SYNTHESIS, CHARACTERIZATION AND PERFORMANCE EVALUATION OF POLYMERIC ADDITIVES FOR LUBRICATING OIL

Thesis Submitted to the University of North Bengal
For the Award of Doctor of Philosophy in
Chemistry

BY

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MARCH, 2013

DECLARATION

I declare that the thesis entitled "SYNTHESIS, CHARACTERIZATION AND PERFORMANCE EVALUATION OF POLYMERIC ADDITIVES FOR LUBRICATING OIL" has been prepared by me under the guidance of Dr. Pranab Ghosh, Associate Professor of Department of Chemistry, North Bengal University. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

This is to certify that Sri Gobinda Karmakar has prepared the thesis entitled "**Synthesis, Characterization and Performance Evaluation of Polymeric Additives for Lubricating Oil",** for the award of PhD degree of the **University of North Bengal,** under my guidance. He has carried out the work at the Department of Chemistry, University of North Bengal, Darjeeling, West Bengal-734013.

Dr. Pranab Ghosh (Research Supervisor and Guide)

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Abstract

Lubricants are usually liquids or semi-liquids used to lubricate the automotive engines or other machineries for their better performance and longevity. Lubricants perform several key functions such as keep moving parts apart, reduce friction, transfer heat, carry away contaminants & debris, transmit power, protect against wear, prevent corrosion, and stop the risk of smoke and fire of objects.

The lubricant contains base oil and an additive package. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property.

In the present work synthesis, characterization and performance evaluation of acrylate based multifunctional additives along with biodegradable multifunctional lubricating oil additives based on vegetable oils (sunflower oil and soybean oil) has been investigated. It comprises synthesis of the additives, characterization of each of them by spectral techniques (IR, NMR), SEC-GPC and viscometric analysis. Finally performances of the additives in base oils mainly as pour point depressant (PPD), viscosity index improver (VII) or modifier (VM) and antiwear performance were evaluated by standard ASTM methods. The shear stability of the polymers was also determined as per ASTM D6022–06 method. Biodegradability of the polymers was tested by disc diffusion method against fungal pathogens and by soil burial degradation test of the polymer films as per ISO 846:1997. Oil thickening property of the polymers has also been investigated and reported here. Thermal stability of the polymers was determined by thermo gravimetric analysis. A greener microwave synthetic procedure for their synthesis along with the conventional thermal method has also been studied. Since

these types of additives are multifunctional in nature i.e. act as PPD, VM and AW at the same time, interest of research on this area gives a new horizon in the lubrication technology.

After a general introduction of the present investigation the whole work has been divided into two parts (Part-I and Part-II). Part-I has discussed about acrylate based polymeric additives and Part-II on the biodegradable polymeric additives based on vegetable oil. Part-I is further divided into three chapters and part-II into four chapters. First chapters of each part discussed about the background of the respective work. The chapter-II of Part-I is further subdivided into two sections (A & B) and discussed about the polymyristyl acrylate based lube oil additive. In sections A of chapter-II, synthesis and characterization of polymyristyl acrylate as a potential additive for lubricating oil has been discussed. In this section homopolymer of myristyl acrylate was synthesized by two different ways; microwave (MW) assisted method and thermal method using benzoyl peroxide (BZP) as initiator. The polymers were characterized by spectroscopic (NMR, IR) and viscometric analysis. Additive performances of each of them [pour point depressant (PPD) and viscosity modifier (VM)] for lubricating oil (lube oil) were also evaluated by standard ASTM methods. Oil thickening property of the polymer has also been investigated and reported here. Thermal stability of the polymer was determined by thermo gravimetric analysis. A comparison of their performances has also been reported. The MW assisted method has appeared to be a cost effective greener approach. The section B of this chapter also discussed about the polymyristyl acrylate as lube oil additive. Here homopolymer of myristyl acrylate was prepared by microwave assisted free radical polymerization method using BZP as initiator with variation of time at a fixed power without any solvent. Then their characterization and performance evaluation were carried out. A comparison of their performances has also been reported. The molecular weights of the polymers were determined from viscosity measurements in toluene at 313K and thermal stability was measured by thermogravimetric analysis (TGA).

Chapter-III of Part-I also contains two sections, A and B and reported about polyacrylate of mixed alcohols as lube oil additive. The section A of chapter-III discussed about the synthesis, characterization and additive performances of the polymer of the acrylate of a mixture of three different alcohols viz. decyl alcohol, dodecyl alcohol and myristyl alcohol and the respective homopolymers viz. poly(decylacrylate), poly(dodecylacrylate) and poly(myristylacrylate). The viscosity measurements of the synthesized polymers in the toluene solution at 313 K were performed and compared. Section B of the same chapter explained about the homopolymer of acrylate of a mixture of myristyl (C14), dodecyl (C12) and decyl (C10) alcohols in 2:1:1 molar ratio prepared by two different ways, microwave (MW) assisted method and thermal method using benzoyl peroxide (BZP) as initiator. The characterization and performance evaluation of the polymers were carried out by the similar methods. Thermal stability of the polymer was determined by thermo gravimetric analysis.

Chapter II of Part-II explained about polymerized sunflower oil as a lube oil additive. In this chapter solvent free synthesis of homopolymer of sunflower oil (SFO) was performed by two different ways; microwave (MW) assisted method and thermal method using benzoyl peroxide (BZP) as initiator. Characterization of the polymers was done by the process as mentioned earlier. Performance evaluation as pour point depressant (PPD), viscosity modifier (VM) or viscosity index improver (VII) and antiwear (AW) in different base oils (BO1, BO2) were carried out by standard ASTM methods. Shear stability, oil thickening property and biodegradability of the polymers have also been investigated and reported here. Thermal stability of the polymers was determined by thermo gravimetric analysis. A comparison of their performances has also been reported. The additive prepared by microwave assisted method showed better viscosity index and pour point values compared to thermally prepared additive.

In chapter-III of Part-II thermal synthesis of homopolymer of soybean oil (SBO) and its copolymer with methyl acrylate, 1-decene and styrene has been carried out using BZP (benzoyl peroxide) as radical initiator. Characterization and performance evaluation of all the polymers were carried out. Biodegradability of the additives prepared against fungal pathogens and microorganisms was tested by disc diffusion (DD) method and soil burial test (SBT) method respectively. Thermal stability and thickening power of each of them have been evaluated and included. The performances have been compared and reported.

Finally in chapter-IV of this Part, comparison of additive performances of homopolymer of sunflower oil (SFO) and soybean oil (SBO) has been investigated.

PREFACE

The thesis is the compilation of the research work carried under the guidance of Dr. Pranab Ghosh in the Department of Chemistry, University of North Bengal during the period 2008 to 2012. It comprises the synthesis, characterization and performance evaluation of polymeric additives for lubricating oil.

The basic functions of a lubricant are lessening the friction and wear between two moving surfaces, heat removal and contaminant suspension. Apart from these, there is much other application for automotive and industrial purposes. Lubricant is basically a combination of lubricating oil or base oil and an additive package (up to 30%). Additives enhance the performance of the lubricating oil already present in lube oil or add some new properties. Additives generally increase the viscosity index, pour point of the base stocks. In modern trends the application of multifunctional additives are focused. So, in my thesis synthesis, characterization and performance evaluation of such type of multifunctional additives has been carried out.

I feel it an imperative to express my sincere gratitude to my guide and supervisor, Dr. Pranab Ghosh, Associate Professor, Department of Chemistry, University of North Bengal, West Bengal for giving me the opportunity to do my research work and for all the help and advice. His encouragement and personal guidance has played a pivotal role in providing a good basis for the present thesis.

I would like to thank all the faculty members of the chemistry department whose valuable advice helped me to do this work. Thanks to Dr. Sajal Das for his advice with NMR, Prof. S.K. Saha for shear stability analysis of the polymers and my colleague Naresh Chandra Roy for his constant inspiration and grammatical error correction of the thesis. I also express my thanks to Dr. Tapan Das for his valuable suggestion regarding my work.

I am immensely thankful to my lab mates. Their expertise and support have been of tremendous help in the completion of this thesis.

Special thanks for Indian Institute of Petroleum, Dehradun for the analysis of antiwear properties of the additives, Indian Oil Corporation Limited and Bharat Petroleum Corporation Limited for the supply of base oils. I also would like to express many thanks to UGC, India for financial assistance of my work.

I wish to give glory to the Almighty, who has given me good health, strength and wisdom in the past decades and the grace to complete this thesis.

I would also like to thank my parents, my wife Rimpa for supporting me to complete this work. I hereby record my appreciation for them, last but not the least.

I dedicate my thesis to my parents.

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Papers Published/Accepted

1. Synthesis and Characterization of Polymyristyl Acrylate as a Potential Additive for Lubricating Oil

   Authors: Pranab Ghosh*, Gobinda Karmakar

   Journal: American Journal of Polymer Science 2012, 2(1): 1-6 DOI: 10.5923/j.ajps.20120201.01
2. Solvent Free Microwave Assisted Synthesis of Poly Myristyl Acrylate - their Characterization and Performance Evaluation as Additives for Lubricating Oil.

   Authors: Pranab Ghosh*, Gobinda Karmakar

   Journal: *Petroleum Science and Technology*

   MS ID: LPET-2012-0027.R5 (Accepted)
3. Evaluation of acrylate-sunflower oil copolymer as viscosity index improvers for lube oils.

   Authors: Pranab Ghosh*, Tapan Das, *Gobinda Karmakar* and Moumita Das.

   Journal: *J. Chem. Pharm. Res., 2011, 3(3):547-556*
4. Synthesis and Characterization of Homo Polymer of Acrylate of Mixed Alcohol and their Performance as Additives for Lubricating Oils.

   Authors: Pranab Ghosh*, *Gobinda Karmakar*, Moumita Das

   Journal: *Petroleum Science and Technology*

   Manuscript ID: *LPET-2011-0045.R2* (Accepted)
5. Synthesis and Characterization of Homo polymer of Acrylate of Mixed Alcohols (Decyl, Dodecyl and Myristyl Alcohol) – A Potential Pour Point Depressant for Lubricating Oils.

   Authors: Pranab Ghosh*, *Gobinda Karmakar*, Moumita Das and Tapan Das.

   Journal: *Petroleum Science and Technology*

Manuscript ID: *LPET-2010-0649.R1* (Accepted)

6. Synthesis and Characterization of Biodegradable Polymer - Used as a Pour Point Depressant for Lubricating Oil.

   Authors: Pranab Ghosh*; Tapan Das; Debabrata Nandi; *Gobinda Karmakar*; Amitava Mandal

   Journal: *International Journal of Polymeric Materials*, 59:1008–1017, 2010
7. Homopolymer of Methyl Acrylate and its Copolymer with Styrene: Synthesis and Characterization.

   Authors: Pranab Ghosh*, Tapan Das, Debabrata Nandi and *Gobinda Karmakar*.

   Journal: *Journal of Polymeric Material, Vol.27, No.4, 2010, 323-334.*

Communicated Papers

8. Article title: Evaluation of Homo and Copolymer of Soybean Oil as a Potential Additive for Lubricating Oil

   Authors: Pranab Ghosh, Gobinda Karmakar

   Journal: Fuel

   Manuscript ID: JFUE-D-12-01911
9. Article title: Evaluation of Sunflower Oil as a Multifunctional Lubricating Oil Additive

   Authors: Pranab Ghosh, Gobinda Karmakar

   Journal: International Journal of Industrial Chemistry

   Manuscript ID: 1000978071902023
10. Article title: GREEN ADDITIVES FOR LUBRICATING OIL

    Authors: Pranab Ghosh, Gobinda karmakar

    Journal: ACS Sustainable Chemistry & Engineering

    Manuscript ID: sc-2013-00027k

Appendix B

List of Published Research Papers in the Proceedings of National/International Seminar/ Conference/Workshop

1. Copolymer of Sunflower Oil with Alkyl Acrylate- Synthesis, Characterization and Performance Evaluation in Lubricating Oil. Tapan Das**,** Debabrata Nandi, **Gobinda Karmakar** and Pranab Ghosh, Page 55 as P-27, proceeding of "International Symposium on Frontiers of Functional Materials",6-7 January, 2009- Department of Chemistry, University of Calcutta, WB, India.
2. Synthesis and Characterization and Viscometric studies of Homo and Copolymer of Decyl Acrylate. Tapan Das**,** Debabrata Nandi, **Gobinda Karmakar** and Pranab Ghosh, proceeding of "11th CRSI National Symposium in Chemistry" 6-8 February 2009. NCL, Pune, India.
3. Greener Macromolecules for Lubricating Oil. Pranab Ghosh and **Gobinda Karmakar**, proceeding of National Seminar on Micro and Macro resources in Biomolecular Technology. Organized by Department of Biotechnology & Microbiology, N.B.U, February 25th – 26th, 2013.
4. LC Blended Acrylate as a Multifunctional Additive for Lubricating Oil. Mahua Upadhyay[a], **Gobinda Karmakar**[a], Molay Das[b] and Pranab Ghosh*[a]. National Seminar On Frontiers in Chemistry-2013. Organized by Department of Chemistry, University of North Bengal, February 28th, 2013.

Appendix C

Abbreviations

1. AW- Antiwear
2. ASTM- American Society for Testing and Materials
3. BPCL- Bharat Petroleum Corporation Limited
4. BO1- Base Oil 1
5. BO2- Base Oil 2
6. BO3- Base Oil 3
7. BZP- Benzoyl peroxide
8. DC- Deb- Chanterjee
9. FBWT- Four Ball Wear Test
10. HPLC- High Performance Liquid Chromatography
11. IOCL- Indian Oil Corporation Limited
12. LOFI- Lube Oil Flow Improvers
13. KV- Kinematic Viscosity
14. Mn- Number average molecular weight
15. Mw- Weight average molecular weight
16. MW- Microwave
17. MHS- Mark-Houwink-Sakurda
18. PMA- Poly Myristyl Acrylate
19. PMR- Proton Magnetic Resonance
20. PDA - Poly Decyl Acrylate
21. PDDA- Poly Dodecyl Acrylate
22. PPD- Pour point depressant
23. PIB- Polyisobutylene
24. VI- Viscosity index
25. VII- Viscosity index improvers
26. VM- Viscosity modifier
27. SB- Schulz-Blaschke

28. SC- Solomon- Ciute
29. TGA- Thermo gravimetric analysis
30. IR- Infra red
31. NMR- Nuclear magnetic resonance
32. GPC- Gel permeation chromatography
33. SEC- Size exclusion chromatography
34. OCP - Olefin copolymers
35. MHS- Mark Houwink Sakurda
36. S1- Source 1
37. S2- Source 2
38. SBO- Soybean Oil
39. SFO- Sunflower Oil
40. THK- Thickening
41. TMS- Tetra Methyl Silane
42. TVL- Temporary Viscosity Loss
43. PVL- Permanent Viscosity Loss
44. PSSI- Permanent Shear Stability Index
45. SSI- Shear Stability Index

Appendix D

Some of the Instruments Used in this Work

Figure 4. Brucker Avance 300 MHz FT-NMR

Figure 5. Shimudzu FT-IR 8300 Spectrometer

Figure 6. Focused mono-mode microwave oven (CEM corporation, Matthews, NC)

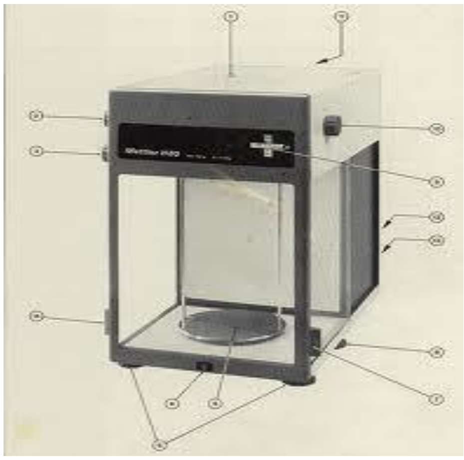


Figure 7. Mettler TA – 3000 system for the determination of TGA

Figure 8. Cloud and pour point test equipment (Wadegati labequip Pvt. ltd, India) having temperature range 0^o to -71°C

General Introduction of the Present Investigation

Engine oil or lubricating oil, used to reduce friction and wear in internal combustion engines, at the dawn of the automotive era was not highly specialized or standardized, and exceedingly frequent oil changes were required. With the development technology increasing demands being placed on engine oils or lubricating oils for automotive engines, high speed machinery and environmental protection. Hence much research effort has been devoted to the process development of improved lubricating oil. Natural petroleum based lubricating oil can’t satisfy all the requirements of modern engines. Hence a large number of functional additives are added to the lube oil to enhance the characteristic properties already present or to impart some new additional properties. Their amount varies from > 1% to 30% or more. The base oil with an additive package is termed as lubricants. These additives are compounds or mixtures when incorporated in base lubricating fluids, supplementing their natural characteristics and improving their field service performance. Additive molecules typically have long, oil soluble, hydrocarbon (non-polar) tails and smaller, hydrophilic (polar) head groups (Fig.1). Since the two parts of the molecule have different solubility's in oil, additives therefore tend to exist colloidally as inverse micelles.

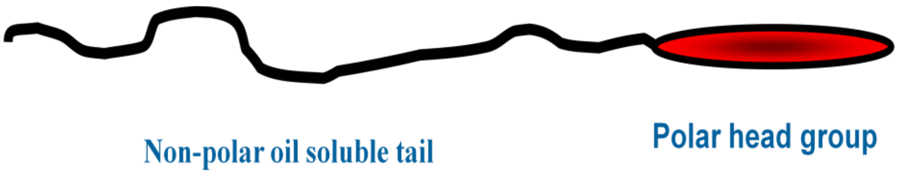


Figure 1. General structure of an additive molecule

Lubricant additives fall into three categories:

a) Surface Additives: The primary purpose of surface additives is to protect lubricated surfaces. Extreme pressure,[1] rust and corrosion inhibitors,[2] tackiness agents, antiwear additives,[3] and oiliness additives are included in this category. These additives coat the lubricated surfaces to prevent wear or rust.

b) Performance-Enhancing Additives: These additives improve the performance of lubricants. Viscosity index improvers,[4] antifoaming agents,[5] emulsifiers,[6] demulsifiers,[7] and pour-point depressants[8] are examples.

c) Lubricant Protective Additives: Lubricant protective additives are employed to protect the lubricant instead of the equipment. Antioxidant[9] and foam inhibitors are examples.

Since the present investigation is based on the synthesis, characterization and performance evaluation of some multifunctional additives having PPD, VII and AW properties, a detailed discussion on them is depicted below.

Extreme pressure (EP), antiwear and rust inhibitors additives coat the lubricated surfaces and prevent wear or rust. Antiwear and extreme-pressure additives function by thermally decomposing to yield compounds that react with the metal surface. These surface-active compounds form a thin layer that preferentially shears under boundary lubrication conditions. Organosulfur and organo-phosphorus compounds, such as organic polysulfides, phosphates, dithiophosphates, and dithiocarbamates are the most commonly used AW and EP.[10] After the discovery of ZDDP (Fig. 2) it rapidly became the most widespread antiwear additive used in lubricants. As a result, many interesting studies have been undertaken on ZDDP with many mechanisms proposed for the antiwear and antioxidant action.[11] Extreme pressure additives form extremely durable protective films by thermo-chemically reacting with the metal surfaces. This film can withstand extreme temperatures and mechanical pressures and minimizes direct contact between surfaces, thereby protecting them from scoring and seizing.

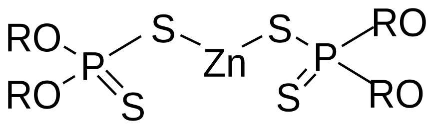
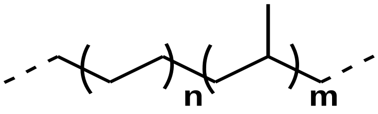
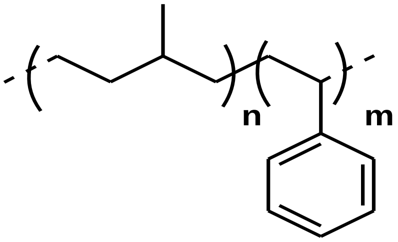


Figure 2. Structure of zinc dialkyl dithio phosphate

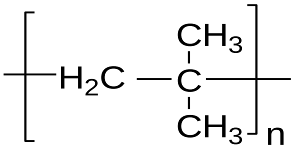
The degree of susceptibility of viscosity of a fluid with rise in temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI).[18] Viscosity index improvers (VII) or viscosity modifier (VM) are additives that resist the change of viscosity of oil with change in temperature. They cause a minimal increase in engine oil viscosity at low temperature, but considerable increase at high temperature. A higher VI value signifies a lesser effect of temperature on viscosity. Performance of viscosity index improvers depends some parameters such as solubility of the polymer in oil, behavior of the polymer molecules in the oil, molecular weight and resistance to shear degradation.[19] The polymer molecule in solution exists as random coil, which is swollen by the lube oil solvent. Polymer solubility generally increases with increasing temperature as the polymer molecules change from tight coils to an open configuration, which has a greater volume. This increase in volume causes increases of the viscosity of the oil, which offsets the normal reduction in viscosity with increasing temperature. Polymers whose stability changes very little with temperature act as thickeners, but are not effective viscosity temperature improvers as those polymers whose solubility is poor at low temperature but good at high temperature. Increasing polymer molecular weight also increases the polymer volume in an oil solution .[20] Consequently, a higher molecular weight polymer will import a higher viscosity index than a lower molecular weight polymer of the same chemical type. Viscosity index improvers are more effective in increasing the viscosity order of low-viscosity oils and become progressively less effective as the viscosity of the base oil increases. By suitable formulation, it is possible to make an engine lubricant which satisfies both the low and high temperature requirements of the SAE viscosity classification system. Commonly used viscosity index improvers (Fig. 3) are polyisobutylene (PIB), polyfumarate esters, polymethylacrylates, olefin copolymers (OCP) i.e. ethylene-propylene copolymer,[21] hydrogenated styrene isoprene copolymer, poly(butadiene-styrene), polybutadiene rubber (PBR) etc.



Ethylene-propylene copolymer (OCP)



Hydrogenated styrene isoprene copolymer

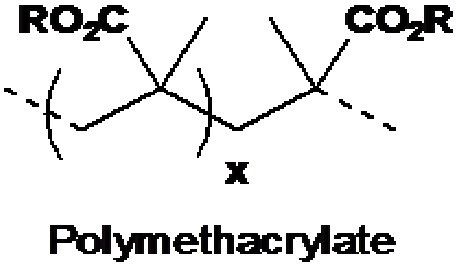


$$\left[-H_2C - \overset{CH_3}{\underset{CH_3}{C}} - \right]_n$$

Polyisobutylene (PIB)

Figure 3. Structure of commomly used viscosity index improvers

The maximum temperature at which the oil just stops flowing is known as pour point of the lube oil which may be defined as the temperature at which the oil sample is no longer considered to flow when subjected to the standardized schedule of quiescent cooling prescribed by standard ASTM method (D97). Pour point depressants, otherwise known as lube oil flow improvers (LOFI), are those additives that improve the low temperature fluidity of the fluid. Typical of those additives that improve the low temperature fluidity of the fluid are C8 to C18 dialkyl fumarate/vinyl acetate copolymers,[12] polymethacrylates, polyacrylates[13] (Figure 4 & 5) ect. They make the oil perform in a desired manner for specific applications.



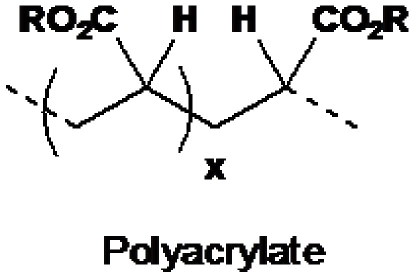


Figure 4. Structure of polymethacrylate   Figure 5. Structure of polyacrylate

The paraffin wax content of the natural oil at a specific temperature (the cloud point) will begin to crystallize. The needle shaped crystals need very little wax to form solid grease – like matrix, which will immobilize the oil. The wax networks will also lead to an increase in oil viscosity. The increase in viscosity is generally temporary as a normal internal combustion engine can generate sufficient shear to disrupt the wax networks and allow the oil to flow. Pour point depressants (PPDs), also known as low-temperature flow improvers and wax crystal modifiers, are polymeric molecules that are added to mineral oil-based lubricants to improve their cold flow properties. Hence to dewax oil to a certain low temperature pour point depressants are added.

Till now several kinds of polymeric additives are synthesized and treated as pour point depressant for lube oil and similar oils. Most of them are acrylate based polymeric additives.[14]

The first formal reports of the action of pour point depressant (PPD) was made by Zimmer, Davis and Frolich[15] following the invention of paraflow by Davis.[16] Ruehrwein reported[17] a certain specificity of action for n-alkyl polymethacrylate in the series dodecyl, tetradecyl, hexadecyl and octadecyl. They reported that the longer alkyl polymers are effective in depressing the pour point of the high pour oils while the shorter alkyl polymers are effective on the lower temperature pour oils.

With the development of engine and transmission technologies to achieve the up growing needs some new additives or new green methodology for their preparation has been investigated on my work. With increasing environmental awareness the research in the area towards the synthesis of bio lubricating oil additive is increasing day by day.[22,23] But reports are still scanty regarding the biodegradability of the additive used. Hence in my present work chemistry of biodegradable multifunctional lubricating oil additive based on vegetable oil (sunflower oil and soybean oil) has also been investigated along with synthetic acrylate based multifunctional additives. The thesis comprises synthesis of the additives, characterization of each of them by spectral techniques (IR, NMR), SEC-GPC and viscometric analysis. Finally performances of the additives mainly as pour point depressant (PPD), viscosity index improver (VII) or modifier (VM) and antiwear performance were evaluated by standard ASTM methods blending in base oils. The shear stability of the polymers was also determined as per ASTM D6022–06 method. Biodegradability of all the polymers was tested by disc diffusion method against fungal pathogens and by soil burial degradation test of the polymer films as per ISO 846:1997. Oil thickening property of the polymers has also been investigated and reported here. Thermal stability of the polymers was determined by thermogravimetric analysis. A greener microwave synthetic procedure for their synthesis along with the conventional thermal method has also been studied. Since these types of additives are multifunctional in nature i.e. act as PPD, VM and AW at the same time, interest of research on this area gives a new horizon in the lubrication technology.

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PART – I

Acrylate Based Lube Oil Additive

Chapter I

1. Background of the present investigation

In recent years, from the viewpoint of global environmental conservation, energy saving with lubricating oil and the extended service life of lubricating oil are the two major problems. In order to solve the problem it is essential to synthesize some new multifunctional additives that not only increase the lifetime of lubricating oil but also increase its field service performances. The use of multifunctional additive in lube oil formulation is well known.[1] All commercial lubricants contain additives to enhance their performance. Their amount varies from > 1% to 30% or more.[2] They boost existing properties; suppress undesirable properties in the base fluids. In general additives are used to (a) reduce the oxidative or thermal degradation of oil, (b) improve pour point of the base oils by dissolving wax crystal deposits at low temperature, (c) increase viscosity index so that the oil does not change its viscosity appreciably with temperature change (d) minimize rust and corrosion, (e) control frictional properties, (f) reduce wear (g) carry away contaminants & debris. They are generally termed as antioxidants,[3] pour point depressants (PPD),[4] viscosity index improver (VII),[5] corrosion inhibitors,[6] extreme pressure agents,[7] antiwear,[8] detergent-dispersants[9] etc. Pour point depressants are designed to prevent wax crystals in lubricants from agglomerating or fusing together at reduced ambient temperatures. If lubricants are not adequately protected with pour point depressants, the flow characteristics can be adversely affected, which may have a negative impact on engine performance and protection. Pour point depressants used earlier were either alkylated aromatic polymers or comb polymers. Comb polymers[10] characteristically have long alkyl chains attached to the backbone of the polymer, with the alkyl groups being of different carbon chain lengths. The mechanism of action for pour point depressants has been the subject of much interest. Early indications were that alkylated aromatic compounds function as pour point depressants by coating the surface of the wax crystals and preventing further growth. More recently, however, it appears that the pour point depressants are either absorbed into the face of the wax crystal if the pour point depressant is an alkyl aromatic or co-crystallize with the wax crystal if it is comb polymer. This co-crystallization sterically inhibits the formation of the three-dimensional network, thus preserving the wax as a distribution of tiny crystals and ensuring the complete fluidity of the oil.

Thus, crystal growth is not prohibited; it is simply directed or channeled along different routes. Light microscopy suggests that wax crystals are typically thin plates or blades, and when a pour point depressant is added to the system, those crystals are smaller and more branched, and thus the pour point depressant may disrupt or redirect crystal growth from different directions into a single direction, and bulkier crystals will be formed. These crystals then can form networks only at much lower temperatures which results in a lower pour point.

