

SYNTHESIS AND APPLICATION OF CHEMICAL ADDITIVES IN THE FIELD OF LUBRICANT FORMULATION

A Thesis submitted to the University of North Bengal

For the Award of
Doctor of Philosophy
in
Chemistry

By

SUJAN KUMAR PAUL, M.Sc.

Under The Supervision of

Prof. Pranab Ghosh

Department of Chemistry
University of North Bengal

June, 2021

Dedicated to
My Parents,
Wife and
Daughter...

DECLARATION

I declare that the thesis entitled “SYNTHESIS AND APPLICATION OF CHEMICAL ADDITIVES IN THE FIELD OF LUBRICANT FORMULATION” has been prepared by me under the guidance of Prof. Pranab Ghosh, Department of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

Sujan Kumar Paul

Sujan Kumar Paul

Department of Chemistry

University of North Bengal

Darjeeling - 734013

West Bengal, India

Date: *24.06.2021*

UNIVERSITY OF NORTH BENGAL

Accredited by NAAC with Grade "A"

Dr. Pranab Ghosh

Professor,
Department of Chemistry,
University of North Bengal
Darjeeling -734013, India



ENLIGHTENMENT TO PERFECTION

Ph: +91 3532776381(O)
+91 9474441468 (M)
Fax: +91 3532699001
Email: pizy12@yahoo.com

Ref. No.....

Dated.....

CERTIFICATE

I certify that Mr. SUJAN KUMAR PAUL has prepared the thesis entitled "*SYNTHESIS AND APPLICATION OF CHEMICAL ADDITIVES IN THE FIELD OF LUBRICANT FORMULATION*", for the award of Ph.D. Degree of the University of North Bengal, under my guidance. He has carried out the research work at the Department of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

Dr. PRANAB GHOSH

Professor,
Department of Chemistry
University of North Bengal
Darjeeling - 734013
West Bengal, India
Date:

Professor
Department of Chemistry,
University of North Bengal
Darjeeling - 734013, India

Urkund Analysis Result

Analysed Document: Sujan Kumar Paul_Chemistry.pdf (D109397701)
Submitted: 6/21/2021 9:01:00 AM
Submitted By: nbuplg@nbu.ac.in
Significance: 8 %

Sources included in the report:

<https://en.wikipedia.org/wiki/Decene>
<https://ir.nbu.ac.in/bitstream/123456789/2628/21/Full%20Thesis%20of%20Koushik%20Dey.pdf>
https://ir.nbu.ac.in/bitstream/123456789/2628/18/12_Part%203_Chapter%203.pdf
<https://ir.nbu.ac.in/bitstream/123456789/1830/23/Thesis%20final.pdf>
<http://14.139.211.59/bitstream/123456789/2760/22/Full%20thesis%20of%20Moumita%20Das.pdf>
https://www.researchgate.net/publication/263982883_Synthesis_and_Evaluation_of_Acrylate_Polymers_in_Lubricating_Oil
https://www.researchgate.net/publication/344001192_Performance_of_higher_polyalkyl_lactate_acrylates_as_viscosity_modifiers_in_vegetable_oils
<http://nopr.niscair.res.in/bitstream/123456789/55626/1/JSIR%2079%2811%29%20990-993.pdf>
http://14.139.211.59/bitstream/123456789/2676/21/21_part%20III_chapter%203.pdf

Instances where selected sources appear:

20



Professor
Department of Chemistry
University of North Bengal
Darjeeling - 734013, India

Sujan Kumar Paul
24.06.2021

ACKNOWLEDGEMENT

At first, I would like to express my heartfelt gratitude and sincerest thanks to my supervisor, Prof. Pranab Ghosh, Department of Chemistry, University of North Bengal, Darjeeling, who has supported me throughout my thesis work with his invaluable guidance. I will always remain grateful to him.

I convey my sincere appreciation to all the faculty members of the Department of Chemistry, the University of North Bengal for their valuable guidance and suggestions.

I bid my gratitude to the authority of the University of North Bengal for providing the facilities and accessibilities related to the research work.

I want to express my respect and thanks to the entire non-teaching staff and all the research scholars of this department for their selfless cooperation. I wish to thank my fellow lab mates for the exciting discussions, with whom I enjoyed many more unforgettable moments during this journey.

I acknowledge them who have directly or indirectly inspired me to make this work happen and also my heartiest thanks go to my friend Dibakar Roy for his immense cooperation throughout my entire journey.

The work would not have materialized without the blessings and support of my parents.

I am ever grateful to my wife Mrs. Nabanita Paul and my daughter Sharanya Paul for their unconditional love, support, and patience.

I am also grateful to the Ex-Headmaster and school management committee, Phansidewa High School (H.S.), Darjeeling, West Bengal for allowing me to carry out my research work.

I especially thank Indian Oil Corporation Limited and Bharat Petroleum Corporation Limited for providing base oils.

Abstract

Lubricants are usually liquids or semi-liquids or in some cases, solids used to lubricate automotive engines or other machines for their better performance and longevity. The other key functions of lubricants are – they keep the moving surface of the engine apart, reduce friction, protect the metal surface against corrosive damage, transfer heat, protect against wear, enhance fuel economy, carry away contaminants, and debris, etc. The main building unit of a lubricant is lubricating oil or lube oil which is the carrier of additives. The additives either enhance the properties already present in lube oil or add some desirable new properties. The present work involved three important steps-

- i. Synthesis of the additives
- ii. Characterization of the synthesized additives and
- iii. Performance evaluation of the additives

The additives synthesized were behenyl, isodecyl, and dodecyl acrylate-based homopolymer and copolymer. In the case of copolymer other monomers used were styrene and 1-Decene. Two important additives- ionic liquid blend homopolymer of behenyl acrylate and poly dodecyl acrylate-based ZnO nanocomposite were also synthesized. Finally, vegetable oil (i.e. castor oil and rapeseed oil) based biodegradable homo and copolymer with styrene were also synthesized. Characterization of the polymers was performed by spectral analysis (FT-IR, ¹H-NMR, and ¹³C-NMR). GPC was used to determine their molecular weight and thermogravimetric analysis (TGA) was used to determine thermal stability. SEM, X-RD, and DLS were used to characterize ZnO nanoparticles. Finally, the performance evaluation of the polymeric additives as viscosity index improver (VII), pour point depressant (PPD), shear stability, anti-wear (AW) was investigated. In the case of vegetable oil-based

polymers, biodegradability was investigated by disc diffusion method against fungal pathogens and also by soil burial degradation test as per ISO 846:1997.

Since all the additives synthesized are multifunctional (VII, PPD, AW, and shear stability improver), interest in research in this area gives a new horizon in the field of lubrication technology.

The thesis starts with a general introduction of the present investigation and then the entire research work has been divided into two parts- **Part-I and Part-II. Part-I** entitled, “**Acrylate Based Polymeric Compounds as Multifunctional Lube Oil Additives**” is divided into five chapters: **Chapter I, Chapter II, Chapter III, Chapter IV, and Chapter V.**

Chapter-I describes the background of the present investigation. The investigation shows that the homopolymer and copolymer of acrylate-based polymers specially dodecyl acrylate, behenyl acrylate, isodecyl acrylate, ionic liquid blend homopolymer of behenyl acrylate, and ZnO nanocomposite of poly dodecyl acrylate are widely used as viscosity index improver (VII) which is also known as viscosity modifier (VM), pour point depressant (PPD) and anti-wear.

Chapter-II entitled, “**A Study of Shear Stability, Thickening and Viscosity Index Properties of Homopolymer of Dodecyl Acrylate and its Copolymer with Styrene and 1-Decene**” describes the synthesis of the homopolymer of dodecyl acrylate (DDA) and two copolymers with styrene and 1-Decene by using azobisisobutyronitrile (AIBN) as initiator. The synthesized polymers were characterized by FT-IR and ¹H-NMR and ¹³C-NMR. Gel Permeation Chromatography (GPC) method was used to determine the molecular weight. The degradation stability towards mechanical shearing (shear stability) of the homopolymer and copolymers at different

concentration levels has been investigated. To understand the relationship between the shear stability of the polymer and the thickening effect, the thickening abilities of the polymer were also determined and compared. Viscosity index and pour point properties of the homopolymer and copolymers were also determined in the base oil.

[This work has been published: Ghosh P., Paul S., Hoque M., (2020), International Journal of Research and Analytical Reviews, 7 (2), 772-779]

Chapter-III entitled, “**A Study as a Potential Multifunctional Additive for Lubricating Oil of Poly Decyl Acrylate-Ionic Liquid Blend**” describes the synthesis of the homopolymer of behenyl acrylate using benzoyl peroxide (BZP) as free radical initiator, characterization, and evaluation for its additive performance in lube oil. The synthesized long-chain acrylate was then blended with phosphonium-based ionic liquid and their characterization was also carried out by spectral method (NMR, IR), thermogravimetric analysis, and gel permeation chromatographic method. The performance of these blends was evaluated by the standard ASTM method in the base oil. The experimental results indicated the multifunctional additive performance of the blend as they effectively provide anti-wear benefit along with pour point depressants and viscosity modifiers properties. A comparison of their performances with the homopolymer has also been evaluated and reported.

Chapter-IV entitled, “**Synthesis and a Comparative Study on Their Performances as Multifunctional Lube Oil Additives of Behenyl and Isodecyl Acrylate Based Polymers**” describes a comparative study on the performance of acrylate-based homo and copolymers as a lube oil additive. The homopolymers of behenyl acrylate, isodecyl acrylate, and their different copolymers with varying percentages of 1-Decene have been synthesized via free radical polymerization using BZP as initiator. All the prepared polymers were characterized by FT-IR and NMR spectroscopy and their

molecular weights were measured by GPC. Their performances as pour point depressant (PPD) and viscosity index improver (VII) in lube oil have been evaluated. Thermo Gravimetric Analysis (TGA) of these polymers accounted for their thermal stability as a polymeric additive. The study revealed that isodecyl acrylate-based additives were better flow improvers than those of behenyl acrylate.

Chapter-V entitled, “**A Study as a Multifunctional Additives of Acrylate Based ZnO Nano Composite for Lubricating Oil**” describes the synthesis of poly dodecyl acrylate and ZnO nanoparticles and characterization of the polymer by spectral method (NMR, IR), thermogravimetric analysis and gel permeation chromatographic method and nanoparticles by SEM, XRD, etc. The synthesized nanoparticles are then incorporated into the poly dodecyl acrylate to prepare polymer nanocomposites (PNCs) by sonication. The PNC is characterized by different analytical techniques. The additive performance of the PNC as Viscosity index improver, pour point depressant and anti-wear is evaluated by standard ASTM methods. From this study, we found that with increasing the concentration of PNC in the base stock, the overall performance of the additive is improved.

[This work has been published: Ghosh P., Paul S., Dey K., (2021), Asian Journal of Nanoscience and Materials 4(2), 159-170]

Part-II entitled, “**Vegetable Oil-based Eco-friendly Lube Oil Additives**” is divided into three chapters: **Chapter I**, **Chapter II**, and **Chapter III**.

Chapter-I describes the background of the present investigation. The investigation shows that homopolymer of vegetable oils and their copolymer with styrene are widely used as viscosity index improver (VII) which is also known as viscosity modifier (VM), pour point depressant (PPD) and anti-wear, and also introduce excellent biodegradability to the base oil.

Chapter-II entitled, “**Synthesis and a Study as a Multifunctional Ecofriendly Lubricating Oil Additives of Castor Oil Based Polymer**” describes the synthesis of the homopolymer of castor oil and copolymer of castor oil with styrene by the thermal method in solvent-free condition at different percentage composition of monomers using benzoyl peroxide (BZP) as initiator. Characterization of the additives was done by spectral technique (FT–IR and NMR spectroscopy). The molecular weight of the prepared additives was determined by Gel permeation Chromatography method (GPC method). The thermal stability of the prepared polymers was determined by Thermo Gravimetric Analysis (TGA). Standard ASTM methods were used to investigate the performance of all the prepared polymers in SN150 mineral oil as viscosity index improver (VII), pour point depressant (PPD), and anti-wear. Biodegradability of all the polymers was determined disc diffusion method.

[This work has been published: Ghosh P., Paul S., Hoque M., (2021), Journal of Macromolecular Science, Part A, 58(5), 329-335]

Chapter-III entitled, “**A Greener Lubricant Formulation using Rapeseed Oil Based Eco-Friendly Lube Oil Additives**” describes the synthesis of the homopolymer of rapeseed oil and its copolymer with styrene. Characterization of the polymer was done by spectral (FT-IR, NMR), thermogravimetric analysis, and GPC. Biocompatibility and multifunctional performances as viscosity index improver, pour point depressant, and anti-war in lube oil compared to conventional additives were investigated using standard ASTM methods. Disc diffusion and soil burial degradation method were used to determine the biodegradability of the prepared polymer.

[This work has been published: Ghosh P., Paul S., Roy D., (2020), International Journal of Petroleum and Petrochemical Engineering, 6(3), 29-37]

PREFACE

The present thesis embodied the results of research work carried out by the author under the supervisor of Prof. Pranab Ghosh, at the department of chemistry, Universality of North Bengal, Dist. Darjeeling, West Bengal, during the period of 2016 to 2021. It comprises the synthesis and characterization of multifunctional lube oil additives. The performance of the prepared additives was evaluated in different mineral base stocks as viscosity index improver, pour point depressant, antiwear, antioxidant, and detergent/dispersant additives. Lubricant is a combination of lubricating oil or base oil and a package of additives. Additives increase the performance of the lubricating oil already present or add some new properties. The key function of a lubricant is to minimize the friction and wear between two moving metal surfaces, remove heat and contaminant suspension. In modern technology, the application of multifunctional lube oil additives is of great interest. In the present work, the author has prepared some multifunctional lube oil additives and additive performances were evaluated in different base stocks. In Part I, acrylate-based synthetic polymeric additives have been synthesized and their performances were evaluated in different base stocks. Synthesis, characterization, and performance evaluation of vegetable oils (castor oil and rapeseed oil) based polymeric additives have been reported in Part II of the thesis.

TABLE OF CONTENTS

Contents	Page No.
Declaration	i
Certificate	ii
Anti-plagiarism Report	iii
Acknowledgement	iv
Abstract	v-ix
Preface	x
Table of Contents	xi-xv
Table of Scheme	xvi
List of Tables	xvii-xix
List of Figures	xx-xxiii
List of Appendices	xxiv
1. Appendix A: List of Paper Published/Accepted/communicated	xxv
2. Appendix B: List of published research papers in the Proceedings of National / International Seminar / Conference / Workshop	xxvi
3. Appendix C: Abbreviations	xxvii-xxviii

General Introduction	1-11
-----------------------------	------

PART I	12
Acrylate Based Polymeric Compounds as Multifunctional Lube Oil Additives	

Chapter I	13-17
Background of The present Investigation	
Chapter II	18
A Study of Shear Stability, Thickening and Viscosity Index Properties of Homopolymer of Dodecyl Acrylate and its Copolymer with Styrene and 1-Decene	
1.2.1 Introduction	19-20
1.2.2 Experimental section	20-21
1.2.3 Measurements	21-22
1.2.4 Results and discussion	22-25
1.2.5 Conclusions	25
1.2.6 References	25
1.2.7 Tables and Figures	26-32
Chapter III	33
A Study as a Potential Multifunctional Additive for Lubricating Oil of Poly Decyl Acrylate-Ionic Liquid Blend	
1.3.1 Introduction	34-35
1.3.2 Materials and method	35-36

Table of Contents

1.3.3 Measurements	37-38
1.3.4 Results and discussion	38-41
1.3.5 Conclusions	41
1.3.6 References	41
1.3.7 Tables and Figures	42-48
Chapter IV	49
Synthesis and a Comparative Study on Their Performances as Multifunctional Lube Oil Additives of Behenyl and Isodecyl Acrylate Based Polymers	
1.4.1 Introduction	50-52
1.4.2 Experimental section	52-54
1.4.3 Measurements	55-56
1.4.4 Results and discussion	56-58
1.4.5 Conclusions	58-59
1.4.6 References	59
1.4.7 Tables and Figures	60-67
Chapter V	68
A Study as a Multifunctional Additives of Acrylate Based ZnO Nano Composite for Lubricating Oil	
1.5.1 Introduction	69-70
1.5.2 Experimental section	70-73
1.5.3 Measurements	73-75

1.5.4 Results and discussion	75-79
1.5.5 Conclusions	79-80
1.5.6 References	80
1.5.7 Tables and Figures	81-87

PART II

88

Vegetable Oil based Eco-friendly Lube Oil Additives

Chapter I	89-92
Background of the present Investigation	
Chapter II	93
Synthesis and a Study as a Multifunctional Ecofriendly Lubricating Oil Additives of Castor Oil Based Polymer	
2.2.1 Introduction	94-95
2.2.2 Experimental section	95-96
2.2.3 Measurements	96-97
2.2.4 Results and discussion	98-101
2.2.5 Conclusions	101
2.2.6 References	101
2.2.7 Tables and Figures	102-113
Chapter III	114
A Greener Lubricant Formulation using Rapeseed Oil Based Eco- Friendly Lube Oil Additives	
2.3.1 Introduction	115-116
2.3.2 Experimental Section	116-117

Table of Contents

2.3.3 Measurements	117-119
2.3.4 Results and discussion	120-124
2.3.5 Conclusions	124
2.3.6 References	124
2.3.7 Tables and Figures	125-132

Bibliography	133-148
---------------------	---------

Index	149-152
--------------	---------

LIST OF SCHEMES

Scheme No.	Title of Scheme	Page No.
Scheme 1.2.1	Reaction for the synthesis of homopolymer of dodecyl acrylate and copolymer with and 1-Decene	20
Scheme 1.3.1	Esterification of acrylic acid with decyl alcohol followed by polymerization of ester	36
Scheme 1.4.1	Reaction for the preparation of isodecyl acrylate and behenyl acrylate	53
Scheme 1.4.2	Reaction for the preparation of homopolymer of isodecyl and behenyl acrylate and copolymer with 1-Decene	54
Scheme 1.5.1	Reaction for the preparation of dodecyl acrylate	71
Scheme 1.5.2	Reaction for the preparation of homopolymer of dodecyl acrylate	72
Scheme 1.5.3	Reaction involved during synthesis of nano-ZnO	73
Scheme 2.2.1	Reaction for the preparation of homopolymer of castor oil and its copolymer with styrene	96
Scheme 2.3.1	Reactions for the preparation of homopolymer of rapeseed oil and copolymer with styrene	117

LIST OF TABLES

Table No.	Title of Table	Page No.
Table 1.2.1	Average molecular weight and TGA values of the prepared polymers and its graphical representation	26
Table 1.2.2	PVL and PSSI Values of the Additives Doped Base Oil	27
Table 1.2.3	Thickening power (THK) of the Additives Doped Base Oil	27
Table 1.2.4	VI values of the Additives Doped Base Oil and its graphical representation	28
Table 1.2.5	Pour Point (PP) of the Additives Doped in Base Oil and its graphical representation	29
Table 1.3.1	Specification of the chemicals used	42
Table 1.3.2	Base oil properties	42
Table 1.3.3	The weight average and number average molecular weights (Mw and Mn) and polydispersity index of the sample and its graphical representation	43
Table 1.3.4	Tribological performance of the samples in two different base oil	44
Table 1.3.5	Anti-Wear Performance of Additive Doped Base Oil its graphical representation under 20 kg load	45
Table 1.4.1	Base Oil (BO) Properties	50
Table 1.4.2	Weight percentage (%) composition, Mn, Mw, and PDI values of polymers (P1 to P8)	50

List of Tables

Table 1.4.3	Pour point (°C) data with respect to the different concentrations of the additives in BO1 and its graphical representation	61
Table 1.4.4	Pour point (°C) data with respect to the different concentrations of the additives in BO2 and its graphical representation	62
Table 1.4.5	Viscosity Index (VI) data with respect to the different concentrations of the additives in BO1 and its graphical representation	63
Table 1.4.6	Viscosity Index (VI) data with respect to the different concentrations of the additives in BO2	64
Table 1.4.7	TGA data of the polymers	64
Table 1.5.1	Properties of base oil	81
Table 1.5.2	Designation and Composition of polydodecylacrylate nano ZnO composites	81
Table 2.2.1	Properties of castor oil	102
Table 2.2.2	Molecular weight of the prepared polymers and its graphical representation	103
Table 2.2.3	Percentage composition and TGA values of the prepared polymers	104
Table 2.2.4	Viscosity index (VI) values of polymer blended base oil	104
Table 2.2.5	Pour point values of polymer blended base oil and its graphical representation	105
Table 2.2.6	Anti-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition and its graphical representation	106
Table 2.2.7	Results of biodegradability test	107

List of Tables

Table 2.3.1	Properties of Rapeseed oil and Base oil	125
Table 2.3.2	Percentage composition and TGA values of the prepared polymers	125
Table 2.3.3	Molecular weight of the prepared polymers	126
Table 2.3.4	Viscosity index (VI) values of polymer blended base oil	126
Table 2.3.5	Pour point values of polymer blended base oil and its graphical representation	127
Table 2.3.6	Anti-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition and its graphical representation	128
Table 2.3.7	Result of biodegradability test by the disc diffusion method and soil burial degradation	129

LIST OF FIGURES

Figure No.	Title of Figure	Page No.
Figure 1	Action mechanism of pour point depressant	3
Figure 2	Structures of some commonly used Pour Point Depressants	3
Figure 3	Structures of some commonly used viscosity index improver	4
Figure 4	Effect of temp. of polymeric additive in lube oil	5
Figure 5	Glycerol monooleate (GMO)	6
Figure 6	Action mechanism of anti-wear additives	6
Figure 7	Donor acceptor bond between AW additive and metal (Fe) surface	7
Figure 8	Structure of a monomeric zinc dialkyl dithiophosphate	7
Figure 9	Action mechanism of dispersant additive	8
Figure 10	General structure of a succinimide based and Mannich Base dispersants	8
Figure 11	Radical trapping by hindered phenols	9
Figure 1.2.1	IR spectra of homo polymer (P-1)	30
Figure 1.2.2	¹ H NMR spectra of homo polymer (P-1)	30
Figure 1.2.3	¹³ C NMR spectra of homopolymer (P-1)	31
Figure 1.2.4	IR spectra of copolymer (P-3)	31
Figure 1.2.5	¹ H NMR spectra of copolymer (P-3)	32
Figure 1.2.6	¹³ C NMR spectra of copolymer (P-3)	32

List of Figures

Figure 1.3.1	FT-IR spectra of polydecyl acrylate	46
Figure 1.3.2	¹ H- NMR spectra of polybehenyl acrylate	46
Figure 1.3.3	¹³ C- NMR spectra of poly behenyl acrylate	47
Figure 1.3.4	Plot of PWL (Percent Weight Loss) vs Temperature (in K)	47
Figure 1.3.5	Plot of photo micrographic images of base oil and additive (P-1, P-2, P-3, and P-4) doped base oil.	48
Figure 1.4.1	FT-IR spectrum of co-polymer of BA- 1-decene (P3)	65
Figure 1.4.2	¹ H NMR spectrum of co-polymer of BA- 1-decene (P3)	65
Figure 1.4.3	¹³ C- NMR spectrum of co-polymer of BA - 1-decene (P3)	66
Figure 1.4.4	FT-IR spectrum of co-polymer of IDA- 1-decene (P7)	66
Figure 1.4.5	¹ H NMR spectrum of co-polymer of IDA - 1-decene (P7)	67
Figure 1.4.6	¹³ C NMR spectrum of co-polymer of IDA - 1-decene (P7)	67
Figure 1.5.1	FT-IR spectra of (a) polymer (A) and (b) polymer/ZnO nano composite (Z-3)	82
Figure 1.5.2	¹ H NMR spectra of polymer (A) and the PNC (Z-3)	83
Figure 1.5.3	¹³ C NMR spectra of polymer (A) and the composite (Z-3)	84
Figure 1.5.4	XRD spectra of prepared ZnO nanoparticles	85
Figure 1.5.5	SEM images (a, b, c and d) of prepared ZnO nanoparticle at different magnifications	85
Figure 1.5.6	TGA data of polymer (A) and polymer/ZnO nanocomposite (Z-1, Z-2 and Z-3)	86
Figure 1.5.7	Plot of viscosity index of the lube oil blended with additives at different concentration levels	86

List of Figures

Figure 1.5.8	Plot of pour point of the lube oil blended with additives at different concentration	87
Figure 1.5.9	Wear scar diamete	87
Figure 2.1	General structure of vegetable oil (triglyceride)	90
Figure 2.2.1	FT-IR spectra of homopolymer of castor oil (P-1)	107
Figure 2.2.2	¹ H NMR of homopolymer of castor oil (P-1)	108
Figure 2.2.3	¹ H NMR of copolymer of castor oil and styrene (P-2)	108
Figure 2.2.4	GPC chromatogram of the copolymer P-1	109
Figure 2.2.5	GPC chromatogram of the copolymer P-2	109
Figure 2.2.6	GPC chromatogram of the copolymer P-3	110
Figure 2.2.7	GPC chromatogram of the copolymer P-4	110
Figure 2.2.8	GPC chromatogram of the copolymer P-5	111
Figure 2.2.9	GPC chromatogram of the copolymer P-1, after biodegradation	111
Figure 2.2.10	GPC chromatogram of the copolymer P-2, after biodegradation	112
Figure 2.2.11	GPC chromatogram of the copolymer P-3, after biodegradation	112
Figure 2.2.12	GPC chromatogram of the copolymer P-4, after biodegradation	113
Figure 2.2.13	GPC chromatogram of the copolymer P-5, after biodegradation	113
Figure 2.3.1	A representative FT-IR spectra of the rapeseed oil – styrene copolymer	129
Figure 2.3.2	A representative ¹ H NMR spectra of rapeseed oil – styrene copolymer	130

List of Figures

Figure 2.3.3	A representative ^{13}C NMR spectra of rapeseed oil-styrene copolymer	130
Figure 2.3.4	FT-IR spectra of the homo polymer of rapeseed oil	131
Figure 2.3.5	^1H NMR spectra of homo polymer of rapeseed oil	131
Figure 2.3.6	^{13}C spectra of homo polymer of rapeseed oil	132
Figure 2.3.7	A representative FT-IR spectra of the copolymer after biodegradability test	132

LIST OF APPENDICES

Appendix	Page No.
Appendix A	xxv
List of paper published/ accepted/communicated	
Appendix B	xxvi
List of oral and poster presentations	
Appendix C	xxvii-xxviii
Abbreviations	

List of Paper Published/Accepted/Communicated

1. Dodecyl Acrylate and its Copolymer with Styrene and 1-Decene: A Study of Shear Stability, Thickening and Viscosity Index Properties P. Ghosh, **S. Paul** and M. Hoque, *International Journal of Research and Analytical Reviews*, **2020**, 7(2), 772-779.
2. Greener Lubricant Formulation: Rapeseed Oil Based Eco-Friendly Lube Oil Additives. P. Ghosh, **S. Paul** and D. Roy, *International Journal of Petroleum and Petrochemical Engineering*, **2020**, 6(3), 29-37.
3. Castor oil based eco-friendly lubricating oil additives. M. Hoque, **S. Paul** and P. Ghosh, *Journal of Macromolecular Science, Part A, Pure and Applied Chemistry*, **2021**, 58(5), 329-335.
4. Koushik Dey, **Sujan Paul**, Pranab Ghosh. Multifunctional additive properties of acrylate based ZnO Nano composite for lubricating oil. *Asian Journal of Nanoscience and Materials*, 4(2) **2021**, 159-170.
5. Dodecylmethacrylate-vinyl acetate copolymer-a multifunctional performance additive for lubricating oil, Dibakar Roy, **Sujan Paul** & Pranab Ghosh, *International Journal of Applied and Natural Sciences (IJANS)*, **2020**, 9(6), 29–36.
6. Synthesis of linseed oil based biodegradable homo and copolymers: role as multifunctional greener additives in lube oil Dibakar Roy, **Sujan Paul**, Sultana Yeasmin & Pranab Ghosh, *Journal of macromolecular Science, Part A Pure and Applied Chemistry*, **2021**, 58, (1), 2–7.
7. Acrylate - Ionic liquid blend: A potential multifunctional additive for lubricating oil, **Sujan Paul**, Dibakar Roy and Pranab Ghosh, *International Journal of Research and Analytical Reviews (IJRAR)*, registration ID-IJRAR 227230 Date **24/10/2020**.
8. Synthesis of behenyl - and isodecyl acrylate based polymers: A comparative study on their performances as multifunctional lube oil additives, Pranab Ghosh, **Sujan Paul** and Sultana Yeasmin, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* - Manuscript ID LMSA-2020-0186.R1, Dated : **06/10/2020**.

Appendix B

List of Seminars/Symposiums/Conferences Attended

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

Abbreviations

1. AIBN - Azobisisobutyronitrile
2. ASTM – American Society for Testing and Materials
3. AW - Antiwear
4. BO1 – Base oil 1
5. BO2 – Base oil 2
6. BO3 – Base oil 3
7. BPCL – Bharat Petroleum Corporation Limited
8. BZP – Benzoyl peroxide
9. CO – Castor oil
10. DMA- Decylmethacrylate
11. DDA- Dodecyl acrylate
12. DAM – Decyl amine
13. DDAM – Dodecyl amine
14. DDMA – Dodecyl methacrylate
15. FBWT – Four Ball Wear Test
16. GPC – Gel Permeation Chromatography
17. HPLC – High Performance Liquid Chromatography
18. IDA- Isodecyl acrylate
19. IL- Ionic Liquid
20. IOCL – Indian Oil Corporation Limited
21. IR – Infra red
22. KV – Kinematic viscosity
23. Mn - Number average molecular weight
24. Mw - Weight average molecular weight
25. NMR – Nuclear magnetic resonance
26. NP- Nanoparticle
27. OAM – Octyl amine
28. OEM- Original equipment manufacturer
29. PMA- Polymethacrylate
30. PNC- Polymer nanocomposite
31. PPD- Pour point depressant

32. PSSI – Permanent shear stability index
33. PVL- Permanent Viscosity Loss
34. SBT – Soil burial test
35. SSI – Shear stability index
36. SIP- Styrene isoprene polymer
37. TMS - Tetramethylsilane
38. TVL – Temporary viscosity loss
39. TGA – Thermo gravimetric analysis
40. VI – Viscosity index
41. VII – Viscosity index improver
42. VM – Viscosity modifier
43. WSD – Wear scar diameter
44. XRD – X-ray diffraction
45. ZDDP- Zinc dialkyl dithiophosphate
46. ZDP – Zinc dithiophosphate

GENERAL INTRODUCTION

Lubricants or lubricating oils are the substances introduced between two moving surfaces (sliding/rolling) to reduce the friction resistance between them. Lubricating oil has been used for a variety of purposes to prevent friction and corrosion on the clashing surfaces, suppress heat generation, keep objects clean and create insulation and rust-preventive effects [1]. Petroleum-based lube oil is a complex mixture of various substances like hydrocarbons, aromatic, naphthenic, paraffinic, etc. which have a molecular weight ranging from C_{20} – C_{50} with a boiling point range from $150^{\circ}C$ to $600^{\circ}C$ [2]. The effectiveness of lube oils solely depends on their rheological properties like viscosity index (VI) i.e. change of viscosity with the change of temperature, low-temperature fluidity, etc. That means a good lube oil should have a very minute change of viscosity with change in temperature [3] and must have flow character at high as well as low temperature [4]. With the development of modern engines and equipment, only the base oils can't fulfill all the requirements of the modern engine and equipment. As a result, scientists are trying to make lubricants that can fulfill most of the requirements of the modern engine and equipment. Research and developments show that only the base oil can't fulfill all the requirements of perfect lube oil. As a result, to improve the performance of lube oil, it is necessary to add some foreign substances, which are called lube oil additives [5]. When additives are added to the base oil then the mixture is called lubricants. Normally lubricants are synthetic polymeric or in some cases nonpolymeric in nature [1]. The additives blended lube oil or lubricants are more compatible with the modern engine. The additives not only increase the performance of the base oils that already present in them but also add some extra properties [6].

Additives perform a wide variety of functions within engine lubricants [6]. These are:

- i. Protect the engine surfaces by performing anti-wear, anti-rust or anti-corrosive properties, which in combination prevent damage to the coatings and surfaces within the engine.
- ii. Modify the physical properties of the lubricant by acting as viscosity modifiers and pour point depressants.
- iii. Prevent and control the effects of engine deposition by acting as antioxidants and dispersants and detergents.
- iv. Increased fuel economy by acting viscosity modifying properties which are due to reduction of friction between moving surfaces or providing favorable viscosity profiles that can lead to improved efficiency.
- v. Reduce pollution by emerging new properties like biodegradability to the lube oil.

Based on the lubricant types different combinations of the quantity of additives are used and the amount of the additives to be added to the lube oil may reach up to 30% [7].

