITIVE***" has been prepared by me under the supervision of Prof. Dr. 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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PREFACE

This thesis is one of the outcomes of my effort under the supervision of Dr. Pranab Ghosh, Professor, Department of Chemistry, University of North Bengal, during the period of December 2015 to June 2021. The basis for this research originally stemmed from my passion for developing multifunctional lube oil additives and vegetable oil-based base stock. As the world moves into the age of engines, there will be a greater need to develop additives and environmentally benign stock lube that can support such operations. Therefore, it was my passion to develop additives as well as base lube that can work under severe conditions in an environment-friendly way.

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

Thank you all for your unwavering support.

ACKNOWLEDGEMENTS

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

I sincerely express my gratitude to my parents for their enormous support, sincere encouragement, inspiration, and belief.

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I sincerely acknowledge Prof. Anirban Misra, Head of the Department, and other faculty members of this department for their kind support.

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

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

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

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

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ABSTRACT

Lubricants are materials that are used for a specific purpose to reduce friction and wear between interacting surfaces and to assist mechanical motion. Lubricants usually contain base oil base lube oil with doping of a certain amount of additives. Additives are generally polymeric substances. The additives either improve the already existing property of the base oil or introduce some new feature into it.

The present research work is entitled “***MODIFICATION OF VEGETABLE OILS AS A POTENTIAL BASE OIL AND A MULTIFUNCTIONAL LUBE OIL ADDITIVE***”, concerned with the synthesis, characterization, and performance evaluation of some multifunctional organic compounds as an additive to lube oil and to evaluate the performance of chemically modified vegetable oils as additive as well as to assess their potential as alternate lubricant base stock. The additives explored in this study are typically based on Polymers made from methacrylate and vinyl acetate. Biodegradable multifunctional lube oil additives based on vegetable oils (Homo and copolymer of castor oil, rapeseed oil, rice bran oil, linseed oil with acrylate, styrene, 1 decene, α - pinene, etc) have also been prepared and investigated. The additives that were synthesized involved a free radical mechanistic pathway by thermal irradiation. Azobisisobutyronitrile (AIBN) or benzoyl peroxide (BZP) were used as free-radical initiators. Another part of this study was to synthesize epoxidized vegetable oils(Linseed oil, Castor oil, Olive oil, Soyabean oil, Sunflower oil) and subsequent epoxy ring-opening with different alcohols (2-ethyl hexanol, dodecanol, n-octanol, 1-decanol, isodecanol). Performance evaluation of these chemically modified vegetable oils revealed that they can be a replacement for mineral lube. The additives, as well as modified vegetable oils, were characterized by spectral techniques ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FT-IR), followed by molecular weight determination by Gel Permeation

Chromatography (GPC) and finally, their thermal stability was assessed by Thermo Gravimetric Analysis (TGA). The additives doped in mineral oil and modified vegetable oils were investigated for their performances as Pour Point Depressant (PPD) and Viscosity Index Improver (VII) as per the standard ASTM (American society for testing and materials) methods. Antiwear properties were ascertained by the Four-Ball Wear test (FBWT). Biodegradability analyses were also conducted for the vegetable oil-based additives by Soil Burial Method (SBT) and Disc Diffusion method (DD) to test their biocompatible nature.

The detailed research work has been divided into **PART-1, PART-2, and PART-3.**

PART-1, entitled “**Methacrylate based polymers as lube oil additive**” is then divided into two chapters, Chapter-1, Chapter-2,

Chapter-1, of Part-1, describes the **background and objective** of this study, the research, and developments made on acrylate and methacrylate-based polymers as a lube oil additive.

Chapter-2 of Part-1, describes the **synthesis, characterization, and performance evaluation of the homopolymers of Dodecyl methacrylate (DDMA) and its copolymers with vinyl acetate**. Homo-polymer of DDMA and four copolymers of dodecyl methacrylate(DDMA) and vinyl acetate (VA) at different molar ratios were synthesized by thermal free radical polymerization method using BZP as radical initiator. All the polymers were characterized by spectral studies, their molecular weights were determined by GPC and they were assessed for their performances as low-temperature flow improvers and viscosity modifiers in the base oil when doped. The results showed that the copolymers have better viscosity modification properties, better low-temperature flow, and an increase in thermal

stability. It is also observed that the viscosity modification and the pour point performance of the additives depend on the concentration of the additives in the base fluid.

**The work has been published: Ghosh P, Roy D, & Paul S, (2020), IJANS 9(6):29-36.*

PART-2 entitled “**Biodegradable multifunctional lube oil additives using modified vegetable oils.**” is again divided into four chapters, Chapter-1, Chapter-2, Chapter-3, and Chapter-4.

Chapter-1, of Part-2, contains the **background and objective** of the present study i.e. the research and development made so far in this area.

Chapter-2 of Part-2, deals with **biodegradable lube oil additives obtained from the homopolymer of castor oil and its copolymers with acrylates**. The polymers were characterized by FT-IR and NMR spectroscopy, their molecular weights were measured by GPC and their thermal stability was determined by TGA. The experimental results showed that the prepared copolymers are better additives than homopolymers. A biodegradability test of all the polymers was carried out by the Disc Diffusion method. From the above study, it was found that the homopolymer and copolymer of castor oil were effective additives in terms of Viscosity Index Improver and Pour Point Depressant, copolymers were more effective than homopolymer. Thermal stability and average molecular weight of copolymers increase with increasing the alkyl chain length of acrylate moiety. Due to the presence of a biodegradable backbone, the polymeric additives were environmentally benign also.

**This work has been published: Ghosh P, Hoque M, Roy D (2020) J Sci Ind Res, 79:537-543.*

Chapter-3 of Part-2, explores the potential of **polymers synthesized from styrene(STY) and Rapeseed oil to act as an environment-friendly multifunctional lubricant oil additive**. A detailed study in this area involved the Synthesis of the homopolymer of rapeseed oil and its copolymer with styrene using thermal irradiation and BZP as free radical initiator. Characterization of the polymer was carried out by spectral (FT-IR, NMR), GPC, and TGA. Biocompatibility and multifunctional performances (Viscosity Index Improver, Pour Point Depressant, and Antiwear) in lube oil compared to conventional additives was investigated using standard ASTM methods. Biodegradability was determined by DD and SBT degradation method. From the above study, it was found that the copolymers were found more effective than the homopolymer as Viscosity Index Improver, Pour Point Depressant, and Antiwear additive for base oil. On the other hand, the presence of rapeseed oil in the additive composition introduces excellent biodegradability too, in the additive.

**This work has been published: Ghosh P, Paul S, Roy D (2020) IJPPE 6(3):29-37.*

Chapter-4, of Part-2, explores the **performance of homopolymer of rice bran oil (RBO) and copolymers with decyl acrylate and α -pinene as multifunctional lube oil additives** at different percentages ratios using thermal irradiation and involve free radical mechanistic pathway. Characterization of the polymers was recorded by spectral technique (FT-IR and NMR spectroscopy). The Gel Permeation Chromatography method (GPC) was used to determine the average molecular weight of the prepared polymers. The Thermo Gravimetric analysis (TGA) method was used to study the thermal stability of the prepared polymers at high temperatures. Standard ASTM methods were used to investigate the performance of all the prepared polymers in two types of base oil as Viscosity Index Improver (VII)

and Pour Point depressant (PPD). The biodegradability of all the polymers was tested by the disc diffusion method and soil burial method. It was found that the average molecular weight of copolymers of RBO with DA is better than RBO with α -pinene. The viscosity index value of the homopolymer of RBO was lower than copolymers and the viscosity index value increases with increasing the percentage of DA or α -pinene in copolymers. The pour point of the lubricant compositions was found to be better for the copolymers of RBO with DA than the copolymers of RBO with α -pinene and the values decreased with the increasing concentration of the lubricant composition. The homopolymer of RBO and copolymers of RBO with α -pinene showed significant biodegradability than copolymers of RBO with DA.

**This work has been published: Ghosh P, Roy D, Hoque M (2020) J.Indian Chem.Soc:97:1-5.*

PART-3 explores the potential of “ **Modification of vegetable oils as multifunctional lube oil additives and a potential base stock**”. This part is again divided into three chapters, Chapter-1, Chapter-2, and Chapter-3.

Chapter-1 of Part-3, deals with the **background and objective** of this study i.e. the research and development in this area so far.

Chapter-2, of Part-3, describes the **opportunity of using linseed oil homo and co-polymers as multifunctional additives to lube oil**. Linseed oil-based biodegradable polymeric additives were prepared and their effectiveness as Pour Point Depressant, Viscosity Index Improver, and their Shear Stability in terms of Permanent Shear Stability Index (PSSI) were evaluated in lube oil. Polymers were proved to act as a good Pour Point Depressant, Viscosity Index Improver, and Shear Stability Improver as well. The copolymers acted like better PPDs than the homopolymer whereas the latter showed better VI improving the property. Keeping in view the environmental issue, the results were quite inspiring. Apart from being

biodegradable and eco-friendly, the linseed oil-based additives might be considered to be potential candidates to replace the traditional harmful organic chemical-based polymeric additives depending on the evaluated parameters. All the additives synthesized in this research illustrated excellent additive performances and, therefore, the outcome of this study can give a new dimension in the field of multifunctional additive research.

**This work has been published: Ghosh P, Roy D, Paul S, Yesmin S (2021) Journal of Macromolecular Science, Part A,58(1):2-7.*

Chapter-3 of Part-3, deals with the “**Synthesis characterization and performance evaluation of chemically modified vegetable oil to be used as lubricant base stock**”. Linseed oil(LO), Castor oil(CO), Olive oil (OLO), Soyabean oil (SBO), Sunflower oil(SFO) epoxide were prepared and are characterized by FTIR and NMR spectroscopy. The reaction of epoxidized linseed oil with 2 ethyl hexanol, dodecanol, n octanol, 1 decanol, and isodecanol in the presence of a catalytic amount of sulfuric acid gave rise to open-ringed products. Oxirene ring-opened products of linseed oil exhibit better low-temperature flow and high viscosity index. Ring opened product with isodecanol and 2 ethyl hexanol showed better results compared to others. ECO, EOLO, ESBO, ESFO rings were also opened through the same procedure using isodecanol and the product exhibited high Viscosity Index and excellent low-temperature flow in this case also. Ring opened product displayed better Thermo Oxidative Stability compared to those vegetable oils from which they are synthesized. Better pour point, high viscosity index, better Thermal-Oxidative stability, and better antiwear property compared to conventional mineral lube make these products an alternative to the latter and more environmentally benign.

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Appendix A

List of papers published/accepted/communicated:-

1. “*Synthesis of linseed oil-based biodegradable homo and copolymers: role as multifunctional greener additives in lube oil*”. Dibakar Roy, Sujan Paul, Sultana Yeasmin & Pranab Ghosh, *Journal of macromolecular Science, Part A Pure and Applied Chemistry*, 2021, VOL. 58, NO. 1, 2–7.
2. “*Greener additives for lube oil: Synthesis and evaluation of rice bran oil-based copolymers as potential lube oil additives*”. Dibakar Roy, Mainul Hoquea and Pranab Ghosh* . *J. Indian Chem. Soc.*, Vol. 97, No. 11a, November 2020, pp.1-5
3. “*Castor Oil and Acrylate based Copolymer as Green Additive for Lubricating Oil*”. Mainul Hoque, Dibakar Roy and Pranab Ghosh*. *Journal of Scientific & Industrial Research*. Vol. 79, June 2020, pp. 537-540.
4. “*Dodecylmethacrylate-vinyl acetate copolymer-a multifunctional performance additive for lubricating oil*”, Dibakar Roy, Sujan Paul & Pranab Ghosh* *International Journal of Applied and Natural Sciences (IJANS)*. ISSN (P): 2319–4014; ISSN (E): 2319–4022 Vol. 9, Issue 6, Oct–Nov 2020; 29–36.
5. “*Greener Lubricant Formulation: Rapeseed Oil Based EcoFriendly Lube Oil Additives*”. Sujan Paul, Dibakar Roy, Pranab Ghosh*. *International Journal of Petroleum and Petrochemical Engineering*. Volume 6, Issue 3, 2020, PP 29-37 ISSN No.: 2454-7980.
6. “*Performance evaluation of chemically modified vegetable oils towards the development of biodegradable greener lubricant base stock*”. Accepted in *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* manuscript ID is LMSA-2021-0124.

Appendix B

List of seminars/symposiums/conferences attended

- UGC sponsored seminar on “*Current Trends in University –Industry Linkages*” organized by the Department of Chemistry, University of North Bengal on March 24, 2017.
- International seminar on “*International Year of the Periodic Table of Chemical Elements-2019*” organized by the Department of Chemistry, University of North Bengal during November 22-23, 2019.
- International Seminar on *Frontiers in Chemistry 2018* organized by Department of Chemistry, University of North Bengal & CRSI North Bengal Local Chapters on August 27, 2017
- 19th CRSI National Symposium in Chemistry (CRSI NSC-19) organized by Department of Chemistry, University of North Bengal, Darjeeling, India, July 14-16, 2016.

Appendix C

Abbreviations

1. AIBN – Azobisisobutyronitrile
2. ASTM – American Society for Testing and Materials
3. A.W.-Anti Wear
4. BO1 – Base oil 1
5. BO2 – Base oil 2
6. BZP – Benzoyl peroxide
7. CO – Castor oil
8. CFI – Cold flow improvers
9. DD- Disc diffusion
10. DA – Decyl acrylate
11. DDA – Dodecyl acrylate
12. DDMA – Dodecyl methacrylate
13. ECO-Epoxy castor oil
14. ELSO-Epoxy linseed oil
15. EOLO-Epoxy olive oil
16. E.Ps.-Extreme Pressure additives
17. ESBO-Epoxy soyabean oil
18. ESFO-Epoxy sunflower oil
19. F.Ms.-Friction Modifiers
20. FT-IR-Fourier transformed infrared
21. GPC – Gel Permeation Chromatography
22. HPLC – High-Performance Liquid Chromatography
23. IDA-Isodecyl acrylate
24. IOCL – Indian Oil Corporation Limited

25. IR – Infrared
26. KV – Kinematic viscosity
27. LSO-Linseed oil
28. M_n – Number average molecular weight
29. M_w – weight average molecular weight
30. NMR – Nuclear magnetic resonance
31. 1-D- decene
32. OA – Octyl acrylate
33. OLO- Olive oil
34. PDI-Polydispersity Index
35. PPD – Pour point depressant
36. PSSI-permanent sheer stability index
37. RBO-Ricebran oil
38. RO-Rapeseed oil
39. SBDT – Soil burial degradation test
40. SBO- Soyabean oil
41. SFO- Sunflower oil
42. ST-Styrene
43. TMS – Tetramethylsilane
44. TGA – Thermogravimetric analysis
45. VI – Viscosity index
46. VII – Viscosity index improver
47. VM – Viscosity modifier
48. ZDDP – Zinc dialkyl dithiophosphate

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GENERAL INTRODUCTION

A lubricant is a substance that is incorporated in an engine to reduce friction and to ease constant movement between metal surfaces in contact[1], thus reducing heat generated on prolonging friction. This property of minimizing friction by a lubricant is known as lubricity. The history of the use of lubricants is thousands of years[2]. During the time of the pyramids, building stones were slid on oil-impregnated lumber. In ancient civilization, soaps were used to reduce friction in wheels. Lubricants based on plant oils and animal fats were used in the Roman era. But with the invention of vacuum distillation of petroleum in the early 1900s, the focus shifted toward petroleum-based materials[3]. Again, with the demanding complexities of modern engines, the demands placed upon the lubricant also became increasing.

To assist the relative motion and to prevent damages, lubricants in form of solid, liquid, or gases are intruded between two surfaces. A gaseous film is usually favored for low contact stress while liquid films are widely used in a most modern engine to perform lubrication over a while. The solid films are usually practical for contacts with low sliding speed[4-5]. The chief ingredient of lubricating oil is the base oil and depending upon nature[4-5], it might be classified as mineral base lube oil, synthetic-based lube oil, or as a lube oil of bio origin.

- **BASE LUBE**

The most commonly used commercial lube oil around the globe is the mineral-based lube and is derived directly or indirectly from refining petroleum. Base oil is extracted as a heavier part of the refining process of crude oil. It is composed of a complex mixture of hydrocarbons and generally includes aromatic, olefinic, paraffinic (linear/branch), and naphthenic hydrocarbons, molecular weights ranging from C₂₀-C₇₀[6]. The synthetic lube oil generally includes poly alpha-olefins,

synthetic esters, silicones, etc., Bio-based lube derived from plants and animal sources.

The lubricating oil provides a fluid layer impregnated between moving metal surfaces and thus, reduces friction and the heat generated by the engines. It also has a huge number of different purposes like increasing liquidity at low temperature reducing temperature variation of viscosity i.e modifying Viscosity Index, wears prevention, inhibiting the formation of rust, protecting the engines against corrosion, etc[7-8].

- **ADDITIVES**

Engine lubricating oil makes up nearly one-half of the world's lubricant market but unfortunately, they do not meet all the requirements of modern engines. Engine oil is, therefore, formulated with a mixture of base oil and a specifically manufactured additive for certain operating conditions. **Additives** are materials that are specifically devised for enhancement of the physical and chemical properties of the base oils, which as a consequence results in enhancing the equipment life and boosting the lubricant performance[9-14]. Devoid of any additives, even the best base oils cannot satisfy all types of industrial requirements. The type and quantity of additives are chosen largely depend upon the lubricant in which it is going to be used (gear oils, hydraulic oils, engine oils, etc.) and on the actual operating environments (materials, loads, temperature, etc.).

Lubricant performance depends collectively on the base oil, the additive used, and its formulation. Usually, only one type of base stock serves the purpose of a particular lubricant but sometimes mixtures of base oils are also used together, doping with a variety of additives. Besides, no single additive can satisfy the desirable performance necessary for the efficient working of an engine. Thus, several

additives are required to satisfy the original equipment manufacturer (OEM) needs and also the consumer needs. Additives are used at different concentrations ranging from 0.05 % to more than 10% by weight of the lubricant. The proportion of additives may even reach 30%[15]. It is obvious that A lubricant without the proper additive is bound to get contaminated by subsequent degradation products of the base oil and, therefore, more frequent systematic oil changes are required.

- **CLASSIFICATION OF ADDITIVES**

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

- **METAL SURFACE PROTECTOR**

They are also known as film-forming agents. This type of additives includes extreme pressure(EP) additives[11-12], anti-wear(AW)[16-17], rust, and corrosion inhibitors[18]or friction modifier(FM). These additives protect the metal surface by making a protective film also called tribo film through adsorption or chemical reaction and thereby inhibit the formation of rust and control wear during prolonged friction in the engine. The three kinds of additives(FM, AW, EP) are collectively called Tribo-Improvers. Detergent and dispersant additives are also considered in this group. Detergents keep surfaces free from deposits and dispersants keep insoluble soot particles suspended by micelles formation with the oleophilic and oleophobic part in their molecular composition thereby protecting the metal film free from any deposits.

- **PERFORMANCE-MODIFIERS**

These additives improve the performances of the lubricants and include viscosity index improver (VII)[6-19], pour point depressants(PPD)[20-21], Additives with high viscosity index keep viscosity change at marginal over a wide temperature range. Lube doped with high PPD inhibits wax crystal formation at lower temperatures hence modifying the attribute of low-temperature flowability in lube oil.VII and PPD additives are also called Rheo Improvers

- **LUBE PROTECTOR**

Out of the many causes of engine malfunction, the major cause is poor lubricant quality arising out of lubricant contamination, deposit formation, oil thickening, ring sticking, etc. The additives which are used to control these actions are known as lubricant protective additives. These additives protect the lubricant instead of the machinery equipment. These types of additives include antioxidants[22], anti-foaming agents[23], Antioxidants terminate the pathways of initiation or propagation or both by quenching free radicals or active molecules. The radical is produced due to thermal or shear stress or due to metal-ligand interaction in the interface. Additives of different kinds and their function are summarised in the following Table 1.

METAL SURFACE PROTECTOR			
ADDITIVE TYPE	PURPOSE	TYPICAL COMPOUNDS	FUNCTIONS
Anti-Wear Agent	Reduce friction and wear, and prevent scoring and seizure	Zinc dithio phosphates, organic phosphates, and acid phosphates; organic sulfur and chlorine compounds; sulfurized fats, sulfides, and disulfides	Chemical reaction with the metal surface to form a film with lower shear strength than the metal, thereby preventing metal-to-metal contact
Corrosion & Rust Inhibitor	Prevent corrosion and rusting of metal parts in contact with the lubricant	Zinc dithio phosphates, metal phenolates, basic metal sulfonates, fatty acids, and amines	Preferential adsorption of polar constituent on the metal surface to provide a protective film and/or neutralization of corrosive acids
Detergent	Keep surfaces free of deposits and neutralize corrosive acids	Metallo-organic compounds of barium, calcium, and magnesium phenolates, phosphates, and sulfonates	Chemical reaction with sludge and varnish precursors to neutralize them and keep them soluble
Dispersant	Keep insoluble soot dispersed in the lubricant	Polymeric alkyl thio phosphonates and alkyl succinimides, organic complexes containing nitrogen compounds	Contaminants are bonded by polar attraction to dispersant molecules, prevented from agglomerating, and kept in suspension due to the solubility of dispersant

PERFORMANCE MODIFIER			
ADDITIVE TYPE	PURPOSE	TYPICAL COMPOUNDS	FUNCTIONS
Pour Point Depressant	Enable lubricant to flow at low temperatures	Alkylated naphthalene and phenolic polymers, polymethacrylates	Modify wax crystal formation to reduce interlocking wax network
Viscosity Improver	Reduce the rate of viscosity change with temperature	Polymers and copolymers of methacrylates, butadiene olefins, and alkylated styrenes	Polymers expand with increasing temperature to counteract oil thickening

LUBE PROTECTOR			
ADDITIVE TYPE	PURPOSE	TYPICAL COMPOUNDS	FUNCTIONS
Anti-Foaming	Prevent lubricant from forming a persistent foam	Silicone polymers and organic copolymers	Reduce surface tension to speed collapse of the foam
Anti-Oxidant	Retard oxidative decomposition	Zinc dithiophosphates, hindered phenols, aromatic amines, sulfurized phenols	Decompose peroxides and terminate free-radical reactions
Metal Deactivator	Reduce the catalytic effect of metals on oxidation rate	Organic complexes containing nitrogen or sulfur, amines, sulfides, and phosphites	Form inactive film on metal surfaces by complexing with metallic ions

Table 1: Lube oil additive of different types

The present study includes the synthesis of some polymeric additives (acrylate, vegetable oil-based) and evaluation of their performance in the base oil as pour point depressant and viscosity index improver, in addition, to synthesize modified vegetable oils and their performance evaluation as stated above so that to identify their potential that they can be used as potential lube base stock. A brief background of these types of additives is described below.

- **POUR POINT DEPRESSANT**

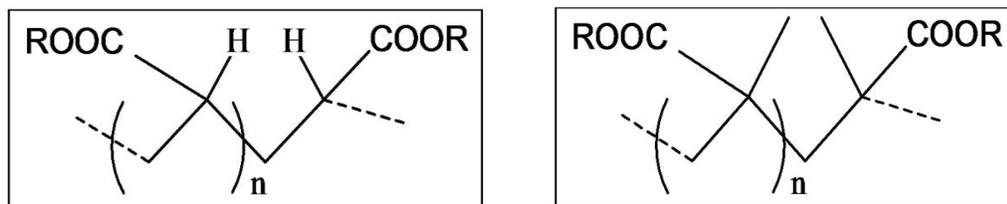
The low-temperature properties are an important part of any lubricating system. The natural paraffinic mineral base oils are always associated with some waxy materials (linear high molecular weight hydrocarbon). At higher temperatures, all the high molecular weight paraffin's remain in a dissolved state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

The higher the wax content in the oil, the greater the flow problems are. Generally, the pour point is proportional to the amount of wax present in the oil and a high pour point means high paraffin content in the oil. During the refining process,

most of the wax present in the crude oil is removed to obtain the base oil but some wax is still desirable for achieving the proper viscosity. The complete removal of paraffinic wax from lube oil is expensive and is very difficult. Extensive dewaxing of the base oil also increases the formation of carbon deposits and decreases the oxidation stability of base oils.

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

Polyalkyl acrylates and methacrylates[31-32] fumarate copolymers[33], ethylene-vinyl acetate copolymers[34], alkyl esters of styrene-maleic anhydride copolymers[35], and few recently used vegetable oil polymers are some of the important additives used as PPD in lubricants[36].



Polyalkyl acrylate

Polyalkyl methacrylate

Figure 1: Structure of some commonly used pour point depressants

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

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



Figure 2: Photomicrograph images of pure lube oil (SN150) at -6°C, & lube oil + 4% (w/w) of DDMA homo polymer at -11.5 °C[58]

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

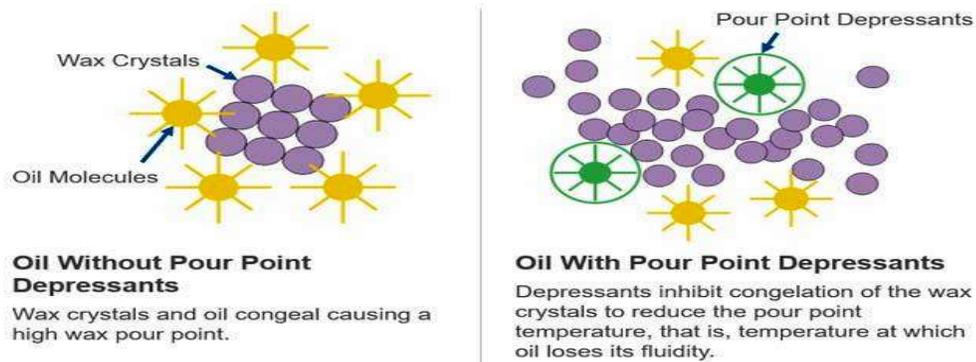


Figure 3: Schematic representation of the action mechanism of additives on wax crystals

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

- **VISCOSITY MODIFIER**

The viscosity of a fluid is the measure of its resistance to steady deformation by tensile stress or shear stress or its resistance to flow. For liquids, it generally refers to the informal concept of thickness. The viscosity of an oil is significant for its cooling and lubricant properties. The effectiveness of lubricating oil in minimizing friction and wear is to a great extent influenced by its viscosity. For oil of high

viscosity, the solid surfaces in contact are fully separated by a thin film of the oil. This condition is known as hydrodynamic lubrication. For low viscous oil, the hydrodynamic pressure generated is insufficient to fully separate the surfaces and, therefore, the two opposing surfaces come into contact with each other. This condition is known as boundary lubrication. The optimum viscosity required for any lubricated system depends on the load to be supported and also on the relative velocities of the surfaces.

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

The dynamic viscosity of a fluid is its resistance to shearing flows where adjacent layers with different speeds move parallel to each other. It is expressed in the unit Pa.S (Pascal-second). On the other hand, the kinematic viscosity of a fluid is the ratio of its dynamic viscosity to the density, both measured at the same temperature. It is commonly expressed in the unit centistokes (cSt; 1 cSt = 0.01 Stoke), whereas its CGS unit is expressed as Stoke.SI unit of kinematic viscosity, meter square per second (m^2/s ; $1 \text{ m}^2/\text{s} = 10^6 \text{ cSt} = 10^4 \text{ St}$).

The viscosity of lubricating oil is also a function of temperature and it should vary as little as possible with the increase or decrease of temperature. It is, therefore, necessary to have some method of determining the viscosities of oils at temperatures other than those at which they are measured. Hence, two different temperatures are

selected (usually 40°C and 100°C) for measuring the viscosities and then plotting these points on special viscosity-temperature charts developed by ASTM (American Society of Testing and Materials)[42]. Viscosity index (VI) is an arbitrary measure to express the change of viscosity with temperature variations[43]. A low VI indicates a relatively high rate of change of viscosity with temperature i.e. it will thin out more at the higher temperature. On the other hand, a higher VI value signifies a lesser effect of temperature on viscosity i.e. the oil will thin out less with increasing temperature[44]. It has been found that the addition of certain oil-soluble polymeric materials to base oil can greatly improve its viscosity properties and thereby the viscosity index. The additives that improve the viscosity index of the oil are known as viscosity index improvers (VII) or alternatively known as viscosity modifiers (VM) [45-46]. VIIs keep the viscosity of the oil at a satisfactory level which provides stable oil film even at increased temperature.

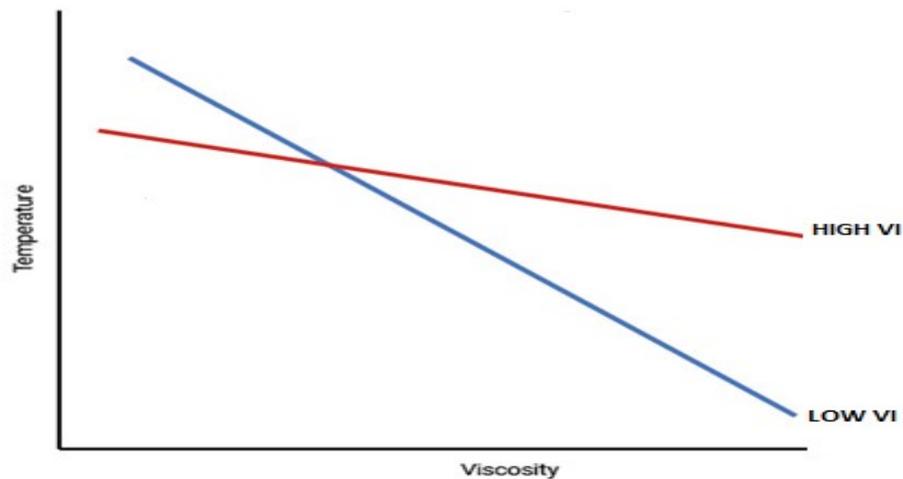


Figure 4: Temperature dependence of viscosity

Acrylate and methacrylate-based polymers are the most commonly used VIIs in lubricants[47]. Some of the other reported VIIs are poly isobutylenes (PIB), olefin copolymer (OCP)[48], ethylene α -olefin copolymers, styrene isoprene copolymer

(SIP), polybutadiene rubber (PBR), poly alkyl styrene[49], maleic anhydride based polymers, and even some vegetable oil-based polymers, etc[36].

The performance of an additive as VII depends on its molecular weight, chemical behavior, shear stability, and also on its solubility in the base oil[50]. The mode of action of VII was first established by Selby in 1958[51]. However, the report presented lacked any physical data supporting the proposed mechanism. Later, in a work of Flory, it was stated that the radius of gyration, R_g , of additive molecules depends on the interactions between the solvent molecules and the polymer chains. The affinity among the polymer chains, in a “poor” solvent, results in the collapse of the polymer chains into compact polymer globules. However, in the case of a “good” solvent, where repulsive forces act between the polymer chains, there occurs an expansion of the globule into random coils[52]. With the rise of temperature, an enhancement in the power of solvation is observed for the solvent and consequently, there occurs an increase in the polymer-solvent interaction. As a result, the polymer molecules further change their shape from tight coil to expanded random coil and thus offset the normal viscosity reduction with increasing temperature. The process of expansion of the coil is reversible as with decreasing temperature the coil contraction occurs[53-55]. Again, the increasing polymer content in the solvent increases the total amount of polymer globules in the solution bringing about a higher viscosity index for the oil.

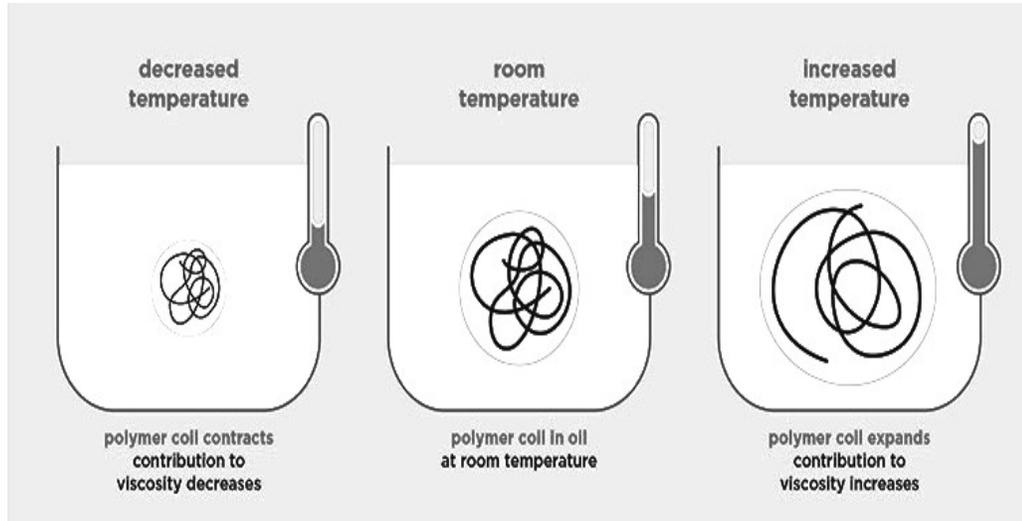


Figure 5: Coil expansion model of viscosity index improvers

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

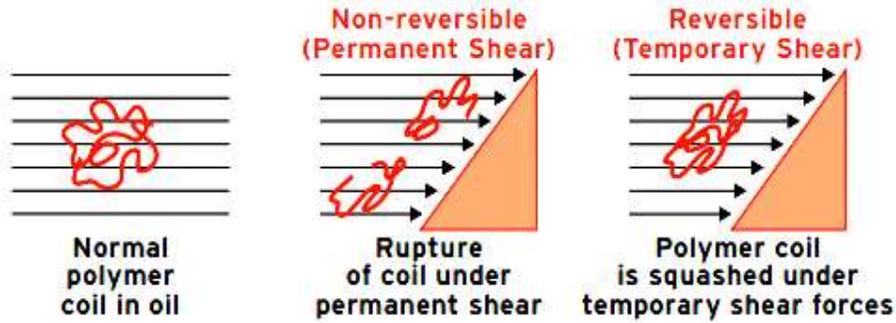


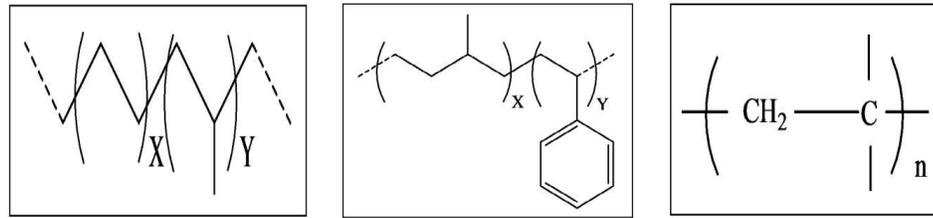
Figure 6: Temporary and permanent shearing of viscosity index improvers

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

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

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

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



Ethylene-propylene copolymer (OCP), Styrene-isoprene copolymer (SIP), Polyisobutylene (PIB)

Figure 7: Structure of some commonly used viscosity index improvers

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

- **TRIBO IMPROVER**

This type of additives is further classified into Friction modifiers (FM), Antiwear(AW), & Extreme Pressure(EP) Additives. FM s are acting low-temperature pressure load where AW s prevent wear in comparatively higher temperature pressure environment. A Stribeck curve in Figure:-9 showed that their effects overlap with each other[57].

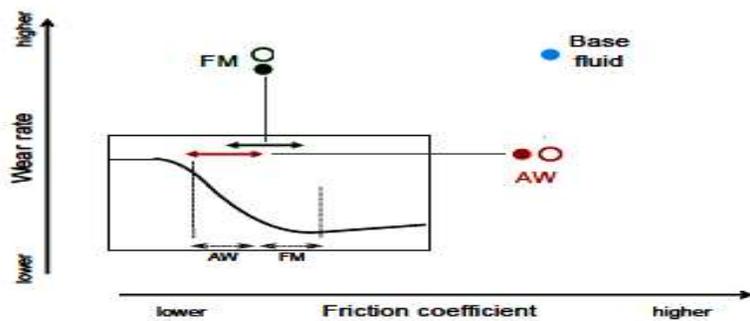


Figure 8: Overlapping effect of tribo improvers

Wear is the deformation of shape at the tribological contact. Wear is a natural process of continuous rubbing of metal parts in a machine. Zinc diethyldithio phosphate (ZDDP) is an effective friction modifier, antiwear, and antioxidant additive and is commonly used in several kinds of lube. The working mechanism of it as AW by surface analysis revealed the formation of inorganic compounds of Zn, S,&P whereas in comparatively low temperature and applied pressure range i.e. in moderate engine condition ZDDP mainly perform through adsorption and thus making a protective film[57].

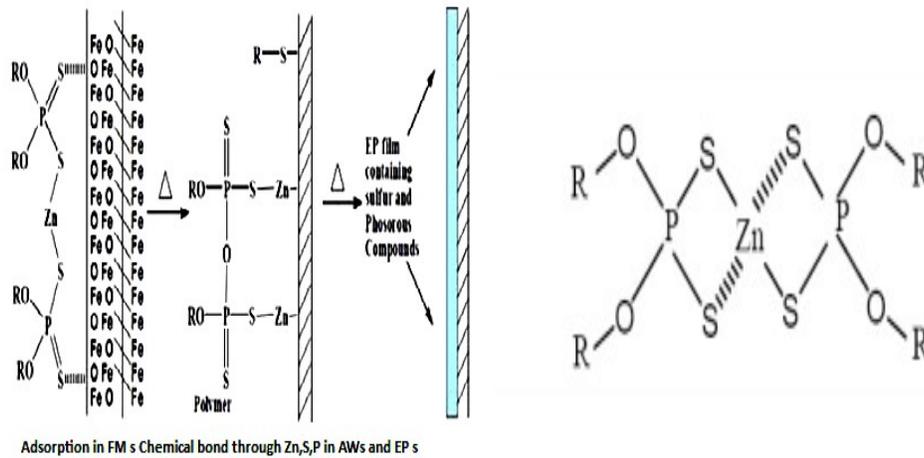


Figure 9: Chemical structure & working of ZDDP as FMs and AWs

The additives may work in an interface (AW, Dispersant,) or bulk(PPD, VII). They can act either chemically (EPs, AWs) or Physically (FMs, Dispersants). According to working function they can be further considered as Tribo-improver, Maintainers, or Rheo –improver relationship between different types of additives is summarised in Table:-2.

Working mechanism	Working site		
	Interface		Bulk
Chemically	Extreme Pressure additive	Anti wear agent	Corrosion Inhibitor
Physically	Dispersant	Anti foam agent	Demulsifier
			Detergent
			Anti-oxidant
			Pour Point depressant
			Viscosity modifier
Working function	Tribo improver	Maintainers	Rheo improvers

Table 2: Relationship of different kinds of additives according to the working mechanism, working site & working function[57].

• **THE OBJECTIVE OF THE PRESENT WORK**

The present work is concerned with the synthesis, characterization, and performance evaluation of some multifunctional organic polymeric additives as well as additives derived from vegetable oil polymer for lube oil and to evaluate the potential of chemically modified vegetable oils as alternate lube base stock. Acrylate, methacrylate based polymers were studied as multifunctional additive. Other molecules used in this study are vinyl acetate, styrene, 1-decene, and α pinene. Some biodegradable multifunctional lube oil additives based on vegetable oils (linseed oil, rapeseed oil, rice bran oil, and castor oil) have also been investigated. Vegetable oil indeed has a fairly high viscosity index and low-temperature flowability compared to mineral-based lube but these are thermally unstable and are prone to auto-oxidation as major fatty acid contains in triglyceride moiety contains unsaturation. Fatty acid composition of some common vegetable oil are summarised in Table 2, and properties of these oils are summarised in Table 3.

Vegetable Oils	C12:0	C14:0	C16:0	C18:0	C16:1	C18:1	C18:2	C18:3	Others
Soybean oil	-	-	11-12	3	0.2	24	53-55	6-7	-
Sunflower oil	-	-	7	5	0.3	20-25	63-68	0.2	-
Rapeseed oil	-	-	4-5	1-2	0.21	56-64	20-26	8-10	9.1 (20:1)
Palm oil	-	1	37-41	3-6	0.4	40-45	8-10	-	-
Rice bran oil	-	-	20-22	2-3	0.19	42	31	1.1	-
Cotton seed oil	-	1	22-26	2-5	1.4	15-20	49-58	-	-
Coconut oil	44-52	13-19	8-11	1-3	-	5-8	0-1	-	-
Corn (Maize) oil	-	-	11-13	2-3	0.3	25-31	54-60	1	-
Peanut/Ground nut	-	-	10-11	2-3	0	48-50	39-40	-	-
Sesame oil	-	-	7-11	4-6	0.11	40-50	35-45	-	-
Safflower oil	-	-	5-7	1-4	0.08	13-21	73-79	-	-
Karanja oil	-	-	11-12	7-9	-	52	16-18	-	-
Jatropha oil	-	1.4	13-16	6-8	-	38-45	32-38	-	-
Rubber seed oil	-	2-3	10	9	-	25	40	16	-
Mahua oil	-	-	28	23	-	41-51	10-14	-	-
Tung oil	-	-	2.67	2.4	-	7.88	6.6	80.46 *	-
Neem oil	-	-	18	18	-	45	18-20	0.5	-
Castor oil	-	-	0.5-1	0.5-1	-	4-5	2-4	0.5-1	83-85 #
Linseed oil	-	-	4-5	2-4	0-0.5	19.1	12-18	56.6	-
Olive oil	-	-	13.7	2.5	1.8	71	10	0-1.5	-

* Alpha-eleostearic acid. # Ricinoleic acid.

Table 3: Fatty acid composition of some common vegetable oils[56].

Vegetable Oils	Iodine Value	Pour Point (°C)	Cloud Point (°C)	Kinematic Viscosity at 40 °C (mm ² /s)	Flash Point (°C)	Density at 15 °C (g/cm ³)
Soybean oil	138-143	-12	-4	29	254	0.914
Sunflower oil	125-140	-15	-9.5	36	274	0.916
Rapeseed oil	98-105	-15	-2	35	246	0.912
Palm oil	48-58	23.6	25.2	39.4	252	0.919
Rice bran oil	103	13	16	38.2	184	0.906
Cotton seed oil	90-119	-4.5	-0.5	34	234	0.918
Coconut oil	8-11	12.7	13.1	27	266	0.918
Peanut/Ground nut/ Arachis oil	84-100	-7	4.5	40	271	0.903
Sesame oil	104-116	-11	-8	36	260	0.918
Karanja oil	81-90	-4	2	38.8	212	0.9358
Jatropha oil	82-98	-6	11	34	225	0.94
Rubber seed oil	104	18	25	33.89	228	0.928
Mahua oil	58-70	11	20	37.18	238	0.945
Neem oil	81	7	13	35.8	200	0.918
Castor oil	83-86	-21	-18	251	229	0.960
Linseed oil	168-204	-15	5	26-29	241	0.938
Safflower oil	145	-7	-2	28.3	260	0.914
Olive oil	75-94	-14	-11	39	177	0.918

Table 4: Physical properties of some common vegetable oils[56].

The oil we used in this study was Linseed oil, Castor oil, and Rapeseed oil as non-edible oil, and Soya bean, Sunflower, Ricebran, and Olive oil as edible oil. The additives (polymeric) were synthesized by thermal irradiation in presence of initiators like azobisisobutyronitrile (AIBN) or benzoyl peroxide (BZP). Another part of this study was to synthesize epoxidized vegetable oils(Linseed oil, Castor oil,

Olive oil, Soyabean oil, Sunflower oil) and subsequent epoxy ring-opening by different alcohols (2-ethyl hexanol, dodecanol, n-octanol, 1-decanol, dodecanol). Performance evaluation of these chemically modified vegetable oils revealed that they can be a replacement for mineral lube.

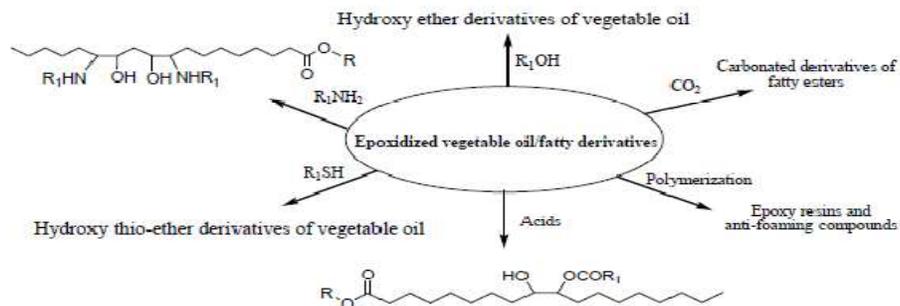


Figure 10: Different pathways to modify epoxy vegetable oil[56].

The additives, as well as modified vegetable oils, were characterized by spectral techniques ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FT-IR), followed by molecular weight determination with gel permeation chromatography (GPC) and finally, assessment of their thermal stability was done by thermogravimetric analysis (TGA). The additives doped in mineral oil and modified vegetable oils were investigated for their performances as pour point depressant (PPD) and viscosity index improver (VII) as per the standard ASTM (American society for testing and materials) methods. Antiwear properties were ascertained by a four-ball wear test. Biodegradability analyses were also conducted for the vegetable oil-based additives by soil burial method and disc diffusion method to test their biocompatible nature.

REFERENCES

References are given in BIBLIOGRAPHY under “**General introduction**”.

PART-1

**METHACRYLATE-BASED
POLYMERS AS A LUBE OIL
ADDITIVE**

PART-1/CHAPTER-1

BACKGROUND AND OBJECTIVE OF THE PRESENT INVESTIGATION

Lube oil is introduced between metal surfaces in an engine to reduce friction and heat generated during prolonged mechanical shear. A good quality lube should protect itself from a destructive Thermo Oxidative environment inside the engine, protect the metal surface from corrosion, and have fair rheological properties. But base lube alone cannot satisfy all requirements of a modern multi-valve, multi-chamber gasoline or diesel engine. The base oils are, therefore, blended with different additives in an expectation to improve their lubrication properties[1]. Additives are generally of a different kind depending upon the requirements. They are selected according to the property need to be modified of base oil and can be blended as a single compound or even as a mixture to attain the desired result.

The success of a lubricant is to deliver the highest level of performance depends upon the interactions of the additives with the base oil following the particular requirement of an engine. Without aided by proper additives, the oil may not protect the engine properly and might lead to engine damage.

As discussed in the “General Introduction” chapter, different additives are of different chemical composition and are manufactured to perform certain functions inside the engine. Surface protector additives act as tribo improvers by forming film between metal parts either by adsorption or by the chemical bond formation and minimize surface contact and prevent wear. Detergent and dispersant additives neutralize corrosive acid and dispersed soot particles and prevent them from deposition on metal surfaces respectively. Rheo improvers modify low-temperature flow (Pour Point Depressant) and modify viscosity for the proper functioning of lube

in a wide temperature variation (Viscosity index improver). An antioxidant is another kind of additive protecting lube from the oxidative environment. No single additive can satisfy the desirable performance necessary for the efficient working of an engine. Thus, several additives are required to satisfy the original equipment manufacturer (OEM) needs and also the consumer needs. Additives are used at different concentrations ranging from 0.05 % to more than 10% by weight of the lubricant. The proportion of additives may even reach 30%. It is obvious that a lubricant without the proper additive is bound to get contaminated by subsequent degradation products of the base oil and, therefore, more frequent systematic oil changes are required. (Zinc diethyl dithiophosphate) ZDDP is a kind of additive that can act as a friction modifier, viscosity improver, and pour point depressant, but it is associated with serious environmental hazards. Among the other desirable properties of additive Viscosity Index Improvers (VII) and Pour Point Depressant (PPD) are the two most important categories. Viscosity is defined as fluid resistance to moving. Viscosity drastically changes with temperature and it is measured with viscosity index. A higher viscosity index implies a lower change of viscosity with temperature and it is desirable inside the engine. VII added to lube to attain this property [11-23]. PPD are substances that reduce wax crystal formation at low temperature maintaining a steady flow of lubricant at lower temperature regions [24-38]. These two properties discussed above are complementary to each other.

Our present study on methacrylate and vinyl acetate homo and copolymers was prepared with an objective to replace harmful additives as well as to ascertain the behavior of the prepared polymers as multifunctional additives.

Various studies of previous researchers following the present line of investigation regarding VII and PPD are being discussed in the following paragraphs.

1. In the year 1937, Rohm and Haas patented the first polymeric PPD, poly alkyl methacrylates (PAMAs) based on waxy alkyl groups. A few years later, Ruehrwein reported the action of n-alkyl polymethacrylate as PPD in the series of methacrylate containing 12 to 18 carbon chains. It was reported that the longer alkyl chain polymers were effective as PPD in the case of high-temperature pour oils, while the shorter alkyl chain polymers were efficient on lower temperature pour oils[39].
2. Gavlin et al. analyzed some acrylates and methacrylates for their PPD properties. Dodecyl methacrylate was chosen by the authors for their work and it was their first acrylic polymer to have excellent PPD properties[40].
3. Several copolymers based on alkyl fumarate and vinyl acetate were synthesized by Borthakur et al. and their effectiveness as PPD was tested on Indian crude oils[41].
4. El-Gamel et al. in the year 1997 reported the synthesis of α -olefin-alkyl methacrylate as PPD for waxy residue fuel. Their study suggested that the polymer containing alkyl group consisting of 21 carbon chain are superior as PPD[42].
5. Abdel-Azim et al. in the year 2006 reported additives based on different esters of acrylic acid and different ratios of styrene to be used as PPD. They reported that the effectiveness of the prepared additives as PPD decreases by increasing the styrene content in the feed[45].
6. Khidr, in the year 2007 prepared four copolymers made from 1-octene or 1-tetradecene and maleic anhydride and esterified them with dodecyl or NAFOL 1822B alcohol. The effectiveness of the copolymers as PPD was tested for crude

oil and it was found that the alkyl chains of the copolymers are a crucial factor for proper interaction of the additives with the crude oil[46].

7. In 2008, Farag prepared different copolymers by varying the molar concentration of cinnamoyloxy ethyl methacrylate and octadecyl acrylate and the PPD performance and rheological characteristics were studied using different concentrations of the prepared additives for two different waxy crude oils[47].
8. El-Ghazawy et al., in the year 2010 reported a novel PPD for waxy crude oil based on alkyl acrylate terpolymers[48]
9. In another work, Khidr reported the preparation of some copolymeric and terpolymeric additives of maleic anhydride and alkyl acrylates of different chain lengths. The polymers were tested for both PPD and wax dispersants for paraffin gas oils and satisfactory results were obtained for the additives[49].
10. Jung et al. in the year 2011, Synthesized and analyzed methacrylate-based polymers as effective flow improvers. Pour point results in doped lube oil were also promising[50].
11. In the year 2014, Decyl acrylate and styrene-based polymers, synthesized by Ghosh et al. exhibit excellent PPD result in doped lube[51].
12. The effectiveness of the polymers like polyvinyl palmitate, polyvinyl caprylate, and copolymers of vinyl palmitate with vinyl acetate as VII were analyzed by Port et al. and found that the additives are efficient viscosity modifiers for lubricating oils[52].
13. Nassar et al. made a comparative study of some polymeric additives prepared by copolymerization of different moles of styrene with different acrylates (decyl, 1-dodecyl, 1-tetradecyl, and hexadecyl) as VIIs. The viscosity modification

properties of the additives were found to increase with the increasing molecular weight of the prepared copolymers[56].

14. Jukic et al. reported dodecyl methacrylate, octadecyl methacrylate, and styrene-based terpolymers as VII for lubricating oil. The amount of styrene in the additive was restricted to 25% by weight. The group reported that the viscosity index increased with increasing molar mass of the additive but the opposite effect was obtained by increasing the styrene percentage[57].
15. Ahmed et al. prepared some additives through polymerization of vinyl acetate and maleic anhydride with different acrylates and studied the effect of concentration, molecular weight, and alkyl chain length on the viscosity index and pour point values of the additives[60]
16. Ghosh et al. reported copolymers of styrene and decyl acrylate and their compatibility as PPD and VM[62].
17. In other work, polymers of myristyl acrylate were synthesized by two different methods viz. thermal method and microwave-assisted method, and their potential to act as PPD and VII were evaluated and compared[63].

REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-1 of Part-1**”.

PART-1/CHAPTER-2

DODECYL METHACRYLATE –VINYL ACETATE HOMO AND COPOLYMERS- A MULTIFUNCTIONAL PERFORMANCE ADDITIVE FOR LUBRICATING OIL

1.2.1 INTRODUCTION

The primary component of lubricating oil used in the modern machine to reduce rolling friction and heat generated is base oil and is derived from a petroleum source, but base oil alone cannot satisfy all engineering requirements. Hence, they are blended with some chemical entities to modify lube behavior or to add extra attributes needed to call additives[1]. Among the various important additives, PPDs, VIIs, and AWs are of prime importance for the effective formulation of the lubricant for their field application. Poly alkyl acrylates, poly alkyl methacrylates, styrene-butadiene copolymers are some of the widely used additives applied in specific composition and architecture for improving the tribological and rheological properties of base lubricating fluids[2]. However, most of the reported additives developed in this area so far, function either simply as VM or as PPD. Moreover, despite their promising properties, only a few of them have been evaluated as multifunctional additives. Therefore, in continuation of our quest to further explore this area of chemistry and to synthesize the effective multifunctional performance additives for lube oil at a reduced cost, this investigation is an attempt to ascertain whether a combination of acrylate and VA group can effectively control the rheological properties of the base fluid. This present work thus reveals the synthesis, characterization, and performance evaluation of additives based on the copolymers of long-chain dodecyl methacrylate and vinyl acetate[15]. A comparative assessment of

the outcome of copolymers as an additive in contrast to the homopolymer of dodecyl methacrylate was also studied. Homopolymer of the prepared dodecyl methacrylate (DDMA) monomer was synthesized and a series of copolymers of it were prepared by varying the ratio between DDMA and vinyl acetate (VA) by free radical polymerization using BZP as initiator. The synthesized polymers were characterized by spectral studies (FT-IR, ¹HNMR, ¹³C NMR) and by Gel Permeation Chromatography (GPC)[13]. Thermogravimetric analysis (TGA) was also carried out to investigate the thermal behavior of the polymers at high temperatures. Performances of the polymers as additives and their responses as PPD and viscosity modifiers in the base oil were evaluated by standard ASTM methods in terms of pour point and viscosity index[15]. Wax crystallization behavior of the additives was analyzed by Photo Micrographic image. The copolymers showed better thermal stability, better flow improving efficiency, and induced better viscosity modification than the homopolymer. It is also observed that the viscosity modification and the pour point performance of the additives depend on the concentration of the additives in the base fluid.