Viscosity index, commonly designated as VI, is an arbitrary numbering scale that measures the resistance power of changes of oil viscosity with changes in temperature. Viscosity index can be classified as follows: low VI - below 35; medium VI - 35 to 80; high VI - 80 to 110; very high VI - above 110. A high viscosity index indicates small oil viscosity changes with temperature. A low viscosity index indicates high viscosity changes with temperature. Therefore, a fluid that has a high viscosity index can be expected to undergo very little change in viscosity with temperature extremes and is considered to have a stable viscosity. A fluid with a low viscosity index can be expected to undergo a significant change in viscosity as the temperature fluctuates. The additives that increase the VI values are termed as viscosity index improvers (VII) or viscosity modifiers (VM).

Most of these additives used as PPD and VII are acrylate based. There are lots of references where polyalkyl acrylates and polyalkyl (meth)acrylates are used for these purpose with great success.[11-17] Bataille et al in the year 1994 has discussed the preparation and characterization of a viscosity index improver for naphthenic and paraffinic base oils.[18] The following patents are also discussed the same.

Patent No. 4,073,738 discloses the use of alkyl acrylate or alkyl methacrylate, wherein the alkyl group side chain can have from 8 to 30 carbon atoms and preferably from 8 to 22 carbon atoms, as a pour point depressant in lube oil.

U. S. Patent No. 4,088,589 claims a combination of pour point depressants of which one can be an oil soluble polymer of an alkyl acrylate or methacrylate which contains a side chain comprising 10 to 18 carbon atoms in the alkyl group.

U. S. Patent No. 3,897,353 discloses oil compositions comprising lubricating oil and a pour point depressant which can be an alkyl methacrylate. These acrylates may be made from monomers wherein the alkyl portion of the ester or the side chain has from 12 to 18 carbon atoms and includes mixtures. However, the polymers of this patent are made from nitrogen- containing monomers.

Patent no. EP 0140274 B1 claimed the use of additives for lubricating oils which contain n-paraffin based on polyalkylmethacrylates and acrylates. US Patent 4490267 disclosed about the preparation of lubricating oil additive by polymerizing C_{1-30}-

alkyl(meth)acrylates. The use of acrylate based pour point depressants also claimed in the US Patent Nos. 6255261, 4867894 and 7718588. US Patent No. 4968444 in 1990 describes the use of mixed polyacrylates as multifunctional lube oil additive.

Very recently issued US Patent No. 8105990 B2 in 2012 discloses the use of poly(methyl acrylate) based viscosity index improver. The U. S. Patent Nos. 3,607,749 and 4,203,854 discloses the application of poly(methacrylate) as viscosity index improvers.

In a recent paper[19]Azim et al has reported the synthesis of some polymeric additive based on styrene-methyl acrylate copolymer as multifunctional (Viscosity Modifier (VM), Pour Point Depressant (PPD), Detergent-dispersant) additives for lube oil. It was found that the efficiency of the prepared compounds as PPD increases with decreasing the concentration of the prepared polymers, increasing the chain length of alkyl groups and increases with decreasing the molecular weight.[20] I.M. El- Gamel[21] has reported the synthesis of methacrylate - C-18 α-olefin copolymer as a potential PPD for waxy residue fuel oil and concluded that polymeric structure with long side chain of average 21 carbons have the potential to decrease the pour point of the oil. In a recent paper[22] Rasha has reported a novel PPD based on methyl acrylates terpolymers.

The use of additives in the lube oil discussed above is the polymers of acrylate or alkyl acrylate esters of long chain monohydric alcohols. The effectiveness of performance of the additives depends on the chain length of the alcohols.[17] These types of additives improve the performances of lubricating oil up to a certain limit. So, if the alcohols of different chain lengths are mixed before esterification with acrylic acid or alkyl acrylic acid followed by polymerization, the extent of additive performances may be changed. However, reports regarding polymer of acrylates of mixed alcohols as multifunctional lube oil additive are scanty.

US 3250715 (Wyman) discloses terpolymers of dialkyl fumarates, vinyl esters and alkyl vinyl ethers for improving the pour point of lubricating oils, and most particularly in which the dialkyl fumartes are prepared from various C_{10} through C_{18} alcohols including tetradecyl alcohol alone as well as alcohol mixtures averaging from 12 to 14 carbon atoms. EP 2081970B1 discloses the use of mixed polyacrylates as pour point depressant. Polymethacrylate copolymers comprised from about 60 to about 96 wt.-percent of a C12-C16 alkyl methacrylate and from about 40 to about 4 weight percent of a C18-C30 alkyl methacrylate showed excellent low temperature properties to lubricating oils. US patent 2992987 discloses about lubricant oil additive composition. In this patent pour point as well as viscosity index of acrylate polymers prepared from alcohol blends have been studed.

From the above literature survey and many other references relating to the application of polyacrylate based lube oil additive the author felt the necessity of doing work on acrylate based polymeric additive for lubricating oil. Since lots of work has already been done on polyalkyl methacrylates, therefore in this part of my work synthesis, characterization and performance evaluation of polymyristyl acrylate and polyacrylate of mixed alcohols (myristyl, dodecyl and decyl alcohol) has been investigated. Microwave irradiation, a greener and cost effective procedure for the synthesis of the polymeric additives has also been studied in comparison to conventional thermal procedure.

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Chapter II

Section A

1.1. Synthesis and Characterization of Polymyristyl Acrylate as a Potential Additive for Lubricating Oil

1.1.1. Introduction

Modern lubricants are formulated from a range of base fluids and chemical additives. The base fluids has several functions but primarily it is the lubricant, providing a fluid layer separating moving surfaces or removing heat and wear particles while keeping friction at a minimum. Many of the properties of the lubricant are enhanced or created by the addition of special chemical additives to the base fluid. For example viscosity modifier (VM) or viscosity index improver (VII),[1] pour point depressant (PPD),[2] antioxidant,[3] corrosion inhibitor,[4] extreme pressure agent[5] etc. The base fluid also functions as the carrier for these additives in solution under all normal working conditions. Multifunctional additives satisfy more than one purpose and hence research throughout the world is increasing directed toward producing such type of additives. In order to improve the pour point (the lowest temperature at which the oil stays flowing) and to meet the requirements of the multigrade engine oil specifications pour point depressants (PPD) are added. PPD functions by depositing or adsorbing on the wax crystals network by markedly reducing the size of the wax crystals formed. Viscosity index improvers (VII) also known as viscosity modifier (VM) are long chain, high molecular weight polymers used to resist the change of viscosity of the oil by increasing the relative viscosity of oil more at high temperatures than at low temperatures.[6-9] The performance of VMs is very often expressed in terms of Viscosity Index (VI), which is an arbitrary number[10] that indicates the resistance of a lubricant to viscosity change with temperature. The higher the VI, the less the viscosity of an oil changes for a given temperature change. The performance of the VII depends on the behavior of the polymer molecules in the oil, where the polymer solubility, molecular weight and resistant to shear degradation are determinant parameters.[9] Oil thickening property of the polymer, which is a direct measure of percent increase in the viscosity of the base stocks for addition of its unit amount of weight, has also been investigated and reported here. This property can also be taken as the measure of extent of interaction of the polymer with the base stock, greater the thickening property; greater is the extent of interaction.[11] Fuel economy may also be predicted by the thickening power of a lube oil additive. Although additives of many diverse types have been developed to meet special lubrication needs, acrylate based polymers as lube oil additive are widely used. Several kinds of poly alkyl acrylates are generally used as performance additive[12] especially as PPD and VM in lubricating oil composition. In this work the additive properties of polymyristyl acrylate have been investigated.

Microwave irradiation is a well-known method for heating and drying materials and is utilized in many private households and industrial applications for this purpose. Both organic and inorganic reactions undergo an immense increase in reaction speed under microwave irradiation compared with conventional heating.[13]Significant improvements in yield and selectivity have also been observed as a consequence of the fast and direct heating of the reactants themselves. Furthermore, high-pressure synthesis is easily accessible for reactions performed in closed vessels, facilitating the use of low boiling solvents and thereby paving the way to environmentally benign reaction conditions.

With this view in mind and as a part of our ongoing studies on the synthesis and evaluation of polymeric additives for lubricating oil, we have undertaken the synthesis of the polymyristyl acrylate under thermal as well as microwave condition. The additives have been prepared, characterized and their performances as PPD and viscosity modifier (VM) along with the thickening properties in different base oils and have been evaluated and compared.

Physical characterization of the polymers was carried out employing spectroscopic (IR and NMR) techniques and thermo gravimetric analysis (TGA). The behavior of the polymeric additives towards a specific solvent / base stock plays a significant role in their action as a performance additive in their end application. Viscometry provides very important data about the interaction of additive in base fluid and hence conformation of polymeric system in the base stock. Again, reports regarding such information are scanty[14] and almost nil for polymers used as lube oil additives, present research also include viscometric study of this polymer. In addition, because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from other techniques, generally in determination of molecular mass of samples with the available literature value of the constants used in the particular equation.

The relationship between viscometric molecular weight and intrinsic viscosity [η] can be described by the Mark-Houwink-Sakurda (MHS) equation:

$$[\eta] = KM^{a} \tag{1}$$

Where, [η] is the intrinsic viscosity in dLg^{-1}, M is the viscosity-average molecular weight, and K and *a* are viscometric constants for given solute-solvent system and temperature. The higher the molecular weight, the more viscous the polymer solution will be. This is reasonable, when a polymer has a higher molecular weight, it has a bigger hydrodynamic volume; that is, the volume that the coiled up polymer takes up in solution. Being bigger, the polymer molecule can block more motion of the solvent molecules. It might be said that it can block off more lanes of the highway. Also, the bigger a polymer is, the stronger its secondary forces are. So the higher the molecular weight, the more strongly the solvent molecules will be bound to the polymer. This enhances the slowing-down of the solvent molecules. A number of mathematical relations are available in literature for the study of viscometric properties of a dilute polymer solution at a particular temperature. The equations used for this purpose are:-

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

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

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

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

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

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

Where, η_r = t/to =time of flow of the solution /time of flow of the pure solvent = relative viscosity or viscosity ratio; η_{sp}= η_r-1= specific viscosity; $[\eta]_h$ = intrinsic viscosity, respective to Huggins equation; $[\eta]_k$ = intrinsic viscosity, respective to Kraemer equation; $[\eta]_m$ = intrinsic viscosity, respective to Martin equation; $[\eta]_{sb}$= intrinsic viscosity or limiting number, respective to Schulz-Blaschke equation. k_h, k_k, k_m and k_{sb} are Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively.

The equations 2 to 5 are used for the determination of intrinsic viscosity by graphical extrapolation method.[15-19] The last two (eqs. (5) and (6)) are applied for single point determination.[16-18] This method has the advantage of being considerably faster and can be adequate when a large number of samples must be analyzed in short period of time, practically in industrial laboratories.

The use of these equations have been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$.[16] Schultz-Blaschke equation is also applied for single point determination where the value of $K_{sb}=0.28$.

1.1.2. Experimental Part

Materials

Myristyl alcohol (CH_3-$(CH_2)_{13}$-OH, 98%, SRL India), and acrylic acid (H_2C = CH-COOH, 99%, Merck) were used as received. Benzoyl peroxide (BZP) ($(C_6H_5CO)_2O_2$, 98 %, LOBA Chemie, India) was used after recrystalization from $CHCl_3$-MeOH mixture. Toluene was purified by distillation after being refluxed for 2 h in presence of sodium and used as a solvent for esterification. Concentrated sulfuric acid (98%, Merck) as a catalyst and hydroquinone (99%, Merck) as an inhibitor were also used for esterification. Base oils were collected from IOCL, India and BPCL, India.

Procedures

Preparation of the ester of myristyl alcohol

The ester was prepared by reacting 0.5 mole of acrylic acid with 0.5 mole myristyl alcohol. The reaction was carried out in a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid and toluene as a solvent. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen and the reactants were agitated using a mechanical stirrer at 500 rpm. The reactants, which were mixed with toluene, were heated gradually from room temperature to 130^{o} C using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester.

Purification of the prepared acrylate ester

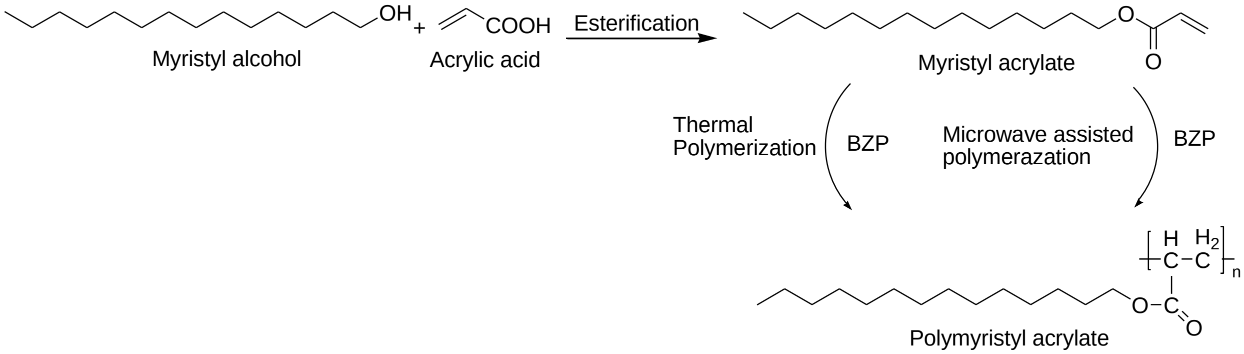
The prepared ester was purified according to the following procedure: a suitable amount of charcoal was added to the ester, allowed to reflux for 3 h and then filtered off. The filtrate was washed with 0.5N sodium hydroxide in a separating funnel and shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide, the ester was then left over night on anhydrous calcium chloride for drying and was then removed by distillation under reduced pressure and was used in the polymerization process.

Thermal polymerization

In a four necked round bottom flask fitted with a mechanical stirrer, condenser, thermometer, an inlet for the introduction of nitrogen, desired mass of the ester was placed without adding any solvent. Then homo polymerization was performed with initiator (BZP) and the reaction temperature was maintained at 80^{o} C for 4 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and to precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 40^{o} C.

Microwave assisted Polymerization

Polymerization was carried out in a focused mono-mode microwave oven (CEM corporation, Matthews, NC) applying 300 WT for 15 minute at 90^{o} C without any solvent by adding 0.01% (w/w) BZP as initiator (Scheme 1).[20]



Scheme 1. Polymerization of myristyl acrylate prepared from myristyl alcohol and acrylic acid by esterification in two different ways

1.1.3. Measurements

Spectroscopic measurements

IR spectra were recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range 400 to 4000 cm^{-1}. NMR spectra were recorded in Brucker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. $CDCl_3$ was used as solvent and TMS as reference material.

Viscometric measurements

Viscometric properties were determined at 40^{o} C in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values $K' = 0.00268$ cm^{2}.s^{-2}, $L = -19.83$ cm^{2}, the volume of the bulb is 3 cm^{3} and length of the capillary 11.3 cm). Experimental determination was carried out by counting flow time of seven different concentrations (0.217 to 0.136 g.cm^{-3}) of the sample solution. The time of flow of the solution was manually determined by using a chronometer. In the single point measurement, the lowest value of solution concentration was chosen for calculation. For the viscosity-average molecular weight determination, the constants K = 0.00387 dl/g and a = 0.725 were employed in Mark Houwink – Sukurda relation.

Thermo gravimetric analysis (TGA)

The thermo grams in air were obtained on a mettler TA – 3000 system, at a heating rate of 10^{o}C / min.

1.1.4. Evaluation

Evaluation of thickening property

Kinematic viscosity of the base oils and that of the polymer doped base oils in different concentrations were evaluated. Thickening power of the polymer was determined by evaluating the percent increase in viscosity of the base stocks by the addition of unit amount of additive.

Evaluation of pour point

The prepared additives were evaluated as pour point depressant using base oils (BO1, BO2 and BO3), each of them collected from two different sources (S1 and S2), through the pour point test according to the ASTM-D97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentrations. The experimental data were noted by taking an average of three experimental results under identical conditions.

Evaluation of viscosity index

Viscosity index of the prepared homopolymers were evaluated in different base stocks according to ASTM D 2270-87 method. The kinematic viscosities of the oils contain the tested compounds which were determined at 40^{0} C and 100^{0} C. Different concentrations ranging from 1.0 to 5.0 wt% were used to study the effect of additive concentration on (VI).

1.1.5. Results and Discussion

The IR absorption at 1732.0 cm^{-1} and 1732.9 cm^{-1} showed the presence of ester carbonyl group of the additives P-1 (thermal method) and P-2 (microwave method) respectively (Fig. 1.1 and 1.2). The broad peaks in the range 1259.4 cm^{-1} and 1263.3 cm^{-1} due to the ester C-O stretching vibration for P-1 and P-2 respectively. Broad peak appeared in the range 1170.7 cm^{-1} to 1056.9 cm^{-1} for C-H stretching vibrations for both the polymers. Peaks in the range 984.6 cm^{-1} to 668.3 cm^{-1} was due to C-H bending vibrations. The ^1H NMR signals in the region 4.15 ppm to 3.641 and 3.642 ppm indicated the presence of $–OCH_2$ group of acrylate chain (Fig. 1.3 and 1.4). Peaks in the range 1.613 to 0.858 ppm were due to C-H bonds of the alkyl groups. Absence of peak between 5 and 6 ppm for P-1 to P-2 polymers indicated the absence of olefinic double bond which indicates effective polymerization in both the case.

The TGA data showed (Table 1.1) that the thermal stability of P-2 is slightly better than P-1. From this result it may also be said that the P-2 is more linear than P-1 which is quite expected.

The intrinsic viscosity values for both the polymers, obtained from different equations (eq. 1 to eq. 6), have little difference (Table 1.2). The higher values indicate that both the polymers have fairly strong interaction with the solvent. k_h values also indicate good solvation which is further supported by the $k_h + k_k$ values (Table 1.3), and thus point towards the formation of the chain like structure of the present polymer as discussed earlier.[21] Molecular weights (viscosity average) for P-1 and P-2 obtained by Mark-Houwink equation using intrinsic viscosity obtained from different equations (eq. 1 to eq. 6) showed excellent correlation (Table 1.4).

Thickening power of both the homopolymers (Table 1.6) as evaluated in different base stocks (Table 1.5) indicated a gradual decrease with the increase in concentration of the additive. This may be because of the fact that the polymer molecule assumes a coiled like aggregation with increase in its concentration in the base stock. The result also showed that the thickening power of the P-1 polymer was slightly higher in comparison to the P-2 polymer. This indicates that as far as the fuel economy is concerned the thermal method is better than the microwave method.

The prepared homopolymers were tested for their effectiveness as viscosity index improvers by measuring the VI of the respective additive doped base oils and the values are given in Table 1.7. The test method (ASTM D 2270-87 method) comprises the determination of the kinematic viscosities of the different base oils containing different concentrations of the additives (ranging between 1% to 5%) at 40^0 and 100^0 C.[22]The data indicated that the VI increases with increasing the concentration of the prepared additives in solution and the VI values of the P-2 polymer are slightly higher in compared to the P-1 polymer in BO1 and BO2 base oils (Figure 1.5 & 1.6), whereas in BO3 base oil the values are nearly equal for both the polymers (Figure 1.7). As the temperature is raised, the lube oil viscosity decreases; meanwhile the polymer molecule expands and as a result of which its hydrodynamic volume increases (Figure 1.8). This increase in the micelle size of the solvated polymer molecules counterbalance the reduction of the viscosity of the lube oils with temperature.[23] This effect is more pronounced in case of P-2 polymer rather than P-1. The increase in concentration of polymer leads to an increase in the total volume of the polymer micelles in the oil solutions. Consequently, higher concentration of additive will impart higher viscosity index.[24]

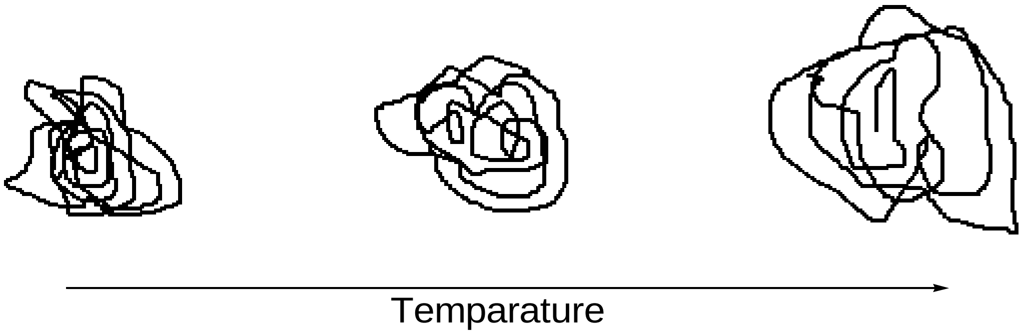


Figure 1.8. Expansion of polymer molecule in oil with increase in temperature

PPD properties of both the polymers as evaluated in different base stocks showed a good depression in the base stocks studied. It was found that the efficiency increases by increasing concentration of the additives and P-2 polymer showed better depression in pour point at higher concentrations than that of the P-1(Figure 1.9 & 1.10). Therefore although both the polymers may be used as potential PPD for the base stocks but the polymer prepared by microwave method is better compared to thermally made polymer.

1.1.6. Conclusion

Comparison on the basis of PPD properties, thermal stability and on the basis of determined VI of the additive blended base oil indicated that the performance of the additive prepared by microwave method is better than that prepared by thermal method. However, both of them are found more or less equally effective as thickeners for the base oils studied. In general, it is observed that, the values of viscosity index and pour point increases with increasing concentration of the additives whereas the thickening power decreases. The studies also indicate that VI values of the additive doped base oils depend on the composition of the base oil. Comparison indicates that MW assisted synthetic method is more economical and may be considered as a greener approach for synthesis of lube oil additive.

1.1.7. Tables and Figures

Tables

Table 1.1. TGA data of polymyristyl acrylate prepared by thermal and microwave induced methods

Sample	Decom. Temp., ^{o}c	PWL
P-1	250/360	12/82
P-2	277/395	14/91

Decom.Temp. Decomposition temperature, *PWL* Percent Weight Loss, P-1 thermally prepared polymer P-2 microwave induced polymer

Table 1.2. Intrinsic viscosity values of polymyristyl acrylates (P-1 and P-2)

Sample	$[\eta]^{a}_{h}$	$[\eta]^{a}_{k}$	$[\eta]^{a}_{m}$	$[\eta]^{a}_{sb}$	$[\eta]^{b}_{sb}$	$[\eta]^{b}_{sc}$	$[\eta]^{b}_{dc}$
P-1	5.397	5.547	5.748	5.873	5.718	5.733	6.097
P-2	5.565	5.717	5.936	6.2	5.878	5.9	6.288

a- viscometric method; *b-* single point determination method; h, k, m, sb, sc and dc refers Huggins, Kraemer, Martin, Schulz- Blaschke, Solomon-Ciuta and Deb-Chatterjee equations respectively

Table 1.3. Viscometric constant values of polymyristyl acrylate samples. k_h, k_k, k_m and k_{sb} are Huggins, Kraemer, Martin and Schulz- Blaschke coefficients respectively

Sample	k_h	k_k	k_m	sky	$k_h+ k_k$
P-1	0.494	0.108	0.316	0.23	0.602
P-2	0.497	0.106	0.316	0.228	0.603

Table 1.4. Molecular weight values (g/mole) of P-1 & P-2 determined by Mark-Houwink equation $[\eta] = KM^{a}$ where, K = 0.00387 and a =0.725

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	21735	22573	23709	24423	23538	23623	25717
P-2	22674	23532	24785	26318	24451	24578	26834

h, k, m, sb, sc, dc refer to the Huggins, Kraemer, Martin, Schulz- Blaschke, Solomon- Ciuta and Deb – Chatterjee respectively. a- extrapolation of graph, b- single point determination

Table 1.5. Base oil properties

Properties	BO1	BO2	BO3
Density ($g.cm^{-3}$) at 40^0C	0.84	0.94	0.97
Viscosity at 40^0C in cSt	6.7	24.229	110.053
Viscosity at 100^0C in cSt	1.77	4.016	10.526
Viscosity Index	80.05	89.02	82.01
Cloud Point,^{0}C	-10	-8	-8
Pour Point,^{0}C	-3	-6	-6

Table 1.6. Thickening Properties of P-1 and P-2

Sample	Base Oil	Additive doped base oils				
		1%	2%	3%	4%	5%
P-1	BO1	16.71	11.49	9.68	8.66	8.52
	BO2	5.59	4.85	4.5	4.17	4.03
	BO3	1.79	1.67	1.49	1.35	1.3
P-2	BO1	7.8	5.64	4.99	4.43	4.39
	BO2	1.05	1.42	1.82	2.04	2.2
	BO3	0.28	0.38	0.45	0.5	0.55

Table 1.7. Viscosity Index Values of P-1 and P-2

Sample	Base Oil	Additive doped base oils				
		1%	2%	3%	4%	5%
P-1	BO1	122.7	135.9	148.8	159.3	161.8
	BO2	118.8	130.7	137.5	146.9	154.1
	BO3	91.71	102.5	109.9	118.4	124.3
P-2	BO1	123	142.1	154.9	162.7	167.7
	BO2	118.9	131.9	141.3	150.1	157
	BO3	92.08	103	111.2	120.2	126

Figures

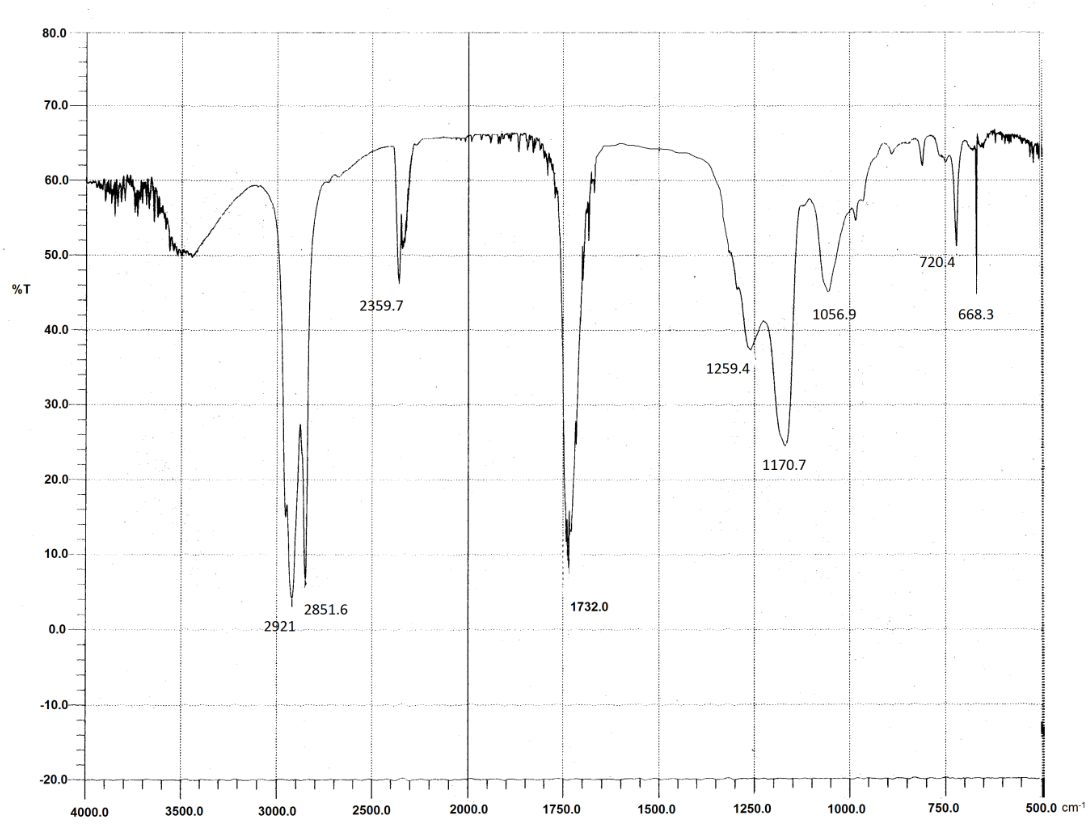


Figure 1.1. FT-IR spectra of thermally prepared polymyristyl acrylate (P-1)