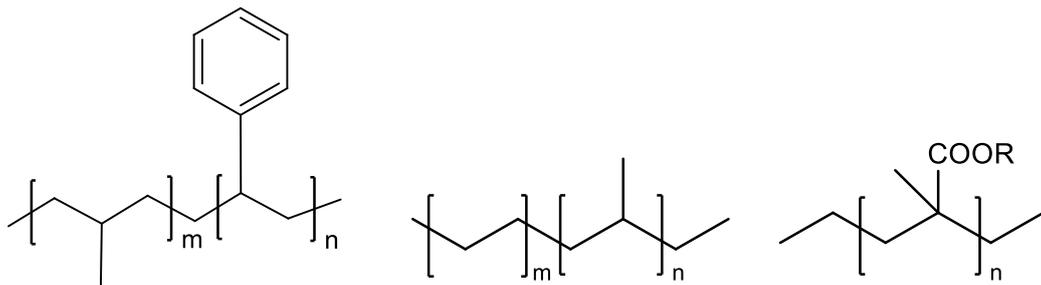
Different types of additives which are generally used in the petroleum base lube oil are: i) Pour Point Depressant (PPD), ii) Viscosity Index Improver (VII) or Viscosity Modifier (VM), iii) Friction Modifier (FM), iv) Anti-wear Additive (AW), v) Detergent, vi) Antioxidant (AO), vii) Extreme Pressure Additive (EP), viii) Dispersant, ix) Anti-foaming Agent, x) Rust and Corrosion Inhibitor.

Pour Point Depressant:

The pour point of an oil is the lowest temperature at which an oil will pour or flow when cooled. Most of the lube oils contain some paraffin wax and complete removal

Viscosity Index Improver:

Viscosity Index (VI) is a unitless arbitrary number of a fluid that measures the change in viscosity with a temperature change. The lower value of VI indicates that viscosity is more affected by a change in temperature and on the other hand higher value of VI indicates that the change of viscosity is very less with temperature change. If the lubricant is too viscous, it will require a large amount of energy to move and if it is too thin, the surfaces will come in contact and friction will increase. Since in the automotive engine during working condition there is a huge change in temperature, the lubricant with lower viscosity index affect badly the engine performance and durability. So to modify the viscosity index of lube oil, there must be added some foreign substance which is called viscosity modifier (VM) or viscosity index improver (VII). VII resists the change of viscosity of lube oil with a change in temperature [17]. High molecular weight polymers like vegetable oil-based polymers, acrylate-based polymers, hydrogenated styrene isoprene copolymer, ethylene-propylene copolymer are widely used as VII.



Hydrogenated styrene isoprene copolymer ethylene-propylene copolymer (OCP) polyalkyl methacrylate

Figure 3: Structures of some commonly used viscosity index improver

This is to be believed that when the oil temperature is low, these polymers curl up into tight balls that flow readily with the oil molecules (**Figure 4**). As the temperature

increases, they expand into large stringy structures that restrict the normal oil flow, which has a thickening effect on the oil. When the oil cools down, the polymers go back to their original shape [18].

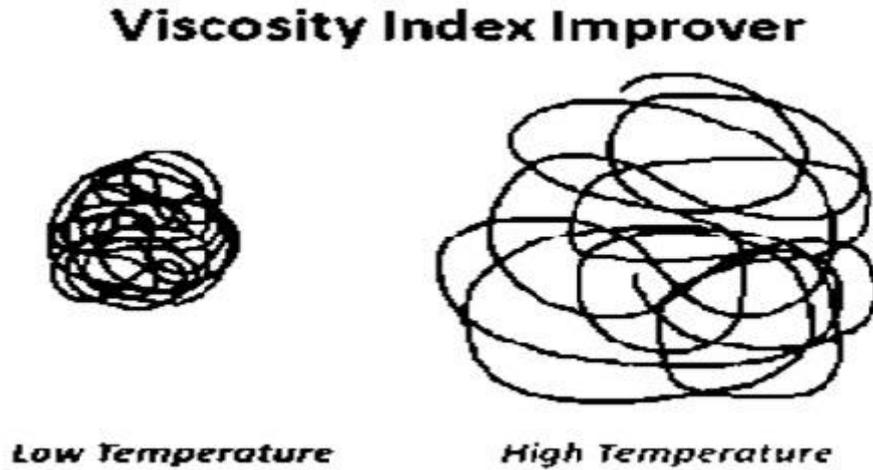


Figure 4: Effect of temp. of polymeric additive in lube oil

Friction Modifier:

Friction modifiers are the additives that are used in lubricants to modify the coefficient of friction (hence the name, Friction Modifiers). Friction modifiers are employed to prevent wear on metal surfaces. These additives help slow down wear and increase fuel economy. The mechanical action of the friction modifier is that they form a polar molecular film by strong adsorption on the surface of the metal. FMs are normally straight-chain hydrocarbons with a polar head group. Generally, the polar head groups are Carboxylic acids or their derivatives amines, amides and their derivatives, phosphoric or phosphonic acids, and their derivatives. The polar head groups are strongly adsorbed on the metal surface and form relatively strong bonds on the other hand the long hydrocarbon tail is left solubilized in the oil. Both the structure of the hydrocarbon chain and the nature of the polar head groups have a strong influence on the contribution to friction reduction. Polyol esters of fatty acids e.g. glyceryl

monooleate, amides of fatty acids, molybdenum compounds e.g. molybdenum dithiocarbamate, sulfurised fats, and esters are the widely used friction modifier.

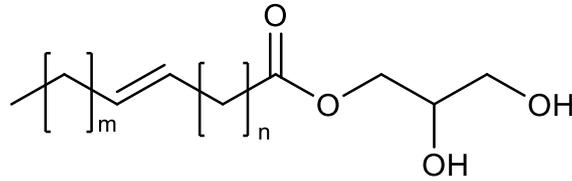


Figure 5: Glycerol monooleate (GMO)

Anti-Wear Additives:

Lubricants form a hydrodynamic multimolecular film on the surface of the metal. When the load is low, the surfaces can't touch each other and which results no wear. However, the formation of a hydrodynamic multimolecular film on metal surfaces is not always possible.

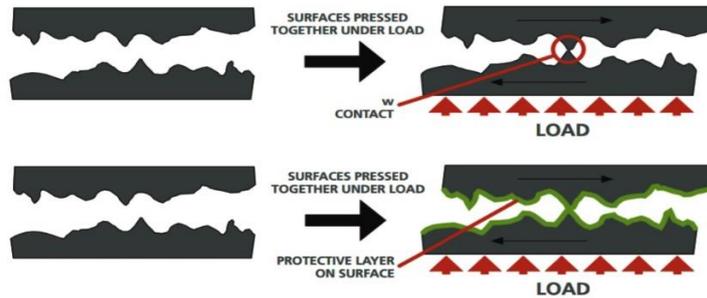


Figure 6: Action mechanism of anti-wear additives

When the load is high and the lubricant's viscosity is not good, the surfaces of the moving parts make contact, shown in **Figure 6**. This metal-metal contact between the lubricated surfaces destroys the boundary lubrication. Under this situation, friction can be minimized by the addition of the anti-wear additives to the metal surface by the formation of the lubricating solid film. Normally anti-wear additives strongly adsorbed or chemisorbed on the metal surface and form a film. When the chemisorption takes place, electrons transfer occurs between additive molecules and metal surfaces [19].

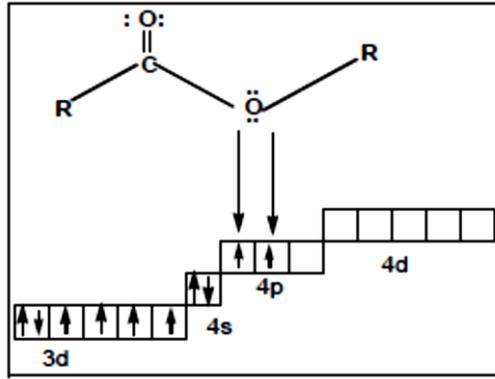


Figure 7: Donor acceptor bond between AW additive and metal (Fe) surface

Some examples of anti-wear additives are zinc dithiophosphate (ZDP), zinc dialkyl dithiophosphate (ZDDP) are used in formulated engine oils [20]. Some Organosulfur, Organophosphorus compounds are used as AW as well as EP additives. It has been found that acrylate-based ZnO nanocomposite, polymeric vegetable oils can also be acted as AW.

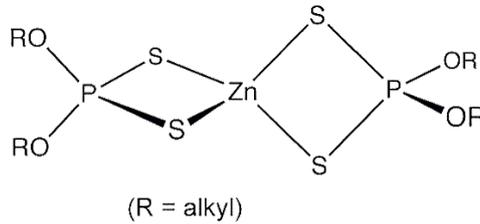


Figure 8: Structure of a monomeric zinc dialkyl dithiophosphate

Detergent and Dispersant Additives:

During the combustion process in the internal combustion engine, several strong acids are formed in the engine oil and deposited on the metal surface [21]. Detergents are substances that neutralized the acids from on the metal surface. Sulfonates, Phenates, Salicylates, phosphates of alkaline earth metals such as Ca and Mg are used as detergent. Heavy metals like Ba are no longer used. Dispersants have ionizable polar heads and hydrocarbon chains that form micelles and trap soot or sludge and also

stabilize larger particles by charge repulsion. By which dispersant additives keep the foreign particles in a finely divided and uniformly dispersant through the lube oil [22].



Figure 9: Action mechanism of dispersant additive

A dispersant molecule has a polar head and the polarity is derived from oxygen or nitrogen moieties and a hydrocarbon tail which is normally polyisobutene, which enables the substrate to be fully oil soluble. Some widely used dispersants are Mannich base and phosphosulphurized Mannich bases of hindered phenols [23], polyisobutylene succinimides [24], amidation products of maleic anhydride and alpha-olefin copolymer [25], etc

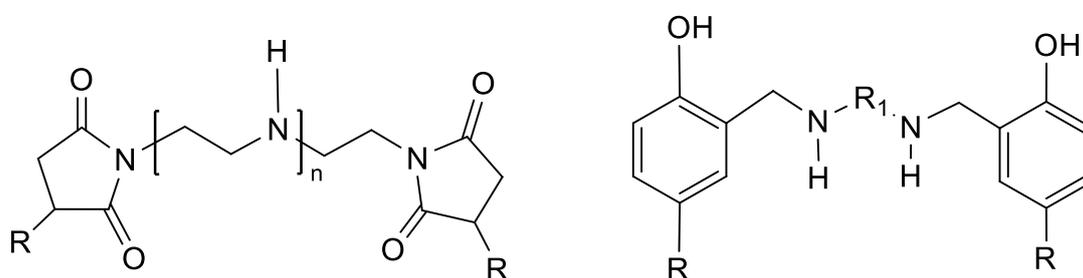


Figure 10: General structure of a succinimide based and Mannich Base dispersants

Antioxidant Additives:

Oxidation of lube oil makes the oil dark and thick. Because during oxidation hydrocarbon chains of lube oil are broken down and form insoluble soot or sludge particles. Because of the oxidation of lube oil, several organic acids are produced which are extremely corrosive towards non-ferrous metals and further oxidation leads to the buildup of polymeric material. These high molecular weight oxygenated polymers cause oil thickening, varnish, and gum deposits on pistons and other engine components.

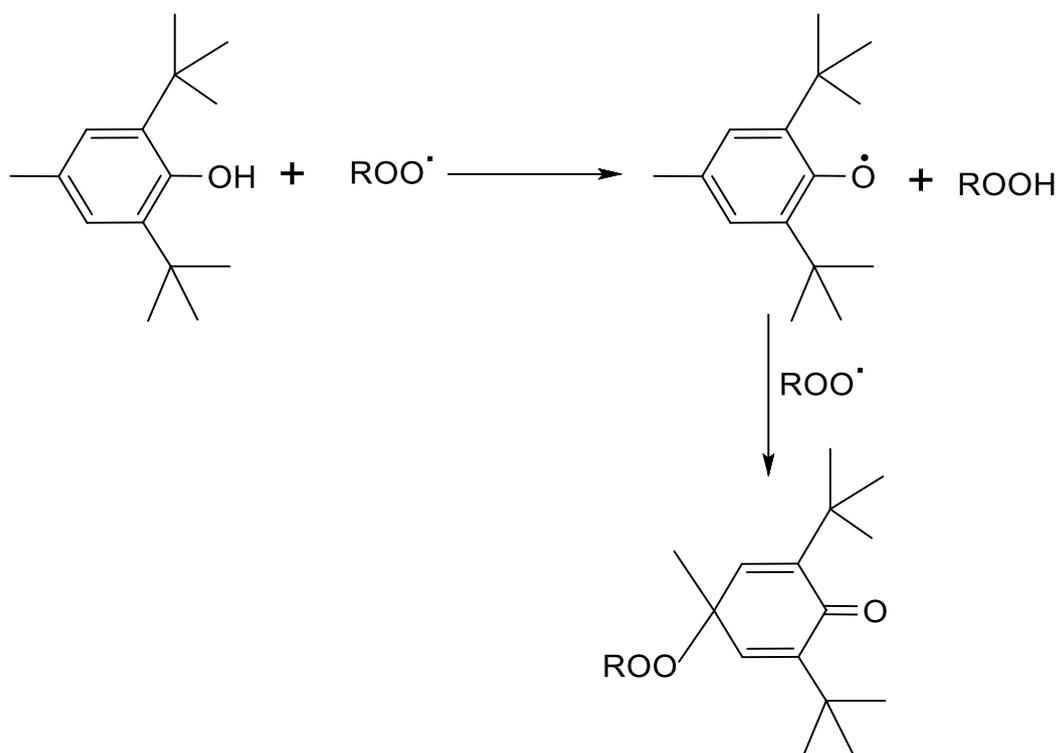


Figure 11: Radical trapping by hindered phenols

Antioxidants work by disrupting the chain propagating steps of the oxidative process by which these insoluble species are formed. The oxidative process is a chain reaction which once started, propagates at an exponential rate producing increasing amounts of free radical or peroxide species [6]. The antioxidants themselves function as either

peroxide decomposers or as free radical traps. Zinc dialkyl dithiophosphate (ZDDPs) can act as antioxidants by destroying the chain propagation steps of the oxidative reaction, by acting as either peroxide decomposers or free radical traps. Hindered alkyl phenols can break down free radicals chain reaction to form stable hindered radicals which are not able to propagate the free radical chain reaction (**Figure 11**).

Although many researchers have studied and reported several additives which are functioning either only as a viscosity modifier [26] or pour point depressant [27] or anti-wear additive [28] or some additives work based on bifunctional properties like viscosity modifier and pour point depressant [29] or viscosity modifier and anti-wear [30] or antioxidants and detergents/dispersants [31] etc. But the research based on polymeric additives that have multifunctional properties is very scanty to date. With the development of engine technology, the modern engines are demanding cost-effective, high quality and environmentally benign additive which have multifunctional performance [32]-[34]. Keeping these in mind, the author has made an effort to form some multifunctional additives in a single additive system to fulfill the above demand. Some acrylate-based like dodecyl acrylate, behenyle, and isodecyl acrylate ionic liquid blends were synthesized and multifunctional additive performance was also evaluated. Keeping in mind, the concept of green technology, the present investigation also comprises the synthesis and evaluation of the performance of vegetable oil-based multifunctional additives. The vegetable oils used in this study are castor oil, rapeseed oil. Our present investigation also comprises the synthesis of acrylic base ZnO nanocomposites as lube oil additives. The additive doped lube oils show excellent multifunctional additive performance along with excellent biodegradability. In brief, the thesis emphasizes on the synthesis of additives followed by characterization as well as performance evaluation of the synthesized additives for

lubricating oils. The characterization was carried out by spectroscopic method, especially FT-IR and NMR. Thermogravimetric (TGA) was used to determine thermal stability. The gel permeation chromatographic (GPC) method was used to determine the molecular weight of the polymers. The characterization of nano-ZnO was performed by CEM, X-RD, and DLS. Finally, the performance of the additives mainly as viscosity modifier (VM), viscosity index improver (VII), pour point depressant (PPD), in few cases anti-wear (AW), antioxidant, and detergent/dispersant was evaluated by standard ASTM method in different base oils. The shear stability of some of the additives was also determined and reported. Biodegradability character was carried out by soil burial test method [35] and disc diffusion method using different fungal pathogens according to ISO 846:1997 rules. To study the mechanism action of pour point, photomicrographic image and power XRD of some of the PPD was carried out. The outcome of our present investigations has some important potential additives for lubricating oil which will be dealt with for commercial application and that will be taken up by our group in near future.

References

References are given in *BIBLIOGRAPHY* under “General Introduction” (Page No. 133-136)

Part I

Acrylate Based Polymeric Compounds as Multifunctional Lube Oil Additives

Chapter I

BACKGROUND OF THE PRESENT INVESTIGATION

With the development of modern technology, original equipment manufacturers (OEM) are trying to make modern and advanced engines. These types of engines require lubricants with multifunctional performance. But the existing lubricants cannot fulfill the requirement of modern engines and technology. Therefore it is necessary to prepare lubricants with multifunctional performance so that they can fulfill all the demands of the modern engine. All the commercially available lubricants contained some additives in them to add additional performance to the lube oil. Additive percentages in lube oil may vary from 1% to 30% or in some cases more [1]. The different types of additives which are normally added to the lube oil to improve its performance are:

- i. Viscosity index improvers (VII) [2].
- ii. Pour point depressant (PPD) [3].
- iii. Anti-rwear additives [4].
- iv. Antioxidant [5].
- v. Detergent/dispersant [6].
- vi. Corrosion inhibitor [7].
- vii. Extreme pressure additives [8].

When these types of additives are added to the lube oil they not only enhance the performance present in it but also add some new properties. Since chemical additives are not cost-effective and very harmful to the environment. So it is necessary to prepare some polymeric additives which are multifunctional so that they can fulfill the demand of modern engine and equipment.

In accordance with the present investigation it is very relevant to include a brief review on viscosity index improver (VII), pour point depressant (PPD), anti-wear (AW) properties, and shear stability. As already discussed in the general introduction the viscosity index (VI) is a unitless arbitrary number of a fluid that measures the change in viscosity with a temperature change. The lower-value of VI indicates that viscosity is more affected by change in temperature on the other hand higher value of VI indicates that the change of viscosity is very less with temperature change. This is because when the oil temperature is low, the polymeric additives are coiled up into tight balls which flow readily with the oil molecules. With the increase in temperature, they expand into large stringy structures that restrict the normal oil flow, resulting in a thickening effect on the oil. When the oil cools down, the polymers go back to their original shape [9], [10]. The polymers which have high molecular weight also increase effective volume in the lube oil solution and as a result, the polymers which have higher molecular weight exhibit a higher value of VI compared to the polymer of the same type with lower molecular weight [11]. The pour point of an oil is the lowest temperature at which an oil will pour or flow when cooled. Most of the lube oils contain some paraffin wax and complete removal of this paraffinic wax from the lube is not only difficult but also expensive. At low temperatures, the wax left in the lubricant base stock comes out of solution as wax crystals, producing a gel-like structure that impedes the flow of lubricant to critical engine parts which badly affects the performance of the engine. The polymeric additives which are used as pour point depressant have some pendant alkyl groups. When copolymers are used as PPD, there should be an appropriate distance between pendant chains with proper monomer ratios in the copolymers [12], [13].

Initially, the mechanical action of PPD assumed that the alkylated aromatic compounds act by coating the surface of the wax crystals and prevent for further growth. More recently it is to be believed that PPD acts by nucleation, co-crystallization, which inhibits the formation of their three-dimensional wax crystal network [14]. The anti-wear additives were used to prevent direct metal-metal contact of the two moving parts of the engine when oil film over the metal surface is broken down. The anti-wear additives increase the life of the machine. Generally strong adsorption or chemisorption takes place between the metal surface and the anti-wear additives and form a film on the metal surface. The shear stability of a lubricant is one of the essential criteria that determine the suitability of the additive in a lubricant formulation. The loss of viscosity of a lubricant under shearing conditions can be expressed in terms of permanent viscosity loss (PVL) or permanent shear stability index (PSSI). The PVL/PSSI value was determined as per the ASTM D-3945 method by the following relation [15].

$$\text{PVL (\%)} = (V_i - V_s) / V_i \times 100 \quad (1)$$

$$\text{PSSI (\%)} = (V_i - V_s) / (V_i - V_o) \times 100 \quad (2)$$

Where,

V_i = Kinematic viscosity of lube oil with polymer before shearing at 100°C

V_s = Kinematic viscosity of lube oil with polymer after shearing at 100°C

V_o = Kinematic viscosity of lube oil at 100°C

The lower the PVL/PSSI value, the higher is the shear stability of the polymer.

The homopolymer and copolymer of acrylate-based polymers specially dodecyl acrylate, behenyl acrylate, isodecyl acrylate, ionic liquid blend homopolymer of

behenyl acrylate, and ZnO nanocomposite of poly dodecyl acrylate are widely used as viscosity index improver (VII) which is also known as viscosity modifier (VM), pour point depressant (PPD) and anti-wear. The homo and copolymers of alkyl acrylate with styrene, 1-Decene are widely used as viscosity index improver (VII), pour point depressant (PPD) anti-wear, and shear stability improver. The following patents discussed the same.

U.S. patent number 5834408 described the procedure for the synthesis and performance evaluation of acrylate-based co-polymers as a pour point depressant in lube oil compositions.

US patent number 4073738 described the application of alkyl methacrylate alkyl acrylate or as PPD for lube oil in which the alkyl group can have 8 to 22 carbon atoms.

U.S. Patent number 3897353 described the oil composition comprising lubricating oil and n-alkyl methacrylate as a point depressant.

U.S. patent number 4968444 described the use of mixed polyacrylates as multifunctional lube oil additives.

There are several numbers of literature available on the efficiency of poly alkyl acrylate as VII and PPD [16]-[18].

From the above literature study, it has been found that alkyl acrylate-based homo and copolymer can be used as potential multifunctional additives for lube oil. In our present investigation, we have synthesized some long chain alkyl acrylate-based homopolymer and copolymer with Styrene and 1-Decene. Our present investigation also comprises ionic liquid and ZnO nanoparticle blended long chain alkyl acrylate-based homopolymer.

References

References are given in *BIBLIOGRAPHY* under “Chapter I of Part I” (Page No. 136-138).

Chapter II

A Study of Shear Stability, Thickening and Viscosity Index

Properties of Homopolymer of Dodecyl Acrylate and its

Copolymer with Styrene and 1-Decene

1.2.1 Introduction

Modern lubricants are composed of a base fluid and a package of chemical additives. When additives are added to the base fluid, they can improve the properties already present or add some new properties [1]. The most important additives which are commonly added to the base fluid are viscosity index improver (VII), pour point depressant (PPD), anti-wear, antioxidant, dispersant, extreme pressure additives, etc. The viscosity index is an indicator which indicates the change in viscosity with temperature change. A higher viscosity index indicates a small change in viscosity with change in temperature. Viscosity index improvers are long-chain, high molecular weight polymeric additives. They function by increasing the relative viscosity of base fluid more at high temperatures than at low temperatures [2]. Oil thickening property of the additives is a direct measure of a percentage increase in the viscosity of the base fluid for the addition of a unit amount of additive. This property indicates the extent of interaction of the additive with the base fluid. The greater is the thickening property, the greater is the extent of interaction. Shear stability is one of the important criteria that determine the suitability of a viscosity index improver in a lubricant composition which is an indicator to indicate the amount of viscosity of oil, may lose during operation [3].

The pour point is the lowest temperature at which the base fluid stops its flowing. The base fluid contains some dissolved paraffinic wax. At low temperatures, the wax crystallizes to form a rigid structure and trap the oil molecules. As a result, the oil will lose its capability to flow. To overcome this problem, some polymeric additives are used as a pour point depressant (PPD). The PPD functions by inhibiting the formation of a wax crystal structure that occurs at low temperatures [4]. In this article, we have prepared a homopolymer of dodecyl acrylate and two copolymers with styrene (10%,

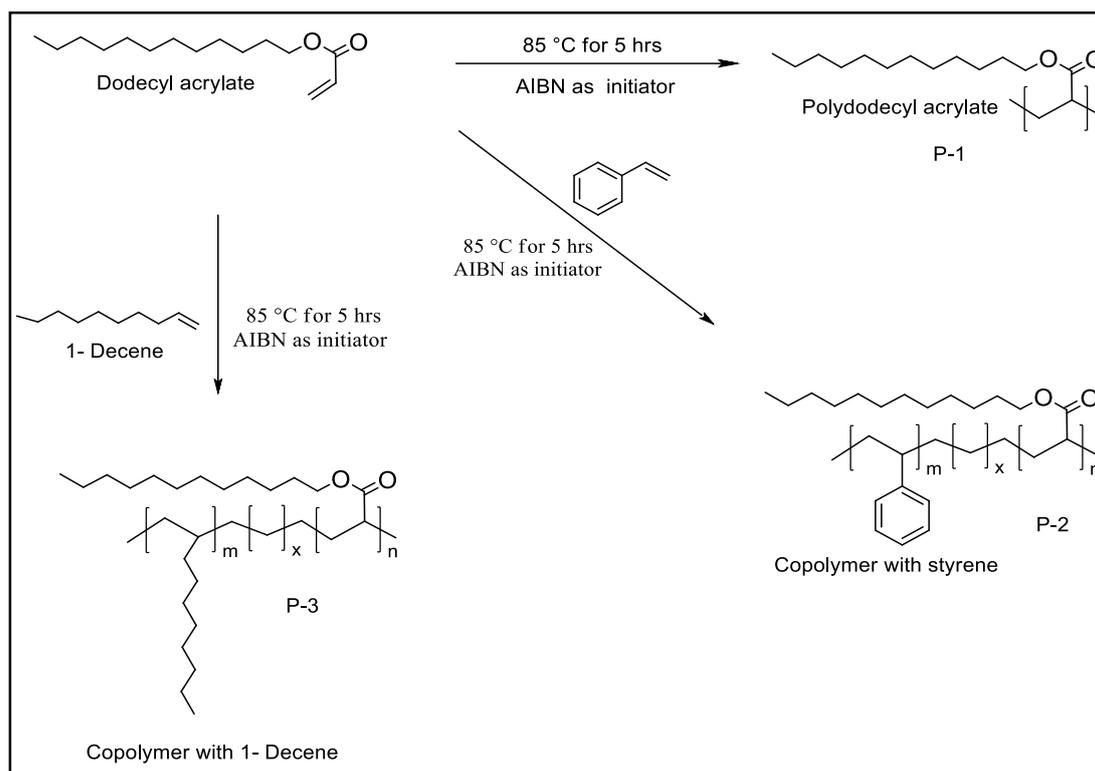
w/w) and 1-Decene (10%, w/w) by using AIBN as initiator and investigated the efficiency of the additives as viscosity index improver and pour point depressant in the base fluid. The shear stability and thickening property of each additive in base fluid have also been investigated and reported here.

1.2.2 Experimental Section

1.2.2.1 Synthesis of the polymers

The copolymers were prepared by taking the monomers of DDA (90%, w/w) and styrene or 1-Decene (10%, w/w) in presence of AIBN initiator without any solvent.

Scheme 1.2.1 Reaction for the synthesis of homopolymer of dodecyl acrylate and copolymer with and 1-Decene



The polymerization was completed in a three-necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. The mixture of monomers was heated to 85°C and then AIBN (0.5% w/w, with respect to the total monomer) was added and continuously heated for 5 hours keeping the temperature constant at 85°C. After the completion of reaction time, the product was

poured into methanol. A precipitate appeared which was filtered off and dried. The homopolymer of DDA was also prepared in the similar procedure. The prepared homopolymer and two copolymers with styrene and 1-Decene were designated as P-1, P-2, and P-3 respectively.

1.2.2.2 Materials

Benzoyl peroxide (LOBA Chemie, India) was used after recrystallization from chloroform-methanol mixture. Styrene (GC 99.8%, Thomas Baker Chemicals Pvt. Ltd., India) and the mineral base oil SN150 were collected from IOCL, Dhakuria, West Bengal, India.

1.2.3 Measurements

1.2.3.1 Spectroscopic measurements

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

1.2.3.2 Molecular weight determination

The average molecular weight was determined by the GPC method (Water 2414) in HPLC grade THF at 35⁰C at a flow rate of 1mL/min

1.2.3.3 Thermogravimetric analysis (TGA)

The thermogravimetric analysis was carried out on a Mettler TA – 3000 system, at a heating rate of 10⁰C / min.

1.2.3.4 Determination of shear stability

The shear stability of a lubricant is one of the essential criteria that determine the suitability of the additive in a lubricant formulation. The loss of viscosity of a lubricant under shearing conditions can be expressed in terms of permanent viscosity loss (PVL)

or permanent shear stability index (PSSI). The PVL/PSSI value was determined as per the ASTM D-3945 method by the following relation [3].

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

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

Where, V_i = Kinematic viscosity of lubricant before shearing at 100°C

V_s = Kinematic viscosity of lubricant after shearing at 100°C

V_o = Kinematic viscosity of lube oil at 100°C

The higher the PVL/PSSI value, the lower is the shear stability of the polymer.

1.2.3.5 Evaluation of thickening property

Kinematic viscosity of the lube oil and that of additive blended lube oil were evaluated at 40°C and 100°C. Thickening power of the lubricant was determined by calculating the percentage increase in viscosity of the lubricant composition by the addition of a unit amount of additive.

1.2.3.6 Determination of viscosity index (VI)

VI of the lubricant composition was determined according to ASTM D 2270-10 method. The kinematic viscosity of the lubricant composition was determined at 40°C and 100°C. Different concentrations of additives [ranging from 1% - 5% (w/w)] were used to study the effect of additive concentration on VI.

1.2.3.7 Determination of pour point

The pour point of the lubricant composition was determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different concentrations ranging from 1% - 5% (w/w).

1.2.4 Result and discussion

1.2.4.1 Spectroscopic analysis

The homopolymer of DDA (P-1) exhibited an IR absorption band at 1735.5 cm^{-1} for the ester carbonyl group. The two peaks at 2854.5 cm^{-1} and 2924 cm^{-1} were due to the characteristic of CH_3CH_2 - group. The peaks at 1464.5 , 1378 , 1241 , and 1152.4 cm^{-1} due to CO stretching vibration and absorption bands at 1068.5 , 969.0 , and 868.2 cm^{-1} were due to bending of C-H bond (**Figure 1.2.1**). In the ^1H NMR of homopolymer, methyl and methylene protons appeared in the range of 0.890 to 1.934 ppm. A broad peak at 3.928 ppm confirmed the protons of $-\text{OCH}_2$ group. There is no peak in the range of 5-6 ppm, indicated that polymerization was completed successfully (**Figure 1.2.2**). In the ^{13}C NMR of homopolymer, the peaks at 177.54 ppm indicated the presence of ester carbon. There was no peak in the range of 120-150 ppm and it confirmed the polymerization (**Figure 1.2.3**). In the IR spectrum of copolymer (P-3), the ester carbonyl group appeared at 1728.2 cm^{-1} . Peaks at 750.4 cm^{-1} and 700.5 cm^{-1} indicated the C-H bond of the phenyl group of styrene (**Figure 1.2.4**). In the ^1H NMR, multiplet peak in the range of 3.933 - 4.156 ppm indicated the protons of $-\text{OCH}_2$. A broad peak in the range of 7.014 - 7.329 ppm indicated the protons of the phenyl group. No peak in the range of 5-6 ppm indicated the confirmation of polymerization (**Figure 1.2.5**). In the ^{13}C NMR, the peaks in the range of 176.8 - 177.7 ppm confirmed the presence of ester carbons. The carbons in the phenyl group appeared in the range of 125.04 - 128.56 ppm (**Figure 1.2.6**). All the spectroscopic data of copolymer P-2 was found approximately the same with the homopolymer, P-1.

1.2.4.2 Analysis of Molecular weight and TGA

The experimental value of number average molecular weight (M_n), weight average molecular weight (M_w), and TGA values of the prepared additives (P-1 to P-3) are given in **Table 1.2.1**. From the data, it is observed that the copolymer P-3 has the highest molecular weight followed by homopolymer P-1. From the TGA values, it is

observed that the additive P-3 is thermally more stable than P-2 and P-1. It may be due to the presence of styrene moiety in P-3 which supports thermally stability.

1.2.4.3 Analysis of shear stability

PVL and PSSI values were calculated in additive doped lube oil at a different concentration ranging from 1% - 5% (w/w) at 100 ° C. The experimental values are listed in **Table 1.2.2**. From the values, it is found that copolymers are more stable under shear (lower PVL/PSSI value) than homopolymer. Among the three additives, the order of stability under shear is P-3 > P-2 > P-1. Moreover, it is also observed that with increasing the concentration of additive to the base oil, the shear stability decreases (higher PVL/PSSI value) [5].

1.2.4.4 Analysis of thickening Property

The thickening power of both homopolymer and copolymers is depicted in **Table 1.2.3** which indicated a gradual decrease with the increase in the concentration of the additive. This may be because of the fact that the additive molecules are assumed to be coiled like aggregation with the increase in concentration to the base oil [6]. From the results, it was observed that the thickening power of the additive P-1 was higher than that of additives P-2 and P-3. This indicated that from the point of view of fuel economy, the additive P-1 is better than additives P-2 and P-3.