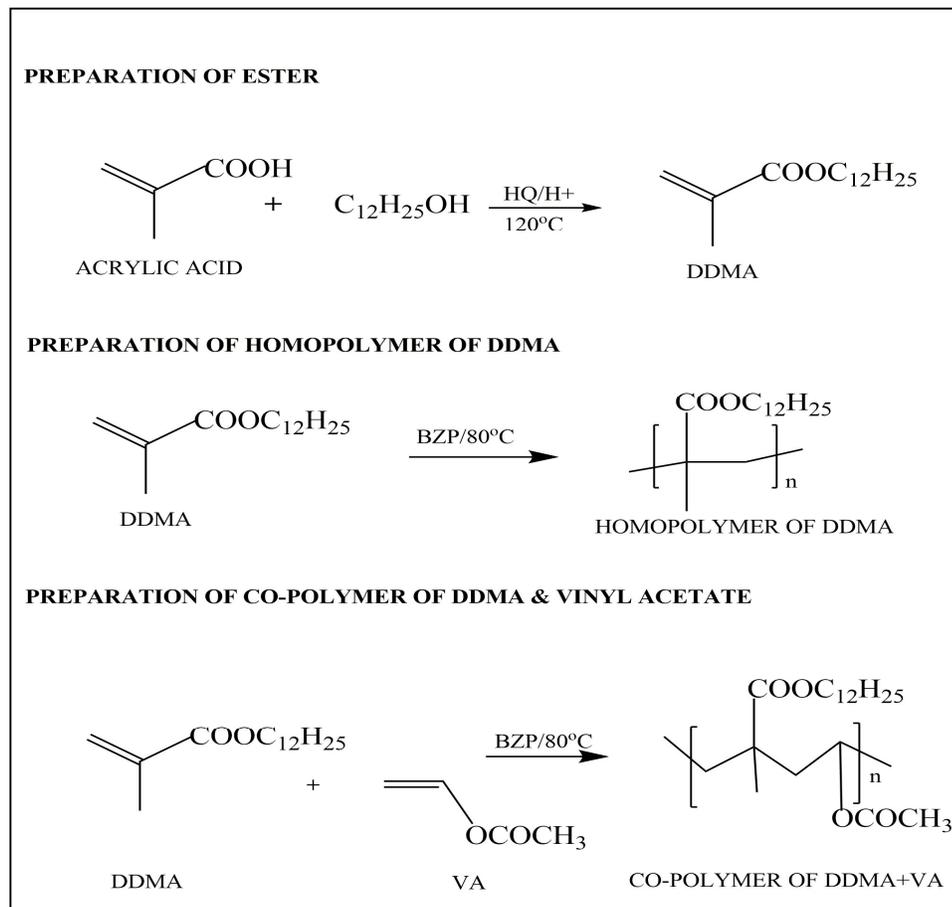
1.2.2 EXPERIMENTAL

1.2.2.1 MATERIALS USED

Dodecyl alcohol (DDA) methacrylic acid was obtained from SRL Pvt., Ltd., (India). and hexane was from SD Fine-Chemical Ltd., (India). Vinyl acetate (VA) was purchased from Acros Organics and methanol was from Thomas Baker Chemicals Pvt., Ltd., (India). Toluene and H₂SO₄ were obtained from Merck Specialties Pvt., Ltd., (India). Benzoyl peroxide (BZP) obtained from Spectrochem Pvt., Ltd. (India) was recrystallized from CHCl₃-CH₃OH before use. Other chemicals were used as received. Indian Oil Corporation Ltd. (IOCL), Dhakuria,

WB, India, provided base oil, and its properties are summarised in the footnote of Table:- 1.2.7.2.

Scheme 1.2.1 Preparation of ester followed by homo and copolymerization



1.2.2.2 PREPARATION OF ESTER (MONOMER) AND ITS PURIFICATION

The ester (dodecyl methacrylate, DDMA) was prepared by reacting 1.1 moles of methacrylic acid with 1 mol of dodecyl alcohol using concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone concerning the total reactants as a polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in the earlier publication[3].

1.2.2.3 PREPARATION OF POLYMERS

The polymers (homo and copolymers) were prepared by free radical polymerization (Scheme:-1.2.1) at different percentage compositions of monomers in presence of BZP as the initiator (0.4% w/w, concerning the total monomer). The process of polymerization and purification was carried out by the procedure as reported in our earlier publication[6].

1.2.3 MEASUREMENTS

1.2.3.1 INSTRUMENTATIONS

- **FT-IR AND NMR SPECTROSCOPY**

Shimadzu FT-IR 8300 (Japan) spectrometer was used within the wavenumber range of 400 to 4000 cm^{-1} at room temperature for recording the IR spectra, using 0.1 mm KBr cells. The NMR spectra were recorded in Bruker Avance 300 MHz (Germany) FT-NMR instrument using CDCl_3 as a solvent and TMS as a reference and 5 mm BBO probe[13].

- **GEL PERMEATION CHROMATOGRAPHY (GPC)**

The average molecular weight (number-average and weight-average) of the additives were measured in Waters (USA) GPC equipment using HPLC grade THF as eluent at room temperature. The system was fitted with a 2414 refractive index detector (polystyrene calibration) and Waters 515 HPLC pump. The PDI (M_w/M_n) was also calculated by GPC[14].

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

The thermo-oxidative stabilities (TGA) or the decomposition pattern of the prepared additives were determined by a Shimadzu TGA-50 (Japan) thermogravimetric analyzer, at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. The percent weight loss (PWL) of mass (of the additives) with a temperature rise was used to measure the

thermal stability of the additives. The PWL was measured according to the following equation,

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

where M_0 = original mass taken and M_1 = Remaining mass after the test. The initial decomposition temperature and the temperature of the complete decomposition of the additives were obtained from the TGA curve[13].

- **PHOTOMICROGRAPH AND WAX MODIFICATION**

The effectiveness of an additive in controlling the crystallization of wax can be studied by a photomicrographic image of the base fluid. The wax modification pattern of the base fluid was analyzed using a Banbros polarizing microscope (BPL-400B, India), with magnification 200X. To control the temperature at 0°C The microscope was connected with a cooling thermostat [13].

1.2.3.2 PERFORMANCE EVALUATION

- **PERFORMANCE EVALUATION AS POUR POINT DEPRESSANTS IN THE BASE OIL**

The effect of additive concentration on the pour point of the lube oil was tested by using different doping concentrations ranging (1% to 5% (w/w) for each of the prepared polymer according to the ASTM D 97-09 method. The Pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India).

- **EVALUATION OF VISCOSITY INDEX**

The VI of the additive doped base fluid was determined using an Ubbelohde viscometer. The viscometer was dried and calibrated with distilled, degassed water, and purified methanol at the experimental temperatures (40°C and 100°C) to determine the value of the viscometric constants[3]. The variation of kinematic

viscosity (ν) of doped lube oil with the change of temperature, was evaluated putting data obtained in the equation,

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

where ρ = density of the experimental solution, t = time of flow of the solution, and K and L are the viscometric constants[4]. The time of flow was recorded using a digital stopwatch. The densities of the solutions were determined with a density meter (Austria, Anton Paar, DMA 4500 M.). The VI, which reflects the variation of kinematic viscosity of oil with temperature, was calculated according to the ASTM D2270 method at five different doping concentrations (ranging between 1 to 5%) of the additives according to the equation,

$$VI = 3.63(60 - 10^n)$$

and n was determined by the equation,

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

where ν_1 and ν_2 are the kinematic viscosities of the additive doped oil at lower and higher temperatures respectively. For the given temperature range, the value of k was determined to be 2.71[5].

1.2.4 RESULT AND DISCUSSION

1.2.4.1 MOLECULAR WEIGHT ANALYSIS

From the experimental values of M_n , M_w , and PDI (polydispersity index) of the prepared homo and copolymers (Table:- 1.2.7.1), the number average molecular weight and weight average molecular weight gradually increases with the increasing percentage of vinyl acetate in the copolymer. DDMA homopolymer. are found more dispersed than The DDMA-VA copolymer.

1.2.4.2 SPECTROSCOPIC ANALYSIS

The homopolymer of dodecyl methacrylate shows an IR absorption band at 1722 cm^{-1} (Figure:-1.2.7.2) corresponds to the ester carbonyl group. For the copolymers of dodecyl methacrylate and vinyl acetate (P-2 to P-5), the IR spectrum(Figure:-1.2.7.5) showed the absorptions ranged between 1716.5 cm^{-1} and 1732.9 cm^{-1} indicate the presence of ester carbonyl groups. In its ^1H NMR spectra, the homopolymer(Figure:-1.2.7.3) showed the presence of the methyl and methylene protons in the range of 0.881 to 1.812 ppm for all alkyl groups and a broad peak at 3.93 ppm for the protons of $-\text{OCH}_2$ group. The absence of any peak in the range of 5-6 ppm confirms the absence of any sp^2 hydrogens in the system and hence indicated the conversion of the monomer into the polymer. In the ^1H NMR of the DDMA-VA copolymers,(Figure:1.2.7.6) a broad peak at 3.93 - 4.16 ppm indicated the protons of $-\text{OCH}_2$ and $-\text{OCH}_3$ groups. Methyl & methylene carbons appeared in the range of 0.87 ppm to 2.63 ppm. The absence of any peak in the range of 5-6 ppm confirmed the conversion of the homopolymer into polymerization successfully.

In ^{13}C NMR of the homopolymer,(Figure:-1.2.7.4) the peaks at 167.60 ppm indicated the presence of ester carbon. The peaks at 64.71 ppm and 64.88 ppm confirmed the presence of $-\text{OCH}_2$ carbon and peaks in the range of 14.13–31.38 ppm accounted for all sp^3 carbon atoms of alkyl groups. The absence of sp^2 carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120-150 ppm. In ^{13}C NMR of the copolymers,(Figure:-1.2.7.7) of vinyl acetate, the peaks at δ 176.73 -177.86 ppm were due to the presence of ester carbonyl group. The peaks at 63.06 - 65.40 ppm corresponded to the $-\text{COCH}_3$ methyl carbon and $-\text{OCH}_2$ carbons, peaks ranging from 14.13–45.22 ppm for all other sp^3 carbons. The absence of a peak

in the range of 120-150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization[15].

1.2.4.3 ANALYSIS OF POUR POINT VALUES

The experimental values of the pour point are given in Table:- 1.2.7.2. The values indicate that all the prepared polymers (P-1 to P-5) perform effectively as better pour point depressants (PPD) and flow improvers (FI) when doped in base lube. The copolymers (P-2 to P-5) are found to better flow improver than the homopolymer (P-1). But with varying concentration, the pour point values do not maintain a linear correlation. The vinyl acetate copolymers (P-2 to P-5) exhibit better results than the homopolymers of DDMA. These polymers are better as FI and may be due to the presence of acetate group in the polymer backbone which reduces the adsorption of the polymer molecule on the wax crystals[7](Abdel-Azim et al., 2005) that happened in the case of flat DDMA homopolymer architecture. The P-5 copolymer having 6% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers[15].

1.2.4.4 ANALYSIS OF THE INFLUENCE OF ADDITIVES ON THE VISCOSITY INDEX VALUE

The data presented in Table:- 1.2.7.3, compared the dependence of the VI values with nature and on the concentrations of the additive, and the results indicated that all the prepared additives modified the viscosity properties of the base fluid. The additive DDMA homopolymer showed the least viscosity modification and with the increase of VA content in the additive feed, the VI values are found to rise gradually in the case of the copolymer. For any viscosity modifier, the potential to improve the VI relies on the conduct of the additive molecules in the base fluid, where its molecular weight, solubility, and chain topology are crucial parameters[11]. Also,

the viscosity of the base fluid depends on the temperature, wherewith an increase in temperature, the viscosity normally decreases[9]. Various researchers suggested that at low temperatures, the additive molecules are poorly soluble in the base fluid and remain in a round coiled up conformation with a minimal effect on the base fluid viscosity[10]. But with the increased solubility and interaction between the additive chains and the solvent molecules at the higher temperature, the additives change their shape from tightly coiled to inflated spread out ones. This successfully thickens the oil and counters the normal reduction in viscosity of the base fluid with increasing temperature[11]. Here the DDMA-VA copolymer additive with 10% VA content in doped lube, P-5 showed the highest VI increment, and this is possibly due to increased degree of solvation and enhanced interaction of the additive having oleophilic ends with the paraffinic base fluid. On the other hand, the additive DDMA, which only consists of dodecyl methacrylate monomers, has a more polar character compared with the others. Due to this polar nature, the additive has less interaction with the base fluid and, therefore, has a lesser solvated volume, consequently leaving it with the lowest VI among others[6]. Moreover, following our earlier publication[13,14], the VI values become more pronounced on increasing the overall additive doping percentage in the base fluid. This is because the increase in the concentration of the additive leads to an increase in the total volume of the polymer coils. These inflated coils, together with their increased interaction with the base fluid leads to a greater thickening effect and subsequently increases the viscosity index of the base stock[12].

1.2.4.5 ANALYSIS OF THE PHOTOMICROGRAPHIC IMAGE

A comparison of the photomicrographs,(Figure:1.2.7.1) of the SN-150 base fluid and the base fluid blended with different polymeric additives indicated that the

original base fluid (pour point = -6°C) showed long rod liked wax crystals in its photomicrographic image whereas additive doped base oils (4%, w/w of DDMA homopolymer solution PP -11.5°C) showed a significant reduction in the shape and size of the wax crystals in their images. Thus, the reduction in the size of wax crystals seems to be responsible for improving the pour point values. Hence, the pour point values obtained earlier are incomplete in correlation with the wax modification results[15].

1.2.5 CONCLUSION

In conclusion, the copolymers of dodecyl methacrylate with vinyl acetate are found effective as a multifunctional additive (flow improver and viscosity improver) for the lube oil. Copolymers with lower molecular weight are more effective as low-temperature flow improvers than copolymers with higher molecular weight. Therefore, the molecular weight of polymer has a significant role concerning the performance of the polymers as flow improvers for lube oil. In addition, the VA copolymer induced excellent VM properties as well when added to the base oil[15].

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for providing Base Oil.

1.2.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-2 of Part -1**”.

1.2.7 TABLES AND FIGURES

TABLE 1.2.7.1

PERCENTAGE COMPOSITION, M_n , M_w , AND PDI VALUES OF POLYMERS (P-1 TO P-5) & GRAPHICAL REPRESENTATION

Polymer code	% of DDMA	% of VA	M_n	M_w	PDI
P-1	100	-	20482	49682	2.4256
P-2	97.5	2.5	22475	33018	1.53
P-3	95	5	24613	35842	1.492
P-4	92.5	7.5	54766	66210	1.164
P-5	90	10	60790	81219	1.31

DDMA = Dodecyl methacrylate, VA = Vinyl acetate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

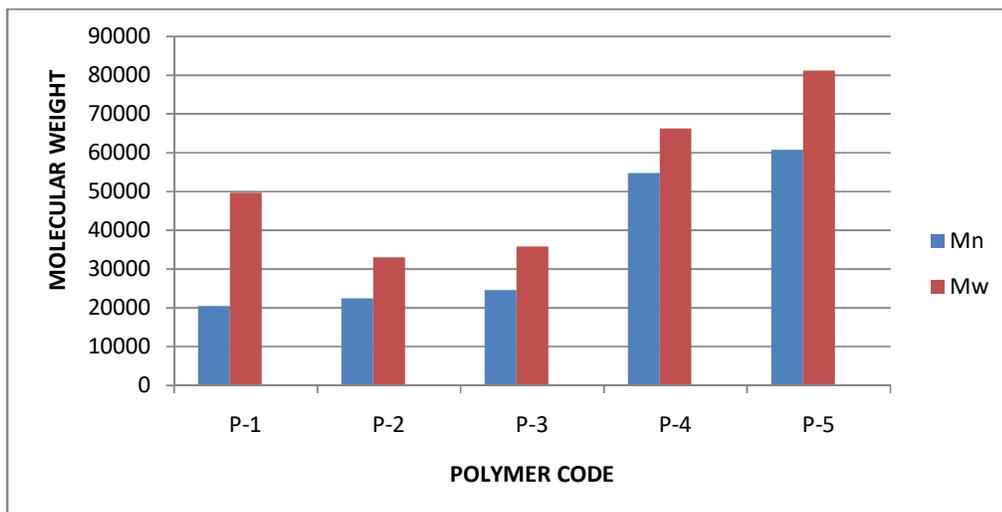


TABLE 1.2.7.2

POUR POINT DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN THE BASE OIL

Polymer	Pour point (°C) of additives doped base oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	-6	-13.5	-12.9	-12	-11.5	-10	-10.3
P-2	-6	-8	-7.8	-7.5	-8.1	-9.2	-10
P-3	-6	-7.5	-6.5	-6	-5.5	-4	-4.5
P-4	-6	-8.5	-8	-7.5	-8	-8.5	-9
P-5	-6	-10	-10.5	-12	-12.5	-13	-13.8

* Properties of the base oil - Density (g.cm⁻³) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 86; Pour point, °C: -6:

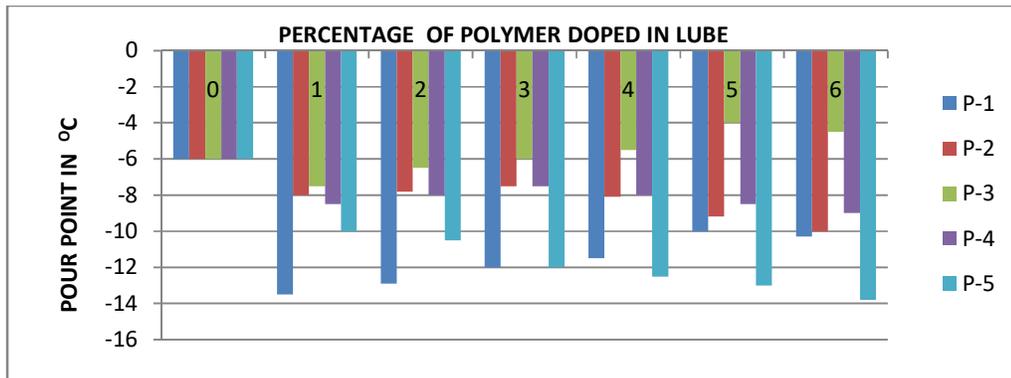


TABLE 1.2.7.3

VISCOSITY INDEX DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN THE BASE OIL & GRAPHICAL REPRESENTATION.

Polymer	The viscosity index of additives doped base oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	86	89	92	102	111	116	120
P-2	86	94	101	107	119	121	126
P-3	86	98	118	123	127	131	135
P-4	86	112	126	128	131	135	139
P-5	86	118	129	130	132	137	138

* Properties of the base oil - Density (g.cm⁻³) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 86; Pour point, °C: -6:

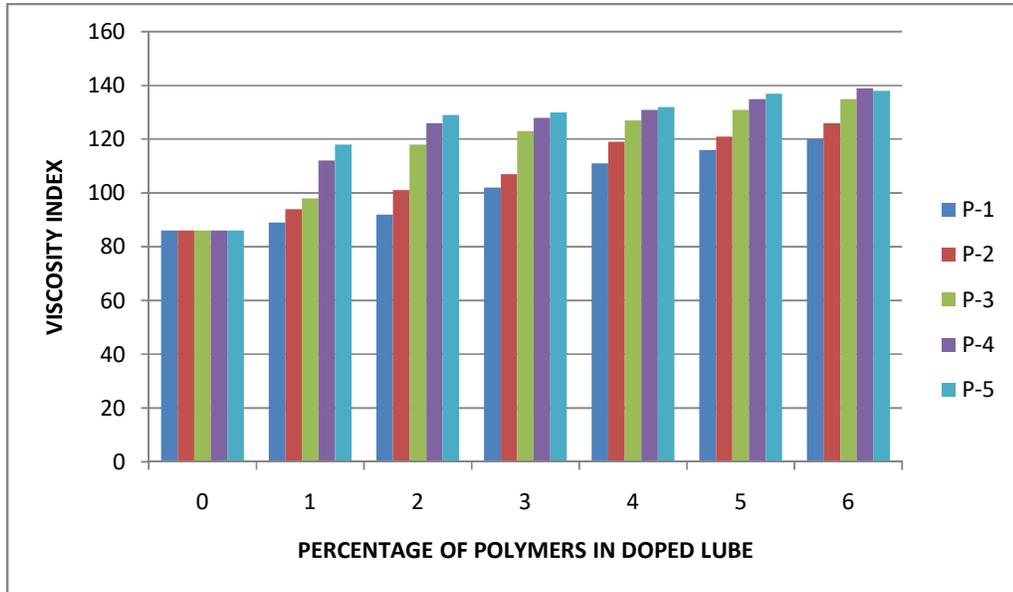
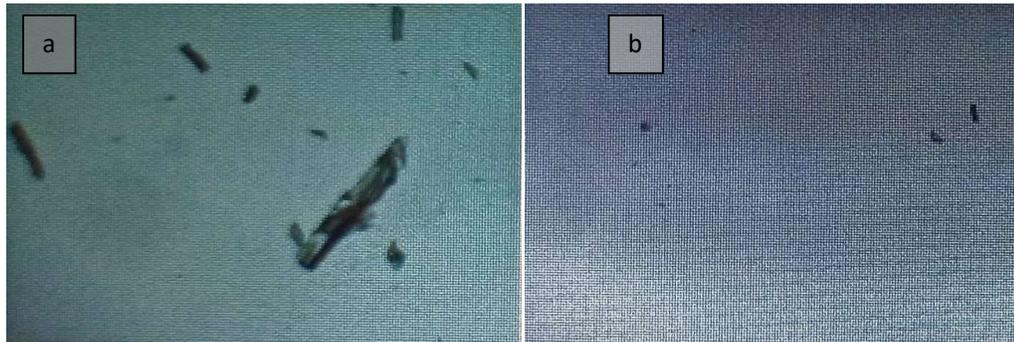


FIGURE 1.2.7.1

PHOTO MICROGRAPHIC IMAGE OF WAX CRYSTAL FORMATION.



Photomicrograph images of (a) pure lube oil ,PP-6°C, (b) lube oil + 4% (w/w) of DDMA homo polymer PP -11.5°C

FIGURE 1.2.7.2

FT IR SPECTRA OF A HOMOPOLYMER OF DDMA(P-1)

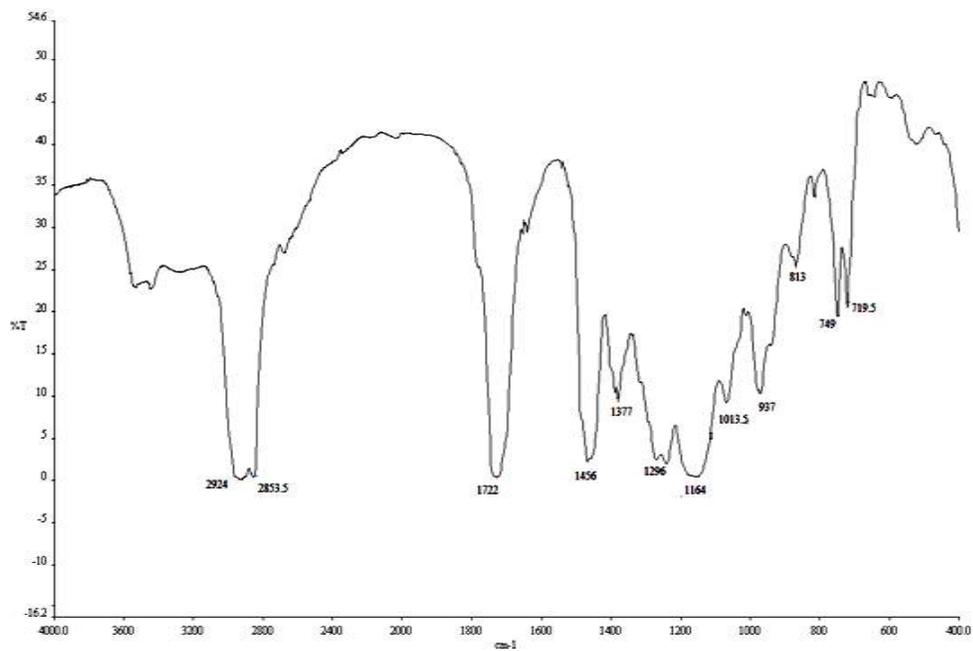


FIGURE 1.2.7.3

¹H NMR SPECTRA OF A HOMOPOLYMER OF DDMA(P-1)

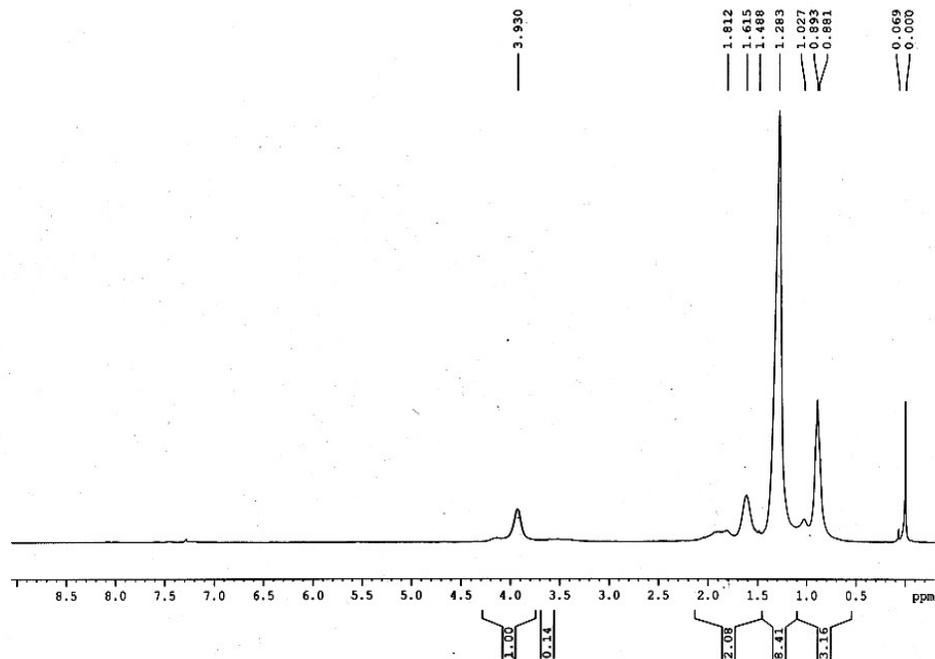


FIGURE 1.2.7.4

¹³C NMR SPECTRA OF A HOMOPOLYMER OF DDMA(P-1)

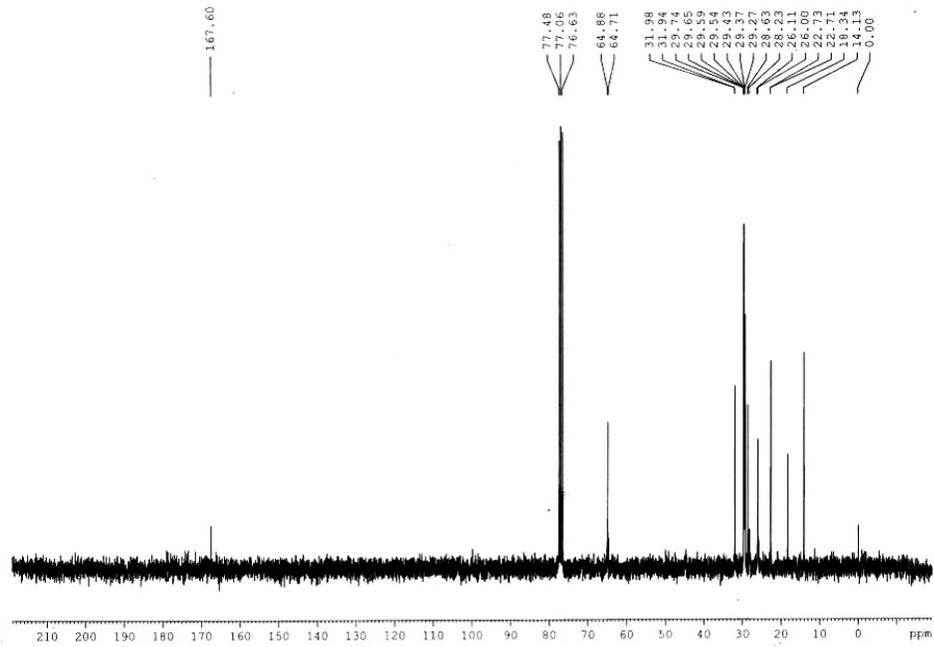


FIGURE 1.2.7.5

FT-IR SPECTRA OF COPOLYMERS (P-2 TO P-5)

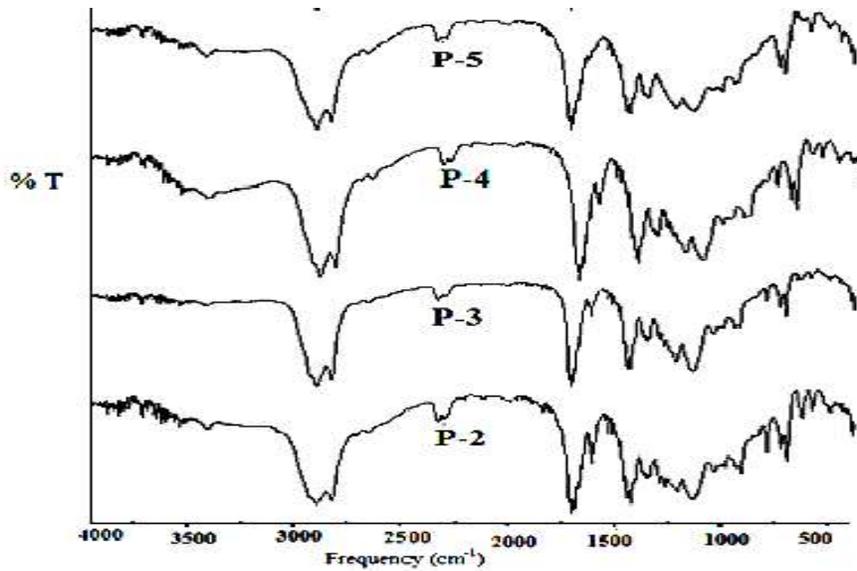


FIGURE 1.2.7.6
¹H NMR SPECTRA OF COPOLYMER (P-2)

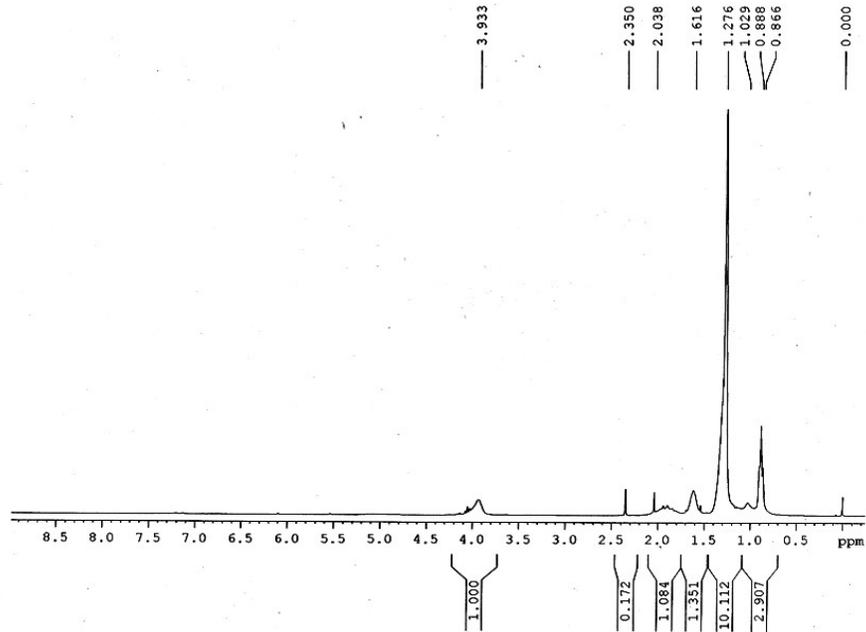
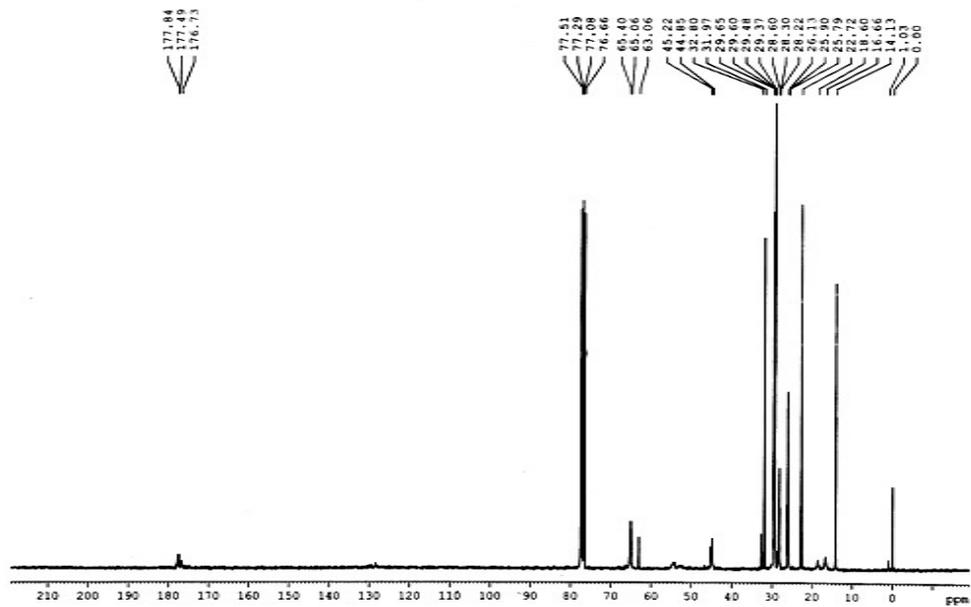


FIGURE 1.2.7.7
¹³C NMR SPECTRA OF COPOLYMER (P-2)



PART-2

BIODEGRADABLE MULTIFUNCTIONAL LUBE OIL ADDITIVES USING MODIFIED VEGETABLE OILS

PART-2/CHAPTER-1

BACKGROUND AND OBJECTIVE OF THE PRESENT INVESTIGATION

The automobile industry is flourishing day by day with the advent of new technologies and ever exploring ideas. Utilization of polymeric additives, their modification to obtain maximum effect with minimum dosage, or application of new potential lubricating additives has remained the key areas of research in this industry. But over the decade environmental issue has become the main concern which has pushed such industries towards a challenging area to adopt comparatively greener initiatives. Hence replacement or minimizing the application of traditional additives through the introduction of biodegradable ones has gained much pace during the years. To maintain the ecosystem, non-conventional sources of energy are getting huge attention, and hence the use of bio-lubricant is very attractive to reduce fossil fuel exploitation and increase its sustainability. A considerable no of research in the area of plant and animal-based oil is happening [1]. Vegetable oils and modified vegetable oils have become sustainable alternatives to petroleum-based materials for industrial applications due to their biodegradability, low toxicity, absence of volatile organic chemicals, easy availability, and relatively low price [2].

Vegetable oils are triglycerides consist of triglycerides (95–97%) and also mono- and diacylglycerides. Saturated fatty acid like tetradecanoic acid(14:0),palmitic acid(16:0),Stearic acid (18:0) and unsaturated fatty acid(MUFA or PUFA) like oleic acid & ricinoleic acid(18:1),linoleic acid(18:2),linoleic acid (18:3) forms tri-ester with glycerol in a varying ratio.

Vegetable oils have been used in various industrial products like wall finishes [3], paints [4], electrodeposition paints [5], water thinnable primers [6], and printing inks [7].

The viscosity Index of most vegetable oils is generally high compared to mineral oil. Another important property of vegetable oils is their high flash point. Most importantly, vegetable oils are renewable biodegradable, less toxic, and may reduce dependency on imported petroleum oils in the future, all of which account for a greener approach. But vegetable oils in their natural form suffer from insufficient oxidative stability due to a high percentage of unsaturation present in their backbone which implies that the untreated oil will get oxidized quite easily and becomes thick and polymerized to plastic-like consistency [8]. But this can be overcome by some modifications such as radical polymerization, epoxidation, transesterification, and selective hydrogenation [9-10].

Plant oil can be classified as edible or non-edible. The largest sources of vegetable oils are annual plants such as soybean, corn, linseed, cottonseed, or peanuts and some oil-bearing perennials such as the palm, olive, or coconut[11]. Among them, soybean oil has conquered one of the most prominent positions mainly because of its availability and composition for the production of biodegradable lubricant additives. Now linseed oil which is a colorless to yellowish oil obtained from the dried, ripened seeds of the flax plant (*Linum usitatissimum*), contains similar triglyceride as that of soybean oil but with a much larger amount of linolenic acid(18:2). Therefore, the level of unsaturation for the triglyceride in linseed oil is somewhat greater than that for soybean oil[12]. The production of linseed oil seeds in India is high enough to make it acceptable from an economic point of view. Most importantly linseed oil is prone to get polymerized by itself and hence can be used as

an impregnator either in natural form or blended with combinations of other oils, resins, or solvents, as a pigment binder in oil paints, as a plasticizer, and hardener in putty, in the manufacture of linoleum and wood finishing [13]. Some recent work on modification of vegetable oil as a potential lube oil additive are summarised below-

1. Cakmakli, B(2004) Investigated linseed oil and its peroxidation in air or oxygen flow at room temperature. The application of these Polymeric peroxides in swell management and tissue engineering was studied[1].
2. Becker, R, Knorr, A (1996) analyzed antioxidant efficiency of low erucic rapeseed oil as an oxidation inhibitor[8].
3. Ashraf, M, S, Ahmed (2007) investigated epoxy vegetable oil for blending with polymers of PMAA to improve physical and mechanical properties. Dehydrated epoxy castor oil was used in this case[13].
4. Ghosh, P, Karmakar, G,(2014) investigated biodegradable multifunctional lube oil additive based on sunflower oil in a solvent-free synthesis of polymers using thermal or MW irradiation using BZP and performance analysis as multifunctional lube additive[14].
5. Ghosh, P, Talukdar, S,(2020) investigated rice-bran oil homo and its copolymer with dodecyl acrylate and styrene as multifunctional additive[15].
6. Ghosh, P, Saha, D(2018) synthesized homo and copolymer of castor oil with alpha-pinene using AIBN as radical initiator and analyzed their additive performance[16].

Due to such versatile application of vegetable oil along with its fruitful properties such as ready to polymerize tendency, high unsaturation, easy availability, and some more, have provoked us to explore it towards the preparation of eco-friendly polymeric additives. Here we have prepared Castor oil and acrylate-based copolymers, Rapeseed oil styrene-based homo and copolymers, and rice-bran oil-based homo and copolymers with acrylate and alpha-pinene as potential lube oil additives followed by their characterization involving FT-IR, NMR, GPC, and their performance terms of VII, PPD, TGA, Biodegradability, antiwear property were monitored.

REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-1 of Part-2**”.

PART-2/CHAPTER-2

BIODEGRADABLE LUBE OIL ADDITIVES OBTAINED FROM THE HOMOPOLYMER OF CASTOR OIL AND ITS COPOLYMERS WITH ACRYLATES

2.2.1 INTRODUCTION

Different additives synthesized from acrylate, vinyl acetate, acid anhydride, etc although exhibit satisfactory performance but generate many environmental issues due to their toxicity and non-biodegradability. Modification of bio-based resources and their use as additives can solve this problem and simultaneously reduces environmental impacts to a notable extent. Edible and non-edible oils based additives have significant advantages compared with synthetic additives owing to their biodegradable properties with minimum toxicity[2] As per viscosity index (VI) [3], low pour point, antiwear property[4], and low volatility[5] modified vegetable oil produce the exceptional outcome. So, modified vegetable oil-based additive to mineral lube has attracted much attention recently. Castor oil is obtained from castor seeds which are available in nature. It contains a high percentage of ricinoleic acid (85-95%)[14] in its triglyceride backbone. Ricinoleic acid is a C-18 fatty acid having a double bond at C-9, C-10, and an -OH functionality at C-12[1]. The triglyceride of castor oil posses trifunctionality, hence it can be modified as a monomer for the preparation of lube oil polymeric additives as well as multifunctional lube base stock also[6]. The alcoholic -OH group in ricinoleic acid is beneficial In this regard.

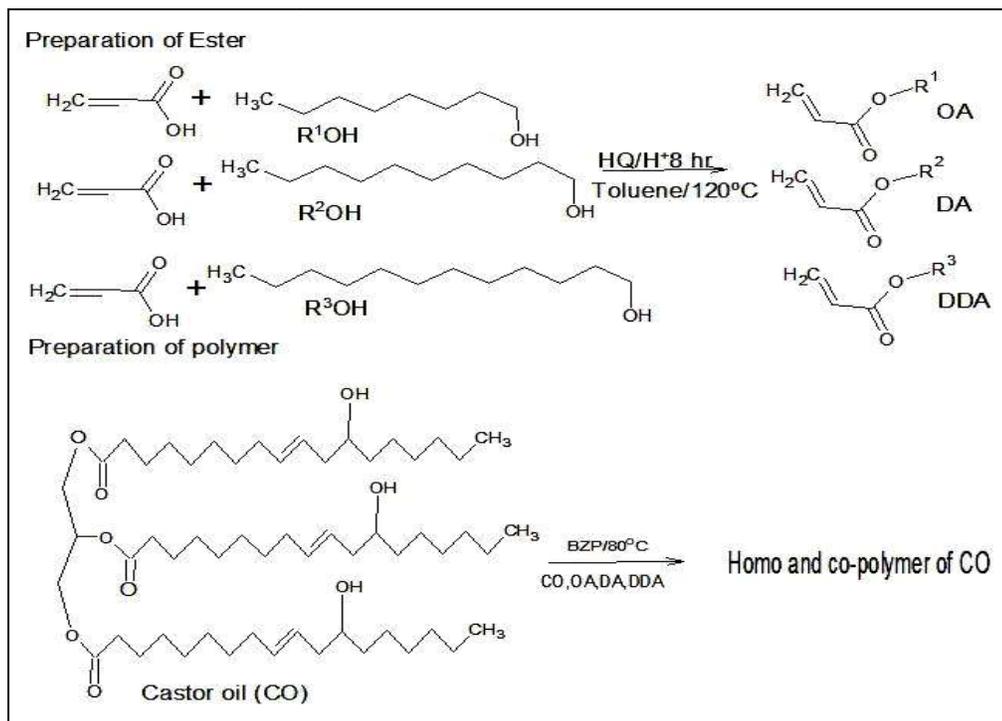
In this present work, we have synthesized three different acrylates by esterification reaction of acrylic acid with long-chain alcohols like octyl alcohol-

OA, decyl alcohol- DA, and dodecyl alcohol-DDA. Homopolymer of castor oil (CO) and three copolymers of castor oil with acrylates (5% w/w) were synthesized by thermal irradiation through free radical polymerization reaction using benzoyl peroxide (BZP) as free radical initiator. Synthesized polymers were characterized by FT-IR and ¹ H NMR, ¹³ C NMR spectroscopy. Gel Permeation Chromatography (GPC) and Thermogravimetric analysis (TGA) method were used to study the average molecular weight and thermal behavior of the polymers at high temperature respectively. Performance evaluation of the polymers as additives in lubricating oil was carefully by suitable doping of the polymer in mineral lube in varying concentrations and assessing properties in terms of thermal stability, viscosity index, pour point, and biodegradability. The outcome revealed that the prepared copolymers are better additives than homopolymer in dopped lube oil[1].

2.2.2 EXPERIMENTAL

2.2.2.1 PREPARATION OF ESTERS

Octyl acrylate (OA), decyl acrylate (DA), and dodecyl acrylate (DDA) were prepared by reacting octyl alcohol, decyl alcohol, and dodecyl alcohol with acrylic acid in the molar ratio of 1.1:1 at 120 °C in toluene (solvent) in the presence of concentrations. H₂SO₄ as a catalyst, 0.25% (w/w) hydroquinone as polymerization inhibitor concerning the total reactants in a Dean-Stark apparatus. The process of esterification and its purification were carried out by the procedure as reported in the earlier publication[7]. Scheme:- 2.2.1 represents the formation of ester followed by polymerization.

Scheme 2.2.1:- Preparation of ester and polymers of castor oil.

(Fatty acid composition of castor oil :- ricinoleic acid-89.5%,linoleic acid-4.2%,oleic acid-3%,linolenic acid-0.3%,other saturated & unsaturated 3%)[14].

2.2.2.2 SYNTHESIS OF THE POLYMERS

Castor oil (95%, w/w) and acrylate (OA, DA, DDA) (5%, w/w) or only castor oil in case of homopolymer in presence of AIBN initiator copolymers were synthesized by thermal free radical polymerization method. The polymerization was carried out in a three-necked RB fitted with a magnetic stirrer, thermometer, condenser, and an inlet for the introduction of nitrogen. The mixture of acrylate and castor oil or only castor oil in the case of the homopolymer was heated at 80 °C without any solvent. Initiator BZP (0.5% w/w, concerning the total monomer) was then added. The system was continuously heated for 5 hours at 80°C. After the completion of the reaction, the product was poured into methanol with continuous

stirring, filtered off, and dried. The prepared homopolymer and three copolymers with OA, DA, and DDA are designated as P-1, P-2, P-3, and P-4 respectively.

2.2.3 MEASUREMENTS

2.2.3.1 INSTRUMENTATIONS

- **SPECTROSCOPIC MEASUREMENTS**

IR spectra were documented on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature by direct loading of the sample in KBr surface within the wavenumber range of 400 to 4000 cm^{-1} . Bruker Avance 300 MHz FT-NMR spectrometer was used to record the ^1H NMR and ^{13}C NMR spectra. CDCl_3 was used as solvent[1].

- **MOLECULAR WEIGHT DETERMINATION**

The average molecular weight was recorded by the GPC method (Water 2414) in HPLC grade THF at 35° C at a flow rate of 1mL/min injecting 20 μl of the polymer solution in HPLC grade THF[1].

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

TGA data were recorded on the Shimadzu TGA-50 system, at a heating rate of 10° C / min[1].

2.2.3.2 PERFORMANCE EVALUATION

- **EVALUATION OF VISCOSITY INDEX**

Viscosity index (VI) is a unitless qualitative parameter that describes the change in viscosity of a particular fluid against a temperature change. Viscosity index (VI) is an important parameter in fluid chemistry. The kinematic viscosity of a

fluid sharply decreases with the increase in temperature. Higher VI value implies fewer changes in viscosity with temperature. Polymeric component added as viscosity index improver (VII) in lube oil adopts complete packed molecular structure resulting in low viscosity at low temperature, whereas in higher temperature the packed coil of polymer opens up resulting higher viscosity. VI is a bulk property and is often called rheo improver in lube oil chemistry. It was calculated according to ASTM D 2270-10 [11]. The kinematic viscosities of the lubricant composition were determined at 40°C and 100°C which are essential to calculate VI according to the equation,

$$v = (Kt - L/t) \rho$$

where ρ is the density of the experimental solution, t is the time of flow of the solution and K and L are the viscometric constants of an Ubbelohde viscometer.

$$VI = 3.63(60 - 10^n)$$

and n was determined by the equation,

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

where v_1 and v_2 are the kinematic viscosities of the additive doped oil at 40 °C and 100°C temperature respectively. For the given temperature range, the value of k was determined to be 2.73.

- **EVALUATION OF POUR POINT**

At lower temperatures, lubricants freeze and form a jelly-like structure. The temperature at which lubricant flow is completely ceased is called the pour point (PP) of that lubricant. This is due to paraffinic wax crystal formation at a lower temperature in lube. This leads to lubricant failure and can cause serious damage to the engine component. Branched alkyl moiety in polymeric additive interacts with the wax and prevents them to crystallize hence inhibit lube to congeal. Polymeric

substances added to improve the low-temperature flow of a lube called pour point depressant(PPD) Pour point of the lubricant composition was determined according to the ASTM D 97-09 [12] method using the cloud and pour point tester model WIL-471 (India). A good pour point depressant additive lowers the pour point of the lubricant composition to a larger scale.

- **BIODEGRADABILITY TEST (DISC DIFFUSION METHOD).**

The biodegradability test was carried against *Alternaria alternate* (AA) fungal. Culture media strain was prepared by mixing the pathogen and suitable amount of potato extract, dextrose, and agar-agar powder in 10:1:1 wt ratios. The mixture was kept in different Petri dishes for different test samples and was kept in an incubator at 37° C for 30 days after the addition of about 2g of the polymer samples in each dish. The pathogen AA growth was confirmed by a change of yellow to blackish color. Polymer samples were recovered from the fungal media by chloroform, purified, and dried. The dried samples were weighed after 30 days, Percentage weight loss was determined and FT-IR spectra were taken[13].

2.2.4 RESULTS AND DISCUSSION

2.2.4.1 SPECTROSCOPIC ANALYSIS

The castor oil homopolymer showed an IR absorption band (Figure:-2.2.7.1) for the carbonyl functionality of the ester moiety in triglyceride at 1740.70 cm^{-1} . The absorption at 2855.9 cm^{-1} and 2927.37 cm^{-1} is due to the vibrating and stretching of the $\text{CH}_3\text{-CH}_2\text{-}$ group. A broad peak at 3447.77 cm^{-1} is due to the -OH group present in castor oil (oleic acid). The absence of absorption in the range of 3005 cm^{-1} to 3008 cm^{-1} due to unsaturated C-H stretching indicates successful polymerization. The IR spectra of the copolymers (P-2 to P-4) are similar. The absorption band at

1741 cm^{-1} -1745.29 cm^{-1} is due to ester carbonyl functionality in triglyceride. FT-IR spectra copolymer are displayed in Figure:-2.2.7.3, Figure:-2.2.7.6 & Figure:-2.2.7.9.

^1H NMR spectra of homopolymer, (Figure:-2.2.7.2) peaks in the range between 4.087- 4.252 ppm indicate the protons of $-\text{COOCH}_2$ group of castor oil and protons of $-\text{OH}$ group of castor oil appears in the range of 3.554 – 3.625 ppm. Methyl and methylene protons appeared in the range of 0.816-2.270 ppm. For copolymer, the peaks that appear in the range between 1.616 – 2.318 ppm indicate the protons of $-\text{COCH}_2$ a group of alkyl acrylate. Peaks at 3.607 – 3.656 ppm indicate the protons of $-\text{OCH}_2$ of acrylate moiety. COOCH_2 group of castor oil peaks appears in the range of 3.988 – 4.156 ppm. The absence of peaks in the chemical shift of 5-6 ppm indicates successful polymerization. ^{13}C NMR spectra of homopolymer, the peaks in the range of 172.95 – 177.41 ppm indicate the carbons of $-\text{COO}-$ (carbonyl) group. The carbons of $-\text{OOCH}_2$ group appear in the range 62.10 – 68.86 ppm. In the case of a copolymer (Figure:- 2.2.7.5), for carbons of $-\text{OCH}_2$ groups of acrylate moiety chemical shift is 58.11 ppm. The carbons of $-\text{OOCH}_2$ group of castor oil appear at 62.78 – 64.87 ppm. The peaks ranging from 166.31- 174.63 ppm confirm the presence of carbons of $-\text{COO}-$ (ester groups). There is no peak in the range of 120 – 150 ppm and it indicates successful polymerization.

2.2.4.2 MOLECULAR WEIGHT DATA ANALYSIS

Number average Molecular weight (M_n), weight average molecular weight (M_w) of the polymers (P-1 to P-4) are shown in Table 2.2.7.1. Experimental data revealed that among the four polymers, P-1 has the lowest, and P-4 has the highest molecular weight. Moreover, it is also observed that with increasing the alkyl chain length of the acrylate moiety in the copolymers, molecular weight increases.

Therefore, the alkyl chain length of acrylate has a determining role during copolymerization as per molecular weight is a concern[1].

2.2.4.3 ANALYSIS OF TGA DATA

From the experimental TGA values of the four polymers, it was observed that polymer P-1 is thermally less stable than the prepared copolymers[1]. This indicates that with the incorporation of acrylate moiety in Castor oil, thermal stability increases compared to homopolymer. Two major decompositions have been observed at 150 ° C and 300 ° C with 25% and 80% weight loss respectively in the case of P-1. An almost identical thermal stability pattern was observed in the case of polymers P-2 to P-4, where two major decompositions were observed at 185 ° C and 358 ° C with 18% and 78% weight loss respectively[1].

2.2.4.4 ANALYSIS OF VISCOSITY INDEX VALUES

VI of lubricant composition was calculated at different concentrations ranging from 1% to 5% (w/w). The experimental values of VI are listed in Table:-
2.2.7.2. The viscosity of lube oil decreases with increasing temperature but an expansion of polymer molecules takes place from tight coil due to increased lube oil – polymer interaction. As a result, the size of the micelle increases. This increased in micelle size prevents the reduction of the viscosity of the lubricant composition. Since the total volume of polymer micelle in lubricant increases, it is observed that higher polymer concentration exhibit higher viscosity index and hence improves the VI property[2]. It is observed that VI increases by incorporation of acrylate moiety in the backbone of the homopolymer of castor oil. This may be due to the higher molecular weight and higher crosslink density of the copolymers. The copolymer P-4 has the highest VI value than the other polymers, P-3, P-2, and P-1. It may be due to higher average molecular weight[1].

2.2.4.5 ANALYSIS OF POUR POINT (PP) VALUES

Pour points of the lubricant composition at different concentration levels ranging from 1%–5% (w/w) are tabulated in Table 2.2.7.3 which indicates that the prepared lubricants have lower Pourpoint than lube oil and hence the prepared polymers can be used as PPD additive. From the data obtained, it is observed that the efficiency as PPD increases up to 3% concentration. The reason for this may be, at this concentration the additive interacts with the paraffinic wax of lube oil effectively and decreases the shape of crystals of the paraffinic wax[9]. Among the prepared four polymers, P-2 showed the best performance as PPD. It may be due to a higher PDI value[1,10].

2.2.4.6 ANALYSIS OF BIODEGRADABILITY TEST RESULTS

The fungal *Alternaria alternata* was used to carry out the biodegradability test. It was found that homopolymer (weight loss 58%) is more biodegradable than the copolymers (weight loss 42%). After biodegradation, the molecular weight of the recovered polymers was also determined by the GPC method and the results were compared with the respective polymers before and after biodegradation and shown in Table 2.2.7.1. Comparative FT-IR spectra were also studied and displayed in Figure:- 2.2.7.12[1].

2.2.5 CONCLUSION

From the above study, it is found that the homopolymer and copolymer of castor oil are effective additives as viscosity index improver and pour point depressant for lubricating oil. Copolymers are more effective than homopolymers. Thermal stability and average molecular weight of copolymers increase with increasing the alkyl chain length of acrylate moiety. Due to biodegradability, the

additives are environmentally benign also. Therefore, this study is a potential approach to formulate a green additive for lubricating oil[1].

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for providing Base Oil.

2.2.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-2 of Part-2**”.