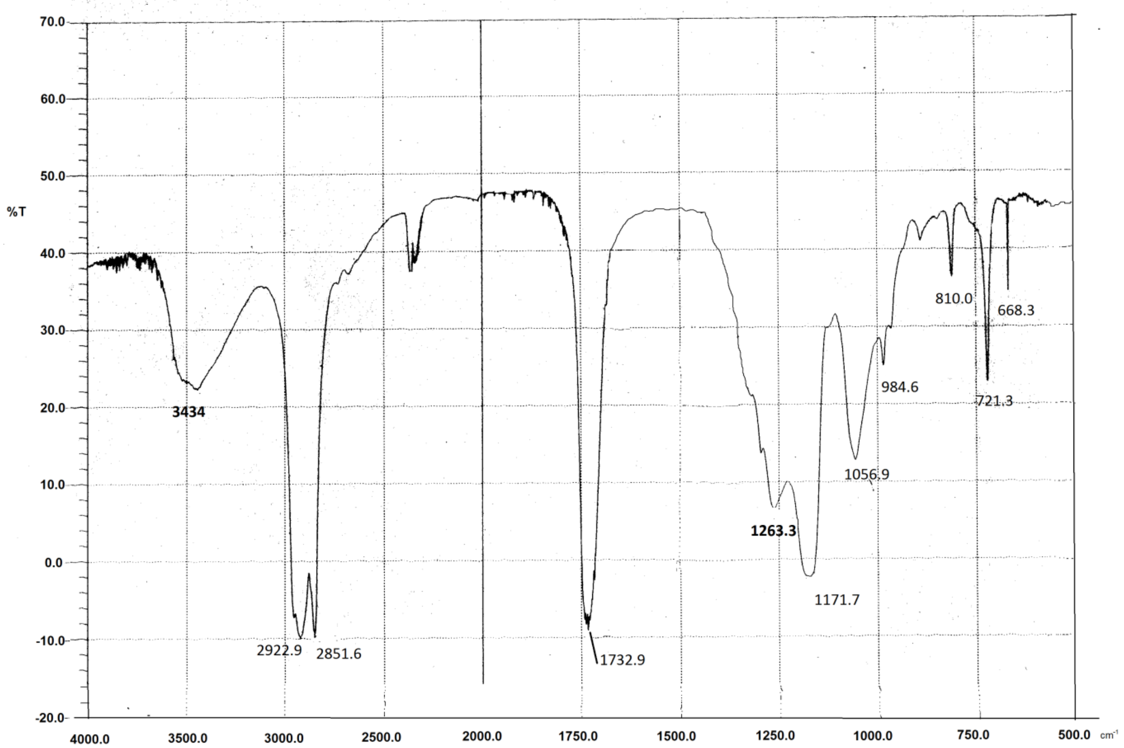


Figure 1.2. FT-IR spectra of polymyristyl acrylate prepared by microwave irradication (P-2)

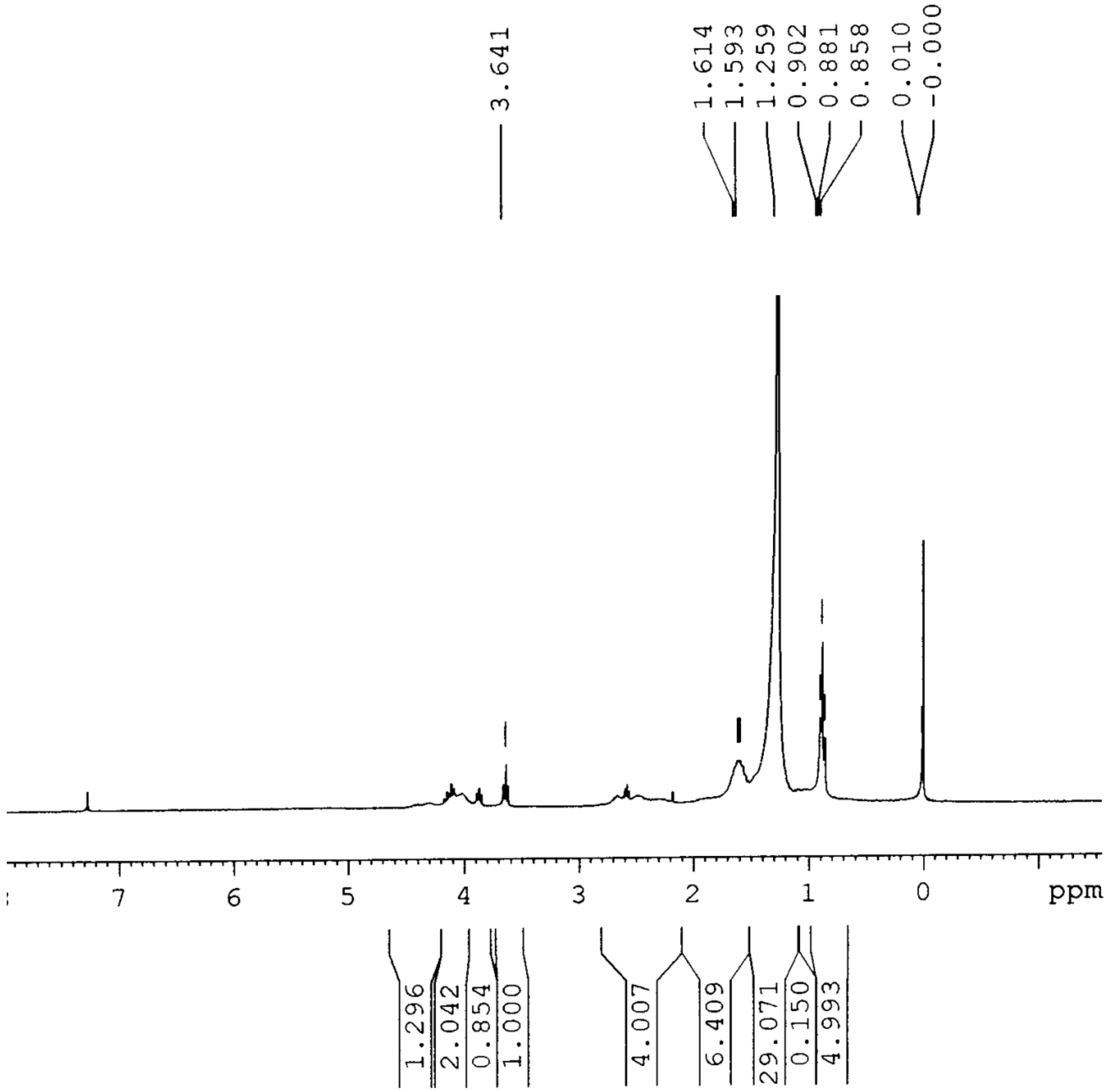


Figure 1.3. ^{1}H NMR of thermally prepared polymyristyl acrylate (P-1)

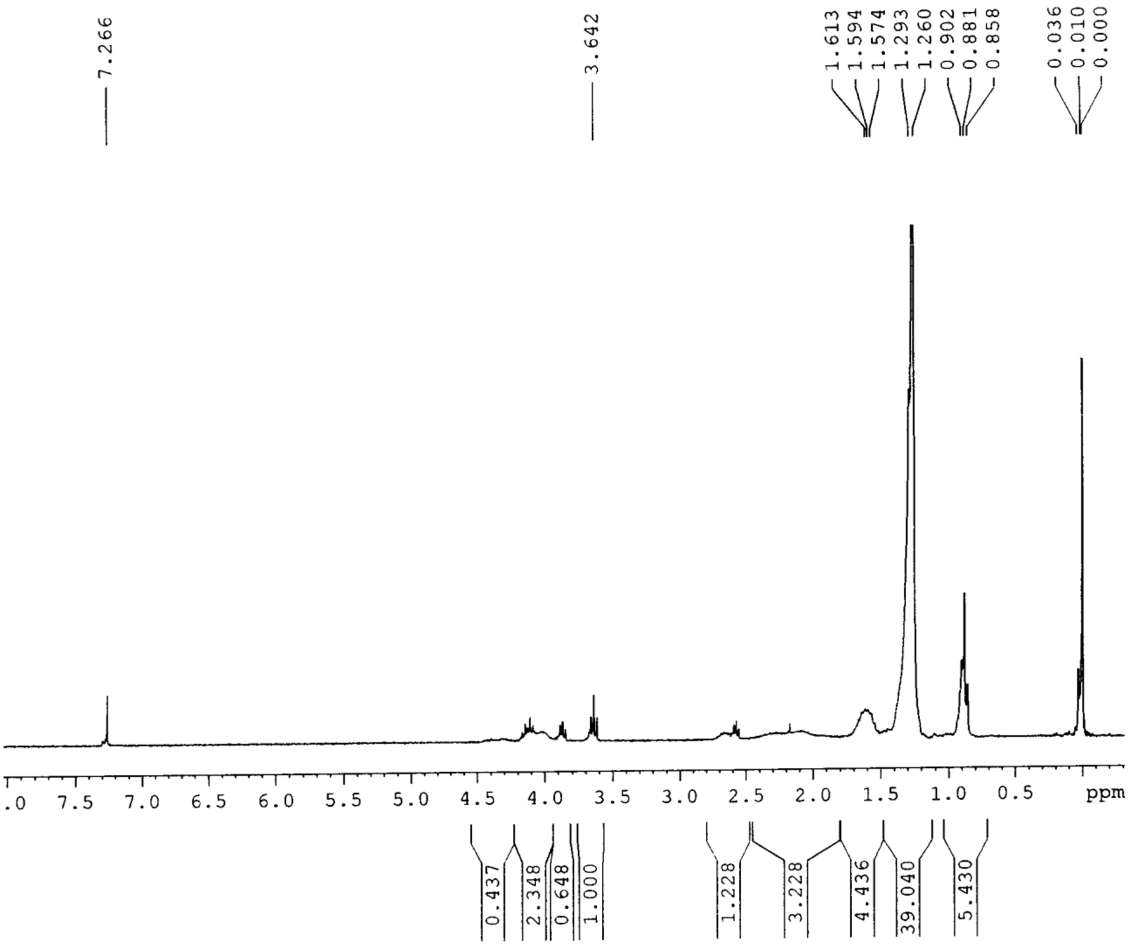


Figure 1.4. ^{1}H NMR of polymyristyl acrylate prepared by microwave irradication (P-2)

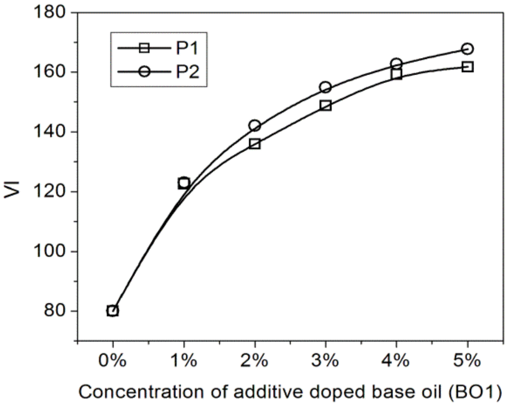


Figure 1.5. Comparison of VI values of the two additives P-1 and P-2 in BO1 base oil.

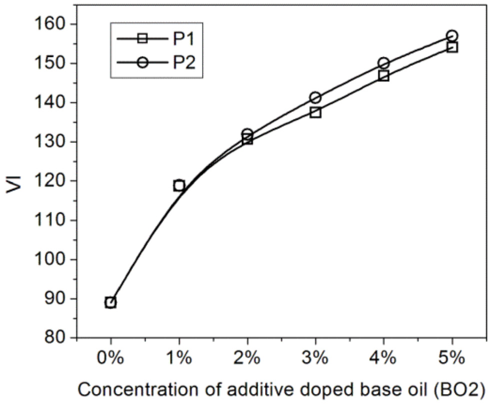


Figure 1.6. Comparison of the VI values of the two polymers P-1 and P-2 in BO2 oil

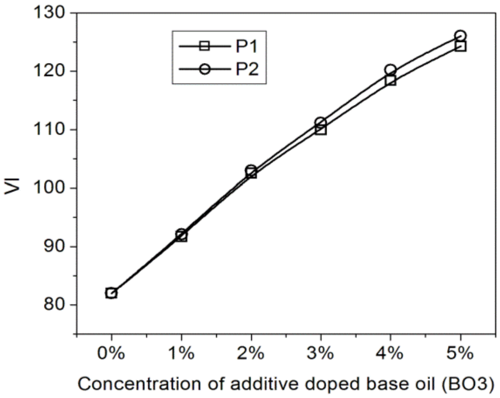


Figure 1.7. Comparison of the VI values of the two polymers P-1 and P-2 in BO3 base oil.

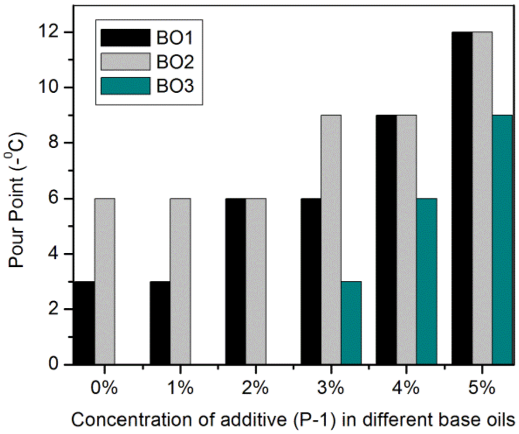


Figure 1.9. Pour Point of P-1 additive doped different base oils

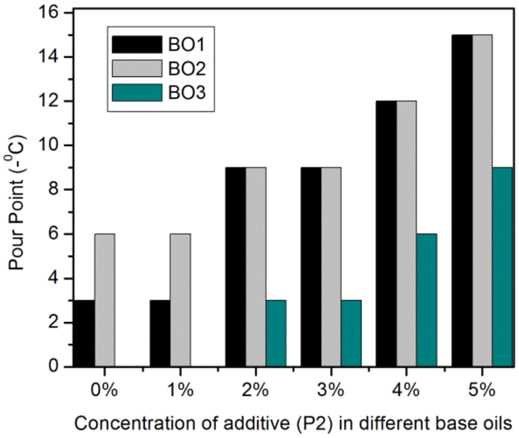


Figure 1.10. Pour Point of P-2 additive doped different base oils

Section B

1.2. Solvent free Microwave Assisted Synthesis of Poly Myristyl Acrylate -Characterization and Evaluation as Additives for Lubricating Oil

1.2.1. Introduction

Microwave irradiation is a well-known method for heating and drying materials and is utilized in many private households and industrial applications for this purpose. Both organic and inorganic reactions undergo an immense increase in reaction speed under microwave irradiation compared with conventional heating.[13]Significant improvements in yield and selectivity have also been observed as a consequence of the fast and direct heating of the reactants themselves. Furthermore, high-pressure synthesis is easily accessible for reactions performed in closed vessels, facilitating the use of low boiling solvents and thereby paving the way to environmentally benign reaction conditions.

With this view in mind and as a part of our ongoing studies on the development of polymeric additives for lube oil, we have undertaken the synthesis of the present acrylate based lube oil additive under microwave condition rather than thermal condition. Nature and morphological aspects of the polymers were tested by their characterization and performance evaluation in lube oils. The results of the present investigation involving the synthesis, characterization including viscometric measurements, evaluation of performance as PPD and VI improvers or viscosity modifier (VM) along with the thickening properties of the mixed acrylate in different base oils have been discussed in this paper.

Physical characterization of the polymers was carried out employing spectroscopic (IR and NMR) techniques and thermo gravimetric analysis (TGA). The behavior of the polymeric additives towards a specific solvent / base stock plays a significant role in their action as a performance additive in their end application. Viscometry provides very important data about the interaction of additive in base fluid and hence conformation of polymeric system in the base stock. In addition, because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from other techniques, generally in determination of molecular mass of samples with the available literature value of the constants used in the particular equation. Hence viscometric study of the additives in base oils has been included in the present study.

The relationship between viscometric molecular weight and intrinsic viscosity [η] can be obtained by the Mark-Houwink-Sakurda (MHS) equation:

$$[\eta] = KM^{a} \tag{1}$$

Where, [η] is the intrinsic viscosity in dL g^{-1}, M is the viscosity-average molecular weight, and K and *a* are viscometric constants for given solute-solvent system and temperature. The higher the molecular weight, the more viscous the polymer solution will be. This is reasonable, when a polymer has a higher molecular weight, it has a bigger hydrodynamic volume; that is, the volume that the coiled up polymer takes up in solution. Being bigger, the polymer molecule can block more motion of the solvent molecules. It might be said that it can block off more lanes of the highway. Also, the bigger a polymer is, the stronger its secondary forces are. So the higher the molecular weight, the more strongly the solvent molecules will be bound to the polymer. This enhances the slowing-down of the solvent molecules. A number of mathematical relations are available in the literature for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation method as explained in sec A of this chapter. The most commonly used equations are:

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

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

Where, $\eta_r = t/t_0$ = time of flow of the solution /time of flow of the pure solvent = relative viscosity or viscosity ratio

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

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

$[\eta]_k$ = intrinsic viscosity, respective to Kraemer equation. k_h, k_k are Huggins, Kraemer coefficients, respectively. The use of these equations have been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$.[19]

1.2.2. Experimental

Materials

The materials used for this work were same as previous work described in sec A.

Preparation of monomer acrylate ester

The ester was prepared by reacting 0.5 mole of acrylic acid with 0.5 mole myristyl alcohol. The reaction was carried out in a resin kettle in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid and toluene as a solvent in nitrogen atmosphere. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403 K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water.

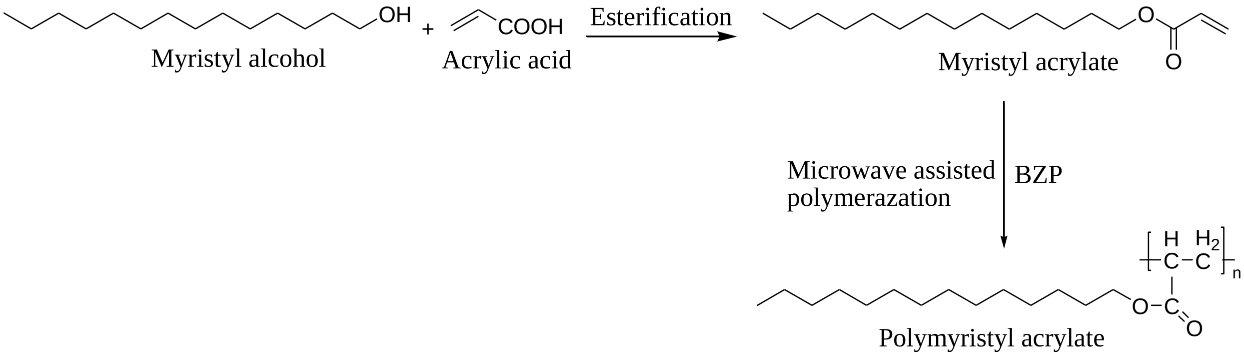
Purification of the prepared acrylate ester

The prepared ester was purified by the method as described in section A of this chapter.

Microwave assisted polymerization

Polymerization of myristyl acrylate, showed in Scheme 1, by microwave irradiation was carried out in a focused mono-mode microwave oven (CEM Corporation, Matthews, NC) in six different reaction times applying 300 WT at 90^0 C without any solvent by adding 0.01% (w/w) BZP as initiator. Hence six different homo polymers of myristyl acrylate, P-1, P-2, P-3, P-4, P-5, and P-6 correspond to reaction times 25 min, 20 min, 15 min, 10 min, 8 min and 2 min respectively are obtained.[20]

Reaction Scheme



Scheme 1. Polymerization of myristyl acrylate prepared from myristyl alcohol and acrylic acid by esterification

1.2.3. Measurements

Spectroscopic measurements

IR spectra were recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range 400 to 4000 cm^{-1}. NMR spectra were recorded in Brucker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. $CDCl_3$ was used as solvent and TMS as reference material.

Viscometric measurements

Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out followed by the procedure as discussed Sec A of this chapter. For determination of viscosity-average molecular weight, the constants K = 0.00387 dl/g and a = 0.725 were employed in Mark Houwink – Sukurda relation (Equation 1).

Thermo gravimetric analysis (TGA)

The thermograms in air were obtained on a mettler TA – 3000 system, at a heating rate of 10^{o}C / min.

1.2.4. Performance Evaluation

Evaluation of viscosity index

Viscosity index of the prepared homopolymers were evaluated in different base stocks (ASTM D 2270-87) from the kinematic viscosity values of the polymer blended base oils at 40^{0} C and 100^{0} C.[22] Effect of additive concentrations on the viscosity index of the lubrication oils was also studied.

Evaluation of thickening property

Kinematic viscosity of the base oils and that of the polymer doped base oils in different concentrations were evaluated. Thickening power of the polymer was determined by evaluating the percent increase in viscosity of the base stocks by the addition of unit amount of additive.[11]

Evaluation of pour point

The prepared additives were evaluated as PPD using base oils (BO1, BO2 and BO3) through the pour point test according to the ASTM-D97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentrations. The experimental data were noted by taking an average of three experimental results under identical conditions.

1.2.5. Results and Discussions

The IR absorption at 1737.7 cm^{-1}, 1733.9 cm^{-1}, 1734.9 cm^{-1}, 1732.9 cm^{-1}, 1732 cm^{-1}, and 1730 cm^{-1} for P-1, P-2, P-3, P-4, P-5, and P-6 respectively showed the presence of ester carbonyl group in them. The broad peaks in the range 1170.7 cm^{-1} to 1190 cm^{-1} for the six homopolymers were due to the ester C-O stretching vibration and peaks in the range 1059.8 cm^{-1} to 668.3 cm^{-1} for C-H bending vibrations. Peaks in the range 1635.5 to 1465.8 cm^{-1} for P-6 indicates the presence of double bond i.e. incomplete polymerization of that additive (Figure 1.11). In Figure 1.2 (mentioned previously) the FT-IR spectra of polymyristyl acrylate prepared by microwave irradiation method has mentioned. The ^{1}HNMR signal in the range δ 3.615 to 4.430 ppm indicates the presence of $–OCH_2$ group of acrylate chain. Absence of peak between δ 5 and δ 6 ppm for P-1 to P-5 polymers indicates the absence of olefinic double bond i.e. effective polymerization whereas the appearance of peaks in the range 1635.5 to 1465.8 cm^{-1} in its IR spectra (Fig. 1.11) supported by the presence of peaks in the range δ 5.775 to 6.416 ppm (Fig 1.12) for P-6 indicates the presence of double bond i.e. incomplete polymerization of that additive.

This implies that the polymerization of myristyl acrylate was not completed at 2 min reaction condition. From this we can say that reaction time below 8 min is not enough for effective polymerization and better results are obtained in the range of 10 –15 min reaction time.

TGA data (Table 1.8) showed that the polymers prepared in the range of 10 -15 min reaction are also better in thermal stability.

The intrinsic viscosity values of the polymers obtained from the equations [Eqs. (2) and (3)] are given in Table 1.8. The higher values imply fairly strong interaction with the solvent. A gradual decrease of the intrinsic viscosity values from P-1 to P-6 indicate that the extent of interaction of each of them with solvent also decreases. k_h values of the polymers from P-1 to P-4 also indicate good salvation which is further supported by the $k_h + k_k$ values, and thus point towards the formation of the chain like structure of the present polymer as discussed earlier.[17] The molecular weights (viscosity average) obtained by Mark-Houwink equation using intrinsic viscosity obtained from the two equations also showed in Table 1.8. A gradual decrease in molecular weight from P-1 to P-6 indicates that at low reaction time the extent of polymerization is low. VI and Thickening power of the homopolymers as evaluated in different base stocks (Table 1.5, sec A) are shown in Table 1.9. In case of P-6 there is no significant improvement of thickening value so it is not shown in the Table 1.9. The data indicates that the VI value increases with increasing the concentration of the prepared additives from P-1 to P-5[24] where as in case of P-6 the VI values decrease. And it was also observed that the VI values of P-4 are higher compared to the other polymers for all additive concentrations in BO1 base oil and at higher concentrations in BO2 base oil (Fig. 1.13). From these values we can say the 15 to 10 min reaction time is ideal for the preparation of the additive. The decrease in VI for P-6 can be explained that 2 min reaction time is not suitable and the additive cannot boost the base oil properties. This is because of the fact that below 10 min reaction time the degree of polymerization decreases and showed minimum at 2 min reaction time.

PPD properties of the polymers (Table 1.10) as evaluated in different base stocks showed a good depression (except P-6) in the base stocks studied. It was found that the efficiency increases by increasing concentration of the additives and P-4 polymer showed better depression in pour point compared to the others. P-3 polymer show almost similar depression in pour point with P-4. But in case of P-6 the pour point of the base oils increases which was not intended.

1.2.6. Conclusion

Considering the performance of the additives it is observed that 10-15 min reaction time under microwave irradiation process showed better result. A gradual decrease in molecular weight (viscosity average) from P-1 to P-6 indicates that at low reaction time the extent of polymerization is relatively low. The study also indicated that the values of VI increase with the increase in concentration of the prepared additives from P-1 to P-5 (P-6 showed very low VI values). It was also observed that the VI values of P-4 are higher compared to the other polymers in the whole range of additive concentrations in BO1 base oil and at higher concentrations in BO2 base oil. From these values it can be concluded that 10 to 15 min reaction time would be ideal for the preparation of the additive under microwave irradiation process. PPD properties of the polymers (Table 4) as evaluated in different base stocks showed a good depression (except P-6) in the base stocks studied and in general the efficiency increases with the increase in additive concentration of the additives in the base oils.