1.2.4.5 Analysis of viscosity index (VI) values

VI values of the prepared additives in base oil are listed in **table 1.2.4**. The viscosity of base oil without any additive decreases with increasing temperature but when additives are added to the base oil, the decrement of viscosity does not occur. At high temperatures, additive molecules in the base oil medium swell up and as a result, the size of the micelle enhances. This enhanced micelle size resists the reduction of the viscosity of the lubricant composition and hence improves VI. It was also found that

at a higher concentration of the lubricant composition, the VI values are higher. This is because, at higher concentration, the micelle size increases and hence improves the VI property [7], [8]. The copolymer P-3 has better VI property than P-2 and P-1. It may be due to the higher molecular weight of P-3.

1.2.4.6 Analysis of Pour point (PP) values

The pour points of the base oil, as well as base oil containing different additives at different concentration levels [1%–5% (w/w)], are given in **Table 1.2.5**. From the experimental values, it is observed that base oil containing additives have lower PP than base oil and hence the prepared additives can be used as PPD. Moreover, it is observed that the efficiency as PPD increases with increasing concentration. The reason behind it may be, at higher concentrations, the interaction between the additive and paraffinic wax present in the base oil is more [9]-[11]. All the three prepared additives are approximately equally effective as PPD. The additive P-3 showed slightly higher performance as PPD than the others two additives.

1.2.5 Conclusions

The study indicated that the copolymers are more stable under shear than homopolymer but the thickening property of a homopolymer is greater than copolymers. This study also indicated that the efficiency of the prepared additives as viscosity index improver and pour point depressant increases with increasing concentration of the additives in the base oil. The viscosity index property of the additives is directly proportional to the average molecular weight but there is no correlation between pour point and average molecular weight

1.2.6 References

References are given in *BIBLIOGRAPHY* under “Chapter II of Part I” (Page No, 138-139).

2.2.7 Tables and figures

Table 1.2.1: Average molecular weight and TGA values of the prepared polymers and its graphical representation

Polymer code	Molecular weight			TGA value	
	M_n	M_w	PDI	Decom. Tem.	PWL
P-1	7731	14155	1.83	172/350	26/84
P-2	6016	8638	1.44	170/320	22/90
P-3	13958	23737	1.7	245/420	20/78

M_n = Number average molecular weight; M_w = Weight average molecular weight; PDI = Polydispersity index; Decom.Tem.=Decomposition temperature; PWL=Percent weight loss

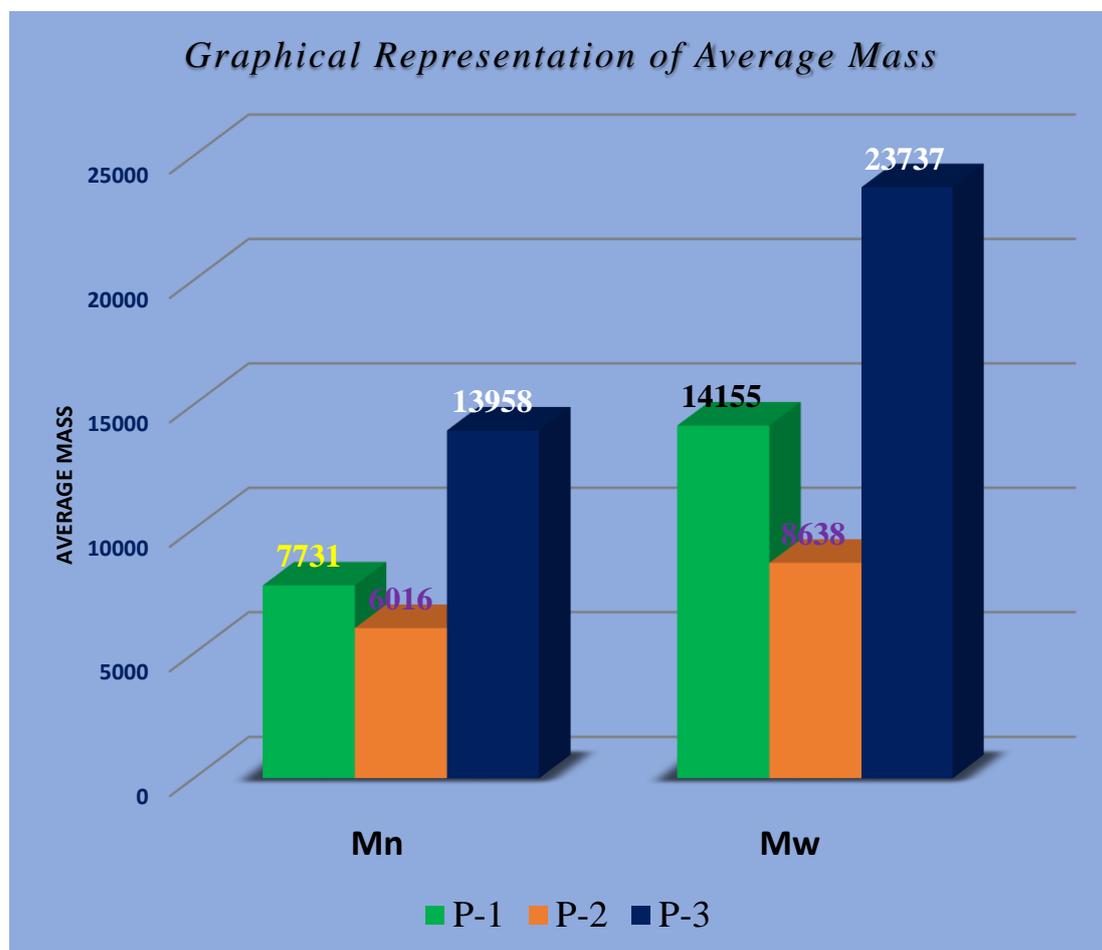


Table 1.2.2: PVL and PSSI Values of the Additives Doped Base Oil

Mass fraction	KV (at 373K)						PVL			PSSI		
	before shear			after shear			P-1	P-2	P-3	P-1	P-2	P-3
	P-1	P-2	P-3	P-1	P-2	P-3						
0.00	3.68	3.68	3.68	3.68	3.68	3.68	0.00	0.00	0.00	0.00	0.00	0.00
0.01	3.84	3.82	3.80	3.83	3.81	3.80	0.23	0.18	0.13	5.76	5.10	4.03
0.02	3.95	3.93	3.92	3.93	3.91	3.90	0.53	0.43	0.38	7.77	6.80	6.35
0.03	4.16	4.14	4.12	4.11	4.10	4.09	1.03	0.84	0.77	9.01	7.67	7.25
0.04	4.29	4.26	4.25	4.22	4.20	4.19	1.67	1.35	1.27	11.84	10.00	9.54
0.05	4.49	4.47	4.46	4.39	4.38	4.37	2.24	2.07	1.97	12.40	11.78	11.34

Table 1.2.3: Thickening power (THK) of the Additives Doped Base Oil.

Mass fraction of the additive	THK(at 313K)			THK(at 373K)		
	P-1	P-2	P-3	P-1	P-2	P-3
0.01	3.07	2.97	2.92	4.23	3.71	3.36
0.02	2.21	2.14	2.12	3.66	3.39	3.2
0.03	1.9	1.87	1.86	3.31	3.12	2.98
0.04	1.74	1.72	1.71	3.12	2.93	2.83
0.05	1.66	1.64	1.63	2.41	2.28	2.21

Table 1.2.4: VI values of the Additives Doped Base Oil and its graphical representation

Mass fraction of the additive	VI		
	P-1	P-2	P-3
0	82	82	82
0.01	90	90	99
0.02	99	98	102
0.03	108	107	110
0.04	112	110	118
0.05	118	115	126

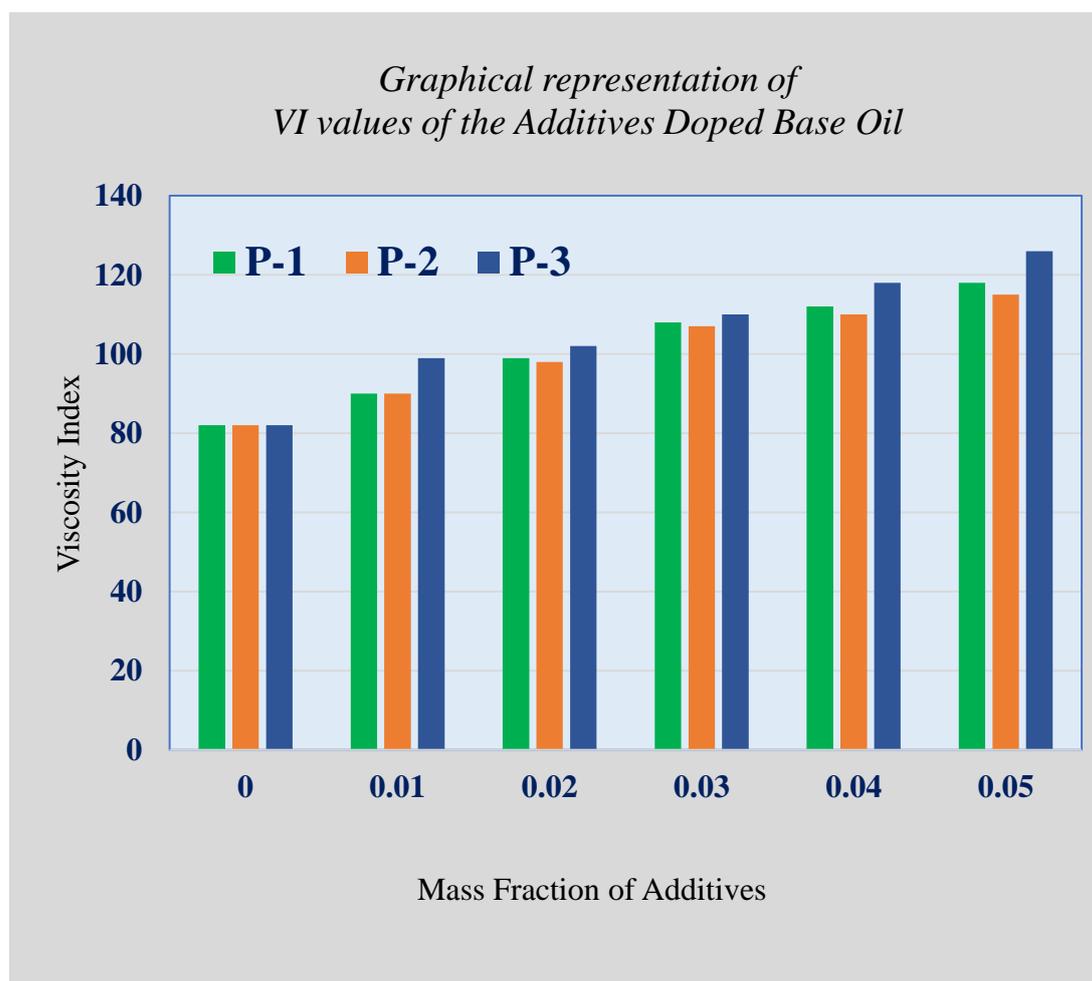
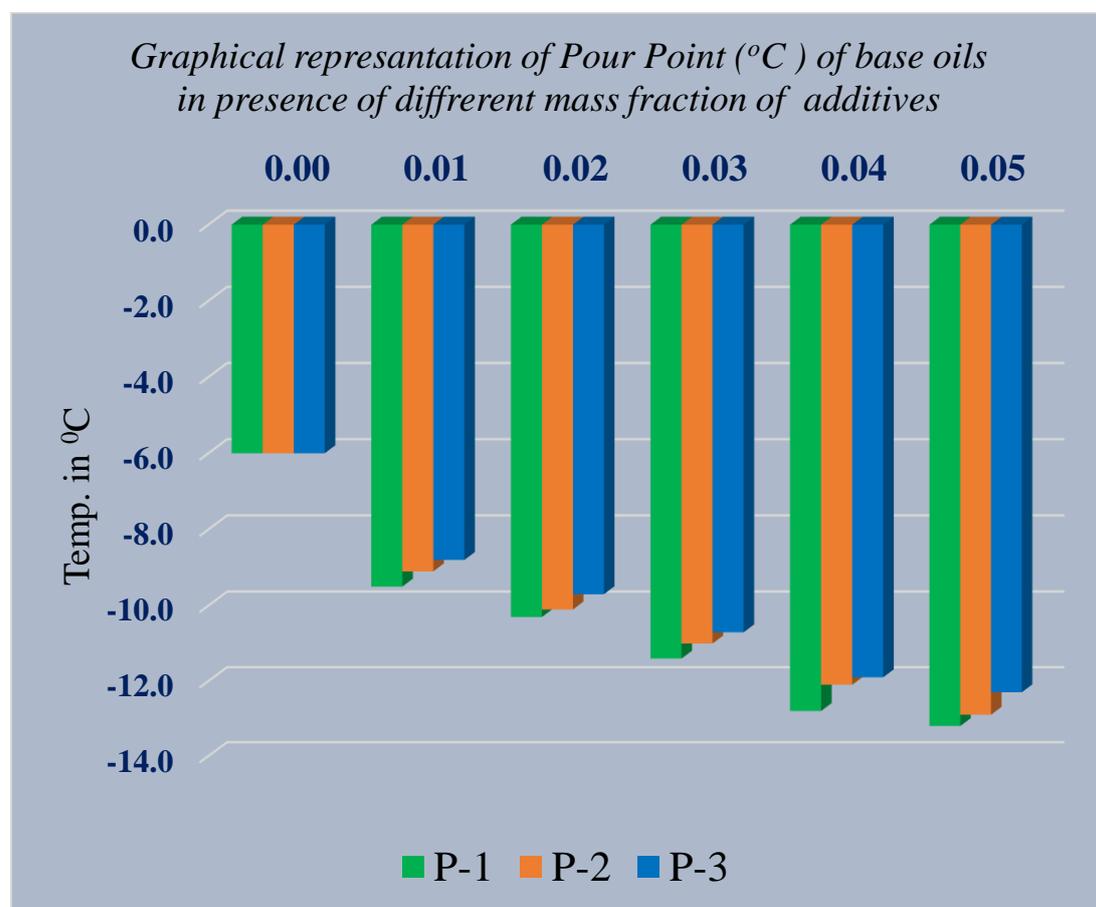


Table 1.2.5: Pour Point (PP) of the Additives Doped in Base Oil and its graphical representation

Mass fraction of the additive	Pour Point ($^{\circ}\text{C}$) of base oils in presence of		
	P-1	P-2	P-3
0.0	-6.0	-6.0	-6.0
0.0	-9.5	-9.1	-8.8
0.0	-10.3	-10.1	-9.7
0.0	-11.4	-11.0	-10.7
0.0	-12.8	-12.1	-11.9
0.1	-13.2	-12.9	-12.3



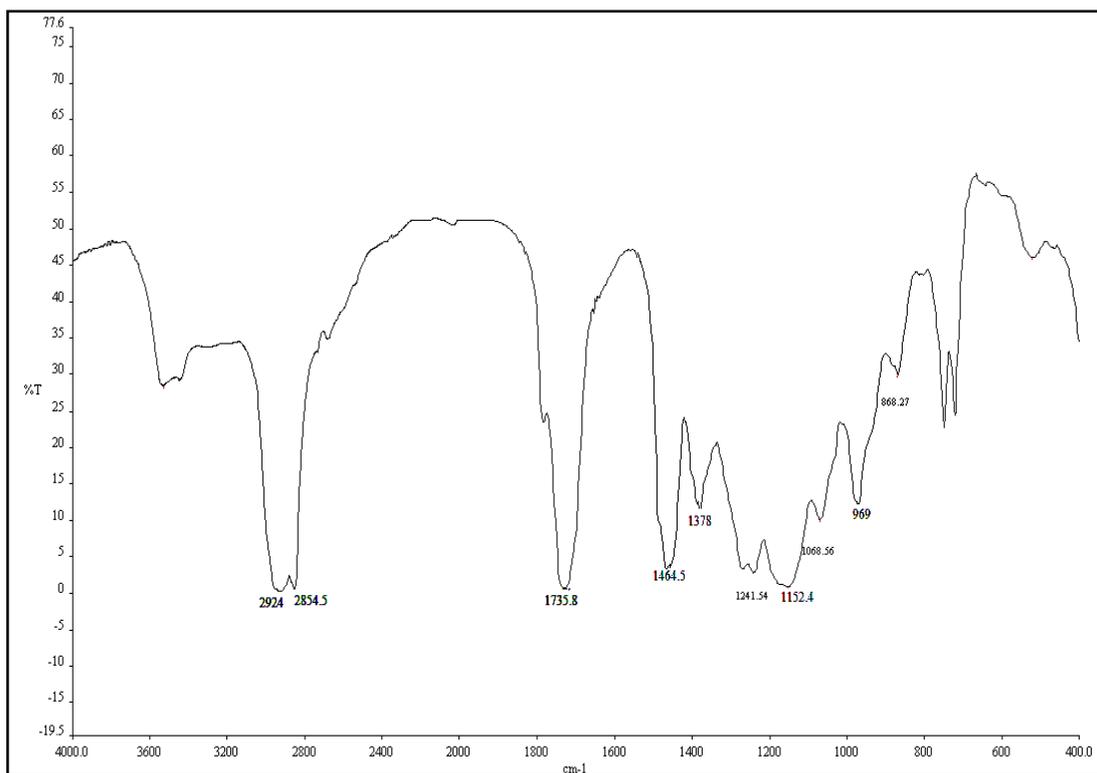


Figure 1.2.1: IR spectra of homopolymer (P-1)

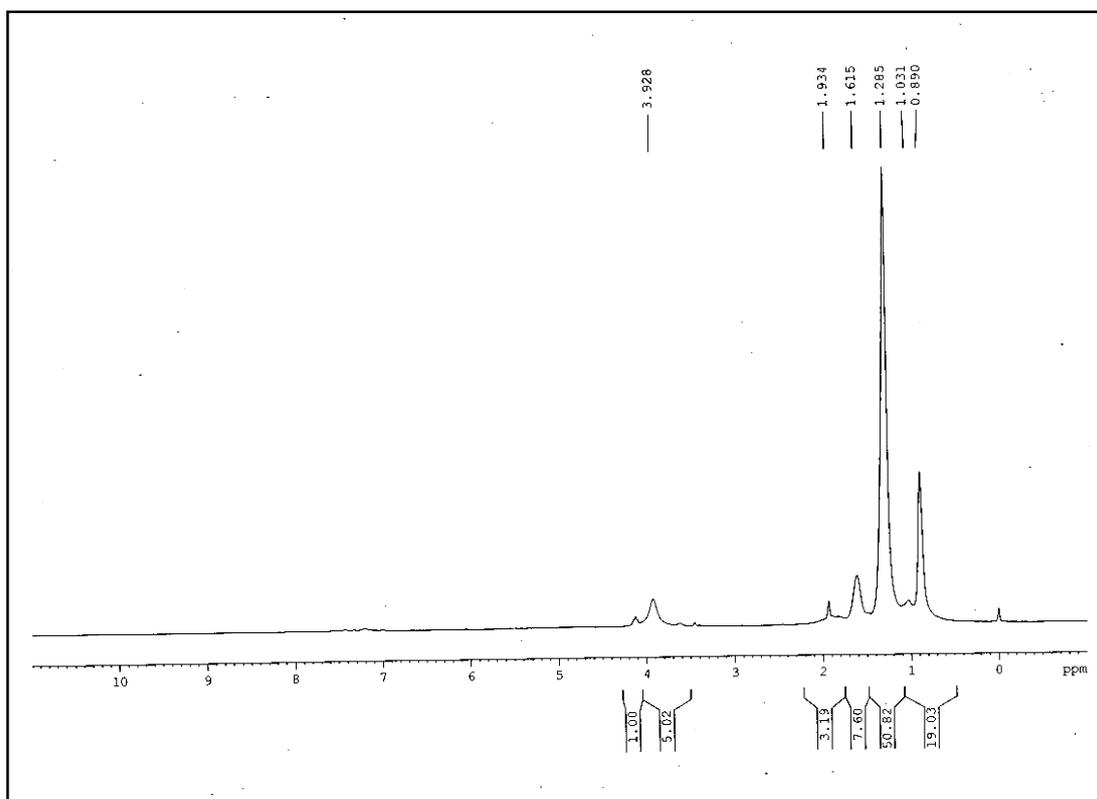


Figure 1.2.2: ¹H NMR spectra of homopolymer (P-1)

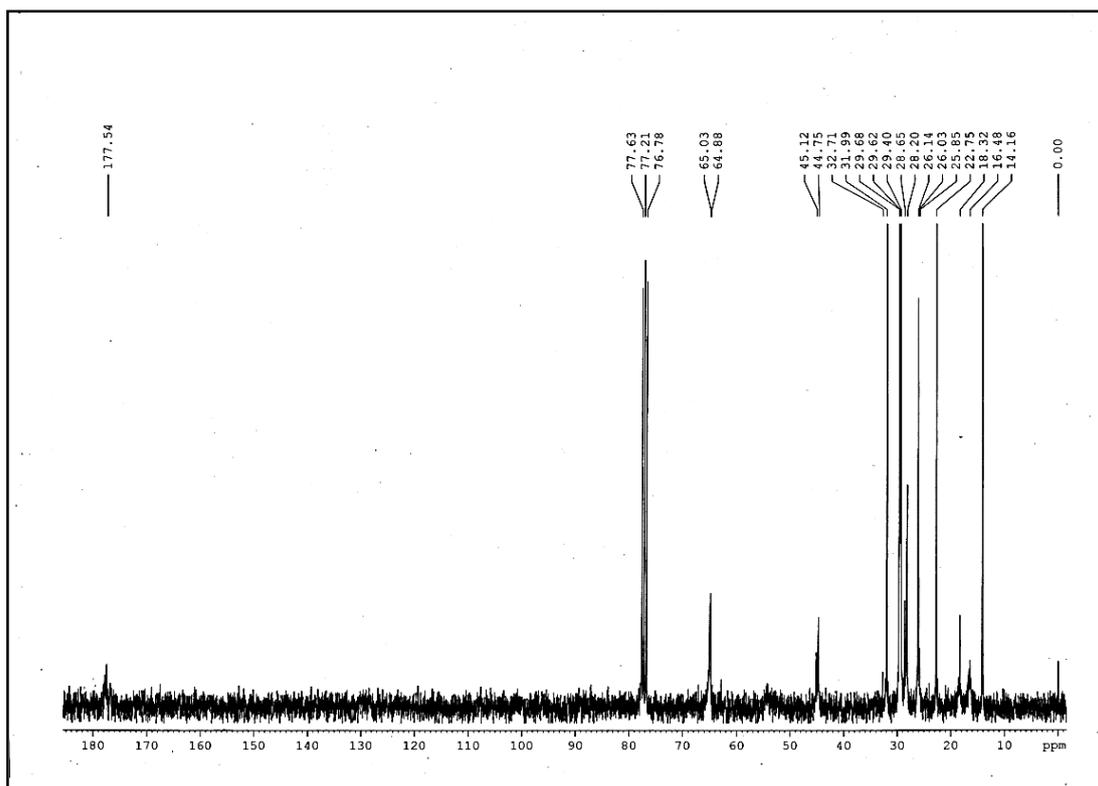


Figure 1.2.3: ^{13}C NMR spectra of homopolymer (P-1)

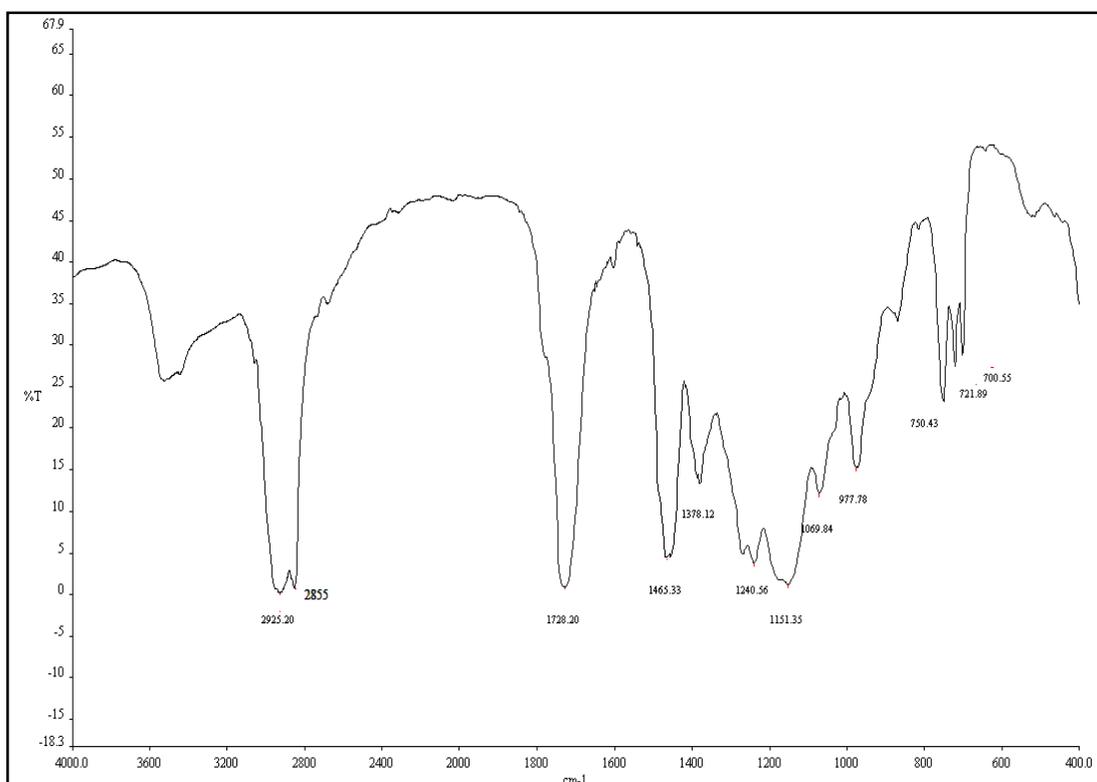


Figure 1.2.4: IR spectra of copolymer (P-3)

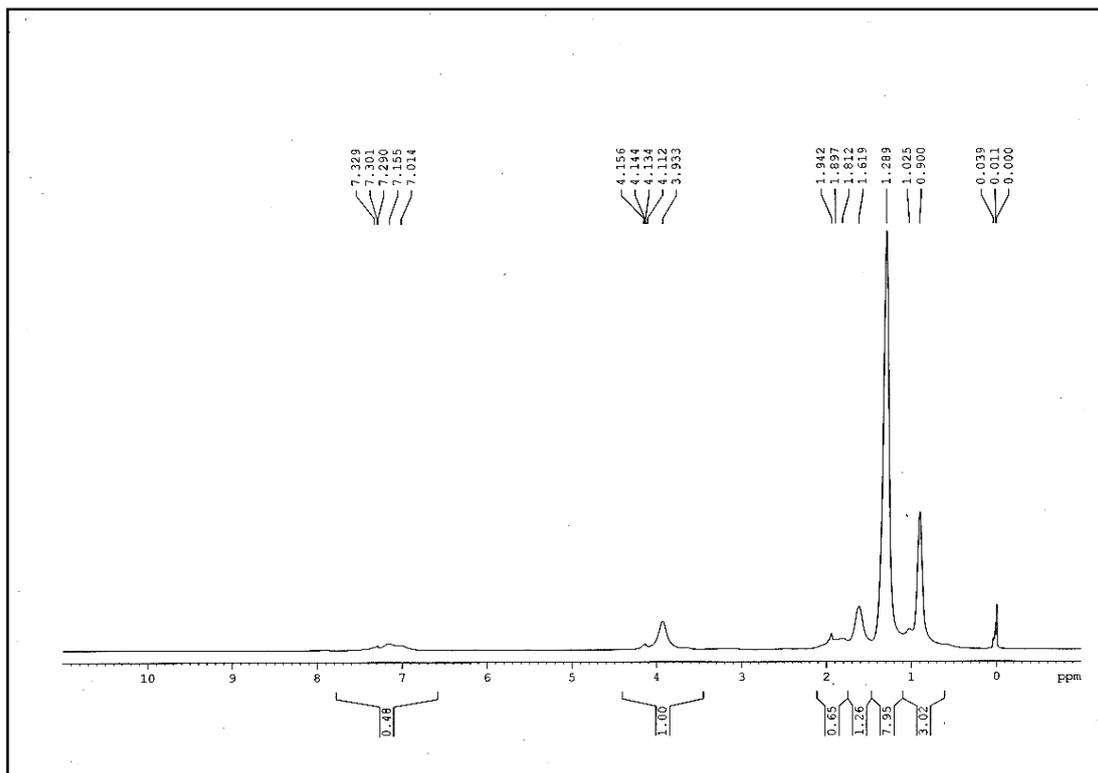


Figure 1.2.5: ^1H NMR spectra of copolymer (P-3)

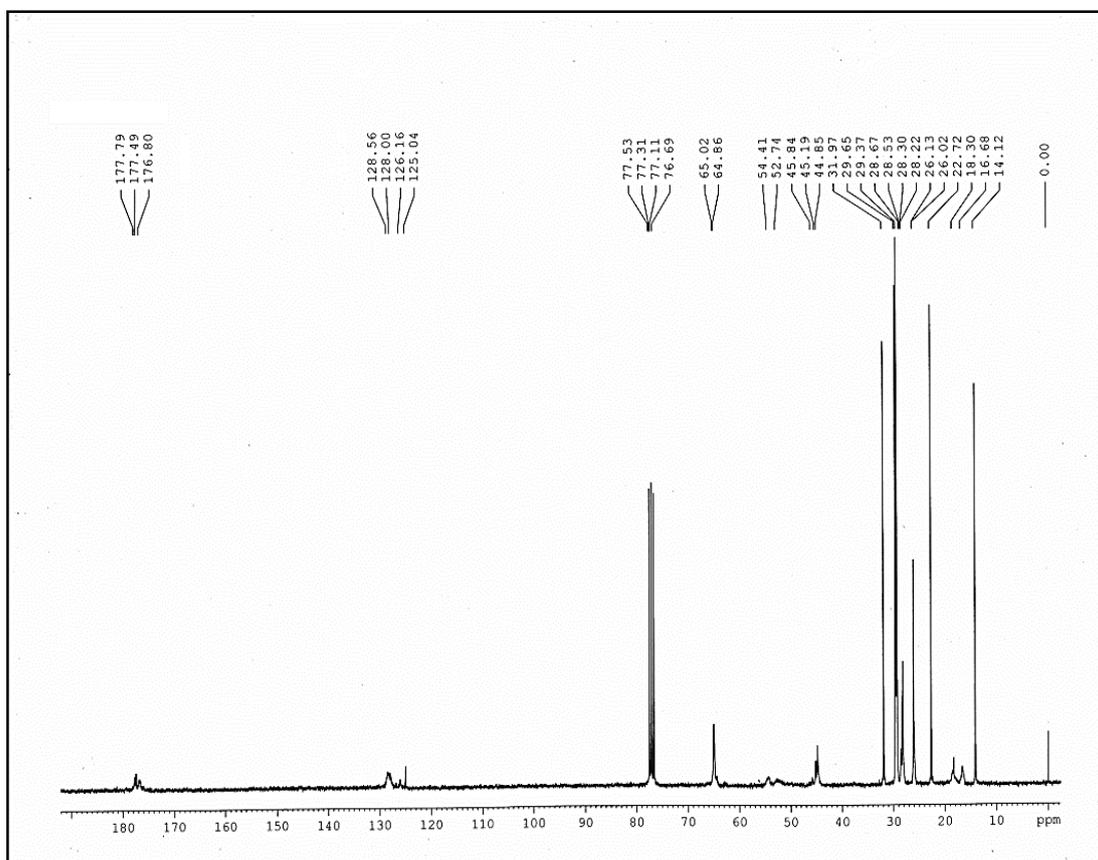


Figure 1.2.6: ^{13}C NMR spectra of copolymer (P-3)

Chapter III

A Study as a Potential Multifunctional Additive for Lubricating Oil of Poly Decyl Acrylate-Ionic Liquid Blend

1.3.1 Introduction

Ionic liquids (more specifically, room temperature ionic liquids (RTIL)) have attracted great interest over the last several years. Ionic liquids (ILs) are broadly referred to as molten salts in a liquid state. Generally, ILs are a specific type of liquid salts with melting temperatures lower than 100⁰C (212⁰F). Unlike ordinary liquids such as water or alcohol, ILs are mostly composed of charged ions as opposed to electrically neutral molecules. Ionic liquids have many good features [1] such as low volatility, non-flammability, low combustibility, high ionic conductivity, high thermo-oxidative stability, eco-friendly, etc. Therefore, they should be the potential candidates for new lubricant formulations and would be suitable for use in severe conditions where conventional oils and greases or solid lubricants fail. ILs have been the subject of research and development for quite a long time. In 2001 ionic liquids (ILs) were first reported [2] as very promising high-performance lubricants and have attracted considerable attention in the field of tribology since then because of their remarkable lubrication and anti-wear capabilities as compared with lubrication oils in general use [3]. In recent times, we have seen dramatically increased interest in this topic. The choice of cation and anion in an ionic liquid (IL), and also the design of ion side chains, regulate the main functions of ionic liquids, which permits creating suitable lubricants and lubricant additives [4]. Limited results of very recent studies have shown the potential for using ionic liquids as a new class of lubricants [1]. Friction and wear reductions have been reported on metallic and ceramic surfaces lubricated by selected ionic liquids compared to conventional hydrocarbon lubricants. It was also suggested that adding a few percent of ionic liquids could improve the lubricating performance of base oils or water. Over the last 15 years, research interest in ILs has expanded into lubrication due to their potential performance as a neat lubricant or additive [5]-[11].