2.2.7 TABLES AND FIGURES

TABLE 2.2.7.1

MOLECULAR WEIGHT OF THE PREPARED POLYMERS & GRAPHICAL REPRESENTATION

Polymer	Average molecular weight (before biodegradation)			Average molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P-1	7928	10022	1.26	4814	5465	1.14
P-2	8948	17515	1.96	7624	13503	1.77
P-3	10972	18048	1.64	9256	14592	1.58
P-4	16246	24228	1.49	15337	20016	1.31

M_n = Number average molecular weight; M_w = Weight average molecular weight; PDI = Polydispersity index

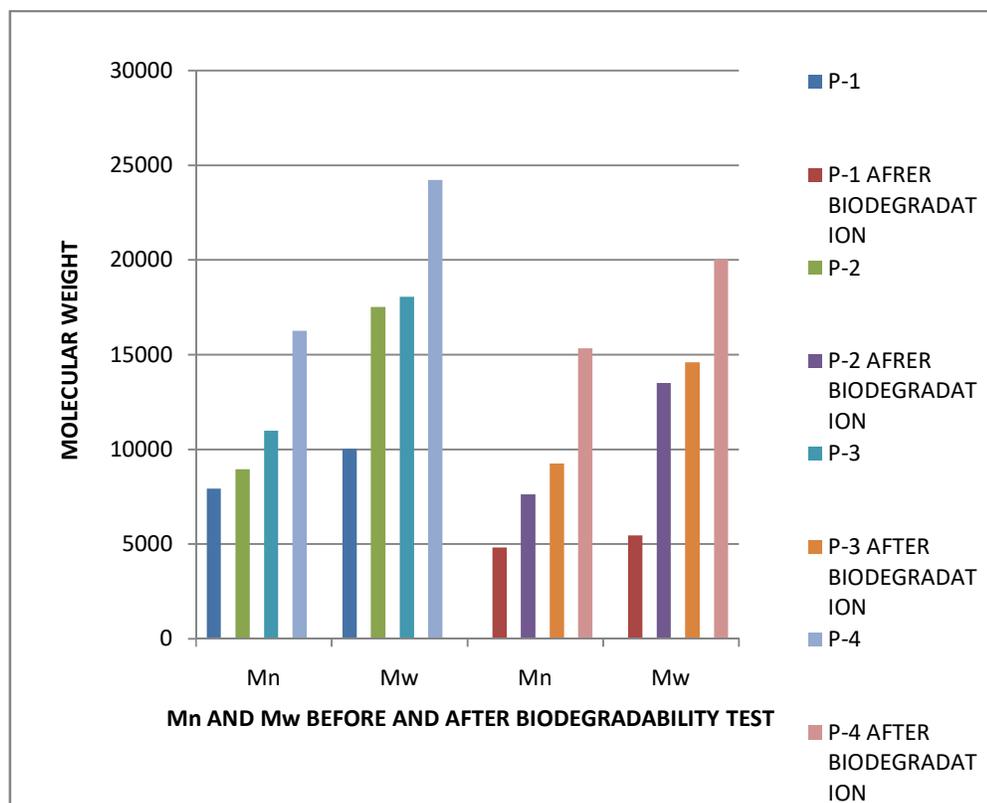


TABLE 2.2.7.2

VISCOSITY INDEX OF POLYMER DOPED LUBRICANTS AT DIFFERENT CONCENTRATIONS (W/W) & GRAPHICAL REPRESENTATION

Polymer	VI of lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	85.2	90	94.5	102	112	116
P-2	85.2	98	104	116	122	134
P-3	85.2	100	108	116	128	138
P-4	85.2	100	112	123	135	145

Properties of the base oil - Density (g.cm^{-3}) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 86; Pour point, °C: -6:

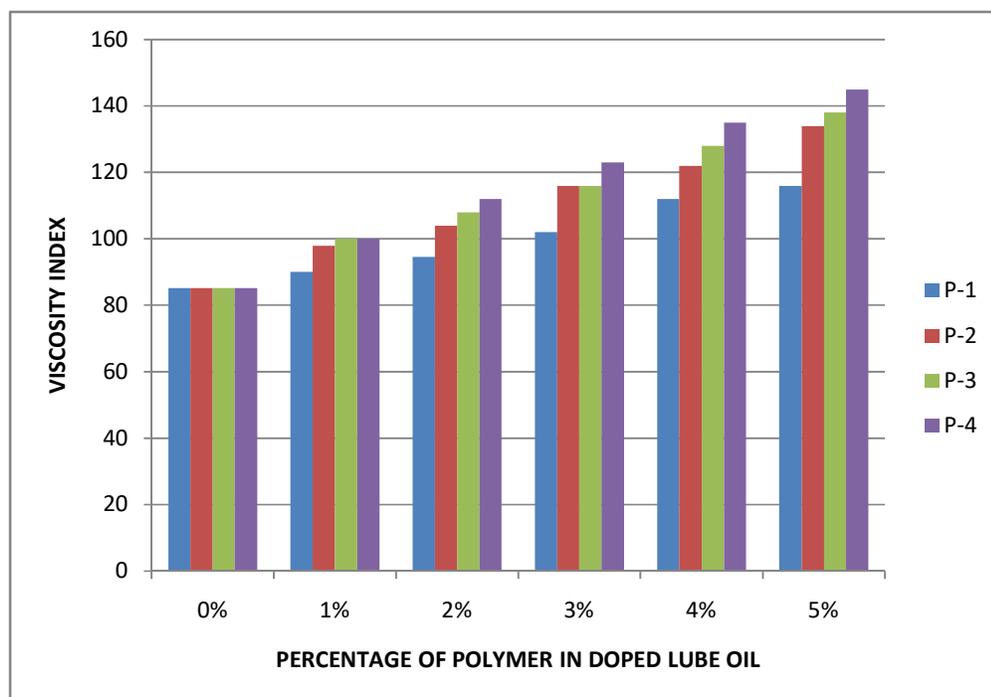


TABLE 2.2.7.3

POUR POINT VALUES OF LUBRICANTS AND GRAPHICAL REPRESENTATION.

Polymer	Pour point (in °C) lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	-6	-9	-12	-14	-15	-15
P-2	-6	-10	-15	-21	-21	-21
P-3	-6	-10	-13	-18	-18	-18
P-4	-6	-10	-13	-17	-17	-17

Properties of the base oil - Density (g.cm⁻³) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 86; Pour point, °C: -6:

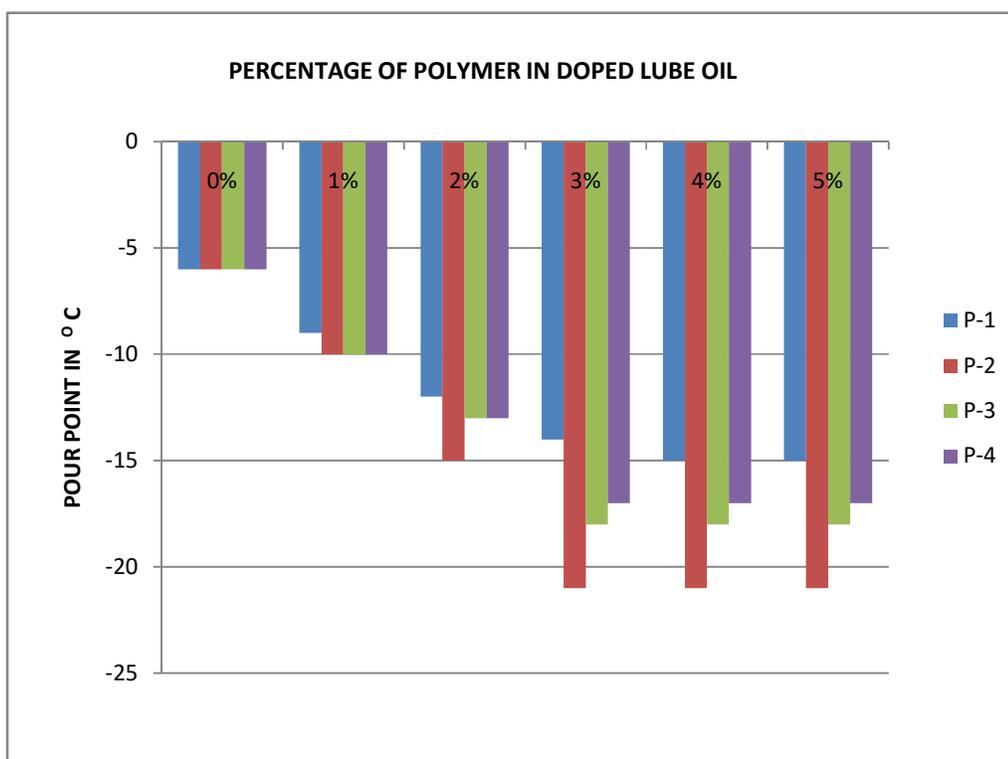


FIGURE 2.2.7.1

FT IR SPECTRA OF THE HOMOPOLYMER OF CASTOR OIL

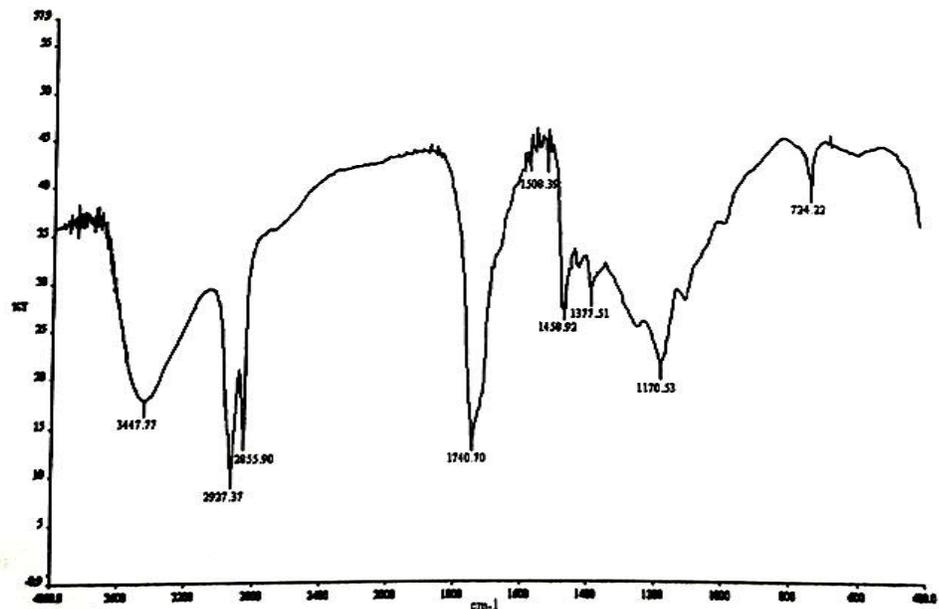


FIGURE 2.2.7.2

¹H-NMR SPECTRA OF THE HOMOPOLYMER OF CASTOR OIL

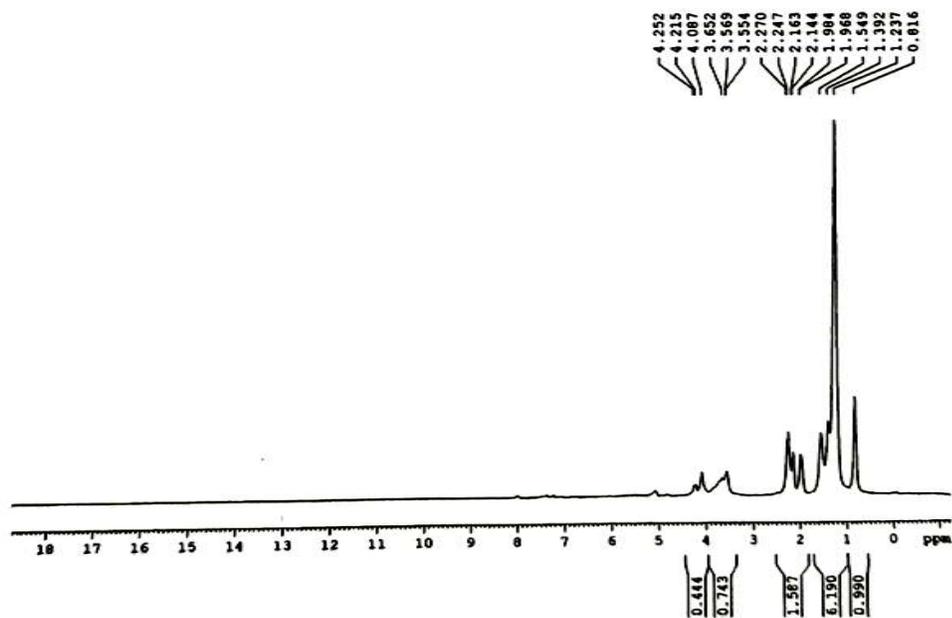


FIGURE 2.2.7.3

FT -IR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND OCTYL ACRYLATE

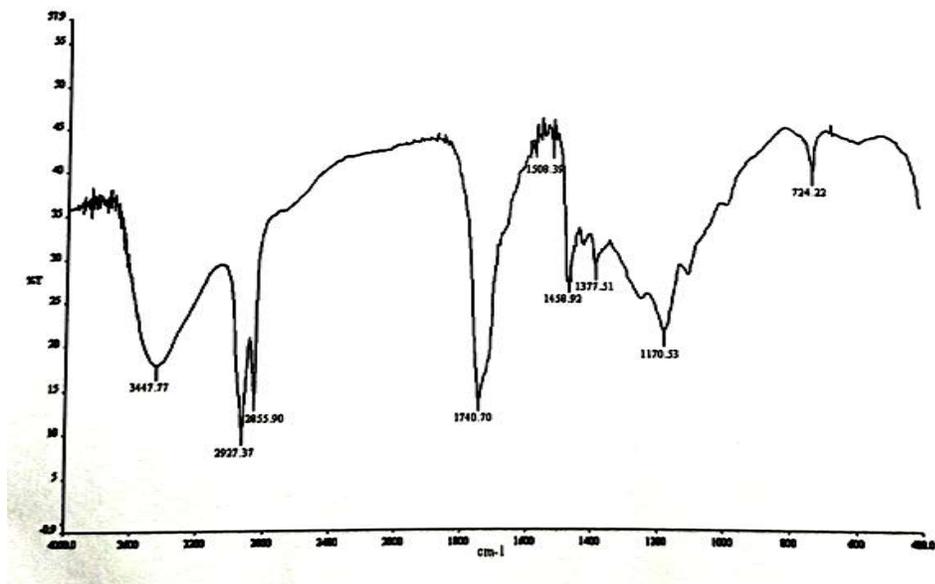


FIGURE 2.2.7.4

¹H-NMR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND OCTYL ACRYLATE

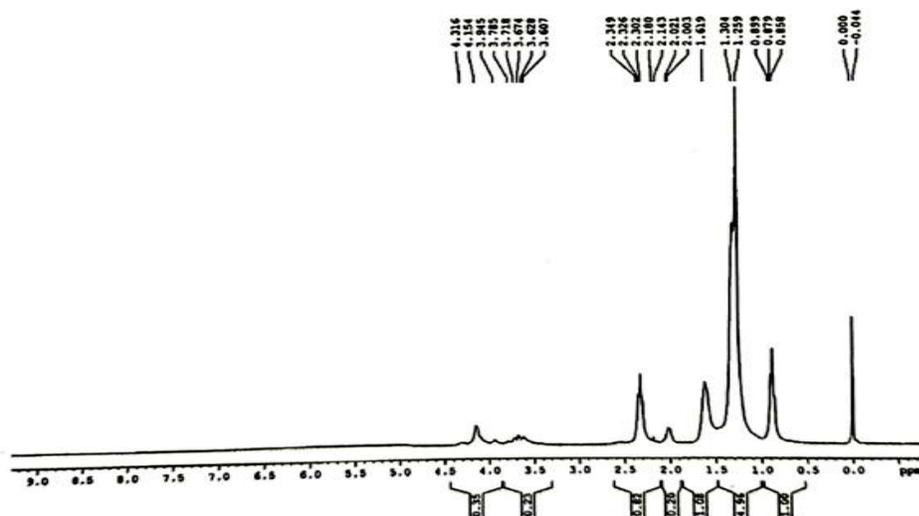


FIGURE 2.2.7.5

¹³C- NMR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND OCTYL .ACRYLATE

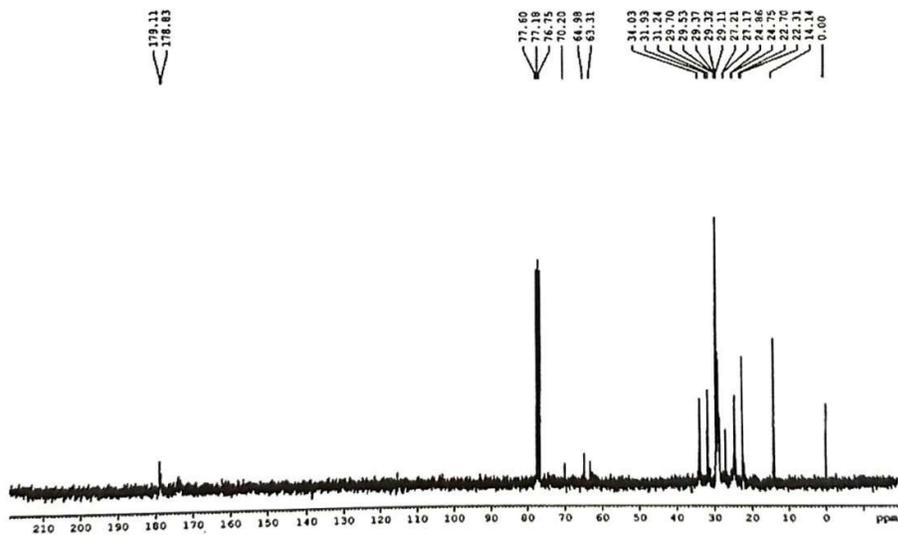


FIGURE 2.2.7.6

FT- IR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND DECYL ACRYLATE

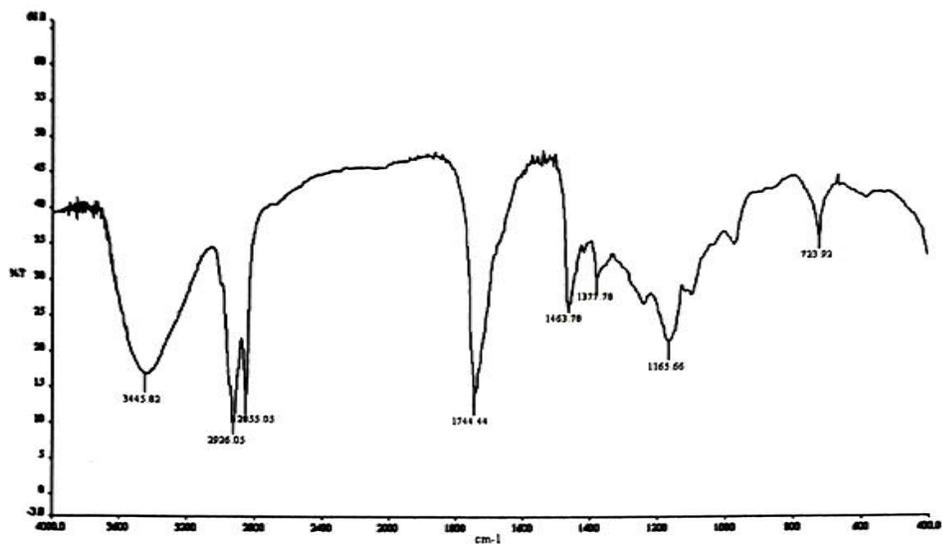


FIGURE 2.2.7.7

¹H- NMR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND DECYL ACRYLATE

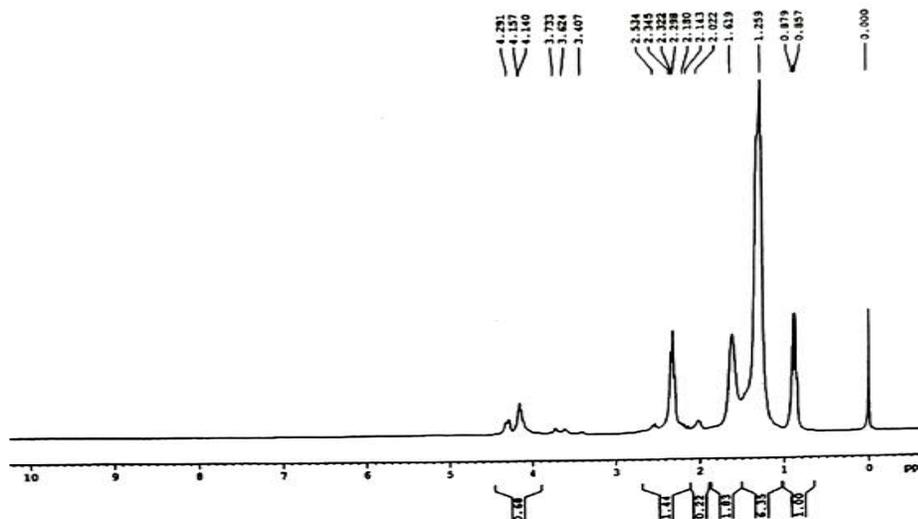


FIGURE 2.2.7.8

¹³C- NMR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND DECYL ACRYLATE

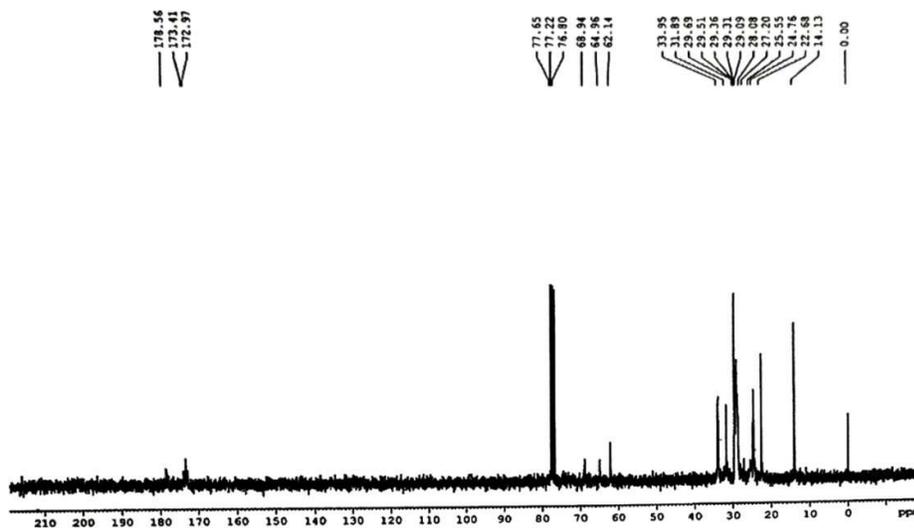


FIGURE 2.2.7.9

FT IR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND DODECYL ACRYLATE

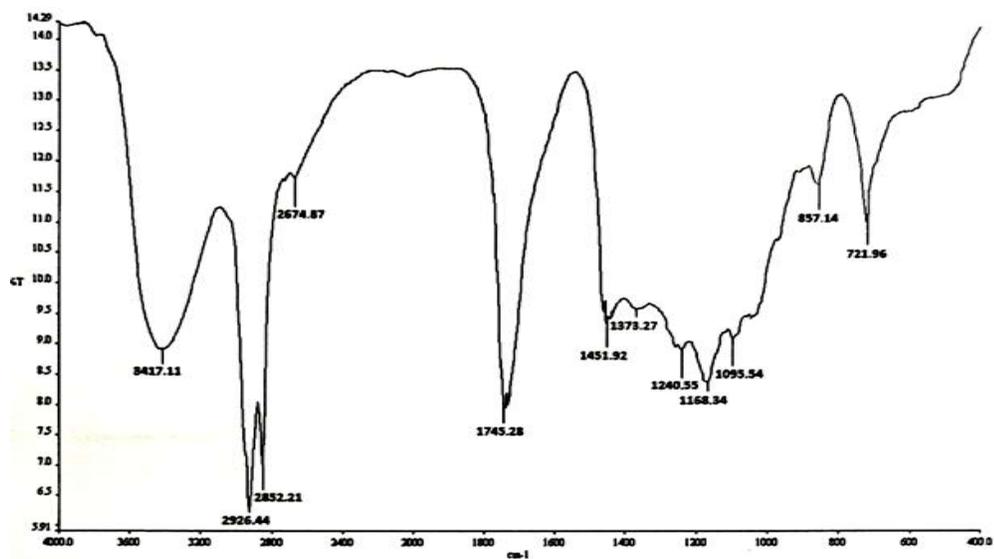


FIGURE 2.2.7.10

¹H-NMR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND DODECYL ACRYLATE

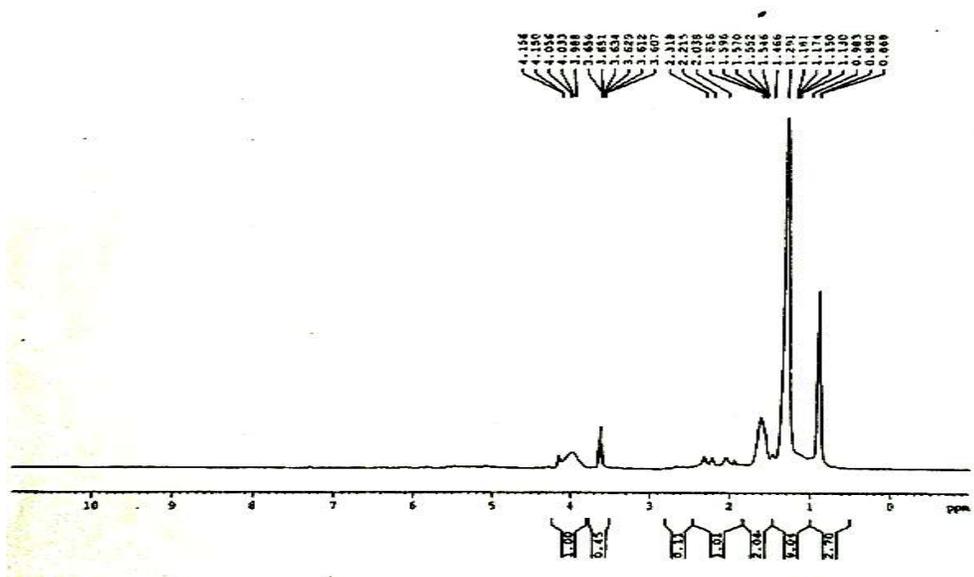


FIGURE 2.2.7.11

¹³C- NMR SPECTRA OF THE COPOLYMER OF CASTOR OIL AND DODECYL ACRYLATE

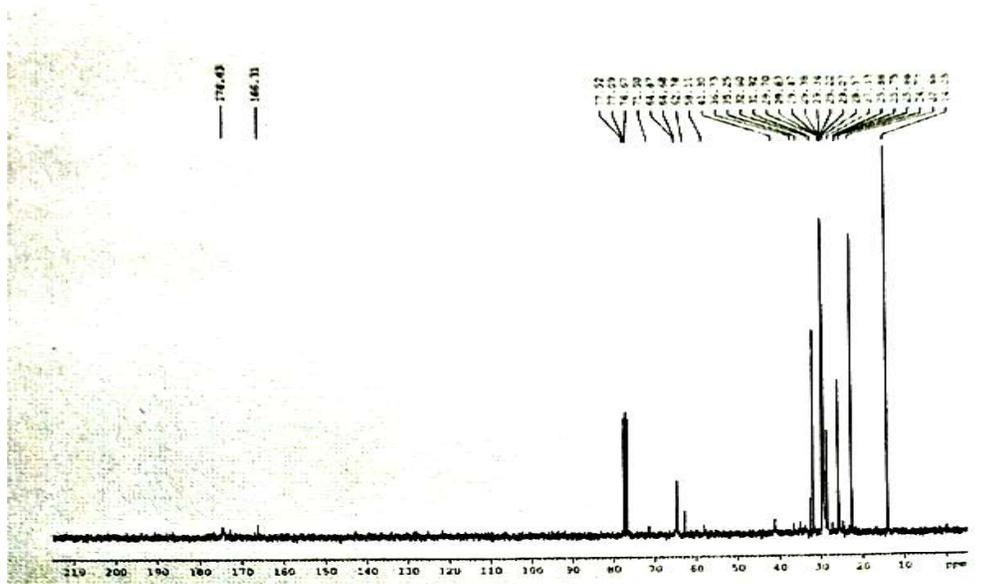
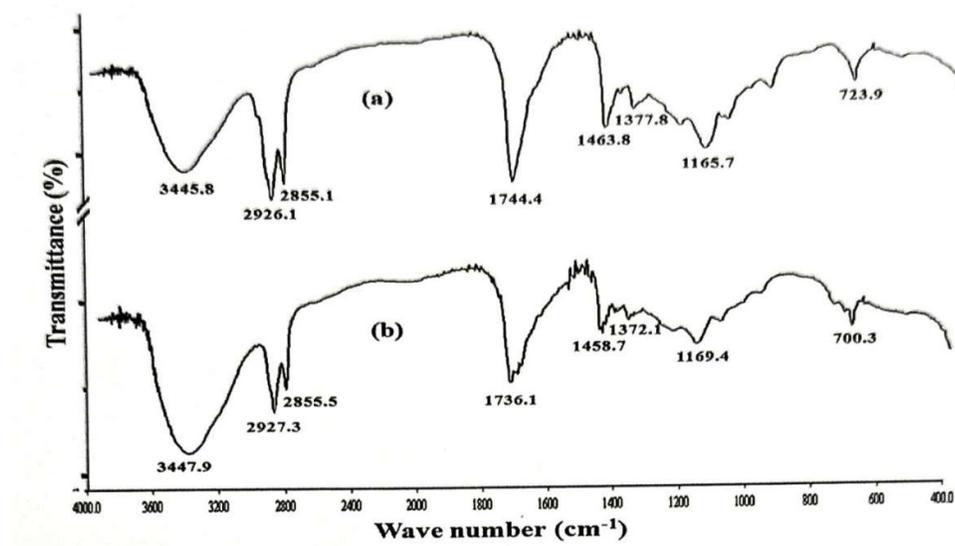


FIGURE 2.2.7.12

BIODEGRADATION OF HOMOPOLYMER OF CASTOR OIL



PART-2/CHAPTER-3

RAPESEED OIL-BASED ECO-FRIENDLY LUBE OIL ADDITIVES

2.3.1 INTRODUCTION

Base lubricating oil is often called base lube obtained from petroleum fraction. Lube oil is a mixture of complex paraffinic, aromatic and naphthenic hydrocarbons. Main purpose of lubrication is to reduce friction between metal surfaces in mutual contact thus minimizing the heat generated in the engine. In maximum cases, base oil alone cannot satisfy all the engine requirements. To increase the effectiveness of a lube certain chemical compositions, called additives are added in a certain percentage (0.03%-30%) in base lube. The additives are of a different kind, either they protect the metal surface or maintain lubrication property intact over a longer period against the adverse condition inside the engine. The addition of additives to lubricating is thus essential for the smooth working of an engine. Lubricants may be described as a suitable combination of base lube and additives and are used to keep moving metal parts apart, reduce friction and heat generated, prevent wear, prevent corrosion and rust, prevent antioxidant, keep base oil clean from corrosive acid (detergent) or keep the soot particle suspended (dispersant), etc. Although, petroleum-based lube or additives exhibit satisfactory performance these toxic chemicals are not biodegradable so they are not environment friendly. Strict regulations are, therefore, currently being imposed in some countries on lube oil-based lubricants together with their non-biodegradable toxic wastes materials [1]. This increasing environmental awareness has provided researchers with the impetus to search for some new, environmentally benign, multifunctional additives. Available vegetable oil, edible or non-edible is a potential candidate in this

field of research. Moreover, they show excellent antiwear properties [11] enhanced extreme pressure (EP) additive performance, exhibited high viscosity index [4], and low volatility [12]. There are lots of research papers where chemically modified vegetable oils have been used as an additive for base oil or base stocks in the formulation of bio-lubricant [7]. Rapeseed oil (RO) is interesting for its high percentage of mono-unsaturated fatty acids(oleic acid 18:1)[14], and its low content in saturated fatty acids in comparison to other edible oils. Rapeseed oil is also frequently used with other vegetable oil in blends (sunflower oil, soybean oil, corn oil, etc.) to improve the fatty acid profile of the oils. It has versatile applications in the nutritional and health field. The unique composition and thermal stability of RO lead us to use suitably modified RO as lube additives. However, research articles regarding such an application of RO as a green multifunctional additive for lubricant are not yet reported. Therefore, in this work, we have synthesized homopolymer of RO (HRO) and the copolymer of it with styrene(STY) in different percentage ratios to get thermally stable, eco-friendly multifunctional lubricant additives[8]. Characterization of the prepared polymer was carried out by spectral (FT-IR, NMR), GPC, and thermogravimetric analysis[2]. Performance evaluation of the prepared polymeric additives as pour point depressant, viscosity index improver, and effective antiwear was evaluated according to respective ASTM methods[5-8]. Keeping in mind the environmental issues over the use of toxic additives in automobile sectors have led to increased attention towards the use of greener environmentally benign components. Working in this field, the Biodegradability of the polymers of RO was determined by disc diffusion(DD) and soil burial degradation(SBD) method[5-8].

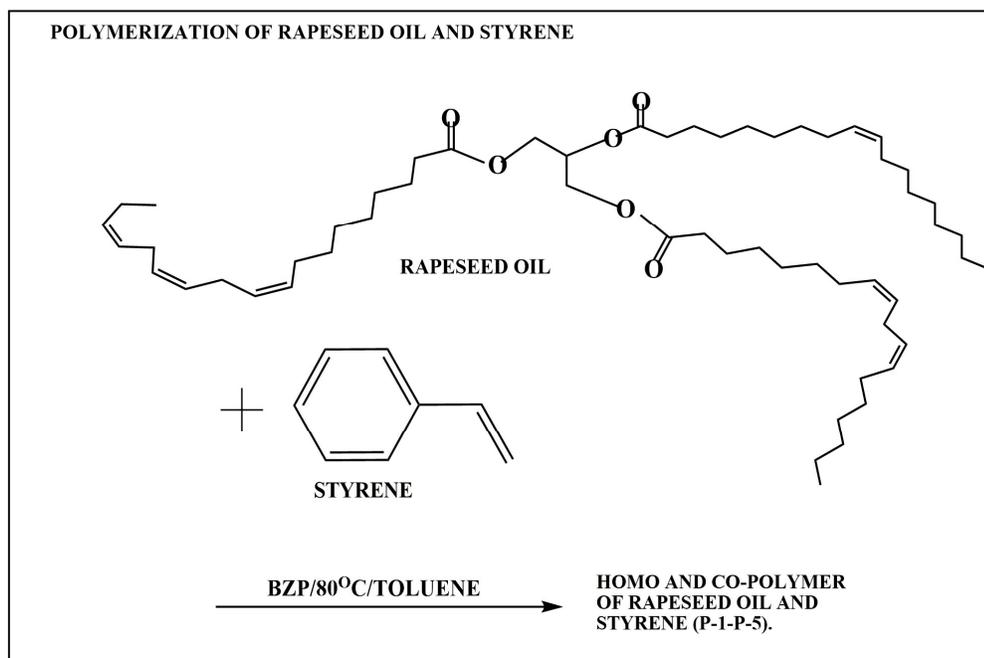
2.3.2 EXPERIMENTAL

2.3.2.1 MATERIALS USED

Rapeseed oil contains monounsaturated fatty acids in a great percentage. Oleic acid(18:1) 60.7%, linoleic acid (8:2) 21.2%, Linolenic acid (18:3) 11.8%[15]. Rapeseed oil (which contains about 90% unsaturation) was collected from a local grocer's shop. Benzoyl peroxide (LOBA chem, India) was used after recrystallization from chloroform-methanol mixture Toluene (GC 99.5%) was obtained from Merck Specialties Pvt. Ltd., (India). Styrene (GC 99.8%, Thomas Baker Chemicals Pvt. Ltd., India) and the mineral base oil SN150 were collected from IOCL, Dhakuria, West Bengal, India. The physical properties of the rapeseed oil and base oil are shown in Table:- 2.3.7.1. Fungal specimens were collected from the Department of Microbiology, North Bengal University, West Bengal, India, a sister department for testing the biodegradability of the polymers.

2.3.2.1 SYNTHESIS OF THE POLYMERS

The copolymers were prepared by taking the monomers, rapeseed oil (RO) and styrene (STY) at different percentage ratios P-1 (RO: STY=100:0), P-2 (RO: STY=98:2), P-3 (RO: STY=96:4), P-4 (RO: STY=94:6), P-5 (RO: STY=92:8), in presence of BZP initiator by conventional thermal free-radical polymerization pathway using toluene as solvent. The polymerization was carried out in a three-necked RB fitted with a magnetic stirrer, thermometer, condenser, and an inlet for nitrogen incorporation. A definite amount of rapeseed oil and styrene was heated to 80 °C and maintained for 20 minutes. Initiator BZP (0.5% w/w, concerning the total monomer wt) was then added the mixture was heated for 6 hrs. The detailed procedure is mentioned in our previous publication [4]. Scheme:- 2.3.1. represents the process of polymerization.

Scheme 2.3.1:- Preparation of polymers of rapeseed oil

- Fatty acid composition of RO:-Oleic acid(18:1) 60.7%,linoleic acid (18:2) 21.2%,Linolenic acid (18:3) 11.8%([14])
- Different percentage ratios of rapeseed oil (RO) and styrene (STY) of different polymers:- P-1 (RO:STY=100:0), P-2 (RO:STY=98:2), P-3 (RO:STY=96:4), P-4 (RO:STY=94:6), P-5 (RO:STY=92:8).[2]

2.3.3 MEASUREMENTS**2.3.3.1 INSTRUMENTATIONS**

- **SPECTROSCOPIC MEASUREMENTS**

IR spectra were documented on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature by direct loading of the sample in KBr surface within the wavenumber range of 400 to 4000 cm^{-1} . Bruker Avance 300 MHz FT-NMR spectrometer was used to record the ^1H NMR and ^{13}C NMR spectra. CDCl_3 and tetramethylsilane (TMS) were used as solvent and reference respectively[2].

- **MOLECULAR WEIGHT DETERMINATION**

The average molecular weight(M_n , M_w) and polydispersity index(PDI) was recorded by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at 35° C at a flow rate of 1mL/min injecting 20 µl of the polymer solution in HPLC grade THF[2].

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

TGA data were measured on the Shimadzu TGA-50 system, at a heating rate of 10° C/ min[2].

2.3.3.2 PERFORMANCE EVALUATION

- **EVALUATION OF VISCOSITY INDEX**

Viscosity index (VI) is a unitless qualitative parameter that describes the change in viscosity of a particular fluid against a temperature change. Viscosity index (VI) is an important parameter in fluid chemistry. The kinematic viscosity of a fluid sharply decreases with the increase in temperature Higher VI value implies fewer changes in viscosity with temperature. Polymeric component added as viscosity index improver (VII) in lube oil adopts complete packed molecular structure resulting in low viscosity at low temperature, whereas at a higher temperature the packed coil of polymer opens up resulting higher viscosity at the higher temperature. VI is a bulk property and is often called rheo improver in lube oil chemistry. It was calculated according to ASTM D 2270-10 [15]. The kinematic viscosities of the lubricant composition were determined at 40°C and 100°C which are essential to calculate VI according to the equations,

$$v = (Kt - L/t) \rho$$

where ρ is the density of the experimental solution, t is the time of flow of the solution and K and L are the viscometric constants of an Ubbelohde viscometer.

$$VI = 3.63(60 - 10^n)$$

and n was determined by the equation,

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

where v_1 and v_2 are the kinematic viscosities of the additive doped oil at 40 °C and 100°C temperature respectively. For the given temperature range, the value of k was determined to be 2.715. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40 °C and 100 °C. The effect of prepared additive concentration on VI was investigated by using different concentrations of lube and additives ranging from 1% - 5% (w/w).

• EVALUATION OF POUR POINT

At lower temperatures, lubricants freeze and form a jelly-like structure. The temperature at which lubricant flow is completely ceased is called the pour point (PP) of that lubricant. This is due to paraffinic wax crystal formation at a lower temperature in lube. This leads to lubricant failure and can cause serious damage to the engine component. Branched alkyl moiety in polymeric additive interacts with the wax and prevents them to crystallize hence inhibit lube to congeal. Polymeric substances added to improve the low-temperature flow of a lube called pour point depressant (PPD). Pour point of the lubricant composition was determined according to the ASTM D 97-09 [16]. method using the cloud and pour point tester model WIL-471 (India). A good pour point depressant additive lowers the pour point of the lubricant composition to a larger scale. The effect of different polymeric additive concentrations on PP was investigated by using different concentrations of lube and additive ranging from 1% - 5% (w/w).

- **EVALUATION OF ANTIWEAR PERFORMANCE**

Wear is the deformation of a metal surface over prolonged rubbing and sliding of metal surfaces in mutual contact. An antiwear agent either involves physical adsorption (moderate engine condition,) acting as friction modifier(FM) or involves in chemical process with electron exchange with metal and additive(extreme engine condition) acting as antiwear (AW) or extreme pressure additive(EP) [16]. The tribo film formation either through physical or chemical process minimizes the formation of wear scar. AW agents are surface protective additives and are often called tribo improvers in lube oil chemistry. The antiwear performance of the lubricant compositions in terms of wear scar diameter (WSD) was determined by Four-ball wear test apparatus (FBWT) (diameter and rotating speed of the ball were 12.7 mm and 1200 rpm respectively). following the ASTM D 4172-94 method[18].

- **BIODEGRADABILITY TEST**

Several tests have been devised for measuring the biodegradability of vegetable oil-based additives, as they have an inherent biodegradability compared to synthetic additives. In the present investigation, it was tested by (a) the disc diffusion method against fungal pathogens [5] and (b) the soil burial degradation test.

(a) DISC DIFFUSION (DD) METHOD

In this method, biodegradation of the prepared additives was tested against four different fungal pathogens, viz. *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA), and *Colletotrichum gloeosporioides* (CG) in a bacteriological incubator (Sigma Scientific Instruments Pvt. Ltd., India). Culture media was prepared, mixing agar powder, potato extract, dextrose, and in a 1:10:1

proportion(w/w). Polymeric additives 1.0 g of each with 2 gms of culture media were placed in Petri dishes and kept at 310 K for 30 days with the different fungal pathogens. The fungal growth was confirmed by a change of color from yellow to blackish. After 30 days, the additive samples were recovered from the fungal media and washed with chloroform, purified, and dried. Finally, the weight loss for each of the samples was calculated[19].

(b) SOIL BURIAL DEGRADATION TEST (SBD TEST)

In this test method, the microorganisms attack the surface of the polymer film (Liu et al., 2010). 1.0 g of each of the polymeric additive was taken to produce the polymer films. The films so obtained were then buried in the soil (containing the microorganisms) in a bacteriological incubator. The soil was placed in a tray, the relative humidity was maintained to 50–60% with the help of a humidity chamber and the temperature was set at 303 K. The soil used in this study was taken from the campus of the North Bengal University (West Bengal, India) with pH 7.3 and moisture content of 25%. The buried polymer films were recovered at regular intervals of 15 days up to 3 months with a different film for each time. Recovered films after the biodegradation test were washed with chloroform, filtered with Whatman grade 41 filtration paper, and dried in a vacuum oven at 323 K. They were then purified by precipitation of their hexane solution by methanol and then dried in a vacuum oven at 323 K. The test was carried as per ISO 846:1997[2,8]. The extent of degradation of the additives in the tests was determined by measuring the percent weight loss (PWL) of the samples. The PWL was determined by the equation,

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

Where M_0 = initial mass and M_1 = remaining mass after the test and subsequent drying until constant weight. The degradation of the polymers was also established

by observing the shift in the IR frequency of the ester carbonyls after the biodegradability test[19].

2.3.4 RESULTS AND DISCUSSION

2.3.4.1 SPECTROSCOPIC DATA ANALYSIS

The spectroscopic data of all the prepared polymers were analyzed to confirm the predicted structure of the additives. In the case of a copolymer, the characteristic IR absorption at 1743 cm^{-1} was for the ester carbonyl group of the rapeseed oil part respectively along with other absorption in the range 2857 cm^{-1} to 2931 cm^{-1} for $-\text{CH}_3$ & $-\text{CH}_2-$ stretching vibration. The peaks at 810 cm^{-1} , 756 cm^{-1} , 724 cm^{-1} , and 695 cm^{-1} were assigned to the phenyl group of styrene. An absorption at around 3000 cm^{-1} was due to the stretching of the C-H bond of an aromatic ring. The absence of absorption in the range of 3005 cm^{-1} to 3008 cm^{-1} due to unsaturated C-H stretching indicates successful polymerization (Figure:-2.3.7.1).

In the ^1H NMR, the methyl protons appear in the range of 0.876 - 0.898 ppm, the methylene protons in the range of 1.287 - 1.621 ppm, and the methine protons appeared in the range of 2.035 - 2.297 ppm for the alkyl chains. A peak at 4.081 ppm indicates the protons of the $-\text{OCH}_2$ group. The peaks in the range of 4.10 - 4.3 ppm indicate the protons of $-\text{COOCH}_2$ group of rapeseed oil. A broad peak in the range of 6.80 - 7.64 ppm indicates the protons of the aromatic ring of styrene in the case of copolymers. The absence of a peak in the range 5-6 ppm indicates polymerization was successful (Figure:-2.3.7.2).

In the ^{13}C NMR of the copolymer, the peaks in the range of 14.14 - 41.03 ppm were due to carbons of all CH_3 and CH_2 groups. The peaks at 58.13 ppm indicate the methine carbons of $-\text{CH}-$ of $-\text{COCH}$ group. The peaks in the range of 60 - 62.08 ppm represent the carbons of $-\text{OCH}_2$ groups. The $-\text{CH}_2$ carbons of $-\text{CH}_2-$

OCOCH₂– group of rapeseed oil showed peaks in the range of 64.61– 68.99 ppm. The aromatic carbons appear in the range of 127.93 -130.88 ppm. The peaks in the range of 165.65 - 173.00ppm confirm the carbons of ester carbonyl groups (Figure:- 2.3.7.3).

In the case of the homopolymer of rapeseed oil, the IR absorption band at 1741 cm⁻¹ (Figure:- 2.3.7.4) showed the presence of the ester carbonyl group. In the ¹H NMR spectra of the homopolymer of rapeseed oil (Figure:-2.3.7.5), the peaks in the range of 4.12- 4.33 ppm indicate the protons of –COOCH₂ group of rapeseed oil, the methyl protons appear in the range of 0.86 - 0.90 ppm, the methylene protons in the range of 1.26 - 1.62 ppm and the methine protons appeared in the range of 2.29 - 2.34 ppm for the alkyl chains (Figure:-2.3.7.5).

In the ¹³C NMR spectra of the homopolymer of rapeseed oil, the ester carbonyl group appears at 173.98 68.91 ppm (Figure:-2.3.7.6). The carbons of – OOCH₂ group appear at 62.07-68.91 ppm.

2.3.4.2 MOLECULAR WEIGHT DATA ANALYSIS

The experimental values of number average molecular weights (M_n) and weight average molecular weights (M_w) of the prepared polymers (P-1 to P-5) are given in Table:-2.3.7.3. From the experimental data, it is seen that among the five polymers, P-5 has the highest molecular weight. This is due to the increased percentage of styrene moiety in polymeric structure. Therefore, the percentage of styrene has a significant role in molecular weight during polymerization. The polydispersity index(PDI) is the ratio between M_w and M_n , which signifies the extent of polymerization i.e. probability of formation of polymers with different chain lengths with varying crosslinking. High PDI polymers have less solubility in lube.

2.3.4.3 ANALYSIS OF TGA DATA

Considering the five prepared polymers (P-1, P-2, P-3, P-4, P-5) thermogravimetric analysis data are given in Table:- 2.3.7.2. From the table, it is observed that the polymer P-1 exhibit higher thermal degradation compared to other copolymers, concluding P-1 is thermally less stable. The thermal degradation of polymers P-3, P-4, and P-5 are almost similar. Major decomposition starts at 160 °C with about 30% weight loss In the case of polymer P-1. Major decomposition starts approximately at 268 °C with 18% weight loss for polymers P-3, P-4, and P-5. Thermal stability increases due to the incorporation of styrene moiety in copolymers. Therefore, styrene has significant importance to improve the thermal stability in copolymers.

2.3.4.4 ANALYSIS OF VISCOSITY INDEX VALUES

VI was measured at different concentrations of polymer in lube ranging from 1% to 5% (w/w) to the base lube. The experimental data of VI are given in Table:- 2.3.7.4. VI values rise with increasing the concentration of polymers in the doped base oil. The viscosity of lubricating oil falls with increasing temperature but an expansion of packet coil of polymer molecules takes place with increasing temperature and due to this, the expanded coil of polymer substance out way the decrease in viscosity of the lubricant [13]. Moreover, increasing the concentration of polymer in lubricating oil leads to an increase in the total volume of polymer coil in doped lube oil and improves the VI property [6]. It has been observed that the VI value increases by incorporation of styrene in the backbone of the copolymer of rapeseed oil, which may be due to the higher crosslinking of the copolymers. The copolymer P-5 has the highest effect on VI increments followed by P-4, P-3, P-2, and P-1. The higher values VI in the case of P-5 containing the maximum percentage of

styrene in the doped lube, are due to greater volume of the solvated additive molecule i.e. micelle compared to others which may be associated with its higher average molecular weights and lower PDI value.

2.3.4.5 ANALYSIS OF POUR POINT VALUES

The Pour points of the lubricants prepared by blending the polymers at different concentration levels ranging from 1%– 5% (w/w) are shown in Table:- 2.3.7.5. All the polymers are performed considerably well as PPD and with increasing concentration, the efficiency of the doped lube in terms of PPD increases up to a certain limit (4% concentration). This indicates that at this concentration, the paraffinic wax of base oil interacts with the polymer effectively and prohibits the crystal of paraffinic wax to congeal [3]. Among the prepared five polymers, P-4 showed better performance as PPD.

2.3.4.6 ANALYSIS OF ANTI-WEAR PROPERTIES

The tribological properties(FM, AW, EP) of the polymer doped base oil compositions were determined by measuring WSD through FBWT apparatus applying 392 N load, and values are given in Table:- 2.3.7.6. Improvement of antiwear performance was observed when lube was blended with polymers and it was reflected in the lower WSD values. Compared to the homopolymer The copolymers exhibit better results. The polymer P-5 at 5% concentration showed the highest reduction in WSD values. This indicates that the film formed by the lubricant between the two moving metal surfaces is very strong. It may be due to higher molecular weight and hence higher number of polar side chains of the ester carbonyl groups and hydroxyl groups present in rapeseed oil [10]. The contribution of the higher percentage of styrene in the polymer feed has also played a significant role in its aromatic ring structure.

2.3.4.7 ANALYSIS OF BIODEGRADABILITY TEST

Biodegradability test results (Table:- 2.3.7.7) with the homopolymer (P-1) and copolymers (P-2 to P-5) showed noticeable decomposition against the fungal pathogens, *Calletotricheme camellia*, and *Alternaria alternata*, though it was expected that homopolymer would show better biodegradability, close observation of the test results revealed considerable biodegradation for all samples. The analysis of the soil burial tests (SBD) indicated that the degradation increased continuously with the time the samples stayed in the test soil. Further, both the homo and copolymer showed significant weight losses against the fungal pathogens, especially against *Alternaria alternate* (AA), in the disc diffusion (DD) test. As expected for a homopolymer of rapeseed oil owing to the presence of the natural monomer unit, it (P-1) showed the highest biodegradability among all the additives in both of the tests. The FT- IR peaks of the polymer P-1 deformed in peak height and intensity after the DD test. The other polymers also showed some shift in their IR peaks but to a lesser extent. The shift and the decrease in the IR peak intensities of the polymers before and after the biodegradation tests together with the PWL of the polymers confirmed the biodegradable nature of the prepared polymers[2].

2.3.5 CONCLUSION

From the above study, it was found that the homopolymer of rapeseed oil and copolymer of it with styrene showed better performance as viscosity index improver, pour point depressant, and antiwear additive for base oil. As a viscosity index improver, pour point depressant, and antiwear additive, the copolymers are found more effective than the homopolymer. On the other hand, the presence of rapeseed oil in the additive composition introduces excellent biodegradability too, in the additive. The average molecular weight and thermal stability of the copolymers

increased with the increase in the percentage of styrene. Therefore, the above study is a potential approach to formulate a green lubricant composition with excellent multifunctional additive properties for lube oil.

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for Base Oil.

2.3.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-3 of Part-2**”.

2.3.7 TABLES AND FIGURES

TABLE 2.3.7.1

PROPERTIES OF RAPESEED OIL AND BASE OIL

RAPESEED OIL		BASE OIL	
PROPERTIES	VALUES	PROPERTIES	VALUES
Saponification index(mg/g)	167-74	Density at 313 K, kg.m^{-3}	868.03
Iodine index(mg/g)	97-100	Viscosity at 313 K	20.31×10
Refractive index at 50°C	1.462	Viscosity at 373 K	3.25×10
Density(g/ml)	0.916	Viscosity index	85
Saturated fatty acid (%)	7.36	Pour point (°C)	-6
Mono unsaturated fatty acid (%)	63.27	Cloud point (°C)	-8
Polyunsaturated fatty acid(%)	28.14	-	-
Oleic acid(g)	60.7	-	-
Linoleic acid ω -6(g)	21.2	-	-
α -Linolenic acid ω -3(g)	11.8	-	-

TABLE 2.3.7.2

PERCENTAGE COMPOSITION AND TGA VALUES OF PREPARED POLYMERS

Polymer code	% composition of monomers		TGA values			
	RO	STY	Decom Temp	PWL	Decom Temp	PWL
P-1	100	0	160	28	320	78
P-2	98	2	210	24	355	85
P-3	96	4	266	17	382	80
P-4	94	6	268	19	382	81
P-5	92	8	268	18	384	79

TABLE 2.3.7.3

THE MOLECULAR WEIGHT OF THE PREPARED POLYMERS BEFORE AND AFTER THE BIODEGRADABILITY TEST & GRAPHICAL REPRESENTATION

Polymer Code	Average molecular weight (before biodegradation)			Average molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P-1	8328	11522	1.31	4132	4645	1.26
P-2	18657	26536	1.34	14211	21427	1.44
P-3	19497	29166	1.43	15512	24876	1.59
P-4	22671	33612	1.88	16536	29271	1.73
P-5	29654	38644	1.29	22320	29664	1.34

M_n = Number average mol. Wt.; M_w = Weight average mol. Wt.; PDI = Poly disparity index

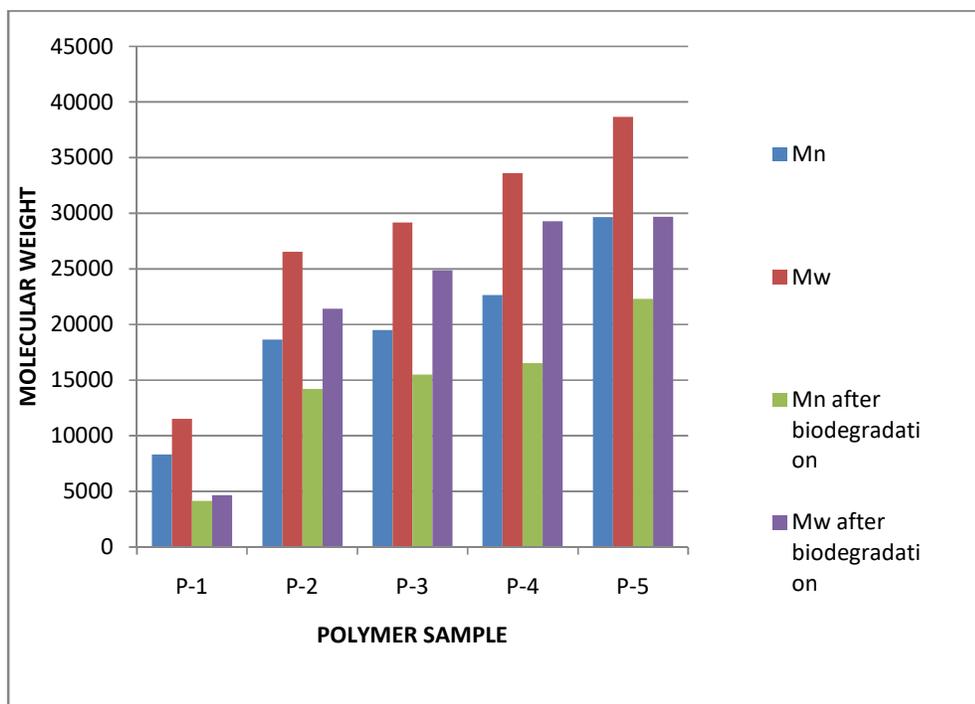


TABLE 2.3.7.4

VISCOSITY INDEX DATA AND GRAPHICAL ILLUSTRATION

Polymer Code	VI of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P-1	85	89	95.5	104	112	118
P-2	85	94	98	112	115	128
P-3	85	96	104	114	123	131
P-4	85	101	106	116	124	133
P-5	85	103.5	111	125	135	145

Properties of the base oil - Density (g.cm^{-3}) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 85; Pour point, °C: -6.

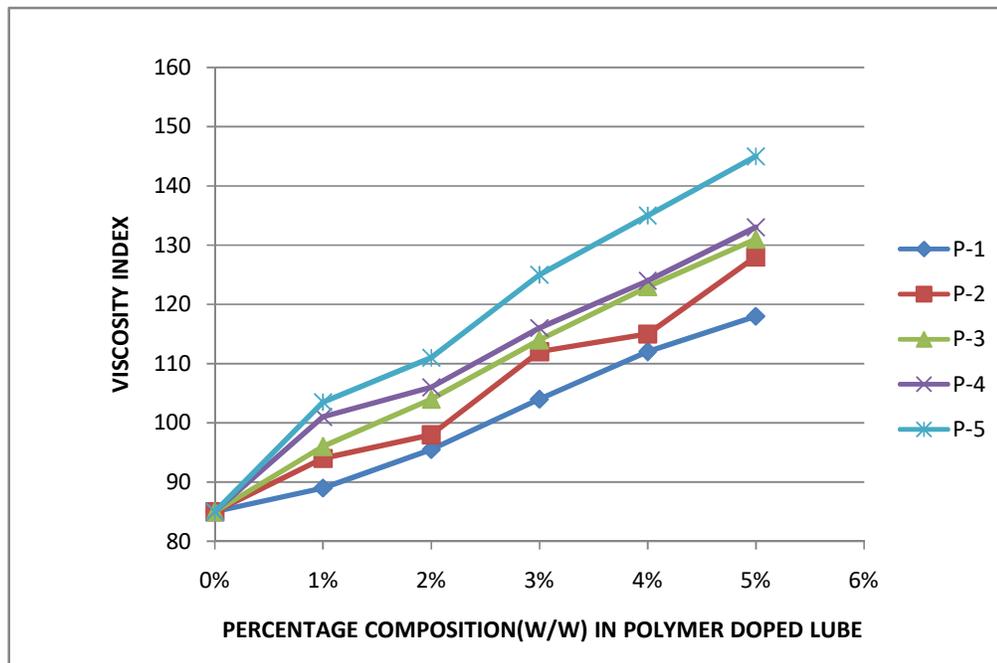


TABLE 2.3.7.5

POUR POINT VALUES OF POLYMER BLENDED BASE OIL & GRAPHICAL REPRESENTATION

Polymer Code	Pour point (° C) of lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	-6	-9	-12	-12	-15	-16
P-2	-6	-10	-12	-16	-18	-16
P-3	-6	-10	-12	-16	-20	-18
P-4	-6	-12	-15	-18	-22	-24
P-5	-6	-10	-15	-18	-18	-22

Properties of the base oil - Density (g.cm⁻³) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 85; Pour point, °C: -6.