1.2.7. Tables and Figures

Tables

Table 1.8. TGA values, Intrinsic Viscosity, Vicometric Constant and Molecular Weight Values (g/mole) Determined by Mark-Houwink Equation, $[\eta] = KM^{a}$ where, K = 0.00387 and a =0.725

Samples	TGA Data		Intrinsic viscosities		Viscometric constants			Molecular weight values	
	Decom. Temp., ^{o}C	PWL	$[\eta]_h$	$[\eta]_k$	k_h	k_k	k_h+k_k	M_h	M_k
P-1	240/370	25/95	6.788	6.682	0.372	0.125	0.497	29821	29181
P-2	250/380	16/96	6.089	6.12	0.42	0.12	0.54	25670	25851
P-3	265/387	15/90	6.072	6.204	0.366	0.148	0.514	25310	26341
P-4	277/395	14/91	5.565	5.717	0.497	0.106	0.603	22674	23532
P-5	245/360	27/94	4.493	4.702	0.574	0.092	0.666	16879	17971
P-6	210/300	30/98	3.29	3.386	0.557	0.078	0.635	10982	11426

h, k refers to Huggins and Kraemer Equations Respectively; PWL is Percent Weight Loss and Decom.Temp. is Decomposition Temperature

Table 1.9. Viscosity Index (VI) and thickening (THK) values of the additive doped base oils

Sample	Base Oil	Additive doped base oils									
		Conc. in ppm ($\times 10^3$)									
		1		2		3		4		5	
		THK	VI	THK	VI	THK	VI	THK	VI	THK	VI
P-1	BO1	14.73	122.44	10.83	135.99	8.79	149.99	8	155.18	7.98	159.47
	BO2	5.18	118.08	4.4	129.83	4.06	137.49	3.86	147.44	3.87	153.83
	BO3	1.61	92.09	1.43	103.01	1.27	110.89	1.23	119.08	1.18	124.85
P-2	BO1	13.33	122.39	8.73	141.35	7.69	151.06	6.94	155.55	7.17	161.26
	BO2	2.79	119.25	3.16	130.36	3.24	139.06	3.26	148.64	3.35	154.91
	BO3	0.97	92.22	0.85	103	0.9	111.02	0.98	119.38	1.02	125.07
P-3	BO1	9.32	122.76	6.71	141.58	6.27	153.54	6.1	156.65	5.6	162.82
	BO2	1.5	119.63	2.08	131.11	2.41	140.22	2.68	149.45	2.89	155.75
	BO3	0.46	92.39	0.57	103.08	0.58	111.45	0.65	120.06	0.67	125.87
P-4	BO1	7.8	123.01	5.64	142.09	4.99	154.93	4.43	162.7	4.39	167.71
	BO2	1.05	118.91	1.42	131.86	1.82	141.29	2.04	150.05	2.2	157.02
	BO3	0.28	92.08	0.38	103	0.45	111.17	0.5	120.2	0.55	126.02
P-5	BO1	5.7	122.65	3.27	141.55	4.32	152.78	3.89	160.86	3.84	166.49
	BO2	0.87	113.82	0.96	126.48	1.36	139.97	1.69	148.9	1.97	155.16
	BO3	0.16	90.33	0.29	101.34	0.36	110.43	0.45	119.38	0.46	125.07
P-6	BO1	-	73.11	-	71.72	-	63.63	-	60.37	-	54.93
	BO2	-	85.32	-	84.19	-	83.46	-	81.56	-	78.2
	BO3	-	81.17	-	80.68	-	79.22	-	78.01	-	77.44

Table 1.10. Pour points of the polymeric additives in different base oils

Polymers	Base Oils	Pour Points of the Additive Doped Base Oils					
		Conc. in ppm (×10^3)					
		0	1	2	3	4	5
P-1	BO1	-3	-3	-3	-6	-6	-9
	BO2	-6	-3	-3	-6	-9	-9
	BO3	0	0	0	-3	-3	-6
P-2	BO1	-3	-3	-6	-6	-9	-9
	BO2	-6	-3	-3	0	-3	-6
	BO3	0	0	-3	-3	-6	-9
P-3	BO1	-3	-3	-9	-9	-12	-12
	BO2	-6	-6	-9	-9	-12	-15
	BO3	0	0	-3	-3	-6	-6
P-4	BO1	-3	-3	-9	-9	-12	-15
	BO2	-6	-6	-9	-9	-12	-15
	BO3	0	0	-3	-3	-6	-9
P-5	BO1	-3	-3	-3	-6	-6	-9
	BO2	-6	-6	-9	-9	-12	-12
	BO3	0	0	0	-3	-3	-6
P-6	BO1	-3	-3	0	0	3	3
	BO2	-6	-3	-3	0	0	3
	BO3	0	0	0	3	3	3

Figure

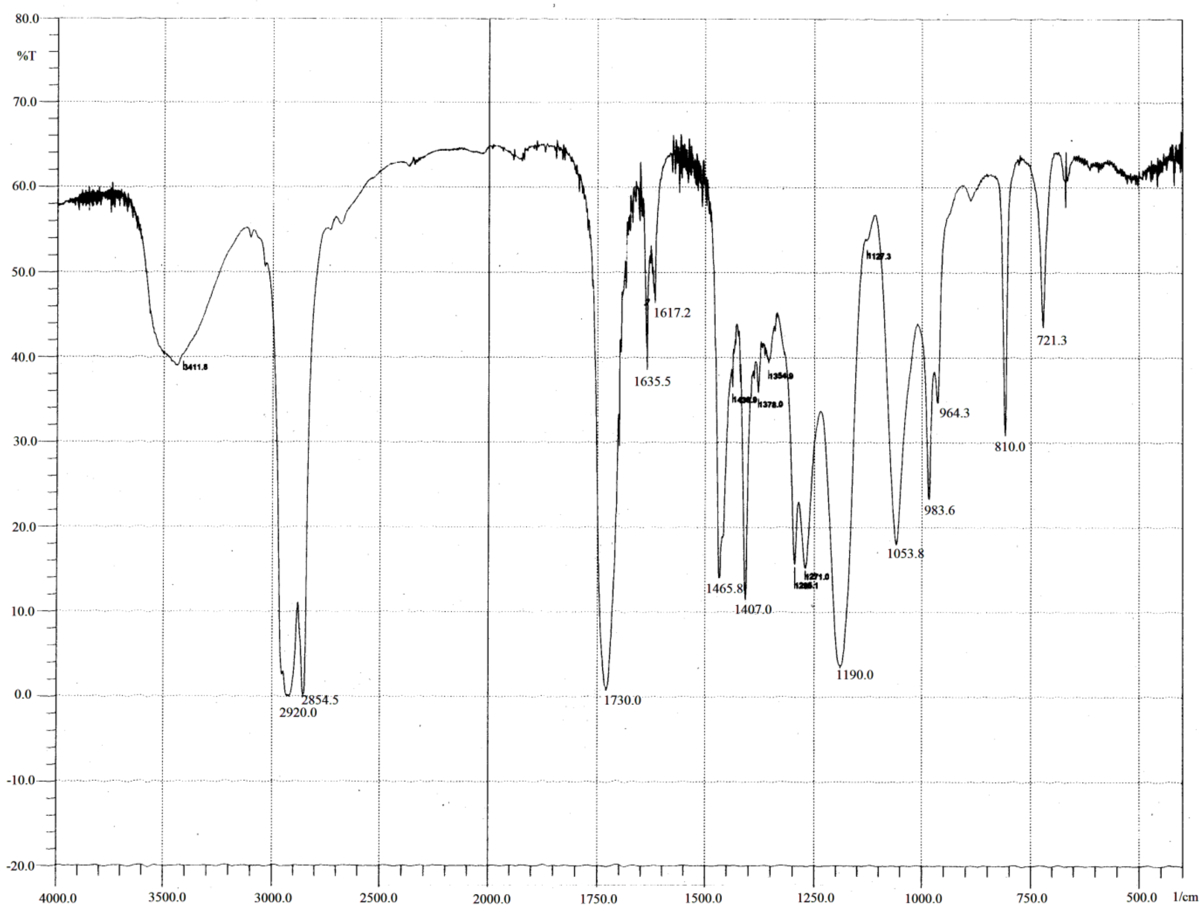
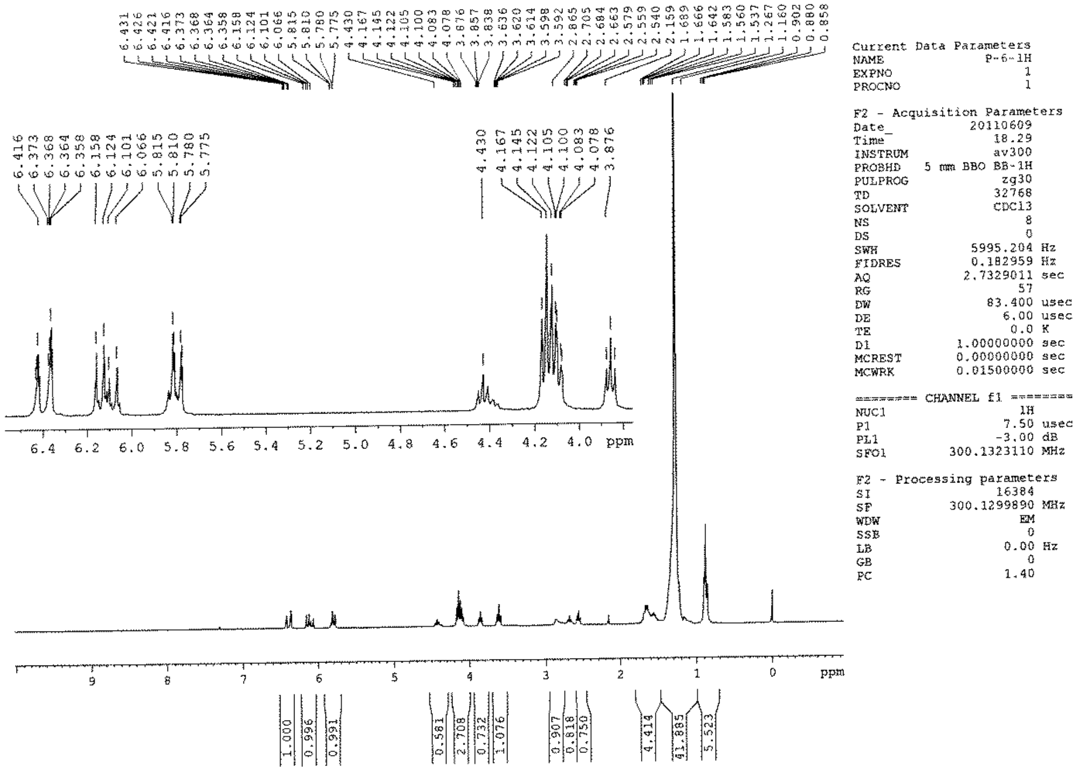


Figure 1.11. FT-IR of Polymyristyl acrylate (P-6) prepared by microwave irradiation (2 min)



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Current Data Parameters
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EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110609
Time                18.29
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PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              5995.204 Hz
FIDRES           0.182959 Hz
AQ              2.7329011 sec
RG                     57
DW                 83.400 usec
DE                   6.00 usec
TE                    0.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                 -3.00 dB
SFO1          300.1323110 MHz