Regarding the use of ILs as neat lubricants, several studies have shown great potential for this purpose [8]-[10]. But at present, considering the high cost of ILs, using a small quantity of ILs as an additive, for engine applications seems to be an economical option. It should be noted, however, that the multiple-recycling of ILs after use could reduce the overall cost of employing ILs [1], [5], [11] in real applications. This is another cost-effective aspect for investigation by the lubricant industry. The Early works were mainly focused on ILs with imidazolium cations based [8], [11]. The interest in phosphonium [1], [2], [8], based ionic liquids has widely grown over the years in line with their increased commercial availability. They have been successfully tested for several applications. In this study, an ionic liquid with phosphonium cation and amide anion based is chosen as a lubricant additive, and studied their different performance such as PPD, VI, and anti-wear property in lube oil, as described in this article.

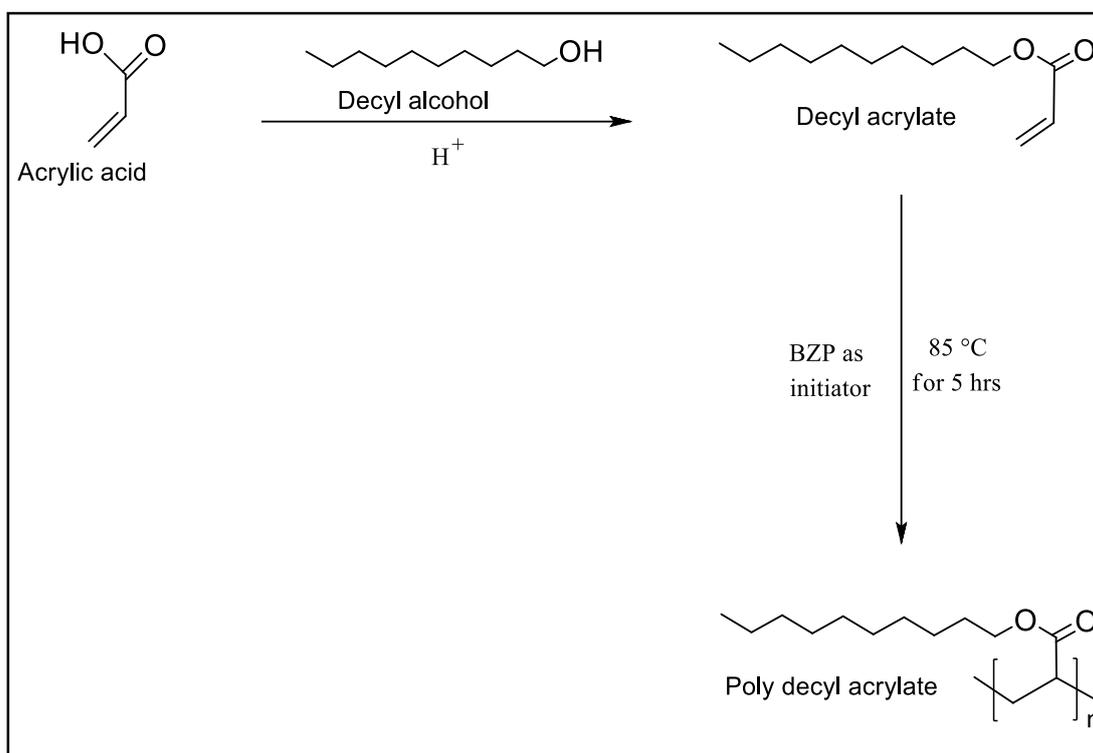
1.3.2 Materials and method

Toluene, hydroquinone, and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (GC Purity 99%) and decyl alcohol was obtained from Sisco Research Laboratories Pvt. Ltd. Ionic liquid [P_{6,6,6,14}][NTf₂] namely Trihexyl (tetradecyl) phosphoniumbis {(trifluoromethyl) sulfonyl} amide was purchased from Sigma-Aldrich Pvt. Ltd. And CH₃OH was purchased from Thomas baker Pvt. Ltd. and were used as received. Benzoyl peroxide (BZP) obtained from the LOBA chemical was recrystallized from CHCl₃-MeOH before use. Specifications of the chemicals are depicted in **Table 1.3.1**. Two different base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in **Table 1.3.2**.

1.3.2.1 Esterification and homopolymerization of DA

Esterification of acrylic acid with decyl alcohols, purification of the prepared esters, and subsequent homopolymerization was carried out following the procedure as reported in earlier publications from our laboratory [12], [13].

Scheme 1.3.1 Esterification of acrylic acid with decyl alcohol followed by polymerization of ester.



1.3.2.2 Preparation of IL-Polymer blend

Polymer-IL blends were prepared by mixing the polymer (**P-1**) with desired amount of IL (100 ppm, 300ppm, 500ppm with respect to the polymer) in a mechanical stirrer at 60°C for one hour. The blended sample was assigned as P-2 (for 100 ppm), P-3 (for 300 ppm), P-4 (for 500 ppm). Four different concentrations (1-4% w/w) of additive (P-1 to P-4) doped base oils, namely BO1 and BO2 were prepared by the addition of a required amount of sample to the base oils.

1.3.3 Measurements

1.3.3.1 Spectroscopic measurements

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

1.3.3.2 Thermogravetric test

The thermograms in the air were obtained on a Mettler TA-3000 system, at a heating rate of 10 K min⁻¹.

1.3.3.3 Molecular weight determination by GPC

The weighted average and number average molecular weights (M_w and M_n) and polydispersity indices of the polymers were measured in Waters' GPC equipment using polystyrene standards for calibration in THF phase [12]. The results are tabulated in **Table 1.3.3**.

1.3.3.4 Pour point determination

The pour point of the prepared polymers in base oils was tested according to the ASTM D97-09 method on a Cloud and Pour Point Tester model WIL-471 (India).

1.3.3.5 Viscosity index determination

Kinematic viscosity (KV) of the polymer was determined separately at 40°C and 100°C by counting the time of flow of polymer solution in base oil using viscometer apparatus and measuring the density of it. According to the ASTM D-7042 method and also by

using the method of viscosity index calculation [14] the viscosity index of each polymer solution was determined.

1.3.3.6 Shear stability determination

Shear stability was determined of various concentrated solutions of pure DA polymer, DA + Ionic liquid blending, and Ionic liquid in lube oil. Tests and calculations were conducted as per the ASTM D- 3945 and ASTM 6022 methods.

1.3.3.7 Anti-wear property determination

Anti-wear (AW) properties of base stocks, as well as additive doped base stocks, were studied in sliding contact using a Four-Ball wear test Machine as per the ASTM D-4172 method. The tests were carried out under the load of 20 kg and 40 kg.

1.3.4 Results and discussion

1.3.4.1 Spectroscopic data

FT-IR spectrum (**Figure 1.3.1**) of poly (decyl acrylate) or homopolymer of decyl acrylate (HDA) exhibited absorption at 1732.0 cm^{-1} due to ester carbonyl stretching vibration. The peak at 1260.0 and 1175.0 cm^{-1} can be explained owing to the C–O (ester bond) stretching vibration and the absorption bands at 975.0 , 750.0 , and 711.0 cm^{-1} were due to the bending of C–H bonds. The broad peak ranging from 2900.0 to 3100.0 cm^{-1} was due to the presence of stretching vibration (C–H bonds). In its ^1H -NMR spectra (**Figure 1.3.2**), homopolymer of DA showed a multiple centered at 3.17 ppm due to the proton of $-\text{OCH}_2$ group; methyl groups of decyl chain showed a broad singlet at 0.73 ppm. The proton decoupled ^{13}C -NMR of the above sample (**Figure 1.3.3**) was in complete agreement with the homopolymer which shows the presence of

the ester carbonyl group at 170.66 ppm and the absence of any sp^2 carbon in the range 130-150 ppm.

1.3.4.2 Thermogravimetric analysis

The plot of TGA data in **Figure 1.3.4** presents a comparison between the thermal stability of homopolymer of DA and its blending with ionic liquid respectively. The analysis reveals that the blend is thermally less stable than the homopolymer.

1.3.4.3 Performance evaluation of the prepared polymers as PPD

The pour point (PP) values of the polymers in both the base oils are tabulated in **Table 1.3.4**, which indicates that their PPD efficiency increases (up to a certain limit) with the increasing concentration of the polymer in base oils. Comparison among the PP values indicates that the efficiency of the polymers as PPD is greater for DA polymers than that of the ionic liquid blend.

1.3.4.4 Photo micrographic analysis

The photomicrographs of lube oil (BO2) with and without different additives are shown in **Figure 1.3.5 (a–e)**. **Figure 1.3.5a**, the photograph of the fresh lube oil showed a large number of crystalline and some needle-shaped wax crystals. But by the addition of polymers the wax crystal size [**Figure 1.3.5(b–e)**] is significantly decreased from a large crystal structure (base oil) to very small dots dispersed in the oil phase of the lube oil, and the polymer which acts as better PPD (reveals by PPD data), decreases the wax size more compared to other. Therefore, a correlation between the depression of pour point and the degree of wax structure modification has been confirmed.

1.3.4.5 Performance evaluation of the prepared polymers as VMs

The VI values in two base oils (measured in four different concentrations) tabulated in **Table 1.3.4** indicates that in both the base oils the values for DA homopolymer are greater than that of its ionic liquid blend but the difference is small, also the VI value

decreases with increasing ionic liquid concentration in the blending feed. This result may be explained based on the molecular weight of the polymers. Again, with the increase in the concentration of the polymers in solution, VI increases. The reason may be that although the viscosity of the lube oil gets decreased at the higher temperature, the polymer molecules may effectively offset this reduction in viscosity by thickening the oil changing its shape from a tight coil to an expanded one due to increased polymer-solvent interaction. The result is an increase in the viscosity of the solution. Again, a higher polymer concentration means an increase in the total volume of polymer coils in the solution which imparts a higher VI compared to a low concentrated polymer solution.

1.3.4.6 Shear stability analysis

Shear stability determined based on PVL (permanent viscosity loss) and PSSI (percent of shear stability index), lesser the value of PVL and PSSI greater the shear stability of the sample. Shear stability determination indicates that the IL-DA blend is more shear stable than that of DA polymer and also shear stability increases with the increasing the IL concentration in the blended feed. This result is clearly explained based on the molecular weights of the sample, the higher the molecular weight greater the possibility of a loss of shear stability of the polymer.

1.3.4.7 Efficiency as anti-wear (AW) additive

Anti-wear contributions of the additives are measured with respect to wear scar diameter (WSD) under two load conditions (20 kg, 40 kg). Effect of additive concentration on the anti-wear performance is also studied. Experiments are conducted at first with pure base oils followed by the additive doped base oils. The WSD measured in all these cases is depicted in **Table 1.3.5**. As was expected, all the samples (P-1 to P-4) show better anti-wear performance compared to pure base oils and IL

blended polymers (P-2 to P-4) are found to be more efficient than pure BA homopolymer (P-1). Also, the performance increases with increasing the IL concentration in the blended feed. Irrespective of base oils or load conditions, WSD decreases (i.e. better AW properties) with increasing additive concentration. That is, both the additives are acting more efficiently at higher concentration levels. A comparison between load conditions indicates that under milder conditions (20 kg load), additives performance is better (lower WSD value).

1.3.5 Conclusions

Evaluation of the performance of the additives indicates that, although the BA homopolymer showed slightly better PPD and viscosity modifier performance compared to its ionic liquid blend, but, the BA+ IL blend is more shear stable than the homopolymer, and shear stability increases with increasing the concentration of IL in blending feed. The investigation also indicates that IL blend polymers show much better anti-wear performance than that of BA homopolymer and the performance increases with increasing the concentration of IL in blending feed.

1.3.6 References

References are given in *BIBLIOGRAPHY* under “Chapter III of Part I” (Page No. 139-140).

1.3.7 Tables and Figures

Table 1.3.1: Specification of the chemicals used

<i>Chemical name</i>	<i>Source</i>	<i>Mole fraction purity</i>
Toluene	Merck Specialities Pvt. Ltd.	0.995
Hydroquinone	Merck Specialities Pvt. Ltd.	0.990
H ₂ SO ₄	Merck Specialities Pvt. Ltd.	-
Acrylic acid	SRL Pvt. Ltd.	0.990
Decanol	S. D. Fine-Chem Ltd.	0.980
Hexane	S. D. Fine-Chem Ltd.	0.995
Methanol	Thomas Baker Pvt. Ltd.	0.980
Benzoyl peroxide	LOBA chemicals	0.980
[P6,6,6,14][NTf ₂]	Sigma-aldrichPvt. Ltd.	-

Table 1.3.2: Base oil properties

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

Table 1.3.3: Weight average and number average molecular weights (M_w and M_n) and polydispersity Index of the sample and its graphical representation

<i>Sample</i>	<i>M_n</i>	<i>M_w</i>	<i>PDI</i>
P-1	10152.00	14287.00	1.40
P-2	9885.00	14114.00	1.42
P-3	9662.00	14011.00	1.45
P-4	9278.00	13825.00	1.49

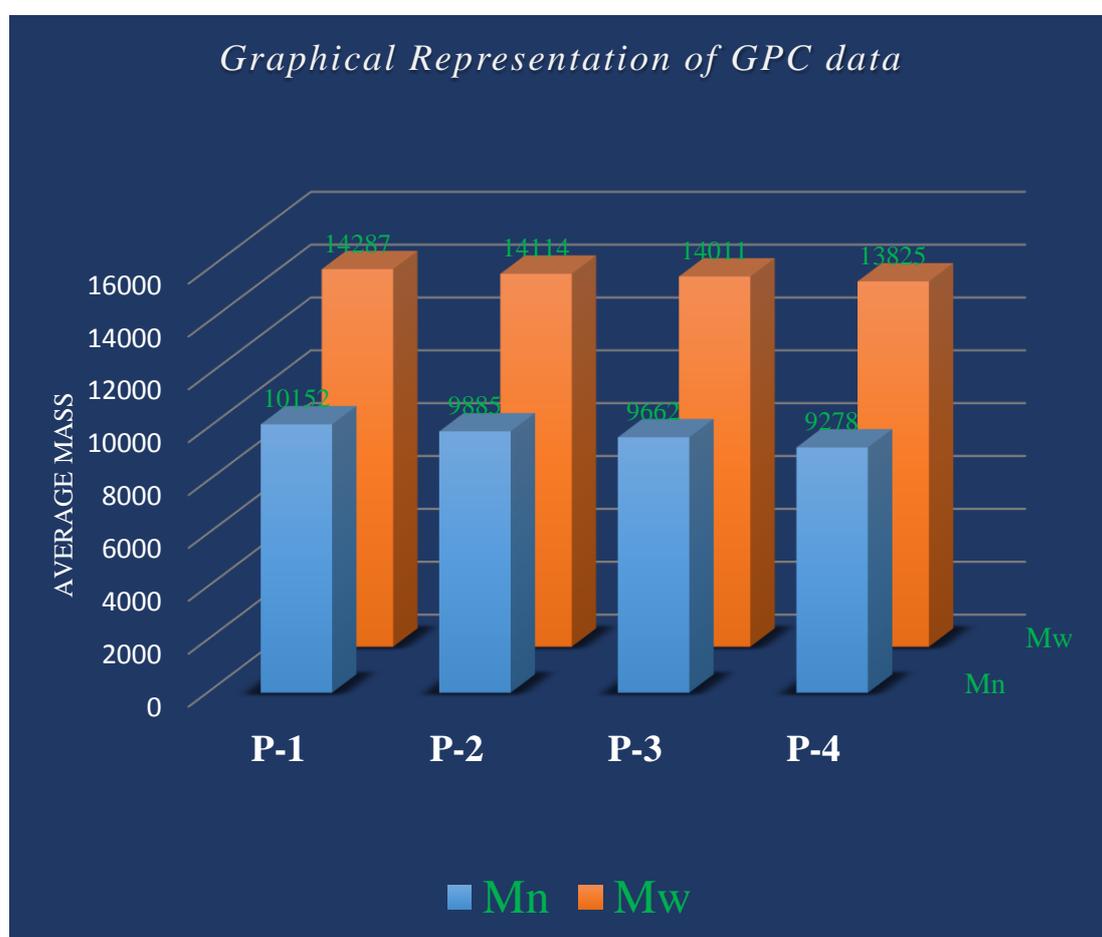
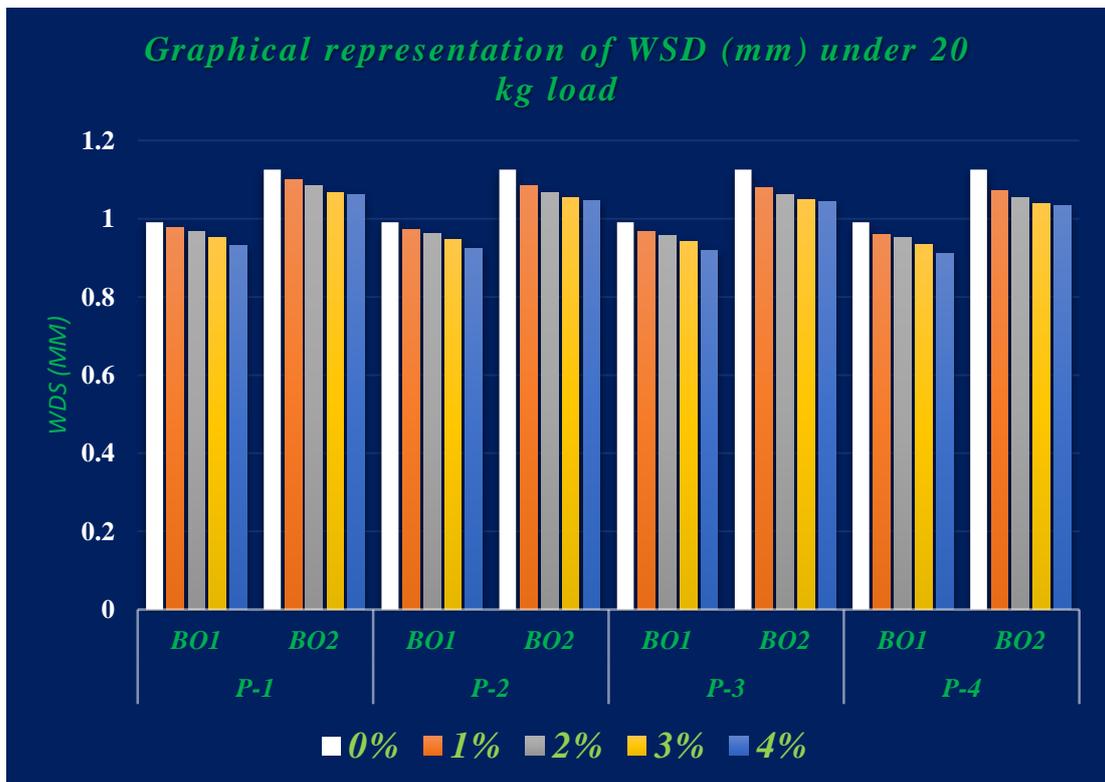


Table 1.3.4: Tribological performance of the samples in two different base oils

Sample	Conc. (%)	BO1				BO2			
		PP	VI	PVL	PSSI	PP	VI	PVL	PSSI
P-1	1	-6	96	0.432	8.978	-9	98	0.435	9.768
	2	-9	105	0.811	9.996	-12	110	0.832	10.778
	3	-12	115	1.353	12.411	-15	128	1.436	13.125
	4	-15	124	1.980	16.821	-18	138	2.112	17.835
P-2	1	-6	92	0.374	7.587	-9	95	0.382	8.421
	2	-6	99	0.644	8.456	-9	105	0.657	9.142
	3	-9	109	1.227	10.234	-12	121	1.259	11.247
	4	-12	119	1.590	15.527	-15	129	1.596	16.223
P-3	1	-6	91	0.298	7.214	-9	94	0.311	8.114
	2	-9	97	0.587	8.145	-12	101	0.590	8.985
	3	-9	105	1.140	9.857	-12	117	1.264	10.141
	4	-12	116	1.372	15.114	-15	123	1.415	15.784
P-4	1	-6	91	0.212	6.984	-9	93	0.242	7.128
	2	-9	95	0.478	8.11	-12	98	0.511	8.541
	3	-9	103	0.985	9.114	-12	113	1.100	9.886
	4	-12	111	1.154	14.954	-15	119	1.173	15.211
<i>PP-Pour Point, VI-Viscosity Index, PVL-Permanent Viscosity Loss, PSSI-Percent of Shear Stability Index.</i>									

Table 1.3.5: Anti-wear Performance data of Additive Doped Base Oil and its graphical representation under 20 kg load

Sample	Base oil	WSD(mm) of additive-base oil blends									
		20 kg load					40 kg load				
Aditives %		0%	1%	2%	3%	4%	1%	2%	3%	4%	
P-1	BO1	0.991	0.979	0.968	0.952	0.931	0.978	0.974	0.965	0.939	
	BO2	1.126	1.101	1.084	1.068	1.061	1.104	1.088	1.071	1.065	
P-2	BO1	0.991	0.973	0.963	0.948	0.925	0.974	0.967	0.959	0.929	
	BO2	1.126	1.085	1.068	1.054	1.047	1.095	1.079	1.065	1.054	
P-3	BO1	0.991	0.967	0.957	0.941	0.919	0.969	0.962	0.952	0.922	
	BO2	1.126	1.08	1.061	1.048	1.043	1.09	1.073	1.059	1.048	
P-4	BO1	0.991	0.961	0.952	0.934	0.912	0.962	0.954	0.943	0.914	
	BO2	1.126	1.072	1.054	1.04	1.033	1.081	1.064	1.05	1.041	



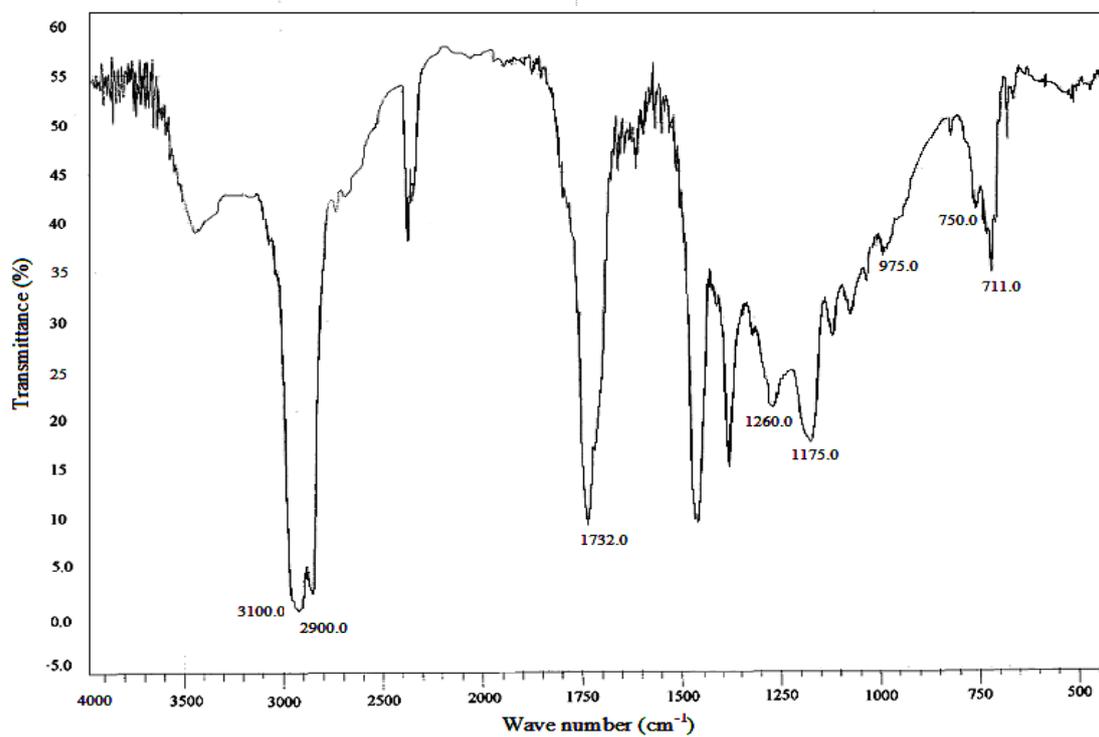


Figure 1.3.1: FT-IR spectra of polydecyl acrylate

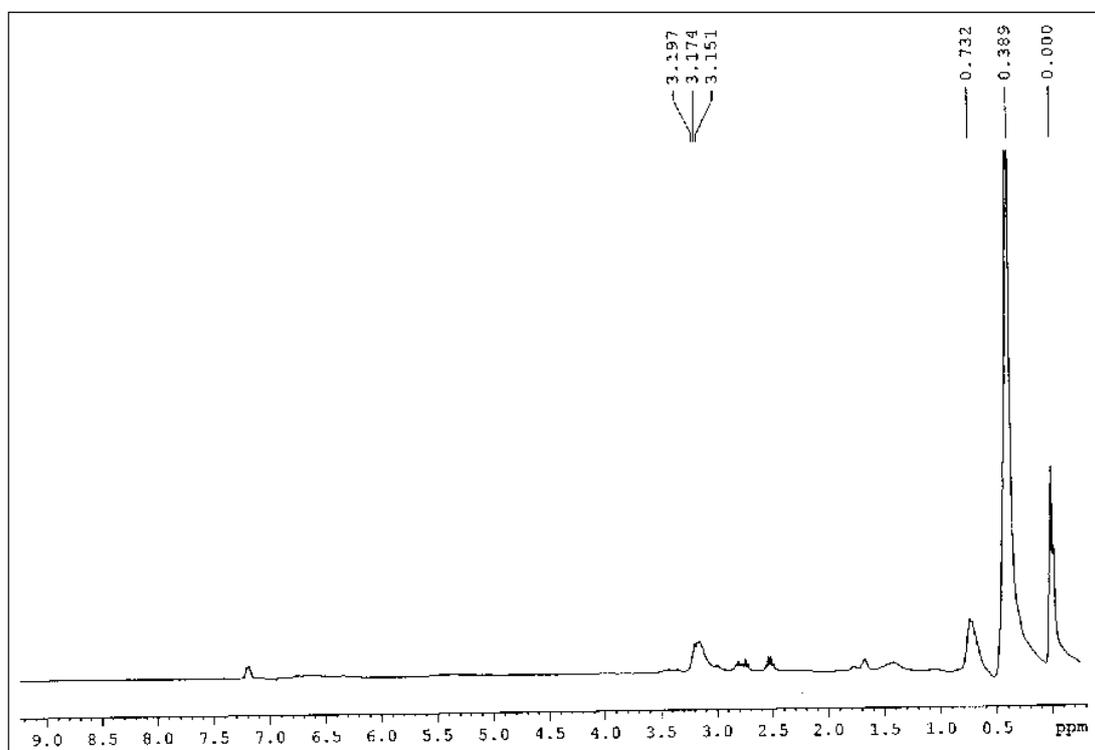


Figure 1.3.2: ¹H- NMR spectra of polydecyl acrylate

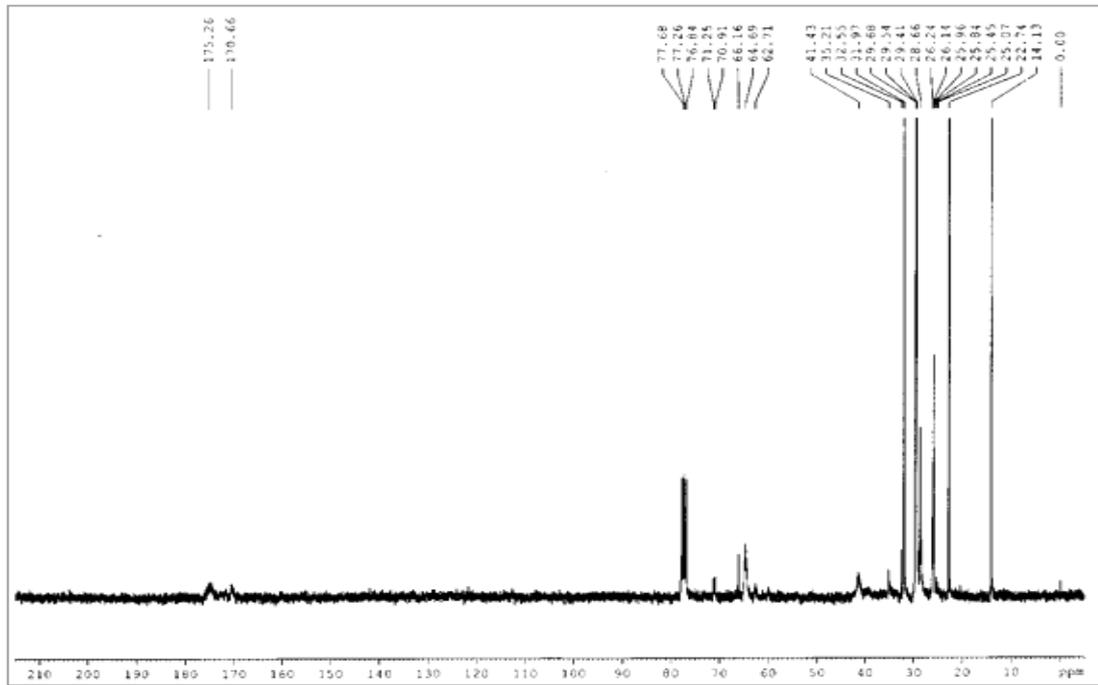


Figure 1.3.3: ^{13}C - NMR spectra of poly behenyl acrylate

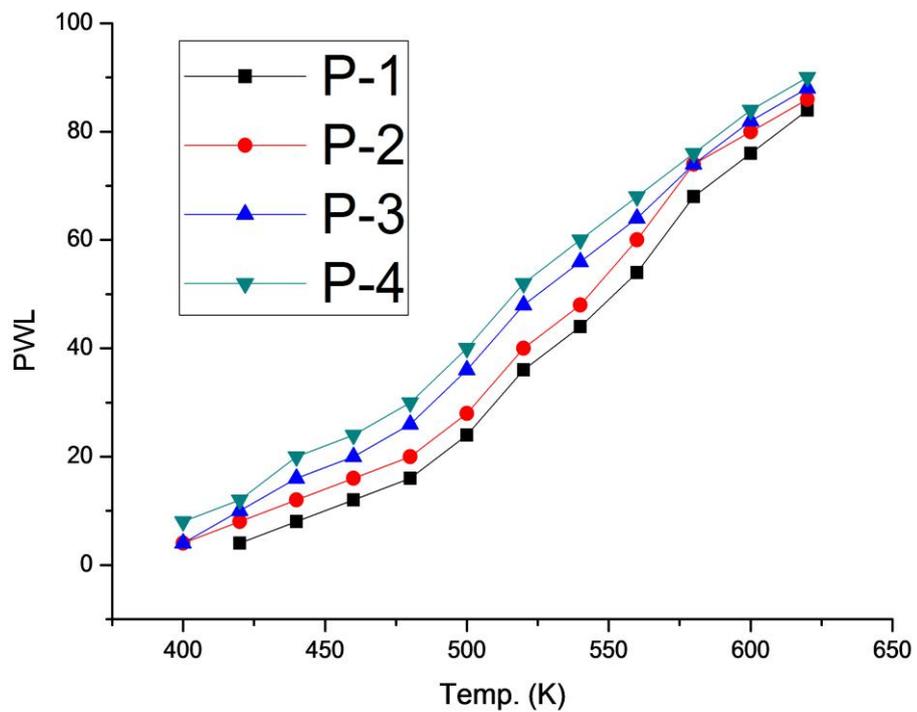


Figure 1.3.4: Plot of PWL (Percent Weight Loss) vs Temperature (in K)



5(a)

Base oil (BO2)



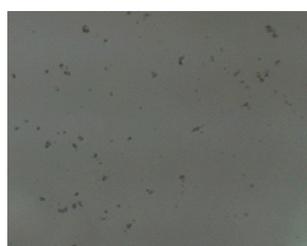
5(b)

P-1 (3%)



5(c)

P-2 (3%)



5(d)

P-3 (3%)



5(e)

P-4 (3%)

Figure 1.3.5(a-e): Plot of photo micrographic images of base oil and additive (P-1, P-2, P-3 and P-4) doped base oil

Chapter IV

Synthesis and a Comparative Study on Their Performances as Multifunctional Lube Oil Additives of Behenyl and Isodecyl Acrylate Based Polymers

1.4.1 Introduction

Modern lubricants consist of the base oil as a major constituent along with some additives required for providing some specific characteristics or sometimes enhancing the existing properties [1]. Antioxidant, detergents, dispersants, corrosion inhibitors, viscosity index improvers (VIIs), pour point depressants (PPDs), anti-wear and antifriction additives are some of the important types of these additives. Out of these, VIIs and PPDs are added in large quantities because the viscosity and fluidity variation with temperature determines the applicability of a lubricant formulation in low and high temperature operational conditions with effective and efficient performance [2]. Utilization of polymeric additives as chemical treatment is considered the most valuable and economic method to inhibit wax precipitation at low temperatures. Basically, these polymeric wax inhibitors consist of a non-polar long hydrocarbon chain of 14 to 25 carbon atoms in addition to a polar segment typically acrylates or acetates. The polar head group is responsible for the modification of wax crystals morphology and the non-polar long hydrocarbon chain renders the interaction between the additives and paraffin [3], [4]. A considerable number of polymeric additives have been created and utilized as PPDs to modify the growing pattern of wax crystals [5]-[7]. Normally, a linear polymer of alkyl methacrylate or acrylate having a pendent alkyl side chain of specific length is used as pour point depressants (PPDs) or flow improvers (FIs) [8]-[11]. PPDs do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates, rather they co-crystallize along with the wax species present in the oil at lower temperature and modify the growing pattern of wax crystal structures. Additionally, the PPD backbone kept the wax crystals apart from each other and because of this steric hindrance, the wax crystals are no longer able to form 3-D matrix which entraps the oil and inhibits

the flow at a lower temperature. Recent studies on the structure–reactivity relationship for the polymers of higher alkyl acrylates and methacrylates [12], [13], promoted the research towards improving processes for the polymerization of *n*-alkyl acrylates with narrow molecular weight distribution (MWD) [14]. Some commercially available properly designed polymeric flow improvers are poly (ethylene–co–vinyl acetate) (EVA) [15], poly (ethylene-butene) (PEB) [16], polymethacrylates [17], and modified maleic anhydride copolymers [4]. Recently Chen et al. reported that polyacrylate polymers with polar building blocks interacted more easily with the paraffin content which would effectively inhibit wax crystal precipitation and improve low-temperature fluidity [18]. Another study supports that an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer having pendant hydrocarbon chain groups [19]. Again, some investigations indicated that molecular weight (MW) and molecular weight distribution (MWD) should also play an important role in the performance as a flow improver [20]. Homopolymers of alkyl methacrylates and acrylates and their copolymers with ethylene, vinyl acetate, etc. are used extensively as pour point depressants and flow improvers in high waxy crude oils, lubricating oils, and fuel oils. These types of polymer contain an alkyl length of more than 14 carbons. Behenyl acrylate (BA) consists of a mixture of C₂₂, C₂₀, and C₁₈ acrylates and is used extensively in the preparation of these additives [13]. Recently development of the novel additives based on copolymers containing *n*-alkyl acrylates has gained huge attention due to their multifunctional nature and the fact that the comb-shaped polymeric additives can be more effective as PPD in lube oil by providing different nucleation sites for the precipitation of wax [21]. Dao in 2017 has reported that copolymers formed by stearyl methacrylate and behenyl acrylate with vinyl acetate using AIBN as initiator give high efficiency to reduce pour point temperature [22]. R.