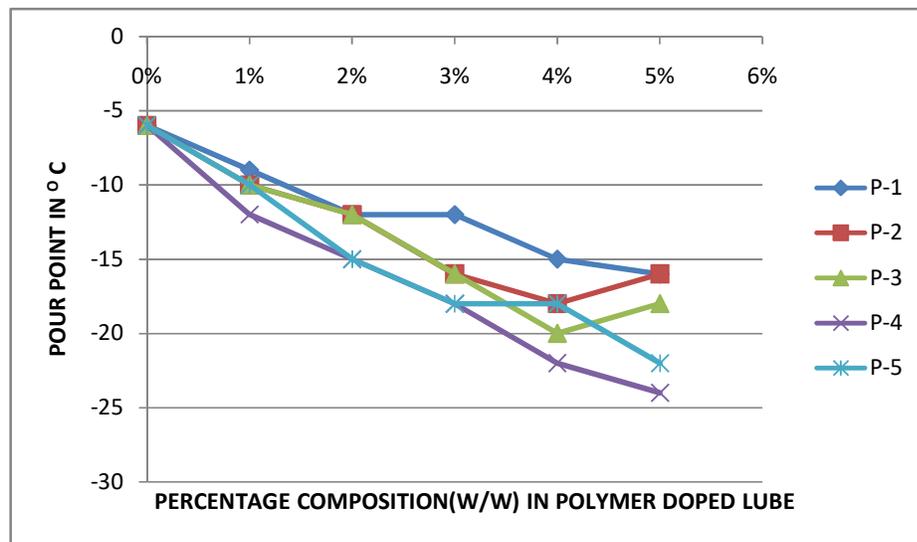


TABLE 2.3.7.6

ANTIWEAR PROPERTY IN TERMS OF WEAR SCAR DIAMETER (WSD IN MM) VALUES OF DIFFERENT LUBRICANT COMPOSITIONS

Polymer Code	WSD of lubricant (in mm) at different polymer concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	1.116	1.067	1.044	1.025	1.007	0.964
P-2	1.116	1.065	1.037	1.023	1.003	0.957
P-3	1.116	1.060	1.028	1.018	0.992	0.955
P-4	1.116	1.052	1.022	1.002	0.958	0.931
P-5	1.116	1.031	1.013	0.992	0.943	0.911

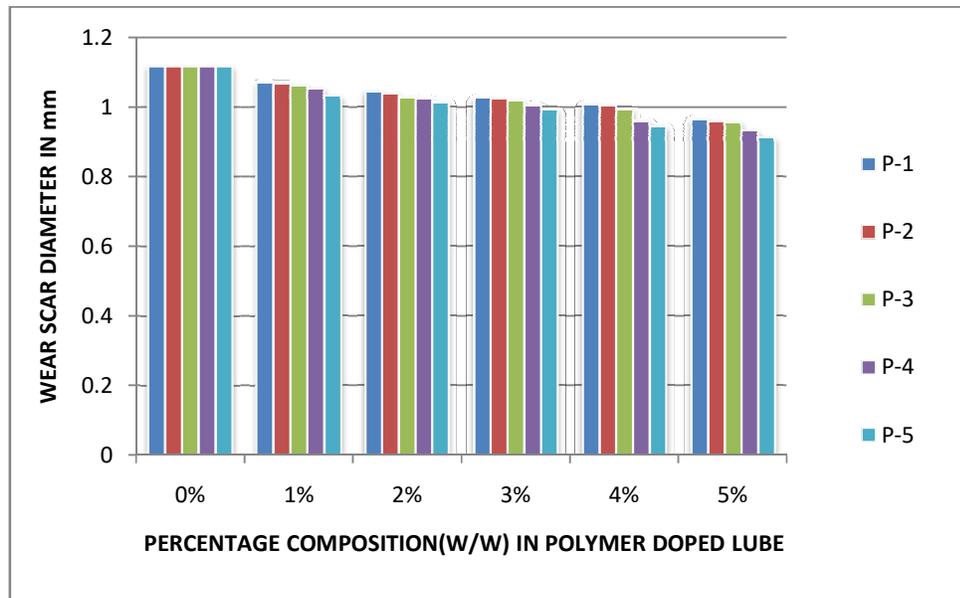


TABLE 2.3.7.7

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	0.45	0	0.62	0	
P-2	0.38	0	0.54	0	0	0.35
P-3	0.30	0	0.48	0	0	0.30
P-4	0.26	0	0.39	0	0	0.25
P-5	0.22	0	0.35	0	0	0.19
CC = Calletotricheme camellia; FE = Fussarium equisitae; AA = Alternaria alternata; CG = Colletrichum gleosproides; CE= Curvularia eragrostidies.						

FIGURE 2.3.7.1

A REPRESENTATIVE FT-IR SPECTRUM OF THE RAPESEED OIL-STYRENE COPOLYMER

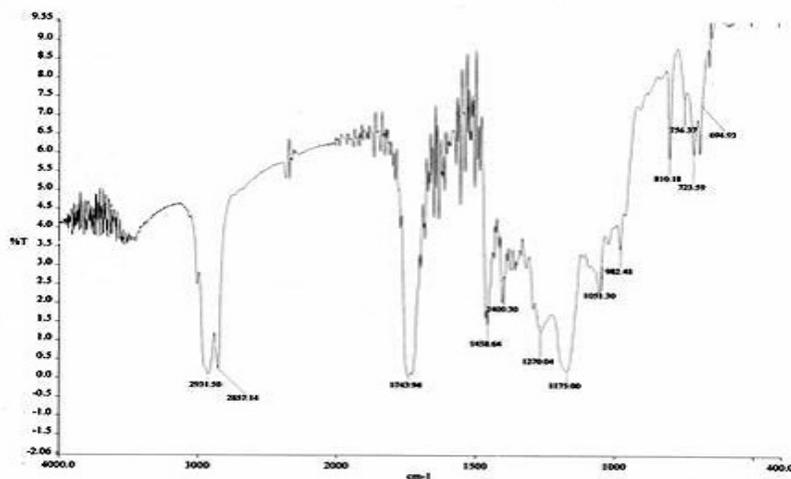


FIGURE 2.3.7.2

A REPRESENTATIVE ¹H NMR SPECTRA OF RAPESEED OIL-STYRENE COPOLYMER

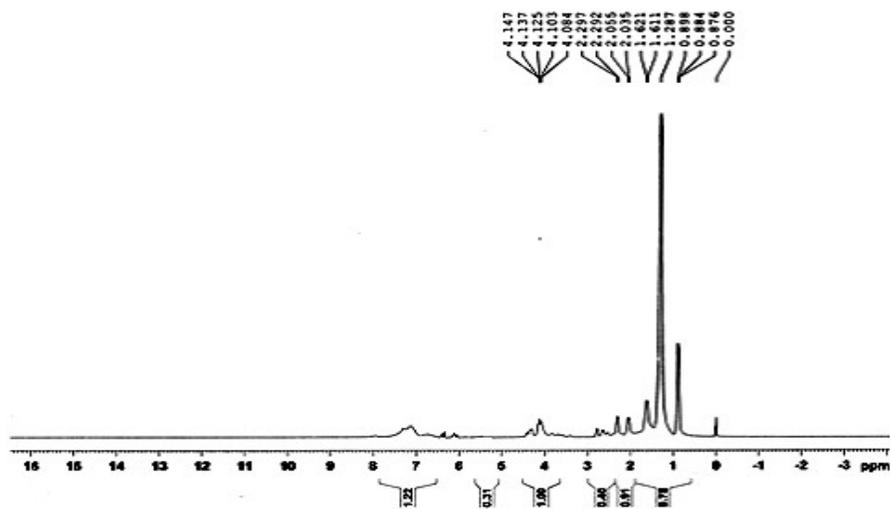


FIGURE 2.3.7.3

A REPRESENTATIVE ^{13}C NMR SPECTRA OF RAPESEED OIL –STYRENE COPOLYMER

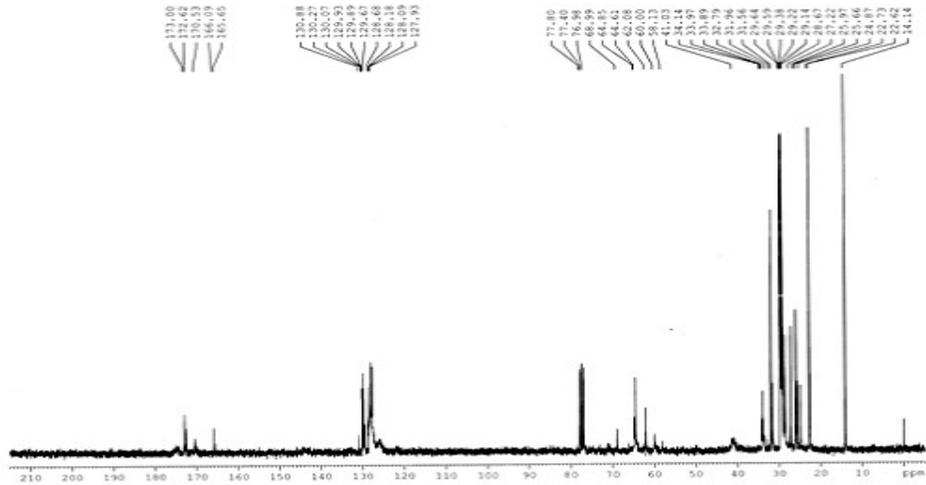
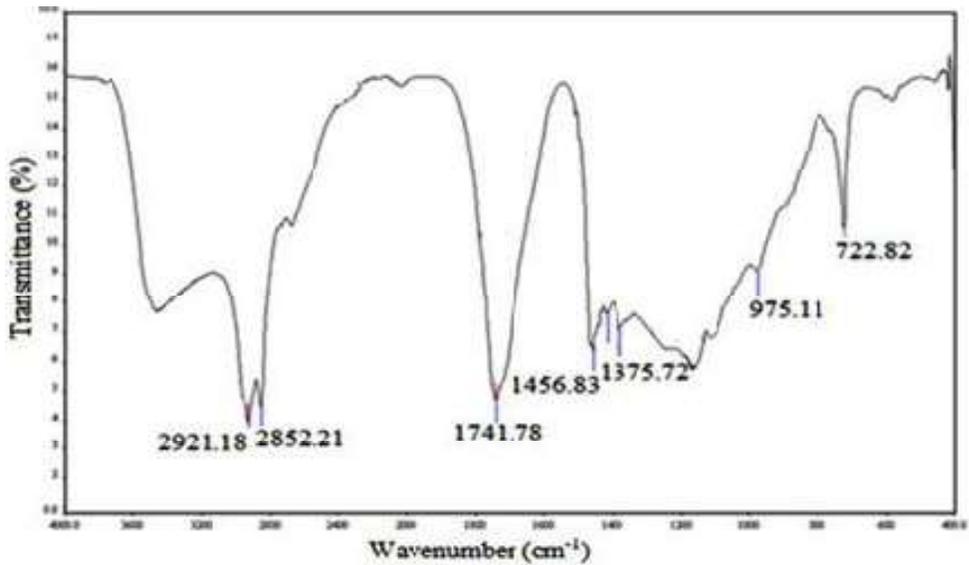


FIGURE 2.3.7.4

FT-IR SPECTRA OF THE HOMOPOLYMER OF RAPESEED OIL



PART-2/CHAPTER-4

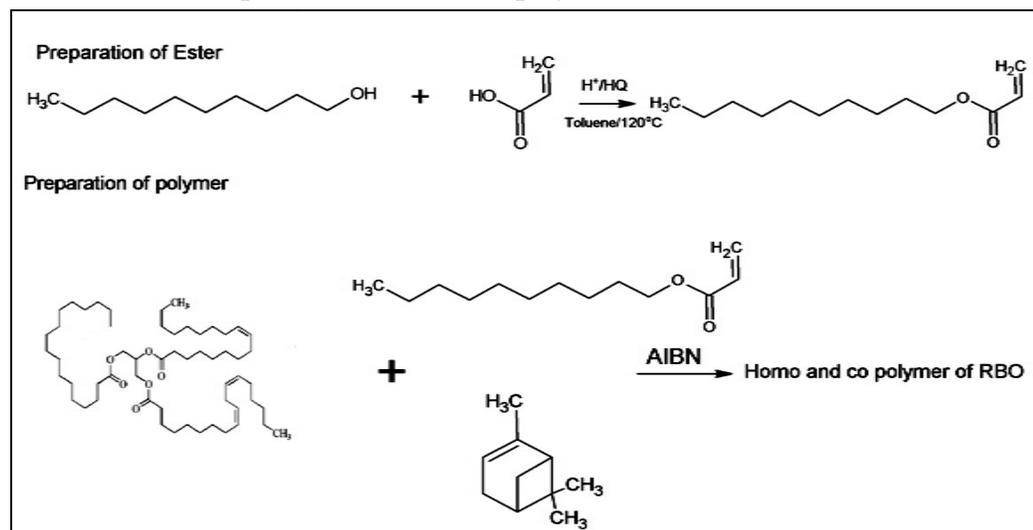
RICE BRAN OIL-BASED HOMO AND COPOLYMERS AS POTENTIAL LUBE OIL ADDITIVES

2.4.1 INTRODUCTION

Lubricating oil additives are the substances which when added to the oil, can either improve the properties already present or incorporate some new feature in it[2]. The most important categories of additives are surface protective additive like friction modifier, antiwear, extreme pressure, detergent, dispersant additive. Performance additive like viscosity improver, pour point depressant. Antioxidant additives protect lubricants from being auto oxidized hence they are lube protective additives of base lube. Additives synthesized from vegetable oils are less toxic and more environmentally benign due to their biodegradable property and low toxicity [3]. Moreover, they exhibit high viscosity index (VI), low pour point, and good antiwear property. Though vegetable oil itself exhibits high viscosity index, low pour point, high dispersant activity, high-temperature stability but unsaturation present in their fatty acid moiety makes them vulnerable to aerial oxidation. After performing certain chemical modifications they can act as a multifunctional lube oil additive. Therefore, more focus has been laid on the research of lube oil additives from vegetable oils. Rice bran oil contains a high percentage of unsaturated triglycerides and can be used as a monomer in free radical polymerization [4]. There are many research papers based on rice bran oil in the field of food[5], pharmaceutical[6], cosmetics[7], industries, etc. However, reports regarding the application of acrylate and alpha-pinene copolymers of rice bran oil as a multifunctional additive for lubricant are very scanty. A recent study in the lubricant industry has given special

attention to the application of plant oil-based additives in lube due to their biocompatibility and enhanced additive performances compared to those toxic chemicals available in the market. In this case, we have prepared a homopolymer of rice bran oil (RBO) and copolymers with decyl acrylate and alpha-pinene at different percentage ratios using a conventional thermal pathway in presence of azobisisobutyronitrile (AIBN) as a free radical initiator[1]. Characterization of the polymers was recorded by spectral technique (FT-IR and NMR spectroscopy). The gel permeation Chromatography method (GPC) was used to determine the average molecular weight of the prepared polymers. Thermogravimetric analysis (TGA) was used to study the thermal stability of the prepared polymers. Standard ASTM methods were used to investigate the performance of all the prepared polymers in two types of base oil as viscosity index improver (VII) and pour point depressant (PPD). Disc diffusion method(DD) and soil burial method(SBT) were used to ascertain the biodegradability of prepared polymers [1].

Scheme 2.4.1:-Preparation of ester and polymer.



Percentage composition(w/w) of major fatty acids in Ricebran oil, Palmitic acid (16:0) 15%, Oleic acid (18:1) 42.5%, Linoleic acid (18:2) 39.2%, Other(saturated or unsaturated) 3.3%[10].

2.4.2 EXPERIMENTAL

2.4.2.1 SYNTHESIS OF THE POLYMERS

The homopolymer of RBO was synthesized by the free radical polymerization method taking the monomers of RBO in presence of the AIBN initiator (Scheme:-2.4.1) The polymerization was carried out in an RB, fitted with a thermometer, magnetic stirrer, condenser, and an inlet for the introduction of air. The monomer was heated to 90° C in presence of toluene as solvent. Initiator AIBN (0.5% w/w, considering total monomer weight) was then added and continuously heated for 5 hours keeping the temperature constant at 90°C. After the completion of the reaction, the product was poured into methanol with continuous stirring, filtered off, and dried. Decyl acrylate was synthesized at 120°C using 1-decanol and acrylic acid in a Dean stark apparatus using H₂SO₄ as the catalyst. The copolymers of RBO with decyl acrylate (DA) (P-1 to P-3) and another set of copolymers of RBO with alpha-pinene (P-4 to P-6) at different percentages ratios were also prepared in a similar procedure. hydroquinone as a free radical quencher, and toluene as solvent[1]. Percentage composition of different monomers in polymers arranged in the following table

Composition in different polymers.

Polymer Code	Specification
P-0	Homopolymer of RBO
P-1	Copolymer ,RBO:DA=9:1 (w/w)
P-2	Copolymer, RBO:DA=8:2 (w/w)
P-3	Copolymer ,RBO:DA=7:3 (w/w)
P-4	Copolymer, RBO:α pinene=9:1 (w/w)
P-5	Copolymer, RBO:α pinene=8:2 (w/w)
P-6	Copolymer, RBO:α pinene=7:3 (w/w)

2.4.3 MEASUREMENTS

2.4.3.1 INSTRUMENTATION

- **SPECTROSCOPIC MEASUREMENTS**

Bruker Avance 300 MHz FT-NMR spectrometer was used to record the NMR spectra by using CDCl_3 as solvent. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wavenumber range of 400 to 4000 cm^{-1} [1].

- **MOLECULAR WEIGHT DETERMINATION**

The average molecular weight was recorded by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at 35° C at a flow rate of 1mL/min[1].

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

TGA data were recorded on the Shimadzu TGA-50 system, at a heating rate of 10° C / min[1].

2.4.3.2. PERFORMANCE EVALUATION

- **EVALUATION OF VISCOSITY INDEX**

Viscosity index (VI) is an important parameter that determines the change of viscosity of the lubricant at high temperatures. A higher value of VI indicates the small change in viscosity at high temperatures. It was calculated according to standards ASTM protocol[12]. The kinematic viscosities of the lubricant composition were determined at 40 °C and 100 °C which are required for the calculation of VI.

- **EVALUATION OF POUR POINT**

Pour point values of the lubricant composition were determined according to the ASTM D 97-09 method[13] using the cloud and pour point tester model WIL-471 (India). A good pour point depressant additive decreases the pour point of the lubricant composition to a larger extent.

- **BIODEGRADABILITY TEST**

- (a) **DISC DIFFUSION METHOD (DD)**

The biodegradability test was carried out for the prepared polymers against *Calletotricheme camellia* (CC), *Fusarium equisetae* (FE), *Alterneria alternate* (AA), *Colletrichum gleosproides* (CG), and *Curvularia eragrostidies* (CE) pathogens. A suitable amount of potato extract, dextrose, and agar powder was mixed to prepare the culture media strain. All the experiments were completed in Petri dishes and were kept incubated at 37° C for 90 days after the addition of about 1g of the polymer sample. The fungal progression was studied by a yellow to blackish color change. After 90 days, the polymer samples were recovered from the fungal media by chloroform, purified, and dried. The dried samples were weighed[14].

- (b) **SOIL BURIAL METHOD (SBT)**

The SBT method was carried out as per ISO 846:1997 standard method. A thin film of polymer sample was prepared by taking 1.5 g of each of the samples separately and then buried in the soil. Then the soils with the samples were incubated in a Bacteriological Incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) at 30° C with a relative humidity of 60% for 90 days and thus subjected to the action of microorganisms present in the soil. After 90 days, the polymer samples were recovered by chloroform and weighed[14].

2.4.4 RESULTS AND DISCUSSION

2.4.4.1 SPECTROSCOPIC ANALYSIS

The homopolymer of RBO (P-0) showed an IR absorption band for the ester carbonyl group at 1745.03 cm^{-1} . The peaks at 2852.4 cm^{-1} and 2924.2 cm^{-1} are the stretching vibration of the $\text{CH}_3\text{-CH}_2\text{-}$ group. (Fig:-2.4.7.1) In the ^1H NMR spectra of homopolymer, the peaks in the range of $4.120\text{-}4.314\text{ ppm}$ indicate the protons of -COOCH_2 group (Figure:-2.4.7.2). In the ^{13}C NMR spectra of homopolymer, the peaks in the range of 174.35 ppm indicate the carbons of an ester carbonyl group. (Figure:-2.4.7.3) The carbons of the -OCH_2 group appear in the range $62.77\text{-}64.71\text{ ppm}$. The IR spectra of three copolymers (P-1 to P-3) are almost similar. The absorption band at 1732 cm^{-1} is due to an ester carbonyl group. (Figure:-2.4.7.4) In the ^1H NMR spectra, peaks at $4.020\text{-}4.124\text{ ppm}$ indicate the protons of -OCH_2 of decyl acrylate moiety. The peaks in the range of $4.311\text{-}4.374\text{ ppm}$ indicate the protons of -COOCH_2 group of RBO. No peaks in the range of $5\text{-}6\text{ ppm}$ indicate that polymerization was carried out successfully. (Figure:-2.4.7.5) In the ^{13}C NMR spectra, peaks ranging from $165.65\text{-}173\text{ ppm}$ confirm the presence of carbons of ester groups (Figure:-2.4.7.6). There is no peak in the range of $120\text{ - }150\text{ ppm}$ and it indicates that polymerization was carried out successfully. The IR spectra of the three copolymers (P-4 to P-6) are almost similar. The absorption at 1745.28 cm^{-1} is due to the ester carbonyl group of RBO moiety. The absence of any peak in the range of $4\text{ - }6\text{ ppm}$ in ^1H NMR and $120\text{ - }150\text{ ppm}$ in ^{13}C NMR spectrum indicated the formation of the copolymer of RBO with α -pinene (Figure:-2.7.4.8-Figure:-2.4.7.9).

2.4.4.2 MOLECULAR WEIGHT DATA ANALYSIS

The experimental value of the number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymers (P-0 to P-6) are shown in Table:- 2.4.7.1. From the experimental data, it was observed that among the seven polymers, the homopolymer of RBO (P-0) and the copolymer P-3, have the lowest and highest molecular weight respectively. Moreover, it is also observed that with increasing the percentage of DA moiety (P-1 to P-3) and alpha-pinene moiety (P-4 to P-6) in the copolymers, the molecular weight increases. A better molecular weight is obtained in the copolymers of RBO and DA than RBO and alpha pinene[1].

2.4.4.3 ANALYSIS OF TGA DATA

From the experimental TGA values of the seven polymers, it was observed that the thermal stability of the homopolymer of RBO (P-0) is less than copolymers. This indicates that when DA or alpha-pinene moiety is introduced in the backbone of RBO oil, the thermal stability increases[1]. Two major decompositions have been observed at 160 ° C and 330 ° C with 23% and 85% weight loss respectively in the case of P-0. The thermal stability of copolymers P-1, P-2, and P-3 are almost identical where two major decompositions were observed at 220 ° C and 482 ° C with 22% and 78% weight loss respectively. The thermal stability of copolymers P-4, P-5, and P-6 is less than other copolymers P-1, P-2, and P-3 but higher than the homopolymer of RBO (P-0).

2.4.4.4 ANALYSIS OF VISCOSITY INDEX (VI) VALUES

VI was calculated at different concentrations ranging from 1% to 5% (w/w) in two types of base oil and the values are listed in Table:- 2.4.7.2. The viscosity of lube oil decreases with increasing temperature but when lube oil is blended with the polymeric additives, the decrement of viscosity stops. At high temperatures,

expansion of additive molecules takes place and as a result, the size of the micelle increases. This increased in micelle size prevents the reduction of the viscosity of the lubricant composition. It is also observed that with the increasing concentration of the lubricant composition, the VI values increase. It may be due to an increase in the total volume of polymer micelle and hence improves the VI property[3]. It was found that the VI value increases by incorporation of DA and alpha-pinene moiety in the backbone of the homopolymer of RBO. This may be due to the higher molecular weight and higher crosslink density of the copolymers[8]. The copolymer P-3 has the highest VI value than the other prepared polymers in both types of base oil. It may be due to higher molecular weight compared to others.

2.4.4.5 ANALYSIS OF POUR POINT (PP) VALUES

The pour points of the base oil containing additives at concentration levels ranging from 1%–4% (w/w) are listed in Table:- 2.4.7.2 for two types of base oil which indicate that the prepared lubricant compositions have lower PP than base oil and hence the prepared additives can be used as PPD. From the experimental data, it is observed that the efficiency as PPD increases up to 3% concentration. The reason may be, at this concentration the interaction between the additive and paraffinic wax of base oil is more effective and decreases the shape of crystals of the paraffinic wax[9-10]. Among the seven polymers, P-3 showed best performance as PPD than the others in both types of base oil.

2.4.4.6 ANALYSIS OF BIODEGRADABILITY TEST RESULTS

Biodegradability test results obtained by using the disk diffusion and soil burial test method are presented in Table:- 2.4.7.3. All the polymers showed significant biodegradability against the pathogens *Calletotricheme camellia* and *Alterneria alternate* only. The mass loss after biodegradation of the prepared

polymers was further confirmed by shifting of IR frequency of the ester carbonyl (Figure:-2.4.7.10) along with other shifted peaks and determining the GPC molecular weight after biodegradation is shown in Table:-2.4.7.1. Among the prepared seven polymers, the homopolymer of RBO (P-0) showed better biodegradation both in disk diffusion as well as soil burial test method[14].

2.4.5 CONCLUSION

A consideration of the chemical structures of DA and alpha-pinene may be taken into consideration to explain the differences of performance between the copolymers of RBO with DA and RBO with alpha-pinene. The average molecular weight of copolymers of RBO with DA is better than RBO with alpha-pinene. A viscosity index value of homopolymer of RBO is lower than copolymers and viscosity index value increases with increasing the percentage of DA or alpha-pinene in copolymers. The pour point of the lubricant compositions is found to be better for the copolymers of RBO with DA than the copolymers of RBO with α -pinene and the values decrease with the increasing concentration of the lubricant composition. The homopolymer of RBO and copolymers of RBO with alpha-pinene showed significant biodegradability than copolymers of RBO with DA.

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for Base Oil.

2.4.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-4 of Part-2**”.

2.4.7 TABLES AND FIGURES

TABLE 2.4.7.1

THE WEIGHT AVERAGE AND NUMBER AVERAGE MOLECULAR WEIGHTS (M_w AND M_n) AND POLYDISPERSITY INDEX OF THE POLYMERS BEFORE AND AFTER THE BIODEGRADABILITY TEST

Polymer samples	Before biodegradability test			After biodegradability test		
	M_n	M_w	PDI	M_n	M_w	PDI
P-0(10:0)	11352	16547	1.45	9321	14536	1.55
P-1(9:1)	20503	27323	1.33	17865	24895	1.39
P-2(8:2)	25953	33523	1.29	21712	31247	1.43
P-3(7:3)	38362	46264	1.2	34231	43135	1.26
P-4(9:1)	14274	19213	1.34	12115	17426	1.43
P-5(8:2)	16936	22721	1.34	14487	20147	1.39
P-6(7:3)	18932	24365	1.28	16548	22335	1.34
P-0 (homopolymer of RBO), P-1 to P-3 (RBO: DA) and P-4 to P-6 (RBO: alpha pinene) w/w, M_n = number average molecular weight; M_w = weight average molecular weight; PDI = polydispersity index.						

TABLE 2.4.7.2

POUR POINT AND VISCOSITY INDEX VALUE OF DIFFERENT POLYMERS AT DIFFERENT CONCENTRATIONS

Property/base oil/(PP/VI)	Con., %	Sample						
		P-0	P-1	P-2	P-3	P-4	P-5	P-6
PP/BO1(-3)	1	-6	-6	-12	-15	-6	-9	-12
	2	-9	-9	-15	-18	-9	-12	-15
	3	-9	-12	-18	-21	-12	-15	-18
	4	-9	-12	-18	-21	-12	-15	-18
PP/BO2/(-6)	1	-9	-9	-15	-18	-9	-12	-15
	2	-12	-12	-18	-21	-12	-15	-18
	3	-12	-15	-21	-24	-15	-18	-21
	4	-12	-15	-21	-24	-15	-18	-21
VI/BO1(80)	1	86	98	100	112	96	98	107
	2	90	101	104	118	98	102	115
	3	96	107	116	125	104	110	123
	4	100	109	120	136	107	116	129
	5	105	119	126	140	115	123	137
VI/BO2(85)	1	94	115	119	121	104	116	120
	2	98	118	123	129	107	117	126
	3	102	128	133	135	110	119	132
	4	109	131	138	142	121	130	138
	5	115	135	141	148	129	133	139
BO = base oil; PP = pour point; VI = viscosity index.								

TABLE 2.4.7. 3

RESULTS OF BIODEGRADABILITY TEST BY THE DISC DIFFUSION METHOD AND SOIL BURIAL TEST METHOD & GRAPHICAL REPRESENTATION

sample	Weight loss in disc diffusion method (in g)					Weight loss in soil burial test (in gm)
	CC	FE	AA	CG	CE	
P-0	0.39	0	0.59	0	0	0.38
P-1	0.35	0	0.51	0	0	0.33
P-2	0.27	0	0.46	0	0	0.29
P-3	0.26	0	0.38	0	0	0.24
P-4	0.35	0	0.56	0	0	0.37
P-5	0.34	0	0.56	0	0	0.35
P-6	0.32	0	0.52	0	0	0.35

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

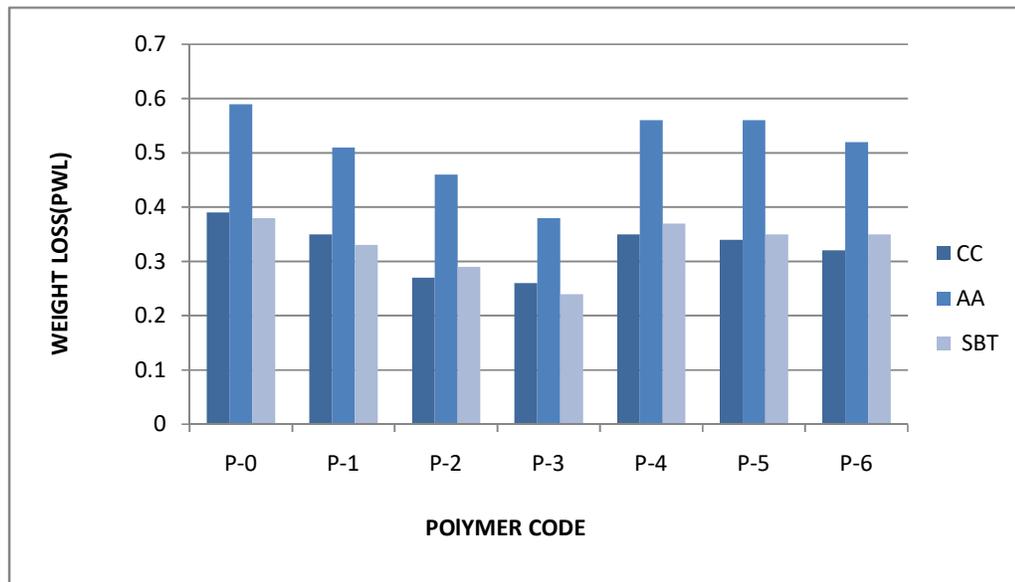


FIGURE 2.4.7.1

FT-IR SPECTRA OF RICE BRAN OIL HOMOPOLYMER

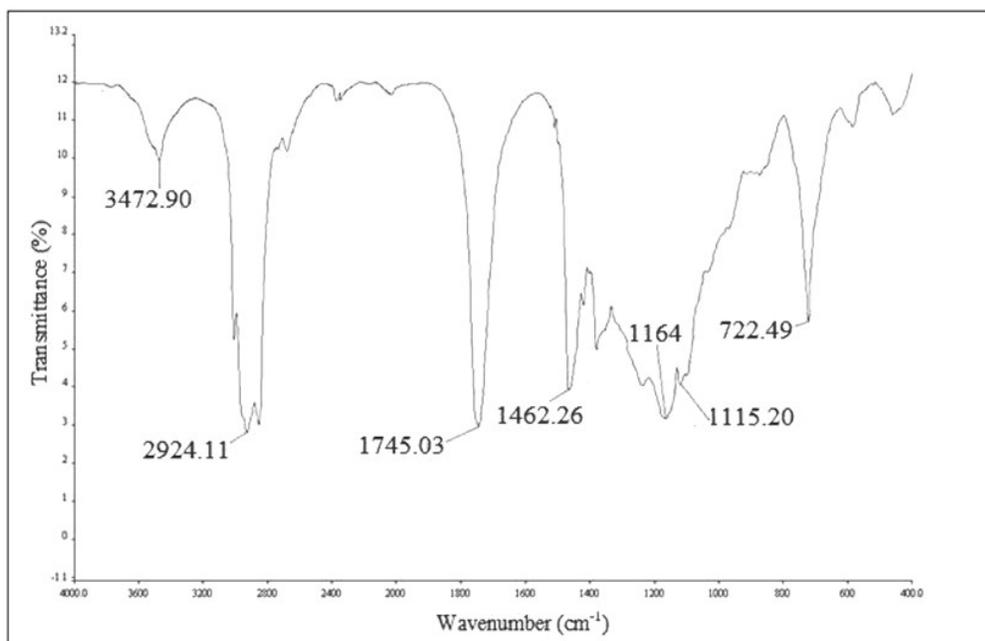


FIGURE 2.4.7.2

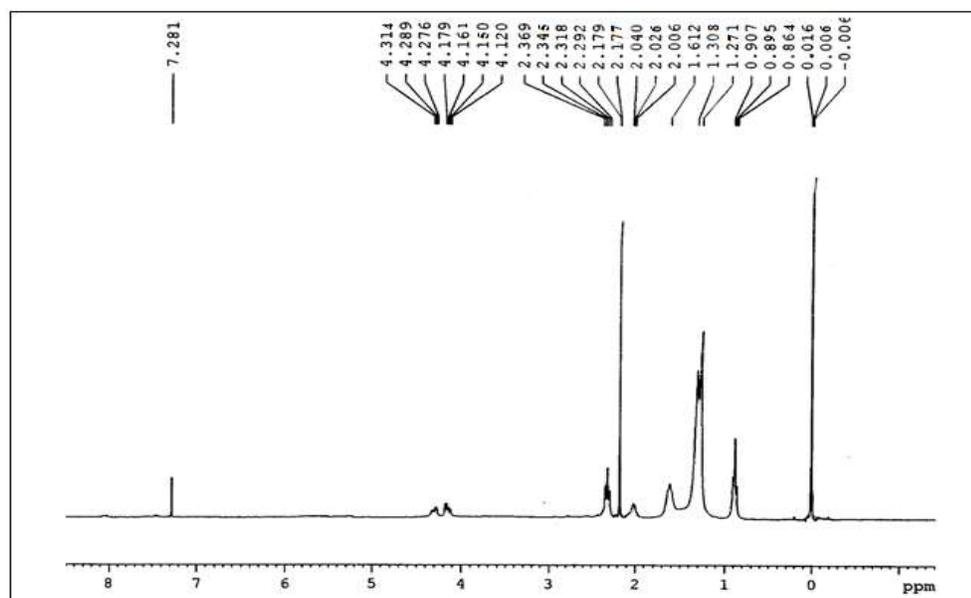
¹H NMR SPECTRA OF RICE BRAN OIL HOMOPOLYMER.

FIGURE 2.4.7.3

¹³C - NMR SPECTRA OF RICE BRAN OIL HOMOPOLYMER

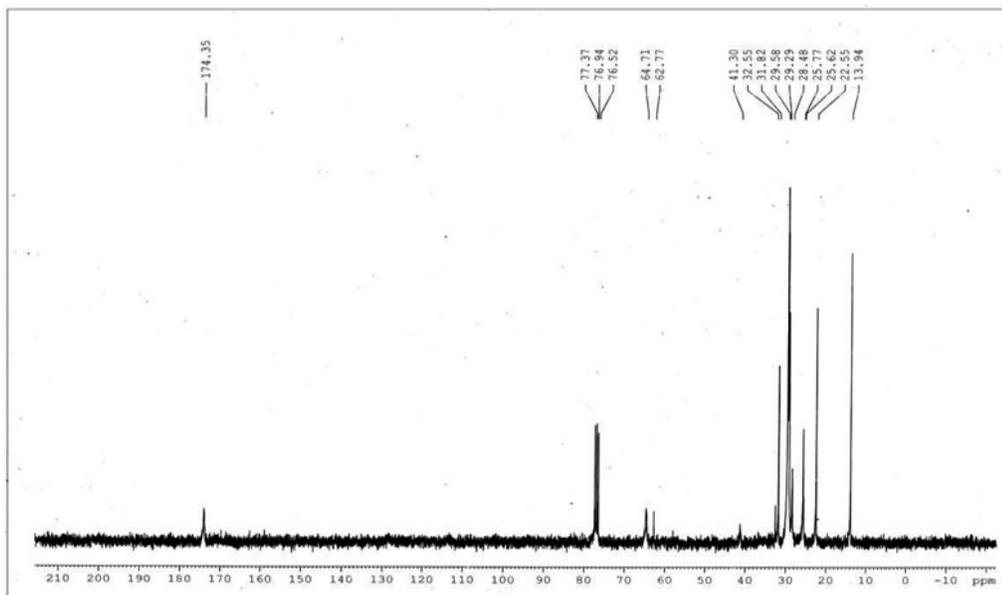


FIGURE 2.4.7.4

FT-IR SPECTRA OF RICE BRAN OIL + DA COPOLYMER

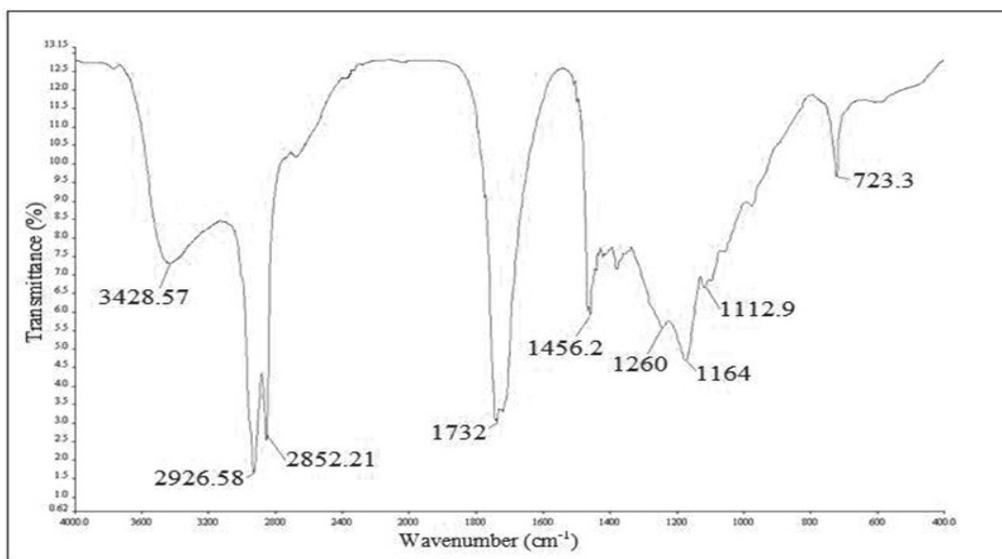


FIGURE 2.4.7.5

¹H NMR SPECTRA OF RICE BRAN OIL + DA COPOLYMER.

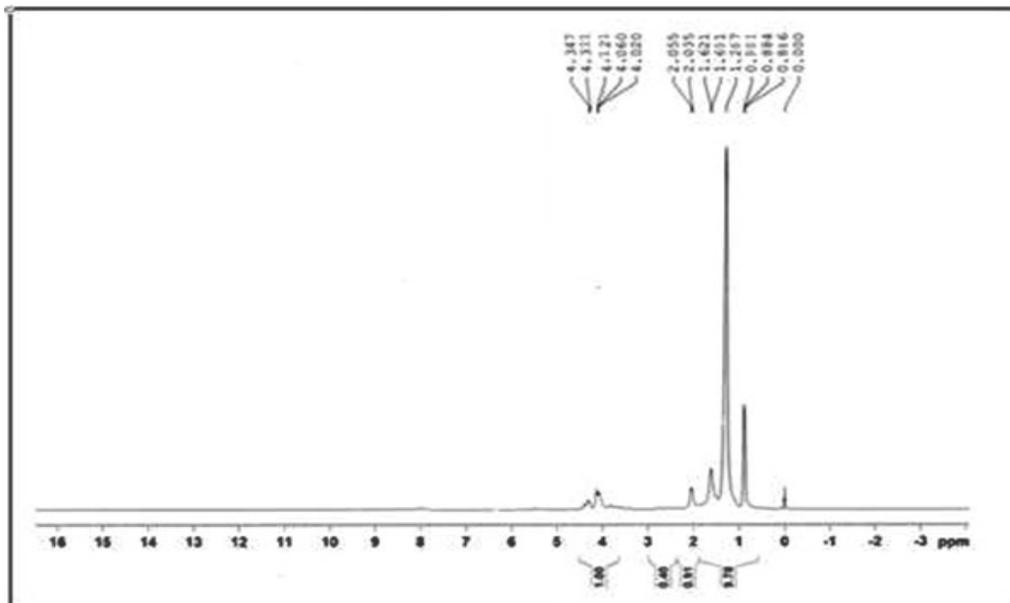


FIGURE 2.4.7.6

¹³C- NMR SPECTRA OF RICE BRAN OIL + DA COPOLYMER

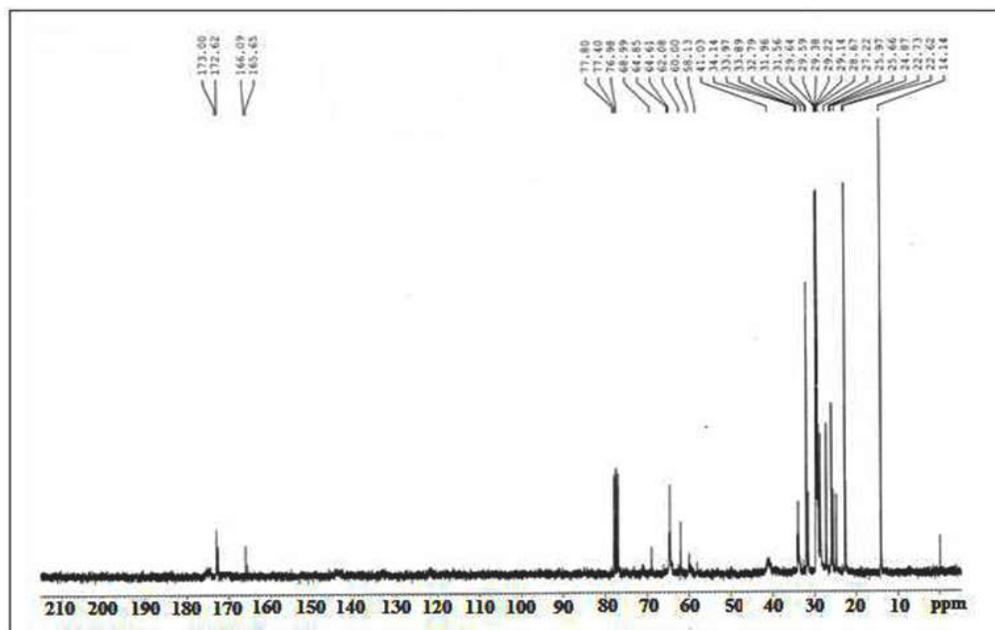


FIGURE 2.4.7.7

FT-IR SPECTRA OF RICE BRAN OIL + ALPHA PINENE

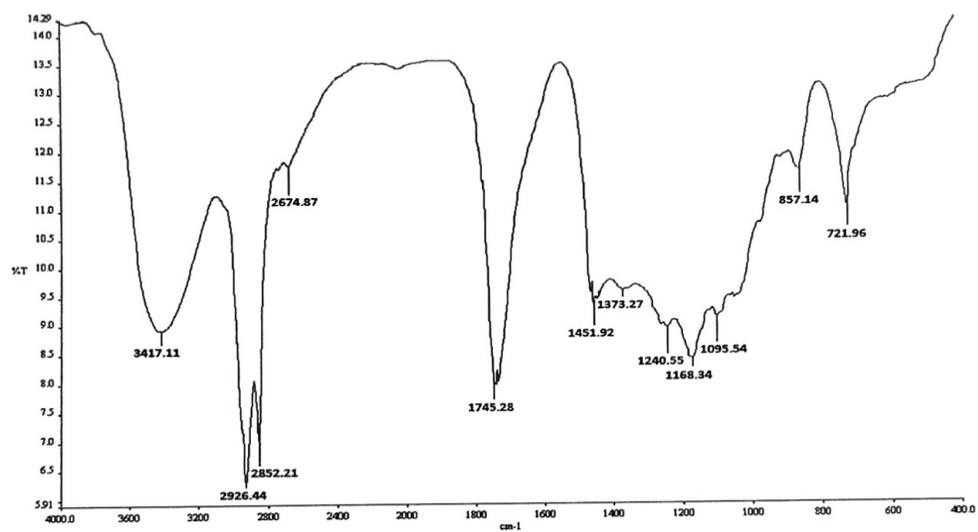


FIGURE 2.4.7.8

¹H NMR, SPECTRA OF RICE BRAN OIL + ALPHA PINENE

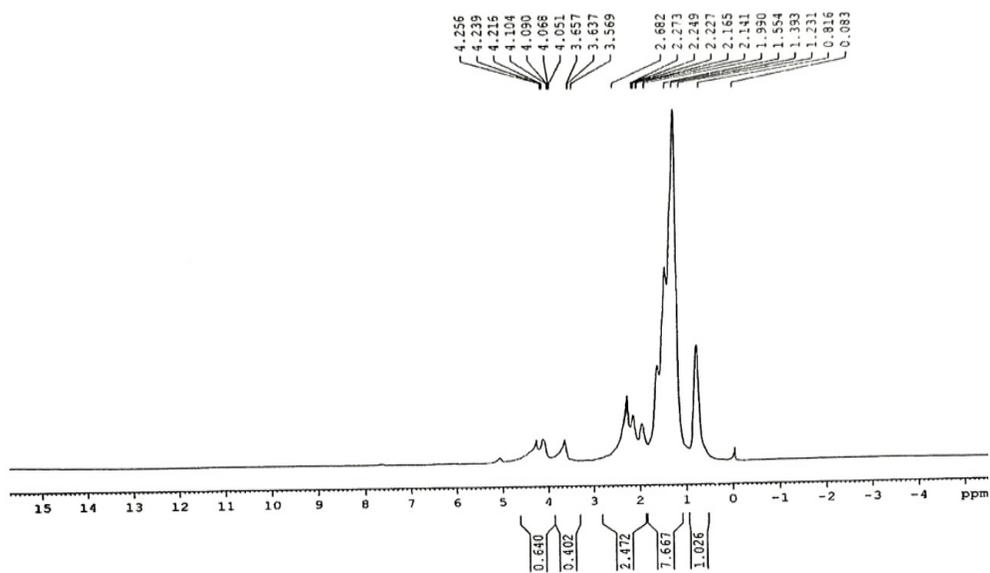


FIGURE 2.4.7.9

¹³C NMR SPECTRA OF RICE BRAN OIL + ALPHA PINENE

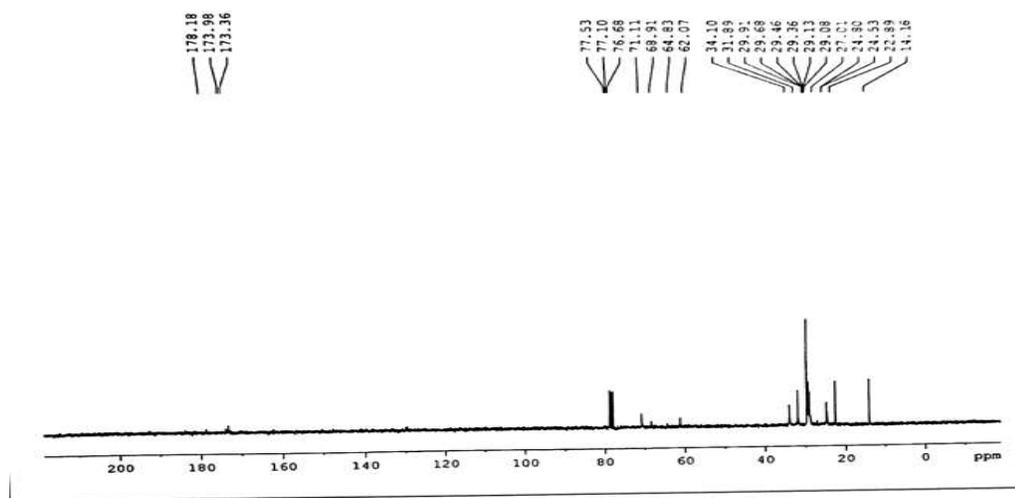
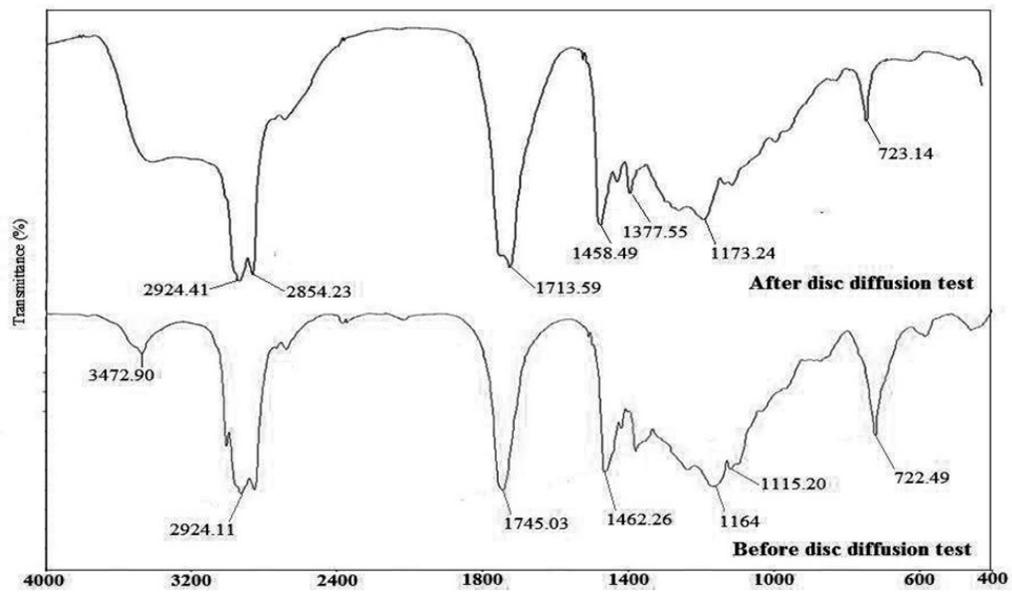


FIGURE 2.4.7.10

COMPARATIVE FT-IR SPECTRA OF RICE BRAN OIL HOMOPOLYMER BEFORE AND AFTER DISC DIFFUSION TEST



PART-3

CHEMICALLY MODIFIED VEGETABLE OILS AS LUBE OIL ADDITIVES AND AS A POTENTIAL LUBE BASE STOCK

PART-3/CHAPTER-1

BACKGROUND AND OBJECTIVE OF THE PRESENT INVESTIGATION

Ever growing lubricant industry requires a continuous flow of oil sources but unfortunately, the most frequent source of base stock or base lubricant is generated from petroleum crude and its sources are limited and gradually decreasing. Despite that mineral, lube has some serious disadvantages like

- They possess poor biodegradability and release toxic chemicals as residue in the environment.
- They have poor tribological and rheological properties.
- Sources are limited and non-renewable [5].

Synthetic lube base stock is considered to be an alternative but they have some serious issues, like-

- They are expensive compared to mineral lube[4].
- They are associated with more environmentally hazardous.
- Biodegradability is not promising.
- They are less miscible with mineral lube, hence can't work together.

Additives that are produced from petroleum resources such as polyacrylate as rheo improver and zinc-diethyl dithiophosphate (ZDDP) as tribo improver brings serious hazards to the environment as they possess heavy metal, and sulfur [1-2]. Friction modifier, molybdenum dithiocarbamate complexes used as solid lubricants, releases heavy metals and sulfur compounds, and their activity decreases with fluid aging [3]. Therefore, research interest in bio-based lubricant additives is also increasing. Although lubricants derived from vegetable oils are more costly than mineral

lubricants, they are a promising alternative to synthetic and mineral oil-based lubricants because they have a high flash point, high viscosity index, better friction properties, high biocompatibility, and low aquatic toxicity [5-7]. With its long fatty acid chain and polar end groups, the structure of vegetable oil thus contains an oleophilic and oleophobic part in their structure, hence, these oils are suitable as a base stock for easily blending different kinds of environmentally acceptable additives, and are used as both boundary and hydrodynamic lubricants[3]. Additives prepared from vegetable oils showed excellent tribological and rheological properties as we observed in our previous chapters where additives prepared from castor oil, rapeseed oil, rice-bran oil exhibit excellent results in this regard. Research in this field of preparing alternate lube base stock and additives was also done.

1. Erhan et al.(2008-2014) patented the use of poly (hydroxy thioether) vegetable oil derivatives as antiwear additives for environmentally friendly industrial oils in automotive applications. Different methods of making fatty acid ester derivatives from unsaturated fatty acids through the formation of their epoxides have also been described by Erhan et al. [9-11].
2. Doll et al.(2014) patented a novel process of preparing chemically modified triglycerides by the reaction of epoxidized triglyceride oils or alkyl esters thereof with phosphorus-based acid hydroxide or esters. The phosphorus-containing triglyceride derivatives so produced have a found utility as antiwear/antifriction additives for industrial oils and automotive applications [12].
3. Biswas et al.(2014) patented a method of preparing nitrogen-containing fatty acid derivatives by reacting epoxidized fatty acids, their esters, or triglyceride oils with amines of cyclic or aromatic hydrocarbons. These fatty acid derivatives

are used as antiwear/antifriction additives for industrial oils and automotive applications[13].

4. Heise, G.L.; Sharma, B.K.; Erhan, S.Z.(2015) synthesized & analyzed the antiwear additive performance of Boron containing vegetable oil U.S. Patent 9156859 B2[14].
5. Ghosh, P, Karmakar, G; (2013-2015) investigated multifunctional additives based on soyabean oil, sunflower oil, and castor oil polymers[17-19].
6. Fox, N.J.; Stachowiak, G.W.(2007) perform a review work on vegetable oil-based lubricant[24].

Vegetable oils can't be used directly as lube because of their low thermal-oxidative stability, low volatility, and high viscosity compared to mineral lube. This can be performed in two different ways: reactions at the carboxyl groups of fatty acids/esters/triglycerides of vegetable oils (transesterification) or reactions at the olefinic functionalities of the fatty acid chain. Different research activities in those areas are discussed below.

- **TRANSESTERIFICATION**

1. A significant reduction of wear scar diameter from the addition of 5% rapeseed oil methyl esters in diesel fuel was disclosed by Sukjit et al. [25]. It was reported that the lubrication performance of diesel base oils was improved when palm oil methyl esters are blended [26,27].

2. Masjuki and Maleque (1997) reported a low wear rate of steel ball bearing while adding palm oil methyl ester in the base oil lubricant [28].