F2 - Processing parameters
SI                  16384
SF            300.1299890 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.40
```

Figure 1.12. ^{1}H NMR spectra of Polymyristyl acrylate (P-6) prepared by microwave irradiation (2 min)

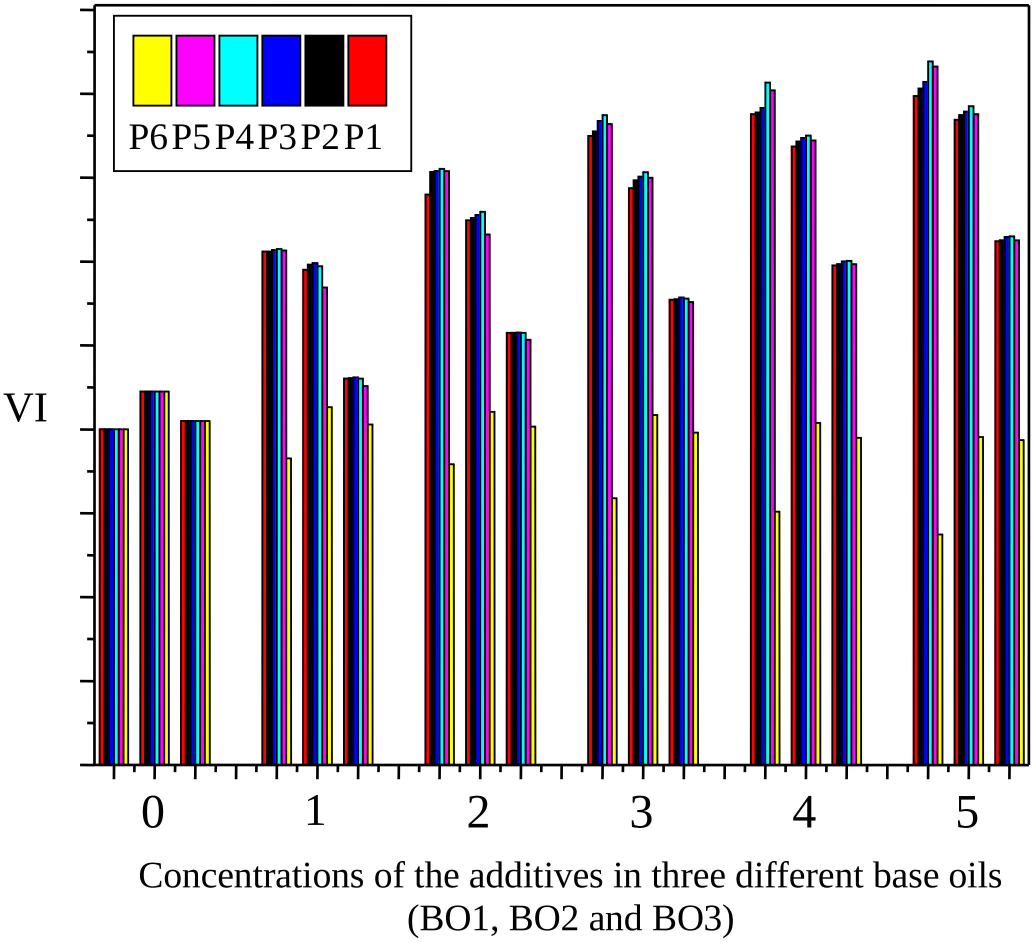

Figure 1.13. VI values in different concentrations of the additive doped base oils. The three groups of columns for each concentration are for three different base oils respectively, different colors indicate different additives.

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PART – II

Biodegradable Polymeric Additives based on Vegetable Oil

2. Background of the present investigation

The increasing focus towards diminishing the impact on environment has driven efforts to develop new, environmentally benign lubricating oil additives. Although synthetic acrylate based additives exhibit satisfactory performances, they are not eco-friendly. Hence research in the area towards the synthesis of bio lubricating oil additive is increasing day by day. But reports are still scanty regarding the biodegradability of the additive used.

Vegetable oils can offer significant environmental advantages with respect to resource renewability, biodegradability,[1] as well as at the same time displaying satisfactory performance in a variety of applications.[2]

Vegetable oils show very high VI [3] and excellent tribological properties such as friction-reducing, wear controlling and improved extreme pressure [4, 5] when used as base stocks or as additive. Generally vegetable oils do not exhibit good pour point values but by means of chemical modification the pour point values can be significantly increased.[6] Lubricant and additives may be petroleum, synthetic, or biological in origin. The lubricants of biological origin include vegetable oils and animal fats that are obtained from seeds, fruits, and animal tissue. Vegetable oils are obtained from renewable resources and are biodegradable. Thus they offer specific environmental benefits over mineral oil-based lubricants. This is significant in applications where the lubricant is lost in the environment, e.g., chain bar lubricants and hydraulic fluids for farm machinery. In addition to environmental benefits, vegetable oils also have certain performance advantages over conventional mineral base stocks.[4, 7] These include low volatility, high viscosity index, and excellent lubricity. Vegetable oils present higher flash point than mineral oils, which always a concern with flammable liquids; they are also safer to humans. Vegetable fats and oils (known by the generic term lipids) comprise, primarily triglycerides, that is, tri esters of long chain carboxylic acids combined with glycerol. Most of these oils contain at least four and sometimes as many as 12 different fatty acids.[8] A general structure of vegetable oil is shown in Figure 3.1. The long chains are the three major constituents of unsaturated long chain fatty acids e.g. linoleic acid, oleic acid and linoleic acid.

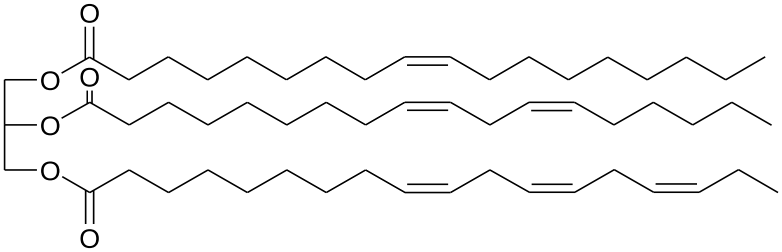

Figure 3.1. General structure of vegetable oil

Vegetable oils are usually good boundary lubricants but the major limitations are their high cost, thermal and oxidative instability. Oxidation stability of vegetable oils depends on the level of unsaturated products present. For good performance, special lubricants requirements must be fulfilled, i.e. good corrosion protection, compatibility with other materials, fair oxidative and hydrolytic stability and low temperature behavior associated with the triglyceride. There are lots of references where vegetable oils are as lube oil additive additives.[9, 10]

In recent publication Franco et al has reported the use of sunflower oil bio fuels, polymeric additives such as ethylene vinyl acetate (EVA) and styrene butadiene styrene (SBS) copolymer in lubricant formulation.[11]

US Patent No 4970010 in the year 1990 has described the use of vegetable oil derivatives as lubricating oil additive. US Patent 6534454 B1 in the year 2003 discussed about the biodegradable vegetable oil composition for lubricant. US Patent 5282989, dated 1994, disclosed the use of sulfurized vegetable oil as lube oil additive (as extreme pressure). US Patent 4925581 (1990) claimed the application of meadowfoam oil and meadofoam oil derivatives as lubricant additive. Sulfurised vegetable wax esters were described in US pat. No. 4152278 to act as an anti wear, friction modifier and extreme pressure additive. The synthesis and evaluation of vegetable oil based lubricant additive which can be used as thermal oxidative stability enhancers and viscosity improvers has discussed in Us pat. No 5229023. US pat. No. 4873008 has described the synthesis and jojoba oil based lube oil additive. Recently in the International Conference on Chemical Processes and Environmental issues (ICCEEI'2012) held on July 15-16, 2012 at Singapore the synthesis of pour point depressant from sunflower oil has been discussed. Thus there exists an ample opportunity to work on this area in order to develop environmental benign lube oil additives with better performance than the conventional synthetic chemical based additive.

From the above literature work the author has felt necessary to undertake a systematic study towards the synthesis, characterization and performance evaluation (mainly PPD, VII and antiwear) of some polymeric additives based on vegetable oil (sunflower oil and soybean oil) for lubricating oil. In order to study the morphological features of the additives in a solvent viscometric analysis were also investigated in my work.

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Chapter II

1.2. Evaluation of Sunflower Oil as a Multifunctional Lubricating Oil Additive

2.1.1. Introduction

The widespread use of nonbiodegradable, synthetic (mainly acrylate-based) polymeric additives has raised many environmental concerns. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. Viscosity index improvers, antifoaming agents, emulsifiers, demulsifiers, and pour-point depressants are example of different kinds of additives. Most of the present day additives are synthetic acrylate based. Due to increasing environmental pollution the direction towards the development of environmentally benign green polymeric additive in the lubricant chemistry is increasing day by day. There are lots of examples where biodegradable vegetable oils[1, 2, 3] are used for the synthesis of such type of polymeric additives. The present investigation comprises the synthesis of a biodegradable multifunctional lubricating oil additive and evaluation of its additive performance in base oils. Sunflower oil has excellent tribological properties and predominantly polyunsaturated fatty acid composition (Table 3.1). Hence in my present work chemistry of biodegradable multifunctional lubricating oil additive based on vegetable oil (sunflower oil) has been investigated. In the present work solvent free synthesis of homopolymer of sunflower oil (SFO) was performed by two different ways; microwave (MW) assisted method and thermal method using benzoyl peroxide (BZP) as initiator. Characterization of the polymers was done by spectral (NMR, IR), GPC and viscometric analysis and finally performance evaluation was tested by standard ASTM methods. In this work homopolymer of sunflower oil was synthesized without adding any solvent by thermal as well as a greener way, microwave assisted method. Their characterization and finally additive performances for their end application were observed by standard ASTM methods.

2.1.2. Experimental

Materials

Refined sunflower oil (almost 87% unsaturation) was collected from S K Oil Industries (India) and used as such. BZP (GC 98%), obtained from Loba Chemie Pvt. Ltd. (India), was recrystallised from $CHCl_3$-MeOH before use. Base oils (BO1 and BO2) were collected from Indian Oil Corporation Limited (IOCL), Dhakuria, West Bengal, India. The fungal specimens were collected from Department of Microbiology, North Bengal University, West Bengal, India.

Thermal polymerization of SFO

Synthesis of homopolymer of SFO (P-1) by thermal method was performed at 90^o C in a four necked round bottom flask for 6 h without adding any solvent. The flask was fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. In this reaction BZP was used as initiator. To terminate the polymerization the reaction mixture was poured into methanol with stirring until the precipitation was completed. It was then purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 40^o C.

Microwave assisted polymerization of SFO

Polymerization of SFO by microwave assisted method[4] was performed in a focused mono-mode microwave oven (CEM corporation, Matthews, NC) applying 300

WT for 30 minute at 90^o C by adding 0.01% (w/w) BZP as initiator. The polymerization process was performed without adding any solvent. The polymer obtained (P-2) was gradually cooled and confirmed by spectral evidences.

Determination of average molecular weight

The average molecular weight of the additives was determined by viscometric method and GPC method. In GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were measured. THF of HPLC grade was used as mobile phase in the Water GPC system (polystyrene calibration) at 40^o C. In viscometric method the viscosity average molecular weight (M) was calculated using Mark Houwink–Sukurda relation (MHS) (Eq. 1) by Ubbelohde OB viscometer at 40^o C taking eight different concentrations (g cm^{-3}) of the polymeric additives in toluene.[5,6] Chronometer was used for recording flow times. The intrinsic viscosity of the additives which is required for their average molecular weight calculation by MHS equation was evaluated by graphic extrapolation method [7, 8, 9] using the equations as discussed in chapter II, sec A (part-I).

MHS equation: $$[\eta] = KM^a \tag{1}$$

The relationship $k_h + k_k = 0.5$ [9] has taken into account to predict the extent of interaction among the polymer and base oil.

2.1.3. Measurements

Spectroscopic measurement

The IR absorption were recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range 400 to 4000 cm^{-1}. 1H NMR spectra were recorded quantitavely in Brucker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. The sample solutions were prepared in deuterated chloroform ($CDCl_3$) and TMS was used as reference material.

Viscometric measurement

Viscometric measurements were carried out at 40^o C in toluene solution using Ubbelohde OB viscometer as per the method discussed in chapter II (sec A), part-I.

Thermal stability measurement by thermo gravimetric analysis (TGA)

The thermal stability was measured in terms of percent degradation of weight of the polymers with the increase in temperature (10^o C/min) by Shimadzu TGA-50 thermobalance in air using an alumina crucible.

Solubility Analysis

Solubility of the prepared polymers in lube oil is a very important factor for their performance evaluation as an effective additive. It was investigated before testing their additive properties (VI, PPD, AW). A good solubility indicates better interaction with the base oil as a result of which show better performance. The reverse effect is observed in case of poor solubility of the polymeric additives in base oil. The solubility test took place by dissolving one gram of the polymer in hundred grams of additive free base oils. The (1g / 100g) mixture has been allowed to stand overnight. This time was enough to produce the required swelling for the polymer. The mixture was agitated by a Teflon covered magnetic stirrer for 20 minutes at 60 °C to disintegrate the gel. To test homogeneity and thermodynamic stability of the mixture, viscosity of two different samples from each solution was measured.

2.1.4. Performance Evaluation

The performance of the additives blended with different base stocks as PPD, VII, thickener and AW was evaluated by standard ASTM methods. The base oils, BO1 and BO2, taken for this work are same as taken for polymyristyl acrylate based lube oil work, mentioned in chapter-II (sec A) of Part-I.

Evaluation of thickening property

Kinematic viscosity (KV) of the base oils and that of the polymer doped base oils in different concentrations (2% to 5%, w/w) were evaluated at 40^{o} C according to ASTM D445-12 method. Thickening power of the polymer was determined by evaluating the percent increase in viscosity of the base stocks by the addition of unit amount of additive.

Evaluation of pour point

The pour point of the base oils (BO1, BO2 and BO3) at different doping concentrations of the additive was evaluated using the WIL-471 cloud and pour point test apparatus model 3 (India) according to ASTM D97-11 method. In order to determine the pour point, the additive is first heated to 45°C in a water bath maintained at 48°C. It is then cooled at a specific rate (by maintaining the specified temperature of the cooling media) and at decrements of 3°C, the container is tilted to check for any movement. The temperature 3°C above the point at which the oil stops moving is recorded as the pour point. As per ASTM D97 method, pour point of mineral oils is defined as the lowest temperature at which movement of the test specimen is observed under the prescribed conditions of the test. In the case of vegetable oils, if the sample is kept under the same condition for an additional period of time, they re-melt and again solidify at a higher temperature. Hence the temperatures of the samples, after 15 minutes of recording the pour point temperatures as described above, are also recorded. As per ASTM D97 method pour points are measured in steps of 3 ºC.

Evaluation of viscosity index

The kinematic viscosities (KV) of the base oils containing different concentrations (ppm) of the additives were determined at 40^0 C and 100^0 C (Table 3.2). Each sample was measured three times in order to minimize the error. Finally, the viscosity index was determined according to ASTM D-2270-10 method.

Evaluation of Permanent Shear Stability Index (PSSI)

Shear stability of the VM is one of the important criteria that determine its suitability in a lubricant formulation. The shear stability of the doped additive has strong influence on multigrade engine oil's ability to retain its viscosity under shearing conditions, experienced by the lubricant while in use. The loss of viscosity of a lubricant under shear can be two kinds, namely a temporary viscosity loss (TVL) or a permanent viscosity loss (PVL).[10] PVL is similar to TVL, except that the viscosity loss is measured by KV before and after shear. The PVL values are more frequently expressed in terms of permanent shear stability index (PSSI) or simply SSI, according to ASTM D6022-01 as follows:

$$\text{PVL (\%)} = (V_i - V_s)/V_i \times 100 \qquad \text{PSSI} = (V_i - V_s / V_i - V_0) \times 100$$

where V_0 = KV of the base fluid before addition of polymer, V_i = KV of unsheared oil, V_s = KV of sheared oil. KV of fresh toluene and sheared polymer solution in toluene was determined by ASTM D- 445 procedure respectively.

Performance as AW

The AW properties were evaluated by FBWT apparatus according to ASTM D 4172-94 method [11] applying two different weld loads, 147 N and 392 N at 75 ^{o} C for 30 min. The rotating speed of the ring was 1200 rpm. The wear scar diameter, show antiwear properties of the oils, was measured adding polymers at different concentration levels.

2.1.5. Biodegradability Test

The microbial degradation of the polymers was tested i) by disc diffusion method [12] against fungal pathogens and ii) by soil burial degradation test as per ISO846:1997.[13] The degradation was confirmed by measuring the shift of IR frequency of the ester carbonyl after the biodegradability test.

Disc Diffusion Method

In this work the biodegradation of the prepared polymer samples were tested against four different fungal pathogens namely *Calletotricheme camellia*, *Fussarium equisitae*, *Alterneria alternate and Colletrichum gleosproides*. All the experiment were performed in petri dishes taking 1.5 g of each of the polymer samples and incubated in a Bacteriological Incubator apparatus at 37^{o} C for 30 days. The All glass apparatus, culture media were autoclaved before use. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. The fungal growth was confirmed by a change of yellow to blackish. After 30 days polymer samples were recovered from the fungal media and washed with chloroform, purified and dried in an open vessel. The dried samples were weighed.

The Soil Burial Test (SBT)

The SBT was conducted as per ISO 846:1997 method. The percentage of degradation of the samples depends on the microbes, pH value and moisture of the soil. Temperature and duration of the experiment also have significant role in the degradation. 1.5 g of each of the additive samples was taken to produce a film and then buried in soil.[14] The soil was collected from North Bengal University campus having 25% moisture and pH 7.2. The test was carried out for 90 days at 38^{o} C with the relative humidity 50% to 60%. After the time period the sample films are recovered, washed (with chloroform), purified and finally dried. The dried samples were weighed. Percentage weight loss (PWL) of the polymeric additives was calculated and given under:

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

Where M_0 is the initial mass and M_1 is the remaining mass after SBT and subsequent drying till constant weight.

2.1.6. Results and Discussion

Spectral Analysis

The IR absorption in the region 1736.8 to 1732 cm^{-1} of the homo polymers of SFO prepared by the two processes showed the presence of ester carbonyl groups. Peaks from 2944.1 to 2851.6 cm^{-1} for C-H stretching and 1454.2 to 1372 cm^{-1} are due to bending vibrations of $-CH_3$ and $–CH_2$ groups. Peaks from 1245.9 to 1069.5 cm^{-1} were due to the ester C-O stretching vibration. The presence of peaks at 1654.8 to 1675 cm^{-1} for olefinic bonds was observed for SFO and their absence indicates the formation of homopolymer. ^{1}H NMR of polymers of SFO showed broad peaks in the range at 4.12 to 4.32 ppm due to ester methylene protons. The proton decoupled ^{13} C NMR of SFO showed peak at 172.9 to 178.7 for protons of $–OCH_2$ groups of the triester. The absence of unsaturation was indicated by the absence of peaks in the range 130 to 150 ppm. The figures from 3.2 to 3.5 clearly showed the IR and NMR spectra of SFO polymers.

The thermal stability obtained from TGA results of the two polymers are shown in Fig. 3.6, where the percent weight loss of the polymers is plotted against increase in temperature (^{o} C). From the figure it is clear that P-2 is thermally more stable compared to P-1.

The intrinsic viscosity values for both the polymers, obtained from two different equations (Eq. 1 and Eq. 2), have little difference. The higher values indicate that both the polymers have fairly strong interaction with the solvent. k_h values also indicate good solvation which is further supported by the $k_h + k_k$ values, and thus point towards the formation of the chain like structure of the present polymer as discussed earlier.[9] Molecular weights (viscosity average, M_n and M_w) for P-1 and P-2 obtained by Mark-Houwink equation and GPC obtained showed excellent correlation (Table 3.3).

Thickening power of both the homopolymers as evaluated in different base stocks indicated a gradual increase with the increase in concentration of the additive (Table 3.4). The result also showed that the thickening power of the P-2 polymer was slightly higher in comparison to the P-1 polymer. This indicates that as far as the fuel economy is concerned the microwave method is better than the thermal method.

The prepared homopolymers were tested for their effectiveness as viscosity index improvers by measuring the VI of the respective additive doped base oils and the values are given in Table 3.4. The test method (ASTM D 2270-10 method) comprises the determination of the KV of the different base oils containing different concentrations of the additives at 40^{o} and 100^{0} C. The data indicates that the VI increases with increasing the concentration of the prepared additives in solution and the VI values of the P-2 polymer are slightly higher in compared to the P-1 polymer in BO1 and BO2 base oils (Figure 3.7). As the temperature is raised, the lube oil viscosity decreases; meanwhile the polymer molecule expands and as a result of which its hydrodynamic volume increases.

The increase in the size of the solvated polymer molecules counterbalance the reduction of the viscosity of the lube oils with temperature.[15] This effect is more pronounced in case of P-2 polymer rather than P-1. The increase in concentration of polymer leads to an increase in the total volume of the polymer micelles in the oil solutions. Consequently, higher concentration of additive will impart higher viscosity index.[16]

Shear stability of both the polymers were evaluated in two base oils (Table 3.5). The stability of the polymers against shear decreases with increasing the PSSI values.[10] It is observed that the PVL values increases with increasing the concentration of polymer and as a result of which the PSSI values also increase. But at higher concentration of the additives the PSSI values decrease. This implies that the stability against shear decreases with increasing the polymer concentration up to a certain limit and at higher concentration it increases. The thermally prepared polymer, P-1 is more shear stable than P-2 (Figure 3.8).

PPD properties of both the polymers (Table 3.6) as evaluated in different base stocks showed a good depression in the base stocks studied. It was found that the efficiency increases by increasing concentration of the additives and P-2 polymer showed better depression in pour point at higher concentrations than that of the P-1. Therefore although both the polymers may be used as potential PPD for the base stocks but the polymer prepared by microwave method is better compared to thermally made polymer.

The AW result (Table 3.7) showed that with increase in the applied load the wear scar diameter decreases and P-2 showed lower scare diameter compared to P-1 in both the base oils(BO1 and BO2). With the increase in concentration of the additives the scare diameter value also decreases. Since larger wear scar diameter indicates severe wear, thus the P-2 additive possessed higher wear resistance properties than P-1 and the base oils.

Analysis of Biodegradability Test Result

Table 3.8 present biodegradability test results obtained by using disk diffusion method and soil burial test method. Polymers of SFO prepared by two different methods showed significant biodegradability against the fungal pathogen, *Alterneria alernata*. Result of soil burial test also indicated the similar extent of biodegradability. It was further confirmed by the shift of IR frequency of the ester carbonyl after the test is over.

2.1.7. Conclusions

Comparison on the basis of PPD properties, AW properties and the determined VI of the additive blended base oils indicated that the performance of the microwave method is better than the thermal method for the additive preparation. However, both of them are found more or less equally effective as thickeners for the base oils studied. The shear stability of P-2 is lower than P-1. In general, it is observed that the values of viscosity index, thickening power and pour point increases with increasing concentration. The studies also indicate that VI values of the additive doped base oils depend on the composition of the base oil. Comparison indicates that MW assisted synthetic method is more economical and may be considered as a greener approach for synthesis of lube oil additive.

2.1.8. Tables and Figures

Tables

Table 3.1. Fatty acid profile of SFO

Fatty Acid (Carbon atoms: Double bonds)	**% Composition (max)**
Saturated	
C 12:0 (lauric acid)	---
C 14:0 (myristic acid)	0.56
C 16:0 (palmitic acid)	6.8 (4-9)
C 18:0 (Stearic acid)	4.2 (1-7)
C 20:0 (arachidic acid)	0.41
Unsaturated	
16:1 (palmitioleic acid)	--
18:1 (oleic acid)	23.3 (14-40)
18:2 (linoleic acid)	60.8 (48-74)
18:3 (linolenic acid)	2.9

Table 3.2. Kinematic Viscosity values of the base oils at different percentage (w/w) of additive concentration at 40 ^{o} C and 100 ^{o} C

Sample	Base Oils	2%		3%		4%		5%	
		KV 40	KV 100	KV 40	KV 100	KV 40	KV 100	KV 40	KV 100
P-1	BO1	7.39	2.24	7.922	2.39	8.22	2.47	8.32	2.49
	BO2	27.6	5.21	28.8	5.51	30.01	5.602	31.51	5.842
P-2	BO1	7.31	2.185	7.51	2.31	8.31	2.61	8.93	2.912
	BO2	27.29	4.92	28.25	5.42	29.82	6.21	31.01	7.18

Table 3.3. Intrinsic Viscosity, Vicometric Constant and Molecular Weight Values (g/mole) Determined by Mark-Houwink Equation and GPC

Samples	Intrinsic viscosities		Viscometric constants			Average molecular weight values			
	$[\eta]_h$	$[\eta]_k$	k_h	k_k	k_h+k_k	M_h	M_k	M_w x10^4	M_n x10^4
P-1	6.784	6.667	0.367	0.126	0.493	29797	29090	3.10	3.02
P-2	6.973	6.762	0.335	0.130	0.465	30949	29661	3.21	3.10

h, k refers to Huggins and Kraemer Equations Respectively

Table 3.4. Viscosity Index (VI) and thickening (THK) values

Sample	Base Oil	Percentage (w/w) of the additives in different base oils							
		2%		3%		4%		5%	
		THK	VI	THK	VI	THK	VI	THK	VI
P-1	BO1	2.761	113	3.822	126	5.177	131	6.208	131
	BO2	1.010	101	1.567	127	2.190	163	3.135	205
P-2	BO1	2.841	121	3.935	131	5.432	128	6.807	131
	BO2	1.093	103	1.619	130	2.259	164	3.198	207

Table 3.5. Shear Stability of the Polymer Doped Base Oil (BO1 and BO2)

Base oils	Conc.	KV				PVL		PSSI	
		Before Shear		After Shear					
		P-1	P-2	P-1	P-2	P-1	P-2	P-1	P-2
BO1	1%	2.125	2.137	2.012	2.011	5.317647	5.896	32.19	34.71
	2%	2.282	2.32	2.105	2.121	7.756354	8.578	34.84	36.45
	3%	2.401	2.428	2.172	2.185	9.537693	10.01	36.52	37.16
	4%	2.515	2.517	2.209	2.208	12.167	12.28	41.3	41.59
	5%	2.588	2.617	2.271	2.282	12.24884	12.8	38.94	39.74
BO2	1%	4.371	4.404	4.214	4.201	3.591855	4.609	44.23	52.32
	2%	4.696	4.729	4.326	4.311	7.879046	8.839	54.41	58.63
	3%	5.116	5.169	4.395	4.401	14.09304	14.86	65.55	66.61
	4%	5.738	5.77	4.562	4.551	20.49495	21.13	68.29	69.5
	5%	6.612	6.656	5.002	5.015	24.34967	24.65	62.02	62.16

Table 3.6. **Pour points of the polymeric additives in different base oils**

Additives	Base oils	Pour points of the base oils doping different percentage (w/w) of additives			
		2%	3%	4%	5%
P-1	BO1	-6	-9	-12	-15
	BO2	-9	-12	-15	-15
P-2	BO1	-6	-9	-15	-18
	BO2	-9	-12	-15	-18

Table 3.7. Anti wear properties of SFO polymer blended base oils

Polymers	Base oils	Wear scar diameter of the base oils at different levels of additive concentrations (in percentage, w/w)									
		Load: 147 ± 2 N (15 ± 0.2 Kgf)					Load: 392 ± 2 N (40 ± 0.2 Kgf)				
		0%	1%	2%	3%	4%	0%	1%	2%	3%	4%
P-1	BO1	0.981	0.955	0.940	0.937	0.934	0.961	0.931	0.925	0.918	0.917
	BO2	1.116	0.996	0.982	0.978	0.973	0.985	0.965	0.957	0.949	0.944
P-2	BO1	0.981	0.951	0.938	0.927	0.921	0.961	0.928	0.922	0.916	0.911
	BO2	1.116	0.982	0.976	0.968	0.964	0.985	0.961	0.953	0.945	0.942

Table 3.8. Result of Biodegradability Test by i) Disc Diffusion Method ii) Soil Burial Degradation for Polymeric Additives

	i) Disc Diffusion Method				**ii) Soil Burial Method**
Polymers	***Calletotricheme Camellia***	**Fussarium Equisitae**	**Alterneria Alternata**	**Colletrichum Gleosproides**	**Microorganism**
	% Wt. Loss	**% Wt. Loss**	**% Wt. Loss**	**% Wt. Loss**	**% Wt. Loss**
P-1	0	0	36	0	20
P-2	0	0	38.7	0	26.7

Figures

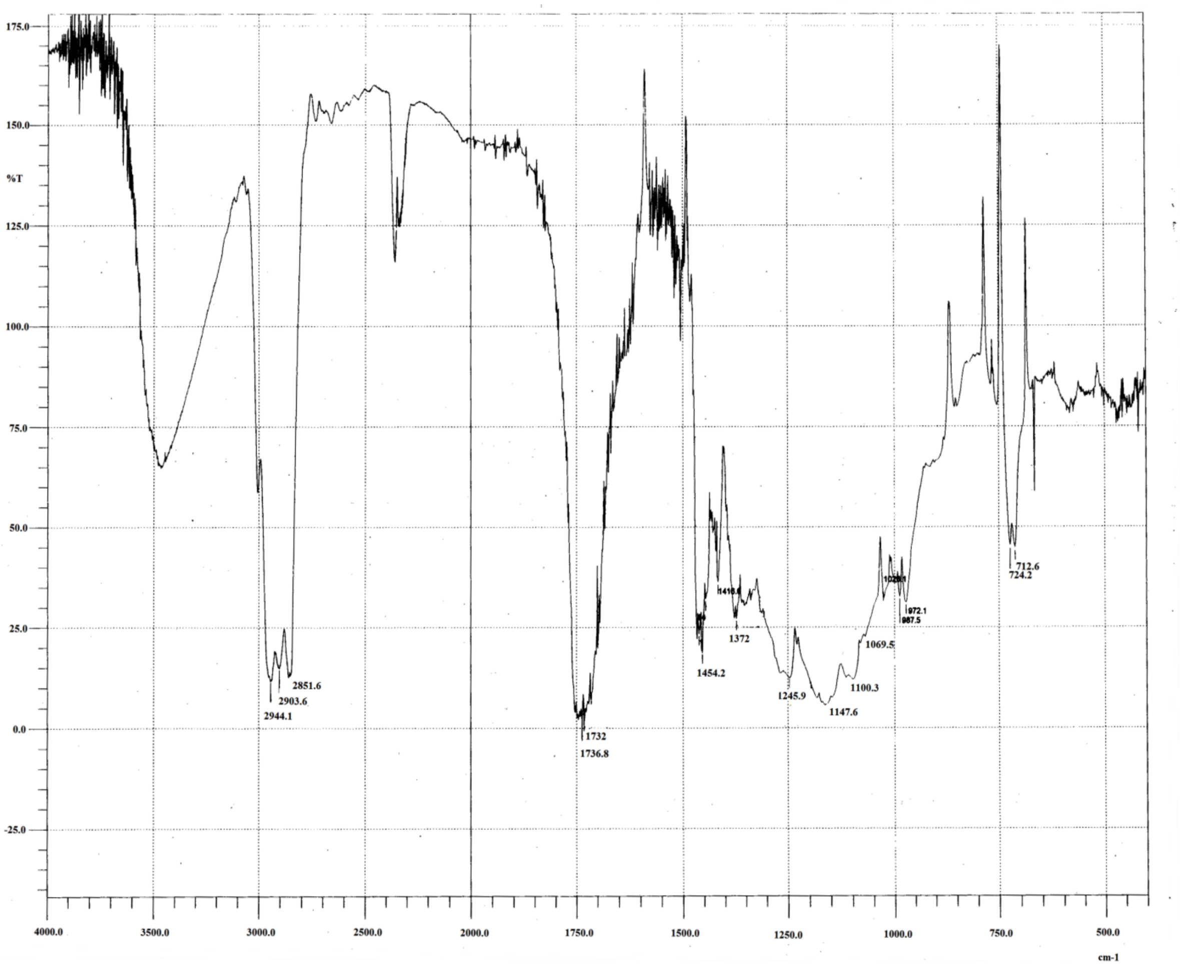

Figure 3.2. FT-IR spectra of thermally prepared SFO polymer (P-1)

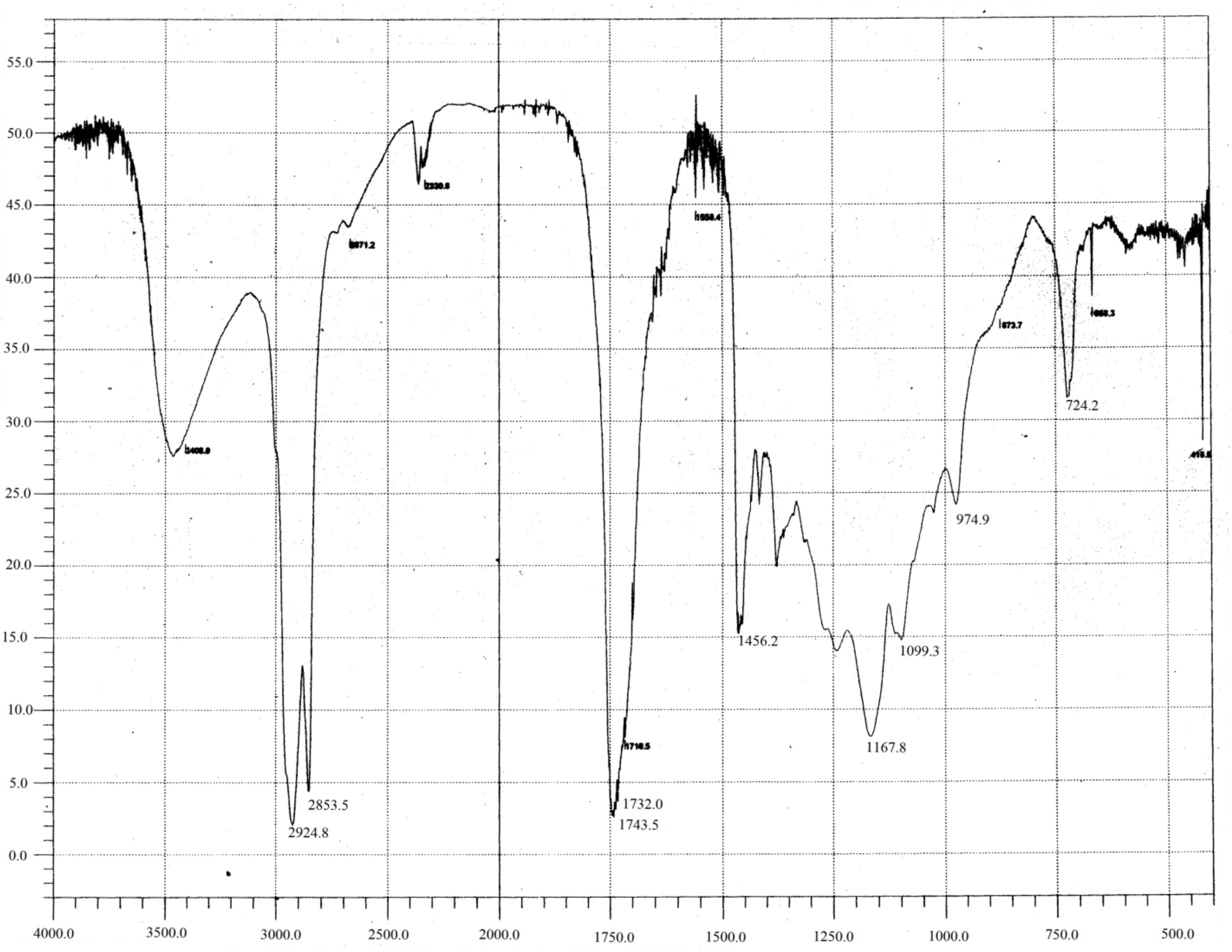

Figure 3.3. FT-IR of SFO polymer prepared by microwave irradiation (P-2)

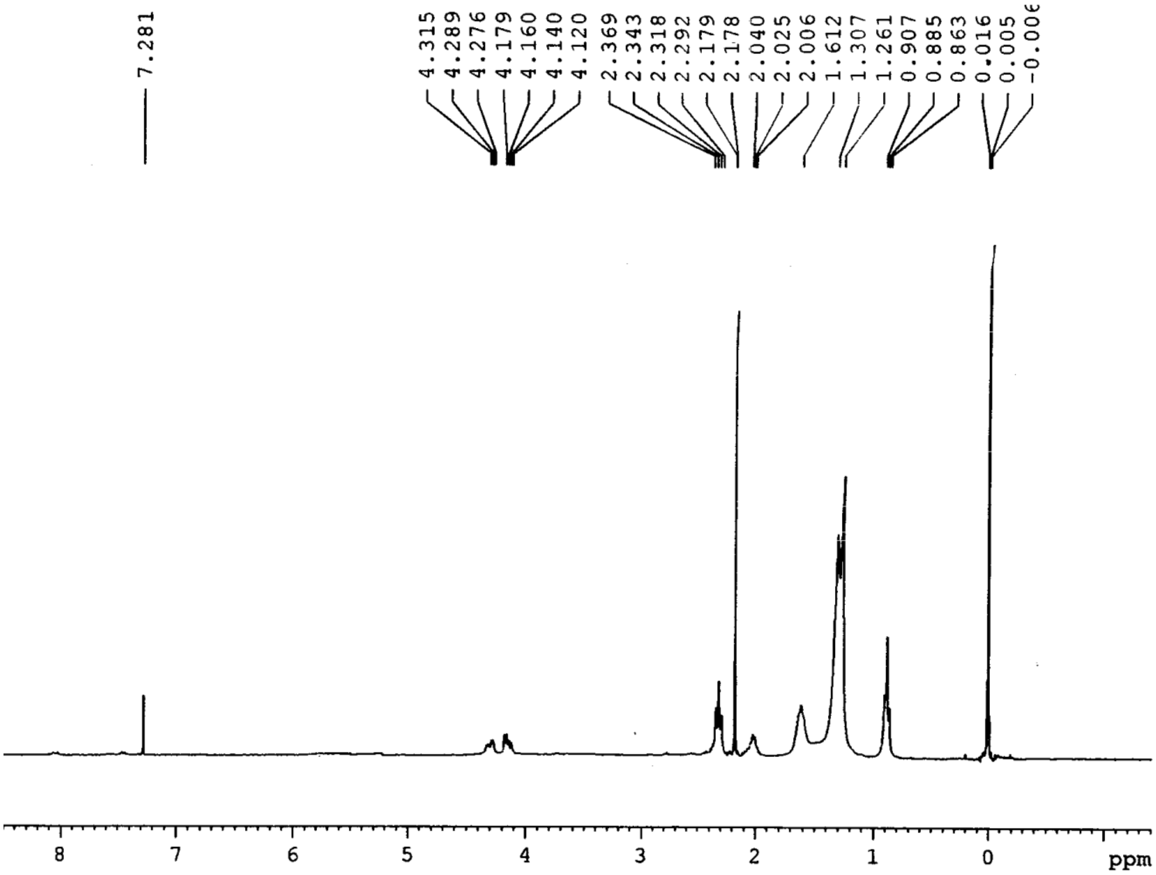

Figure 3.4. ^{1}H NMR of thermally prepared SFO polymer (P-1)

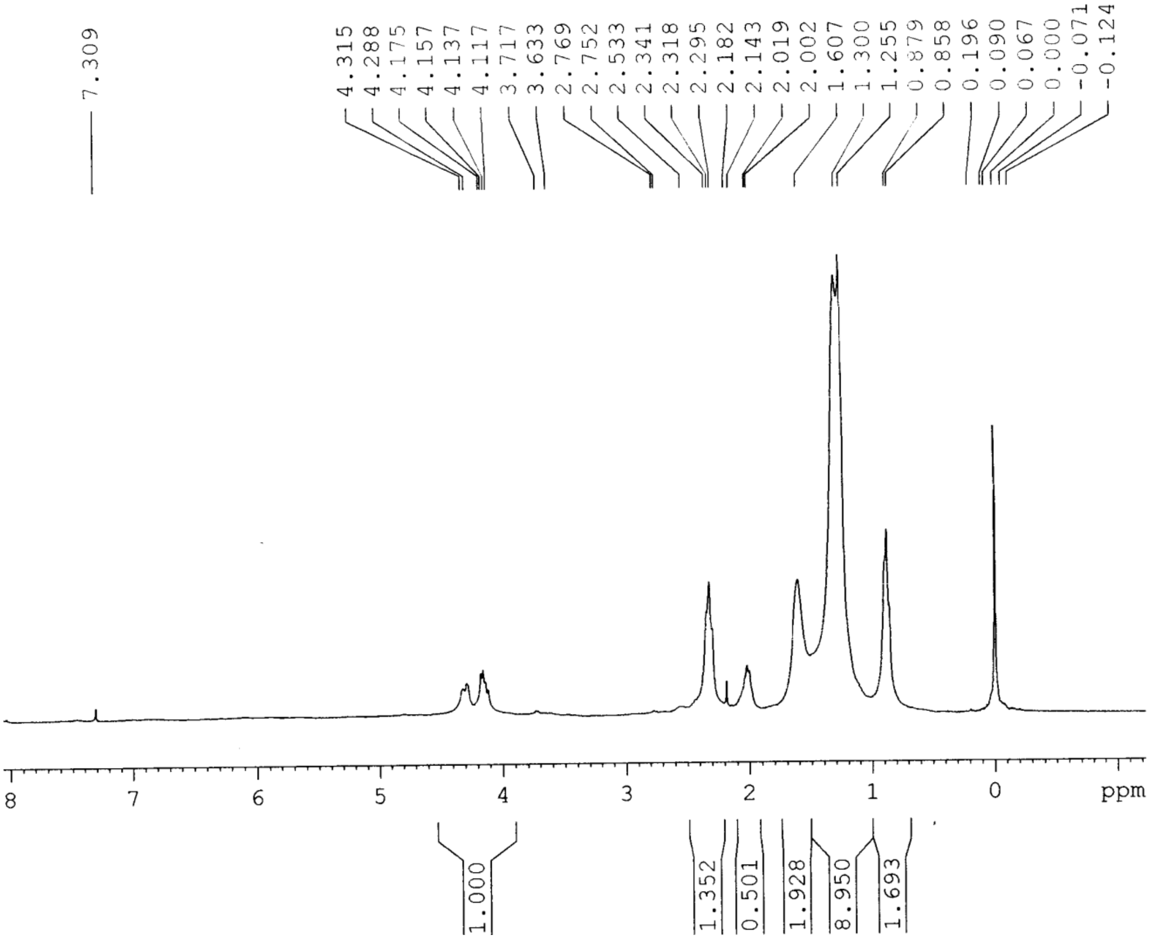

Figure 3.5. 1H NMR of homopolymer of SFO prepared by microwave method (P-2)

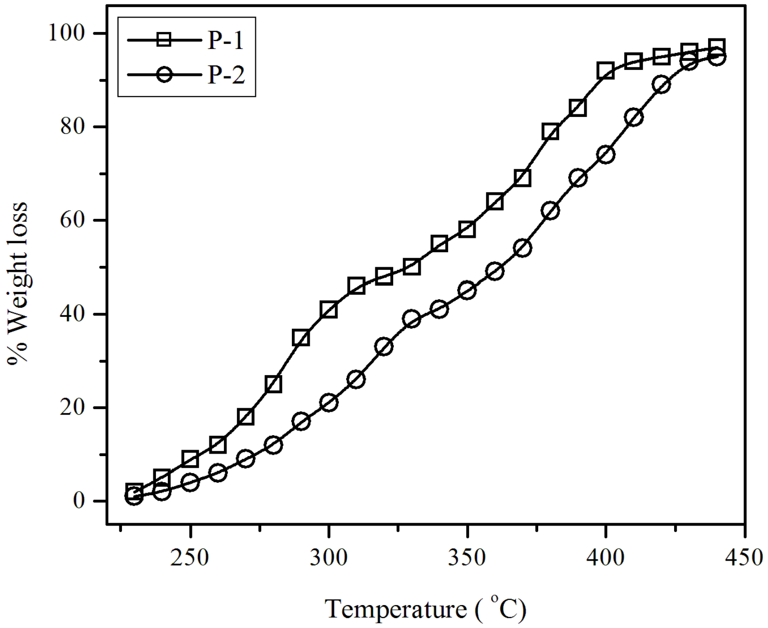

Figure 3.6. TGA analysis results of the SFO polymers (temperature increases at 10 °C/min)

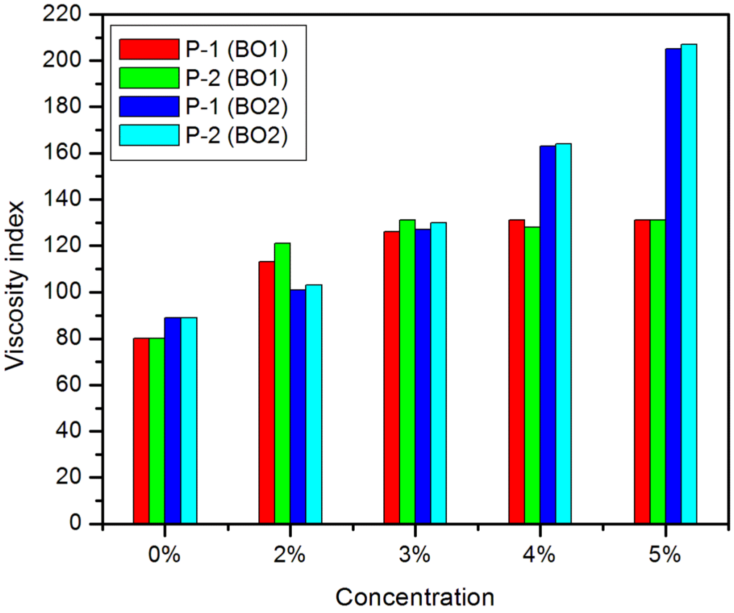

Figure 3.7. VI values of base oils (BO1 and BO2) blended with different percentage (w/w) of SFO polymer

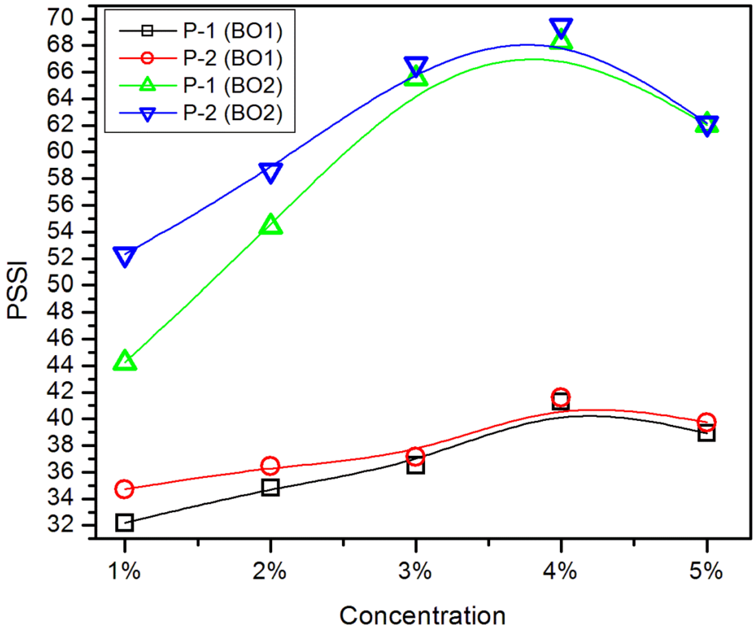

Figure 3.8. PSSI values of the two base oils (BO1 and BO2) blended with different percentage (w/w) of additives

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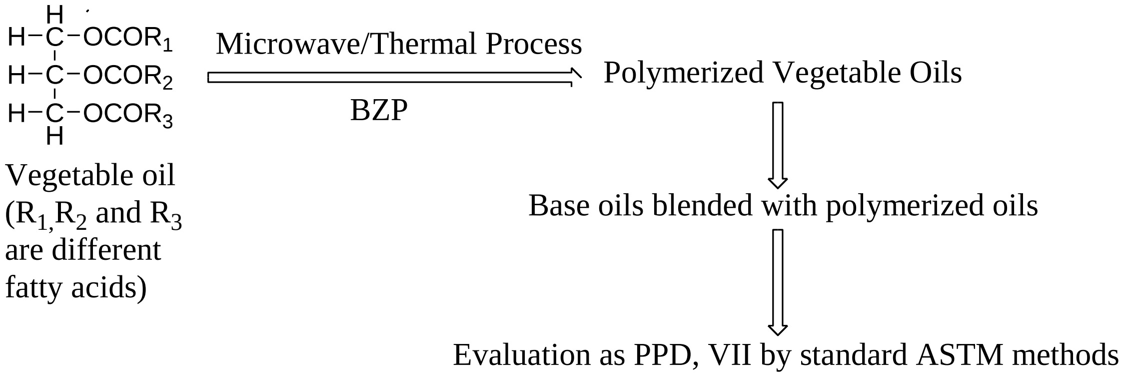
1.3. Evaluation of Homo and Copolymer of Soybean Oil as a Potential Additive for Lubricating Oil

2.2.1. Introduction

All commercial lubricants contain additives to enhance their performance. Their amount varies from greater than 1% to 30% or more. They boost the properties already present and reduce the properties which are undesirable in the base fluids. Since multifunctional additives[1] induce more than one of the above performances, research in this area is increasing day by day. Different types of polymeric additives[2] are used to improve the performance and longevity of lubricants, a major portion of them are acrylate base.[3] But with increasing environmental awareness the research in the area towards the synthesis of bio lubricating oil additive based on vegetable oil is increasing day by day.[4] Vegetable oils are natural products and contain mainly triglycerides of long chain carboxylic acids combined with glycerol. In addition, they have recognized biodegradability, non toxicity and high viscosity index. It is reported that vegetable oils has certain advantages over the conventional base oils in respect of their properties and performances in a variety of application.[5, 6] They show excellent tribological properties such as antiwear and friction modifier etc in lubricant formulation.[5,7] Reported biodegradability, renewability, excellent tribological properties and lubrication performance of soybean oil (SBO) [8] has prompted us to investigate the performance of its copolymers as a potential source of eco-friendly lubricating oil additive. The composition of the fatty acids present in SBO[9] is cited in Table 3.9. The copolymers of SBO with methyl acrylate, 1-decene and styrene in two different concentrations were prepared; characterized and their performances as lube oil additive were tested and compared. In addition, biodegradability of each of them was also tested.

Structure and morphology of the polymeric additives in lube oil plays a significant role in determining the performance of the additive blended lube oils in operation.[10] Thus, it is anticipated that viscometric studies of the dilute solution of polymers may provide valuable information regarding the base stock employed and conformation of the polymer chain in dilute solutions. Therefore, the study may be very useful for evaluating the performance of polymer blended lube oils, where the structure and morphology plays a significant role. Despite this, such information regarding lube oil additives is not yet emphasized. An outline of the present work is shown in the following scheme 1.



Scheme 1: Polymerization of vegetable oil by microwave and thermal method

2.2.2. Experimental Section

Materials

Refined SBO (85% unsaturated), collected from Sarvottam Vegetable Oil Refinery Private Limited (Indore, India) and toluene (GC 99.5%) from Merck (Mumbai, India). BZP (GC 98%), obtained from Loba Chemie Pvt. Ltd. (India), was recrystallised from $CHCl_3$-MeOH before use. Styrene (GC 99%, Acros Organics, USA), methyl acrylate (GC 99%, Thomas Baker (Chemicals) Pvt. Limited, Mumbai, India) and 1-decene (GC 95%, Acros Organics, USA) were used as received. Base oils were collected from IOCL, Dhakuria, West Bengal, India. The fungal specimens were collected from Department of Microbiology, North Bengal University, West Bengal, India.

Synthesis of the Polymer

Synthesis of homopolymer of SBO, a triglyceride ester of glycerol with long chain carboxylic fatty acids (Fig. 3.9), and its copolymers with methyl acrylate, 1-decene and styrene in two different concentrations (5% and 10%) were performed. The reaction was carried out in a four necked round bottom flask fitted with a mechanical stirrer, condenser, thermometer, an inlet for the introduction of nitrogen at 90^o C for 6 hours in toluene solvent. The polymerization was performed with initiator (BZP). At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymers were further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 40^o C.

Determination of Viscosity Average Molecular Weight

The average molecular weight of the polymeric additives prepared was determined by viscometric technique using Mark Houwink–Sukurda (MHS) relation.[6] The experiment was carried out by Ubbelohde OB viscometer at 313 K taking eight different concentrations in g cm^{-3} (0.218 to 0.137) of the polymeric additives in toluene and chronometer was used for recording their flow times. During this experiment adequate precautions against evaporation of the solvent were taken. For the determination of viscosity average molecular weight by MHS equation the intrinsic viscosity was calculated by graphical extrapolation method[10, 11, 12] using Huggins and Kraemer equation as discussed in chapter II (part-II). Thus the viscometric study, which is indeed a function of size of the molecule of the polymers in solution may yield very useful parameters required for the choice of end application of the polymers.

The relationship $k_h + k_k = 0.5$[13] has taken into account to predict the extent of interaction among the polymer and base oil.

2.2.3. Analytical Methods

Spectroscopic Analysis

The spectral characterization was done by FT-IR and 1H NMR measurements of the samples. Shimudzu FT-IR 8300 and Brucker Avance 300 MHz FT-NMR spectrometers were used in that case. IR spectra were taken within the range 400 to 4000 cm^{-1} using 0.1 mm KBr cells at room temperature. For 1H NMR, 5 mm BBO probe, $CDCl_3$ solvent and TMS as reference material were used.

Viscometric Analysis

The viscometric measurements for the determination of intrinsic viscosity and molecular weight were performed at 313 K using toluene solvent as was reported in chapter II, sec A (Part-I).

Thermal Stability Analysis

The thermo-oxidative stability of all the polymers was determined by thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating rate of 10^{o} C /min. The percent weight loss (PWL) of the polymers with rise in temperature was calculated.

2.2.4. Performance Evaluation

Evaluation of Thickening Property