K. Singh et al. have reported the successful synthesis, characterization, and performance evaluation of two homopolymers of C₁₈ alkyl acrylate and N,N-dimethylacrylamide and their three copolymers as synthesized by using 1:1, 1:2, and 2:1 monomer ratios as VII and PPDs in polyol base oil taking the homopolymers as reference [2]. B. Subrahmanyam et al. had presented a thorough study on the effect of initiator concentration and monomer concentration on the molecular weight and molecular weight distribution in behenyl acrylate polymerization. They found that at a higher concentration of initiator and monomer, the branching reactions led to gel formation in behenyl acrylate polymerization. They reported that viscosity of the polymerizing medium also influenced the high conversion polymerization in alkyl acrylate polymerization [13].

Thus growing demand for the requirement of high performance characteristics and increasing environment related concerns have forced the researchers to develop new multifunctional polymeric additives so that maximum activity can be achieved with a minimum dosage. In this present context, we have prepared homopolymers of behenyl acrylate and isodecyl acrylate and further their copolymers with 1-Decene at variable percentage. All the prepared polymers have been characterized by FT-IR and NMR spectroscopy. Their thermal stability and molecular weight were determined and then they were evaluated as VII and PPD in lube oil.

1.4.2 Experimental section

1.4.2.1 Materials

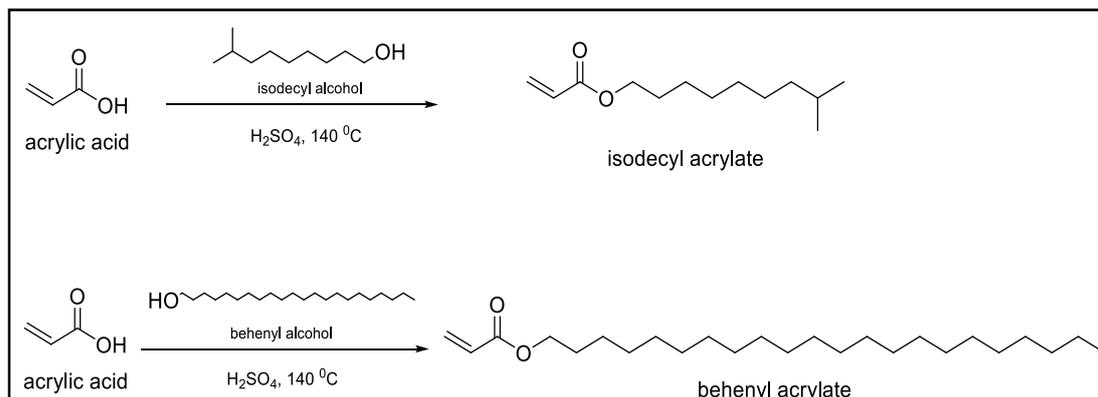
Isodecyl alcohol (98%, SRL Pvt. Ltd.), behenyl alcohol (Merck Specialties Pvt. Ltd.), 1-decene (95%, Acros organics), and acrylic acid (Merck Specialties Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Chem Ltd.), and Methanol (98%, Thomas Baker Pvt. Ltd.) were

used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and Benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd.) was used as received. The properties of the used base oils are tabulated in **Table 1.4.1**.

1.4.2.2 Preparation of esters

The ester (Isodecyl acrylate, IDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of isodecyl alcohol. The reactants were mixed with toluene along with few drops of concentrated sulphuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as a polymerization inhibitor in a resin kettle, and heated gradually from room temperature to 140°C using a well-controlled thermostat under a slow stream of deoxygenated nitrogen. The extent of esterification was monitored by the amount of liberated water. Another ester (Behenyl acrylate, BA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of behenyl alcohol following the same procedure.

Scheme 1.4.1 Reaction for the preparation of isodecyl acrylate and behenyl acrylate



1.4.2.3 Purification of prepared esters

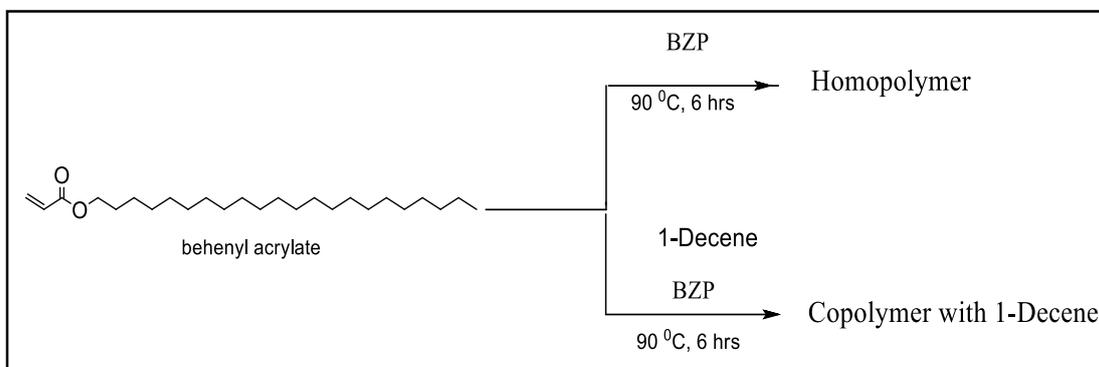
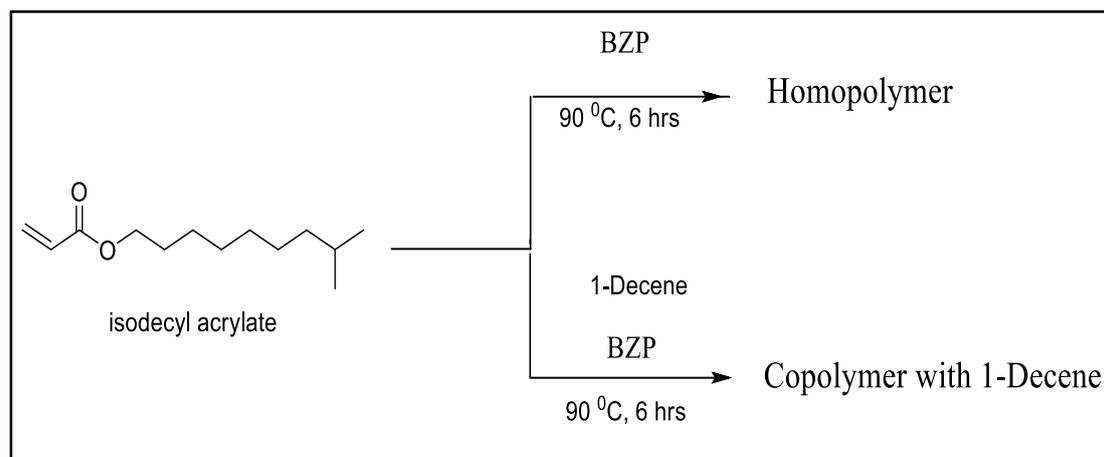
The prepared esters were refluxed for 3 hours with a suitable amount of charcoal and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separatory funnel several times to ensure the complete removal of untreated acid. The ester was

then washed repeatedly with distilled water to remove any traces of sodium hydroxide. The purified ester was then left overnight on calcium chloride. It was then removed by distillation under reduced pressure. Then the ester was ready to be used in the polymerization process.

1.4.2.4 Preparation of the polymers

The polymers (homo and copolymers) were prepared by free radical polymerization at different percentage compositions of monomers (**Table 1.4.2**) in presence of BZP as an initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of the polymer was carried out by the procedure as reported in our earlier publication [23].

Scheme 1.4.2 Reaction for the preparation of homopolymer of isodecyl and behenyl acrylate and copolymer with 1-Decene



1.4.3 Measurements

1.4.3.1 Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 35°C temperature at a flow rate of 1mL/min. The values are given in **Table 1.4.2**.

1.4.3.2 Spectroscopic Measurements

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

1.4.3.3 Performance evaluation as pour point depressants in base oil

The effect of additive concentration on the pour point of two base oils (BO1 and BO2) was tested by using different doping concentrations ranging from 1% to 6% (% w/w) for each of the prepared polymers. According to the ASTM D 97-09 method, the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India) given in **Tables 1.4.3 & Table 1.4.4**.

1.4.3.4 Performance evaluation as viscosity index improver (VII)

Viscometric parameters were determined according to ASTM D 2270-10. The kinematic viscosity of the base oils containing the polymers determined at 40°C and 100°C. Different concentrations of the polymers in the base oil (% w/w) from 1% to 6% was used to study the effect of concentration on VI of the additive-doped lube oil. All of the experimental data given in **Table 1.4.5 & Table 1.4.6** were noted by taking an average of three experimental results under identical conditions in each case.

1.4.3.5 Determination of thermogravimetric analysis (TGA) data

TGA data (Table 1.4.7) was measured on Mettler TA-3000 system, at a heating rate of 10K min^{-1} . The variation of temperature within the range was $\pm 10^{\circ}\text{C}$ during the experiment. The uncertainty in determining percent weight loss (PWL) within the range was $\pm 1.5\%$.

1.4.4 Results and discussion

1.4.4.1 Molecular Weight Analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w), and polydispersity index data (PDI) of the prepared polymers are given in Table 1.4.2.

Analyzing the experimental data, it was found that the homopolymer of behenyl acrylate (P_1) had a higher number average and weight average molecular weight than the others. Again in terms of polydispersity index (PDI), this polymer is less polydispersed which indicates better uniformity. With an increasing concentration of 1-Decene, the polymers (P_2 , P_3 & P_4) exhibited a higher polydispersity index. Among the polymers of IDA (P_5 to

P_8), the copolymer of 95% IDA and 5% 1-Decene (P_8) showed the highest number average and weight average molecular weight and lowest polydispersity index.

1.4.4.2 Spectroscopic analysis

In FT-IR spectroscopy almost all the polymers being acrylate produced similar spectra. Peaks around $1733\text{--}1738\text{ cm}^{-1}$ clearly indicated the presence of the ester carbonyl group in each case. Absence of peaks above 3000 cm^{-1} indicates the absence of C=C unsaturation which supports complete polymerization in all the cases. In ^1H NMR spectra, peaks appeared in the range of $3.93\text{--}4.32\text{ ppm}$ clearly indicated the presence of $-\text{OCH}_2-$ protons. Here again, the absence of peaks around 6 ppm indicated

the absence of C=C unsaturation and hence supported total polymerization. In ^{13}C NMR spectra, peaks at 170.34–177.8 ppm indicated the presence of ester carbonyl carbon. The peaks at 59.78–65.99 ppm corresponded to the $-\text{OCH}_2-$ carbons, peaks ranging from 13.95–45.22 ppm for all other sp^3 carbons. Again no peak in the range of 120–150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization.

1.4.4.3 Performance evaluation as pour point depressant

The pour point data are given in **Tables 1.4.3** & **Table 1.4.4** clearly prove that the prepared polymers are good pour point depressants for both the base oils except the homopolymer of behenyl acrylate (P_1) which exhibited very little depletion in pour point in both cases (BO1 & BO2). The very high molecular weight of this polymer might be the reason for its low solubility in the base oils which discards its effectiveness as PPD. But the copolymers of behenyl acrylate and 1-Decene have been proved to be effective PPDs in both the base oils. Comparing all the pour point data, it can be said that the homopolymer of IDA (P_5) and its copolymers (P_6 to P_8) are better pour point depressants and among them all, P_5 polymer gave the best result. Branching in the alkyl chain of these polymers might be the reason behind this observation. Almost in all the cases the pour point depression curves get flattened above 4% concentration since at higher concentration the polymers suffer lower solubility and hence their effectiveness as PPD also diminishes.

1.4.4.4 Performance evaluation as viscosity index improver

Solubility of the polymer, its molecular weight, and composition play an important role in its performance as a viscosity index improver [24]. It is said that polymers exist as random coils in base oil solutions. As the temperature increases the solubility of the polymer increases and it unfolds itself to an open configuration of higher volume and

hence overall higher viscosity is exhibited at higher temperature by polymer-doped base oil. This activity offsets the normal trend of a decrease in viscosity with an increase in temperature [25]. It is seen from **Tables 1.4.5 & Table 1.4.6** that all the prepared polymers are effective viscosity index improvers for both the base oils. Here again, due to very high molecular weight and hence lower solubility, the homopolymer of behenyl acrylate (P₁) is least effective as VII among all. On the other hand, the homopolymer of IDA (P₅) has been proved to be the best viscosity index improver in both the base oils. The rests are almost comparable VIIs. With increasing concentration of the polymer in the base oil, the total volume of the polymer micelle increases, and hence the viscosity index data also increases [26].

1.4.4.5 Analysis of TGA data

The thermal studies confirmed that all the prepared polymers are thermally stable (**Table 1.4.7**). Lower the percent weight loss (PWL) higher will be the thermal stability. Therefore, among the prepared polymers, the copolymer of behenyl acrylate and 1% 1-Decene (P₂) is thermally most stable while the homopolymer of behenyl acrylate (P₁) is thermally least stable. Higher thermal stability of the additives indicated their suitability as lubricant additives.

1.4.5 Conclusion

The above study may be summarized as follows. All the prepared polymers have been evaluated as effective multifunctional and thermally stable additives for lube oil. In terms of molecular weight, the homopolymer of behenyl acrylate exhibited the highest number average and weight average molecular weight. Further, the PDI value accounts for better uniformity in this polymer than others. But this polymer is very much less effective as PPD as well as VII which may be attributed to its solubility problem. All the other polymers have been proved to be good flow improvers in both the base oils.

Especially the homopolymer of isodecyl acrylate resulted the highest depression in pour point in both cases. This polymer was also proved to be the best VII among all the prepared ones.

1.4.6 References

References are given in *BIBLIOGRAPHY* under “Chapter IV of Part I” (Page No. 140-143).

1.4.7 Tables and Figures

Table 1.4.1: Base Oil (BO) Properties

<i>Physical Property</i>	<i>BO1</i>	<i>BO2</i>
Density (gcm^{-3} at 40 °C)	0.837	0.868
Viscosity at 40 °C in cSt	7.136	23.392
Viscosity at 100 °C in cSt	1.856	3.915
Pour Point (PP in °C)	-3	-6
Cloud Point (°C)	-10	-8
<i>BO1, BO2 collected from IOCL, Dhakuria, West Bengal</i>		

Table 1.4.2: Weight percentage (%) composition, M_n , M_w , and PDI values of polymers (P₁ to P₈)

<i>Polymer</i>	<i>% of BA</i>	<i>% of IDA</i>	<i>% of 1-D</i>	M_n	M_w	<i>PDI</i>
P ₁	100	–	–	22574	333217	1.50
P ₂	99	–	1	117472	218347	1.86
P ₃	97	–	3	114428	215067	1.88
P ₄	95	–	5	112692	213115	1.89
P ₅	–	100	–	131593	231034	1.76
P ₆	–	99	1	138208	236429	1.71
P ₇	–	97	3	141356	240259	1.70
P ₈	–	95	5	145256	243593	1.68
<i>BA = Behenyl acrylate, IDA = Isodecyl acrylate, 1-D = 1-Decene, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index</i>						

Table 1.4.3: Pour point (°C) data with respect to the different concentrations of the additives in BO1 and its graphical representation

Additive	1%	2%	3%	4%	5%	6%
P ₁	-4.9	-5.4	-6.0	-6.0	-5.8	-5.1
P ₂	-6.0	-6.5	-7.2	-7.8	-8.1	-8.0
P ₃	-8.1	-8.6	-9.2	-9.4	-9.4	-9.1
P ₄	-10.9	-11.2	-11.6	-12.1	-12.0	-12.0
P ₅	-14.0	-14.6	-15.0	-15.2	-15.1	-15.0
P ₆	-9.4	-10.8	-11.6	-12.4	-12.3	-12.3
P ₇	-11.1	-11.8	-12.2	-12.9	-12.9	-12.4
P ₈	-11.9	-12.5	-13.4	-13.6	-13.6	-13.3

Concⁿ represents concentration in % w/w

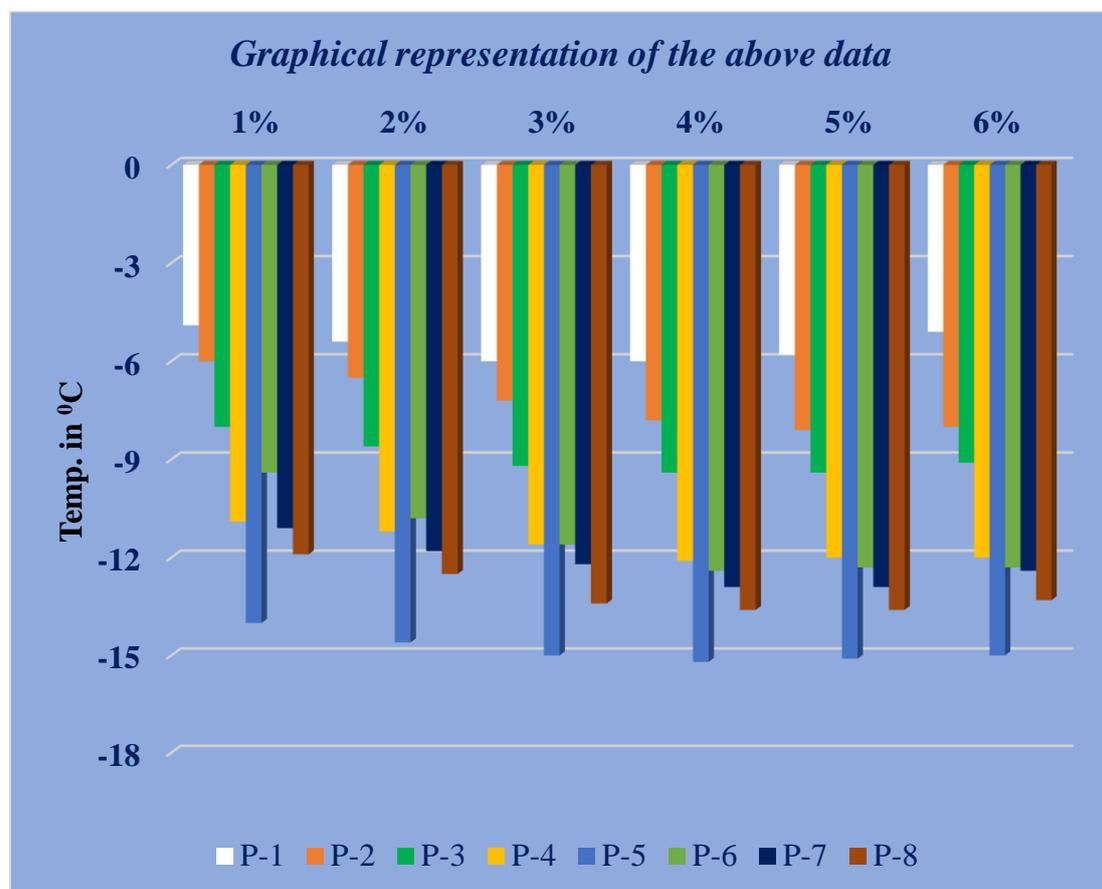


Table 1.4.4: Pour point (°C) data with respect to the different concentrations of the additives in BO2 and its graphical representation

Additive	1%	2%	3%	4%	5%	6%
P ₁	-8.4	-9.0	-9.4	-9.8	-9.8	-9.6
P ₂	-12.5	-13.1	-13.5	-14.1	-14.6	-14.6
P ₃	-12.4	-12.9	-13.2	-13.8	13.8	-13.7
P ₄	-12.0	-12.6	-13.2	-13.8	-14.2	-14.2
P ₅	-18.0	-18.5	-19.4	-19.8	-20.0	-20.0
P ₆	-15.8	-16.4	-17.0	-17.3	-17.7	-17.7
P ₇	-16.1	-16.8	-17.2	-17.6	-17.9	-17.4
P ₈	-14.0	-14.3	-14.8	-15.1	-15.4	-15.0

Concⁿ represents concentration in % w/w

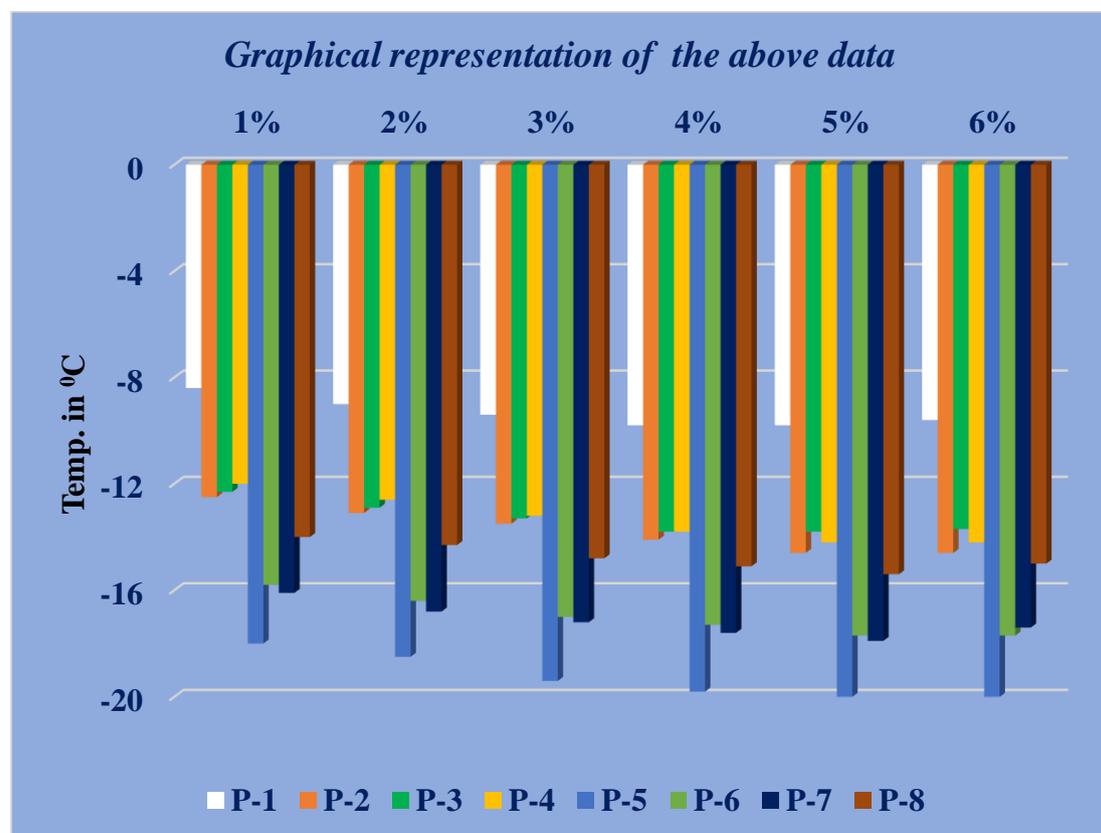


Table 1.4.5: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO1 and its graphical representation

Additive	0%	1%	2%	3%	4%	5%	6%
P ₁	85	90	92	94	95	99	102
P ₂	85	92	95	99	101	105	109
P ₃	85	88	90	93	95	101	103
P ₄	85	86	88	90	94	97	100
P ₅	85	91	103	119	125	130	136
P ₆	85	86	87	89	91	97	103
P ₇	85	89	93	97	103	107	112
P ₈	85	98	102	108	111	114	120

Concⁿ represents concentration in % w/w

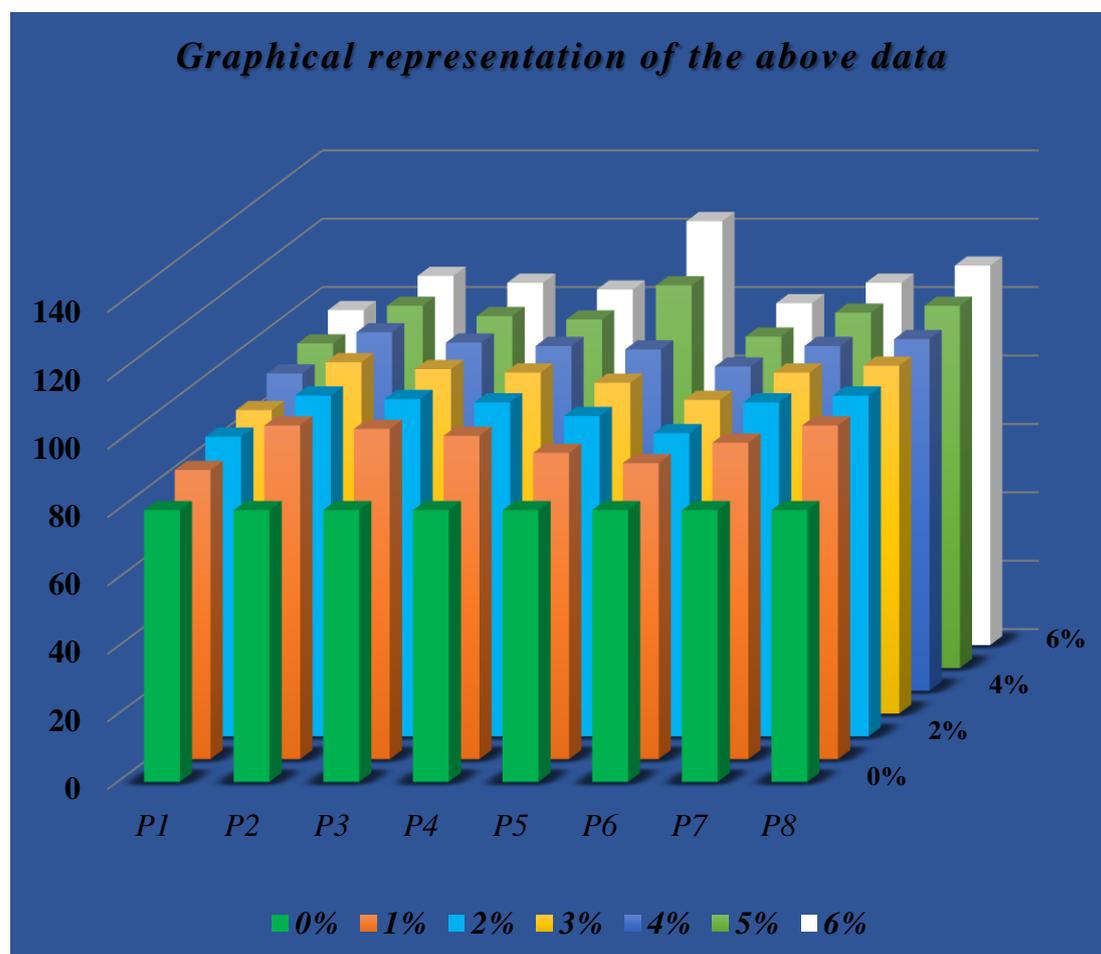


Table 1.4.6: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO2

<i>Additive</i>	<i>0%</i>	<i>1%</i>	<i>2%</i>	<i>3%</i>	<i>4%</i>	<i>5%</i>	<i>6%</i>
P₁	80	85	88	89	93	95	98
P₂	80	98	100	103	105	106	108
P₃	80	97	99	101	102	103	106
P₄	80	95	98	100	101	102	104
P₅	80	90	94	97	100	112	124
P₆	80	87	89	92	95	97	100
P₇	80	93	98	100	101	104	106
P₈	80	98	100	102	103	106	111
<i>Concⁿ represents concentration in % w/w</i>							

Table 1.4.7: TGA data of the polymers

<i>Polymer</i>	<i>Decomposition temperature</i>	<i>Percent weight loss (PWL)</i>
P₁	250/340	23/86
P₂	250/360	12/82
P₃	260/380	14/85
P₄	250/380	13/80
P₅	260/320	14/80
P₆	240/320	14/86
P₇	240/320	13/87
P₈	250/320	14/90

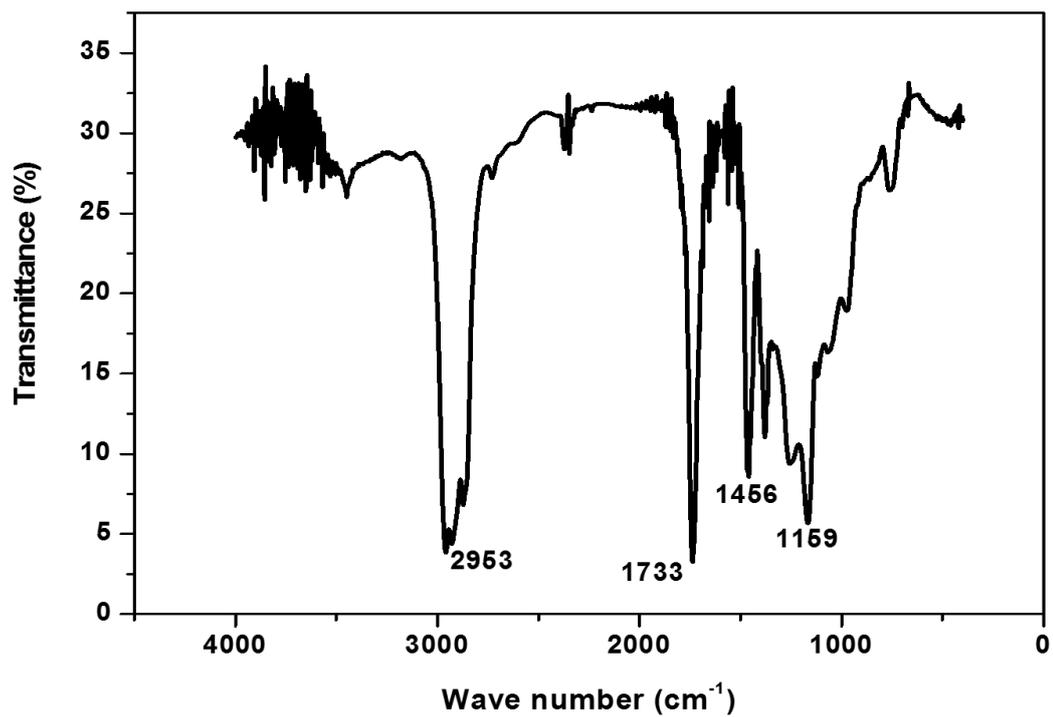


Figure 1.4.1: FT-IR spectrum of co-polymer of BA- 1-Decene (P3)