3. Malavolti et al. have synthesized biodiesels through the transesterification of castor oil with various alcohols in the presence of trimethylchlorosilane (TMSCl) as an acidic mediator[29].

4. The potential use of castor oil methyl esters as lubricants, with their high viscosity, low pour point, and good lubricity, was explained by Madankar et al. [30].

Glycerol obtained can be used as water-based lube, or it has other utility in the diversified chemical field[31].

- **REACTION AT OLEFINIC PART OF VEGETABLE OIL**

Epoxidation of fatty acids/esters and their application as a bio lubricant: One of the most important steps in preparing a bio lubricant (base stock and/or additive) from vegetable oils is the epoxidation of its olefinic functionalities. Vegetable oils epoxide can be prepared using peracid([32-34]. Because of their higher reactivity, the oxirane rings of the epoxides can easily be opened by different reagents such as acids, alcohols, thiols, and amines to provide different value-added compounds such as lubricants (base stocks/additives), bio-plasticizers, and other industrially useful chemicals. The epoxidized vegetable oils/fatty esters are used to prepare antiwear/anti frictional additives for lubricants. Because of their higher solubility in vegetable oils.

1. Schafer et al. described the development of corrosion-protection additives from an epoxidized methyl ester of an unsaturated fatty acid and a sulphonic acid[35].
2. Rowland et al. disclosed different antifriction additives from an epoxidized ester of fatty acids to reduce lead corrosion in lubricants and fuels [36].

3. Hydroxy thioether derivatives of vegetable oils prepared by opening the epoxy rings of epoxidized soybean oil with common organic thiols are used as sustainable antiwear/anti frictional additives for lubricants [37-38].

The incorporation of sulfur in the triglyceride backbone introduces polar functionalities in the molecule which improved the adsorption power of the derivatives on the metal surface resulting in reduced wear and friction coefficient. Ester hydroxy derivatives of methyl oleate, obtained by opening the epoxy rings of epoxidized methyl oleate by different organic acids (propionic, octanoic, hexanoic, or 2-ethyl hexanoic acid) showed better pour point and cloud point values [28]. They also showed improved thermo-oxidation stability and tribological and lubricity properties when used as lubricant additives.

Some research-based on linseed oil was very interesting in this regard as Linseed oil has found various applications in the polymer industry as well as in the petroleum industry. In a study, linseed oil polyesteramide in combination with dehydrated castor oil was blended with polymethyl methacrylate to obtain a bioartificial polymer with improved mechanical and physical properties [40-41]. In another study, epoxidized linseed oil was used to prepare a natural viscosity increasing agent from polyvinyl chloride (PVC) and triethyl-lene glycol ester of gum rosin [42]. Epoxidized linseed oil is often used as lubricants or plasticizers and secondary stabilizers for halogen-containing polymers [43]. In a study, Linseed oil biodiesel was produced by the transesterification process and its effect was investigated on engine performance and exhaust emissions which showed that linseed biodiesel and fuel blends acted quite similar to the standard diesel fuel, but in the case of the former exhaust emissions was generally improved [44]. V A Markov et al. have established in their study that the physical and chemical properties of a

mixture of 90% diesel fuel and 10% linseed oil are quite similar to petroleum diesel fuels characteristics and also application of this mixture as motor fuel minimized the emission of exhaust toxic components such as nitric oxides, carbon monoxide and unburned hydrocarbons [45]. P. P. Chahande has successfully prepared a novel polymeric surfactant that is biodegradable and eco-friendly as well, based on linseed oil, rosin, and sorbitol [46]. Birten Cakmakli et al. have prepared a series of biodegradable synthetic branched graft copolymers of linseed oil with methyl methacrylate and reported their potential application in tissue engineering due to their cell adhesion and development [47] S. M. Ashraf et al. have prepared a blend of polyvinyl alcohol and epoxidized linseed oil to use it as a plasticizer and corrosion-resistant coating film of good toughness, flexibility and low water absorption [40-41]

In this part of our study, we discussed the scope opportunity of using chemically modified linseed oil as additives or as lube base stock

In Chapter 1, we discussed Linseed oil-based biodegradable polymeric additives and their effectiveness as pour point depressant, viscosity index improver, and their shear stability in terms of permanent shear stability index (PSSI) has been evaluated. Polymers were proved to act as a good pour point depressant, viscosity index improver, and shear stability improver as well. The copolymers acted like better PPDs than the homopolymer whereas the latter showed better VI improving the property. Keeping in view the environmental issue, the results are quite inspiring. Apart from being biodegradable and eco-friendly, the linseed oil-based additives may be considered to be potential candidates to replace the traditional harmful organic chemical-based polymeric additives depending on the evaluated parameters. All the additives synthesized in this research illustrated excellent additive

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

In chapter 2, the performance evaluation of chemically modified vegetable oil to be used as lubricant base stock. Linseed oil(LO), castor oil(CO), olive oil (OLO), Soyabean oil (SBO), sunflower oil(SFO) epoxide were discussed. The product prepared were characterized by FTIR and NMR spectroscopy. The reaction of epoxidized linseed oil with 2 ethyl hexanol, dodecanol, n octanol, 1 decanol, and isodecanol in the presence of a catalytic amount of sulfuric acid gave rise to open-ringed products. Oxirene ring-opened products of linseed oil exhibit better low-temperature flow and high viscosity index. Ring opened product with isodecanol and 2 ethyl hexanol showed better results compared to others. ECO, EOLO, ESBO, ESFO rings were also opened through the same procedure using isodecanol and the product exhibits high viscosity index and excellent low-temperature flow in this case also. Ring opened product displays better Thermo Oxidative Stability compared to those vegetable oils from which they are synthesized. Better pour point, high viscosity index, better thermal-oxidative stability, and better antiwear property compared to conventional mineral lube make these products an alternative to the latter and more environmentally benign.

However, there are some limitations to using vegetable oils. The major component of vegetable oils is a triglyceride of long-chain fatty acids of mostly unsaturated carbon atoms. The double bonds of the fatty acid chains are not conjugated. They have low thermo-oxidative stability, poor bio-resistance, poor hydrolytic stability, and poor fluidity at lower temperatures [21–23]. Therefore, they cannot be used directly as lubricant-based stocks/additives. The presence of unsaturation in the chain makes vegetable oils fragile to oxidative degradation [24].

This ultimately results in an insoluble deposit formation in vegetable oils which increases oil acidity, viscosity, corrosion, and volatility. The production and processing cost of vegetable oil is another constrain. A Huge consumption of edible oil worldwide and low production of nonedible oil makes it difficult to replace mineral lube with modified vegetable oil-based lube. These limitations can, however, be mitigated by chemically modifying vegetable oils to reach the desired performance level without increasing the cost. Extensive research in this field is going on worldwide to produce lubricant base stocks or additives from vegetable oils [25–28].

REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-1 of Part-3**”.

PART-3/CHAPTER-2

LINSEED OIL-BASED BIODEGRADABLE HOMO AND COPOLYMERS- MULTIFUNCTIONAL GREENER ADDITIVES IN LUBE OIL

3.2.1 INTRODUCTION

Lubricant is important for the smooth rubbing of metal parts in a modern engine. Lubricant reduces friction and heat generated inside the engine compartment. Base lube extracted from crude petroleum fraction and mixed with suitable additives to perform the diversified function in a different engine in different working conditions. Petroleum lube is non-renewable and its source is limited whereas additives are generally used having a serious environmental impact. Vegetable oils on the contrary have many properties in favor of their use as lube or lube additive (high viscosity index, low pour point, thermal stability). Moreover, their biocompatibility attracts many researchers in this field of research using vegetable oil as potential lube or lube additive. Vegetable oil contains a fair amount of unsaturation due to the presence of unsaturated fatty acid (oleic acid, linolenic acid, linoleic acid) in their composition. Oxidative instability due to the unsaturation prevents their direct use. This can be overcome by suitable modification (polymerization, transesterification, epoxidation). Vegetable oils either in original form or after some simple modification have drawn huge attention as sustainable alternatives to petroleum-based materials for industrial applications due to their biodegradability, low toxicity, easy availability, and relatively low price. These are considered to be the most important renewable feedstock towards the synthesis of bio-based multifunctional polymeric additives for the lubricant industry. In this present context linseed oil-based biodegradable polymeric additives using styrene,1-

decene, isodecyl acrylate, n octyl acrylate have been synthesized and their effectiveness as pour point depressant, viscosity index improver, and their shear stability in terms of permanent shear stability index (PSSI) have been evaluated in lube oil[1].

3.2.2. EXPERIMENTAL

3.2.2.1 MATERIALS USED

Linseed oil was bought from the local market; its density was 0.93 g/mL at 25 °C, saponification value was 189.6, and iodine no. was 188.0 [1]. Toluene (GC 99.5%) was collected from Merck (Mumbai, India). Styrene (99%, Sigma–Aldrich), 1–decene (95%, Acros Organics), octyl alcohol, isodecyl alcohol, and acrylic acid (99%, LOBA Chem Pvt. Ltd.) was used as received. Hexane (99.5%, S. d Fine Chem Ltd.) and Methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use[2]. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. The mineral base oil (BO) was collected from IOCL, Dhakuria, West Bengal, India, and its properties are listed in Table 3.2.7.1.

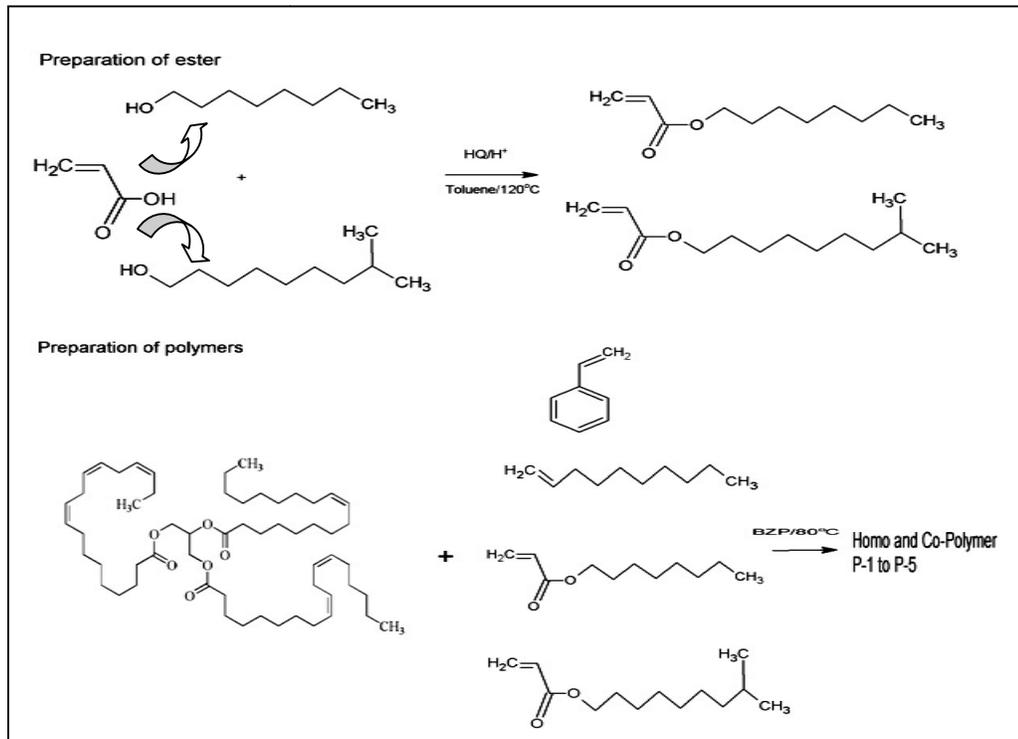
3.2.2.2 PREPARATION OF ESTERS AND THEIR PURIFICATION

The ester (isododecyl acrylate, IDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of isododecyl alcohol in a Dean-Stark apparatus adding concentrated H₂SO₄ as a catalyst, 0.25 % hydroquinone concerning the total reactants as a polymerization inhibitor, and toluene as a solvent. Another ester (octyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol in a similar reaction condition stated above. The method of esterification and its purification were carried out by the process as reported in the earlier publication [5].

3.2.2.3 SYNTHESIS OF THE POLYMERS AND THEIR PURIFICATION

Preparation of homopolymer of linseed oil (P-1) and its copolymers with styrene (5% w/w): P-2, 1-decene (5% w/w): P-3, IDA (5% w/w): P-4 and OA (5% w/w): P-5 respectively (Scheme:-3.2.1) [1], were carried out in a four-necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen at 90 °C for 6 hours by a free radical pathway in the presence of toluene as solvent and BZP as an initiator (0.5% w/w, concerning the total monomer). At the end of the reaction time, the reaction mixture was poured into methanol to terminate the polymerization process and precipitate the polymer. The polymers were further purified by repeated precipitation of their hexane solution by methanol followed by drying under vacuum at 40 °C [1].

Scheme 3.2.1:- Preparation of esters and polymers



P-1 homopolymer of linseed oil ,P-2-P-5 Copolymers of linseed oil with styrene,1decene,isodecyl acrylate, n-octylacrylate (5% w/w)

3.2.3 MEASUREMENTS

3.2.3.1 INSTRUMENTATION

- **SPECTROSCOPIC MEASUREMENTS**

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

- **GEL PERMEATION CHROMATOGRAPHY (GPC)**

The average molecular weight (number-average and weight-average) of the additives were measured in Waters (USA) GPC equipment using HPLC grade THF as eluent at room temperature. The system was fitted with a 2414 refractive index detector (polystyrene calibration) and Waters 515 HPLC pump. The PDI (M_w/M_n) was also calculated by GPC.

3.2.3.2 PERFORMANCE EVALUATION

- **PERFORMANCE EVALUATION AS POUR POINT DEPRESSANTS (PPDS) IN LUBE OIL**

The effect of additive concentration on the pour point of the base oil was tested by using different doping concentrations ranging from 1% to 6% (w/w) for each of the prepared polymers. According to the ASTM D 97-09 [8] method, the Pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India) given in Table:- 3.2.7.2.

- **PERFORMANCE EVALUATION AS VISCOSITY INDEX IMPROVER (VII)**

Viscometric properties were determined for the base oil doped with different concentrations (1% to 6% w/w) of the prepared homo and copolymers of linseed oil using an Ubbelohde OB viscometer[9]. The obtained results are tabulated in terms of kinematic viscosity (KV) data at 40 °C, 100 °C, and viscosity index (VI) data in Tables:- 3.2.7.3 & 3.2.7.4.

- **SHEAR STABILITY MEASUREMENT**

When subjected to mechanical agitation or stress inside the engine compartment a polymer in the lube component may lose its viscosity in terms of two different ways such as Temporary Viscosity Loss (TVL) and Permanent Viscosity Loss (PVL) [7] The latter occurs due to mechanical degradation of polymer molecules and is often expressed in terms of Permanent Shear Stability Index (PSSI) using the equations,

$$\begin{aligned} \text{PVL (\%)} &= [(V_i - V_s)/V_i] \times 100 \\ \text{PSSI (\%)} &= [(V_i - V_s) / (V_i - V_o)] \times 100 \end{aligned}$$

Where V refers to Kinematic Viscosity (KV) at 100 °C.

V_o = KV of the oil before the addition of polymer.

V_i = KV of the oil after the addition of polymer.

V_s = KV of the oil after shearing.

The PVL and PSSI values are measured here preparing 1%–6% solutions of the prepared homo and copolymers of linseed oil in the base oil under consideration as per ASTM D–3945-93 [10] method. The values are given in Table 3.2.7.6.

3.2.4 RESULTS AND DISCUSSION

3.2.4.1 SPECTROSCOPIC ANALYSIS

All the absorptions at ν 1733, 1740, 1742, 1744, and 1743 cm^{-1} for the homopolymer of linseed oil, P–1 and its copolymers P–2, P–3, P–4 and P–5 respectively showed the presence of ester carbonyl group. Peaks ranging from ν 1452 to 1169 cm^{-1} were due to CO stretching vibration and the peaks from ν 2846 to 2932 cm^{-1} were the stretching vibration of the paraffinic C–H bonds of $-\text{CH}_3$ and $-\text{CH}_2-$ groups. Peaks at ν 723 cm^{-1} and ν 700 cm^{-1} were attributed to the C–H bonds of the styrene which was observed only in the case of P–2.

The ^1H NMR of homo and copolymer of linseed oil showed peaks in the range of 3.01 to 4.9 ppm due to $-\text{OCH}_2-$ groups. The peaks that appeared in the range of 2.318 to 2.983 represent the $-\text{OH}$ groups of linseed oil. The peaks ranging from 0.51 to 1.30 ppm and 1.41 to 2.41 ppm indicate methyl and methylene protons respectively. The peaks that appeared in the range of 7.12 to 7.33 ppm indicate protons of the benzene ring of styrene moiety (for P–2 only).

The proton decoupled ^{13}C NMR showed peaks at 164 to 177 ppm for ester carbons. The peaks that appeared in the range of 52 to 69 ppm represent the carbons of $-\text{OCH}_2-$ groups. The peaks of methyl and methylene carbons appeared in the range of 14 to 41 ppm. The carbons of the benzene ring showed peaks in the range of 125 to 133 ppm (for the polymer of P–2 only).

3.2.4.2 PERFORMANCE EVALUATION AS POUR POINT DEPRESSANT

Based on the pour point data (Table:- 3.2.7.2), it is obvious that all the prepared polymers of Linseed oil are good pour point depressants for the base oil under consideration. Comparatively the copolymers showed better efficiency than the homopolymer. Among these all, copolymer of Linseed oil and isodecyl acrylate has been proved to be the best PPD. The presence of the polar acrylate group in association with the long alkyl chain of the ester group is supposed to play a crucial role here which inhibits the formation of 3-D matrix of paraffin wax at a lower temperature [11] In almost all the cases, the optimum results were obtained at 4 or 5% concentrations but above this, the effect was diminished may be due to lower solubility.

3.2.4.3 PERFORMANCE EVALUATION AS VISCOSITY INDEX IMPROVER

Viscosity may be regarded as the most important and deciding parameter for a lubricant. Lesser change in viscosity concerning temperature results in a high VI value which is quite an essential requirement for a good lubricant so that even at a higher temperature it does not lose its viscous characteristic at ease. All the prepared polymers of linseed oil have shown a promising result in this area (Table:- 3.2.7.3, 3.2.7.4 and 3.2.7.5). The kinematic viscosity of the petroleum base oil has increased dramatically when doped with these polymers. These polymers have drastically improved the viscosity index of the base oil above 200 which recommends these polymers as a quite useful lubricant additive at a higher range of temperatures. In general, it may be summarized that all the prepared polymers of linseed oil are impressive viscosity index improvers for the base oil. The homopolymer (P-1) has outplayed the copolymer here which is quite an inspiring result. With the increasing concentration of the added polymers, the viscosity index increases very slowly.

Polymer micelles in the base oil solutions may responsible slow but steady increase in VI at higher concentrations [6].

3.2.4.4 SHEAR STABILITY INDEX ANALYSIS

It is evident from the table that viscosity change after shear is minute in all the cases (Table:- 3.2.7.5). Hence it is obvious that in presence of the additives the base oil under mechanical shear experienced molecular degradation at a marginal basis and thus sustains its viscometric properties for a long-range. PVL and PSSI data (Table:- 3.1.7.6) unanimously account for the prepared polymers to be treated as lubricant additives even at higher shearing conditions. The PVL and PSSI values increase steadily with an increase in the concentration of the additives in the base oil.

3.2.4.5 MOLECULAR WEIGHT ANALYSIS

From the experimental values of M_n , M_w , and PDI (polydispersity index) of the prepared homo and copolymers (as tabulated below, Table:- 3.2.7.7), it is clear that polydispersity index is lowest in case of homopolymer, P-1 and highest in case of P-3 (copolymer of LSO and 1-decene). It is reflected in viscosity index data that P-3 has the lowest VI due to low solubility. The excellent PDI values for homopolymer are also following its high viscosity index.

3.2.5 CONCLUSION

Linseed oil-based some greener additives have been provided here which are proved to be good pour point depressant, viscosity index improver, and shear stable as well. The copolymers acted like the better PPDs than the homopolymer whereas as a VII the latter excels. All the prepared polymers are shear-stable as well which implies that even under mechanical shear, in presence of these additives in minute concentration, the lube oil can retain its viscosity and hence its lubricant property quite effectively. Keeping in view the environmental issue, the results are quite

inspiring. Apart from being biodegradable and eco-friendly, the linseed oil-based additives may be considered to be potential candidates to replace the traditional harmful organic chemical-based polymeric additives depending on the evaluated parameters at least[1].

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for providing Base Oil.

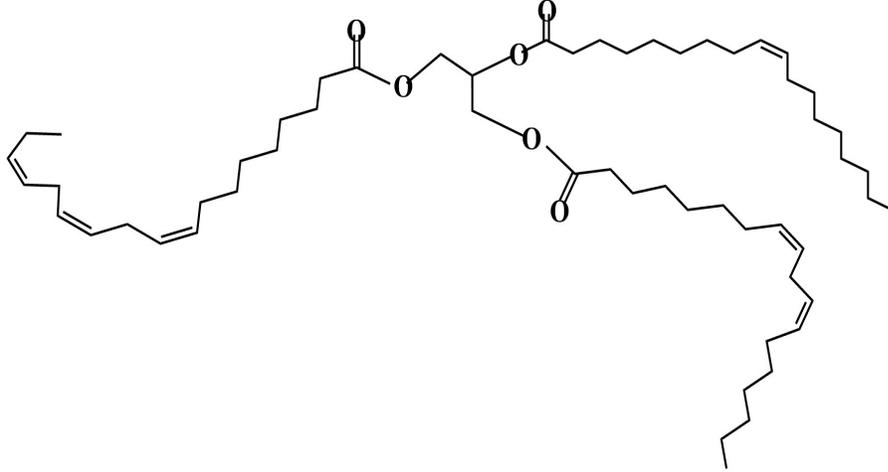
3.2.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-2of Part-3**”.

3.2.7 TABLES AND FIGURES

FIGURE 3.2.7.1

TRIGLYCERIDE IS FOUND IN LINSEED OIL AND ITS FATTY ACID COMPOSITION.



FATTY ACID COMPOSITION OF LSO

Fatty Acid	% Composition
Palmitic acid (16:0)	4.90-8.00
Stearic acid (18:0)	2.24-4.59
Oleic acid (18:1)	13.44-19.39
Linoleic acid (18:2)	12.25-17.44
Linolenic acid (18:3)	39.90-60.42

* J Food Sci Technol DOI 10.1007/s13197-013-1247-9

TABLE 3.2.7.1

BASE OIL (BO) PROPERTIES

Physical Property	BO*
Density (g cm^{-3} at 40 °C)	0.95
Viscosity at 40 °C in cSt	24.211
Viscosity at 100 °C in cSt	4.47
Viscosity Index (VI)	89.87
Pour Point (PP in °C)	-6
Cloud Point (°C)	-8

* BO collected from IOCL, Dhakuria, West Bengal

TABLE 3.2.7.2

POUR POINT (°C) DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN BASE OIL (BO)

Additive	1%	2%	3%	4%	5%	6%
P ₁	-12.5	-11.9	-11.5	-10.8	-9.7	-9.8
P ₂	-14.0	-14.4	-15.0	-15.3	-15.7	-15.7
P ₃	-15.0	-14.4	-13.6	-14.5	-15.1	-15.0
P ₄	-17.0	-17.1	-17.3	-17.4	-17.4	-17.1
P ₅	-14.0	-14.7	-15.2	-15.8	-16.0	-15.9

* Conc represents concentration in % w/w

TABLE 3.2.7.3

KINEMATIC VISCOSITY (KV) DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN BASE OIL (BO)

Conc	KV ₁					KV ₂				
	P ₁	P ₂	P ₃	P ₄	P ₅	P ₁	P ₂	P ₃	P ₄	P ₅
1	158.14	165.24	173.17	169.43	181.3	34.32	35.55	34.89	35.18	35.51
2	160.34	167.3	173.91	172.54	182.37	34.93	35.87	35.51	36.67	36.21
3	164.23	169.41	174.95	174.9	184.59	35.72	36.41	35.87	37.15	36.48
4	169.54	171.21	178.13	176.56	186.13	36.79	36.91	36.43	37.54	36.9
5	172.74	172.16	180.84	180.15	187.5	37.89	37.19	36.97	38.34	37.34
6	173.11	175	181.13	182	188.15	38.91	37.82	37.53	38.93	37.78

*Conc represents concentration in % w/w; KV₁ & KV₂ represent kinematic viscosity at 40 °C & 100 °C respectively.

TABLE 3.2.7.4

VISCOSITY INDEX (VI) DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN BASE OIL (BO)

Additive	1%	2%	3%	4%	5%	6%
P ₁	262	264	264	265	268	274
P ₂	262	262	263	264	264	265
P ₃	249	252	253	253	254	257
P ₄	255	261	261	262	263	264
P ₅	244	247	247	248	249	251

*Conc represents concentration in % w/w

TABLE 3.2.7.5

KINEMATIC VISCOSITY DATA AFTER SHEAR (KV_s) CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN BASE OIL (BO)

Additive	1%	2%	3%	4%	5%	6%
P ₁	33.21	33.58	34.13	35.03	35.69	36.31
P ₂	34.42	34.39	34.52	34.64	34.71	34.96
P ₃	33.98	34.29	34.39	34.71	35.02	35.39
P ₄	34.35	35.7	36.06	36.29	36.95	37.38
P ₅	34.52	35.07	35.19	35.49	35.77	36.09

*Conc represents concentration in % w/w

TABLE 3.2.7.6

PVL & PSSI DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN BASE OIL (BO)

Conc	PVL					PSSI				
	P ₁	P ₂	P ₃	P ₄	P ₅	P ₁	P ₂	P ₃	P ₄	P ₅
1	3.23	3.18	2.61	2.36	2.79	3.72	3.63	2.99	2.7	3.19
2	3.86	4.13	3.43	2.64	3.14	4.43	4.71	3.93	3.01	3.59
3	4.45	5.19	4.13	2.93	3.54	5.09	5.92	4.71	3.33	4.03
4	4.78	6.15	4.72	3.33	3.82	5.44	6.7	5.38	3.78	4.35
5	5.81	6.67	5.27	3.62	4.2	6.58	7.58	6	4.1	4.78
6	6.68	7.56	5.7	3.98	4.47	7.55	8.57	6.47	4.5	5.07

*Conc represents concentration in % w/w

TABLE 3.2.7.7

M_n & M_w AND PDI VALUES OF THE PREPARED POLYMERS & GRAPHICAL REPRESENTATION.

Polymer code	composition	% of LSO	M_n	M_w	PDI
P-1	Homo LSO	100	40210	42371	1.053
P-2	LSO+STY(5%)	95	78932	84080	1.065
P-3	LSO+1-D (5%)	95	20125	38374	1.905
P-4	LSO+IDA(5%)	95	36427	55410	1.521
P-5	LSO+ n OA(5%)	95	71832	81420	1.133

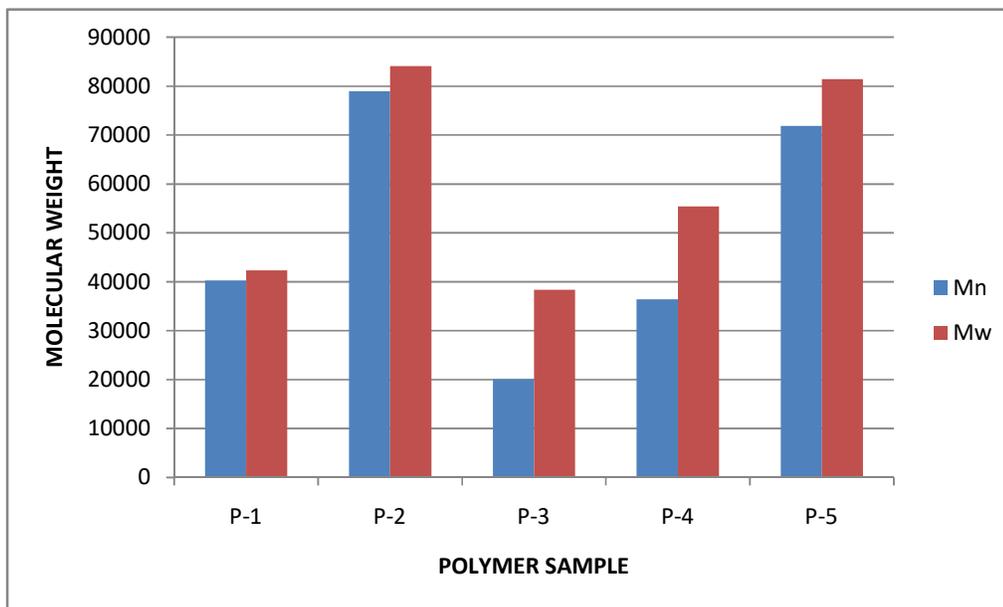


FIGURE 3.2.7.2

FT-IR SPECTRA OF THE HOMOPOLYMER OF LINSEED OIL (P-1)

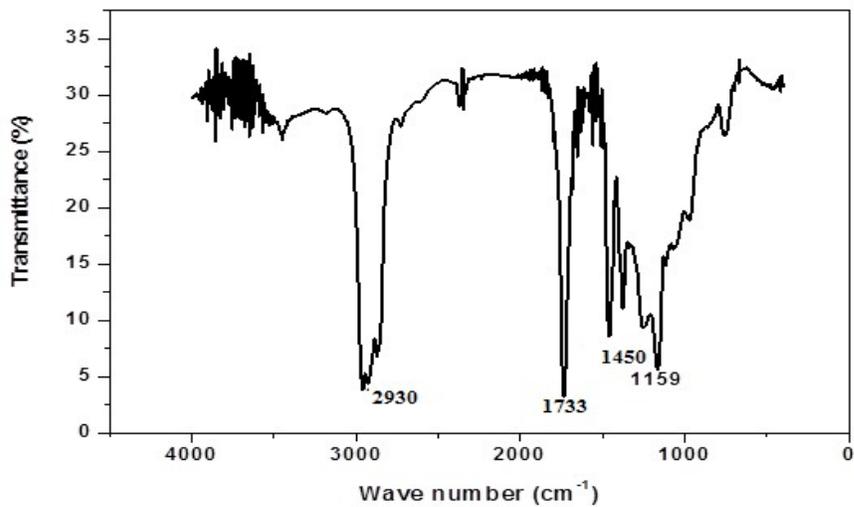


FIGURE 3.2.7.3

¹³C NMR SPECTRA OF THE HOMOPOLYMER OF LINSEED OIL (P-1)

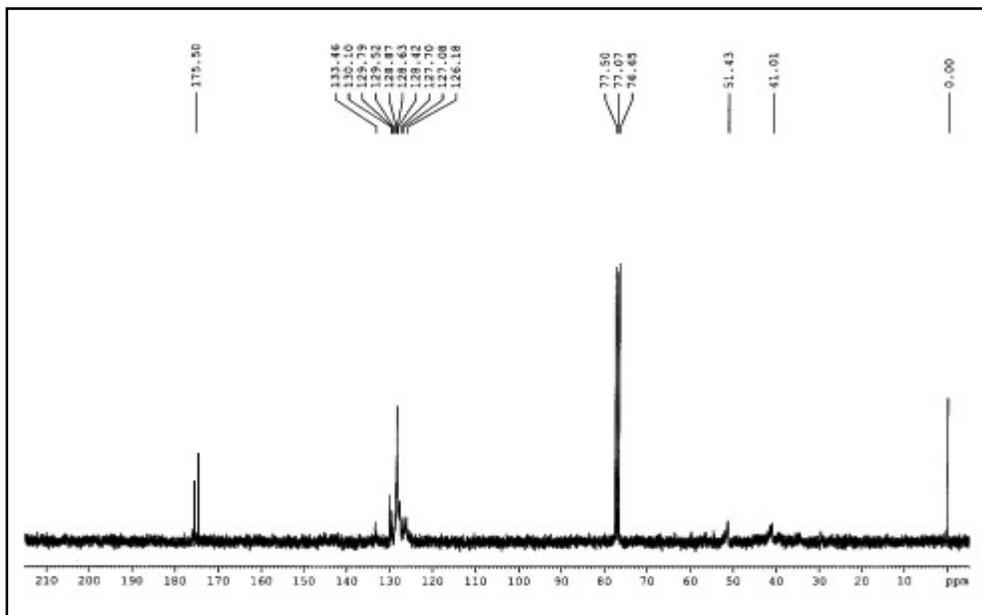


FIGURE 3.2.7.4

FT-IR SPECTRA OF THE COPOLYMER OF LINSEED OIL, STYRENE (P-2)

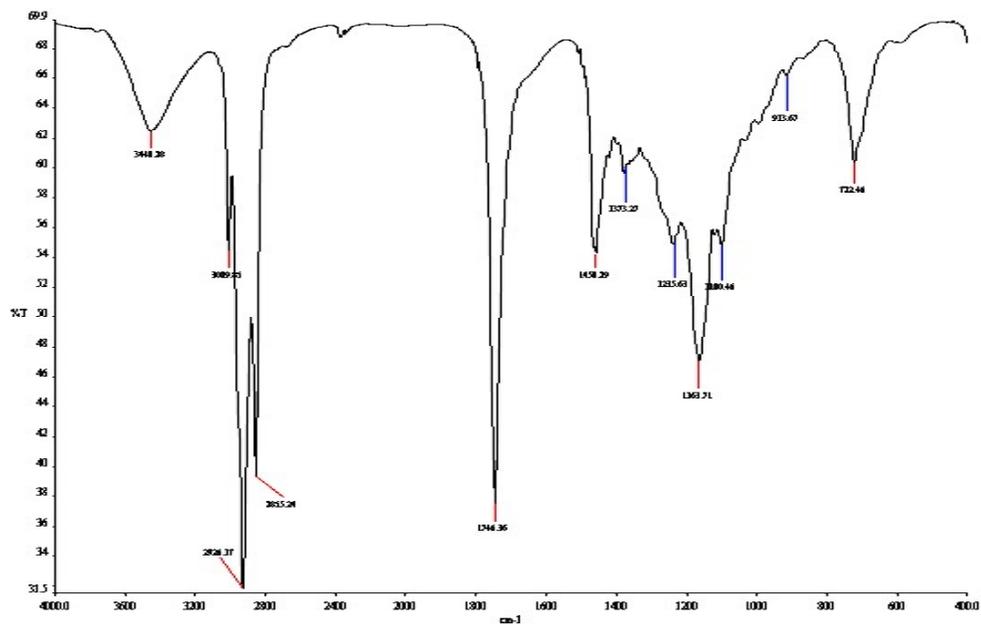


FIGURE 3.2.7.5

¹H NMR SPECTRA OF THE COPOLYMER OF LINSEED OIL, STYRENE (P-2)

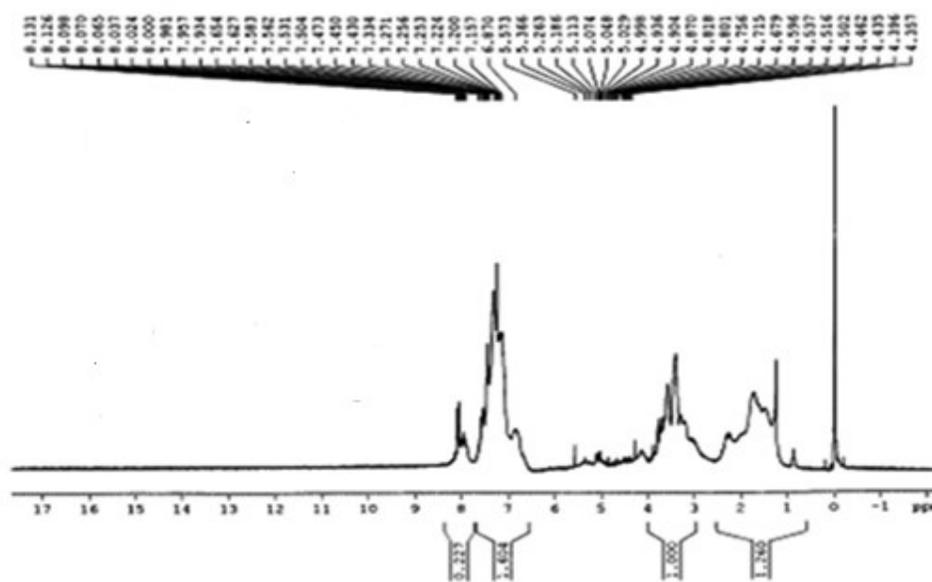


FIGURE 3.2.7.6

^{13}C NMR SPECTRA OF THE COPOLYMER OF LINSEED OIL, STYRENE (P-2)

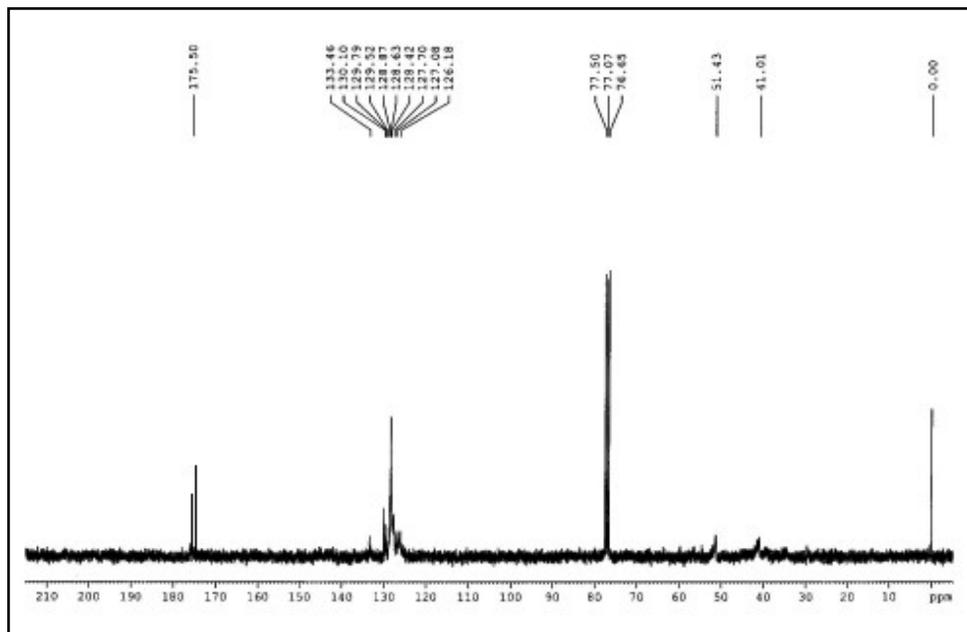


FIGURE 3.2.7.7

^{13}C NMR SPECTRA OF THE COPOLYMER OF LINSEED OIL, 1-DECENE (P-3)

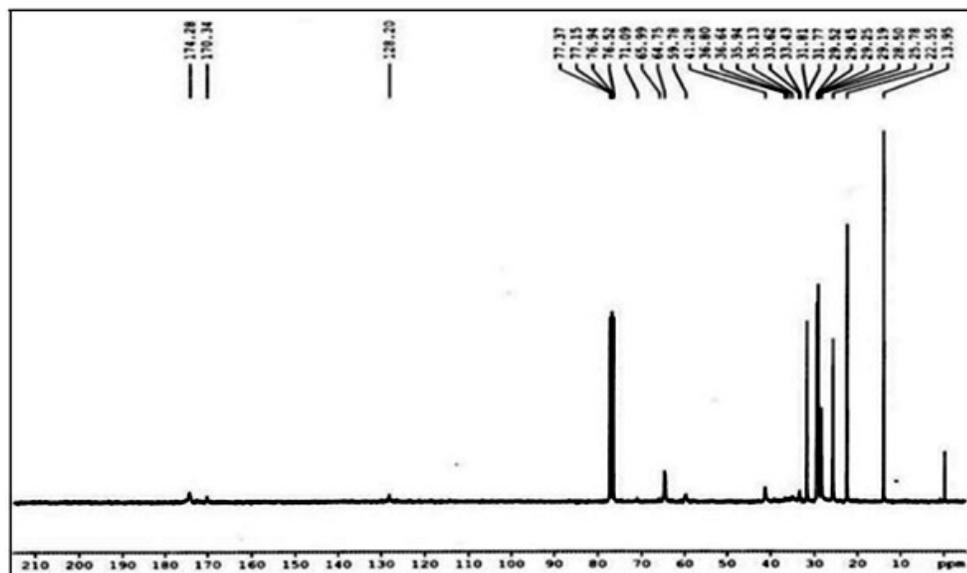


FIGURE 3.2.7.8

FT-IR SPECTRA OF THE COPOLYMER OF LINSEED OIL, OA (P-5)

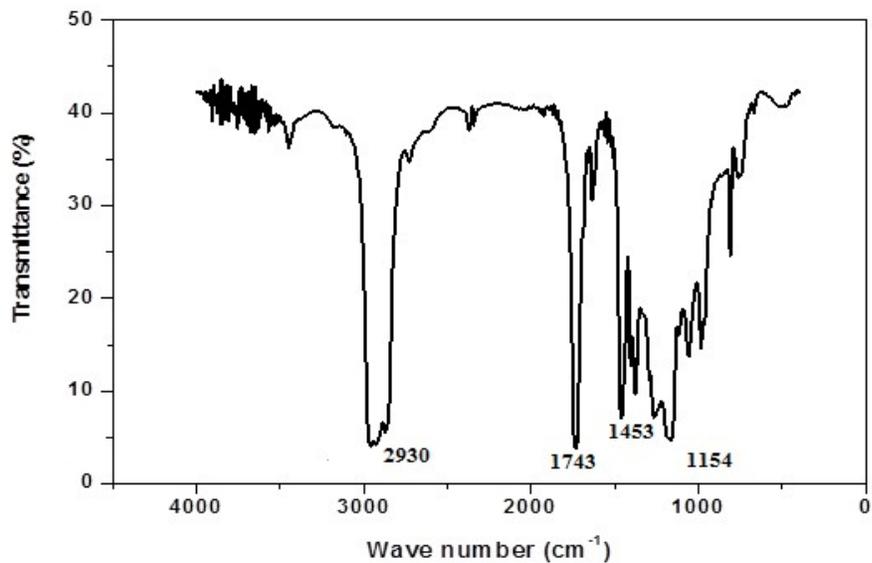


FIGURE 3.2.7.9

¹H NMR SPECTRA OF LINSEED OIL, OA COPOLYMER (P-5)

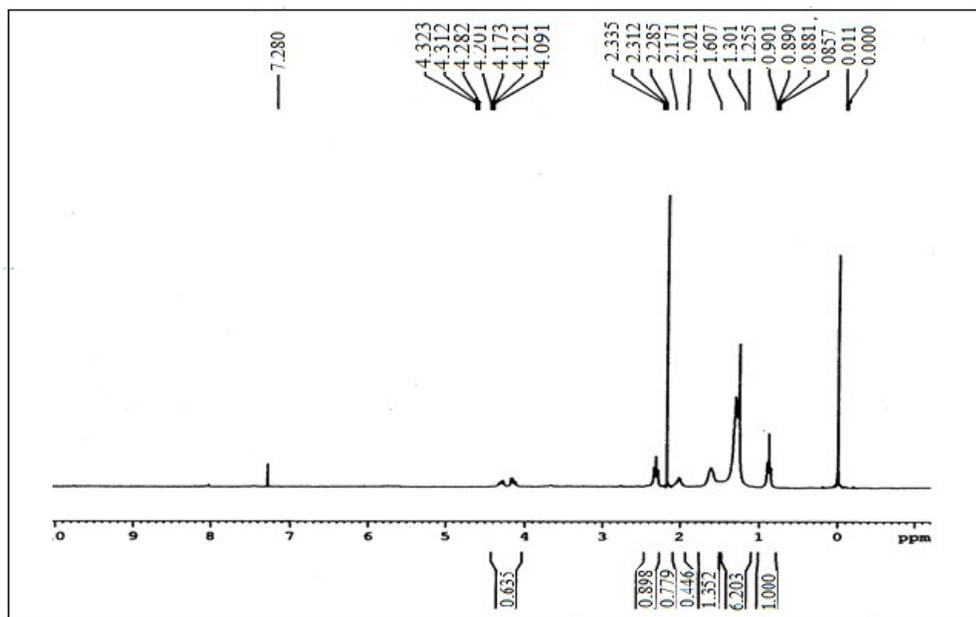


FIGURE 3.2.7.10

¹³C- NMR SPECTRA OF LINSEED OIL, OA COPOLYMER (P-5)

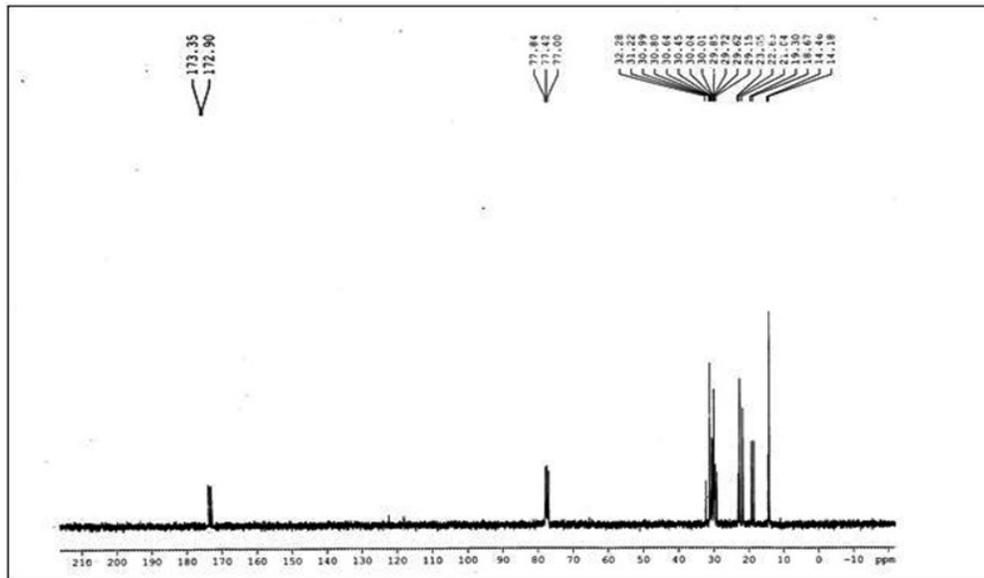


FIGURE 3.2.7.11

GPC OF THE HOMOPOLYMER OF LINSEED OIL.

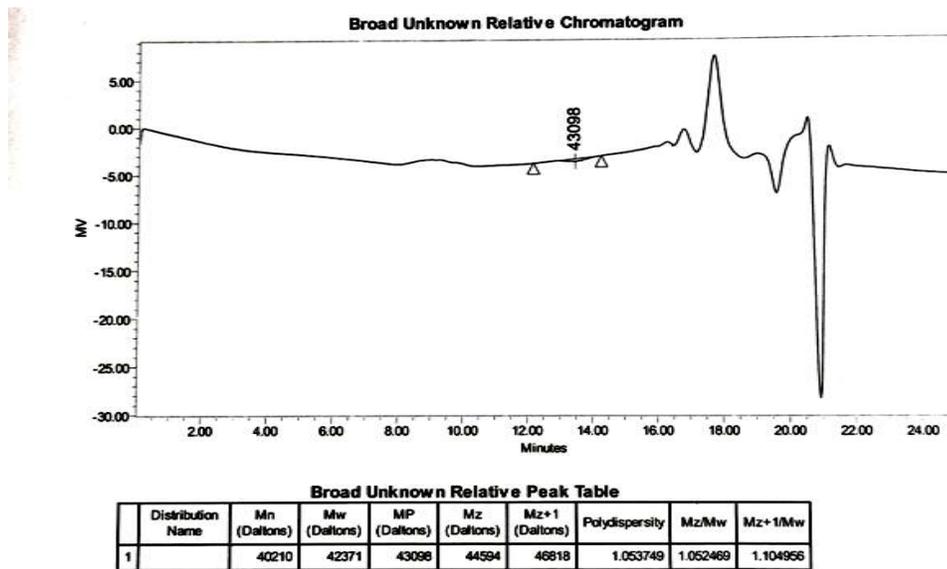


FIGURE 3.2.7.12

GPC OF THE COPOLYMER OF LINSEED OIL+STYRENE

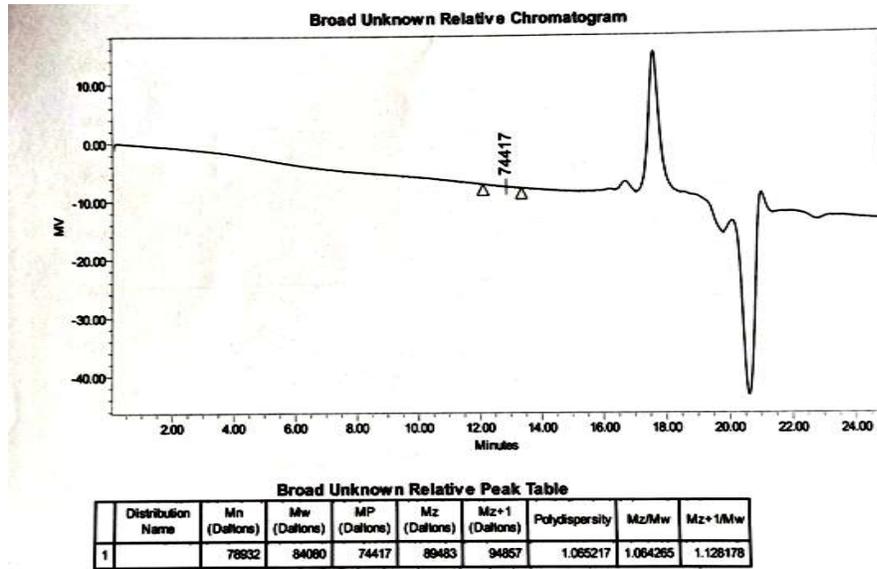


FIGURE 3.2.7.13

GPC OF THE COPOLYMER OF LINSEED OIL+1-DECENE

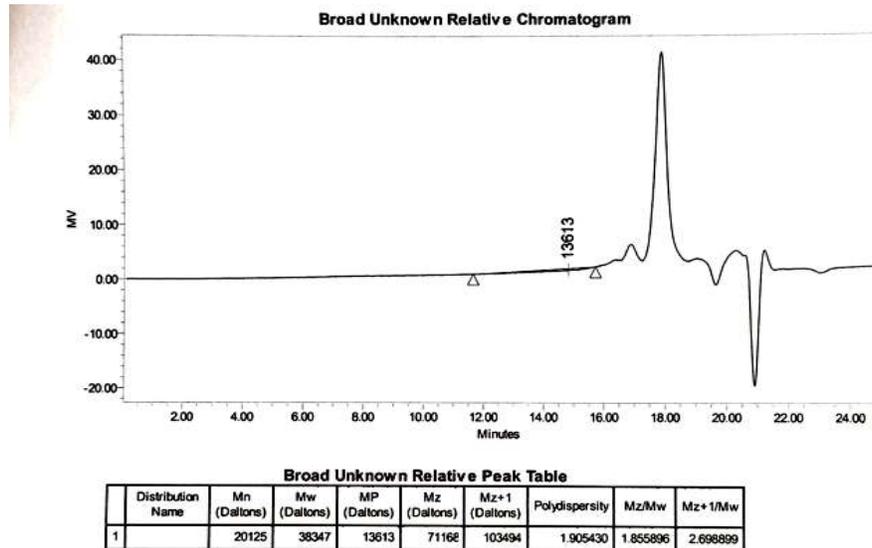


FIGURE 3.2.7.14

GPC OF THE COPOLYMER OF LINSEED OIL+ISODECYL ACRYLATE

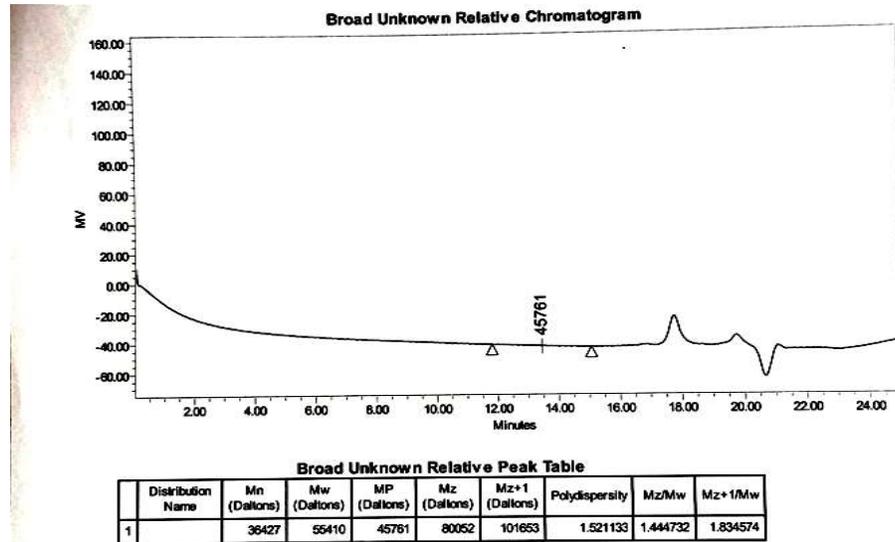
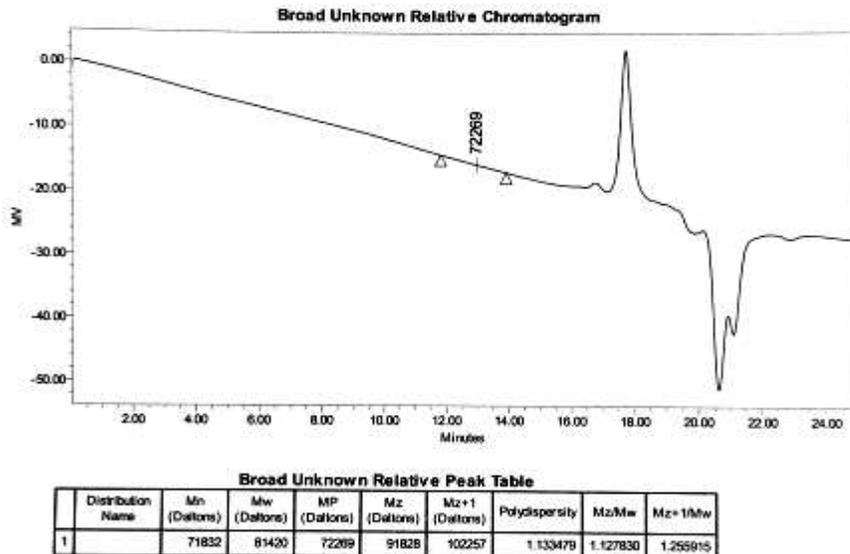


FIGURE 3.2.7.15

GPC OF THE COPOLYMER OF LINSEED OIL+OCTYL ACRYLATE



PART-3/CHAPTER-3

PERFORMANCE EVALUATION OF CHEMICALLY MODIFIED VEGETABLE OILS TOWARDS THE DEVELOPMENT OF BIODEGRADABLE GREENER LUBRICANT BASE STOCK

3.3.1 INTRODUCTION

Environment-friendly biodegradable lubricants, based on plant oil could replace or partially substitute conventional mineral oil is a big challenge. They have excellent rheological properties. (Vegetable oils have high viscosity index (above 200) high flash point as well. Despite having huge advantages and being biodegradable and environment friendly, vegetable oils suffer from some inherent limitations mainly low thermo-oxidative stability due to the presence of polyunsaturation [6]. Hence untreated vegetable oils cannot be used directly as a lubricant. However, this problem can be solved by some chemical modifications such as transesterification, epoxidation, selective hydrogenation, polymerization, etc. High contents of unsaturated fatty acid in most vegetable oils can be converted into epoxy fatty acid by conventional epoxidation, [11]. Epoxidized vegetable oil can act as a raw material for the synthesis of a variety of chemicals including polyols, glycol, carbonyl compound, lubricants, plasticizers for polymer, etc. because of the high reactivity of oxirane ring [7]. Castor oil is obtained from castor seeds which are available in nature. It contains a high percentage of triacylglycerol of ricinoleic acid (85–95%) which is a C–18 fatty acid having a double bond at C–9 and a hydroxyl group at C–12. Due to the trifunctional nature of castor oil, it can be used as a monomer for the preparation of lube oil polymeric additives as well as base stock

with multifunctional properties. Castor oil contains hydroxyl monounsaturated triglycerides which via hydrogen bonding raises the viscosity to a very good level. Castor oil has higher viscosity index compared to super-refined mineral oils [8]. In our earlier work, castor oil was explored towards the synthesis of multifunctional greener additives for lubricating oil[9]. Soyabean oil, one of the most abundant and inexpensive renewable sources towards the formulation of high molecular weight polymers, consists of polyunsaturated fatty acids with the main component being linoleic acid (50% w/w) [10]. Hong–Sik Hwang, Sevim Z. Erhan studied the properties of synthetic lubricant base stocks from epoxidized soybean oil and Guerbet alcohols [11]. Linseed oil is also another potential candidate in this field in which the level of unsaturation for the triglyceride is somewhat greater than that for soybean oil [12] In our previous work linseed oil-based biodegradable homo and copolymers were prepared towards the development of multifunctional greener additives for lube oil[13]. Olive oil is also a potential candidate in the lubricant industry as it is commercially available, cheap, and contains about 86 % of total active unsaturation. P. Ghosh et al. have conducted several studies on sunflower oil-based lubricants and additives which accounted for its vast application in the lubricant industry[14-16]. Due to high viscosity index and low pour point, these vegetable oils can be treated as a source of potential lube base stock. Lack of Thermal stability due to the unsaturation present in the triglyceride moiety is the main reason that they cannot be used directly as lube. In this context, we made epoxides of vegetable oils followed by epoxy ring-opening by different alcohols and studied their properties to determine whether they can be treated as alternate lubricant base stock. The main constituents of vegetable oils are triglycerides (95–97%). The general structure of triglyceride found in most of the vegetable oils is

shown in Figure 3.3.7.1. In our present study Vegetable oils like linseed oil (LO), castor oil (CO), olive oil (OLO), soybean oil (SBO), and sunflower oil (SFO) were epoxidized and characterized by FTIR and NMR spectroscopy. The reaction of epoxidized linseed oil with 2-ethyl hexanol, dodecanol, n-octanol, 1-decanol, and isodecanol in the presence of a catalytic amount of H₂SO₄ provided ring-opened products. These ring-opened products of linseed oil exhibited better low-temperature flow i.e. better pour point (PP) and high viscosity index (VI). Ring opened products with isodecanol and 2 ethyl hexanol showed better results compared to others. CO, OLO, SBO, SFO epoxide rings were also opened through the same procedure using isodecanol and the products exhibited high viscosity index and excellent low-temperature flow as well. Ring opened products displayed better thermal stability when passed through thermogravimetric analysis (TGA) compared to the mineral base oil. Better pour point, high viscosity index value, thermo oxidative stability, and better antiwear (AW) property make these products an environmentally benign alternative to mineral lubricating oil. The presence of unsaturated fatty acids like oleic, linoleic, linolenic, etc and saturated fatty acids like tetradecanoic, palmitic, stearic has been responsible for its versatile applications such as in-wall finishes[1], paints[2], electrodeposition paints [3], water thinnable primers[4], and printing inks [5], etc.