The thickening property of polymer indicates the extent of interaction of the polymer with base oil. Thickeners are added to lubricants to reduce the degree of change in viscosity seen at high and low temperatures. They increase the viscosity of the base stock at higher temperature. It was calculated by measuring the percent of increase in the kinematic viscosity of the base oils after addition of the polymers by unit amount at 40^{o} C.

Evaluation of Pour Point

The pour point of the base oils (BO1 and BO2) at different doping concentrations of the additive was evaluated based on ASTM-D97 method[14] as mentioned in chapter-II of this part. The test was carried out by using cloud and pour point test equipment (Wadegati labequip Pvt ltd, India) having temperature range 0^{o} to -71°C.

Evaluation of Viscosity Index

Viscosity index is an arbitrary number indicates the resistance of change of viscosity of base oil with change in temperature. A high value of it indicates relatively small change in viscosity with the temperature change. Additive increases this index thereby improve the performance of the base oil. It was calculated by measuring kinematic viscosity of the base oils (BO1 and BO2) at different levels of additive concentrations (ppm) at 40° and 100° C according to ASTM D 2270-87 method.

2.2.5. Biodegradability Test

The main advantage of using vegetable based additives over synthetic acrylate based ones is its excellent biodegradability. The biodegradability of the additives was tested by DD and SBT methods (ISO 846:1997)[15] after a certain period of time. A shift in IR frequency of the ester carbonyl group after the test confirmed the degradation.

Disc Diffusion (DD) Method

In DD method biodegradation of the prepared polymer samples were tested in Bacteriological Incubator apparatus against different fungal pathogens following the method as previously mentioned (chapter II, part-II). Here the polymeric samples were incubated for 30 days at 310 K and 1.5 g of each of the sample was taken. The fungal pathogens taken for this test were *Calletotricheme amellia*, *Fussarium equisitae*, *Alterneria alternata* and *Colletrichum gleosproides*. After the time period the samples were recovered, washed several times with chloroform and dried. Finally the percentage weight loss for each of the samples was calculated.

Soil Burial Test (SBT) method

In SBT 1.5 g of each of the additive samples were taken to produce a film and then buried in soil.[16] The soil sample was collected from North Bengal University campus having 25% moisture and pH 7.2. The test was carried out at 303 K with the relative humidity 60% for 3 months. The procedure follows the ISO 846:1997 norms. After the time period the sample films are recovered, washed with chloroform for several times, purified and finally dried. The dried samples were weighed. The degradation was calculated in terms of percentage weight loss of the polymeric additives as given under. The extent of degradation was calculated in terms of percentage weight loss (%WL) of the samples as follows:

$\%WL = [(M_0-M_1)/M_0] \times 100$

Where M_0 is the initial mass and M_1 is the remaining mass after SBT and subsequent drying till constant weight.

2.2.6. Results and Discussion

The IR absorption at 1745.5, 1740, 1732, 1741, 1736.8, 1737.7 and 1732 cm^{-1} for homopolymer of SBO (S-1), copolymer with methyl acrylate (10%) (S-2), methyl acrylate (5%) (S-3), 1-decene (10%) (S-4), 1-decene (5%) (S-5), styrene (10%) (S-6) and styrene (5%) (S-7) respectively showed the presence of ester carbonyl group. Peaks at 1167.8 to 1155 cm^{-1} were due to the C-O stretching vibration of the ester carbonyl and from 1099.3 cm^{-1} to 712.6 cm^{-1} for C-H bending vibrations. The absence olefinic peaks for the polymers and its presence for their respective monomers support the phenomenon. Absorptions recorded from 2851.6 to 2944.1 cm^{-1} for the paraffinic C-H bonds. Figures from 3.10 to 3.13 clearly mentioned the IR spectra of homo and copolymers of SBO. ^{1}H NMR of homo and copolymers of SBO (Figures 3.14 to 3.17) showed broad peaks in the range at 4.080 to 4.327 ppm due to ester carbonyl protons of the triglyceride. Peaks appeared in the range 0.820 to 0.911 ppm, 1.220 to 1.608 ppm and 2.000 to 2.770 ppm for methyl and methylene protons respectively. The proton decoupled ^{13}C NMR showed peaks at 172.91 to 173.97 for protons of $-OCH_2$ groups of the triester. The absence of unsaturation was indicated by the absence of peaks in the range 130 to 150 ppm. The percent incorporation of different monomers in SBO was determined by NMR and FT-IR method and given in Table 3.10.

The thermal analysis report of the polymers shown in Table 3.11 indicates that the thermal stability of S-4 and S-5 are slightly better than rest of the polymers. Thus it appears that the copolymer of soybean oil with 1-decene is more linear and hence thermally more stable than the others.

The average molecular weight values of the polymers as reported in Table 3.11 showed that the molecular weight of the homopolymer of SBO is slightly higher than its copolymers which is in consistence with their corresponding intrinsic viscosity values. The higher intrinsic viscosity value indicates a fairly strong interaction of the polymer S-1 with the solvent. k_h values also indicate good solvation which is further supported by the $k_h + k_k$ values, thus the formation of the chain like structure of the present polymer is quite obvious.[11]

The VI data, as given in Table 3.12, indicated that the additive doped base oils show very high VI values compared to the base oils. It reveals that the hydrodynamic volume of the additive molecules in base oils become bigger and increases with increase in temperature.[17] The homopolymer of SBO showed excellent results. The incorporation of styrene and 1-decene to SBO enhances the VI values whereas copolymer of SBO with methyl acrylate (S-2 & S-3) showed least VI (Fig. 3.18 & Fig. 3.19).

The thickening power of copolymer of soybean oil with methyl acrylate (S-2 and S-3, Table 3.12), evaluated in different base stocks, is higher compared to the other polymers. This shows that considering the fuel economy, S-2 and S-3 provide better performance. Better thickening effect was observed at lower concentrations.

Table 3.13 showed that the PPD properties of the additives in different base stocks (BO1, BO2) gradually improve with an increase in their concentrations [except S-4 and S-5]. The copolymer of soybean oil with methyl acrylate exhibits better PPD (Fig. 3.20 & 3.21) performance compared to the others.

The results of the biodegradability test (Table 3.14) obtained by DD method showed significant degradation against fungal pathogen, Alterneria alternata. Result of soil burial test also indicated the similar extent of biodegradability. The shift in IR frequency of the ester carbonyl group of the recovered samples confirmed the degradation.

2.2.7. Conclusion

From the above discussion it is clear that all the copolymers of SBO (except that with methyl acrylate) including its homopolymer show excellent viscosity index. The VI values of the base oils gradually increase with the increase in concentration of the doped additives. A gradual increase in the VI values with an increase in the concentration of the additive in base oil is also observed. Homopolymer of soybean oil and its copolymer with methyl acrylate showed significant biodegradability against the fungal pathogen, *Alterneria alternata*. Soil burial test also support this. The S-2 and S-3 additives also show excellent pour point depressant properties when doped in base oil compared to other additives. So it may be concluded that in terms of pour point and biodegradability the homopolymer of SBO and its copolymer with methyl acrylate gives better performance compared to the other polymers whereas rest of the copolymers show better VI performance.

2.2.8. Tables & Figures

Tables

Table 3.9. Fatty acid profile of SBO

Fatty Acid (carbon atoms : double bonds)	% Composition (max)
Saturated	
C 12:0 (lauric acid)	-
C 14:0 (myristic acid)	0.1
C 16:0 (palmitic acid)	11
C 18:0 (Stearic acid)	2.8
Unsaturated	
16:1 (palmitioleic acid)	0.21
18:1 (oleic acid)	24
18:2 (linoleic acid)	55.8
18:3 (linolenic acid)	5.1
20:1 (gadoleic acid)	0.1

Table 3.10. Composition of the Monomers in the Copolymers in Terms of Mass Fraction Determined by PMR and FT-IR Spectro Photometric Method. S-1 is homopolymer of SBO and S-2 to S-7 are the copolymers of SBO with different monomers

Polymer sample	Percentage (w/w) of monomer in the feed		Percent incorporation of methyl acrylate by PMR method	Percent incorporation of methyl acrylate by FT-IR method
	SBO	Methyl Acrylate		
S-1	100	-	-	-
S-2	90	10	3.9	4.6
S-3	95	5	1.8	2.0
Polymer sample	SBO	1-Decene	Percent incorporation of 1-Decene by PMR method	Percent incorporation of 1-Decene by FT-IR method
S-4	90	10	3.5	3.7
S-5	95	5	1.7	1.9
Polymer sample	SBO	Styrene	Percent incorporation of styrene by PMR method	Percent incorporation of methyl acrylate by FT-IR method
S-6	90	10	3.2	3.5
S-7	95	5	1.5	1.8

Table 3.11. TGA values, Intrinsic Viscosity, Vicometric Constant and Molecular Weight Values (g/mole) Determined by Mark-Houwink Equation where h, k refers to Huggins and Kraemer Equations Respectively; PWL is Percent Weight Loss and Decom.Temp. is Decomposition Temperature

Samples	TGA Data		Intrinsic viscosities		Viscometric constants			Molecular weight values	
	Decom. Temp., ^{o}c	PWL	$[\eta]_h$	$[\eta]_k$	k_h	k_k	k_h+k_k	M_h	M_k
S-1	250/360	28/91	9.621	9.157	0.348	0.117	0.465	48246	45066
S-2	300/380	24/86	6.585	7.614	0.869	0.078	0.946	28598	34939
S-3	330/400	15.9/86	5.895	6.625	0.781	0.081	0.861	24549	28838
S-4	280/420	6.9/79.3	6.6798	7.564	0.778	0.086	0.864	29168	34625
S-5	290/420	9.5/95	7.0372	7.883	0.756	0.086	0.842	31342	36656
S-6	290/390	11.5/73	6.98	7.589	0.66	0.093	0.753	30991	34781
S-7	260/410	9.4/93.7	7.283	7.738	0.595	0.097	0.692	32862	35726

Table 3.12. **Viscosity Index (VI) and thickening (THK) values of the additive doped base oils**

Sample	Base Oil	Additive doped base oils							
		Conc. in ppm (×10^3)							
		2		3		4		5	
		THK	VI	THK	VI	THK	VI	THK	VI
S-1	BO1	6.783	132	6.51	170	7.12	211	6.79	227
	BO2	6.75	140	6.15	200	4.92	227	4.97	256
S-2	BO1	10.49	113	8.19	127	7	135	6.69	138
	BO2	23.94	113	17.24	133	13.83	153	11.8	177
S-3	BO1	13.51	116	9.998	134	8.13	145	7.19	160
	BO2	18.06	122	13.15	144	10.97	173	9.66	189
S-4	BO1	6.052	156	5.92	199	5.37	232	4.57	240
	BO2	6.87	150	5.41	212	4.48	234	4.24	262
S-5	BO1	13.8	142	6.37	184	9.14	218	8.32	232
	BO2	5.41	152	5.1	210	4.03	242	3.59	270
S-6	BO1	11.49	162	8.85	201	7.98	232	6.98	242
	BO2	5.49	166	4.06	211	3.46	244	2.82	272
S-7	BO1	14.1	152	10.44	192	8.58	217	7.28	236
	BO2	6.21	162	4.57	199	3.84	231	3.11	268

Table 3.13. **Pour points of the polymeric additives in different base oils**

Polymers	Base Oils	Pour points (^{o} C) Concentrations (ppm x 10^3) of the additives 2	3	4	5
S-1	BO1	-6	-7	-8	-12
	BO2	-6	-8	-9	-15
S-2	BO1	-6	-9	-12	-18
	BO2	-6	-9	-15	-18
S-3	BO1	-6	-8	-9	-15
	BO2	-6	-9	-12	-15
S-4	BO1	-7	-7	-6	-6
	BO2	-8	-7	-6	-5
S-5	BO1	-8	-7	-6	-6
	BO2	-9	-8	-7	-6
S-6	BO1	-6	-6	-9	-12
	BO2	-6	-6	-10	-15
S-7	BO1	-6	-7	-8	-10
	BO2	-6	-8	-9	-12

Table 3.14. Result of Biodegradability Test by i) Disc Diffusion Method ii) Soil Burial Degradation for Polymeric Additives

Polymers	i) Disc Diffusion Method				ii) Soil Burial Method
	Calletotricheme Camellia	Fussarium Equisitae	Alterneria Alternata	Colletrichum Gleosproides	Microorganism
	% Wt. Loss	% Wt. Loss	% Wt. Loss	% Wt. Loss	% Wt. Loss
S-1	0	0	10.6346	0	12.53
S-2	0	0	3.38078	0	7.62
S-3	0	0	2.55164	0	9.87
S-4	0	0	0.82305	0	5.73
S-5	0	0	1.86625	0	6.97
S-6	0	0	1.45808	0	4.78
S-7	0	0	2.22603	0	5.92

Figures

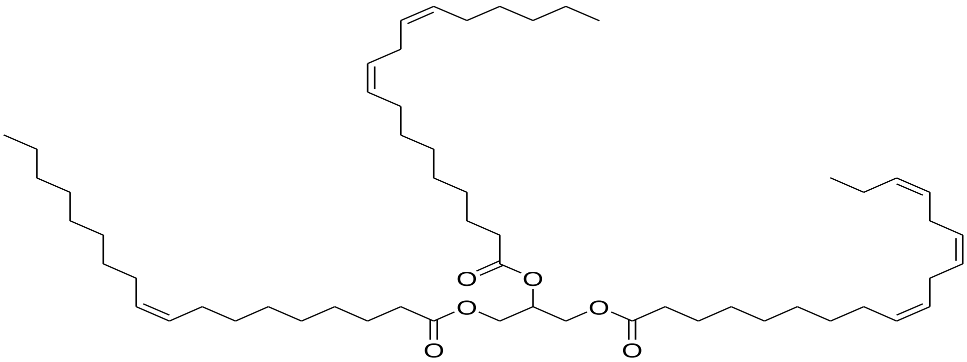


Figure 3.9. General structure of SBO (long chains are the three major unsaturated fatty acid constituents of SBO)

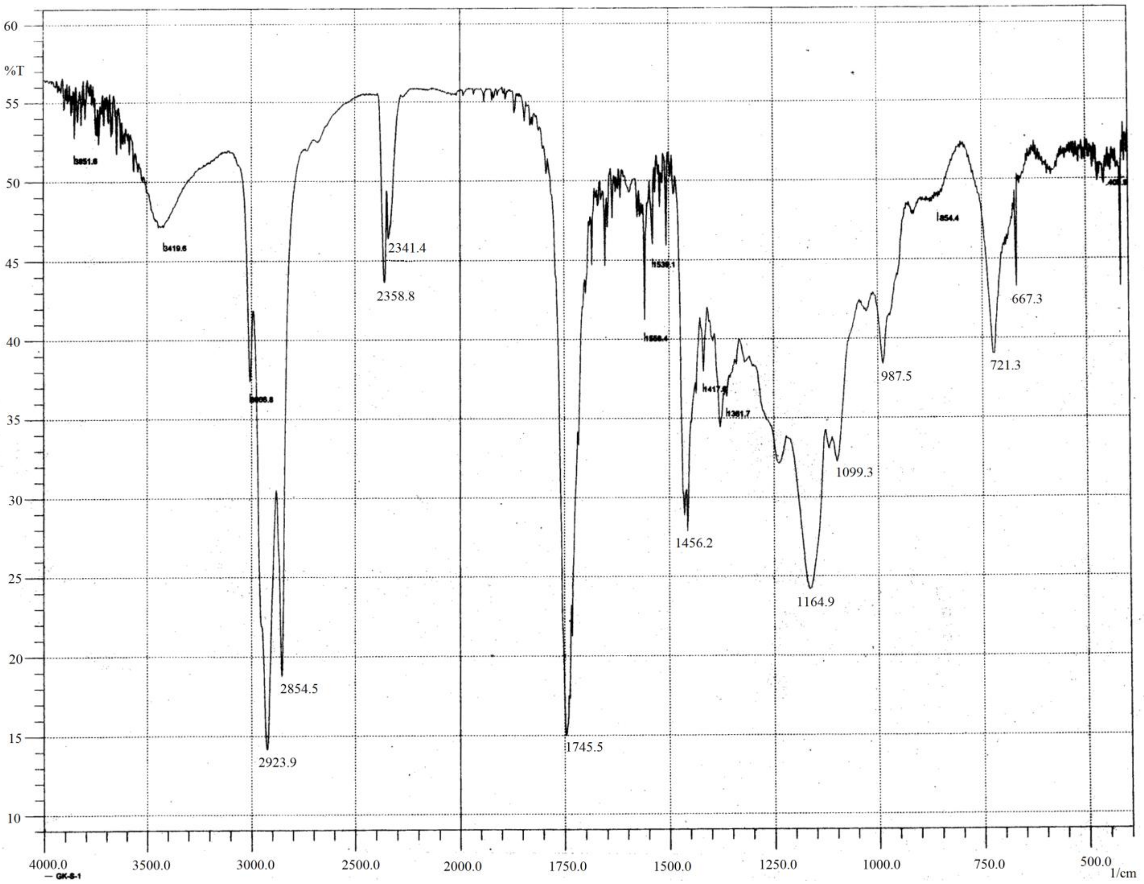


Figure 3.10. FT-IR spectra of homopolymer of SBO (S-1)

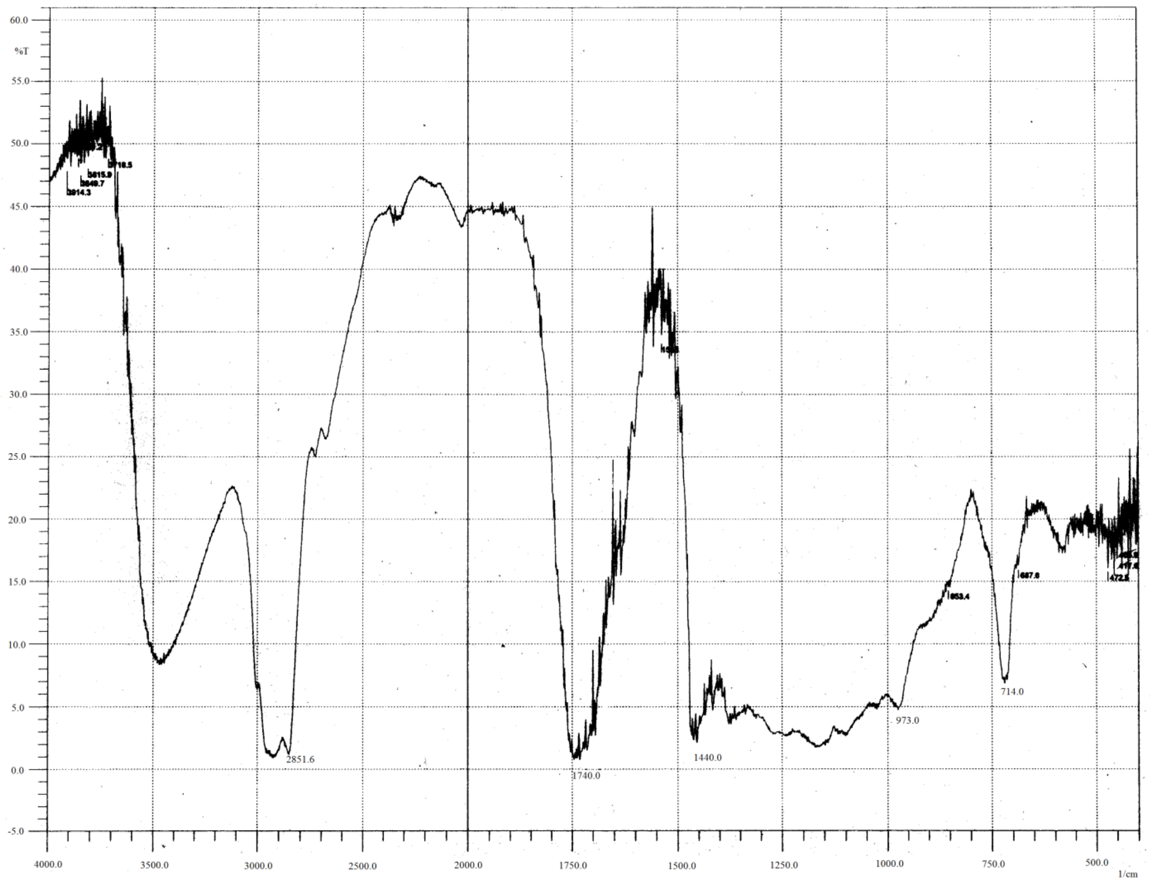


Figure 3.11. FT-IR spectra of copolymer of SBO with methyl acrylate (10%) (S-2)

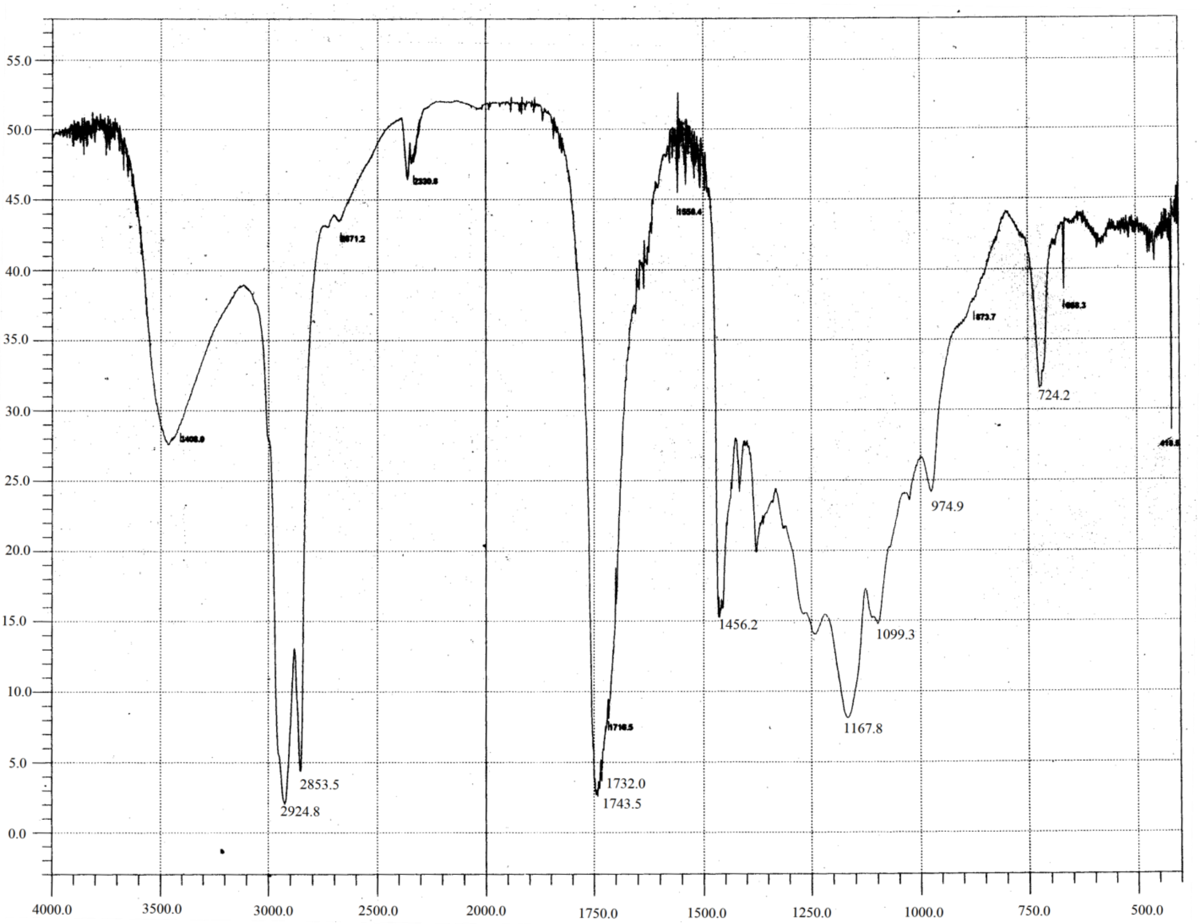


Figure 3.12. FT-IR spectra of copolymer of SBO with 1-decene (10%) (S-4)

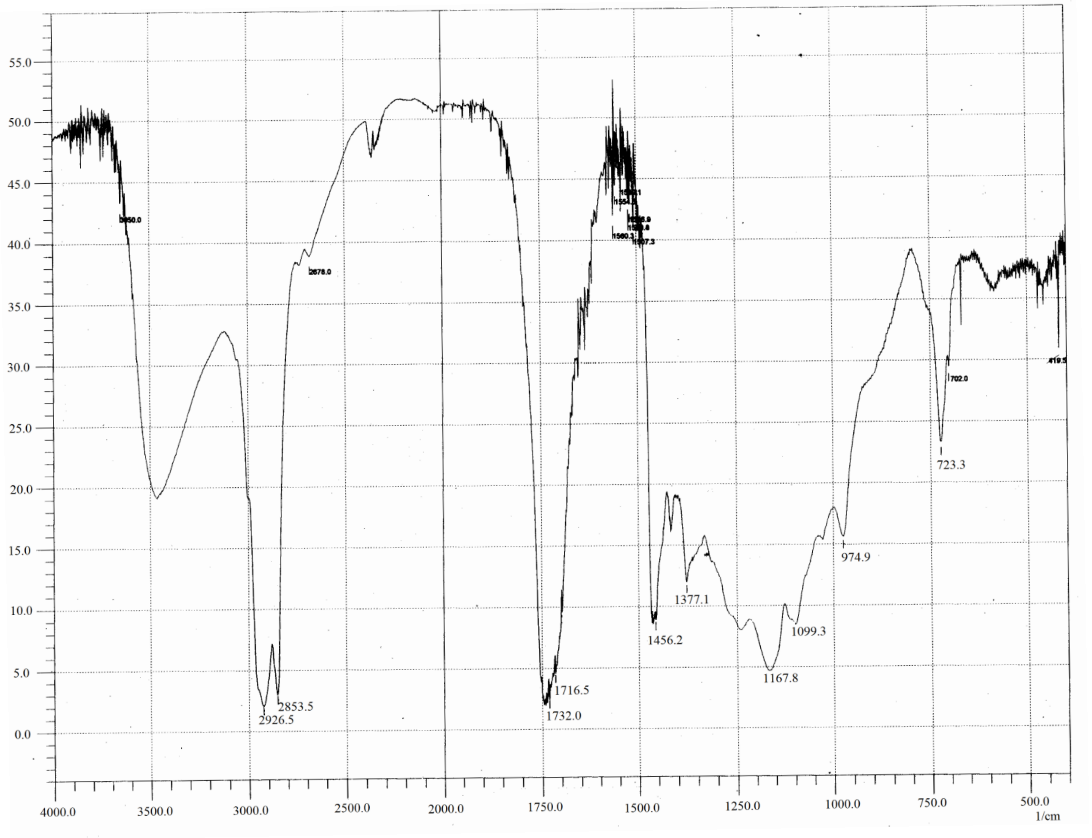


Figure 3.13. FT-IR spectra of copolymer of SBO with styrene (10%) (S-6)

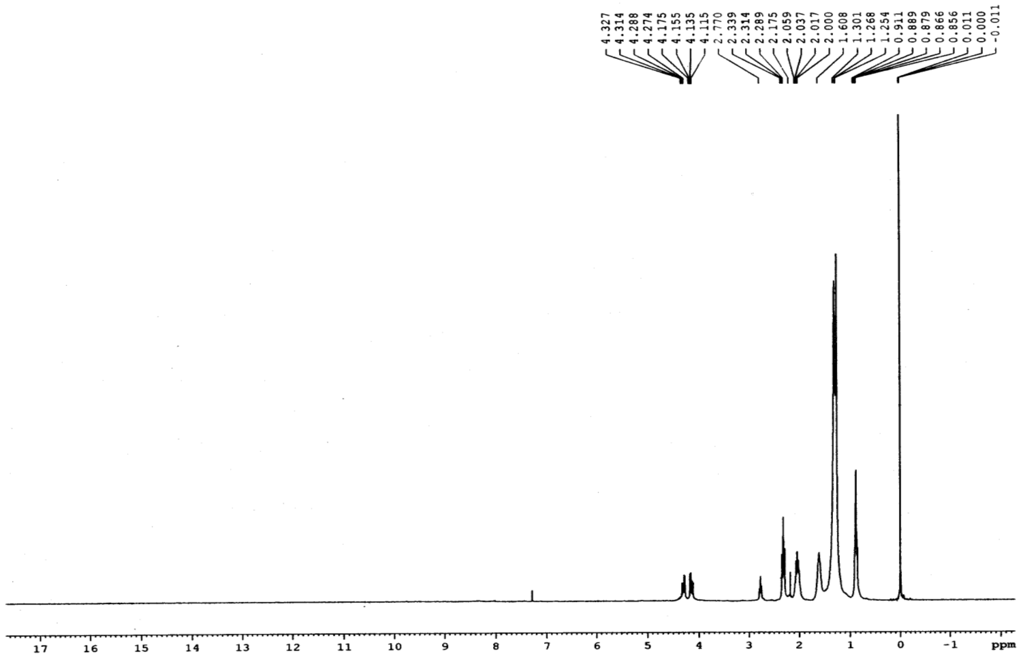


Figure 3.14. 1H NMR of homopolymer of SBO (S-1)

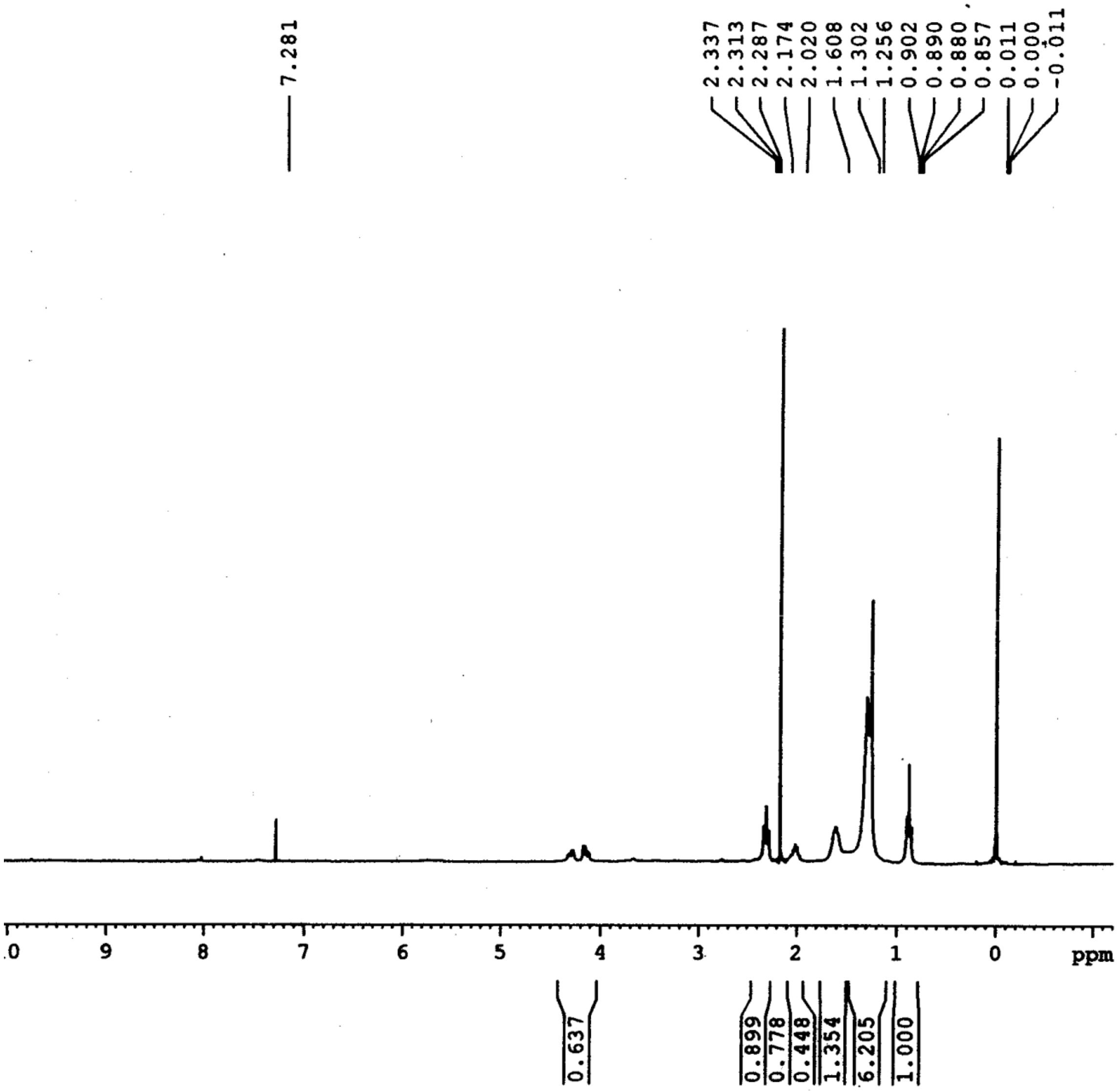


Figure 3.15. 1H NMR of copolymer of SBO with methyl acrylate (10%) (S-2)

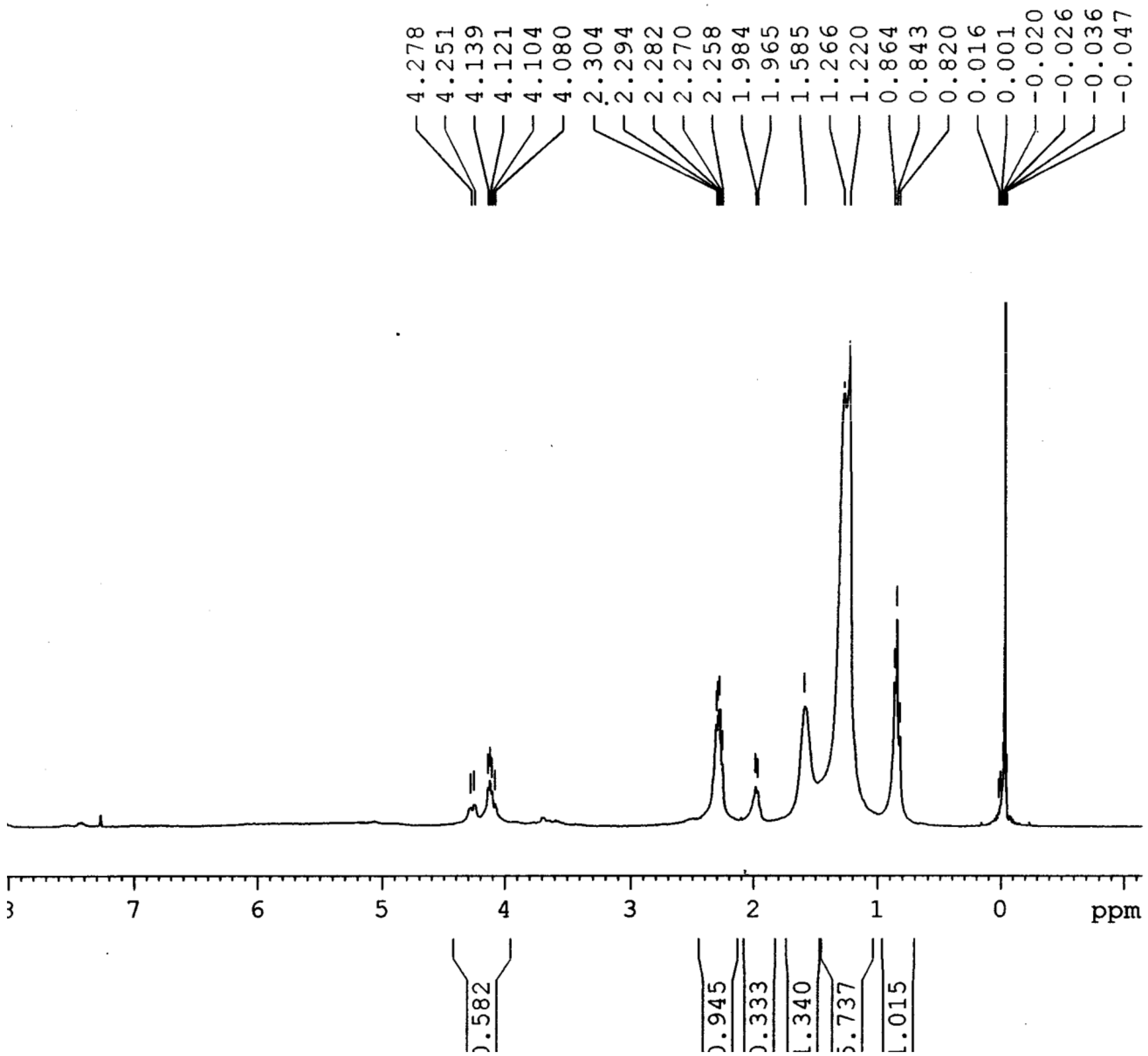


Figure 3.16. 1H NMR of copolymer of SBO with 1-Decene (10%) (S-4)

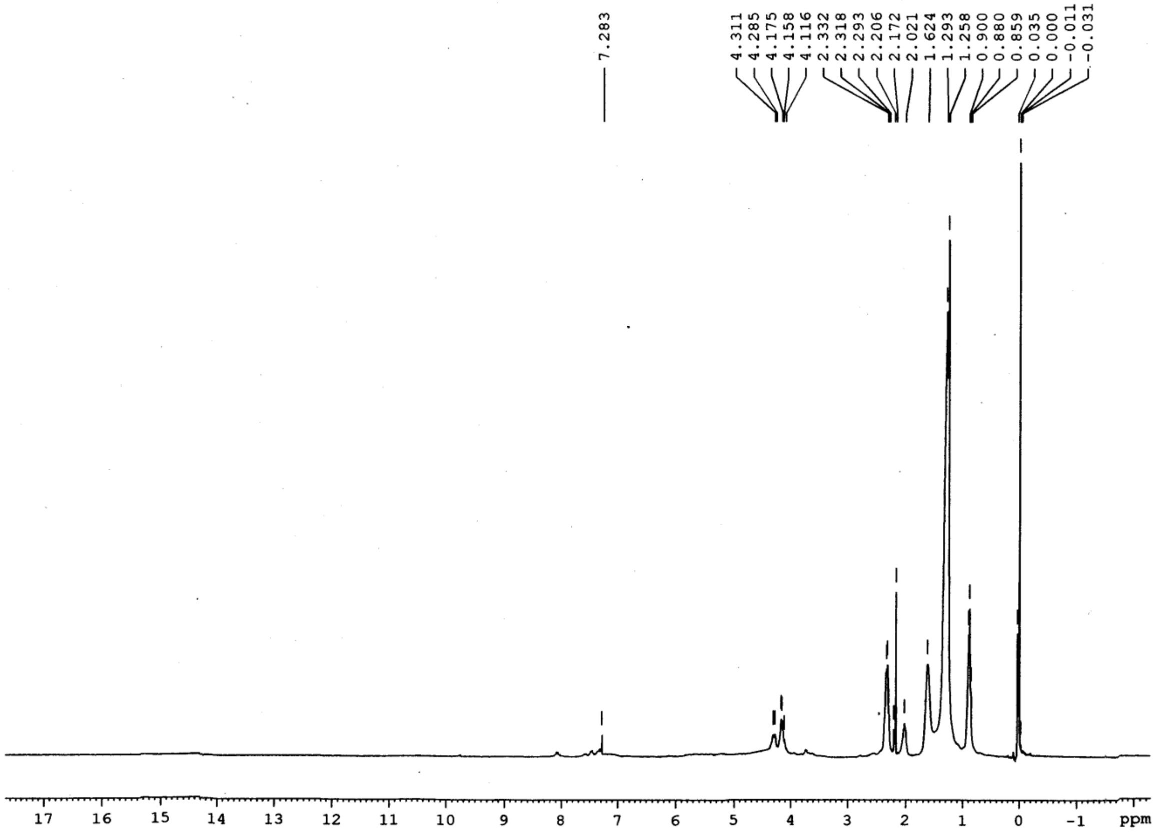


Figure 3.17. 1H NMR of copolymer of SBO with styrene (10%) (S-6)

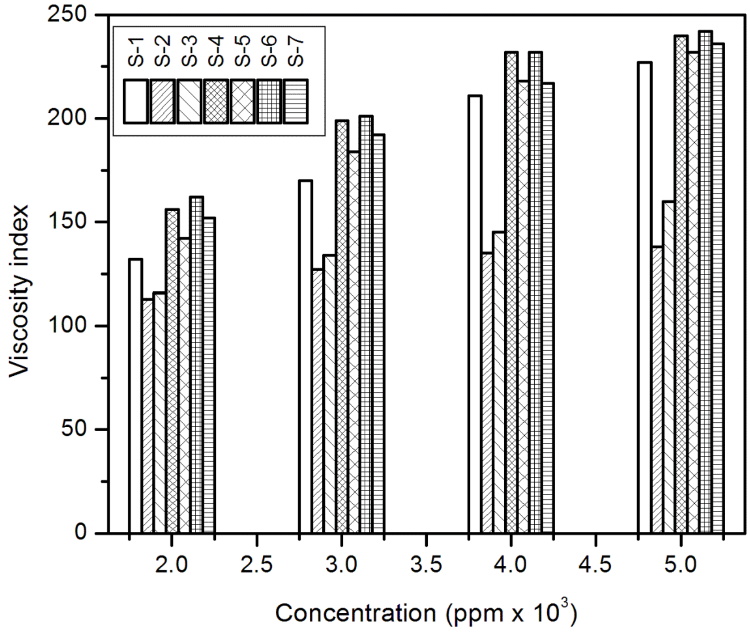


Figure 3.18. Viscosity index values of the BO1 base oil at different levels of additive concentrations (ppm × 10^3)

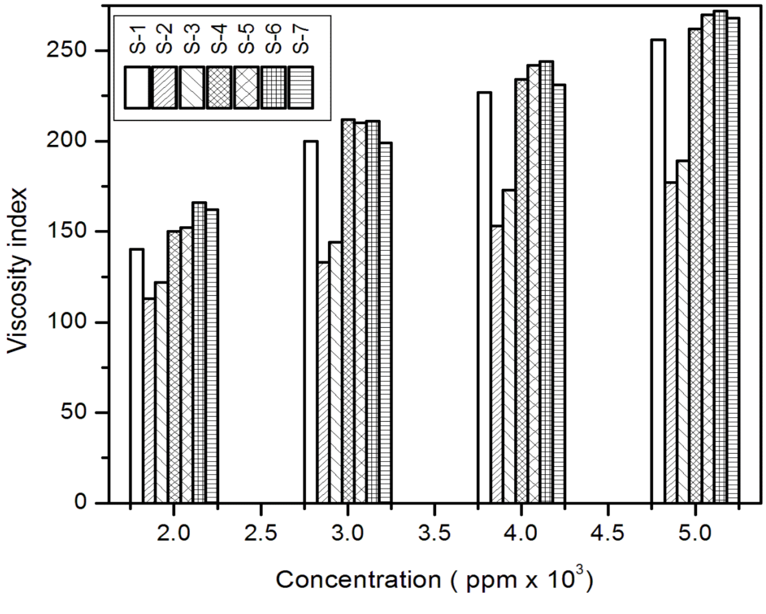


Figure 3.19. Viscosity index values of the BO2 base oil at different levels of additive concentrations (ppm × 10^3)

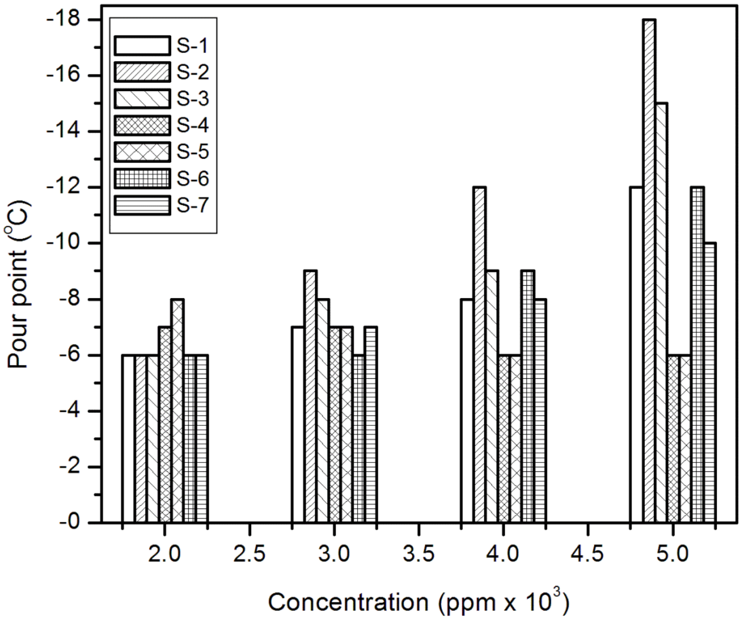


Figure 3.20. Pour points of the BO1 base oil doped with additives at different concentrations (ppm x 10^3)

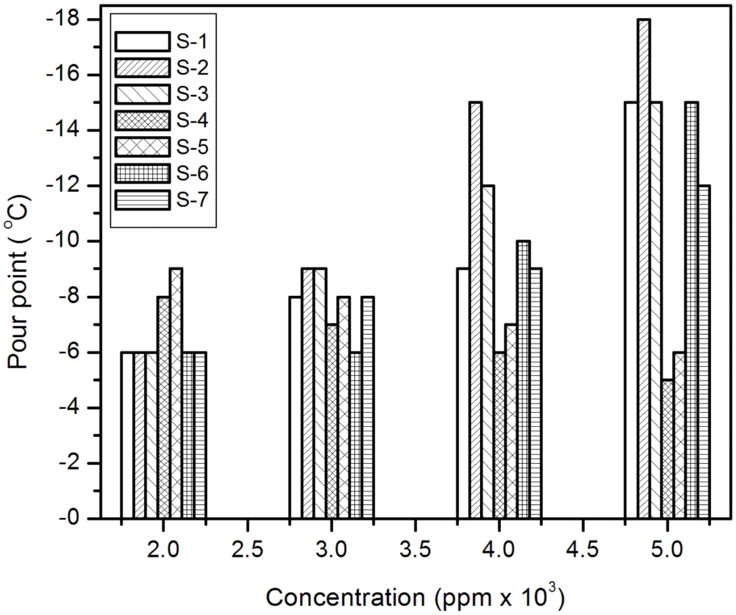


Figure 3.21. Pour points of the BO2 base oil doped with additives at different concentrations (ppm x 10^3)

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2.3. Comparison of Additive Performances of Homopolymer of Sunflower Oil and Soybean Oil

2.3.1. Introduction

Lubricants are widely used to reduce the friction between the surfaces of moving parts and thereby reduce the wear and prevent damage to the parts. The reduction of friction and wear results from the formation of a lubricant film separating the rubbing surfaces. The thickness of the lubricant film depends upon constituent chemistry (base oil and additives), as well as upon the operating conditions, specifically the applied load and the sliding velocity. At a sufficiently high load, lubricant may be expelled from the friction zone, leaving the rubbing surface unlubricated. In this case, severe friction and wear occur. Most lubricants are comprised principally of a base stock or lube oil (mainly petroleum origin) which is generally a mixture of high molecular weight hydrocarbons and an additive package. The field application performance cannot be met simply by mineral oil and it is therefore necessary to blend performance additives with them. One of the major problems in the case of mineral oil is the formation of wax crystal net work at low temperature that inhibits the normal flow properties of the base oil. Other problems associated with the lube oils are, the change in viscosity of the base stocks with the change in temperature, low thermo-oxidative stability and tribological behavior etc. To overcome these drawbacks additives with suitable formulation are blended with the base stocks. These additives, polymeric in nature, improved the field service performance of the base lubricating fluids. Additive molecules typically have long, oil soluble, hydrocarbon (non-polar) tails and smaller, hydrophilic (polar) head groups. Since the two parts of the molecule have different solubility's in oil, additives therefore tend to exist in the colloidal form as inverse micelles. Viscosity index improvers,[1] antioxidant,[2] detergent-dispersant,[3] antiware [4] and pour-point depressants [5] are some of the important additives added to lube oil.

Although additives of many diverse types have been developed to meet the needs of modern lubricants, acrylate based polymers for lube oil additives are widely used since long time.[6] These conventional acrylate base additives are extremely harmful for the biosphere. Compared to mineral oils, vegetable oils have many promising natural properties including good lubricity, good resistance to shear, a high flash point, and a high viscosity index and low evaporative loss.[7, 8, 9] Vegetable oils are primarily triglycerides, that is, tri esters of long chain fatty acids (both saturated and unsaturated) combined with glycerol and most of these oils contain at least four and sometimes as many as 12 different fatty acids. The fatty acid composition of SFO and SBO was given in Table 3.15.

There are examples where vegetable-based oils have been used as lubricating oils as an alternative of petroleum based oils. [10, 11, 12]But one thing is that these vegetable oils are costly, in general, are about twice as expensive as petroleum-based oils. Beside this, they have very low oxidation stability and cold temperature properties.[13] The main reason for the thermal and oxidative instability of plant-based oils is the structural "double bond" elements in the fatty acid part and the "β-CH group" of the alcoholic components.[14] Thus it is anticipated that polymerization of the oil of plant origin may effectively increase their thermal stability and their use as an additive into the lube oil will not only add performance but also will maintain the overall cost of the product.

Therefore in the present investigation the polymers of sunflower and soybean oil have been synthesized, characterized (IR, NMR and viscometric method) and their additive performances were tested and compared.

2.3.2. Experimental Section

Materials