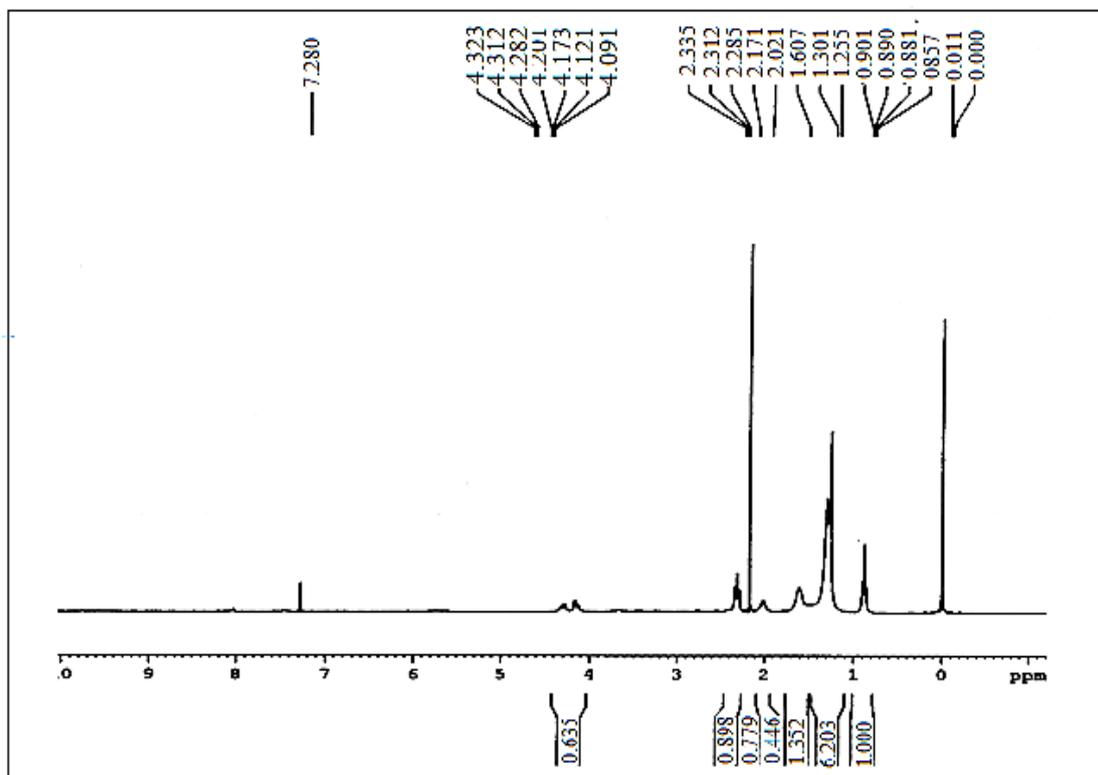


Figure 1.4.2: ¹H NMR spectrum of co-polymer of BA- 1-Decene (P3)

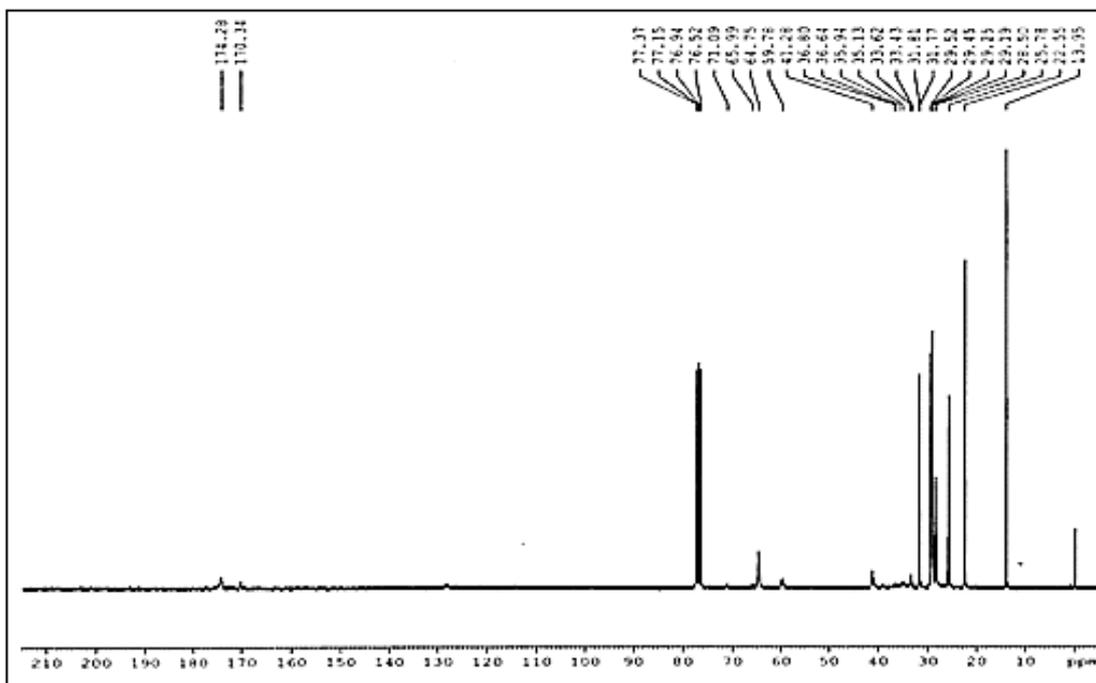


Figure 1.4.3: ^{13}C - NMR spectrum of co-polymer of BA - 1-Decene (P3)

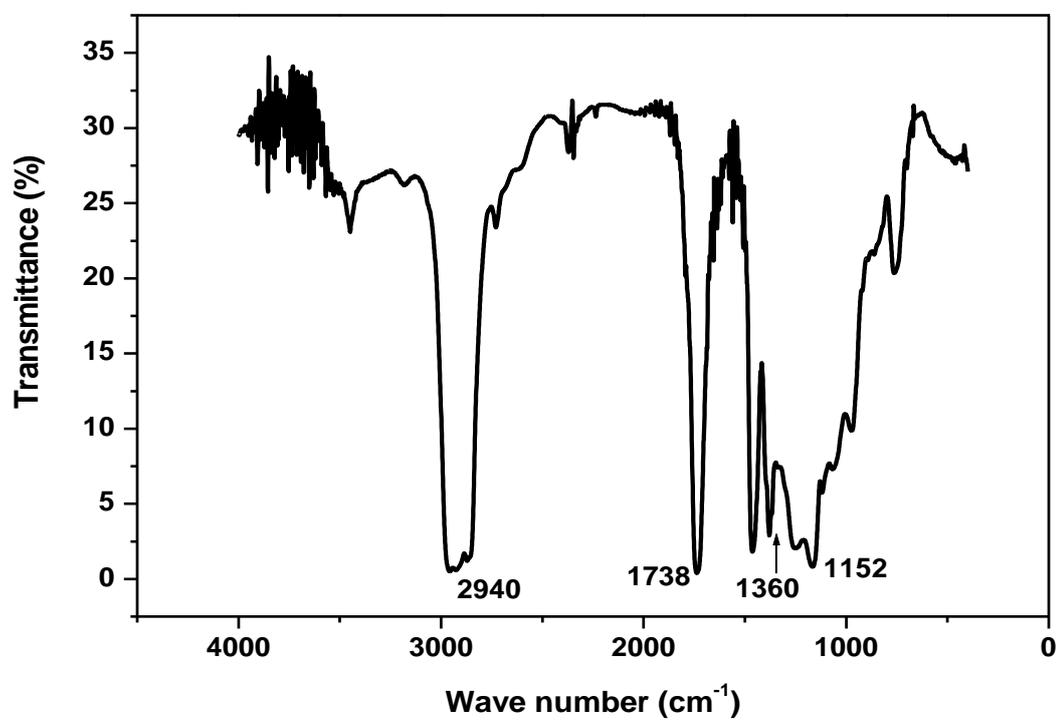


Figure 1.4.4: FT-IR spectrum of co-polymer of IDA- 1-Decene (P7)

Chapter V

A Study as a Multifunctional Additives of Acrylate Based ZnO Nano Composite for Lubricating Oil

1.5.1 Introduction

Service life, economic efficiency, and engine operation are directly or indirectly depend on the quality, performance, and sensible use of the oils [1], [2]. The two major constituents of tribology are friction and wear. The service of the machine automatically increases when this friction and wear under controlled and reduced. This ultimately saves money. The awareness of the subject, i.e. identification of tribological problems and their proper solution can give rise to a considerable saving. According to some estimation, losses due to unawareness of tribology are about 6 % of its gross national product in the United States. Thus the significance of friction reduction and wear management cannot be overemphasized for economic reasons and long-term dependability. In this regard, researchers are focused on the application of nanoparticles (NPs) in lube oil. Nanoparticles blended lubricating oils can boost the properties of extreme pressure anti-wear, and friction reduction capability and hence improved the service life of the machine [3]. The anti-wear and friction reduction action is depended on the characteristics of nanoparticles, for example, shape, size, and concentration. Due to its large surface area nanoparticles are dissimilar from other materials. As a result, nanoparticles are very reactive compared to their bulk form. Now a day, generally used nanoparticles are oxides based- Al_2O_3 , CuO , ZnO , metals- Al , Cu , nonmetals- graphite, carbon nanotubes, layered composites- $\text{Al}-\text{Al}_2\text{O}_3$, $\text{Cu}+\text{C}$, functional nanoparticles, etc. Due to their unique structure and performance, ZnO nanoparticles have been attracted considerable interest among different kinds of nanoparticles [4]-[7]. ZnO nanoparticle has a huge surface area, high surface energy, high diffusion, strong adsorption characteristics. Apart from that, ZnO NPs have attracted increasing attention because these NPs can be easily synthesized and it is a greener material i.e, biocompatible and nontoxic [8]. Nano-sized base oil additives are

appropriate for heavy load, low speed, high-temperature work, and have excellent extreme pressure resistance, and anti-wear resistance performance, and better lubrication properties. When ZnO nanoparticles are used as lube oil additive, not only enhance the tribological properties of base oils but also potentially reduce the cost of lube oil. On the other hand, due to its hydrophilic-oleophobic nature, nano-ZnO is poor oil soluble. It needs to depend on the role of dispersant, ultrasonic dispersion, or strong agitation to disperse nano-ZnO particles in the base oils [9]-[13]. So, nano-ZnO particles alone do not show other kinds of additive performance. Therefore, to disperse ZnO nanoparticles to lube oil to develop a multifunctional performance additive, ZnO nanoparticles were first dispersed acrylate-based polymer matrix by sonication. Since acrylate-based polymer was known to perform as a good viscosity index improver [14]-[16] and pour point depressant [17]. The main objective of this research work is to study the multifunctional additive property of polymer-ZnO nanocomposites for lube oil. In our previous work, we made a polyacrylate-nano magnetite composite [18] and polyacrylate-Liquid crystal composite [19] to study the multifunctional additive performance. In continuation of our work, here we have introduced nano ZnO into the polyacrylate system to study the multifunctional additive properties (tribological performance, viscosity index improver, pour point depressant) of this polymer-ZnO nanocomposite.

1.5.2 Experimental Section

1.5.2.1 Materials and methods

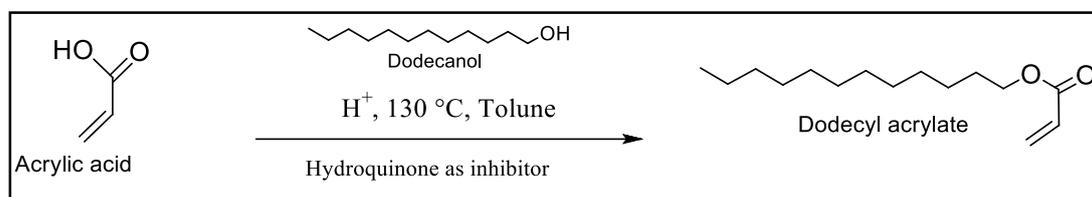
Dodecyl alcohol, acrylic acid, hydroquinone, and BZP were purchased from Merck specialties Pvt. Ltd. India. Toluene, Methanol, hexane, and conc. H₂SO₄ was purchased from Thomas baker Pvt. Ltd. India. BZP was recrystallized from CHCl₃-MeOH.

NaOH and ZnCl₂ were purchased from Merck specialties Pvt. Ltd. India. The base oil was collected from the IOCL, Dhakuria, Kolkata, India.

1.5.2.2 Preparation of dodecyl acrylate by esterification

Dodecyl acrylate (DDA) was prepared by the esterification process of dodecyl alcohol with acrylic acid in the mole ratio of 1:1.1. The reaction was performed in a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone is added with respect to the reactants as a polymerization inhibitor, and toluene used as a solvent. The reaction was performed under a nitrogen atmosphere. The reaction mixture was heated gradually from room temperature to 130⁰C using a well-controlled thermostat. The extent of the reaction was monitored by observing the amount of liberated water during the reaction to give the ester, dodecyl acrylate (DDA).

Scheme 1.5.1 reaction for the preparation of dodecyl acrylate



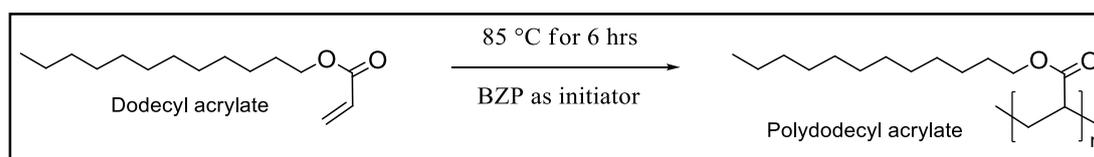
1.5.2.3 Purification of the prepared monomer

A desired amount of charcoal was added to the ester to purify the product. After that, it was reflux for 3 h and then filtered. The filtrate was washed frequently with 0.5N sodium hydroxide solution to ensure the complete removal of unreacted acid. Then to remove traces of sodium hydroxide, purified ester was washed several times with distilled water. The prepared ester was then left on calcium chloride overnight and recollected by distillation under reduced pressure. This purified ester was used in the polymerization reaction.

1.5.2.4 Preparation of homopolymer of dodecyl acrylate

The polymerization was carried out in a four-necked round bottom flask furnished with a condenser, stirrer, thermometer, and an inlet for the nitrogen insertion. The required amounts of dodecyl acrylate and benzoyl peroxide (BZP) as initiator were taken in the flask and toluene was also added as a solvent. The reaction temperature was controlled at 85⁰C for 6 hours. After that, the reaction mixture was added into methanol solvent with constant stirring to cease the polymerization, and then a precipitate appeared. The precipitate (the polymer) was further purified by frequent precipitation with methanol followed by drying under vacuum at 40⁰C.

Scheme 1.5.2 Reaction for the preparation of homopolymer of dodecyl acrylate



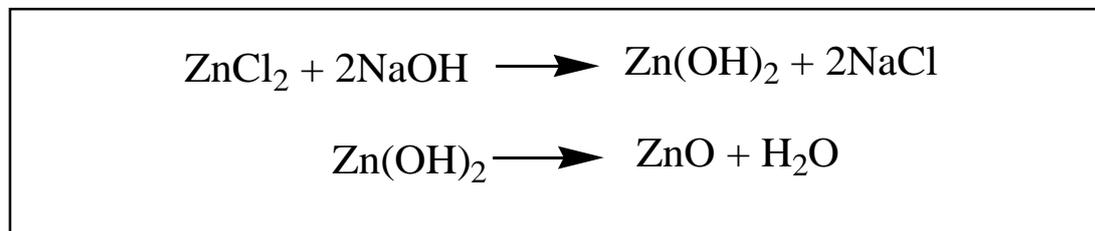
1.5.2.5 Preparation of ZnO nanoparticle

5.5 g of ZnCl₂ was dissolved in 100ml of distilled water in a beaker. The solution was kept under constant stirring with a magnet till ZnCl₂ dissolved in the distilled water. The temperature of the solution was increased to 90⁰C by electric hot plate heating. Meanwhile, 20 g of NaOH was dissolved in 100ml of distilled water in a separate vessel. From the prepared NaOH solution, 16 ml of NaOH is added to the beaker with constant stirring, drop by drop through the inner wall of the beaker. Without any precipitation, the aqueous solution turned into a milky white colloid. After completing the addition of NaOH, the reaction was allowed to proceed for another 2 hrs. After completion of the reaction, the solution was allowed to settle and the supernatant solution was removed by washing with distilled water 5 times. After washing, the ZnO

nanoparticles were dried at 100⁰C for 30 min. and then changed into powder form [20].

The reaction involved is given below:

Scheme 1.5.3 Reaction involved during synthesis of nano-ZnO



1.5.2.6 Preparation of poly dodecyl acrylate- ZnO nanocomposites

PDDA- ZnO nanocomposites were prepared by mixing the PDDA/toluene solution and nano- ZnO particles. The PDDA- ZnO suspension was prepared as follows: 5g of PDDA were dissolved in toluene and the required amount (0.5, 1, and 1.5mg) of nano- ZnO particles were added into the PDDA/toluene solution under the ultrasonic wave and vigorous stirring to prepare 100, 200 and 300 ppm blend and it is depicted in **Table 1.5.2**. The suspension was then poured into a glass plate and allows the toluene to evaporate naturally and a semi-solid mass of polymer-nanocomposites was obtained.

1.5.3 Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wavenumber range of 400–4000 cm⁻¹. NMR spectra were recorded in Bruker Advance NEO 400 MHz FT-NMR spectrometer using a 5 mm BBO probe using CDCl₃ as solvent and TMS as reference material.

1.5.3.1 Characterization of nano- ZnO by SEM, X-RD, and DLS

The synthesized ZnO-nanoparticles were characterized by Field Emission Scanning Microscope (FE-SEM, INSPECT F50, FEI) and XRD analysis is recorded using an

Advance D8, Bruker instrument with 2θ angle from the range of $20-90^\circ$. The DLS of the suspension was performed on a Malvern Zetasizer ver 6.01. For the DLS study suspension of NPs in water was prepared by taking a concentration of 5 mg/mL.

1.5.3.2 Determination of molecular weight by GPC

By GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) was determined. The polydispersity index was also calculated. In this method HPLC grade THF (0.4%, w/v) was used as mobile phase in the water 2414 GPC system (polystyrene calibration) at 35°C with a flow rate of 1 ml/min and the injection volumes are set to 20 μL . The data of this study is given in supporting information.

1.5.3.3 Thermogravimetric analysis (TGA)

The thermal stabilities of the prepared homopolymer and polymer nanocomposites were determined by a thermogravimetric analyzer (Shimadzu TGA-50) using an alumina crucible in air. The system was run at a heating rate of $10^\circ\text{C}/\text{min}$. The percentage of weight loss (PWL) with the rise in temperature was calculated.

1.5.3.4 Evaluation as viscosity modifier

The viscosity index (VI) of the polymeric additives was determined in a paraffinic base oil to evaluate the efficiency of the prepared polymeric additives as viscosity modifiers (VM). The viscosity index (VI) of different concentrations of the additives in the base oils was evaluated in two base oils according to the ASTM D2270 method and following the equations as reported by Tanveer and Prasad [21]. Five different concentrations ranging from 1 wt % to 5 wt % of the polymeric sample solutions were used to study the effect of additive concentration on VI.

1.5.3.5 Evaluation as pour point depressant

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

1.5.3.6 Evaluation of the tribological performance of prepared additives

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

1.5.4 Results and discussion

1.5.4.1 Spectroscopic analysis

The FT-IR spectrum of homopolymer dodecyl acrylate (A) and its nanocomposites (Z-3) is shown in **Figure 1.5.1**. The absorption band (**Figure 1.5.1a**) at 1734.56 cm^{-1} indicated the ester stretching vibration along with other peaks at 1458.40, 1169.67, 1070.96, 721.65 cm^{-1} . **Figure 1.5.1b** of polymer/ZnO nanocomposites showed absorption band for ester carbonyl group at 1728 cm^{-1} along with other peaks at 1465.98, 1167.99, 1070.96, 721.63 cm^{-1} . This shifting of carbonyl stretching frequency may be due to some association of nano magnetite and poly dodecyl acrylate. The peaks in the range at 1458.40, 1465.98 cm^{-1} are for asymmetric and symmetric bending vibrations of C-H bonds of $-\text{CH}_3$ and $-\text{CH}_2-$ groups of polymers and its nanocomposites. Peaks in the range of 1169.67, 1167.99, 1070.96 cm^{-1} are due

to C-O stretching vibration of the carboxylate ester group. Peaks at about 721 cm^{-1} are for C-H bending vibration of the paraffinic chain. Broad peaks in the range 2924.08 to 2937 cm^{-1} are for stretching vibration of paraffinic C-H bonds of $-\text{CH}_2-$ groups. In the infra-red region, the peaks at 454.6 cm^{-1} correspond to Zinc oxide nanoparticles which show the stretching vibration of Zn-O bond [24]. There is no significant peak observed in the range of the carbon-carbon double bonds region which supported the formation of the polymer.

The ^1H NMR spectra of A and Z-3 are shown in **Figure 1.5.2** & **Figure 1.5.2a** represents the spectrum of A which showed broad singlet centered at 4.013 to 4.293 ppm due to the protons of $-\text{OCH}_2$ group. Methyl protons of the dodecyl chain appeared between 0.866 ppm and 0.878 ppm and the absence of singlet between 5 ppm and 6 ppm implies the absence of any vinylic proton in the polymer. The ^1H NMR of polymer nanocomposites (**Figure 1.5.2b**) showed a peak at 4.001 and 3.627 ppm due to the protons of $-\text{OCH}_2$ group of the acrylate polymer and methyl and methylene protons appeared in the range of 0.851 to 0.884 ppm.

In the ^{13}C NMR spectrum of A, the carbonyl carbon appeared at 174.3 ppm along with other sp^3 carbons appeared in the range of 64.72 to 13.94 ppm and it is shown in **Figure 1.5.3**. The ester carbonyl of the nanocomposite (Z-3) appeared at 174.5 ppm as shown in **Figure 1.5.3b**. Peaks appeared in the range from 65 to 14.19 ppm are for the SP^3 carbons of alkyl chains of PNC. The intensity of peaks decreases compared to the pure polymer as depicted in NMR spectra. Hence it can be concluded that ZnO nanoparticles formed a co-ordinate type of bond with ester group of A which lower the stretching frequency of ester carbonyl.

1.5.4.2 Characterization of nano- ZnO (by XRD, SEM, and DLS)

Figure 1.5.4 shows the X-ray diffraction pattern of ZnO nanoparticles. The nanoscale range of particles in the prepared materials was indicated by a definite line broadening of the X-RD peaks. The eight most intense diffraction peaks located at 31.84° , 34.52° , 36.33° , 47.63° , 56.71° , 62.96° , 68.13° , and 69.18° have been observed which is in good agreement with a research work published elsewhere [25]. Moreover, it also suggests that the synthesized nanoparticles were free of impurities as it does not show any characteristics of XRD peaks other than nano-ZnO peaks. **Figure 1.5.5** represents the scanning electron micrograph (SEM) of the ZnO nanoparticles at different magnifications. These SEM pictures substantiate the formation of ZnO nanoparticles. These pictures confirm the approximately spherical shape of the ZnO nanoparticles. It also can be seen from the pictures that the size of the nano-ZnO is in the range of 15 to 20 nm. The intensity plot showed the relative intensity of light scattered by ZnO NPs. DLS measures the hydrodynamic diameter of the particles. The plot showed only one peak with a mean hydrodynamic size (Z-Average) of 474.6 nm and PDI 0.713. The obtained particle sizes are bigger than those shown in the SEM images due to the agglomeration of the particles [26]. The plot of the size distribution report by the intensity of ZnO NPs as obtained by the experiment was mentioned in the supporting information.

1.5.4.3 Thermogravimetric analysis

The TGA data of the polymer (A) and polymer/ZnO nanocomposites (Z-1, Z-2, and Z-3) are represented in **Figure 1.5.6**. It was seen from the figure that, the thermal stability of all nano blended composites is higher than that of A. At 380°C , the

percentage of decomposition of the polymer (A) and nanocomposites from Z-1 to Z-3 was 32.42%, 22.88%, 22.09%, and 21.29% respectively, whereas, at 490°C, the percent of weight loss of A, Z-1, Z-2, and Z-3 was 93.71%, 74.86%, 74.08%, and 73.27% respectively. Hence thermal stability of the polymer/ZnO nanocomposites (Z-1, Z-2, and Z-3) was improved by dispersion of the nano-ZnO into the A. This enhancement of thermal stability may be due to the reduction of the mobility of the polymer chain and the tendency of nanoparticles to remove free radicals [27]

1.5.4.4 Efficiency of additive as viscosity modifier

Figure 1.5.7 represents the viscosity index values of the lubricants blended with the additives. It is observed that the viscosity index (VI) values of the polymer/nano-ZnO composites of different compositions (Z-1, Z-2, and Z-3) at different concentration levels are better than the pure polymer (A). Again with both types of additives, there is always a steady increase of VI values with the increase in additive concentration. An increase in the concentration of the additives leads to an increase in the total volume of polymer micelles in the solutions. The additional increase of volume compared to the pure polymer may be due to the fact that the nanoparticles present in the polymer matrix lead to the polymer chain separated from each other. For all concentrations, the viscosity index values of the prepared polyacrylate-ZnO nanocomposites are higher than polyacrylate- magnetite nanocomposites. The values of the viscosity index of polyacrylate-magnetite nanocomposites are reported in our previous work [18].

1.5.4.5 Efficiency of additive as pour point depressant

Different level of percentage concentration varying from 1 wt% to 5 wt% of the additives in the base oil was tested as PPD and the results are depicted in **Figure 1.5.8**. The results showed that the additives (A, Z-1, Z-2, and Z-3) are efficient as PPD and

the efficiency decreases with increasing additive concentration. The PPD property of all the blended composites is very similar to that of A. That means, incorporation of nanoparticles into the polymer matrix does not affect the PPD property compared to polymer (A). The decrease of pour point is only significant at low concentration (1%). Battez et. al, reported that with higher concentration (more than 0.4 wt%) of the ZnO NPs, no changes in the pour point have been observed [28], [29]. As reported earlier in our previous work, the pour point depressant property of polyacrylate-magnetite nanocomposites is more or less the same as studied with polyacrylate-ZnO nanocomposites [18].

1.5.4.6 Tribological performance

The tribological properties of all the lubricant compositions (A, Z-1, Z-2, and Z-3) were determined by measuring WSD by FBWT apparatus employing 40 kg load and the results were depicted in **Figure 1.5.9**. The AW performance of the base oil is significantly enhanced when the additives are blended with it and is indicated by the lower WSD values of the lubricant compositions. The nano-ZnO blended composites exhibited better anti-wear performance compared to only polymer (A) and the performance becomes increasingly better with increasing the number of nanoparticles in the polymer matrix as is shown in **Figure 1.5.9**. The tribological performance of all the lubricant compositions was excellent but less significant than polyacrylate-magnetite nanocomposites as reported in our previous work [18].

1.5.5 Conclusion

In this study, nano-ZnO was synthesized with better size distribution (15-20 nm) which was established and characterized by SEM, XRD, and DLS study. The interaction of nano-ZnO with PDDA was studied by FT-IR analysis and it suggests that there is

definite interaction between them. All the ZnO nanoparticles blended composites showed excellent performance as anti-wear and viscosity modifier additives for lube oil but they did not improve the pour point significantly compared to pure polyacrylate. Moreover, the thermal stability of polymer was also improved by the incorporation of nano ZnO into the polymer matrix as shown in the thermogravimetric analysis. This change in the properties of the polymer is also evidence of nano-polymer interaction in the blended composites. This study clearly put more insight into the formulation of nano-based multifunctional lubricating oil additives. Therefore, the above study is definitely a potential approach to design multifunctional additives for lubricating oil with better thermal stability.

1.5.6 References

References are given in *BIBLIOGRAPHY* under “Chapter IV of Part I” (Page No. 143-144).