3.3.2 EXPERIMENTAL

3.3.2.1 MATERIAL USED

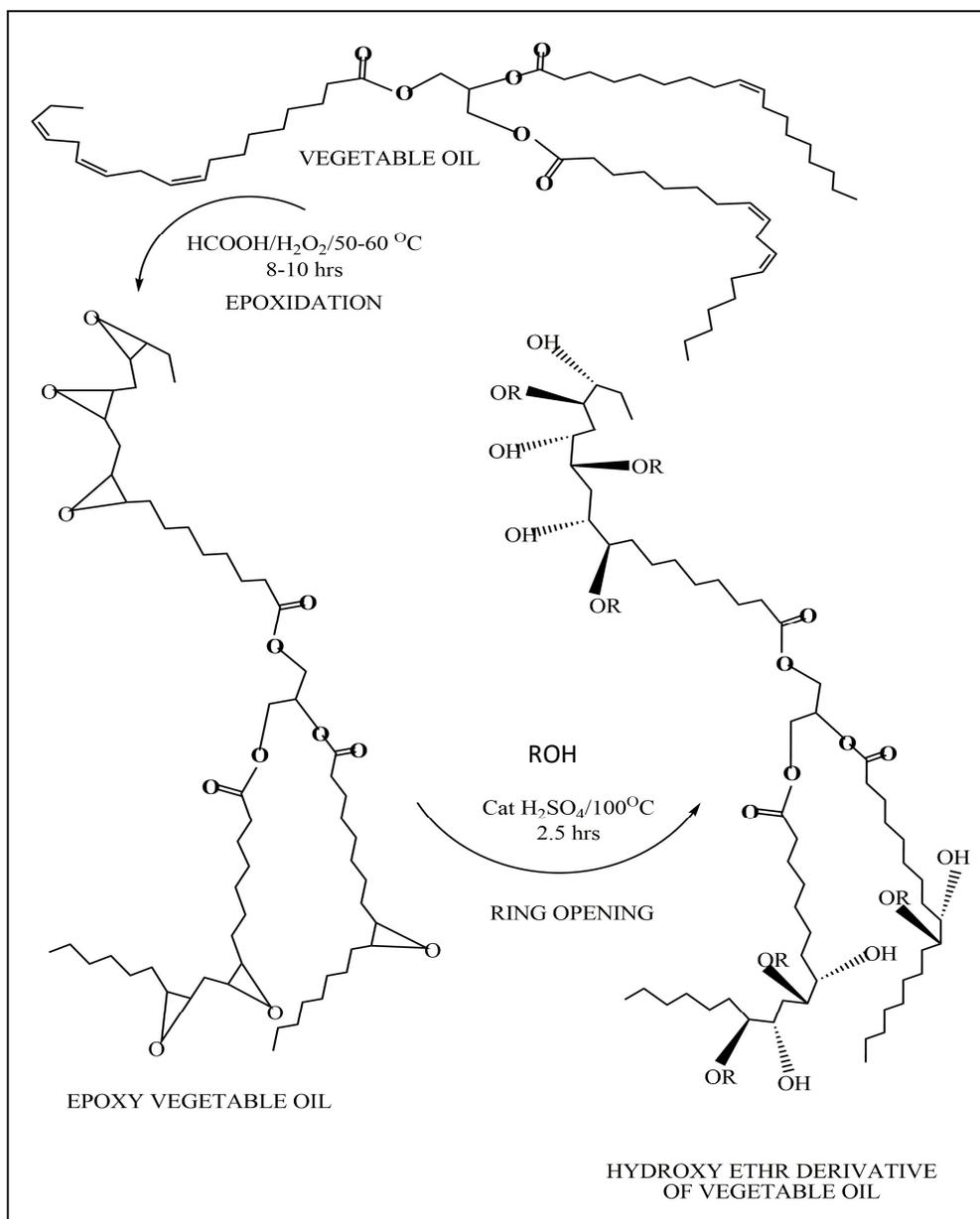
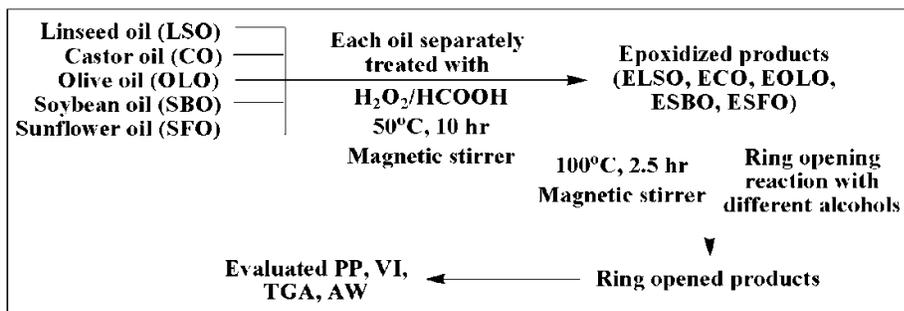
Linseed oil, castor oil, olive oil, sunflower oil, and soybean oil were brought from a local market and used directly. The physical properties of the vegetable oils and the mineral base oils are given in Table:- 3.3.7.1. The fatty acid composition of the vegetable oils is given in Table:- 3.3.7.2 H₂O₂ (30%) used at it was bought from

MERCK. Formic acid (98% Thomas Baker Pvt Ltd Ind), Concentrated H₂SO₄ (98% MERCK), 2-ethyl hexanol (99%Sigma Aldrich), dodecanol (99% Sigma Aldrich), n-octanol (99% LOBA Chemicals Pvt Ltd Ind), 1-decanol (99%Sigma Aldrich), isodecanol (99% LOBA chemical Pvt Ltd Ind) were used after distillation.

3.3.2.2 VEGETABLE OIL EPOXIDATION AND ITS PURIFICATION

At first, linseed oil and formic acid (1.0: 0.4 molar ratio) were mixed in a 2 neck RB fitted with a condenser & set over a water bath at a temperature of 50⁰C and speed of 550 RPM on a magnetic stirrer. The mixture was stirred for 10 min. To start the epoxidation, hydrogen peroxide (30 %) was gradually changed into the mixture during the first 5 hr of reaction in the molar ratio of 1: 1.7 concerning the oil and peroxide[11]. After charging of H₂O₂ was completed, the reaction continued by mixing and controlling the temperature at 50^o C for a further 5 hr. After that, the mixture was cooled down and neutralized by water. Diethyl ether was used to enhance the separation of the oil production from the water phase. The final product was dried out by heating less than 50^oC. Three replications were performed concurrently. Similarly, castor oil epoxide and epoxide of other vegetable oils were prepared[11]. Epoxides have active sites and are further treated with different sets of chemicals to obtain end products with the diversified application. The epoxides were characterized by FTIR and NMR spectra and used for the next step.

Scheme 3.3.1:-Preparation of epoxy vegetable oil and subsequent ring-opening



3.3.2.3 RING-OPENING REACTION OF VEGETABLE OIL EPOXIDE

A mixture of epoxidized linseed oil (ELSO) and 2-ethyl hexanol (1:5 molar ratio of epoxide and alcohols) was heated at 90°C with stirring. Sulfuric acid (2%) was added dropwise and the mixture was stirred at 100°C for 2.5 hr. When the reaction mixture turned brownish, it was cooled by adding ice and saturated aqueous sodium bicarbonate. It was extracted with ethyl acetate, dried over anhydrous Na₂SO₄. The remaining solvent was evaporated under vacuum at 80°C to have the ring-opened product [11]. Similar reactions were carried out using dodecanol, n-octanol, 1-decanol, and isodecanol under the same reaction condition stated above. Castor oil epoxide (ECO), olive oil epoxide (EOLO), soybean oil epoxide (ESBO), sunflower oil epoxide (ESFO) was treated with isodecanol in 1: 2.5 molar ratio of epoxide and alcohol under the same reaction condition to have the ring-opened products. The ring-opening reaction was monitored by the disappearance of epoxy ring hydrogen.

3.3.3 MEASUREMENTS

3.3.3.1 INSTRUMENTATION

- **SPECTROSCOPIC MEASUREMENTS**

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

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

TGA data were recorded on Shimadzu TGA-50 system, at a heating rate of 10° C/min. Results are summarised in Table:- 3.3.7.3. The uncertainty in determining percent weight loss (PWL) within the range was $\pm 1.2\%$.

3.3.3.2 PERFORMANCE EVALUATION

- **PERFORMANCE EVALUATION - POUR POINT**

The pour point of the ring-opened products was measured according to the ASTM D 97-09 [18] method using cloud and pour point tester model WIL-471 (India) and a comparison was carried out against base oil. The pour point data are given in Table:- 3.3.7. 4.

- **PERFORMANCE EVALUATION - VISCOSITY INDEX**

Viscosity index (VI) is the change of viscosity with temperature and is a unitless parameter. The higher the value of VI, the smaller is the change of viscosity at high temperature. It was calculated according to ASTM D 2270-10 [17]. The kinematic viscosities of the lubricant composition were determined at 40°C and 100°C which are essential to calculate the VI. A comparison of VI data between the ring-opening products of ELSO and ECO with base oil is listed in Table:- 3.3.7.5.

- **PERFORMANCE EVALUATION - ANTIWEAR TEST**

The antiwear performance of the ring-opened products was evaluated by Four-ball Wear Test apparatus (FBWT) following the ASTM D 4172-94 [19] method. In this experiment, the wear scar diameter (WSD), a parameter for the determination of antiwear (AW) performance of the oils, has been measured applying weld load of 392 N (40 Kg) at 75°C for 60 min. The results are tabulated in Table:- 3.3.7.6.

3.3.4 RESULT AND DISCUSSION

3.3.4.1 SPECTROSCOPIC ANALYSIS

Spectral data of all the vegetable oils give an almost similar result. IR absorption band around 1745 cm^{-1} corresponds to the C=O stretching in the ester carbonyl group in triglyceride moiety in vegetable oil, a broad peak at 3437.95 cm^{-1} corresponds to the –OH group present in the castor oil (ricinoleic acid). Epoxidized vegetable oils produce a new absorption around 822 cm^{-1} and 845 cm^{-1} which indicate the presence of an epoxy ring. The ring-opened products have absorption ranging from 1738 cm^{-1} to 1740 cm^{-1} (Figure:-3.3.7.3 for ELSO) corresponding to the ester C=O group in the ring-opened epoxidized vegetable oils. Broad absorption ranging from 3420 cm^{-1} to 3450 cm^{-1} corresponds to the –OH group in the ring-opened product. Completion of the ring-opening reaction was confirmed by checking the disappearance of epoxy signals at 1158 , 845 , and 822 cm^{-1} in the IR spectrum (Figure:- 3.3.7.8 for ELSO+isodecanol).

The ^1H NMR data of the epoxidized vegetable oils exhibited the presence of secondary and primary glycerol proton at δ 5.10–5.20 ppm and 4.10–4.30 ppm, respectively. The proton signal centered at δ 3.00 ppm is evident for the presence of epoxy protons. This is further substantiated by the disappearance of the olefinic proton signals in the region between δ 5.34–5.43 ppm. The broad intense signal observed in the region δ 1.26–1.63 ppm is due to the presence of many methylene protons. Furthermore, the proton signal at δ 0.89 ppm is characteristic of terminal methyl groups. Ring-Opening product of the epoxides of linseed oil, castor oil, olive oil, soybean oil, and sunflower oil with isodecanol exhibited a similar appearance in NMR spectra. In the ring-opened products, peaks around δ 3.00 ppm corresponding to epoxy protons are absent.

The ^{13}C NMR data also indicated the presence of the carbonyl carbon (O=C) at δ 173.06 ppm, glycerol (CH) at δ 68.95ppm, and glycerol (CH₂) at δ 62.04–64.99ppm, methylene carbons (CH₂) at δ 22.64–34.03 ppm, and methyl carbon (CH₃) at δ 14.06 ppm. On inspection of the ^{13}C NMR spectrum of linseed oil, there are diagnostic signals in the region δ 120–130 ppm which accounted for the olefinic carbons. These signals were not detected in the epoxidized linseed oil which justifies the disappearance of the double bonds and formation of epoxides. This is further supported by the observed increase in the intensity of the epoxy carbon. Furthermore, the triglyceride structure remained intact after epoxidation. Other vegetable oils also produced similar peaks.

3.3.4.2 ANALYSIS OF THERMAL STABILITY

TGA data (Table:- 3.3.7.3) supported that the prepared products were thermally more stable than the mineral base oil. A lower PWL value indicates higher thermal stability. It is found that the percentage of degradation of the ring-opened products of the vegetable oil epoxides at a particular temperature is lower compared to the mineral base oil. This observation simply implies that chemically modified vegetable oils are far resistant against thermal degradation than the mineral base oil under consideration. At 473 K mineral base oil degrades almost completely (PWL 98) whereas the chemically modified vegetable oils degrade almost completely (PWL around 90) above 600K. From this point of view, these chemically modified vegetable oils are more reliable as lubricant base stock.

3.3.4.3 ANALYSIS OF POUR POINT DATA

From Table:- 3.3.7.4 data it is observed that the ring-opening product of ELSO with 2 ethyl hexanol, isodecanol; and ECO, EOLO, ESBO, ESFO with isodecanol exhibited better low-temperature flow. This may be attributed to the

morphology of the branched alcohol moiety that hinders the formation of the wax crystal network. This result implies that at lower temperatures these chemically modified vegetable oils are easier to handle than the mineral base oil.

3.3.4.4 ANALYSIS OF VISCOSITY INDEX DATA

Viscosity may be the most important parameter for lube oil. Vegetable oil has fare viscosity index (Table:- 3.3.7.1) but due to the low thermal-oxidative stability, it can't be directly used as a lubricant. After modification of vegetable oils, they can be considered for comparison with mineral oil. Table:- 3.3.7.5 indicates the possibility of using them as lube base stock. These data sought for the utilization of chemically modified vegetable oils over a broad temperature range since they can sustain their viscosity at an elevated temperature quite well.

3.3.4.5 ANALYSIS OF ANTIWEAR PERFORMANCE DATA

The tribological properties of the lubricant compositions at different mass fractions were determined by measuring WSD values through the FBWT apparatus. By analyzing Table:- 3.3.7.6 data it is evident that the modified vegetable oils produce less wear in engine condition. The chemically modified vegetable oils strengthen the film through chemical and physical bonding between polar functional groups and metal atoms on the metallic surface. Due to the presence of long polar fatty ester chains of these oils showed better AW property compared to the mineral base oil. Due to polar -OH groups, the ring-opened products form comparatively stronger bonds with metal atoms and exhibit better AW property. Among all the chemically modified vegetable oils under consideration, a ring-opened product of castor oil epoxide exhibited the best result in terms of antiwear performance.

3.3.5 CONCLUSION

Epoxidation followed by ring-opening reaction with suitable alcohols has provided an efficient easy route towards the formation of vegetable oil-based biodegradable and thermally stable lubricant base stock with the better low-temperature flow, viscometric properties, and antiwear performance. These chemically modified vegetable oils can be used directly or in a mixture with mineral base lube for better performance. The above study accounts for the replacement of toxic mineral base oil with environment-friendly, biodegradable greener vegetable oil-based products as lubricant base stock.

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for providing Base Oil.

3.3.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-3 of Part-3**”.

3.3.7 TABLES AND FIGURES

FIGURE 3.3.7.1

GENERAL STRUCTURE OF TRIGLYCERIDE FOUND IN VEGETABLE OIL.

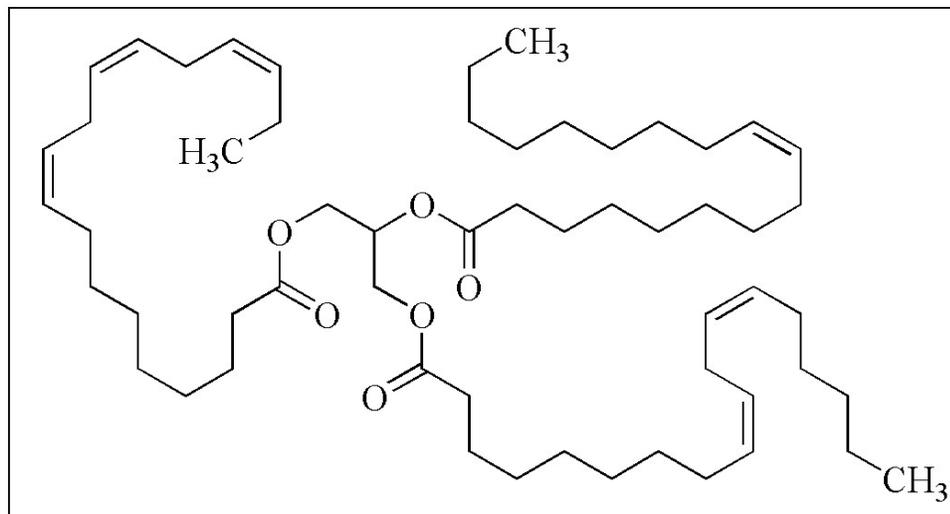


TABLE 3.3.7.1

PHYSICAL PROPERTIES OF BASE OIL (BO), LINSEED OIL (LSO), CASTOR OIL (CO), OLIVE OIL (OLO), SOYBEAN OIL (SBO), SUNFLOWER OIL (SFO)[20]

Physical properties	BO*	LSO	CO	OLO	SBO	SFO
Density (gcm^{-3} at 25°C)	0.95	0.93	0.88	0.92	0.86	0.91
Viscosity at 40°C in cSt	24.211	15.22	173	41.7	28	33.8
Viscosity at 100°C in cSt	4.47	6.33	15	8.8	7.55	8.1
Pour Point (PP in $^{\circ}\text{C}$)	-6	-21	-27	-2	-9	-17
Flash Point ($^{\circ}\text{C}$)	225	>280	200	316	252	245

*BO collected from IOCL, Dhakuria, West Bengal

TABLE 3.3.7.2

FATTY ACID (IN %) COMPOSITION OF VEGETABLE OILS [20]

Vegetabl oil	Palmitic acid (16:0)	Stearic acid (18:0)	Oleic acid (18:1)	Ricinoleic acid (18:1)	Linoleic acid (18:2)	Linolenic acid (18:3)
Olive	14	2	64	–	16	2
Castor	3	3	9	75	10	–
Soybean	6	5.2	20.2	–	63.7	5
Linseed	5	4	19.1	–	15.3	56.6
sunflower	6.1	5.3	21.4	–	66.4	–

TABLE 3.3.7.3

TGA DATA OF THE MODIFIED VEGETABLE OILS IN COMPARISON TO THE BASE OIL

Sample	Decomposition temperature (K)	Percent weight loss (PWL)
Base Oil	393/473	38/98
ELSO + 2-Ethyl hexanol	451/573	15/90
ELSO + Dodecanol	453/571	14/93
ELSO + n-Octanol	468/608	15/92
ELSO + 1-Decanol	470/610	15/96
ELSO + Isodecanol	483/613	13/91
ECO + Isodecanol	483/603	21/95
EOLO + Isodecanol	473/613	14/92
ESBO + Isodecanol	453/598	18/96
ESFO + Isodecanol	462/593	14/91

TABLE 3.3.7.4

POUR POINT DATA OF MODIFIED VEGETABLE OILS IN COMPARISON TO BASE OIL AND GRAPHICAL REPRESENTATION.

Sample	Pour point in °C
Base Oil	-6
ELSO + 2-Ethyl hexanol	-15
ELSO + Dodecanol	-2
ELSO + n-Octanol	-7.2
ELSO + 1-Decanol	-3.6
ELSO + Isodecanol	-18.4
ECO + Isodecanol	-22
EOLO + Isodecanol	-19.4
ESBO + Isodecanol	-18
ESFO + Isodecanol	-17

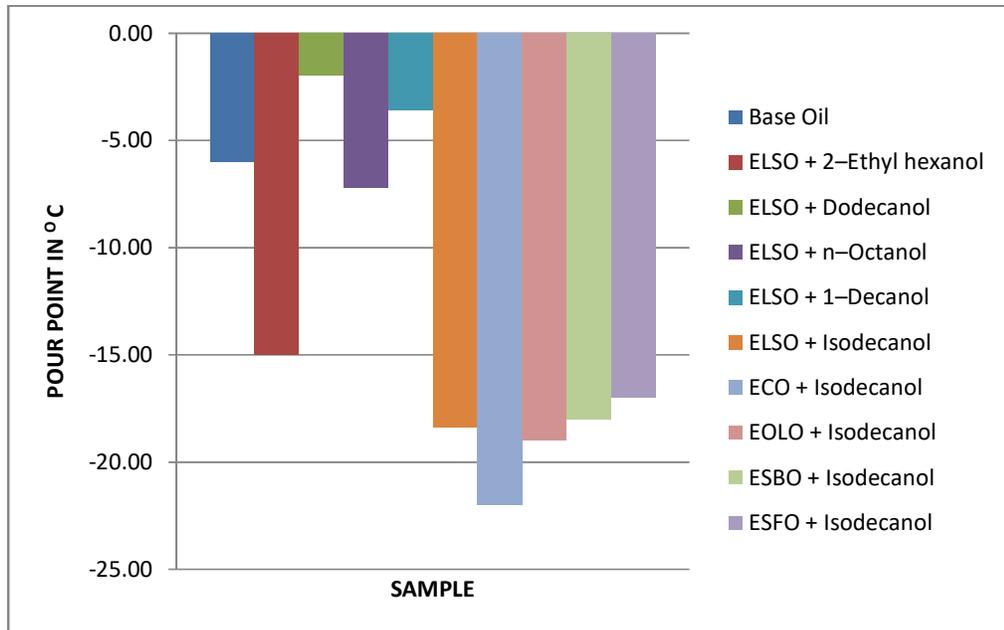


TABLE 3.3.7.5

VISCOSITY INDEX DATA OF MODIFIED VEGETABLE OILS IN COMPARISON TO BASE OIL AND GRAPHICAL REPRESENTATION.

Sample	Viscosity index
Base Oil	89.87
ELSO + 2-Ethyl hexanol	248
ELSO + Dodecanol	256
ELSO + n-Octanol	238
ELSO + 1-Decanol	259
ELSO + Isodecanol	264
ECO + Isodecanol	138
EOLO + Isodecanol	154
ESBO + Isodecanol	268
ESFO + Isodecanol	207

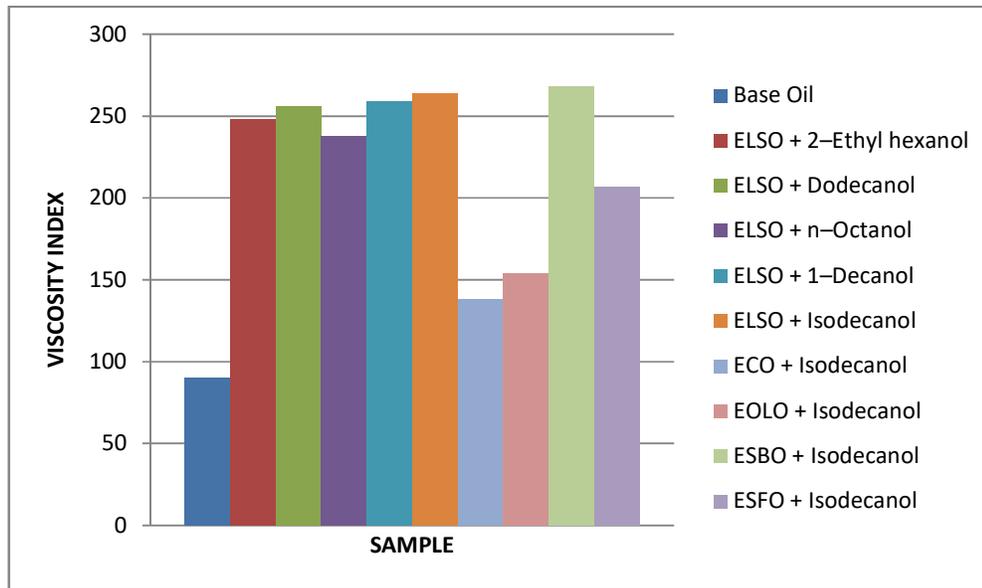


TABLE 3.3.7.6

WEAR SCAR DIAMETER (WSD) VALUES OF THE MODIFIED VEGETABLE OILS IN COMPARISON TO THE BASE OIL AND GRAPHICAL REPRESENTATION.

Sample	WSD x 10 ⁻³ (m)
Base Oil	1.119
ELSO + 2-Ethyl hexanol	0.868
ELSO + Dodecanol	0.835
ELSO + n-Octanol	0.856
ELSO + 1-Decanol	0.882
ELSO + Isodecanol	0.868
ECO + Isodecanol	0.616
EOLO + Isodecanol	0.989
ESBO + Isodecanol	0.776
ESFO + Isodecanol	0.798

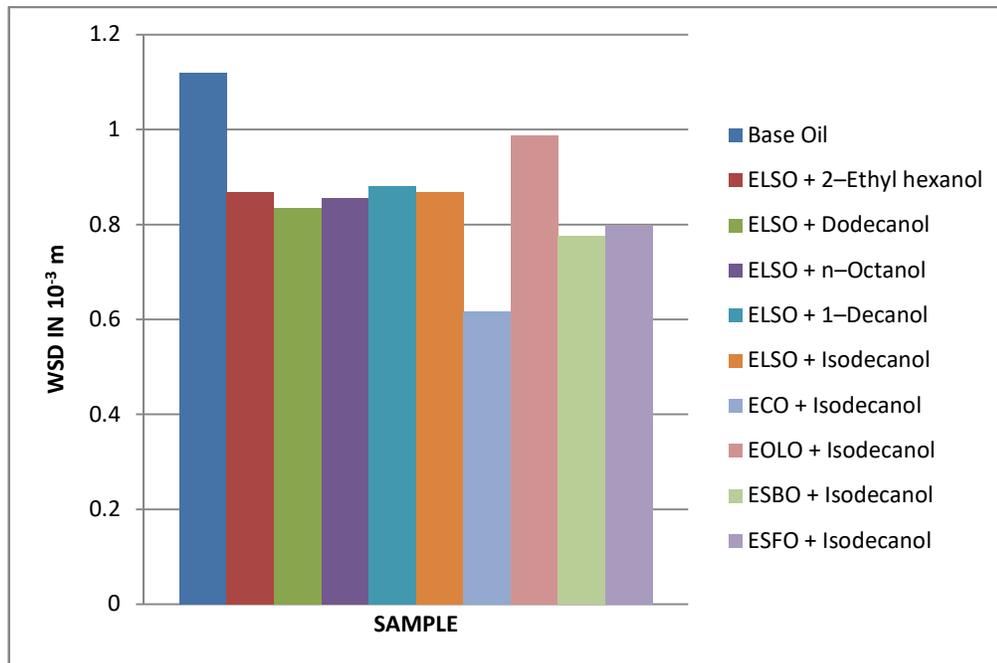


FIGURE 3.3.7.2

FT IR SPECTRA OF LINSEED OIL (LSO)

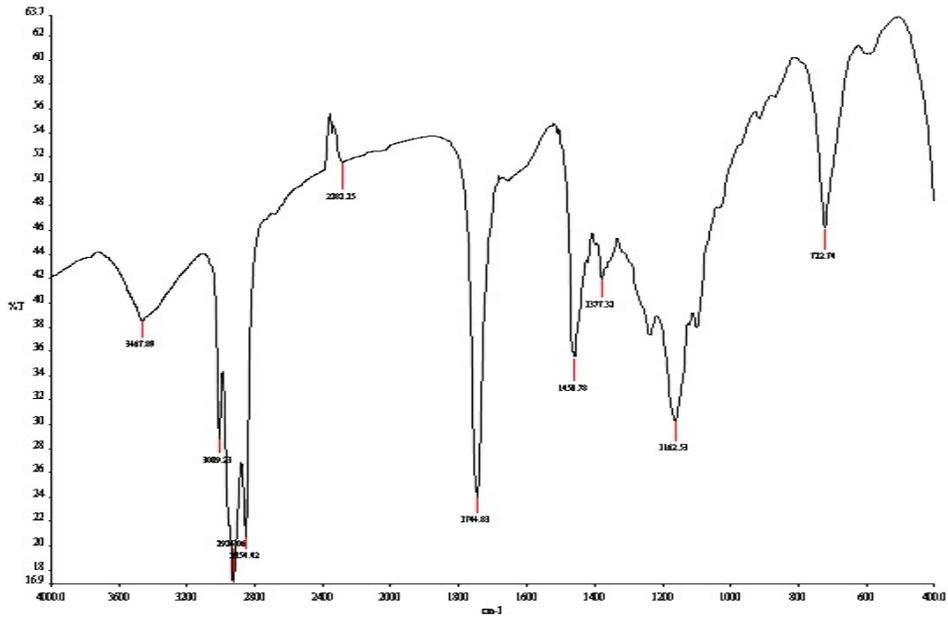


FIGURE 3.3.7.3

FT IR SPECTRA OF EPOXY LINSEED OIL (ELSO)

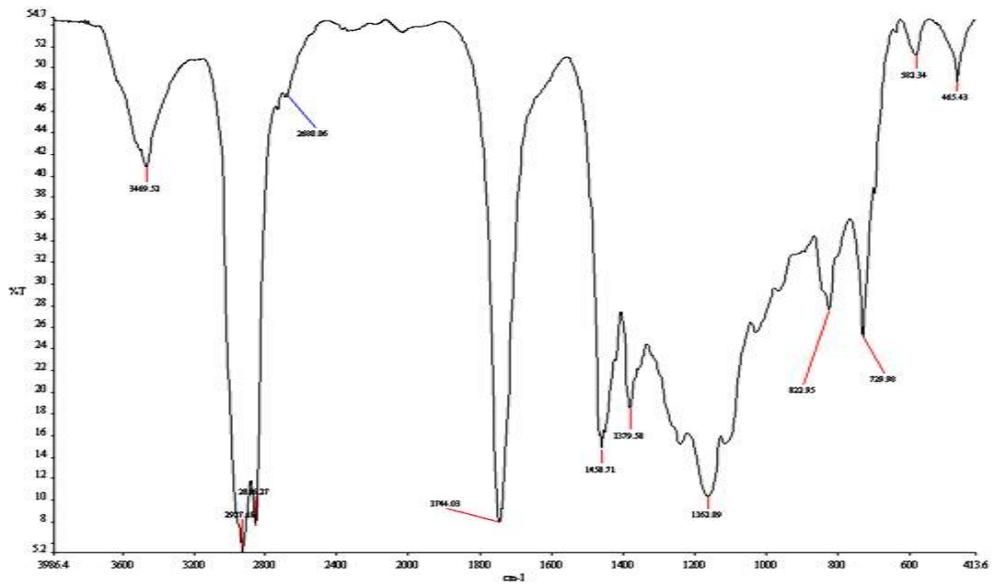


FIGURE 3.3.7.4

FT IR SPECTRA OF ELSO+2ETHYLHEXANOL

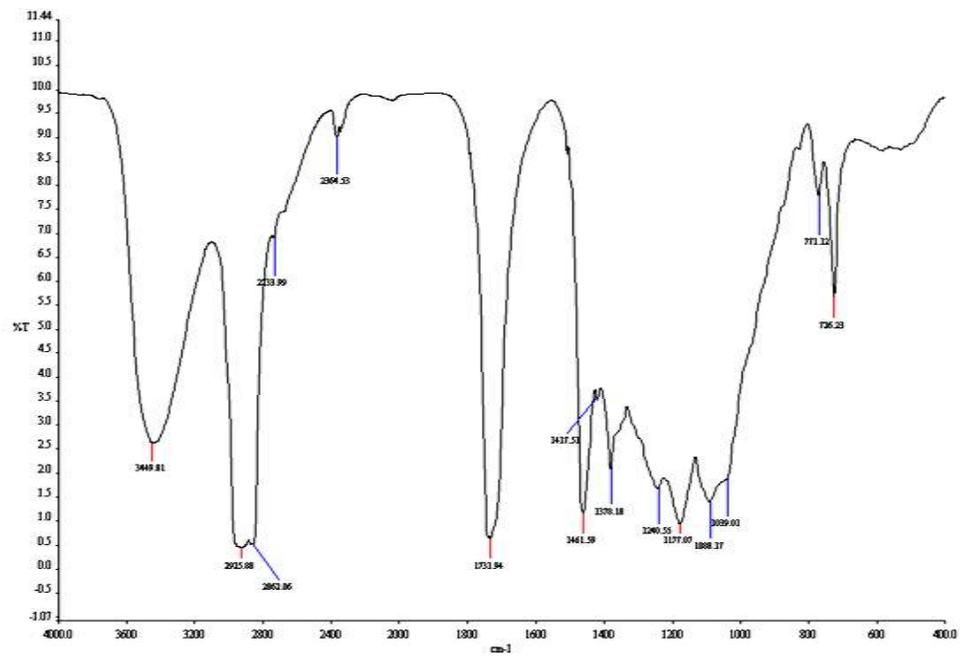


FIGURE 3.3.7.5

FT IR SPECTRA OF ELSO+DODECANOL

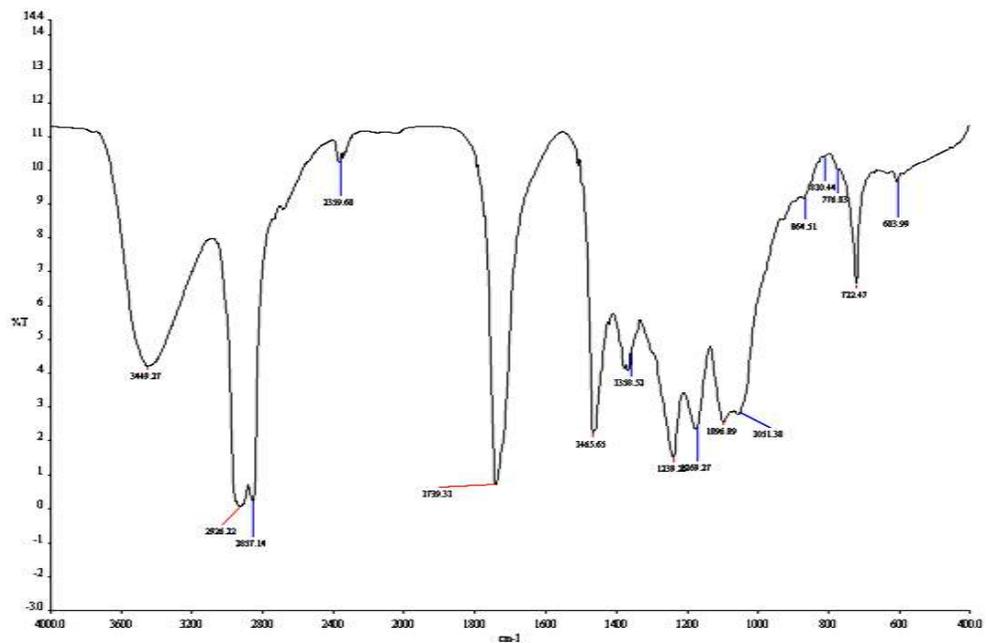


FIGURE 3.3.7.6

FT IR SPECTRA OF ELSO+N-OCTANOL

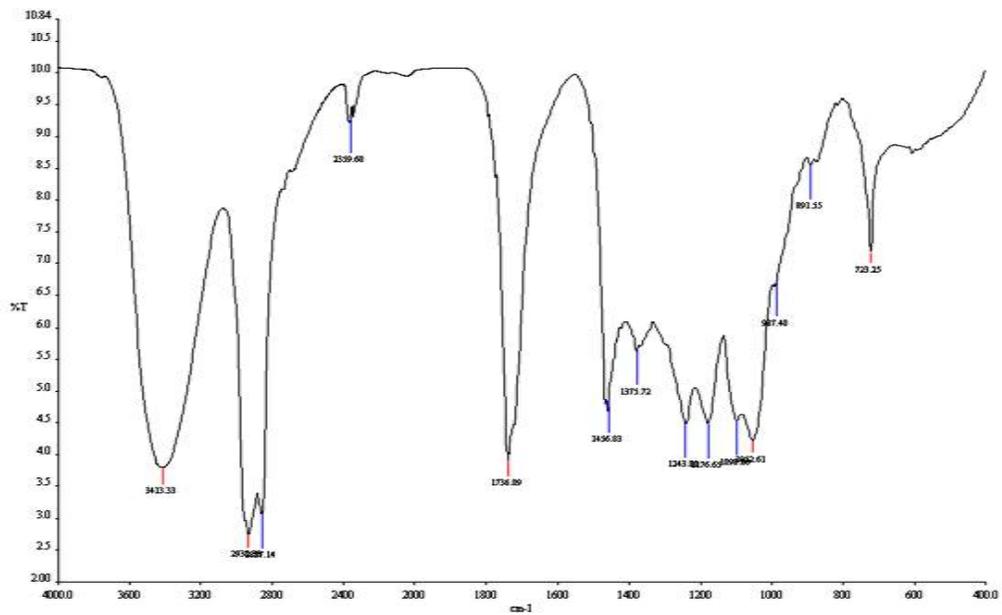


FIGURE 3.3.7.7

FT- IR SPECTRA OF ELSO+1-DECANOL

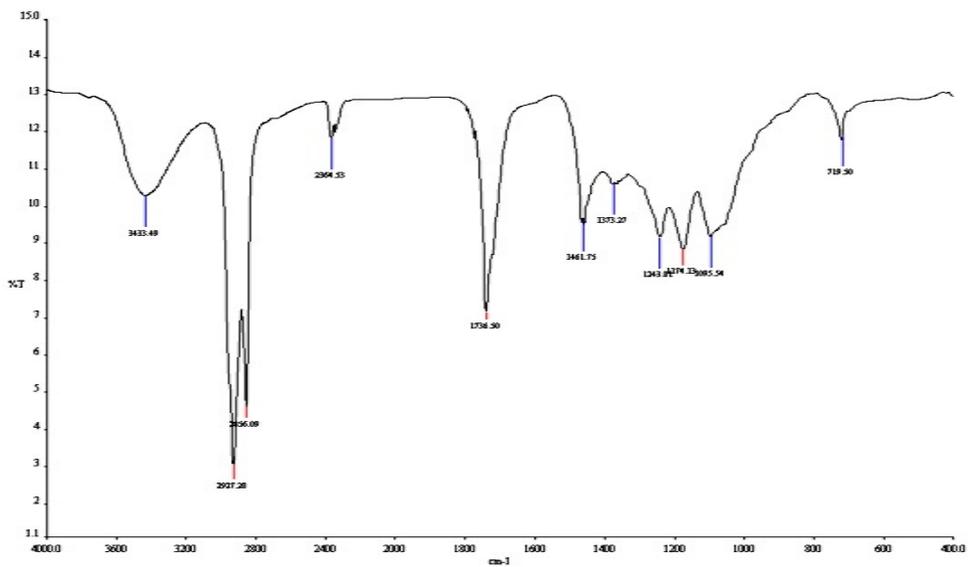


FIGURE 3.3.7.8

FT IR SPECTRA OF ELSO+ISODECANOL

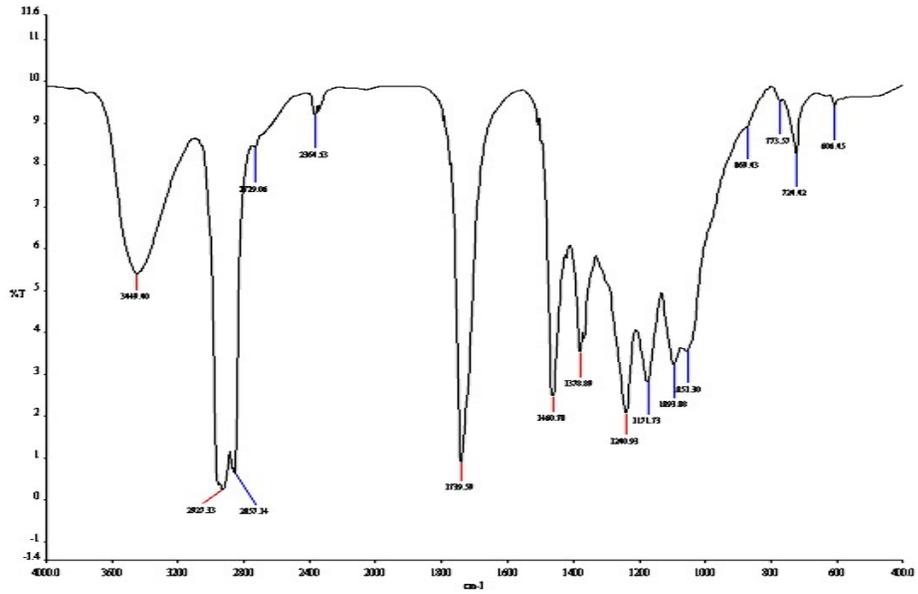


FIGURE 3.3.7.9

FT IR SPECTRA OF ECO+ISODECANOL

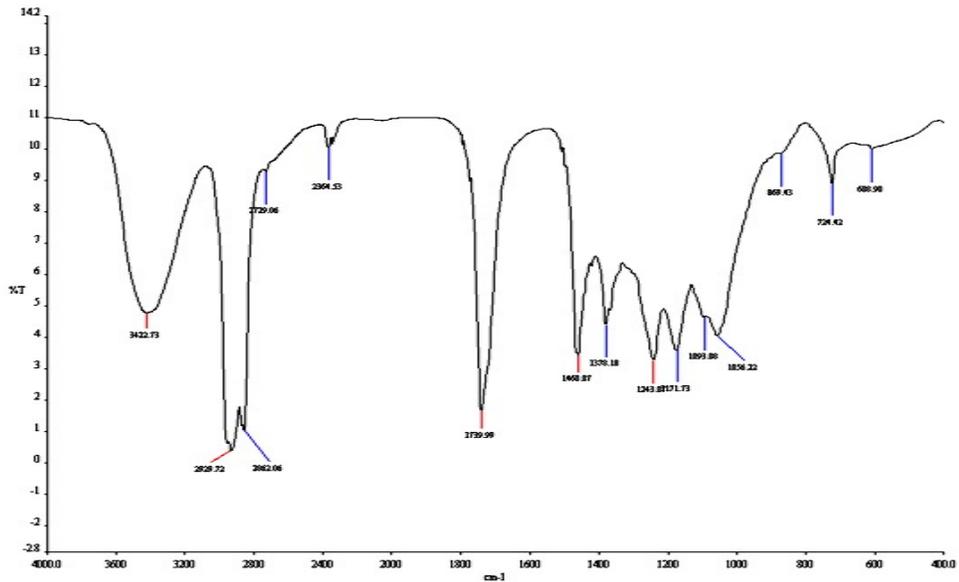


FIGURE 3.3.7.10

FT IR SPECTRA OF EOLO+ISODECANOL

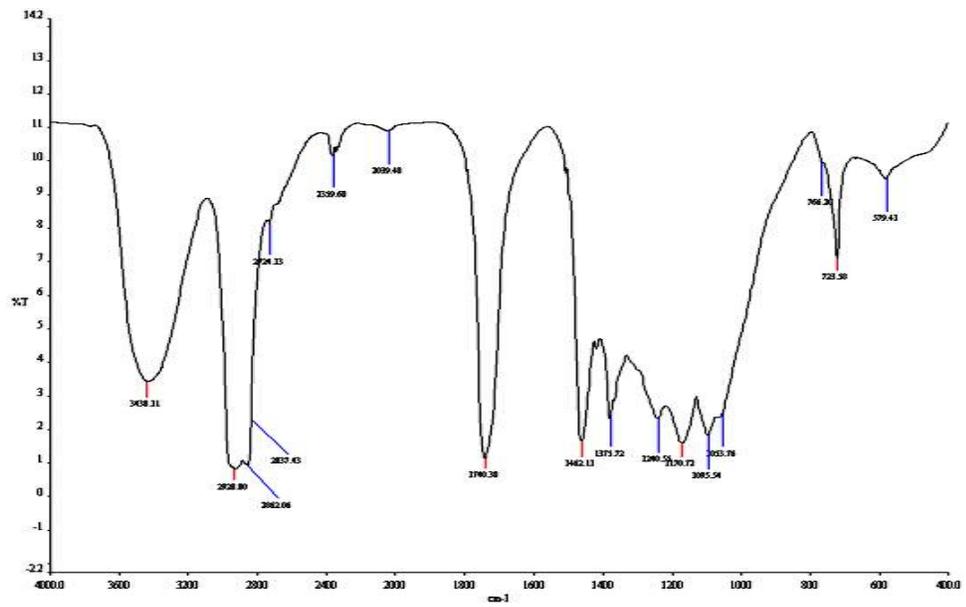


FIGURE 3.3.7.11

FT- IR SPECTRA OF ESBO+ISODECANOL

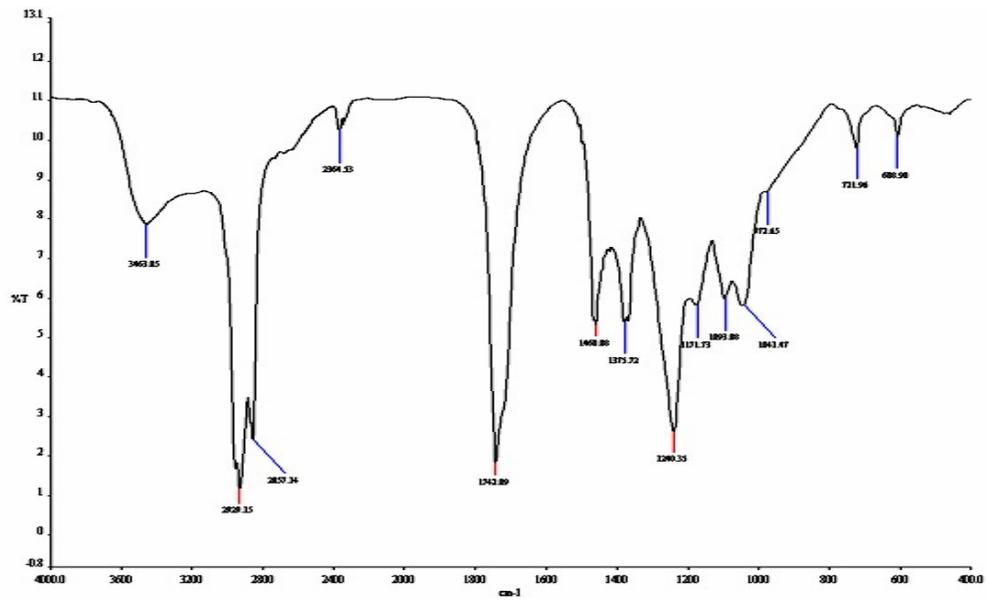


FIGURE 3.3.7.12

FT IR SPECTRA OF ESFO+ISODECANOL

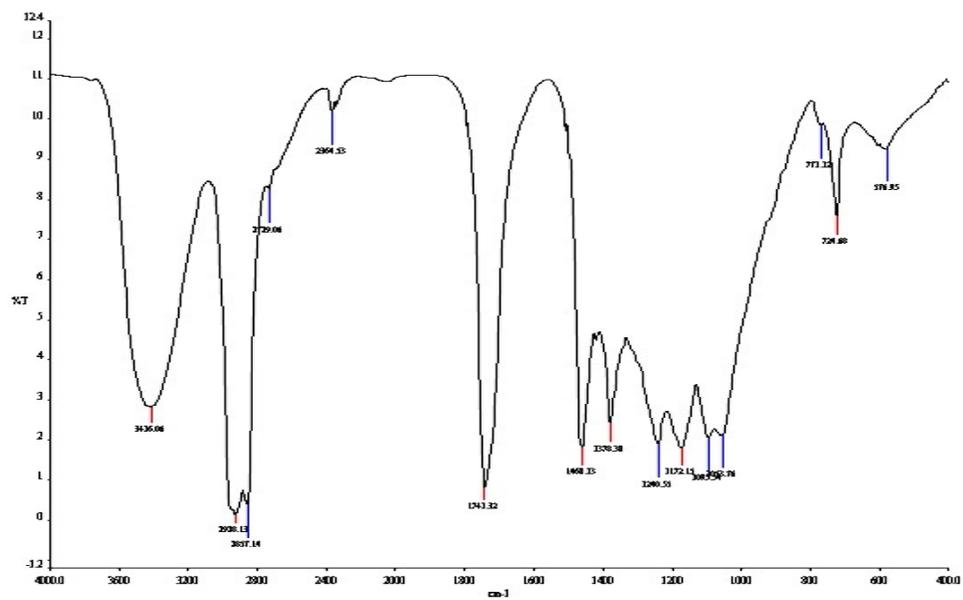


FIGURE 3.3.7.13

REPRESENTATIVE ^1H NMR SPECTRA OF (A)LSO,(B) ELSO

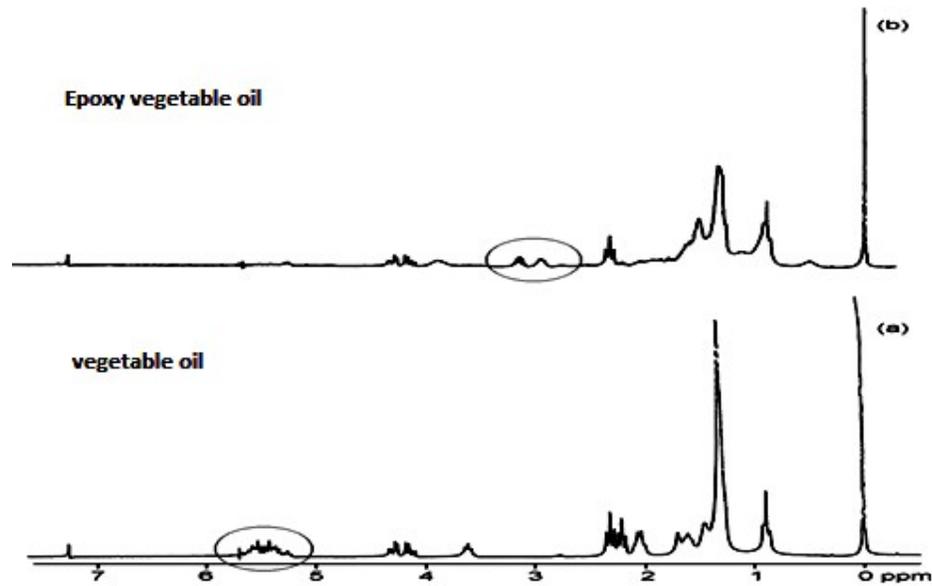


FIGURE 3.3.7.14

REPRESENTATIVE ^1H NMR SPECTRA OF ELSO+ ISODECANOL

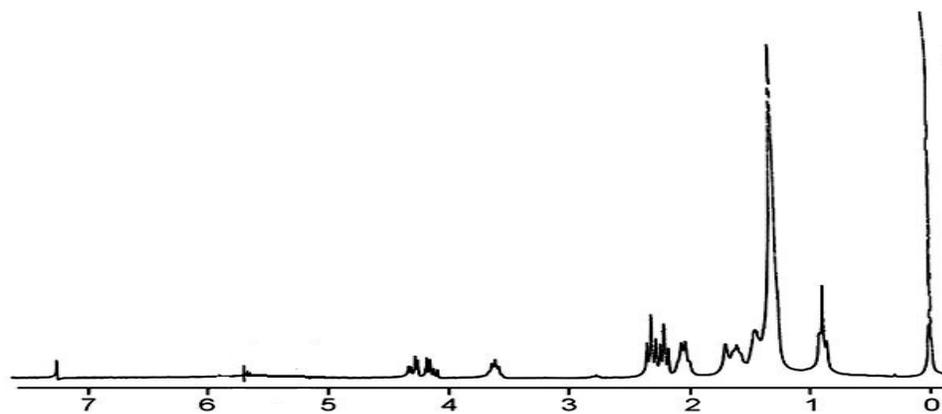


FIGURE 3.3.7.15

^{13}C NMR SPECTRA OF LSO

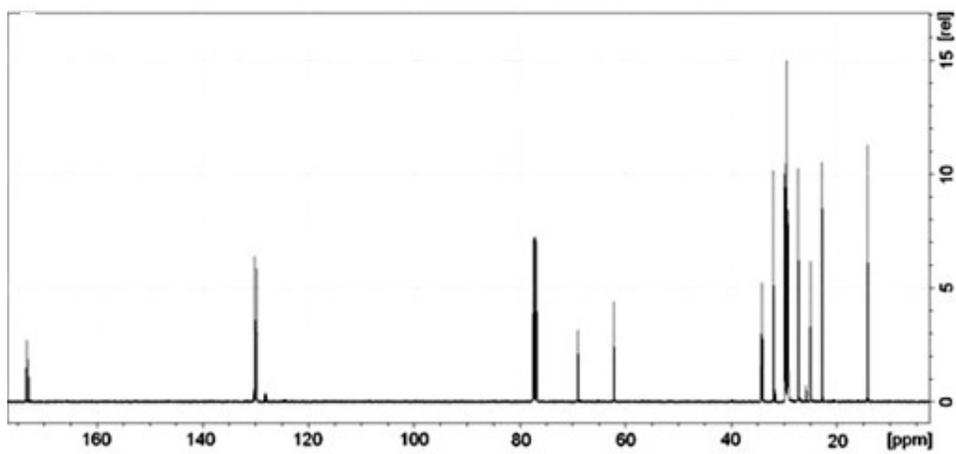
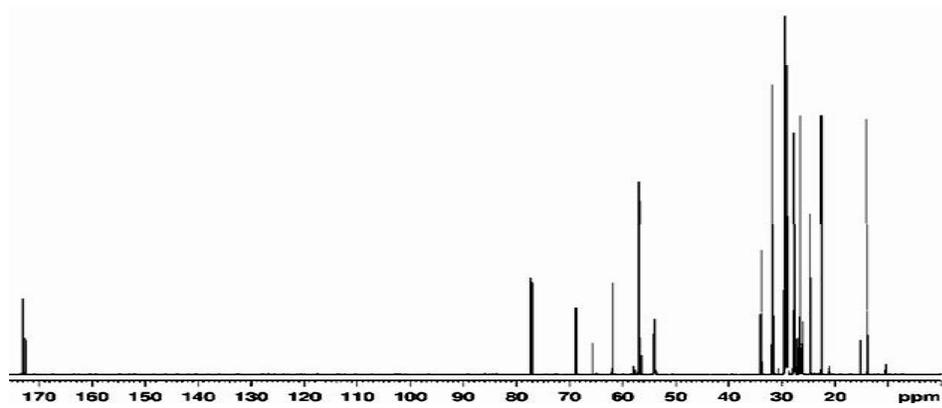


FIGURE 3.3.7.16

^{13}C NMR SPECTRA OF ELSO



BIBLIOGRAPHY

REFERENCES

GENERAL INTRODUCTION

1. Lansdown, AR, (2004). Lubrication and lubricant selection: a practical guide, (*Third Edn.*). ASME Press, New York.
2. Persson BNJ (2000). Sliding friction, physical principles, and applications. Springer-Verlag, Germany. [https://doi.org/10.1002/\(SICI\)1096-9853\(200001\)24:1<95::AID-NAG37>3.0.CO;2-J](https://doi.org/10.1002/(SICI)1096-9853(200001)24:1<95::AID-NAG37>3.0.CO;2-J).
3. Pirro DM, Webster M, Daschner E (2016) Lubrication fundamentals (Third Edn.). CRC Press.
4. Stachowiak, G, Batchelor, A, (2013). Engineering tribology (4th Edn.). Elsevier, Amsterdam.
5. Abdullah, SF. (2009). Study on nanoparticles as an additive in lubricant towards sustainability of energy in industrial engineering. *J Energy Environ* 1:34-37.
6. Bataille, P, Sharifi-Sanjani, N, Evin, E. (1994). Preparation and characterization of viscosity index improver for naphthenic and paraffinic base oils. *J Sol Chem*. 23:325-338.
7. Dorinson A, Ludema, KC. (1985). Mechanics and chemistry in lubrication. Elsevier, Amsterdam.
8. Jones, MH, Scott, D. (1983). Industrial tribology. Elsevier, Amsterdam.
9. Mortier, RM, Fox, MF, Orszulik, ST. (2010). Chemistry and technology of lubricants, (Third Edn.). Springer, Dordrecht. <https://doi.org/10.1007/978-1-4020-8662-5>.
10. Xiangqiong, Z, Heyang, S, Wenqi, R, Zhongyi, H, Tianhui, R. (2005). Tribological study of trioctylthiotriazine derivative as lubricating oil additive. *Wear*. 258:800-805.
11. Li, W, Jiang, C, Chao, M, Wang, X. (2014). Natural garlic oil as a high-performance, environmentally friendly, extreme pressure additive in lubricating oils. *ACS Sustain Chem Eng*. 2:798-803.
12. Rastogi, RB, Maurya, JL, Jaiswal, V, Tiwari, D. (2012). Lanthanum dithiocarbamates as potential extreme pressure lubrication additives. *Int J Ind Chem* 3:32-41.