Refined SFO and SBO were collected from S K Oil Industries (India) (Table 3.15), benzoyl Peroxide (GC 98%), obtained from LOBA chemicals, was recrystallised from $CHCl_3$-MeOH before use. Base oils, 70 N (BO1) and 150 N (BO2) were collected from IOCL, Dhakuria, West Bengal, India. The fungal specimens were collected from Department of Microbiology, North Bengal University, West Bengal, India.

Synthesis of the Polymer

The microwave synthesis of homopolymer of SFO (S-1) and SBO (S-2) was carried out in a focused mono-mode microwave oven (CEM corporation, Matthews, NC) applying 300 WT for 30 minute at 90^0 C without any solvent by adding 0.01% (w/w) BZP as initiator.

Determination of average molecular weights of the polymers

The average molecular weight of the additives was determined by GPC and viscometric method. The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured in GPC method. In this method the samples were dissolved in tetrahydrofuran (0.4%, wt/vol) (used as mobile phase) in the Water GPC system (polystyrene calibration) at 313 K. In viscometric method viscosity average molecular weight (M_v, viscosity average) was calculated by Mark Houwink–Sukurda relation (Eq. (1)).

$$[\eta] = KM_v{}^a \tag{1}$$

Where, [n] is the intrinsic viscosity in dL g^{-1}, M_v is the viscosity-average molecular weight, and K and *a* are viscometric constants for given solute-solvent system and temperature. The intrinsic viscosities of the dilute polymer solution at a particular temperature can be evaluated by a number of mathematical relations by graphic extrapolation method mentioned in chapter II, part-I. The most commonly used equations are:

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

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

Where, $n_r = t/t_o$ = relative viscosity or viscosity ratio i.e. time of flow of the solution /time of flow of the pure solvent, $n_{sp} = n_r - 1$ = specific viscosity, [n] = intrinsic viscosity, k is reaction coefficient and C is concentration (g cm^{-3}). The subscripts h and k denote for Huggins and Kraemer equation respectively. In MHS equation, the constants K = 0.00387 dLg^{-1} and a = 0.725 were employed and adequate precautions against evaporation of the solvent during viscometric measurements were taken.

The use of these equations have been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$.[15]

2.3.3. Analytical Methods

Spectroscopic Analysis

The IR absorption of the two polymers were recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range

400 to 4000 cm^{-1}. 1H NMR spectra were recorded in Brucker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. $CDCl_3$ was used as solvent and TMS as reference material.

Viscometric Analysis

Viscometric measurements were carried out at 313 K in toluene solution using Ubbelohde OB viscometer for seven different concentrations (0.218 to 0.137 g cm^{-3}) of the sample solution. The time of flow of the solution was manually determined by using a chronometer. For the viscosity-average molecular weight calculation by Mark Houwink – Sukurda relation the constants K = 0.00387 dl/g and a = 0.725 [15] were employed.

Thermo Gravimetric Analysis (TGA)

The thermal stability was measured by Shimadzu TGA-50 thermobalance in terms of percent degradation of weight of the polymers with the increase in temperature (10^{o} C/min) in air using an alumina crucible.

2.3.4. Performance Evaluation

Evaluation of Thickening Property

Kinematic viscosity of the base oils and that of the polymer doped base oils in different concentrations were evaluated. Thickening power of the polymer was determined by evaluating the percent increase in viscosity of the base stocks by the addition of unit amount of additive.

Evaluation of Pour Point

The pour point of the base oils (BO1 and BO2) at different doping concentrations of the additive was evaluated using the WIL-471 cloud and pour point test apparatus model 3 (India) according to ASTM-D97 method discussed in chapter II, part-II.

Evaluation of Viscosity Index

Viscosity index of the prepared polymers were evaluated in different base stocks (BO1 and BO2) according to ASTM D 2270 method. The kinematic viscosities of the base oils containing different concentrations (ppm) of the additive were determined at 40^0 C and 100^0 C. Each sample was measured three times in order to minimize the error. Finally, the viscosity index was determined according to the ASTM D-2270 formula.

Evaluation of Shear Stability Index

The shear stability of the two polymer solutions in base oils were determined by the ASTM methods. The kinematic viscosities before and after shear were evaluated. Then permanent viscosity loss (PVL) and permanent shear stability index (PSSI) were determined by ASTM D6022–06 formula.

2.3.5. Biodegradability Test

Biodegradability is the most important aspect with regard to the environmental fate of a substance. Vegetable based oils are also easily biodegradable under anaerobic conditions, whereas mineral oils are not.[10, 16] Ultimate biodegradation is when the substance is totally converted by microorganisms into carbon dioxide, water, mineral salts, and biotic mass. Several tests have been developed to measure biodegradability. Here the microbial degradation of the polymers were tested i) by disc diffusion method [17] against fungal pathogens and ii) by soil burial degradation test of polymer films as per ISO 846:1997[18] and by measuring the shift of IR frequency of the ester carbonyl after the biodegradability test.

Disc Diffusion Method

In this process biodegradation of the prepared polymer samples were tested against four different fungal pathogens namely *Calletotricheme camellia*, *Fussarium equisitae*, *Alterneria alternata*, *Colletrichum gleosproides*. All glass apparatus, culture media were autoclaved before use. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. The fungal growth was confirmed by a change of yellow to blackish. The experiment was performed in Petri dishes and was incubated at 310 K for 30 days after addition of definite weight of polymer samples. The whole process was carried out in inoculation chamber. After 30 days polymer samples were recovered from the fungal media and washed with chloroform, purified and dried in an open vessel. The dried samples were weighed.

The Soil Burial Degradation Test

In soil burial degradation, the effect of microorganisms arises on the surface of the polymer film.[19] The films of polymer samples were buried in soil (pH 7.2, soil moisture 25%). The soil used in this study had been taken from North Bengal University (West Bengal, India) campus. The soil was taken in a tray, in which the relative humidity was adjusted to 50 % to 60 % and temperature was thermo stated at 303 K with the help of a humidity chamber. The soil was conditioned for 1 week before it was used for the actual test. The buried films were removed at regular intervals of 15 days up to a span of 3 months. Recovered films were washed with chloroform, purified and dried in a vacuum oven at 50^0 C to constant weight. The weights of the sample, before and after drying were recorded. The percentage of weight loss of the samples was calculated as follows:

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

Where M_0 is the weight of the original films before SBT and M_1 is the weight of residual films after SBT and subsequent drying till constant weight for different times. As the exposure time increased, the weight of the biodegradable mulching film decreased gradually. It is possibly due to the erosion from soil microorganism constantly.

2.3.6. Results and Discussion

FT-IR spectra of the two polymers SFO and SBO are shown in Figure 3.3 and 3.22. The absorptions at 1745.5 and 1732 cm^{-1} are for the homo polymer of SBO and SFO showed the presence of ester carbonyl group. Broad peak in the region 1164.9 and 1167.8 cm^{-1} were due to the ester C-O stretching vibration of the two additives S-2 and S-1 respectively. Peaks appeared in the region 1099.3 cm^{-1} to 721.3 cm^{-1} were for C-H bending vibrations. Absorptions observed in the region 2854.5 and 2923.9 cm^{-1} were for the paraffinic C-H bonds of S-2 and that of from 2853.5 to 2924.8 cm^{-1} for S-1. ^{1}H NMR of homopolymer of SFO and SBO showed broad peaks in the range at 4.117 to 4.315 ppm due to ester carbonyl protons of the triglyceride (Figures 3.5 and 3.23). Peaks appeared in the range 0.857 to 0.911 ppm, 1.255 to 1.607 ppm and 2.001 to 2.769 ppm for methyl and methylene protons respectively. In Figures 3.24 and 3.25 the proton decoupled ^{13}C NMR showed peaks in the range 172.91 to 178.92 ppm for protons of –OCH_2 groups of the triester. The absence of unsaturation was indicated by the absence of peaks in the range 130 to 150 ppm.

The TGA data showed in Table 3.16 indicated that lower thermo-oxidative stability of both soybean and sunflower oil could be significantly increased by their polymerization and the homopolymer of sunflower oil (S-1) show better result than the homopolymer of soybean oil (S-2).

The intrinsic viscosity values calculated by two different equations (eq. 1 and eq. 2)) for both the polymers are also shown in Table 3.17. The higher intrinsic viscosity value for S-2 indicates that the polymer of soybean oil has fairly strong interaction with the solvent. The k_h + k_k value of S-2 also supports that in base oil the solubility of S-2 is better than S-1, and thus point towards the formation of the chain like structure. From the intrinsic viscosity values, the viscosity average molecular weights (M_v) were obtained.

Thickening power of both the homopolymers (Table 3.17) as evaluated in different base stocks indicated a gradual increase with the increase in concentration of the additive. This may be because of the fact that the polymer molecule assumes a coiled like aggregation with increase in its concentration in the base stock. The result also showed that the S-2 polymer exibit better thickening effect than S-1 polymer. This indicates that as far as the fuel economy is concerned the polymer of soybean oil performs better than the polymer of sunflower oil.

The prepared homopolymers were tested for their effectiveness as viscosity index improvers by measuring the VI of the respective additive doped base oils by ASTM D 2270 method [15] and the values are given in Table 3.17. The test method comprises the determination of the kinematic viscosities of the different base oils containing different concentrations of the additives at 40^0 and 100^0 C. The data indicates that the VI increases with increasing the concentration of the prepared additives in solution and the S-2 polymer show higher VI in compared to the S-1 polymer in BO1 and BO2 base oils (Fig. 3.26). As the temperature is raised, the polymer molecule expands and because of which its hydrodynamic volume increases. This increase in the micelle size of the solvated polymer molecules counterbalanced the reduction of the viscosity of the lube oils with temperature.[20] This effect is more pronounced in case of S-2 polymer rather than S-1. The increase in concentration of polymer leads to an increase in the total volume of the polymer micelles in the oil solutions. Consequently, higher concentration of additive will impart higher viscosity index.[1]

The PSSI of both the polymers was evaluated as per ASTM D6022–06 method in two base oils (Table 3.18). The stability of the polymers against shear decreases with increasing the PSSI values.[21] It is observed that with increasing concentration of the additive the PVL values increases and because of which the PSSI values increase (Fig. 3.27). This may be explained based on molecular weight of the polymers. With increase in polymer concentration molecular mass distribution increases and the system undergoes degradation.The higher PSSI values of S-2 compared to S-1 reveals that the homopolymer of soybean oil is relatively less stable against shear.

The result of the biodegradability tests (Table 3.19) in both disc diffusion and SBT method indicate that the polymers S-1 and S-2 show significant degradation against fungal pathogen Alterneria Alternata and microorganisms present in the soil.

PPD properties of both the polymers (Table 3.20) as evaluated in different base stocks showed a good depression in the base stocks studied. It was found that the efficiency increases by increasing concentration of the additives and S-1 polymer showed better depression in pour point than that of the S-2 (Fig. 3.28). Therefore, it may be said that although both the polymers may be used as potential PPD for the base stocks the homopolymer of sunflower oil is better compared to soybean oil.

2.3.7. Conclusion

From the above discussion, it is clear that except the PPD properties, polymer of soybean oil show better additive performances as is tested in the present investigation in comparison to the homopolymer of sunflower oil. However, when PPD properties and biodegradability were considered, polymer of sunflower oil showed better performance.

2.3.8. Tables and Figures

Tables

Table 3.15. Fatty acid profile of soybean oil and sunflower oil

Fatty Acids (carbon atoms : double bonds)		% Composition	
		Soybean oil	Sunflower oil
Saturated	C 12:0 (lauric acid)	0.16	0.29
	C 14:0 (myristic acid)	0.28	0.56
	C 16:0 (palmitic acid)	11	7.5 (4-9)
	C 18:0 (Stearic acid)	4.1	4 (1-7)
	C 20:0 (arachidic acid)	0.31	0.41
Unsaturated	16:1 (palmitioleic acid)	0.26	0.30
	18:1 (oleic acid)	22	23 (14-40)
	18:2 (linoleic acid)	54	60 (48-74)
	18:3 (linolenic acid)	7.5	2.9

Table 3.16. Thermal Stability (TGA data)

Sample	**Decom. Temp., ^{o}c**	**PWL**
Homopolymer of Sunflower Oil (S-1)	340/410	38/94
Homopolymer of Soybean Oil (S-2)	350/440	25/93

Decom.Temp. Decomposition temperature, *PWL* Percent Weight Loss

Table 3.17. Intrinsic Viscosity, Vicometric Constant and Molecular Weight Values (g/mole) Determined by Mark-Houwink Equation where h, k refers to Huggins and Kraemer Equations Respectively; PWL is Percent Weight Loss and Decom.Temp. is Decomposition Temperature

Samples	Intrinsic Viscosities		Viscometric constants			Average Molecular weight values			
						Viscosity Average (M_v)		GPC	
	$[\eta]_h$	$[\eta]_k$	k_h	k_k	k_h+k_k	M_h	M_k	$M_w \times 10^4$	$M_n \times 10^4$
S-1	7.281	6.879	0.275	0.139	0.414	32849	30374	3.51	3.30
S-2	9.58	9.167	0.356	0.1165	0.4725	47962.6	45134	4.85	4.64

Table 3.18. Viscosity Index (VI) and thickening (THK) values of the additive doped base oils

Sample	Base Oil	Additive doped base oils							
		Conc. in ppm (×10^3)							
		2		3		4		5	
		THK	VI	THK	VI	THK	VI	THK	VI
S-1	BO1	2.841	121	3.935	131	5.432	158	6.807	161
	BO2	1.093	135	1.619	150	2.259	164	3.198	198
S-2	BO1	6.06	130	6.38	169	6.731	201	6.363	211
	BO2	5.718	141	5.326	172	3.788	220	4.103	238

Table 3.19. Shear Stability of the Polymer Doped Base Oils (BO1 and BO2)

Base oils	Conc. in ppm (×10^3)	K.V				PVL		PSSI	
		Before Shear		After Shear					
		S-1	S-2	S-1	S-2	S-1	S-2	S-1	S-2
BO1	1	2.137	2.28	2.011	2.1	5.896	8.57143	34.71	35.5731
	2	2.32	2.34	2.121	2.13	8.578	9.85915	36.45	37.1025
	3	2.428	2.58	2.185	2.26	10.01	14.1593	37.16	39.7022
	4	2.517	2.85	2.208	2.37	12.28	20.2532	41.59	44.6097
	5	2.617	3.01	2.282	2.45	12.8	22.8571	39.74	45.3074
BO2	1	4.404	4.85	4.201	4.4	4.609	10.2273	52.32	53.9568
	2	4.729	5.45	4.511	4.58	8.839	18.9956	58.63	60.6695
	3	5.169	6.6	4.401	4.85	14.86	36.0825	66.61	67.7245
	4	5.77	7.02	4.551	4.97	21.13	41.2475	69.5	68.2423
	5	6.656	7.9	5.015	5.18	24.65	52.5097	62.16	70.0309

Table 3.20. Result of Biodegradability Test by i) Disc Diffusion Method ii) Soil Burial Degradation for Polymeric Additives (S-1 and S-2)

Pathogen used	Polymer	Initial Wt. (g)	Final Wt. (g)	% Wt. Loss
Disc Diffusion Method				
Calletotricheme Camellia	S-1	0.5843	0.5783	1.03
	S-2	0.5785	0.5705	1.38
Fussarium Equisitae	S-1	0.5874	0.5768	1.80
	S-2	0.5658	0.5532	2.23
Alterneria Alternata	S-1	0.5742	0.3814	33.58
	S-2	0.5483	0.4010	26.86
Colletrichum Gleosproides	S-1	0.5921	0.5765	2.63
	S-2	0.5651	0.5445	3.64
Curvularia Eragrostidies	S-1	0.5610	0.5580	0.53
	S-2	0.5531	0.5501	0.54
Soil Burial Degradation Test				
Microorganism Present in Soil	S-1	0.5881	0.4215	28.33
	S-2	0.5972	0.4528	24.18

Table 3.21. Pour points of the polymeric additives in different base oils

Polymers	Base Oils	Pour Points of the Additive Doped Base Oils Conc. in ppm (×10^3)			
		2	3	4	5
S-1	BO1	-6	-9	-15	-18
	BO2	-9	-12	-15	-18
S-2	BO1	-6	-9	-9	-12
	BO2	-6	-8	-9	-12

Figures

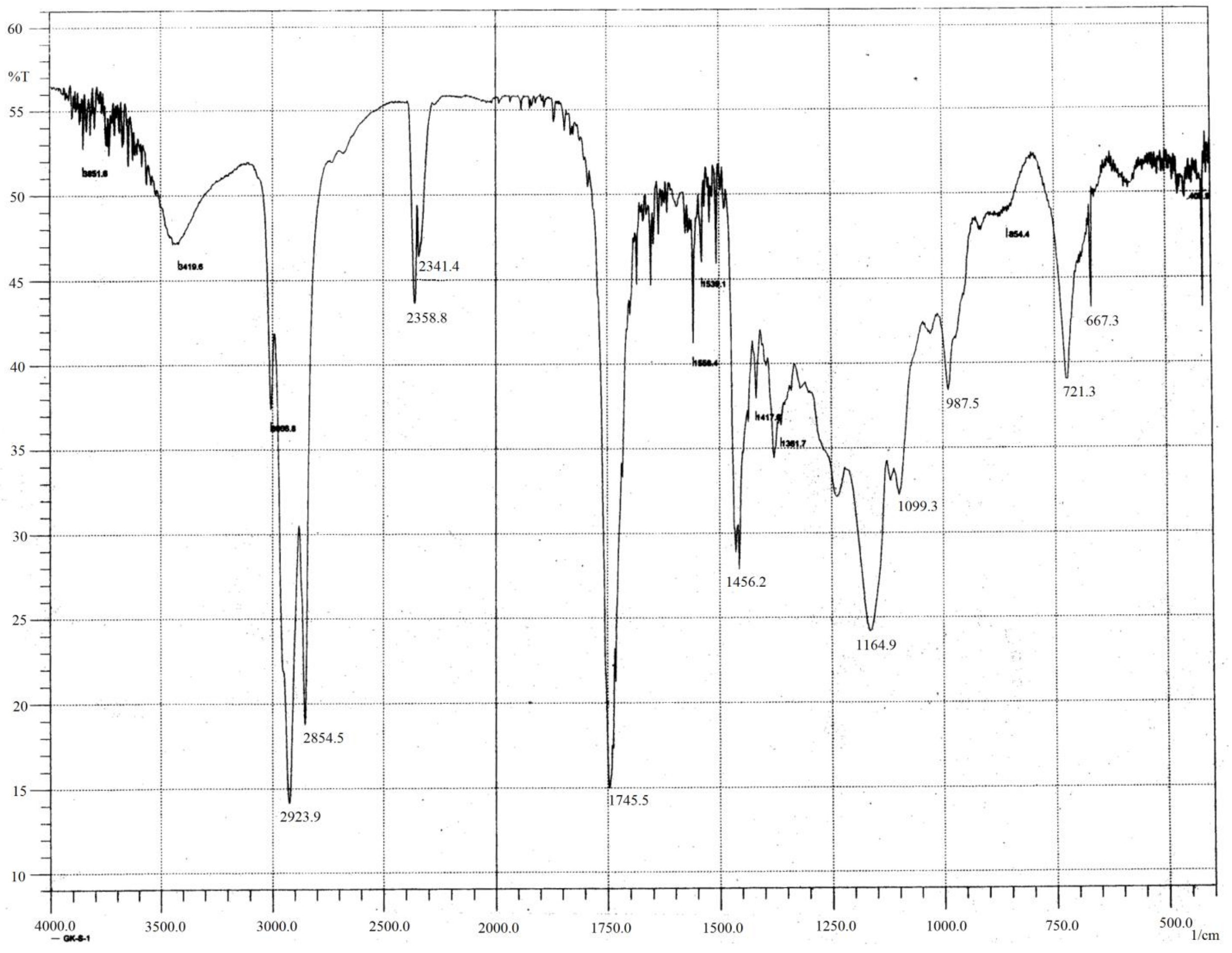

Figure 3.22. FT-IR of homopolymer of SBO

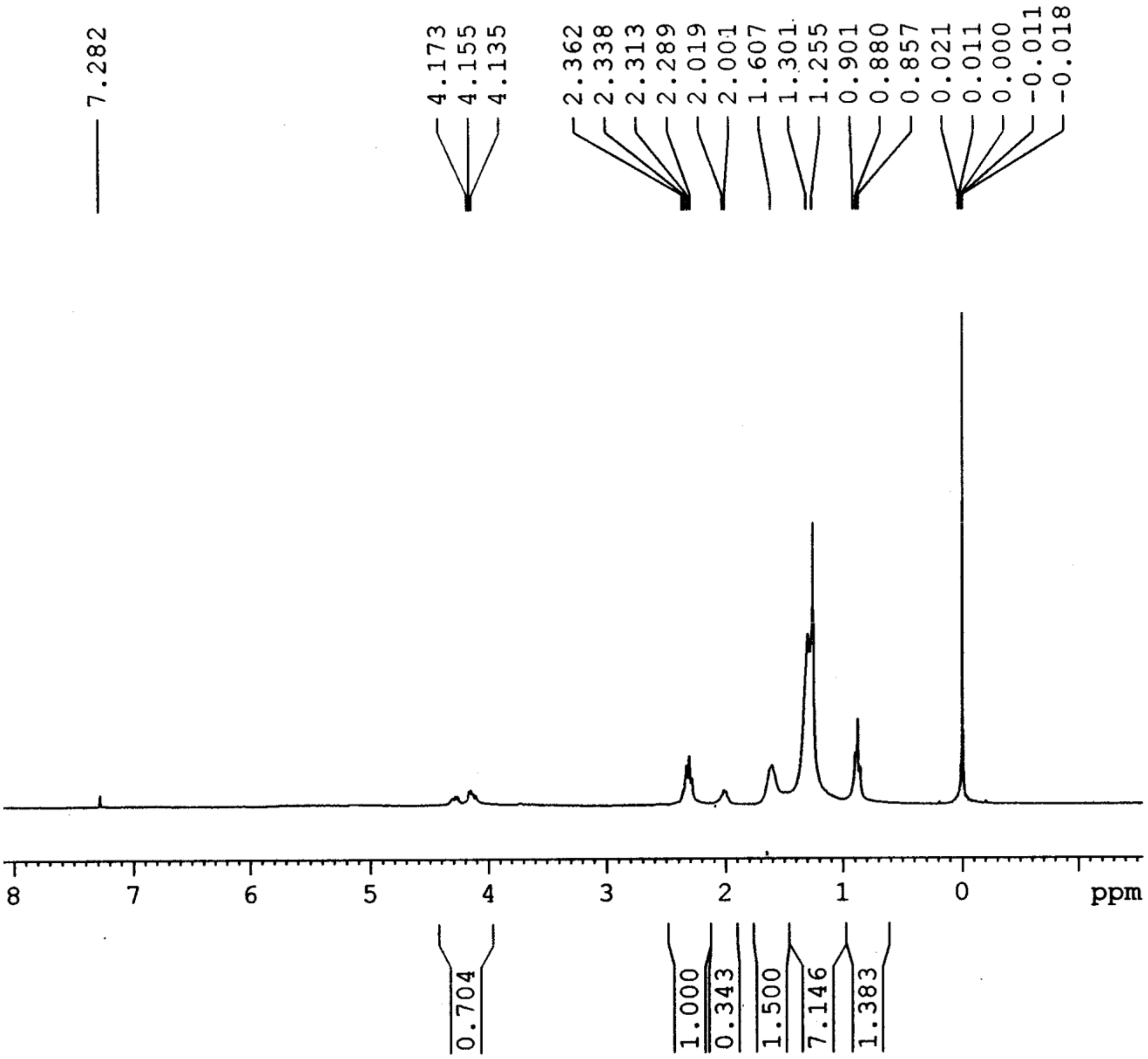

Figure 3.23. 1H NMR of homopolymer of SBO

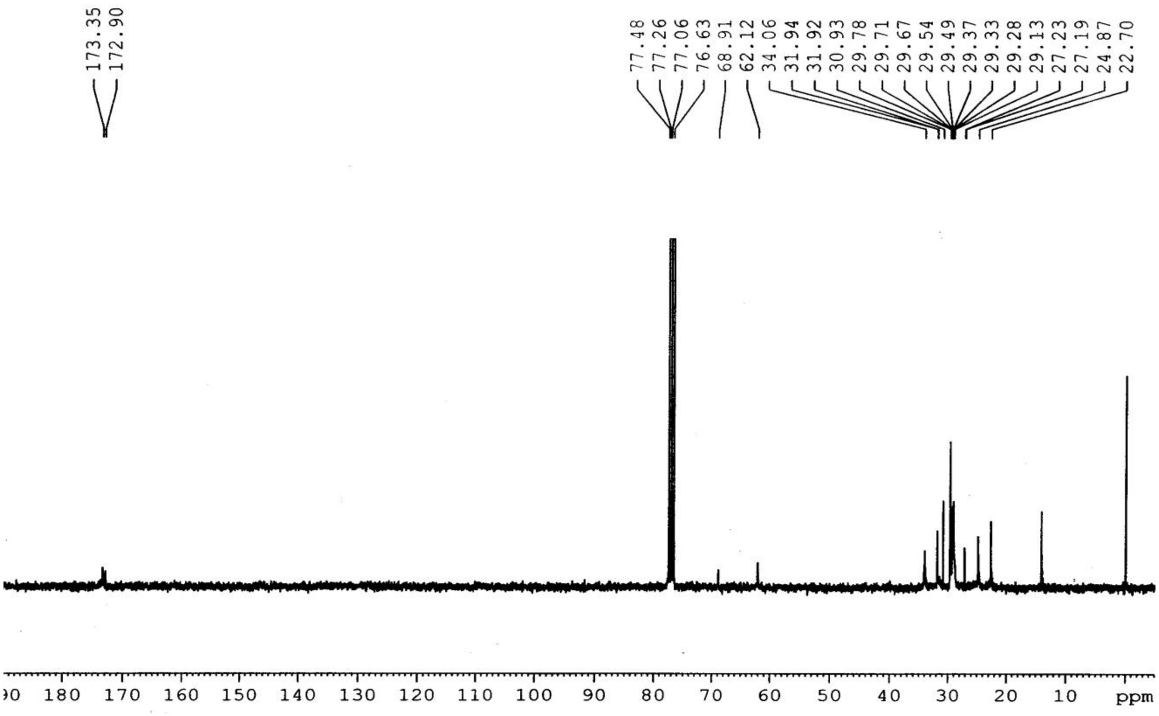

Figure 3.24. ^{13}C NMR spectra of homopolymer of SFO

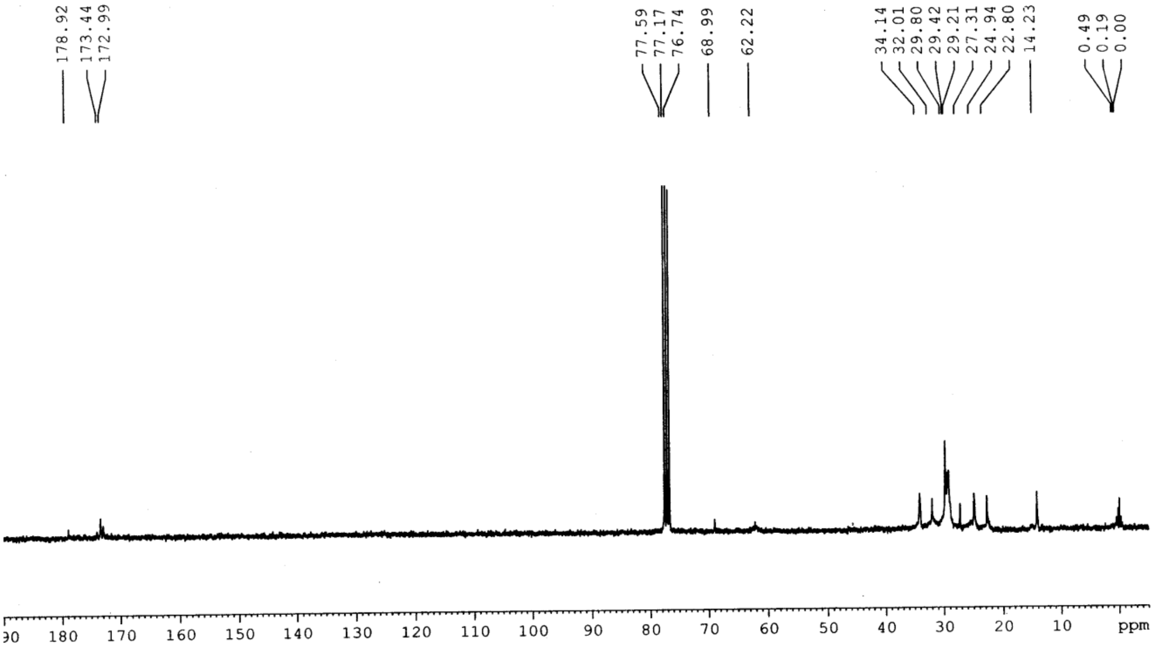

Figure 3.25. ^{13}C NMR spectra of homopolymer of SBO

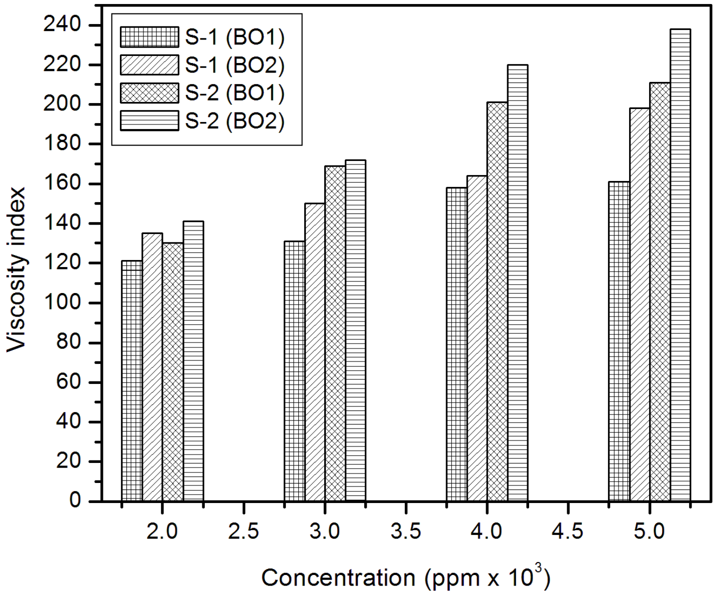

Figure 3.26. Viscosity index values of the two base oils at different levels of S-1 and S-2 additive concentrations (ppm × 10^3)

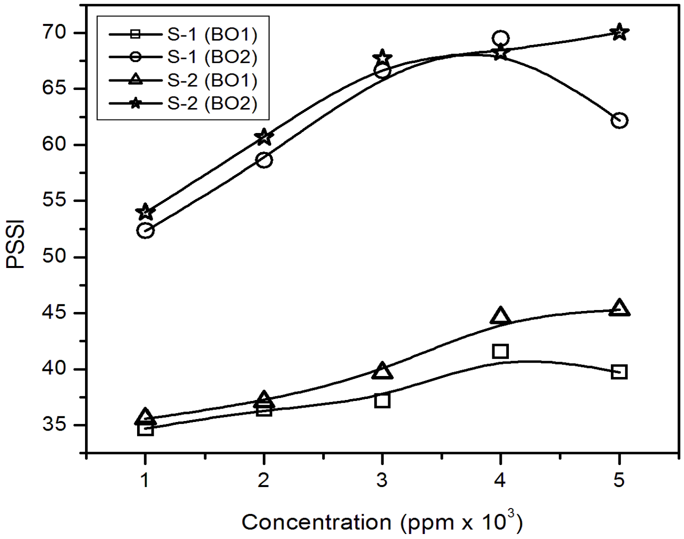

Figure 3.27. PSSI values of the base oils doped with SFO and SBO polymer at different concentration levels

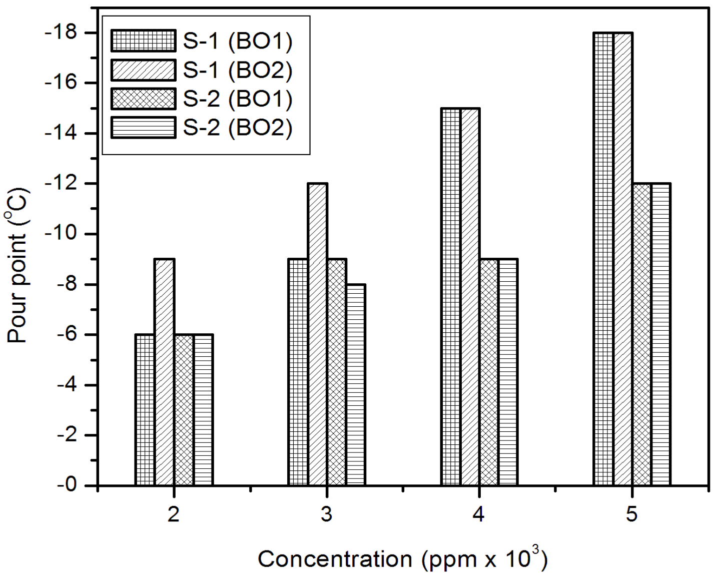

Figure 3.28. Pour point values of the two base oils at different levels of SFO and SBO polymer concentrations (ppm × 10^3)

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