1.5.7 Tables and Figures

Table 1.5.1: Properties of base oil

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

Table 1.5.2: Designation and Composition of polydodecylacrylate nano ZnO composites

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

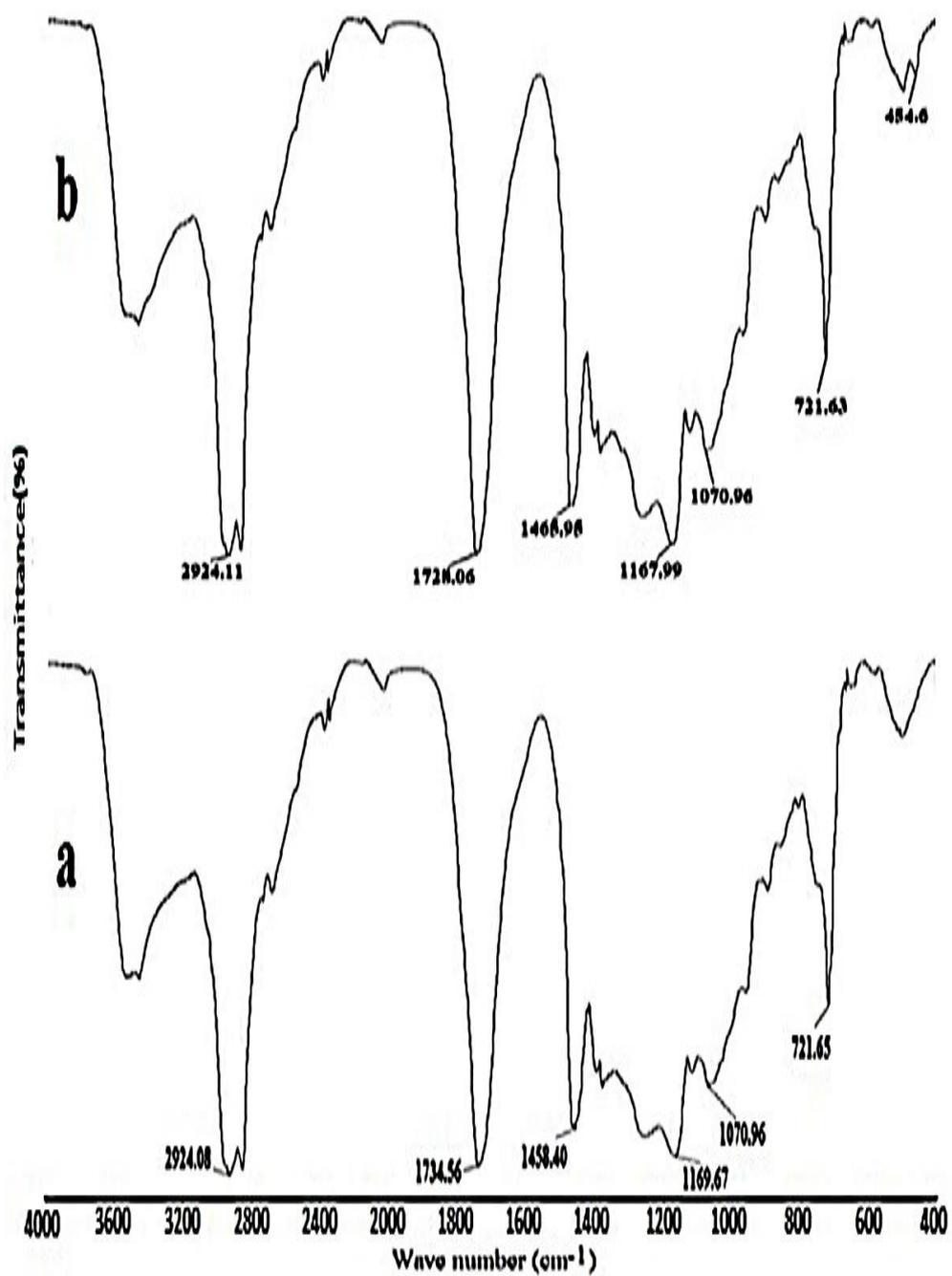


Figure 1.5.1: FT-IR spectra of (a) polymer (A) and (b) polymer/ZnO nano composite (Z-3)

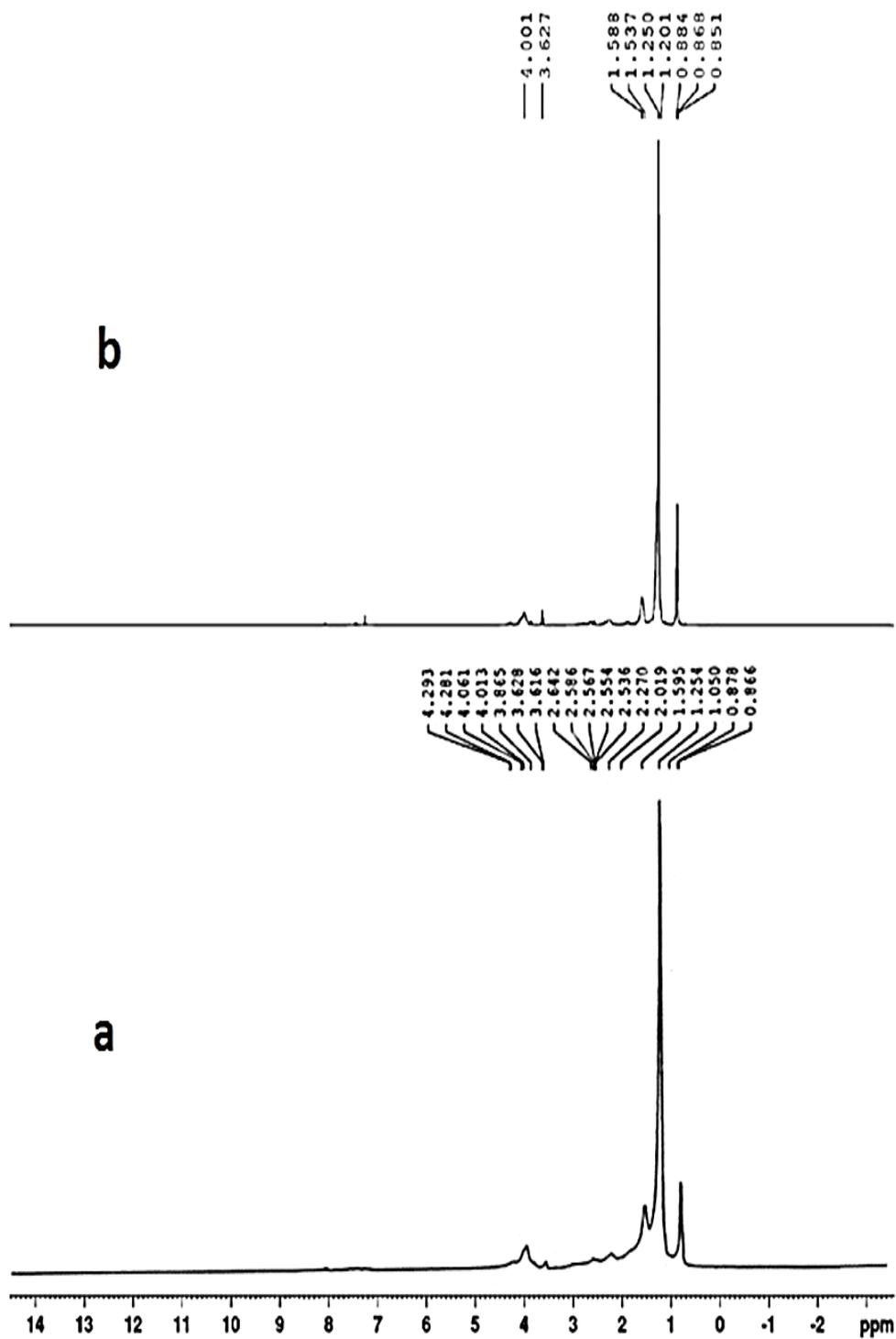


Figure 1.5.2: ^1H NMR spectra of polymer (A) and the PNC (Z-3)

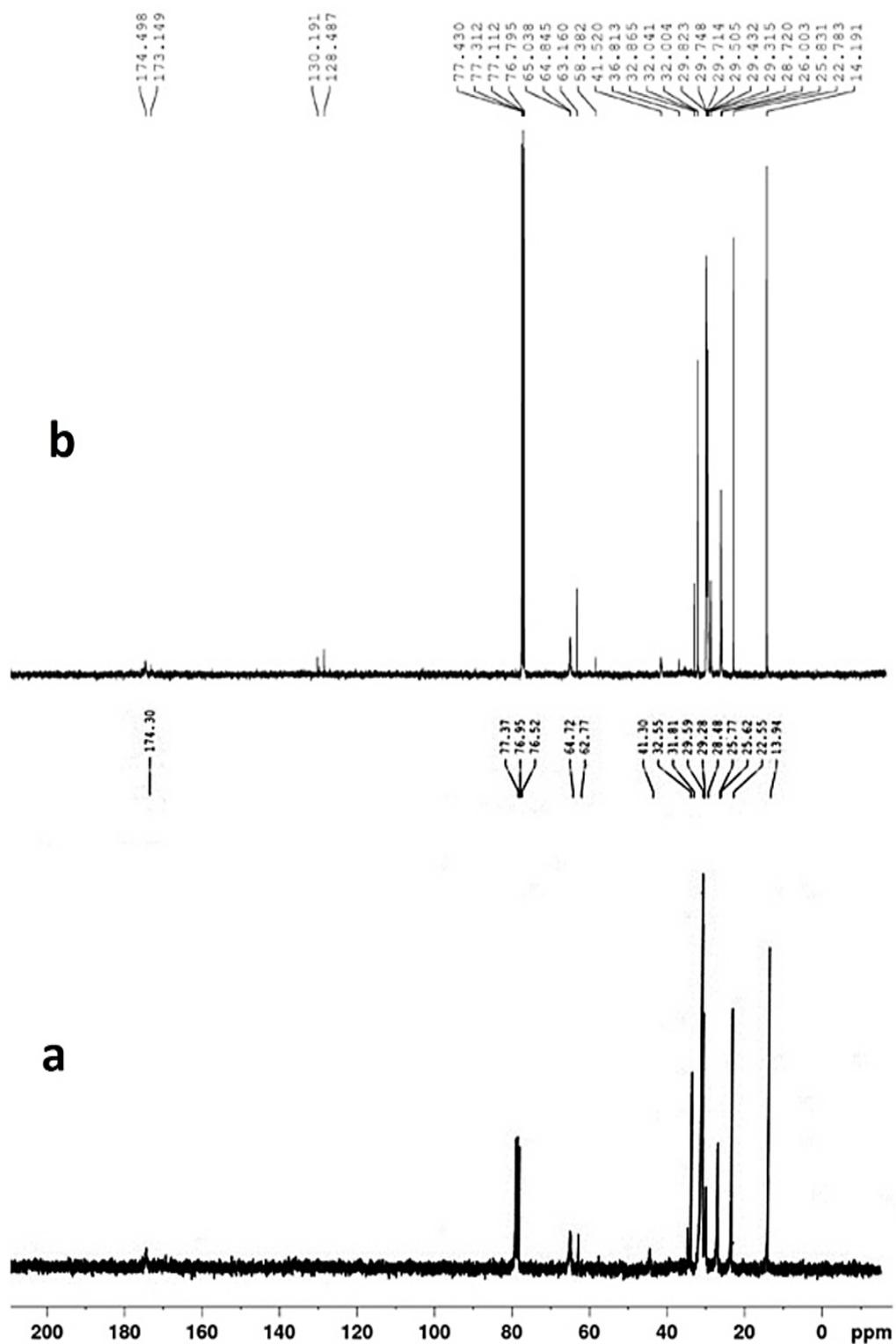


Figure 1.5.3: ^{13}C NMR spectra of polymer (A) and the composite (Z-3)

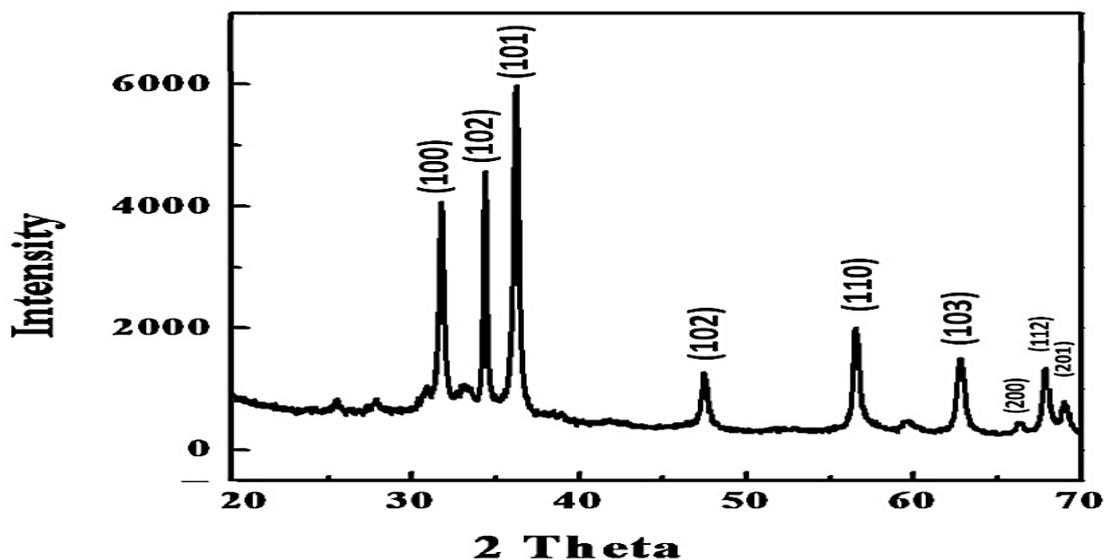


Figure 1.5.4 XRD spectra of prepared ZnO nanoparticles

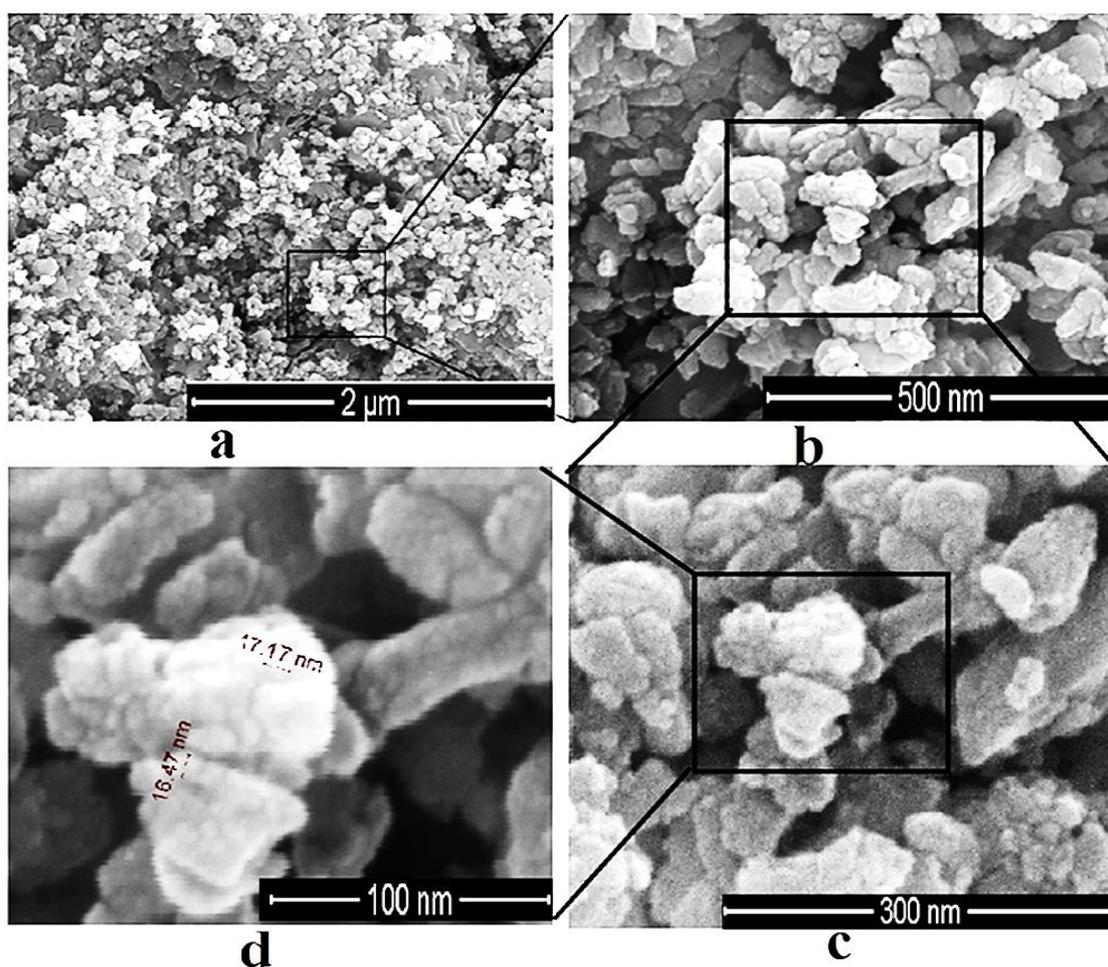


Figure 1.5.5: SEM images (a, b, c and d) of prepared ZnO nanoparticle at different magnifications

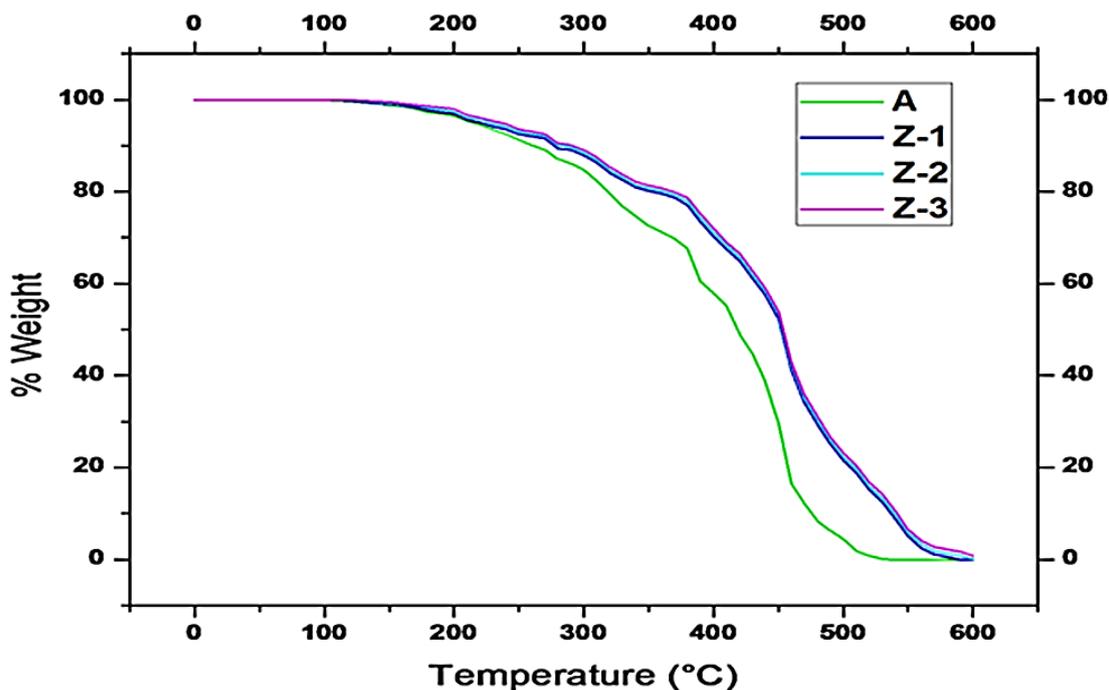


Figure 1.5.6: TGA data of polymer (A) and polymer/ZnO nanocomposite (Z-1, Z-2 and Z-3)

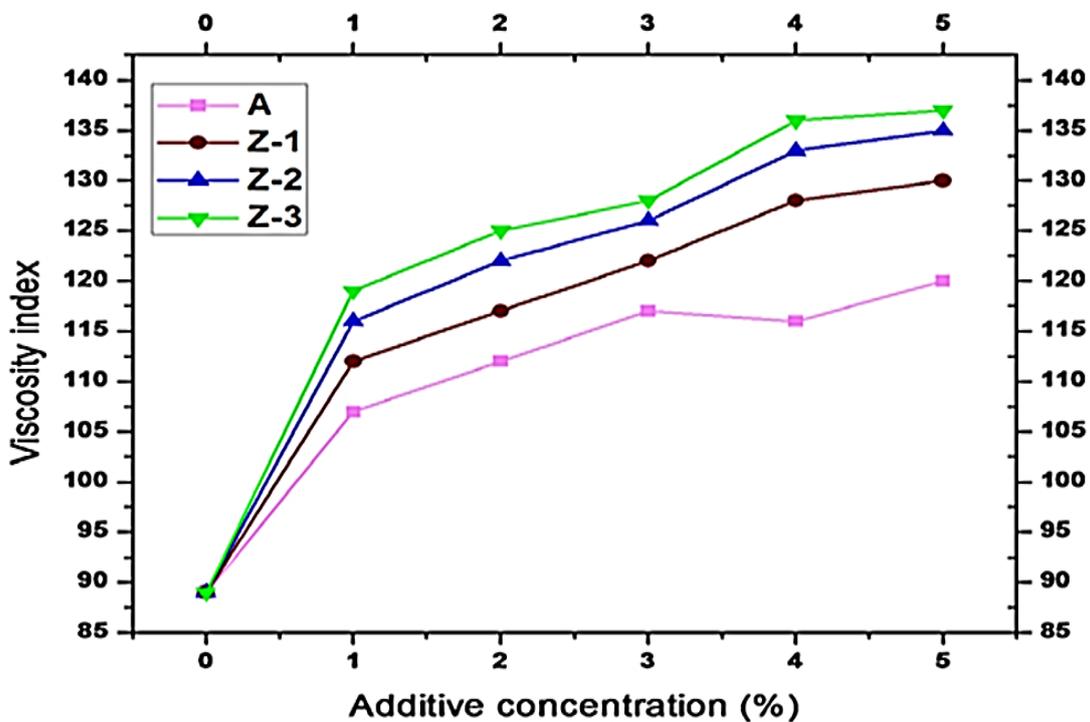


Figure 1.5.7: Plot of viscosity index of the lube oil blended with additives at different concentration levels

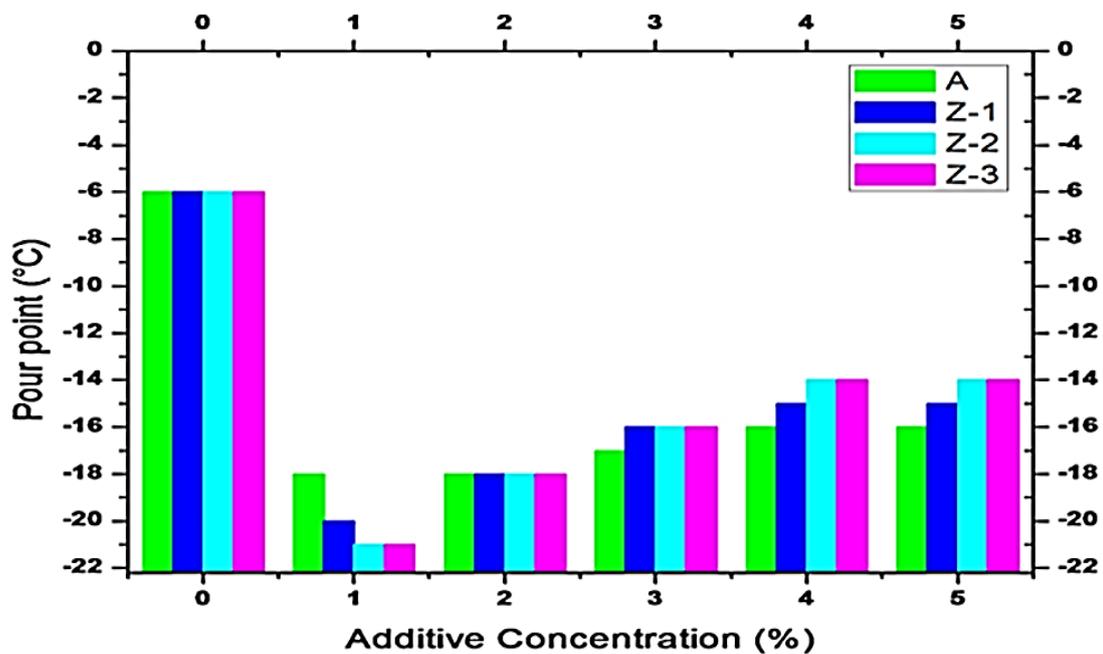


Figure 1.5.8: Plot of pour point of the lube oil blended with additives at different concentration

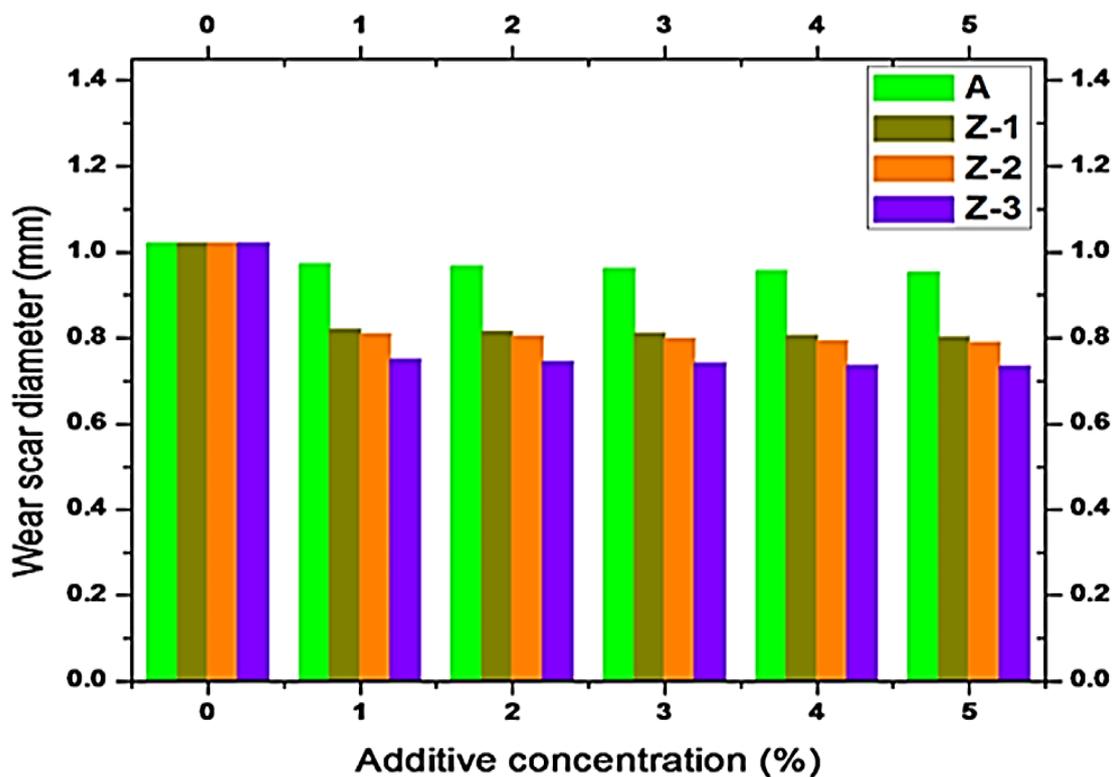


Figure 1.5.9: Wear scar diamete

Part II

Vegetable Oil-based Eco-friendly Lube Oil Additives

Chapter I

BACKGROUND OF THE PRESENT INVESTIGATION

Mineral lubricants are not environmentally friendly because of their non-biodegradability and toxicity [1], [2]. Mineral lubricants contaminate drinking water, soil, seawater, affect human health, aquatic animal, plant life to a great extent. Therefore strict specifications on various environmental issues such as toxicity, biodegradability, health, and safety emissions are required in certain specific areas [3]. For this reasons demand are being placed on the lube oil production company to produce biodegradable and environmentally benign lube oil and the lubricant industries have been trying to prepare bio-degradable lubricants which are of superior quality to those based on petroleum [4]. Most of the additives which are generally used in lubricating oil are synthetic ester and are very harmful to the environment. The additives prepared from vegetable oils (Triglycerides of long-chain carboxylic acids) for lube oils are highly accepted from the viewpoint of the increasing global environmental solutions [5]. The most commonly used vegetable oils are soya bean oil, rapeseed oil, sunflower oil, castor oil, neem oil, Karanja oil, mahua oil [6], etc. All of the vegetable oils contain triglycerides of long-chain carboxylic acids. These vegetable oils are biodegradable and non-toxic.

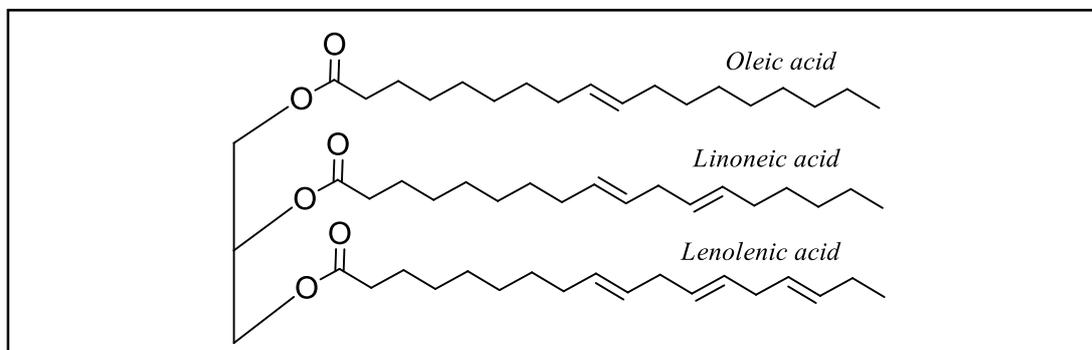


Figure 2.1 General structure of vegetable oil (triglyceride)

In the competition of vegetable oils with mineral oils, vegetable oils have high viscosity index [7], excellent tribological properties [8], high flash point, and low volatility. Therefore vegetable oil can be used in various applications such as self-lubricants or lubricant additives, additives in polymer, etc. Though vegetable oils don't have satisfactory pour points but pour point values can be improved by chemical modification [9]. There are some drawbacks of vegetable oil-based lubricants or additives. They have poor oxidation and thermal stability, high temperature-sensitive tribological behaviour, and poor cold flow improvers are considered as the limitations for their application in the field of industrial lubricants [10], [11]. But the limitations can be modified through chemical modification [12] of the olefin group or carboxylic group or fatty acid chain. There are several references from where it is evident that the chemically modified vegetable oils have eminent scope for use as base fluids.

Vinci et al have prepared a Thermo oxidative stable lubricant based on methyl 12-hydroxy stearate which is a derivative of castor oil with 70% renewable carbon content [13]. Regueira et al studied the compressibility and the viscosities of vegetable oils for their use as a hydrolytic fluid and lubricant [14]. Joseph et al studied and found that a mixture of amine and phenolic antioxidants can be applied to increase the thermo oxidative stability of vegetable oils when used as lubricant base oil at a temperature around 120⁰C [15]. There are numbers of references where vegetable oils are used as mineral lube oil additives or as lubricants [16]-[18] U.S. patent number 4970010 described that vegetable oil derivatives can be used as lubrication oil additives. U.S. patent number 522 9023 described the synthesis of vegetable oil-based lubricant additive that can be used as thermo oxidative stability enhancer and viscosity modifiers. In 2009 Franco et al reported that the blending of high oleic sunflower oil (HOSO) with polymeric additives, such as ethylene-vinyl acetate and styrene-

butadiene-styrene (SBS) copolymers at different concentrations in the lubricant formulation and studied the enhanced Kinetic viscosity and viscosity index [19]. In 2015 Nasser et al showed that homo and copolymer of jojoba oil as lubrication oil additives and the performance of the additives was evaluated as viscosity index improver and pour point depressant [20]. In 1993 Bisht et al reported that the application of jojoba oil as an additive in lubricating oil base stocks. They reported that jojoba oil or its compound can enhance properties such as viscosity index improver, antifoam antiwear antirust, and fiction reduction properties to the blend with lubricating oil [21]. In 2013 Karmakar et al studied the homopolymer soybean oil and sunflower oil as lube oil additives. The performance of additives in lube oil was studied as viscosity index improver (VII) and pour point depressant (PPD) [22]. Again in 2015 Karmakar et al reported the soybean oil and its copolymer with 1-Decene, styrene, and methyl acrylate. The performance of these additives was evaluated as PPD, VII, and AW in different lube oils. In 2011, Ghosh et al reported the copolymer of sunflower oil with decyl acrylate and methyl acrylate, and their performances were evaluated as VII for lube oil [23]. Again in 2014 Ghosh et al reported the homopolymer of sunflower oil as lube oil additives. They prepared the homopolymer by two different methods. Thermal and microwave methods and the performance of the polymer were evaluated as viscosity index improver, pour point depressant, and anti-wear for lube oil [24].

From the above literature study, it is clear that vegetable oil-based homo and copolymers are very effective as lube oil additives because of their natural sources and biodegradable nature. Considering the present demand of green technology, in our present investigation we have prepared castor oil and rapeseed oil base eco-friendly lube oil additives i.e. homopolymer of castor oil and rapeseed oil and copolymer with styrene and their performance as viscosity index improve (VII) pour point depressant

(PPD), antiwear additive for base oils were studied. The biodegradability of the prepared vegetable oil-based additives was also studied in different methods and showed considerable biodegradability in all cases.

References

References are given in *BIBLIOGRAPHY* under “Chapter II of Part I” (Page No. 144-146)

Chapter II

Synthesis and a Study as a Multifunctional Ecofriendly Lubricating Oil Additives of Castor Oil Based Polymer

2.2.1 Introduction

Lubricating oil is a complex mixture of paraffinic, aromatic, and naphthenic hydrocarbons, and the main function is to lubricate the engine. The functioning and longevity of lubricating are very poor in an automotive engine without any additive. Therefore, the addition of additives to lubricating oil is very essential for the smooth running of the modern engine. Lubricants are generally liquids or semiliquids which are used to lubricate the automotive engine for their longevity and better performances. The main functions of lubricating oil are to reduce friction, to keep moving parts apart, transfer heat, protect against wear, prevent rust and corrosion, as detergents/dispersants as an antioxidant, etc. The petroleum-based lubricants exhibit satisfactory performance but they are not environmentally benign due to their ecotoxicity and non-biodegradability. The research on vegetable oils as base stocks or their derivatives as additives for base stocks is increasing significantly due to their biodegradable property and availability in nature. Moreover, they show excellent anti-wear properties [1]; enhanced extreme pressure (EP) additives performance [2]; high viscosity index [3] and low volatility [4]. There are lots of research papers, where chemically modified vegetable oils have been used as an additive for base oil or base stocks in the formulation of bio-lubricant [5]. Castor oil contains a high percentage of triacylglycerols of ricinoleic acid (85–95%) which is a C–18 fatty acid. It contains a double bond at C–9 and a hydroxyl group at C–12 [6]. Castor oil is widely used in different important fields such as lubricants, pharmaceuticals, paints, adhesives, rubber, cosmetics, etc. [7]. The high flash point and due to the presence of polar hydroxyl group of castor oil make it efficient in the synthesis of additives for lubricating oil as well as bio lubricant [8], [9]. However research articles regarding the application of castor oil–styrene copolymer green multifunctional additive for

lubricant are very scanty. Therefore, in this work we have synthesized homopolymer of castor oil and copolymer with styrene in different percentage ratios to get thermally stable, cost-effective as well as eco-friendly lubricant additives. Styrene was chosen because due to incorporation it enhances the thermal stability of lubricant. Performance evaluation of polymeric additives was carried out as pour point depressant, viscosity index improver, and antiwear according to the respective ASTM method.

2.2.2 Experimental section

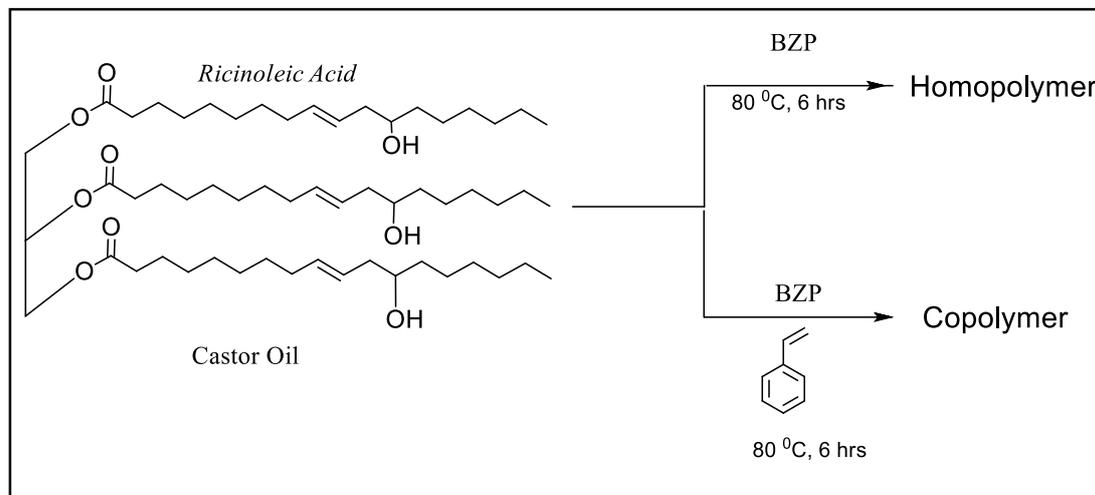
2.2.2.1 Materials

Castor oil (~85% unsaturation) was collected from the local grocery store and its fatty acid composition and properties are given in **Table 2.2.1**. Benzoyl peroxide (98%, LOBA Chemie, India) was used after recrystallization from the chloroform-methanol mixture. The mineral base oil SN150 was collected from IOCL, Dhakuria, West Bengal, India.