13. Ahmed, NS, Nassar, AM. (2009). Lubricating oil additives based on polyalkylpolyamines. *Int J Polymer Mater.* 58:178-190.
14. Habib, OMO, Hassan, HM, Moawad EB, El-Hadidy M. (2010). The evaluation of some heterocycles as antioxidant additives for lubricating oils. *Pet Sci Technol.* 28:1059-1067.
15. Rizvi. SQA (2009). A comprehensive review of lubricant chemistry, technology, selection, and design. ASTM International, West Conshohocken, PA.
16. Stepuro, OS, Rebrov, IY, Borshchevskii, SB, Mikhailova, OL. (1984). Antiwear additives and corrosion inhibitors for lubricating oils. *Chem Technol Fuels Oils.* 20:196-200.
17. Masabumi, M, Hiroyasu, S, Akihito, S, Osamu, K. (2008). Prevention of oxidative degradation of ZnDTP by microcapsulation and verification of its antiwear performance. *Tribol Int.* 41:197-204.
18. Ludema, KC. (1996). Friction, wear, lubrication. A textbook in tribology. CRC Press. pp. 124-134.
19. Nassar, AM (2008). The behaviour of polymers as viscosity index improvers. *Pet Sci Technol.* 26:514-522.
20. Florea, M, Catrinoiu, D, Paul, L, Balliu, S. (1999). The influence of chemical composition on the pour point depressant properties of methacrylate copolymers used as additives for lubricating oils. *Lubr Sci.* 12:31-34.
21. Ahmed, NS, Nassar, AM. (2009). Lubricating oil additives based on polyalkylpolyamines. *Int J Polymer Mater.* 58:178-190.
22. El-Ashry, El-SH, El-Rafey, ME, El-Nagdi, MH, Abou-Elnaga, HH, Bakry, WMA, Boghdady, YM. (2006). Synthesis of benzotriazole derivatives as antioxidants for industrial lubricating oils. *Lubr Sci.* 18:109-118.
23. Page, MA, Sunkara, HB, Wijesekera, KS. Lubrication oil compositions. U.S 20120004152 A1.
24. Gavlin, G, Swire, EA, Jones, Jr. SP. (1953). Pour point depression of lubricating oils. *Ind Eng Chem.* 45:2327-2335.
25. Ming, TC, Ramli, N, Lye, OT, Said, M, Kasim, Z (2005) Strategies for decreasing the pour point and cloud point of palm oil products. *Eur J Lipid Sci Technol.* 107:505-512.

26. Bjorndalen, N, Mustafiz, S, Islam, MR. (2003). Numerical modeling of petroleum fluids under microwave irradiation for improved horizontal well performance. *Int Commun Heat Mass Transfer*. 30:765-774.
27. Rocha, NO, Gonzalez, G, Vaitsman, DS. (1998). Magnetic field effect on paraffin deposition. *Quim NoVa* 12:11-17. <http://dx.doi.org/10.1590/S0100-40421998000100002>.
28. Khidr, TT. (2007). Synthesis and evaluation of copolymers as pour-point depressants. *Pet Sci Technol* 25:671-681.
29. Soldi, RA, Oliveira, ARS, Barbosa, RV, Ceasar-Oliveira, MAF. (2007). Polymethacrylates: Pour point depressants in diesel oil. *Eur Polym. J* 43:3671-3678.
30. Jung, KM, Chun, BH, Park, SH, Lee, CH, Kim, SH. (2011). Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricant oil. *J Appl Polym Sci*. 120:2579-2586.
31. Ghosh, P, Das, M, Upadhyay, M, Das, T, Mandal, A. (2011). Synthesis and evaluation of acrylate polymers in lubricating oil. *J Chem Eng Data* 56:3752-3758.
32. Ghosh, P, Das, T, Nandi, D. (2011). Synthesis, characterization, and viscosity studies of homopolymer of methyl methacrylate and copolymer of methyl methacrylate and styrene. *J Soln Chem*. 40:67-78.
33. Borthakur, A, Chanda, D, Dutta Choudhury, SR, Rao, KV, Subrahmanyam, B. (1996). Alkyl fumarate-vinyl acetate copolymer as flow improver for high waxy Indian crude oils. *Energy Fuels*. 10:844-848.
34. Andre, LCM, Elizabete, FL. (2001). The influence of vinyl acetate content of the poly (ethylene-co-vinyl acetate) (EVA) additive on the viscosity and the pour point of Brazilian crude oil. *Pet Sci Technol*. 19:197-204.
35. Ghosh, P, Hoque, M. (2015). Synthesis and performance evaluation of vinyl acetate-maleic anhydride-based polymeric additives for lube oil. *Pet Sci Technol*. 33:1182-1189.
36. Karmakar, G, Ghosh, P. (2013). Green additives for lubricating oil. *ACS Sustain Chem Eng*. 1:1364-1370.
37. Pedersen, KS. (2003). Influence of wax inhibitors on wax appearance temperature pour point and viscosity of waxy crude oils. *Energy Fuels*. 17:321-328.

38. Zhang, J, Wu, C, Li, W, Wang, Y, Han, Z. (2003). Study on performance mechanism of pour point depressants with differential scanning calorimeter and X-ray diffraction methods. *Fuel* 82:1419-1426.
39. Kuzmić, AE, Radošević, M, Bogdanić G, Sricá V, Vuković, R. (2008). Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives. *Fuel*. 87:2943-2950.
40. Wang, SL, Flamberg, A, Kikabhai, T. (1999). Select the optimum pour point depressant. *Hydrocarbon Process*. 59:59-62.
41. Srivastva, SP, Tandon, RS, Verma, PS, Saxena, AK, Joshi, GC, Pathak, SD. (1992). Crystallization behavior of n-paraffins in Bombay high middle distillate wax/gel. *Fuel*. 71:533-537.
42. Pirro, DM, Wessol, AA. (2001). *Lubrication Fundamentals, (Second Edn.)*. Marcel Dekker Inc. New York. pp 1-68.
43. Onyeji, LI, Aboje, AA. (2011). The effect of additive on the viscosity index of lubricating oil (engine oil). *Int J Eng Sci Tech*. 3:1864-1869.
44. Tanveer, S, Prasad, R (2006) Enhancement of viscosity index of mineral base oils. *Ind J Chem Technol*. 13:398-403.
45. Quinchia, LA, Delgado, MA, Valencia, C, Franco, JM, Gallegos, C. (2010). Viscosity modification of different vegetable oils with EVA copolymer for lubricant applications. *Ind Crops Prod*. 32:607-612.
46. Nassar, AM, Ahmed, NS. (2010). Study the influence of some polymeric additives as viscosity index improvers pour point depressants and dispersants for lube oil. *Pet Sci Technol*. 28:13-26.
47. Van Horne, WL. (1949). Polymethacrylates as viscosity index improvers and pour point depressants. *Ind Eng Chem*. 41:952-959.
48. Rudnick, LR. (2009). *Lubricant additives: chemistry and applications, (2nd Edn.)*. CRC press.
49. Mikeska, LA, Fulton, SC. (1937). Resinous material. U S 2072120 A.
50. Eckert, RJA, Covey, DF. (1986). Development in the field of hydrogenated diene copolymer as viscosity index improvers, 5th International Colloquium. Technische akademie, Esslingen.
51. Selby, TW. (1958). The non-newtonian characteristics of lubricating oils. *ASLE Trans* 1:68-81.

52. Covitch, MJ, Trickett, KJ. (2015). How polymers behave as viscosity index improvers in lubricating oils. *Adv Chem Eng Sci* 5:134-151.
53. Abdel-Azim, A, Nasser, AM, Ahmed, NS, Kamal, RS. (2011). Multifunctional lube oil additives based on octadecene-maleic anhydride copolymer. *Pet Sci Technol.* 29:97-107.
54. Canter, N. (2011). Viscosity index improvers. *Tribol Lubr Technol.* 67:10-22.
55. Callais, P, Schmidt, S, Macy, N. (2004). The effect of controlled polymer architecture on VI and other rheological properties. *SAE Tech Paper.* 2004-01-3047. <https://doi.org/10.4271/2004-01-3047>.
56. Karmakar, G, Ghosh, P, Sharma, K, B.(2017). Chemically modifying vegetable oils to prepare green lubricants. *Lubricants.* 5:44.
57. Minami, Ichiro, (2017), "Molecular science of lube additives". *Appl, Sci,* 7(5):445
58. Ghosh P, Roy D, & Paul S, (2020), "Dodecyl methacrylate –Vinyl acetate copolymer- A multifunctional performance additive for lubricating oil", *IJANS* 9(6):29-36.

PART-1

CHAPTER-1

1. Pirro, DM, Wessol, AA (2001). *Lubrication fundamentals.* New York, Marcel Dekker. 37-43.
2. Mohamed, MM, El, Naga HHA, El, Meneir, MF. (1994). Multi-functional viscosity index improvers. *J Chem Technol Biotechnol.* 60:283-289.
3. Roveda AC, Trindade MAG (2018) Alternative multifunctional additives for biodiesel stabilization: perspectives for more efficiency and more cost-effectiveness. In: Trindade M (Eds.), *Increased biodiesel efficiency.* Green energy and technology, Springer, Cham.
4. Jatti VS, Singh TP, (2015). Copper oxide nanoparticles as friction-reduction and antiwear additives in lubricating oil. *J Mech Sci Technol.* 29:793-798.
5. Cai G, Zhang L, Ma L, Eli W (2015) Synthesis and characterization of polybutylacrylate viscosity index improver with anti-wear function. *Lubr Sci* 27:209-216.

6. Ghosh P, Das M, Upadhyay M, Das T, Mandal A (2011) Synthesis and evaluation of acrylate polymers in lubricating oil. *J Chem Eng Data* 56:3752-3758.
7. Ghosh P, Upadhyay M, Das MK (2014) Studies on the additive performance of liquid crystal blended polyacrylate in lubricating oil. *Liq Cryst* 41:30-35.
8. Li B, Wang X, Liu W, Xue Q (2006) Tribochemistry and antiwear mechanism of organic-inorganic nanoparticles as lubricant additives. *Tribol Lett* 22:79-84.
9. Ahmed NS, Nassar AM, Nasser RM, Abdel Raouf ME, El-Kafrawy AF (2014) Novel terpolymers as pour point depressants and viscosity modifiers for lube oil. *Pet Sci Technol* 32:680-687.
10. Ahmed NS, Nassar AM, Nasser RM, Khattab AF, Abdel-Azim AA (2012) Synthesis and evaluation of some polymers as lubricating oil additives. *J Disper Sci Technol* 33:668-675.
11. Stachowiak G, Batchelor A (2001) *Engineering tribology (2nd Edn.)*. Boston: Butterworth-Heinemann.
12. Bondi, A.A. (1951) *Physical chemistry of lubricating oils*. Reinhold publishing corp., New York.
13. Stambaugh RL (1997) Viscosity index improvers and thickeners. In: Mortier RM, Orszulik ST (Eds.), *Chemistry and technology of lubricants*. Springer, Dordrecht.
14. Nassar AM (2008) The behavior of polymers as viscosity index improvers. *Pet Sci Technol* 26:514-522.
15. Covitch MJ, Trickett KJ (2015) How polymers behave as viscosity index improvers in lubricating oils. *Adv Chem Eng Sci* 5:134-151.
16. Muller HG (1978) Mechanism of action of viscosity index improvers. *Tribol Int* 11:189-192.
17. Lariviere D, Asfour AFA, Hage A, Gao JZ (2000) Viscometric properties of viscosity index improvers in lubricant base oil over a wide temperature range. Part I: Group II base oil. *Lubr Sci* 12:133-143.
18. Sen A, Rubin ID (1990) Molecular structures and solution viscosities of ethylene-propylene copolymers. *Macromolecules* 23:2519-2524.

19. Abdel-azim A, Nasser AM, Ahmed NS, Kamal RS (2011) Multifunctional lube oil additives based on octadecene-maleic anhydride copolymer. *Pet Sci Technol* 29:97-107.
20. Abdel-Azim A, Huglin MB (1983) Selective solvation of polystyrene in tetralin/ cyclohexane mixtures. *Polymer* 24:1308-1312.
21. Eckert RJ A, Covey DF (1988) Developments in the field of hydrogenated diene copolymers as viscosity index improvers. *Lubr Sci* 1:65-80.
22. Chu B, Ying Q, Grosberg AY (1995) Two-stage kinetics of single-chain collapse. Polystyrene in cyclohexane. *Macromolecules* 28:180-189.
23. Tao F, Wang X, Che B, Zhou D, Chen W, Xue G, Zou D, Tie Z (2008) Probing the contraction and association of polystyrene chains in semidilute solution by non-radiative energy transfer. *Macromol Rapid Commun* 29:160-164.
24. Garcia MC, Carbognani L, Urbina A, Orea M (1998) Paraffin deposition in oil production. Oil composition and paraffin inhibitors activity. *Pet Sci Technol* 16:1001-1021.
25. Cristante M, Selves JL, Grassy G, Colin JP (1993) Structure-activity relationship study on paraffin inhibitors for crude oils (INIPAR model II). *Anal Chim Acta* 274:303-316.
26. Coutinho JAP, Cauphin C, Daridon JL (2000) Measurements and modelling of wax formation in diesel fuels. *Fuel* 79:607-616.
27. Huiyang Z, Weibang Z, Zhuomei L (1991) Synthesis of polymers with a long side chain of N-alkyl esters and their effects on pour-point depression of oil. *J Appl Polym Sci* 43:919-924.
28. Ke-Jian L, Min LG (1997) PSM as pour point depressant for diesel. *Pet Sci Technol* 15:707-714.
29. Jung KM, Chun BH, Park SH, Lee CH, Kim SH (2011) Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricant oil. *J Appl Polym Sci* 120:2579-2586.
30. Wu CJ, Zhang JL, Li W, Wu N (2005) Molecular dynamics simulation guiding the improvement of EVA-type pour point depressant. *Fuel* 84:2039-2047.
31. Wuhua C, Zongchang Z, Caoyong Y (2010) The interaction of waxes with pour point depressants. *Fuel* 89:1127-1132.

32. EI-Gamal IM, Al-Sabbagh AM (1996) Polymeric additives for improving the flow properties of waxy distillate fuels and crudes. *Fuel* 75:743-750.
33. Holder GA, Winkler J (1965) Wax crystallization from distillate fuels II: Mechanism of pour depression. *J Inst Pet* 51:235-242.
34. Zhang J, Wu C, Li W, Wang Y, Han Z (2003) Study on performance mechanism of pour point depressants with differential scanning calorimeter and X-ray diffraction methods. *Fuel* 82:1419-1426.
35. Denis J, Durand JP (1991) Modification of wax crystallization in petroleum products. *Oil Gas Sci Technol* 46:637-649.
36. Fremel TV (1993) Mechanism of action of pour-point depressants. *Chem-Tech Fuels Oil* 29:400-403.
37. Huiyang Z, Weibang Z, Zhuomei L (1991) Synthesis of polymers with long side chain of N-alkyl esters and their affects on pour-point depression of oil. *J Appl Polym Sci* 43:919-924.
38. Kumar MNS (1989) Review on polymeric and copolymeric pour point depressants for waxy crude oils and studies on Bombay high crude oil. *Quart J Technol* 15:47-62.
39. Ruehrwein RA (1951) Specificity of pour point depressants in lubricating oils. 3rd World Petroleum Congress. Hague, Netherlands.
40. Gavlin G, Swire EA, Jr. Jones SP (1953) Pour point depression of lubricating oils. *Ind Eng Chem* 45:2327-2335.
41. Borthakur A, Chanda D, Dutta Choudhury SR, Rao KV, Subrahmanyam B (1996) Alkyl fumarate-vinyl acetate copolymer as flow improver for high waxy Indian crude oils. *Energy Fuels* 10:844-848.
42. EI-Gamal IM, Atta AM, Al-Sabbagh AM (1997) Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* 76:1471-1478.
43. Ke-Jian L, Yuchun Z (1998) A study on three kinds of alcohols esterified copolymer of maleic anhydride and olefins as pour-point depressant for diesels. *Pet Sci Technol* 16:971-977.
44. Ke-Jian, L, Yuchun Z (1999) A study on alcohols mixture esterified copolymer of maleic anhydride with mixed olefins, acrylic alkyl ester, and styrene as a pour-point depressant for diesels. *Pet Sci Technol* 17:51-56.

45. Abdel-Azim AAA, Nassar AM, Ahmed NS, Kamal RS (2006) Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. *Pet Sci Technol* 24:887-894.
46. Khidr TT (2007) Synthesis and evaluation of copolymers as pour-point depressants. *Pet Sci Technol* 25:671-681.
47. Farag RK (2008) Poly (cinnamoyloxy ethyl methacrylate-co-octadecyl acrylate) as flow improver for Egyptian waxy crude oils. *Int J Polymer Mater* 57:189-202.
48. El-Ghazawy RA, Farag RK (2010) Synthesis and characterization of novel pour point depressants based on maleic anhydride-alkyl acrylate terpolymers. *J Appl Polym Sci* 115:72-78.
49. Khidr TT (2011) Pour point depressant additives for waxy gas oil. *Pet Sci Technol* 29:19-28.
50. Jung KM, Chun BH, Park SH, Lee CH, Kim SH (2011) Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricating oil. *J Appl Polym Sci* 120:2579-2586.
51. Ghosh P, Das T (2014) Synthesis and characterization of homopolymer of decyl acrylate and its copolymer with styrene and evaluation of their performance as a pour point depressant in lubricating oil. *Pet Sci Technol* 32:1448-1457.
52. Port WS, O'Brien JW, Hansen JE, Swern D (1951) Viscosity index improvers for lubricating oils. *Ind Eng Chem* 43:2105-2107.
53. Yorulmaz Y (1983) Alkylated polymers as lube oil additives. *J Mater Sci* 18:1638-1644.
54. Coutinho FMB, Teixeira SCS (1993) Polymers used as viscosity index improvers: A comparative study. *Polym Test* 12:415-422.
55. Reza PHM, Faraahani EV, Maryam G, Mahmoud G (2005) Synthesis and characterization of olefin copolymers as viscosity modifiers for engine oil. *Iran Polym J* 14:549-557.
56. Nassar AM, Ahmed NS, Kamal RS, Abdel-Azim AAA, El-Nagdy EI (2005) Preparation and evaluation of acrylate polymers as viscosity index improvers for lube oil. *Pet Sci Technol* 23:537-546.

57. Jukic A, Vidovic E, Janovic Z (2007) Alkyl methacrylate and styrene terpolymers as lubricating oil viscosity index improvers. *Chem-Tech Fuels Oils* 43:386-394.
58. Ahmed NS (2008) Lubricants additives from maleate copolymers. *Pet Sci Technol* 26:298-306.
59. Mohammed MF, Mahdi Abd M (2012) Effect of temperature on lubricating oil and poly(methyl methacrylate) additive. *Diyala J Eng Sci* 5:205-220.
60. Ahmed NS, Nassar AM, Nasser RM, Khattab AF, Abdel-Azim AAA (2008) Synthesis and evaluation of some polymeric compounds as pour point depressants and viscosity index improvers for lube oil. *Pet Sci Technol* 26:1390-1402.
61. Castro LV, Vazquez F (2008) Copolymers as flow improvers for Mexican crude oils. *Energy Fuels* 22:4006-4011.
62. Ghosh P, Nandi D, Das T (2013) Preparation, compatibility studies and evaluation of polymer mixture of decyl acrylate and its copolymer with styrene as lubricating oil additives. *Am J Polym Sci* 3:35-45.
63. Ghosh P, Karmakar G (2012) Synthesis and characterization of polymyristyl acrylate as a potential additive for lubricating oil. *Am J Polym Sci* 2:1-6.

PART-1

CHAPTER-2

1. Mortier RM, Fox MF, Orszulik ST, (2010) *Chemistry and Technology of Lubricants*, Springer, Heidelberg, USA, 3rd edn.
2. Czech Z, Kowalczyk A, Kabatc J, Świdarska J, (2013) Thermal Stability of Poly(2-Ethylhexyl acrylates) used as Plasticizers for Medical Application. *Polym Bull*, 70. 1911–1918.
3. Zhang J, Wu C, Li W, Wang Y, Han Z(2003) Study on Performance Mechanism of Pour Point Depressants with Differential Scanning Calorimeter and X-ray Diffraction Methods. *Fuel*, 82 .1419–1426. 34.
4. Fang L, Zhang X, Ma J, Zhang B. (2012) Investigation into a Pour Point Depressant for Shengli Crude Oil. *Ind Eng Chem Res*, 51 11605–11612.
5. Kuzmić AE, Radošević M, Bogdanić G, Srića V, Vuković R, (2008) Studies on the Influence of Long Chain Acrylic Esters Polymers with Polar Monomers as Crude Oil Flow Improver Additives, *Fuel*, 87 .2943–2950.

6. Karmakar G, Ghosh P, (2015) Soybean Oil as a Biocompatible Multifunctional Additive for Lubricating Oil, ACS Sustain Chem Eng, 3 19–25.
7. Abdel Azim A A, Amal M N, Nehal S A, Rasha S K, Nagdy E I, (2005) Preparation and Evaluation of Acrylate Polymers as Viscosity Index improves for Lube Oil, Pet Sci-Tech, 23 .537–546.
8. Strate GV, Struglinski MJ, (1991). Polymers as Lubricating-Oil Viscosity Modifier. In: Schultz DN, Glass JE (eds) Polymers as Rheology Modifiers. ACS Symposium Series.
9. Chanda, M,(2013) Introduction to polymer science and chemistry: a problem solving approach, CRC Press, Boca Raton, 2nd edn.
10. Nassar AM, (2008). The behavior of Polymers as Viscosity Index Improvers. Pet Sci Tech, 26 .514–522.
11. Abdel-Azim A, Nasser AM, Ahmed NS, Kamal RS, (2011) . Multifunctional Lube Oil Additives based on Octadecenemaleic anhydride Copolymer, Pet Sci Tech, 29 .97–107.
12. Abdel-Azim A A A, Abdel-Aziem RM, (2001) . Polymeric Additives for improving the Flow Properties and Viscosity Index of Lubricating Oils, J Polym Res,8.111–118.

PART -2

CHAPTER-1

1. Adhvaryu, A. and Erhan, S. Z. (2002). Epoxidized soybean oil as a potential source of high-temperature lubricants. Industrial Crops and Products 15:247–254.
2. Arrietaa, P. M., Sampera, D. M., Jimenez-Lopeza, Aldasa, M. M. and Lopez, J. (2017). Combined effect of linseed oil and gum rosin as natural additives for PVC. Industrial Crops and Products 99:196–204.
3. Ashraf, M. S., Ahmad, S., Riaz, U., Alam, M., and Sharma, O. H. (2007). Investigation of miscibility of linseed oil epoxy with poly(vinyl alcohol). Journal of Macromolecular Science, Part A: Pure and Applied Chemistry 44:1115–1120.
4. Ashraf, M. S., Ahmad, S., Riaz, U., Alam, M., and Sharma, O. H. (2007). Miscibility behavior of blend of polyesteramides of linseed oil and

- dehydrated castor oil with poly(methacrylic acid). *Journal of Applied Polymer Science* 103:1367–1374.
5. Becker, R. and Knorr, A. (1996). An Evaluation of antioxidants for vegetable oils at elevated temperatures. *Lubrication Science* 8:95–117.
 6. Behbahani, T. J. (2014). Experimental investigation of the polymeric flow improver on waxy oils, *Petroleum & Coal* 56(2):139–142.
 7. Cakmakli, B., Hazer, B., Tekin, O. Z., Kizgut, S., Koksall, M. and Menciloglu, Y. (2004). Synthesis and characterization of polymeric linseed oil grafted methyl methacrylate or styrene. *Macromol. Biosci.* 4:649–655.
 8. Chahande, P. P. (2014). Low foaming ecofriendly detergents based on linseed oil and resin for detergent. 1:202–209.
 9. Chaurasiya, K. S. and Suhane, A. (2017). The prospects of linseed oil based bio lubricant in machine application: A review. *International Journal for Scientific Research & Development* 5:1909–1911.
 10. Fox, J. N. and Stachowiak, W. G. (2007). Vegetable oil–based lubricants–A review of oxidation. *Tribol. Int.* 40:1035–1046.
 11. Gajbhiye, P. G. And Gogte, B. B. (2005) *Chemical Engg World*, 40:92.
 12. Ghosh, P., Pantar, A. V., and Sarma, A. S. (1998). Shear stability of polymers used as viscosity modifier in lubricating oils, *Indian Journal of Chemical Technology* 5:309–314.
 13. Ghosh, P, Saha, D.K.(2019) “Synthesis, characterization, and performance evaluation of long chain methacrylate-octene copolymer for lubricant formulation”, *Journal of Macromolecular Science, Part A*, 56:1050-1059.
 14. Ghosh, P, Hoque, M, Nandi, D (2015) “Homo and Co-polymers of Decyl methacrylateas performance additives for Lube Oil”, *Petroleum Science and Technology*,33(8):920-927.
 15. Ghosh P, Roy D,& Paul S,(2020), “Dodecyl methacrylate –Vinyl acetate copolymer- A multifunctional performance additive for lubricating oil”, *IJANS* 9(6):29-36.
 16. Hui, Y. H. (1995). *Bailey’s industrial oil and fats products, edible oil, and fat Products: General Application*. 5th edn., 1, Wiley, Blackwell, 19–44.
 17. Kharkate, S. K and Gogte, B. B. (2005). *Surface coating Australia* 42:91.
 18. Lambourne, R, (1987). *Paint and surface coatings theory and practice*,ellis horwood limited, New York 440.

19. Markov, A. V., Kamaltdinov, G. V. and Savastenko, A. A. (2018). Petroleum diesel fuel and linseed oil mixtures as engine fuels. *J. Phys.: Conf. Ser.* 944 012077.
20. Nassar, A. M. (2008). The behaviour of polymers as viscosity index improvers, *Petrol. Sci. Technol.* 26:514–522.
21. Phate, B.W. & Gogte, B.B. (2005). *Paint India*, LV:71.
22. Sahin, S. And Ogut, H. (2018). Investigation of the effects of linseed oil biodiesel and diesel fuel blends on engine performance and exhaust emissions. *Internatinal Journal of Automotive Engineering and Technologies* 4: 149–157.
23. Sawant, V.D. (2000). *Paint India*, LV9500:78–80.
24. Sinadinovic-Fiser, S., Jankovic, M. and Petrovic, Z. S. (2001). Kinetics of in Situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. *Journal of the American Oil Chemists' Society* 78:725–731.

PART -2

CHAPTER-2

1. Ghosh P, Hoque M, Roy D (2020) Castor Oil and Acrylate based Copolymer as Green Additive for Lubricating Oil *J Sci Ind Res*,79:537-543.
2. Karmakar G & Ghosh P, (2013). Green additives for lubricating oil, *ACS Sustainable Chem Eng*, 1 .1364–1370.
3. Balamurugan K, Knangasabapathy N & Mayilsamy K, (2010) . Studies on Soyabean oil-based lubricant for diesel engine, *J Sci Ind Res*, 69 .794–797.
4. Kumar G S, Balamurugan A, Vinu S, Radhakrishnan M & Senthilprabhu G, (2012). Tribological and emission studies on two-stroke petrol engine lubricated with sunflower methyl ester, *J Sci Ind Res*, 71 .562–565.
5. Samarth N B & Mahanwar P A, (2015). Modified vegetable oil based additives as a future polymeric material—Review, *Open J Org Polym Mater.* 1–22.
6. Ghosh P, Hoque M & Karmakar G, (2018) . Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant, *Polym Bull*, 75 .501–514.
7. Chinchkar D S, Satpute S T, & Kumbhar N R, (2012) . Castor oil as green lubricant: A Review, *Int J Eng Res Technol*, 1 .1–3.

8. Ghosh P, Das M, Upadhyay M, Das T & Mandal A, (2011). Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil, *J Chem Eng Data*, 56 .3752–3758.
9. Al-Sabagh A M, Sabaa M W, Saad G R, Khidr T T & Khalil T M, (2012) . Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties, *Egypt J Petrol*, 21 .19–30.
10. Ghosh P, Hoque M & Nandi D, (2015) .Homo and copolymers of decyl methacrylate as performance additives for lube oil, *Pet Sci Technol*, 33 .920–927.
11. ASTM D2270-10(2016), Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C, ASTM International, West Conshohocken, PA, 2016, www.astm.org)
12. ASTM D97-09, (2009)Standard Test Method for Pour Point of Petroleum Products, ASTM International, West Conshohocken, PA, www.astm.org
13. Ghosh, Pranab & Hoque, & Karmakar, Gobinda. (2017). Terpolymers based on sunflower oil/alkyl acrylate/styrene as sustainable lubricant additive. *Polymer Bulletin*. 74. 10.1007/s00289-016-1863-4.
14. Thiyagarajan, Prakash & Varuvel, Edwin & Martin, Leenus & Nagalingam, B.. (2018). Effect Of Ternary Blends Of Bio-Ethanol, Diesel And Castor Oil On Performance, Emission And Combustion In A Ci Engine. *Renewable Energy*. 122. 10.1016/j.renene.2018.01.070.

PART -2

CHAPTER-3

1. Betton, CI, (2010). Lubricants and Their Environmental Impact. In: *Chemistry and Technology of Lubricants*, Eds. Mortier RM, Fox MF, Orszulik ST, Springer, The Netherlands, pp. 435-457.
2. Ghosh, P, Paul, S, Roy, D (2020). Greener lubricant formulation: rapeseed oil based eco friendly lube oil additives. *IJPPE* ,vol6,issue 3,pp 29-37.
3. Chandure AS, Umare SS, (2007). Synthesis, Characterization and Biodegradation Study of Low Molecular Weight Polyesters. *Int J Polym Mater* 56: 339–353.

4. El-Gamal, I.M., Atta, A. M., and Al-Sabbagh, A. M. (1997). Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* 76:1471–1478.
5. Ghosh, P., Hoque, M., and Karmakar. G. (2018). Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant. *Polym. Bull.* 75:501-514
6. Ghosh P, Das T, Nandi D, Karmakar G, Mandal A (2010) Synthesis and characterization of biodegradable polymer: Used as a pour point depressant for lubricating oil. *Int J Polym Mater* 59: 1008–1017
7. Karmakar, G., and Ghosh, P. (2013). Green additives for lubricating oil. *ACS Sustainable Chem. Eng.* 1:1364–1370.
8. Karmakar, G., and Ghosh, P. (2015). Soybean oil as a biocompatible multifunctional additive for lubricating oil. *ACS Sustainable Chem. Eng.* 3: 19–25.
9. Ghosh P, Karmakar G (2014) Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int J Ind Chem* 5: 7
10. Liu M, Huang Z, Yang Y (2010) Analysis of biodegradability of three biodegradable mulching films. *J Polym Environ* 18: 148–154.
11. Masjuki, H. H., Maleque, M. A. (1997). Investigation of the anti-wear characteristics of palm oil methyl ester using a four-ball tribometer test. *Wear* 206: 179 –186.
12. Shanta, S. M., Molina, G. J., and Soloiu, V. (2011). Tribological effects of mineral-oil lubricant contamination with biofuels: A pin-on-disk tribometry and wear study. *Adv. Tribol.* doi:10.1155/2011/820795.
13. Sharma, B. K., Adhvaryu, A., and Erhan, S. Z. (2009). Friction and wear behavior of thioether hydroxyl vegetable oil. *Wear* 42:353–358.
14. Tanveer, S., Sharma, U. C., and Prasad, R. (2006). Rheology of multigrade engine oils. *Indian J. Chem. Technol.* 13:180–184.
15. Cracking of a rapeseed vegetable oil under realistic FCC conditions, (2007), *Applied Catalysis B Environmental* 72(1-2):44-61).
16. ASTM D2270-10(2016), Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C, ASTM International, West Conshohocken, PA, (www.astm.org)

17. ASTM D97-09, (2009) Standard Test Method for Pour Point of Petroleum Products, ASTM International, West Conshohocken, PA, www.astm.org.
18. Ichiro Minami,(2017) Review Molecular Science of Lubricant Additives. MDPI, Appl.Sci2017,7,445
19. ASTM D4172-20, (2020) Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method), ASTM International, West Conshohocken, PA, www.astm.org.
20. Ghosh, Pranab & Hoque, & Karmakar, Gobinda. (2017). Terpolymers based on sunflower oil/alkyl acrylate/styrene as sustainable lubricant additive. Polymer Bulletin. 74. 10.1007/s00289-016-1863-4.

PART-2

CHAPTER-4

1. Ghosh P, Hoque M, Roy D (2020) Castor Oil and Acrylate based Copolymer as Green Additive for Lubricating Oil J Sci Ind Res,79:537-543
2. P. Ghosh, D. Nandi, and T. Das, (2010) J. Chem. Pharm. Res, 2(4), 122.
3. G. Karmakar and P. Ghosh, (2013), ACS Sustainable Chem. Eng., 1, 1364.
4. S. Rani, M. L. Joy, and K. P. Nair, (2015), Indian Crop. Prod., 65, 328.
5. K. Rajnarayana, M. C. Prabhakar and D. R. Krishna, (2001), Indian J. Physiol. Pharmacol., 45(4), 442.
6. M. B. Reena and B. R. Lokesh, (2007), J. Agric. Food Chem., 55(25), 10461.
7. K. Wuttikul and P. Boonme, (2016), Drug Deliv. Transl. Res., 6(3), 254.
8. S. Jerbic, J. P. Vukovic and A. Jukic, (2012)Ind. Eng. Chem. Res , 51, 1914.
9. P. Ghosh, T. Das, D. Nandi, G. Karmakar,(2010), and A. Mandal, Int. J. Polym, 59, 1008.
10. H. P. Soni and D. P. Kiranbala Bharambe, (2008), Energy Fuels, 22, 3930
11. Kangabam, Rajiv & Medhabati, Kangabam & Nongalleima, Khumukcham & Devi, Huidrom. (2014). The Potential of Dark Purple Scented Rice-From Staple Food to Nutraceutical. Current World Environment. 9. 867-876. 10.12944/CWE.9.3.38.
12. Ghosh P, Hoque M & Nandi D, (2015) Homo and copolymers of decyl methacrylate as performance additives for lube oil, Pet Sci Technol, 33 .920–927.

13. ASTM D2270-10(2016), Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C, ASTM International, West Conshohocken, PA, 2016, www.astm.org)
14. ASTM D97-09, (2009), Standard Test Method for Pour Point of Petroleum Products, ASTM International, West Conshohocken, PA, www.astm.org
15. Ghosh, Pranab & Hoque, & Karmakar, Gobinda. (2017). Terpolymers based on sunflower oil/alkyl acrylate/styrene as sustainable lubricant additive. *Polymer Bulletin*. 74. 10.1007/s00289-016-1863-4.

PART- 3

CHAPTER-1

1. Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, (2011), A. Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil. *J. Chem. Eng. Data* 56, 3752–3758.
2. Johnson, D.W.; Hils, J.E. (2013), Phosphate Esters, Thiophosphate Esters, and Metal Thiophosphates as Lubricant Additives. *Lubricants* .1, 132–148.
3. Karmakar, Gobinda; Ghosh, Pranab; Sharma, Brajendra K.(2017). "Chemically Modifying Vegetable Oils to Prepare Green Lubricants" *Lubricants* 5, no. 4: 44.
4. Ripple, D.E.; Fuhrmann, J.F.(1989), Performance comparisons of synthetic and mineral oil crankcase lubricant base stocks. *Lubr. Sci.* 6, 209–232.
5. Salimon, J.; Salih, N.; Yousif, E. (2010) Biolubricants: Raw materials, chemical modifications, and environmental benefits. *Eur. J. Lipid Sci. Technol*, 112, 519–530.
6. Salimon, J.; Abdullah, B.M.; Yusop, R.M.; Salih, N. (2014) Synthesis, reactivity and application studies for different biolubricants. *Chem. Cent. J*, 8, 16. [PubMed]
7. Li, W.; Jiang, C.; Chao, M.; Wang, X. (2014) Natural Garlic Oil as a High-Performance, Environmentally Friendly, Extreme Pressure Additive in Lubricating Oils. *ACS Sustain. Chem. Eng*, 2, 798–803. [CrossRef]
8. Ossia, C.V.; Han, H.G.; Kong, H. (2008), Additive properties of saturated very long chain fatty acids in castor and jojoba oils. *J. Mech. Sci. Technol.* 22, 1527–1536.

9. Erhan, S.Z.; Adhvaryu, A.; Sharma, B.K. (2017) Poly(hydroxy thioether) Vegetable Oil Derivatives Useful as Lubricant Additives. U.S. Patent 7,279,448 B2, 9 October 2007. *Lubricants*, 5, 44–52.
10. Erhan, S.Z.; Doll, K.M.; Sharma, B.K. Method of Making Fatty Acid Ester Derivatives. U.S. Patent 8,173,825 B2, 8 May 2012.
11. Erhan, S.Z.; Doll, K.M.; Sharma, B.K. Method of Making Fatty Acid Ester Derivatives. U.S. Patent 20,080,154,053 A1, 26 June 2008.
12. Doll, K.M.; Sharma, B.K.; Suarez, P.A. Process to Prepare a Phosphorous Containing Vegetable Oil Based Lubricant Additive. U.S. Patent 8,822,712 B1, 2 September 2014.
13. Biswas, A.; Doll, K.M.; Cheng, H.N.; Sharma, B.K. Process for Preparation of Nitrogen-Containing Vegetable Oil-Based Lubricant Additive. U.S. Patent 8,841,470 B1, 23 September 2014.
14. Heise, G.L.; Sharma, B.K.; Erhan, S.Z. Boron Containing Vegetable Oil Based Antiwear/Antifricition Additive and Their Preparation. U.S. Patent 9,156,859 B2, 13 October 2015.
15. Erickson, F.L.; Anderson, R.E.; Landis, P.S. Vegetable Oil Derivatives as Lubricant Additives. U.S. Patent 5,282,989, 1 February 1994.
16. Erickson, F.L.; Anderson, R.E.; Landis, P.S. Meadowfoam Oil, and Meadowfoam Oil Derivatives as Lubricant Additives. U.S. Patent 4,925,581, 15 May 1990.
17. Karmakar, G.; Ghosh, P. (2015) Soybean Oil as a Biocompatible Multifunctional Additive for Lubricating Oil. *ACS Sustain. Chem. Eng.* 3, 19–25.
18. Ghosh, P.; Karmakar, G. (2014) Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int. J. Ind. Chem.*, 5. [CrossRef]
19. Karmakar, G.; Ghosh, P. (2013) Green Additives for Lubricating Oil. *ACS Sustain. Chem. Eng.* 1, 1364–1370.
20. Ghosh, P.; Hoque, M.; Karmakar, G. (2017) Castor oil as a potential multifunctional additive in the formulation of eco-friendly lubricant. *Polym. Bull.*
21. Meijer, M.; Masjuki, H.H.; Kalam, M.A.; Shahabuddin, M.; Hazrat, M.A.; Liaquat, A.M. (2012), Palm oil methyl ester and its emulsions effect on

- lubricant performance and engine components wear. *Energy Procedia*,14, 1748–1753.
22. Liu, Z.; Sharma, B.K.; Erhan, S.Z.; Biswas, A.; Wang, R.; Schuman, T.P. (2015) Oxidation and low-temperature stability of polymerized soybean oil-based lubricants. *Thermochim. Acta*, 601, 9–16.
23. Adhvaryu, A.; Erhan, S.Z.; Liu, Z.S.; Perez, J.M. 2000, Oxidation kinetic studies of unmodified and genetically modified vegetable oils using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochim. Acta* 364, 87–97.
24. Fox, N.J.; Stachowiak, G.W. 2007, Vegetable oil-based lubricants—A review of oxidation. *Tribol. Int.* 40, 1035–1046. [CrossRef]
25. Sujit, E.; Dearn, K.D. 2011, Enhancing the lubricity of an environmentally friendly Swedish diesel fuel MK1. *Wear* 271, 1772–1777. [CrossRef]
26. Maleque, M.A.; Masjuki, H.H.; Haseeb, A.S.M.A. 2000, Effect of mechanical factors on tribological properties of palm oil methyl ester blended lubricant. *Wear* 239, 117–125.
27. Masjuki, H.H.; Maleque, M.A. 1996, The effect of palm oil diesel fuel contaminated lubricant on sliding wear of cast irons against mild steel. *Wear* 198, 293–299.
28. Masjuki, H.H.; Maleque, M.A. 1997, Investigation of the anti-wear characteristics of palm oil methyl ester using a four-ball tribometer test. *Wear* 206, 179–186.
29. Malavolti, M.; Brandi, A.; Salvini, A.; Giomi, D. 2015, Transesterification of castor oil with trimethylchlorosilane: Simultaneous formation of fatty acid alkyl esters and α -monochlorohydrin. *RSC Adv.* 5, 77341–77347.
30. Madankar, C.S.; Pradhan, S.; Naik, S.N. Parametric study of reactive extraction of castor seed (*Ricinus communis* L.) for methyl ester production and its potential use as bio lubricant. *Ind. Crops Prod.* 2013, 43, 283–290.
31. Shi, Y.J.; Minami, I.; Grahm, M.; Bjorling, M.; Larsson, R. 2014, Boundary and elastohydrodynamic lubrication studies of glycerol aqueous solutions as green lubricants. *Tribol. Int.* 69, 39–45.
32. Cai, S.; Wang, L. 2011, Epoxidation of Unsaturated Fatty Acid Methyl Esters in the Presence of SO₃H-functional Brønsted Acidic Ionic Liquid as Catalyst. *Chin. J. Chem. Eng.* 19, 57–63.

33. Abdullah, B.M.; Salimon, J. 2010, Epoxidation of Vegetable Oils and Fatty Acids: Catalysts, Methods, and Advantages. *J. Appl. Sci.* 10, 1545–1553.
34. Saithai, P.; Lecomte, J.; Dubreucq, E.; Tanrattanakul, V. 2013 Effects of different epoxidation methods of soybean oil on the characteristics of acrylated epoxidized soybean oil-co-poly(methyl methacrylate) copolymer. *eXPRESS Polym. Lett.*, 7, 910–924.
35. Schafer, V.; Kohler, R.; Pauli, A.; Fessenbecker, A. (1994), Corrosion Protection Additives Based on Epoxides. U.S. Patent 5,368,776 A, 29 .
36. Rowland, R.G.; Migdal, C.A. Epoxidized Ester Additives for Reducing Lead Corrosion in Lubricants and Fuels. Patent EP 1805284A1, 11 July 2007.
37. Sharma, B.K.; Adhvaryu, A.; Erhan, S.Z. 2006, Synthesis of Hydroxy Thioether Derivatives of Vegetable Oil. *J. Agric. Food Chem.* 54, 9866–9872. [PubMed]
38. Sharma, B.K.; Adhvaryu, A.; Erhan, S.Z. 2009 Friction and wear behavior of thioether hydroxy vegetable oil. *Tribol. Int.*, 42, 353–358.
39. Varshney, H.; Ahmad, A.; Rauf, A. (2013) Ring Opening of Epoxy Fatty Esters by Nucleophile to Form the Derivatives of Substituted β -Amino Alcohol. *Food Nutr. Sci.*, 4, 21–24.
40. Ashraf, M. S., Ahmad, S., Riaz, U., Alam, M., and Sharma, O. H. (2007). Investigation of miscibility of linseed oil epoxy with poly(vinyl alcohol). *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 44:1115–1120.
41. Ashraf, M. S., Ahmad, S., Riaz, U., Alam, M., and Sharma, O. H. (2007). Miscibility behavior of blend of polyesteramides of linseed oil and dehydrated castor oil with poly(methacrylic acid). *Journal of Applied Polymer Science* 103:1367–1374.
42. Arrietaa, P. M., Sampera, D. M., Jimenez-Lopez, Aldasa, M. M. and Lopez, J. (2017). Combined effect of linseed oil and gum rosin as natural additives for PVC. *Industrial Crops and Products* 99:196–204.
43. Gichter, R. and Miiller, H. (1987). *Plastics additives handbook*, Hanser, Munich, 2nd edn. 282.
44. Sahin, S. And Ogut, H. (2018). Investigation of the effects of linseed oil biodiesel and diesel fuel blends on engine performance and exhaust

- emissions. *International Journal of Automotive Engineering and Technologies* 4: 149–157.
45. Markov, A. V., Kamaltdinov, G. V. and Savastenko, A. A. (2018). Petroleum diesel fuel and linseed oil mixtures as engine fuels. *J. Phys.: Conf. Ser.* 944 012077.
46. Chahande, P. P. (2014). Low foaming ecofriendly detergents based on linseed oil and resin for detergent. 1:202–209.
47. Cakmakli, B., Hazer, B., Tekin, O. Z., Kizgut, S., Koksall, M. and Menciloglu, Y. (2004). Synthesis and characterization of polymeric linseed oil grafted methyl methacrylate or styrene. *Macromol. Biosci.* 4:649–655.

PART-3

CHAPTER-2

1. Cakmakli, B.; Hazer, B.; Tekin, O. Z.; Kizgut, S.; Koksall, M.; Menciloglu, Y. (2004), Synthesis and Characterization of Polymeric Linseed Oil Grafted Methyl Methacrylate or Styrene. *Macromol. Biosci.* 4, 649–655. DOI: 10.1002/mabi.200300117.
2. Fox, J. N.; Stachowiak, W. G. (2006). Vegetable Oil-Based Lubricants—A Review of Oxidation. *Tribol. Int.*, 40, 1035–1046. DOI: 10.1016/j.triboint.10.001.
3. Phate, B. W.; Gogte, B. B. (2005), Eco-Friendly Liquid Detergents Based on Malenised Vegetables Oils. *Paint India, LV* . 3, 71–76.
4. Gajbhiye, P. G.; Gogte, B. B. (2005), Eco-Friendly Malenized Oils for Liquid Detergent. *Chem. Eng. World.* 40, 92.
5. Lambourne, R. (1987), *Paint and Surface Coatings Theory and Practice*; Ellis Horwood Limited: New York. Vol. 440.
6. Kharkate, S. K.; Gogte, B. B. Testing of Eco-friendly Detergent Powder and Liquid Detergent. *Surf. Wait. Aust.* 2005, 42, 91.
7. Chahande, P. P. Low Foaming Eco-Friendly Detergents Based on Linseed Oil and Resin for Detergent. *Int. Jr. Res. Biosci. Agri. Tech.* 2014, 2, 202–209.
8. Becker, R.; Knorr, A. (1996), An Evaluation of Antioxidants for Vegetable Oils at Elevated Temperatures. *Lubr. Sci.* 8, 95–117. DOI: 10.1002/lr.3010080202.

9. Sinadinovic, F. S.; Jankovic, M.; Petrovic, Z. S. (2001) Kinetics of In Situ Epoxidation of Soybean Oil in Bulk Catalyzed by Ion Exchange Resin. *J. Am. Oil Chem. Soc.* 78, 725–731. DOI: 10.1007/s11746-001-0333-9.
10. Adhvaryu, A.; Erhan, S. Z. (2002). Epoxidized Soybean Oil as a Potential Source of High-Temperature Lubricants. *Ind. Crop. Prod.* 15, 247–254. DOI: 10.1016/S0926-6690(01)00120-0.
11. Hui, Y. H. *Bailey's Industrial Oil and Fats Products, Edible Oil and Fat Products: General Application*, 5th ed.; Wiley: Blackwell, Vol. 1; pp. 19–44.
12. Howell, A. B.; Betso, R. S.; Meltzer, A. J.; Smith, B. P.; Debney, F. M. (1995). Thermal Degradation of Epoxidized Soybean Oil in the Presence of Chlorine-Containing Polymers. *Thermochim. Acta* 1990, 166, 207–218. DOI: 10.1016/0040-6031(90)80182-X.
13. Chaurasiya, K. S.; Suhane, A. (2017) The Prospects of Linseed Oil Based Bio Lubricant in Machine Application: A Review. *Int. J. Sci. Res. Dev.* 5, 1909–1911. PAPER ID: IJSRDV5I21612.
14. Sharma, O. H.; Alam, M.; Riaz, U.; Ahmad, S.; Ashraf, M. S. (2007), Miscibility Behavior of Blend of Polyesteramides of Linseed Oil and Dehydrated Castor Oil with Poly(methacrylic acid). *J. Appl. Polym. Sci.* 103, 1367–1374. DOI: 10.1080/00914030600904611.
15. Arrieta, M. P.; Samper, M. D.; Jimenez-Lopez, M.; Aldas, M.; Lopez, J. (2017), Combined Effect of Linseed Oil and Gum Rosin as Natural Additives for PVC. *Ind. Crop. Prod.* 99, 196–204. DOI: 10.1016/j.indcrop.2017.02.009.
16. Gichter, R.; Miiller, H. (1987) *Plastics Additives Handbook*, 2nd ed.; Hanser: Munich; p. 282.
17. Sahin, S.; Ogut, H. (2018), Investigation of the Effects of Linseed Oil Biodiesel and Diesel Fuel Blends on Engine Performance and Exhaust Emissions. *Int. J. Auto. Eng. Technol.* 4, 149–157. DOI: 10.18245/ijaet.476775.
18. Markov, A. V.; Kamaltdinov, G. V.; Savastenko, A. A. (2018), Petroleum Diesel Fuel and Linseed Oil Mixtures as Engine Fuels. *J. Phys: Conf. Ser.* 944, 012077. DOI: 10.1088/1742-6596/944/1/012077.

19. Chahande, P. P. (2014), Low Foaming Ecofriendly Detergents Based on Linseed Oil and Resin for Detergent. *Int. J. Res. Bios. Agric. Technol.* 1, 202–209. 6 D. ROY ET AL.
20. Ashraf, M. S.; Ahmad, S.; Riaz, U.; Alam, M.; Sharma, O. H. (2007) Investigation of Miscibility of Linseed Oil Epoxy with Poly(vinyl alcohol). *J. Macromol. Sci. A*, 44, 1115–1120. DOI: 10.1080/10601320701524260.
21. Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. (2011) Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil. *J. Chem. Eng. Data*, 56, 3752–3758. DOI: 10.1021/je2003435.
22. Ghosh, P.; Pantar, A. V.; Sarma, A. S. Shear Stability of Polymers Used as Viscosity Modifier in Lubricating Oils. *Indian J. Chem. Technol*, 5, 309–314.
23. Behbahani, T. J. (1998), Experimental Investigation of the Polymeric Flow Improver on Waxy Oils. *Pet. Coal* 2014, 56, 139–142.
24. Nassar, A. M.(2008) The Behaviour of Polymers as Viscosity Index Improvers. *Pet. Sci. Technol*, 26, 514–522. DOI: 10.1080/10916460600806101.

PART-3

CHAPTER-3

1. Phate, B. W.; Gogte, B. B. (2005) *Paint India*, LV, 3, 71–76.
2. Gajbhiye, P. G.; Gogte, B. B. (2005), *Chemical Engg World*. 40, 92.
3. Lambourne, R.V,(1987), *Paint and surface coatings theory and practice*, ellis horwood limited, New York. 440.
4. Kharkate, S. K; Gogte, B. B.(2005) *Surface waiting Australia*. 42, 91.
5. Sawant, V. D. *Paint India*, LV. 2000, 9500, 78–80.
6. Becker, R.; Knorr, A.(1996), An Evaluation of antioxidants for vegetable oils at elevated temperatures. *Lubr. Sci.* 8, 95–117. DOI: [10.1002/lis.3010080202](https://doi.org/10.1002/lis.3010080202).
7. Myshkin, K. N.; Grigoriev, Ya. A.; Kavaliova, N. I.(2017), Influence of Composition of Plant Oils on Their Tribological Properties. *Tribol. Indus.* 39, 207–210. DOI 10.24874/ti.2017.39.02.07.
8. Asadauskas, S.; Perez, J. M.; Duda,(1997), *J. L. Lubr. Eng.*, 53, 35. Lubrication

9. Castor oil based multifunctional greener additives for lubricating oil. *Curr. Environ. Eng.* 2017, 4, 197–206. DOI: 10.2174/2212717804666170609121546.
10. Hazer, D. B.; Kilicay, E.; Hazer, B. (2012) Poly (3-hydroxyalkanoate)s: Diversification and Biomedical Applications. A State of the Art Review. *Mater. Sci. Eng. C* 32, 637–647. DOI: 10.1016/j.msec.2012.01.021.
11. Hwang, S. H.; Erhan, Z. S. (2006), Synthetic lubricant basestocks from epoxidized soybean oil and Guerbet alcohols. *Indus. Crops Prod.* 23, 311–317. DOI: [10.1016/j.indcrop.2005.09.002](https://doi.org/10.1016/j.indcrop.2005.09.002).
12. Howell, A. B.; Betso, R. S.; Meltzer, A. J.; Smith, B. P.; Debney, F. M. (1990) Thermal degradation of epoxidized soybean oil in the presence of chlorine-containing polymers. *Thermochimica Acta*. 166, 207–218. DOI: [10.1016/0040-6031\(90\)80182-X](https://doi.org/10.1016/0040-6031(90)80182-X).
13. Roy, D.; Paul, S.; Yeasmin, S.; Ghosh, P. (2020), Synthesis of linseed oil based biodegradable homo and copolymers: Role as multifunctional greener additives in lube oil. *J. Macromol. Sci. A* 58, 1–6. DOI: 10.1080/10601325.2020.1812400.
14. Ghosh, P.; Karmakar, G. (2014), Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int. J. Ind. Chem.* 5, 7. DOI: 10.1007/s40090-014-0007-7.
15. Ghosh, P.; Das, T.; Nandi, D.; Karmakar, G.; Mandal, A. (2010) Synthesis and characterization of biodegradable polymer–used as a pour point depressant for lubricating oil. *Int. J. Polym. Mater.* 59, 1008–1017. DOI: 10.1080/00914037.2010.504156.
16. Ghosh, P.; Das, T.; Karmakar, G.; Das, M. (2011), Evaluation of acrylate–sunflower oil copolymer as viscosity index improvers for lube oils. *J. Chem. Pharm. Res.* 3, 547–556.
17. ASTM D2270-10(2016), Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C, ASTM International, West Conshohocken, PA, 2016, www.astm.org)
18. (ASTM D97-09, (2009), Standard Test Method for Pour Point of Petroleum Products, ASTM International, West Conshohocken, PA, www.astm.org)

19. ASTM D4172-20,(2020), Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method), ASTM International, West Conshohocken, PA, www.astm.org.)
20. Karmakar, Gobinda; Ghosh, Pranab; Sharma, Brajendra K.(2017). "Chemically Modifying Vegetable Oils to Prepare Green Lubricants" *Lubricants* 5, no. 4: 44.

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Synthesis of linseed oil based biodegradable homo and copolymers: role as multifunctional greener additives in lube oil

Dibakar Roy , Sujan Paul , Sultana Yeasmin & Pranab Ghosh

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Synthesis of linseed oil based biodegradable homo and copolymers: role as multifunctional greener additives in lube oil

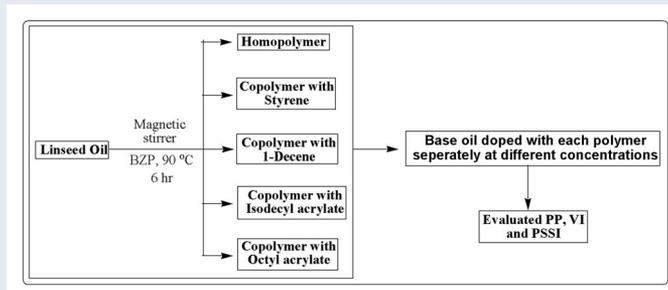
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ABSTRACT

Homopolymer of linseed oil and its four copolymers with styrene, 1-decene, isodecyl acrylate and octyl acrylate, respectively, have been synthesized in this present context. The prepared polymers are characterized by NMR and FTIR spectroscopy. The molecular weights have been measured by gel permeation chromatography. Their effectiveness as pour point depressant (PPD), viscosity index improver (VII) and their shear stability in terms of permanent shear stability index have been evaluated in lube oil. The copolymers acted as better PPDs than the homopolymer whereas the homopolymer of linseed oil excelled as VII. Further it was observed that all the prepared polymers were stable enough under severe mechanical shear.

GRAPHICAL ABSTRACT



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Biodegradability; polymeric additive; linseed oil; pour point; viscosity index; shear stability

1. Introduction

Automobile industry is flourishing day by day with the advent of new technologies and ever exploring ideas. Utilization of polymeric additives, their modification to obtain maximum effect with minimum dosage or application of new potential lubricating additives has remained the key areas of research in this industry. But over the decade environmental issue has become the main concern which has pushed such industries toward a challenging area to adopt comparatively greener initiatives. Hence, replacement or minimizing the application of traditional additives through the introduction of biodegradable ones has gained much pace during the years. To maintain the ecosystem, nonconventional sources of energy are getting huge attention and hence the use of biolubricant is very attractive to reduce fossil fuels exploitation and increase its sustainability. A large research body has been engaged to increase attention toward the possible utilization of renewable resources as raw materials for the production of both chemicals and polymeric materials. Today, natural oils and fats are considered to be

the most important class of renewable sources for the production of biodegradable polymers.^[1] Vegetable oils and modified vegetable oils have become attractive sustainable alternatives to petroleum-based materials for industrial applications due to their biodegradability, low toxicity, absence of volatile organic chemicals, easy availability and relatively low price.^[2]

Vegetable oils have gained huge attention in lubricant industry mainly because of their molecular composition and structure. They mainly consist of triacylglycerides (95–97%) and also monoacylglycerides and diacylglycerides. They consist both of unsaturated fatty acids (oleic, linoleic, linolenic etc.) and saturated fatty acids (tetradecanoic, palmitic, stearic and etc.). Vegetable oils have been used in various industrial products like wall finishes^[3]; paints^[4]; electrodeposition paints^[5]; water thinnable primers^[6] and printing inks.^[7] Vegetable oils also have a very high viscosity index (VI) above 200 compared to 90 or 100 for most petroleum oils. Another important property of vegetable oils is their high flash point. Most importantly, vegetable oils are

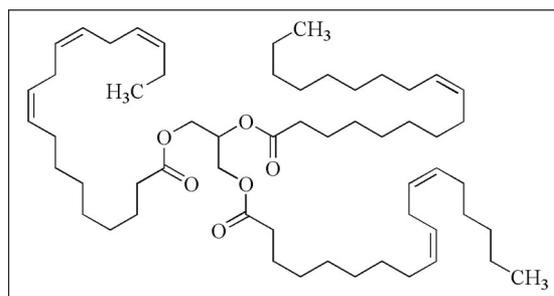


Figure 1. Triglyceride found in linseed oil.

biodegradable, less toxic, renewable and they reduce dependency on imported petroleum oils, all of which account for a greener approach. But vegetable oils in their natural form suffer from insufficient oxidative stability which implies that the untreated oil will get oxidized quite easily and becomes thick and polymerized to a plastic like consistency mainly due to presence of unsaturation.^[8] But this barrier can be overcome by some modifications such as transesterification, epoxidation and selective hydrogenation.^[9,10]

The largest sources of vegetable oils are annual plants such as soybean, corn, linseed, cottonseed or peanuts and some oil-bearing perennials such as the palm, olive or coconut.^[11] Among them, soybean oil has conquered one of the most prominent positions for the production of biodegradable lubricant additives mainly because of its availability and composition. Now linseed oil (LSO) which is a colorless to yellowish oil obtained from the dried, ripened seeds of the flax plant (*Linum usitatissimum*), contains similar triglyceride as that of soybean oil but with much larger amount of esterified linolenic acid. Therefore, the level of unsaturation for the triglyceride in LSO is somewhat greater than that for soybean oil.^[12] The representative triglyceride found in LSO is shown in Figure 1. The production of LSO seeds in India are high enough to make it acceptable from economic point of view. Most importantly LSO is prone to get polymerized by itself and hence can be used as an impregnator either in natural form or blended with combinations of other oils, resins or solvents, as a pigment binder in oil paints, as a plasticizer and hardener in putty, in the manufacture of linoleum and in wood finishing.^[13]

LSO has found various applications in polymer industry as well as in petroleum industry. In a study, LSO polyesteramide in combination with dehydrated castor oil was blended with polymethyl methacrylate to obtain a bioartificial polymer with improved mechanical and physical properties.^[14] In another study, epoxidized LSO was used to prepare a natural viscosity increasing agent from polyvinyl chloride and triethylene glycol ester of gum rosin.^[15] Epoxidized LSO is often used as lubricants or plasticizer and secondary stabilizer for halogen-containing polymers.^[16] In a study, LSO biodiesel was produced by transesterification process and its effect was investigated on engine performance and exhaust emissions which showed that linseed biodiesel and fuel blends acted quite similar to the standard diesel fuel, but in case of the former exhaust emissions was generally improved.^[17] Markov et al. have established in their study that the physical and chemical properties of a mixture of 90% diesel fuel and 10% LSO are quite similar to petroleum

Table 1. Base oil (BO) properties.

Physical property	BO
Density (gcm^{-3} at 40 °C)	0.95
Viscosity at 40 °C in cSt	24.211
Viscosity at 100 °C in cSt	4.47
Viscosity index (VI)	89.87
Pour point (PP in °C)	-6
Cloud point (°C)	-8

BO collected from IOCL, Dhakuria, West Bengal.

diesel fuels characteristics and also application of this mixture as motor fuel minimized the emission of exhaust toxic components such as nitric oxides, carbon monoxide and unburned hydrocarbons.^[18] Chahande has successfully prepared a novel polymeric surfactant which is biodegradable and eco-friendly as well, based on LSO, rosin and sorbitol.^[19] Cakmakli et al. have prepared a series of biodegradable synthetic branched graft copolymers of LSO with methyl methacrylate and reported their potential application in tissue engineering due to their cell adhesion and development.^[11] Ashraf et al. have prepared a blend of poly vinyl alcohol and epoxydized LSO to use it as a plasticizer and corrosion resistant coating film of good toughness, flexibility and low water absorption.^[20]

Due to such versatile application of LSO along with its fruitful properties such as ready to polymerize tendency, high unsaturation, easy availability and some more, have provoked us to explore it toward the preparation of eco-friendly polymeric additives. Here, we have prepared homopolymer of LSO and its copolymer with styrene (ST), 1-decene (1-D), isodecyl acrylate (IDA) and octyl acrylate (OA) separately and investigated their potential application as multifunctional lube oil additive.

2. Experimental section

2.1. Materials

LSO was bought from the local market; its density was 0.93 g/mL at 25 °C, saponification value was 189.6 and iodine no. was 188.0. Toluene (GC 99.5%) was collected from Merck (Mumbai, India). ST (99%, Sigma-Aldrich), 1-D (95%, Acros organics), octyl alcohol, isodecyl alcohol and acrylic acid (99%, LOBA Cheme Pvt. Ltd., India) were used as received. Hexane (99.5%, S. d Fine Cheme Ltd., India) and Methanol (98%, Thomas Baker Pvt. Ltd., India) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd., India) and benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd., India) were purified by recrystallization before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd., India) was used as received. The mineral base oil (BO) was collected from IOCL, Dhakuria, West Bengal, India and its properties are listed in Table 1.

2.2. Preparation of esters and their purification

The ester (IDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of isododecyl alcohol in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization

Table 2. Molecular weight and polydispersity index data.

Additive	M_n	M_w	PDI
P ₁	42456	51560	1.21
P ₂	32539	38396	1.18
P ₃	22286	31869	1.43
P ₄	28350	35438	1.25
P ₅	25059	33580	1.34

P₁ is homopolymer of linseed oil; P₂, P₃, P₄ and P₅ are copolymers of linseed oil with styrene, 1-D, IDA and OA, respectively.

inhibitor and toluene as a solvent. The process was carried out in a resin kettle which was heated gradually from room temperature to 130 °C using a well-controlled thermostat under a slow stream of deoxygenated nitrogen. The extent of esterification was monitored by the amount of liberated water.^[21] Another ester (OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol following the same procedure.

The prepared esters were refluxed for 3 h with suitable amount of charcoal and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separatory funnel several times to ensure complete removal of untreated acid. The esters were then washed repeatedly with distilled water to remove any traces of sodium hydroxide. The purified esters were then left overnight on calcium chloride which was then removed by distillation under reduced pressure. Then, the esters were ready to be used in the polymerization process.

2.3. Synthesis of the polymers and their purification

Preparation of homopolymer of LSO (P₁) and its copolymers with ST (5% w/w): P₂, 1-D (5% w/w): P₃, IDA (5% w/w): P₄ and OA (5% w/w): P₅, respectively, were carried out in a four necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of deoxygenated nitrogen at 90 °C for 6 h by free radical polymerization in the presence of toluene as solvent and BZP as initiator (0.5% w/w, with respect to the total monomer). At the end of the reaction time, the reaction mixture was poured into methanol to terminate the polymerization process and precipitate the polymer. The polymers were further purified by repeated precipitation of their hexane solution by methanol followed by drying under vacuum at 40 °C.

3. Measurements

3.1. Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by gel permeation chromatography method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 35 °C temperature at a flow rate of 1 mL/min. The values are given in Table 2.

3.2. Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within

Table 3. Pour point (°C) data with respect to the different concentrations of the additives (% w/w) in base oil (BO).

Additive	1%	2%	3%	4%	5%	6%
P ₁	-12.5	-11.9	-11.5	-10.8	-9.7	-9.8
P ₂	-14.0	-14.4	-15.0	-15.3	-15.7	-15.7
P ₃	-15.0	-14.4	-13.6	-14.5	-15.1	-15.0
P ₄	-17.0	-17.1	-17.3	-17.4	-17.4	-17.1
P ₅	-14.0	-14.7	-15.2	-15.8	-16.0	-15.9

the wave number range of 400 to 4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe, CDCl₃ solvent and tetramethylsilane as reference material.

3.3. Storage stability test

The storage stability of the prepared polymers in the lube oil was determined using ASTM D7603-13 method. It is the standard method of storage stability and compatibility in Automotive Gear Oils.

3.4. Performance evaluation as pour point depressants (PPDs) in lube oil

The effect of additive concentration on pour point of the BO was tested by using different doping concentrations ranging from 1% to 6% (w/w) for each of the prepared polymer. According to the ASTM D 97-09 method, the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India) given in Table 3.

3.5. Performance evaluation as viscosity index improver (VII)

Viscometric properties were determined for the BO doped with different concentration (1% to 6% w/w) of the prepared homo and copolymers of LSO using an Ubbelohde OB viscometer. The time of flow of the solution was manually determined by using a chronometer. In a single measurement, the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2%. Precautions regarding prevention of evaporation of solvent were taken in all the cases. The obtained results are tabulated in terms of kinematic viscosity (KV) data at 40 °C, 100 °C and VI data in Tables 4 and 5.

3.6. Shear stability measurement

When subjected to mechanical shear or stress, a polymer may lose its viscosity in terms of two different ways such as temporary viscosity loss (TVL) and permanent viscosity loss (PVL).^[22] The latter occurs due to mechanical degradation of polymer molecules and is often expressed in terms of permanent shear stability index (PSSI) using the equations,

Table 4. Kinematic viscosity (KV) data with respect to the different concentrations of the additives in base oil (BO).

Conc ⁿ	KV ₁					KV ₂				
	P ₁	P ₂	P ₃	P ₄	P ₅	P ₁	P ₂	P ₃	P ₄	P ₅
1	158.14	165.24	173.17	169.43	181.30	34.32	35.55	34.89	35.18	35.51
2	160.34	167.30	173.91	172.54	182.37	34.93	35.87	35.51	36.67	36.21
3	164.23	169.41	174.95	174.90	184.59	35.72	36.41	35.87	37.15	36.48
4	169.54	171.21	178.13	176.56	186.13	36.79	36.91	36.43	37.54	36.90
5	172.74	172.16	180.84	180.15	187.50	37.89	37.19	36.97	38.34	37.34
6	173.11	175.00	181.13	182.00	188.15	38.91	37.82	37.53	38.93	37.78

Concⁿ represents concentration in % w/w; KV₁ and KV₂ represent kinematic viscosity at 40 °C and 100 °C, respectively.

Table 5. Viscosity index (VI) data with respect to the different concentrations of the additives (% w/w) in base oil (BO).

Additive	1%	2%	3%	4%	5%	6%
P ₁	262	264	264	265	268	274
P ₂	262	262	263	264	264	265
P ₃	249	252	253	253	254	257
P ₄	255	261	261	262	263	264
P ₅	244	247	247	248	249	251

Table 6. Kinematic viscosity data after shear (KV_s) with respect to the different concentrations of the additives (% w/w) in base oil (BO).

Additive	1%	2%	3%	4%	5%	6%
P ₁	33.21	33.58	34.13	35.03	35.69	36.31
P ₂	34.42	34.39	34.52	34.64	34.71	34.96
P ₃	33.98	34.29	34.39	34.71	35.02	35.39
P ₄	34.35	35.70	36.06	36.29	36.95	37.38
P ₅	34.52	35.07	35.19	35.49	35.77	36.09

Table 7. PVL and PSSI data with respect to the different concentrations (Concⁿ) of the additives (% w/w) in base oil (BO).

Conc ⁿ	PVL					PSSI				
	P ₁	P ₂	P ₃	P ₄	P ₅	P ₁	P ₂	P ₃	P ₄	P ₅
1	3.23	3.18	2.61	2.36	2.79	3.72	3.63	2.99	2.70	3.19
2	3.86	4.13	3.43	2.64	3.14	4.43	4.71	3.93	3.01	3.59
3	4.45	5.19	4.13	2.93	3.54	5.09	5.92	4.71	3.33	4.03
4	4.78	6.15	4.72	3.33	3.82	5.44	6.70	5.38	3.78	4.35
5	5.81	6.67	5.27	3.62	4.20	6.58	7.58	6.00	4.10	4.78
6	6.68	7.56	5.70	3.98	4.47	7.55	8.57	6.47	4.50	5.07

$$\begin{aligned} \text{PVL (\%)} &= [(V_i - V_s)/V_i] \times 100 \\ \text{PSSI (\%)} &= [(V_i - V_s)/(V_i - V_o)] \times 100 \end{aligned}$$

where, V refers to KV at 100 °C. $V_o =$ KV of the oil before addition of polymer $V_i =$ KV of the oil after addition of polymer $V_s =$ KV of the oil doped with polymer after shearing.

The PVL and PSSI values are measured here preparing 1–6% solutions of the prepared homo and copolymers of LSO in the BO under consideration as per ASTM D-3945 method. The values are given in Tables 6 and 7.

4. Results and discussion

4.1. Molecular weight analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity index data (PDI) of the prepared polymers are given in Table 2. The obtained data clearly accounts for successful polymerization in each case. Among all the

polymers, the homopolymer of LSO (P₁) exhibited highest molecular weight. The polydispersity index in each polymer is near about one which implies that the prepared polymers are less polydisperse.

4.2. Spectroscopic analysis

All the absorptions at ν 1733, 1740, 1742, 1744 and 1743 cm^{-1} for the homopolymer of LSO, P₁ and its copolymers P₂, P₃, P₄ and P₅, respectively, showed the presence of ester carbonyl group. Peaks ranging from ν 1452 to 1169 cm^{-1} were due to CO stretching vibration and the peaks from ν 2846 to 2932 cm^{-1} were the stretching vibration of the paraffinic C–H bonds of $-\text{CH}_3$ and $-\text{CH}_2-$ groups. Peaks at ν 723 cm^{-1} and ν 700 cm^{-1} were attributed to the C–H bonds of the phenyl group of ST which was observed only in case of P₂.

The ¹H NMR of homo and copolymer of LSO showed broad peaks in the range of 3.012 to 4.99 ppm due to $-\text{OCH}_2-$ groups. The peaks appeared in the range of 2.318 to 2.983 represent the $-\text{OH}$ groups of LSO. The peaks ranging from 0.51 to 1.30 ppm and 1.41 to 2.41 ppm indicate methyl and methylene protons, respectively. The peaks appeared in the range of 7.12 to 7.33 ppm indicate protons of benzene ring of ST moiety (for P₂ only).

The proton decoupled ¹³C NMR showed peaks at 164 to 177 ppm for ester carbons. The peaks appeared in the range of 52 to 69 ppm represent the carbons of $-\text{OCH}_2-$ groups. The peaks of methyl and methylene carbons appeared in the range of 14 to 41 ppm. The carbons of benzene ring showed peaks in the range of 125 to 133 ppm (for the polymer of P₂ only).

4.3. Storage stability test analysis

Performance of a polymeric additive especially as PPD or VII depends largely on its solubility in the lube oil used. It is seen that at higher temperature the solubility of the polymers increases while at lower temperature solubility decreases. The molecular weight also plays a part here. Higher the molecular weight of the polymer lower is the solubility. Again with increasing concentration of the additive in the BO especially above 4% the solubility diminishes which is sharply reflected in the PP and VI data.

4.4. Performance evaluation as PPD

Based on the pour point data (Table 3), it is obvious that all the prepared polymers of LSO are good PPD for the BO under consideration. Comparatively the copolymers showed better efficiency than the homopolymer. Among these all, copolymer of LSO and IDA has been proved to be the best PPD. Presence of polar acrylate group in association with long alkyl chain of the ester group is supposed to play the crucial role here which inhibits the formation of 3-D matrix of paraffin wax at lower temperature.^[23] In almost all the cases, the optimum results were obtained at 4 or 5%

concentrations but above this the effect was diminished may be due to lower solubility.

4.5. Performance evaluation as VII

Viscosity may be regarded as the most important and deciding parameter for a lubricant. Lesser change in viscosity with respect to temperature results in high VI value which is quite an essential requirement for a good lubricant so that even at higher temperature it does not lose its viscous characteristic at ease. All the prepared polymers of LSO have shown a promising result in this area (Tables 4 and 5).

The KV of the petroleum BO has increased dramatically when doped with these polymers. These polymers have drastically improved the VI of the BO above 200 which recommends these polymers as quite useful lubricant additive at higher range of temperatures. In general, it may be summarized that all the prepared polymers of LSO are impressive VIIs for the used BO at least. The homopolymer (P₁) has outplayed the copolymer here which is quite an inspiring result. With increasing concentration of the added polymers, the VI increases very slowly. Increase in the total volume of the polymer micelles in the BO solutions may attribute to the slow but steady increase in VI at higher concentrations.^[24]

4.6. Shear stability index analysis

It is evident from table that viscosity change after shear is minute in all the cases (Table 6). Hence, it is obvious that in presence of the additives the BO under mechanical shear experienced molecular degradation at a marginal basis and thus sustains its viscometric properties for a long range.

PVL and PSSI data (Table 7) unanimously account for the prepared polymers to be treated as lubricant additives even at higher shearing condition. The PVL and PSSI values increase steadily with increase in concentration of the additives in BO.

5. Conclusion

LSO-based biodegradable additives have been investigated here, which have proved to be good PPDs and VIIs. They exhibited enough stability against mechanical shear as well. The copolymers were better PPDs than the homopolymer of LSO. But as VII the homopolymer predominated over the copolymers. In presence of these additives in minute concentration, the lube oil could retain its viscosity and hence its lubricant property quite effectively even under mechanical shear, keeping in view the environmental issue, the results are quite inspiring. Apart from being biodegradable and eco-friendly, the LSO-based additives may be considered to be potential candidates to replace the traditional harmful organic chemical based polymeric additives depending on the evaluated parameters at least.

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References

- [1] Cakmakli, B.; Hazer, B.; Tekin, O. Z.; Kizgut, S.; Koksall, M.; Menciloglu, Y. Synthesis and Characterization of Polymeric Linseed Oil Grafted Methyl Methacrylate or Styrene. *Macromol. Biosci.* **2004**, *4*, 649–655. DOI: [10.1002/mabi.200300117](https://doi.org/10.1002/mabi.200300117).
- [2] Fox, J. N.; Stachowiak, W. G. Vegetable Oil-Based Lubricants—A Review of Oxidation. *Tribol. Int.* **2007**, *40*, 1035–1046. DOI: [10.1016/j.triboint.2006.10.001](https://doi.org/10.1016/j.triboint.2006.10.001).
- [3] Phate, B. W.; Gogte, B. B. Eco-Friendly Liquid Detergents Based on Malenised Vegetables Oils. *Paint India, LV* **2005**, *3*, 71–76.
- [4] Gajbhiye, P. G.; Gogte, B. B. Eco-Friendly Malenised Oils for Liquid Detergent. *Chem. Eng. World* **2005**, *40*, 92.
- [5] Lambourne, R. *Paint and Surface Coatings Theory and Practice*; Ellis Horwood Limited: New York, **1987**; Vol. 440.
- [6] Kharkate, S. K.; Gogte, B. B. Testing of Ecofriendly Detergent Powder and Liquid Detergent. *Surf. Wait. Aust.* **2005**, *42*, 91.
- [7] Chahande, P. P. Low Foaming Eco-Friendly Detergents Based on Linseed Oil and Resin for Detergent. *Int. Jr. Res. Biosci. Agri. Tech.* **2014**, *2*, 202–209.
- [8] Becker, R.; Knorr, A. An Evaluation of Antioxidants for Vegetable Oils at Elevated Temperatures. *Lubr. Sci.* **1996**, *8*, 95–117. DOI: [10.1002/lis.3010080202](https://doi.org/10.1002/lis.3010080202).
- [9] Sinadinovic, F. S.; Jankovic, M.; Petrovic, Z. S. Kinetics of In Situ Epoxidation of Soybean Oil in Bulk Catalyzed by Ion Exchange Resin. *J. Am. Oil Chem. Soc.* **2001**, *78*, 725–731. DOI: [10.1007/s11746-001-0333-9](https://doi.org/10.1007/s11746-001-0333-9).
- [10] Adhvaryu, A.; Erhan, S. Z. Epoxidized Soybean Oil as a Potential Source of High-Temperature Lubricants. *Ind. Crop. Prod.* **2002**, *15*, 247–254. DOI: [10.1016/S0926-6690\(01\)00120-0](https://doi.org/10.1016/S0926-6690(01)00120-0).
- [11] Hui, Y. H. *Bailey's Industrial Oil and Fats Products, Edible Oil and Fat Products: General Application*, 5th ed.; Wiley: Blackwell, **1995**; Vol. 1; pp. 19–44.
- [12] Howell, A. B.; Betso, R. S.; Meltzer, A. J.; Smith, B. P.; Debney, F. M. Thermal Degradation of Epoxidized Soybean Oil in the Presence of Chlorine-Containing Polymers. *Thermochim. Acta* **1990**, *166*, 207–218. DOI: [10.1016/0040-6031\(90\)80182-X](https://doi.org/10.1016/0040-6031(90)80182-X).
- [13] Chaurasiya, K. S.; Suhane, A. The Prospects of Linseed Oil Based Bio Lubricant in Machine Application: A Review. *Int. J. Sci. Res. Dev.* **2017**, *5*, 1909–1911. PAPER ID: IJSRDV5I21612.
- [14] Sharma, O. H.; Alam, M.; Riaz, U.; Ahmad, S.; Ashraf, M. S. Miscibility Behavior of Blend of Polyesteramides of Linseed Oil and Dehydrated Castor Oil with Poly(methacrylic acid). *J. Appl. Polym. Sci.* **2007**, *103*, 1367–1374. DOI: [10.1080/00914030600904611](https://doi.org/10.1080/00914030600904611).
- [15] Arrieta, M. P.; Samper, M. D.; Jiménez-López, M.; Aldas, M.; López, J. Combined Effect of Linseed Oil and Gum Rosin as Natural Additives for PVC. *Ind. Crop. Prod.* **2017**, *99*, 196–204. DOI: [10.1016/j.indcrop.2017.02.009](https://doi.org/10.1016/j.indcrop.2017.02.009).
- [16] Gichter, R.; Müller, H. *Plastics Additives Handbook*, 2nd ed.; Hanser: Munich, **1987**; p. 282.
- [17] Sahin, S.; Ogut, H. Investigation of the Effects of Linseed Oil Biodiesel and Diesel Fuel Blends on Engine Performance and Exhaust Emissions. *Int. J. Auto. Eng. Technol.* **2018**, *4*, 149–157. DOI: [10.18245/ijaet.476775](https://doi.org/10.18245/ijaet.476775).
- [18] Markov, A. V.; Kamaltdinov, G. V.; Savastenko, A. A. Petroleum Diesel Fuel and Linseed Oil Mixtures as Engine Fuels. *J. Phys: Conf. Ser.* **2018**, *944*, 012077. DOI: [10.1088/1742-6596/944/1/012077](https://doi.org/10.1088/1742-6596/944/1/012077).
- [19] Chahande, P. P. Low Foaming Ecofriendly Detergents Based on Linseed Oil and Resin for Detergent. *Int. J. Res. Bios. Agric. Technol.* **2014**, *1*, 202–209.

- [20] Ashraf, M. S.; Ahmad, S.; Riaz, U.; Alam, M.; Sharma, O. H. Investigation of Miscibility of Linseed Oil Epoxy with Poly(vinyl alcohol). *J. Macromol. Sci. A* **2007**, *44*, 1115–1120. DOI: [10.1080/10601320701524260](https://doi.org/10.1080/10601320701524260).
- [21] Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil. *J. Chem. Eng. Data* **2011**, *56*, 3752–3758. DOI: [10.1021/je2003435](https://doi.org/10.1021/je2003435).
- [22] Ghosh, P.; Pantar, A. V.; Sarma, A. S. Shear Stability of Polymers Used as Viscosity Modifier in Lubricating Oils. *Indian J. Chem. Technol.* **1998**, *5*, 309–314.
- [23] Behbahani, T. J. Experimental Investigation of the Polymeric Flow Improver on Waxy Oils. *Pet. Coal* **2014**, *56*, 139–142.
- [24] Nassar, A. M. The Behaviour of Polymers as Viscosity Index Improvers. *Pet. Sci. Technol.* **2008**, *26*, 514–522. DOI: [10.1080/10916460600806101](https://doi.org/10.1080/10916460600806101).



Castor Oil and Acrylate based Copolymer as Green Additive for Lubricating Oil

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In this work, the authors synthesized three different acrylates by esterification reaction of acrylic acid with three different long chain alcohols (octan -1-ol, decan -1-ol and dodecan -1-ol). Homopolymer of castor oil (CO) and three copolymers of castor oil with acrylates were prepared by free radical polymerization method in the presence of azobisisobutyronitrile (AIBN) as initiator. FT-IR and NMR spectral technique were used to characterize the synthesized polymers. The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by gel permeation chromatography (GPC) method. Thermo gravimetric analysis (TGA) method was used to study the thermal behaviour of the prepared polymers at high temperature. Performances of the polymers as additives in lubricating oil were carefully assessed in terms of viscosity index and pour point. The experimental results showed that the prepared copolymers are better additives than homopolymer. Disc diffusion method was applied to carry out the biodegradability test of all the prepared polymers.

Key words: Esterification, Homopolymer, Viscosity index, Biodegradability

Introduction

The lube oil additives synthesized from acrylate, maleic anhydride, vinyl acetate etc exhibit better performance but they are not environmentally benign. It is due to their inability to biodegradation. The application of bio-based products for the synthesis of lube oil additives has solved this problem. The additives synthesized from vegetable oils have potential advantages compared to the synthetic additives owing to their less toxic and biodegradable properties.¹ They have high viscosity index (VI)², low pour point, excellent antiwear property³ and low volatility.⁴ So, the application of additives derived from vegetable oils for base oil to formulate green lubricant composition has found greater attraction recently.

Castor oil is obtained from castor seeds which is available in nature. It comprises 85–95% triacylglycerol of ricinoleic acid which is a C-18 fatty acid having a double bond at C-9 and a hydroxyl group at C-12. Due to trifunctional nature of castor oil, it can be used as a monomer for the preparation of lube oil polymeric additives as well as base stock also.^{5,6}

The present work comprises preparation of homopolymer of castor oil and different copolymers

with octyl acrylate, decyl acrylate and dodecyl acrylate to get better performing and thermally more stable green lubricant additives. Performance of the polymers was evaluated as viscosity index improver (VII) and pour point depressant (PPD) additives in mineral base oil according to respective standard ASTM method.

Materials and Methods

Experimental Section

Preparation of esters

Octyl acrylate (OA), decyl acrylate (DA) and dodecyl acrylate (DDA) were prepared by reacting acrylic acid with octan -1-ol, decan -1-ol and dodecan -1-ol respectively in the molar ratio of 1.1:1 in the presence of conc. H_2SO_4 as a catalyst, 0.25% (w/w) hydroquinone with respect to the total reactants as polymerization inhibitor and toluene as solvent by using Dean Stark apparatus. The details of esterification reaction and the purification were carried out by the procedure as reported in the earlier publication.⁷

Synthesis of the polymers

The copolymers were synthesized by free radical polymerization method taking the monomers of castor oil (95%, w/w) and acrylate (5%, w/w) in presence of AIBN as initiator. The polymerization reaction was

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completed in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the passing of nitrogen. The mixture of castor oil and acrylate was heated to 80°C without any solvent. Initiator AIBN (0.5% w/w, with respect to the total monomer) was then added and continuously heated for 5 hour keeping the temperature constant at 80°C. After the completion of reaction, the product was poured into methanol with continuous stirring, filtered off and dried. The homopolymer of castor oil was also prepared in the similar procedure. The prepared homopolymer and three copolymers with OA, DA and DDA are designated as P-1, P-2, P-3 and P-4 respectively.

Spectroscopic measurements

Bruker Avance 300 MHz FT-NMR spectrometer was used to record the NMR spectra and CDCl_3 was used as solvent. IR spectra were documented on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} .

Molecular weight determination

The average molecular weight was recorded by GPC method (Water 2414) in HPLC grade THF at 35°C at a flow rate of 1 mL/min.

Thermo gravimetric analysis (TGA)

TGA data was recorded on Shimadzu TGA-50 system, at a heating rate of 10 °C/min.

Performance Evaluation

Evaluation of viscosity index

Viscosity index (VI) is an important parameter to determine the change of viscosity of the lubricant composition with increasing temperature. Higher the value of VI, smaller is the change of viscosity at high temperature. It was calculated according to ASTM D 2270-10. The kinematic viscosities of the lubricant composition were determined at 40°C and 100°C which are required to calculate the VI.

Evaluation of Pour point

Pour point values of the lubricant composition were measured according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). A good pour point depressant additive lowers the pour point of the lubricant composition to a larger scale.

Biodegradability test (Disc diffusion method)

The biodegradability test was carried out for the prepared polymers against *Alterneria alternata* fungal. Culture media strain was made by mixing a suitable amount of potato extract, dextrose and agar powder. All the experiments were completed in petri dishes and were kept in incubator at 37°C for 30 days after addition of about 2 g of the polymer sample. The fungal growth was confirmed by a change of yellow to blackish colour. After 30 days, the fungal media was dissolved in chloroform and the polymer samples were recovered, purified and dried. The dried samples were weighed.

Results and Discussion

Spectroscopic analysis

The homopolymer of castor oil showed IR absorption band for the ester carbonyl group at 1735.1 cm^{-1} . The peaks at 2854.4 cm^{-1} and 2922.2 cm^{-1} are the stretching vibration of $\text{CH}_3\text{-CH}_2\text{-}$ group. A broad peak at 3442.9 cm^{-1} is due to -OH group present in castor oil. The IR spectra of three copolymers (P-2 to P-4) are almost similar. The absorption band at 1732.08 cm^{-1} is due to ester carbonyl group.

In the ^1H NMR spectra of homopolymer, the peaks in the range of 4.12–4.323 ppm indicate the protons of -COOCH_2 group of castor oil and the peaks in the range of 3.60–3.72 ppm indicate protons of -OH group of castor oil. In case of copolymer, the peaks in the range of 1.616–2.318 ppm indicate the protons of -COCH- group of alkyl acrylate. Peaks at 3.607–3.656 ppm indicate the protons of -OCH_2 of acrylate moiety. The peaks in the range of 3.988–4.156 ppm indicate the protons of -COOCH_2 group of castor oil. No peaks in the range of 5–6 ppm indicate that both homo and copolymerization was carried out successfully.

In the ^{13}C NMR spectra of homopolymer, the peaks in the range of 172.95–177.41 ppm indicate the carbons of ester carbonyl group. The carbons of -OOCH_2 group appear in the range 62.10–68.86 ppm. In case of copolymer, the peak at 58.11 ppm indicates the carbons of -OCH_2 groups of acrylate moiety. The carbons of -OOCH_2 group of castor oil appear at 62.78–64.87 ppm. The peaks ranging from 166.31–174.63 ppm confirm the presence of carbons of ester carbonyl groups. There is no any peak in the range of 120–150 ppm and it indicates that both homo and copolymerization was completed successfully.

Molecular weight data analysis

The experimental data of number average molecular weight (M_n), weight average molecular weight (M_w) of the polymers (P-1 to P-4) are shown in Table 1. From the data, it is been observed that among the four polymers, P-1 and P-4 have the lowest and highest molecular weight respectively. Moreover, it is also observed that with increasing the alkyl chain length of the acrylate moiety in the copolymers, the molecular weight increases. Therefore, length of alkyl group in acrylate moiety has an important role during copolymerization.

Analysis of TGA data

From the experimental TGA values of the four polymers, it was observed that polymer P-1 is thermally less stable than the prepared copolymers. This indicates that when acrylate moiety is introduced in the backbone of castor oil, the thermal stability increases. Two major decompositions have been observed at 150°C and 300°C with 25% and 80% weight loss respectively in case of P-1. The thermal stability of copolymers P-2, P-3 and P-4 are almost identical where two major decompositions were observed at 185°C and 358°C with 18% and 78% weight loss respectively.

Analysis of viscosity index values

VI of lubricant composition was calculated at different concentration levels ranging from 1% to 5% (w/w). The experimental values of VI are listed

Table 1 — Molecular weight of the prepared polymers

Polymer Code	Average molecular weight (before biodegradation)			Average molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P-1	7928	10022	1.26	4814	5465	1.14
P-2	8948	17515	1.96	7624	13503	1.77
P-3	10972	18048	1.64	9256	14592	1.58
P-4	16246	24228	1.49	15337	20016	1.31

M_n = Number average molecular weight; M_w = Weight average molecular weight;

PDI = Polydispersity index

Table 2 — Viscosity index (VI) values of lubricants

Polymer Code	VI of lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	85.2	90	94.5	102	112	116
P-2	85.2	98	104	116	122	134
P-3	85.2	100	108	116	128	138
P-4	85.2	100	112	123	135	145

in Table 2. As the temperature increases, the viscosity of lube oil decreases but expansion of polymer molecules take place from tight coil due to increased lube oil - polymer interaction. As a result, the size of micelle increases and this increased in micelle size prevents the reduction of the viscosity of the lubricant composition. It is observed that a higher polymer concentration showed a higher viscosity index compared to a lower one since the total volume of polymer micelle in lubricant increases and hence improves the VI property.¹ It is observed that VI increases by incorporation of acrylate moiety in the backbone of homopolymer of castor oil. This may be due to higher molecular weight and higher crosslink density of the copolymers. The copolymer P-4 has highest VI value than the other polymers, P-3, P-2 and P-1. It may be due to higher average molecular weight compared to others.

Analysis of Pour point values

The pour points of the lubricant composition at different concentration levels ranging from 1%–5% (w/w) are tabulated in Table 3 which indicates that the prepared lubricants have lower PP than lube oil and hence the prepared polymers can be used as PPD additive. From the experimental data, it is observed that the efficiency as PPD increases up to certain limit (3% concentration). The reason for this may be, at this concentration the additive interacts with the paraffinic wax of lube oil effectively and decreases the shape of crystals of the paraffinic wax.⁸ Among the prepared four polymers, P-2 showed best performance as PPD. The higher PDI value may be the reason for better performance.⁹

Analysis of biodegradability test results

The fungal *Alternaria alternata* was used to carry out the biodegradability test. It was found that homopolymer (weight loss 58%) is more biodegradable than the copolymers (weight loss 42%).

Table 3 — Pour point values of lubricants

Polymer Code	Pour point (0°C) lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	-6	-9	-12	-14	-15	-15
P-2	-6	-10	-15	-21	-21	-21
P-3	-6	-10	-13	-18	-18	-18
P-4	-6	-10	-13	-17	-17	-17

After biodegradation, the molecular weight of the recovered polymers was also determined by GPC method and the results were compared with the respective polymers before biodegradation and listed in Table 1.

Conclusions

From the above study, it is found that the homopolymer and copolymer of castor oil are effective additives as viscosity index improver and pour point depressant for lubricating oil. Copolymers are more effective than homopolymer. Thermal stability and average molecular weight of copolymers increase with increasing the alkyl chain length of acrylate moiety. Due to biodegradability character, the additives are environmentally benign also. Therefore, this study is definitely a potential approach to formulate a green additive for lubricating oil.

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References

- 1 Karmakar G & Ghosh P, Green additives for lubricating oil, *ACS Sustainable Chem Eng*, **1** (2013) 1364–1370.
- 2 Balamurugan K, Knangasabapathy N & Mayilsamy K, Studies on Soyabean oil based lubricant for diesel engine, *J Sci Ind Res*, **69** (2010) 794–797.
- 3 Kumar G S, Balamurugan A, Vinu S, Radhakrishnan M & Senthilprabhu G, Tribological and emission studies on two stroke petrol engine lubricated with sunflower methyl ester, *J Sci Ind Res*, **71** (2012) 562–565.
- 4 Samarth N B & Mahanwar P A, Modified vegetable oil based additives as a future polymeric material—Review, *Open J Org Polym Mater*, **5** (2015) 1–22.
- 5 Ghosh P, Hoque M & Karmakar G, Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant, *Polym Bull*, **75** (2018) 501–514.
- 6 Chinchkar D S, Satpute S T, & Kumbhar N R, Castor oil as green lubricant: A Review, *Int J Eng Res Technol*, **1** (2012) 1–3.
- 7 Ghosh P, Das M, Upadhyay M, Das T & Mandal A, Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil, *J Chem Eng Data*, **56** (2011) 3752–3758.
- 8 Al-Sabagh A M, Sabaa M W, Saad G R, Khidr T T & Khalil T M, Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties, *Egypt J Petrol*, **21** (2012) 19–30.
- 9 Ghosh P, Hoque M & Nandi D, Homo and copolymers of decyl methacrylate as performance additives for lube oil, *Pet Sci Technol*, **33** (2015) 920–927.



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Greener additives for lube oil: Synthesis and evaluation of rice bran oil based copolymers as potential lube oil additives

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During the last few years, the lubricant industry has given special attention towards the application of vegetable oil based additives for lube oil due to their biocompatibility and enhanced additive performances compared to conventional additives. In this article, the author reported the preparation of homopolymer of rice bran oil (RBO) and copolymers with decylacrylate and alpha pinene at different percentage ratios in the presence of azobisisobutyronitrile (AIBN) as initiator. Characterization of the polymers was recorded by spectral technique (FT-IR and NMR spectroscopy). Gel permeation chromatography method (GPC) was used to determine the average molecular weight of the prepared polymers. Thermo gravimetric analysis (TGA) method was used to study the thermal stability of the prepared polymers at high temperature. Standard ASTM methods was used to investigate the performance of all the prepared polymers in two types of base oil as viscosity index improver (VII) and pour point depressant (PPD). Biodegradability of all the polymers was tested by disc diffusion method and soil burial method.

Keywords: Homopolymer, copolymer, viscosity index, pour point, biodegradability.

Introduction

Lubricating oil additives are the substances which when added to the oil, they can improve the properties already present or add some new properties¹. The most important properties of lubricants are viscosity index improver (VII) pour point depressant (PPD), antiwear, extreme pressure, antioxidant, dispersant etc. Lube oil additives synthesized from vegetable oils are more environmentally benign due to their biodegradable property and low-toxicity². Moreover, they exhibit high viscosity index (VI), low pour point and good antiwear property. Therefore, more focus has been laid on the research of lube oil additives from vegetable oils.

Rice bran oil contains high percentage of unsaturated triglycerides and can be used as monomer in the free radical polymerization³.

There are many research papers based on rice bran oil in the field of food⁴, pharmaceutical⁵, cosmetics⁶, industries etc. However, reports regarding the application of acrylate

and alpha pinene copolymers of rice bran oil as multifunctional additive for lubricant are very scanty.

In the present work, we have prepared the homopolymer of rice bran oil and different copolymers with decyl acrylate and alpha pinene to achieve potential greener lubricant additives. The performance of the additives in two types of base oil were evaluated as viscosity index improver (VII) and pour point depressant (PPD) according to respective standard ASTM methods.

Experimental

Synthesis of the polymers: The homo polymer of RBO was synthesized by free radical polymerization method taking the monomers of RBO in presence of AIBN initiator. The polymerization was carried out in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. The monomer was heated to 90°C in presence of toluene as solvent.

Initiator AIBN (0.5% w/w, with respect to the total monomer) was then added and continuously heated for 5 h keeping the temperature constant at 90°C. After the completion of reaction, the product was poured into methanol with continuous stirring, filtered off and dried. The three copolymers of RBO with decyl acrylate (DA) and another three copolymers of RBO with alpha pinene at different percentage ratio were also prepared in the similar procedure.

Spectroscopic measurements: Bruker Avance 300 MHz FT-NMR spectrometer was used to record the NMR spectra by using CDCl₃ as solvent. 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 to 4000 cm⁻¹.

Molecular weight determination: The average molecular weight was recorded by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at 35°C at a flow rate of 1 mL/min.

Thermo gravimetric analysis (TGA): TGA data was recorded on Shimadzu TGA-50 system, at a heating rate of 10°C/min.

Performance evaluation

Evaluation of viscosity index: Viscosity index (VI) is an important parameter which determines the change of viscosity of the lubricant at high temperature. Higher value of VI indicates the small change in viscosity at high temperature. It was calculated according to ASTM D 2270-10. The kinematic viscosities of the lubricant composition were determined at 40°C and 100°C which are required for the calculation of VI.

Evaluation of pour point: Pour point values of the lubricant composition were determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). A good pour point depressant additive decreases the pour point of the lubricant composition to a larger extent.

Biodegradability test: Biodegradability test was carried out by two methods – (i) Disc diffusion (DD) method and (ii) Soil burial test (SBT) method.

Disc diffusion method: The biodegradability test was car-

ried out for the prepared polymers against *Calletotricheme camellia* (CC), *Fussarium equisetiae* (FE), *Alternaria alternata* (AA), *Colletrichum gleosproides* (CG) and *Curvularia eragrostidies* (CE) pathogens. A suitable amount of potato extract, dextrose and agar powder were mixed to prepare culture media strain. All the experiments were completed in petridishes and were kept incubator at 37°C for 90 days after addition of about 1 g of the polymer sample. The fungal growth was confirmed by a change of yellow to blackish colour. After 90 days, the polymer samples were recovered from the fungal media by chloroform, purified and dried. The dried samples were weighed.

SBT method: The SBT method was carried out as per ISO 846:1997 standard method. A thin film of polymer sample was prepared by taking 1.5 g of each of the samples separately and then buried in soil. Then the soils with the samples were incubated in a Bacteriological Incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) at 30°C with relative humidity of 60% for 90 days and thus subjected to the action of microorganisms present in the soil. After 90 days, the polymer samples were recovered by chloroform and weighed.

Results and discussion

Spectroscopic analysis: The homopolymer of RBO (P-0) showed IR absorption band for the ester carbonyl group at 1732.5 cm⁻¹. The peaks at 2852.4 cm⁻¹ and 2924.2 cm⁻¹ are the stretching vibration of CH₃-CH₂- group. In the ¹H NMR spectra of homopolymer, the peaks in the range of 4.02–4.22 ppm indicate the protons of -COOCH₂ group. In the ¹³C NMR spectra of homopolymer, the peaks in the range of 170.95–176.41 ppm indicate the carbons of ester carbonyl group. The carbons of -OCH₂ group appear in the range 64.10–68.86 ppm. The IR spectra of three copolymers (P-1 to P-3) are almost similar. The absorption band at 1734.08 cm⁻¹ is due to ester carbonyl group. In the ¹H NMR spectra, peaks at 3.607–3.656 ppm indicate the protons of -OCH₂ of decyl acrylate moiety. The peaks in the range of 3.988–4.156 ppm indicate the protons of -COOCH₂ group of RBO. No peaks in the range of 5–6 ppm indicate that polymerization was carried out successfully. In the ¹³C NMR spectra, peaks ranging from 168.31–172.63 ppm confirm the presence of

carbons of ester groups. There is no any peak in the range of 120–150 ppm and it indicates that polymerization was carried out successfully. The IR spectra of three copolymers (P-4 to P-6) are almost similar. The absorption band at 1736.02 cm^{-1} is due to ester carbonyl group of RBO moiety. The absence of any peak in the range of 4–6 ppm in ^1H NMR and 120–150 ppm in ^{13}C NMR spectrum indicated the formation of copolymer of RBO with α -pinene.

Molecular weight data analysis: The experimental value of number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymers (P-0 to P-6) are shown in Table 1. From the experimental data, it was observed that among the seven polymers, the homopolymer of RBO (P-0) and the copolymer P-3, have the lowest and highest molecular weight respectively. Moreover, it is also observed that with increasing the percentage of DA moiety (P-1 to P-3) and α -pinene moiety (P-4 to P-6) in the copolymers, the molecular weight increases. A better molecular weight is obtained in the copolymers of RBO and DA than RBO and alpha pinene.

Table 1. The weight average and number average molecular weights (M_w and M_n) and polydispersity index of the polymers before and after biodegradability test

Polymer samples	Before biodegradability test			After biodegradability test		
	M_n	M_w	PDI	M_n	M_w	PDI
P-0 (10:0)	11352	16547	1.45	9321	14536	1.55
P-1 (9:1)	20503	27323	1.33	17865	24895	1.39
P-2 (8:2)	25953	33523	1.29	21712	31247	1.43
P-3 (7:3)	38362	46264	1.20	34231	43135	1.26
P-4 (9:1)	14274	19213	1.34	12115	17426	1.43
P-5 (8:2)	16936	22721	1.34	14487	20147	1.39
P-6 (7:3)	18932	24365	1.28	16548	22335	1.34

P-0 (homopolymer of RBO), P-1 to P-3 (RBO: DA) and P-4 to P-6 (RBO: α -pinene) w/w, M_n = number average molecular weight; M_w = weight average molecular weight; PDI = polydispersity index.

Analysis of TGA data: From the experimental TGA values of the seven polymers, it was observed that homopolymer of RBO (P-0) is thermally less stable than the prepared copolymers. This indicates that when DA or α -pinene moiety is introduced in the backbone of RBO oil, the thermal stability increases. Two major decompositions have been observed at 160°C and 330°C with 23% and 85% weight

loss respectively in case of P-0. The thermal stability of copolymers P-1, P-2 and P-3 are almost identical where two major decompositions were observed at 220°C and 482°C with 22% and 78% weight loss respectively. The thermal stability of copolymers P-4, P-5 and P-6 is less than other copolymers P-1, P-2 and P-3 but higher than homo polymer of RBO (P-0).

Analysis of viscosity index (VI) values: VI was calculated at different concentrations ranging from 1% to 5% (w/w) in two types of base oil and the values are listed in Table 2. The viscosity of lube oil decreases with increasing temperature but when lube oil is blended with the polymeric additives, the decrement of viscosity stops. At high temperature, expansion of additive molecules takes place and as a result, the size of micelle increases. This increased in micelle size prevent the reduction of the viscosity of the lubricant composition. It is also observed that with increasing concentration of the lubricant composition, the VI values increases. It may be due to increase of total volume of polymer micelle and hence improves the VI property². It was found that VI value increases by incorporation of DA and α -pinene moiety in the backbone of homopolymer of RBO. This may be due to higher molecular weight and higher crosslink density of the copolymers⁷. The copolymer P-3 has the highest VI value than the other prepared polymers in both types of base oil. It may be due to higher molecular weight compared to others.

Analysis of pour point (PP) values: The pour points of the base oil containing additives at concentration levels ranging from 1%–4% (w/w) are listed in Table 2 for two types of base oil which indicate that the prepared lubricant compositions have lower PP than base oil and hence the prepared additives can be used as PPD. From the experimental data, it is observed that the efficiency as PPD increases up to 3% concentration. The reason may be, at this concentration the interaction between the additive and paraffinic wax of base oil is more effective and decreases the shape of crystals of the paraffinic wax^{8,9}. Among the seven polymers, P-3 showed best performance as PPD than the others in both types of base oil.

Analysis of biodegradability test results: Biodegradability test results obtained by using the disk diffusion and soil burial test method are presented in Table 3. All the polymers showed

Table 2. Pour point (°C) and VI values of lubricant in different concentration

Property/base oil/(PP/VI)	Conc. (%)	Sample						
		P-0	P-1	P-2	P-3	P-4	P-5	P-6
PP/BO1(-3)	1	-6	-6	-12	-15	-6	-9	-12
	2	-9	-9	-15	-18	-9	-12	-15
	3	-9	-12	-18	-21	-12	-15	-18
	4	-9	-12	-18	-21	-12	-15	-18
PP/BO2(-6)	1	-9	-9	-15	-18	-9	-12	-15
	2	-12	-12	-18	-21	-12	-15	-18
	3	-12	-15	-21	-24	-15	-18	-21
	4	-12	-15	-21	-24	-15	-18	-21
VI/BO1(80)	1	86	98	100	112	96	98	107
	2	90	101	104	118	98	102	115
	3	96	107	116	125	104	110	123
	4	100	109	120	136	107	116	129
	5	105	119	126	140	115	123	137
VI/BO2(85)	1	94	115	119	121	104	116	120
	2	98	118	123	129	107	117	126
	3	102	128	133	135	110	119	132
	4	109	131	138	142	121	130	138
	5	115	135	141	148	129	133	139

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

significant biodegradability against the pathogens *Calleotricheme camellia* and *Alterneria alternate* only. The mass loss after biodegradation of the prepared polymers was further confirmed by shifting of IR frequency of the ester carbonyl along with other shifted peaks and determining the GPC molecular weight after biodegradation shown in Table

Table 3. Results of biodegradability test by the disc diffusion method and soil burial test method

Sample	Weight loss in disc diffusion method (in g)					Weight loss in soil burial test (in g)
	CC	FE	AA	CG	CE	
P-0	0.39	0	0.59	0	0	0.38
P-1	0.35	0	0.51	0	0	0.33
P-2	0.27	0	0.46	0	0	0.29
P-3	0.26	0	0.38	0	0	0.24
P-4	0.35	0	0.56	0	0	0.37
P-5	0.34	0	0.56	0	0	0.35
P-6	0.32	0	0.52	0	0	0.35

CC = *Calleotricheme camellia*; FE = *Fussarium equisetiae*; AA = *Alterneria alternate*; CG = *Colletrichum gleosporoides*; CE = *Curvularia eragrostidies*.

1. Among the prepared seven polymers, the homopolymer of RBO (P-0) showed better biodegradation both in disk diffusion as well as soil burial test method.

Conclusion

A consideration of the chemical structures of DA and α -pinene may be taken into consideration to explain the differences of performance between the copolymers of RBO with DA and RBO with α -pinene. Average molecular weight of copolymers of RBO with DA is better than RBO with α -pinene. A viscosity index value of homopolymer of RBO is lower than copolymers and viscosity index value increases with increasing the percentage of DA or α -pinene in copolymers. The pour point of the lubricant compositions is found to be better for the copolymers of RBO with DA than the copolymers of RBO with α -pinene and the values decrease with the increasing concentration of the lubricant composition. The homopolymer of RBO and copolymers of RBO with α -pinene showed significant biodegradability than copolymers of RBO with DA.

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References

1. P. Ghosh, D. Nandi and T. Das, *J. Chem. Pharm. Res.*, 2010, **2(4)**, 122.
2. G. Karmakar and P. Ghosh, *ACS Sustainable Chem. Eng.*, 2013, **1**, 1364.
3. S. Rani, M. L. Joy and K. P. Nair, *Indian Crop. Prod.*, 2015, **65**, 328.
4. K. Rajnarayana, M. C. Prabhakar and D. R. Krishna, *Indian J. Physiol. Pharmacol.*, 2001, **45(4)**, 442.
5. M. B. Reena and B. R. Lokesh, *J. Agric. Food Chem.*, 2007, **55(25)**, 10461.
6. K. Wuttikul and P. Boonme, *Drug Deliv. Transl. Res.*, 2016, **6(3)**, 254.
7. I. S. Jerbic, J. P. Vukovic and A. Jukic, *Ind. Eng. Chem. Res.*, 2012, **51**, 1914.
8. P. Ghosh, T. Das, D. Nandi, G. Karmakar and A. Mandal, *Int. J. Polym. Mater.*, 2010, **59**, 1008.
9. H. P. Soni and D. P. Kiranbala Bharambe, *Energy Fuels*, 2008, **22**, 3930.