2.2.2.2 Synthesis of the polymers

The copolymers were prepared by taking the monomers of castor oil and styrene at different ratios (**Table 2.2.3**) in presence of BZP as the initiator by free radical polymerization method without any solvent. The polymerization was carried out in a three-necked round bottom flask with a magnetic stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. In the flask, a definite amount of castor oil and styrene was heated to 80⁰ C and maintained for 20 minutes. Initiator BZP (0.5% w/w, with respect to the total monomer) was then added and heated for 6 hours keeping the temperature constant at 80⁰C.

Scheme 2.2.1 Reaction for the preparation of homopolymer of castor oil and its copolymer with styrene



2.2.3 Measurements

2.2.3.1 Spectroscopic measurements

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

2.2.3.2 Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at 35 °C at a flow rate of 1 mL/min.

2.2.3.3 Thermogravimetric analysis (TGA)

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

2.2.3.4 Performance evaluations of viscosity index

Viscosity index (VI) is an important parameter that determines the change of viscosity of the lubricant with temperature change. It was calculated according to ASTM D 2270–10. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40⁰C and 100⁰C

2.2.3.5 Evaluation of pour point

The pour point of the additive blended lube oil was determined according to the ASTM D 97–09 method using the cloud and pour point tester model WIL–471 (India).

2.2.3.6 Evaluation of anti-wear performance

The antiwear performance in terms of wear scar diameter (WSD) of the lubricant compositions was determined by Four–ball wear test apparatus (FBWT) following the ASTM D 4172–94 method. In this experiment, 392 N (40 Kg) load at 75⁰C for 60 min was applied to measure the wear scar diameter. The rotating speed and diameter of the ball were 1200 rpm and 12.7 mm respectively.

2.2.3.7 Biodegradability test (Disc diffusion method)

The biodegradability test was carried out for the prepared polymers against *Alternaria alternata* fungal. All the experiments were carried out in Petri dishes and were kept *in an* incubator at 37⁰C for 30 days after the addition of about 1g of the polymer sample. The change of yellow to blackish colour confirmed fungal growth. Culture media strain was prepared by mixing a suitable amount of potato extract, dextrose, and agar powder. After 30 days, the polymer samples were collected from the fungal media by CHCl₃ and then purified and dried. The dried samples were weighed.

2.2.4 Results and discussion

2.2.3.1 Spectroscopic data analysis

The homopolymer of castor oil exhibited an IR absorption band at 1735.0 cm^{-1} for the ester carbonyl group. The peaks at 2854.4 cm^{-1} and 2922.1 cm^{-1} are the stretching vibration of $-\text{CH}_2-\text{CH}_3$ group. A broad peak at 3442.9 cm^{-1} is due to the free $-\text{OH}$ group present in castor oil (**Figure 2.2.1**). The absorptions peak at 1739.5 cm^{-1} indicates the presence of the ester carbonyl group in the copolymer. Peaks at 724.5 cm^{-1} and 699.9 cm^{-1} were showed the presence of C-H bond of the phenyl group of styrene in the copolymer. In the ^1H NMR spectra of the homopolymer of castor oil, the peaks in the range of 4.118–4.323 ppm indicates the protons of $-\text{COOCH}_2$ group of castor oil. The peaks in the range of 3.60–3.71 ppm are for the $-\text{OH}$ group of castor oil. No peaks in the range of 5–6 ppm indicate the polymerization was carried out successfully. The broad peaks that appeared in the range of 7.16 to 7.83 ppm indicate the protons of the benzene ring of styrene moiety in the copolymer. In the ^{13}C NMR spectra of the homopolymer of castor oil, the ester carbonyl group appears in the range of 172.95–177.41 ppm. The carbons of $-\text{OOCH}_2$ group of castor oil appear at 62.10–68.86 ppm. The peak at 71.50 ppm is the carbon which is joined to $-\text{OH}$ group of castor oil. No peaks in the range of 120–150 ppm indicate that polymerization was carried out successfully. The carbons of the benzene ring showed peaks in the range of 125.35 to 132.89 ppm in the copolymer. The peaks in the range of 172.86 to 176.77 ppm indicate the presence of the ester carbonyl group in the copolymer.

2.2.3.2 Molecular weight data analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) of the prepared polymers (P-1 to P-5) are given in **Table 2.2.2**. From the experimental data, it is seen that among the five polymers, P-5 has the

highest molecular weight. Moreover, it is also observed that with increasing the percentage of styrene in the backbone of castor oil, the molecular weight increases. Therefore, the percentage of styrene has a significant role during polymerization.

2.2.3.3 Analysis of TGA data

The TGA values of the five polymers are given in **Table 2.2.3**. From the table, it is clear that the thermal degradation of polymer P-1 is higher than the other polymers which signifies that P-1 is thermally less stable. The thermal degradation of polymers P-3, P-4, and P-5 are almost identical. In the case of polymer P-1, major decomposition starts at 155⁰C with a 30% weight loss. For polymers P-3, P-4, and P-5, major decomposition starts approximately at 265⁰C with 18% weight loss. Due to the copolymerization of castor oil with styrene, the thermal stability increases. Therefore, copolymerization with styrene has significant importance to improve thermal stability.

2.2.3.4 Analysis of viscosity index values

VI was calculated at different concentrations ranging from 1% to 5% (w/w) to the base oil. The experimental values of VI are given in **Table 2.2.4**. From the table, it is found that VI values increase with increasing the concentration of polymers in the base oil. The viscosity of lubricating oil decreases with increasing temperature but an expansion of polymer molecules takes place with increasing temperature and due to this, the size of the micelle increases. This increased in micelle size interfere with the reduction of the viscosity of the lubricant [10]. Moreover, with increasing the concentration of polymer in lubricating oil leads to an increase in the total volume of polymer micelle in lube oil and improves the VI property [11]. It has been observed that the VI value increases by the incorporation of styrene in the backbone of the homopolymer of castor oil. This may be due to the higher crosslink density of the copolymers. The copolymer

P-5 has the highest effect on VI increments followed by P-4, P-3, P-2, and P-1. The higher values VI in the case of P-5 are due to the greater volume of the solvated additive molecule i.e. micelle compared to others. This may be due to its higher average molecular weights and lower PDI value.

2.2.3.5 Analysis of Pour point values

The pour points of the lubricants prepared by blending the polymers at different concentration levels ranging from 1% to 5% (w/w) are shown in **Table 2.2.5**. All the polymers are effective as PPD and the efficiency as pour point increases with increasing the concentration of polymers up to a certain limit (4% concentration). This indicates that at this concentration, the polymer interacts with the paraffinic wax of base oil effectively and decreases the size of crystals of the paraffinic wax [12]. Among the prepared five polymers, P-4 showed better performance as PPD. It may be due to a higher PDI value.

2.2.3.6 Analysis of anti-wear properties

The tribological properties of the lubricant compositions were determined by measuring WSD through FBWT apparatus applying 392 N load and values are given in **Table 2.2.6**. The anti-wear performance of the lube oil is significantly improved when the polymers are blended with it and is reflected in the lower WSD values of the lubricant compositions. The copolymers showed better results compared to the homopolymer. The polymer P-5 at 5% concentration showed the highest reduction in WSD values compared to the other polymers. This indicates that the film formed by the lubricant between the two moving metal surfaces is very strong. It may be due to higher molecular weight and hence higher number of polar side chains of the ester carbonyl groups and hydroxyl groups present in castor oil [13], [14].

2.2.3.7 Analysis of biodegradability test results

The biodegradability test was carried out against *A. alternate* fungal. The percentage loss of mass after biodegradation of the polymers is given in **Table 2.2.7**. After biodegradation, the molecular weight of the recovered samples was determined by the GPC method and the results were compared with the respective samples before biodegradation and given in **Table 2.2.2**. Among the five polymers, polymer P-1 is highly biodegradable and polymer P-5 is the least [14].

2.2.5 Conclusions

From the above study, it was found that the homopolymer of castor oil and copolymer with styrene showed better performance as viscosity index improver, pour point depressant, and antiwear additive for base oil. Copolymers are more effective than homopolymers. The average molecular weight and thermal stability of copolymers increase with increasing the percentage of styrene. Due to biodegradability, the additives are eco-friendly also. Therefore, the above study is definitely a potential approach to formulate a green lubricant composition.

2.2.6 References

References are given in *BIBLIOGRAPHY* under “Chapter II of Part II” (Page No.146-147).

2.2.7 Tables and Figures

Table 2.2.1: Properties of castor oil

<i>Physical properties</i>	
Density (g.cm ⁻³) at 40 °C	0.95
Kinematic Viscosity (c St) at 40 °C	225.7
Kinematic Viscosity (c St) at 100 °C	18.5
Viscosity index	91
Flash point	210 °C
Pour point	-6 °C
Cloud point	-4 °C
<i>Chemical composition</i>	
<i>Fatty acids</i>	<i>Average percentage range</i>
Ricinoleic acid	83–85
Oleic acid	4–5
Linoleic acid	2–3
α – Linoleic acid	0.5–1
Stearic acid	0.5–1
Palmitic acid	0.5–1
Dihydroxystearic acid	0.3 – 0.5

Table 2.2.2: Molecular weight of the prepared polymers and its graphical representation

Polymer Code	Average molecular weight (before biodegradation)			Average molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P-1	7928	10022	1.26	4014	4865	1.2
P-2	17879	25736	1.44	13432	20766	1.55
P-3	18897	28669	1.52	15302	24585	1.6
P-4	16671	32312	1.94	15846	28772	1.8
P-5	34170	42644	1.25	31320	39664	1.3

P-1=100% CO; P-2=97.5% CO + 2.5% sty; P-3=95% CO+5% sty; P- 4=92.5% CO + 7.5% sty; P-5=90% CO +10% sty; CO=castor oil; Sty=styrene; Mn=number average molecular weight; Mw=weight average molecular weight; PDI= polydispersity index.

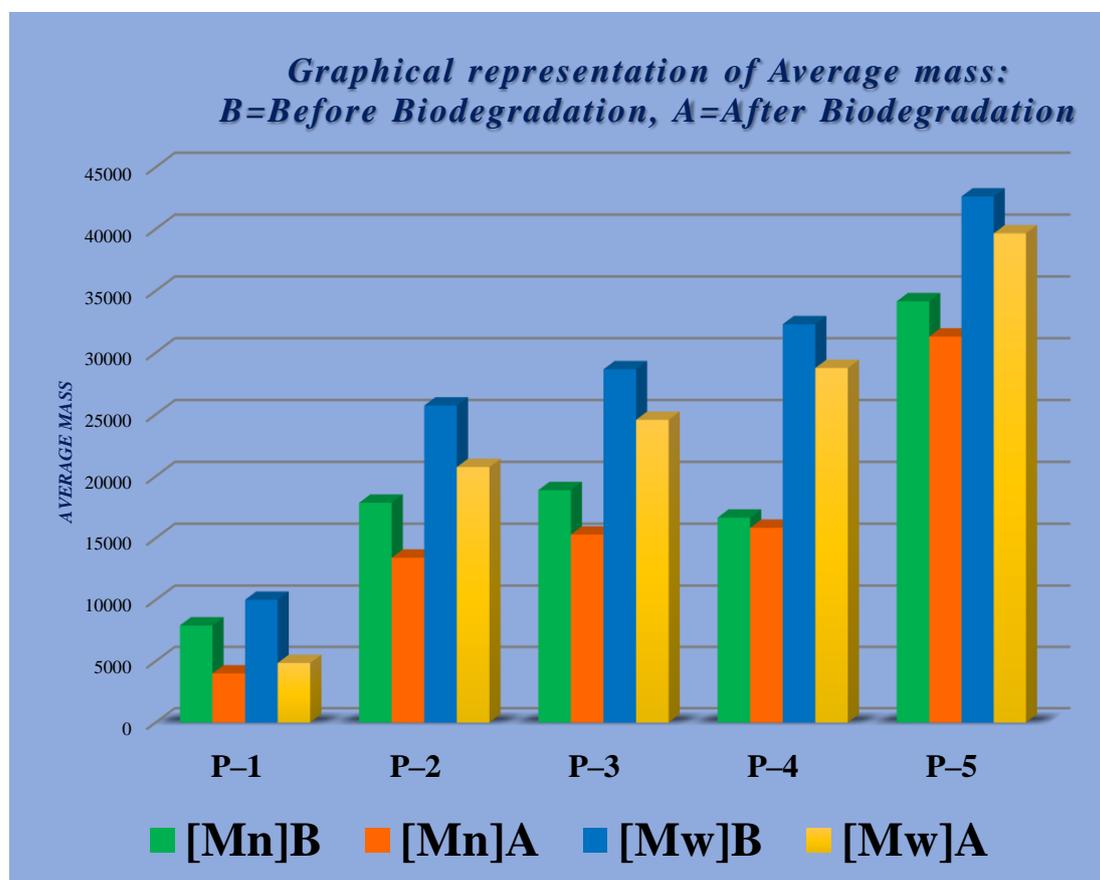


Table 2.2.3: Percentage composition and TGA values of the prepared polymers

<i>Polymer Code</i>	<i>% of monomers</i>		<i>TGA values</i>	
	CO	Sty	Decom. Temp.	PWL
P-1	100	0	155/310	30/82
P-2	97.5	2.5	210/350	24/84
P-3	95	5	262/376	18/80
P-4	92.5	7.5	265/378	18/82
P-5	90	10	265/382	17/78

CO = Castor oil; Sty = Styrene; Decom. Temp.=Decomposition temperature;
PWL= Percentage weight loss.

Table 2.2.4: Viscosity index (VI) values of polymer blended base oil

<i>Polymer Code</i>	<i>VI of polymer blended base oil at different concentrations(w/w)</i>					
	0%	1%	2%	3%	4%	5%
P-1	85.2	90	94.5	102	112	116
P-2	85.2	96	100	110	116	128
P-3	85.2	96	102	114	122	130
P-4	85.2	100	106	114	124	131
P-5	85.2	100.5	110	122.5	132	142

Table 2.2.5: Pour point values of polymer blended base oil and its graphical representation

Polymer Code	Pour point (0°C) of lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	-6	-9	-12	-14	-15	-15
P-2	-6	-9	-12	-15	-16	-16
P-3	-6	-10	-12	-16	-17	-17
P-4	-6	-11	-15	-18	-22	-22
P-5	-6	-10	-14	-16	-16	-16

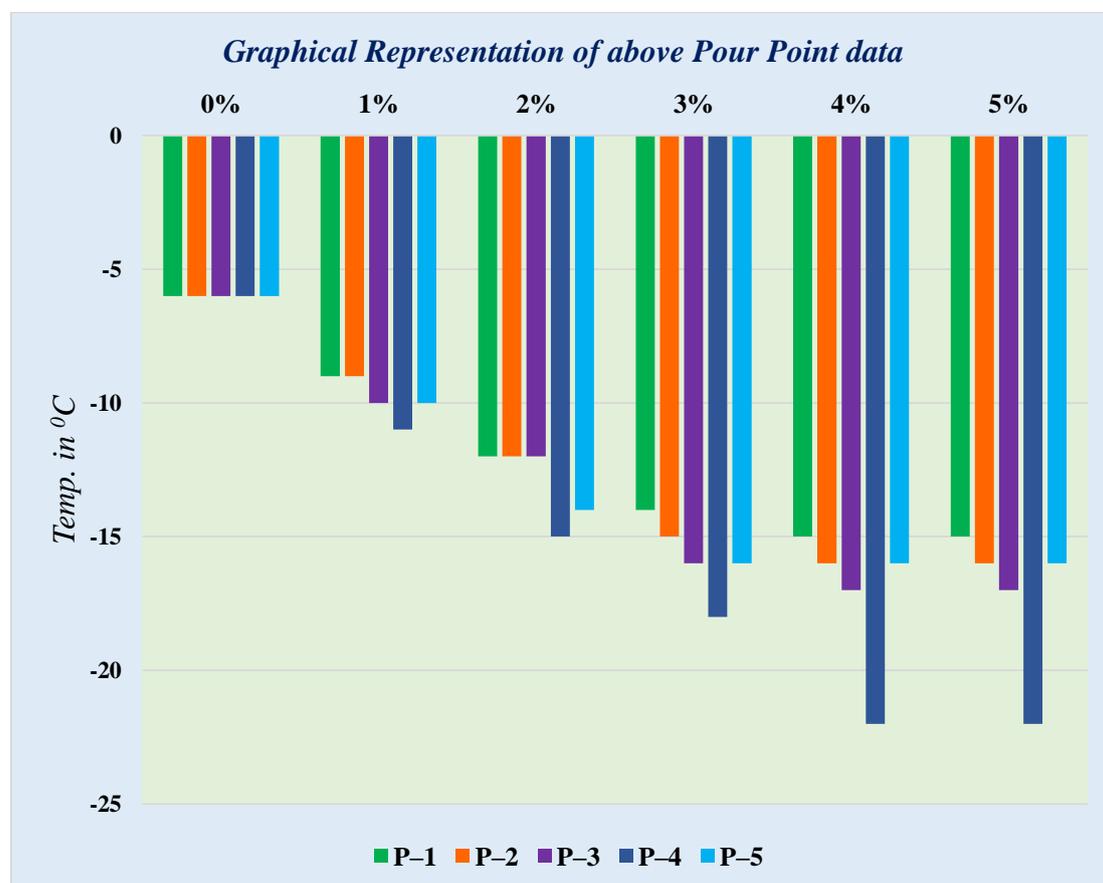


Table 2.2.6: Ant-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition and its graphical representation

Polymer Code	WSD of lubricant (in mm) at different polymer concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	1.119	1.069	1.052	1.036	1.008	0.98
P-2	1.119	1.066	1.048	1.032	1.002	0.972
P-3	1.119	1.062	1.04	1.028	0.992	0.964
P-4	1.119	1.051	1.038	1.02	0.978	0.948
P-5	1.119	1.034	1.022	1.002	0.95	0.926

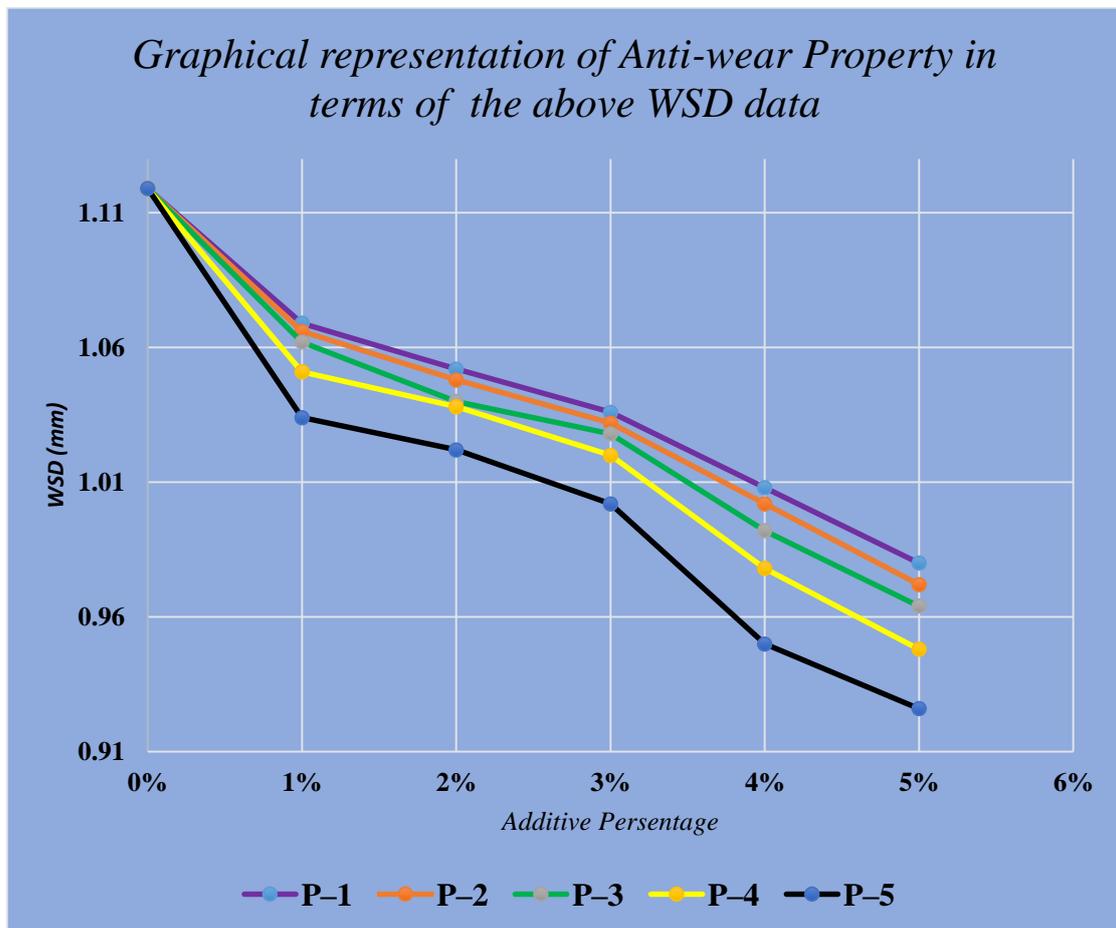
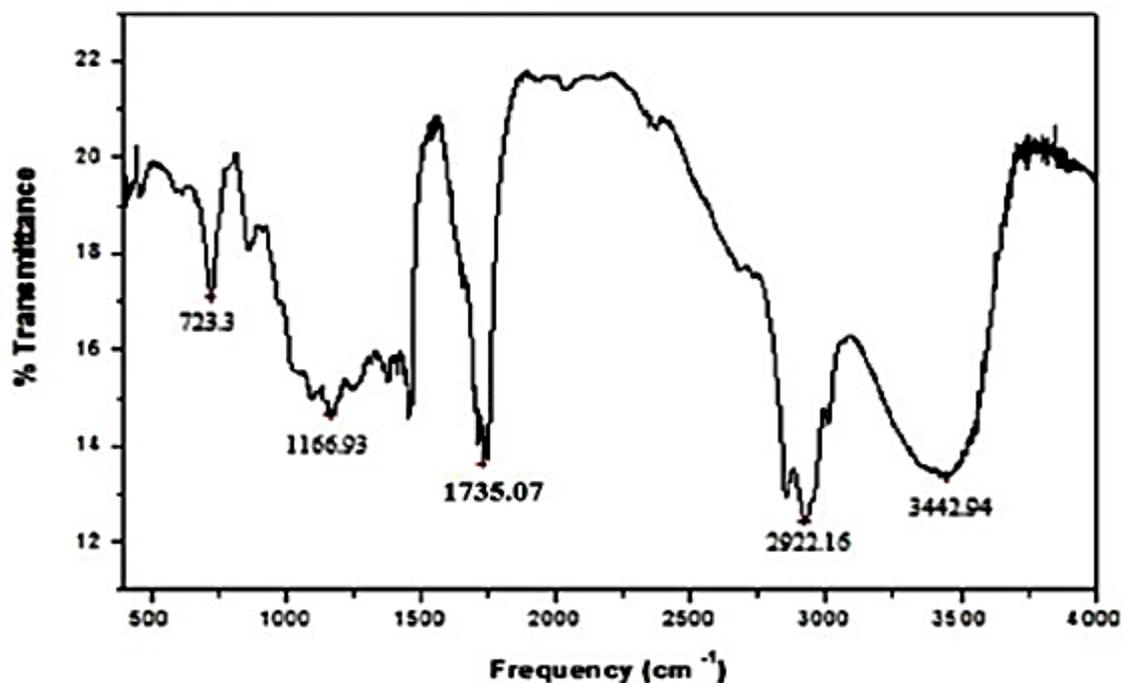


Table 2.2.7: Results of biodegradability test

<i>Fungal pathogens</i>	<i>Polymer code</i>	<i>Incubation periods(days)</i>	<i>Initial weight (gm)</i>	<i>Final weight (gm)</i>	<i>Weight loss %</i>
<i>Alternata</i>	P-1	30	1.02	0.55	46.0
	P-2	30	1.04	0.68	34.6
	P-3	30	1.05	0.71	32.4
	P-4	30	1.00	0.78	22.0
	P-5	30	1.08	0.91	15.7

**Figure 2.2.1: FT-IR spectra of homopolymer of castor oil (P-1)**

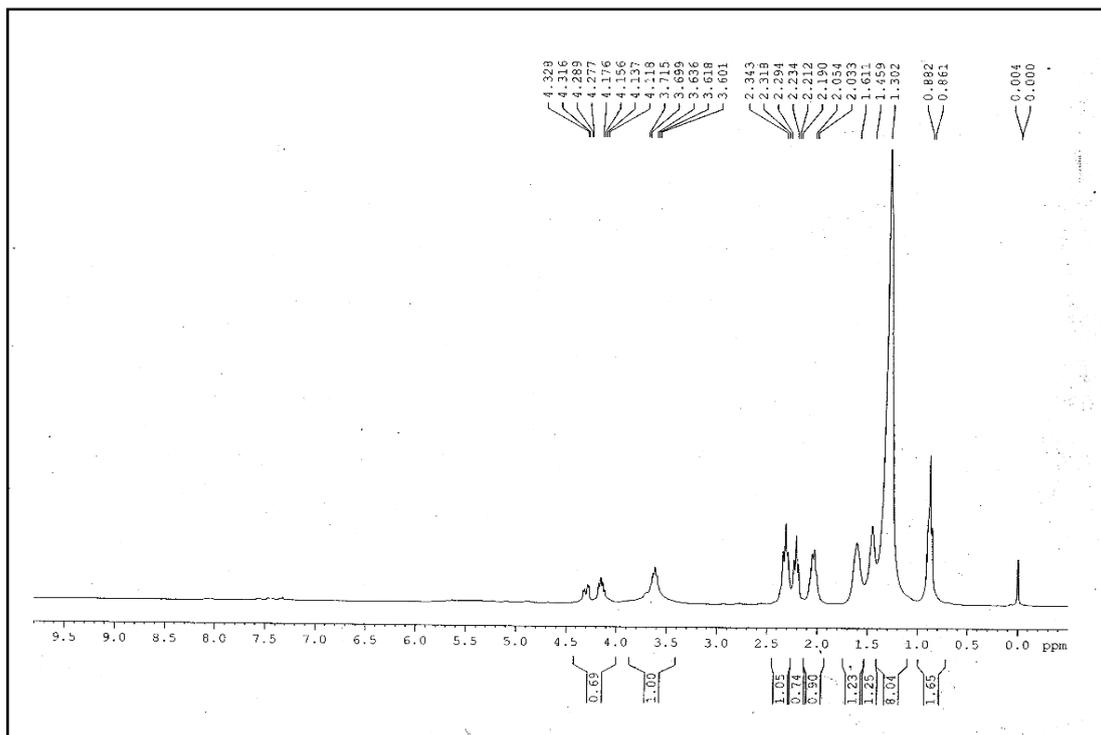


Figure 2.2.2: ^1H NMR of homopolymer of castor oil (P-1)

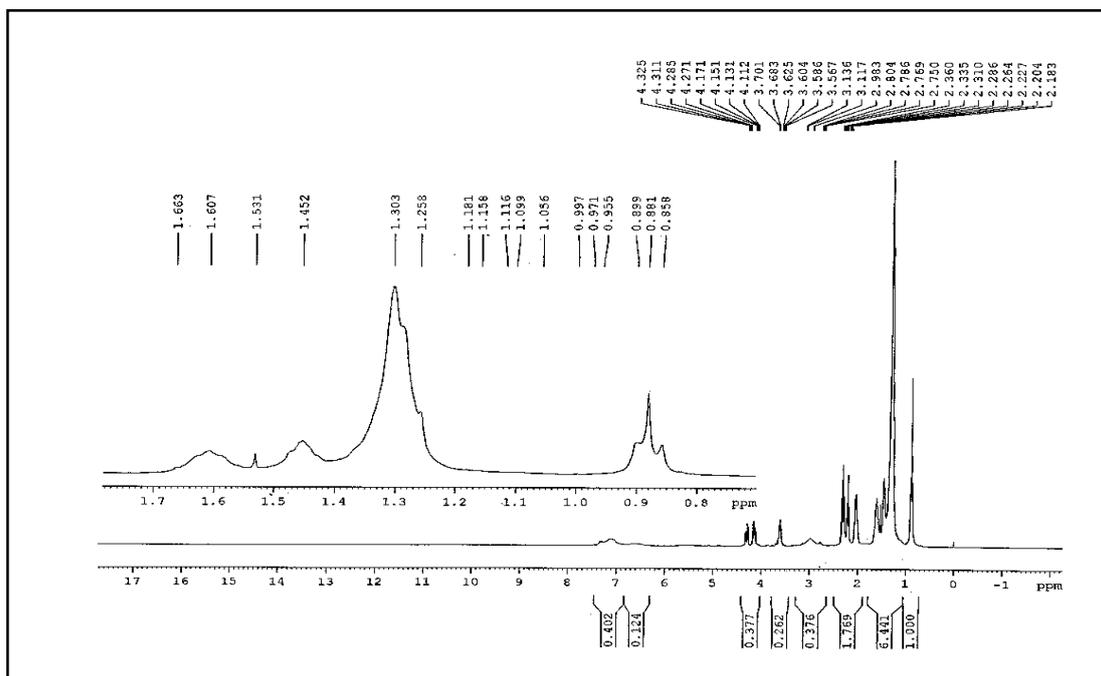


Figure 2.2.3: ^1H NMR of copolymer of castor oil and styrene (P-2)

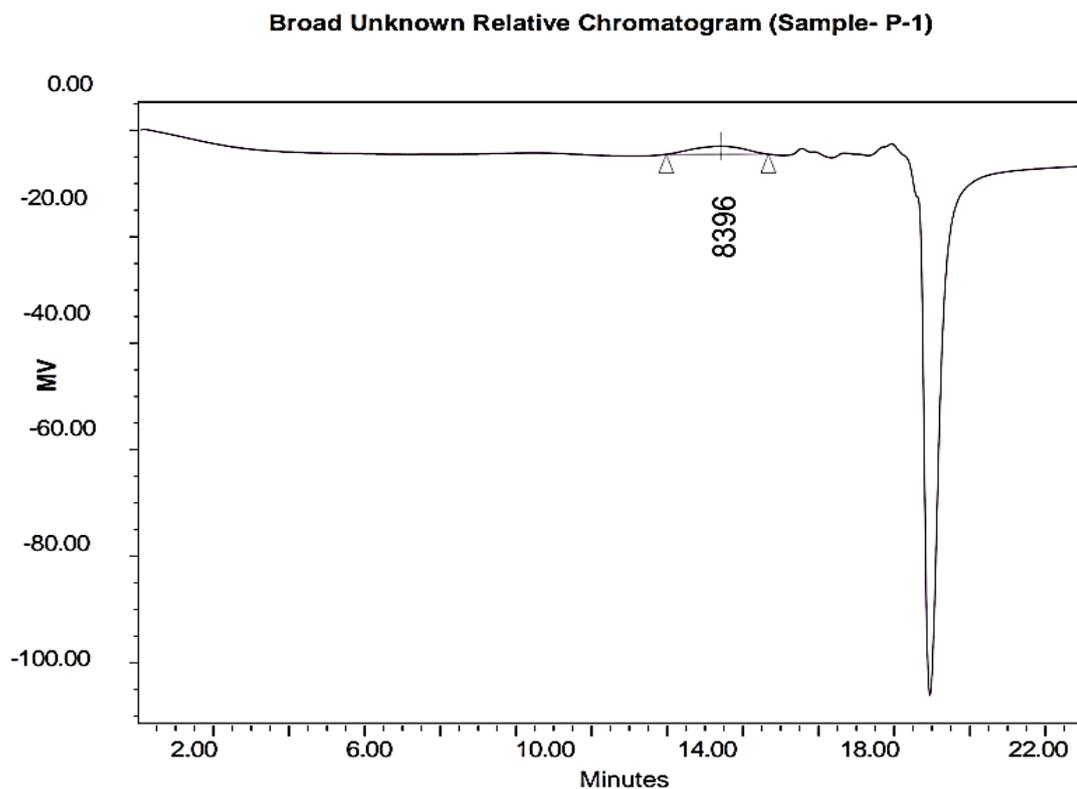


Figure 2.2.4: GPC chromatogram of the copolymer P-1

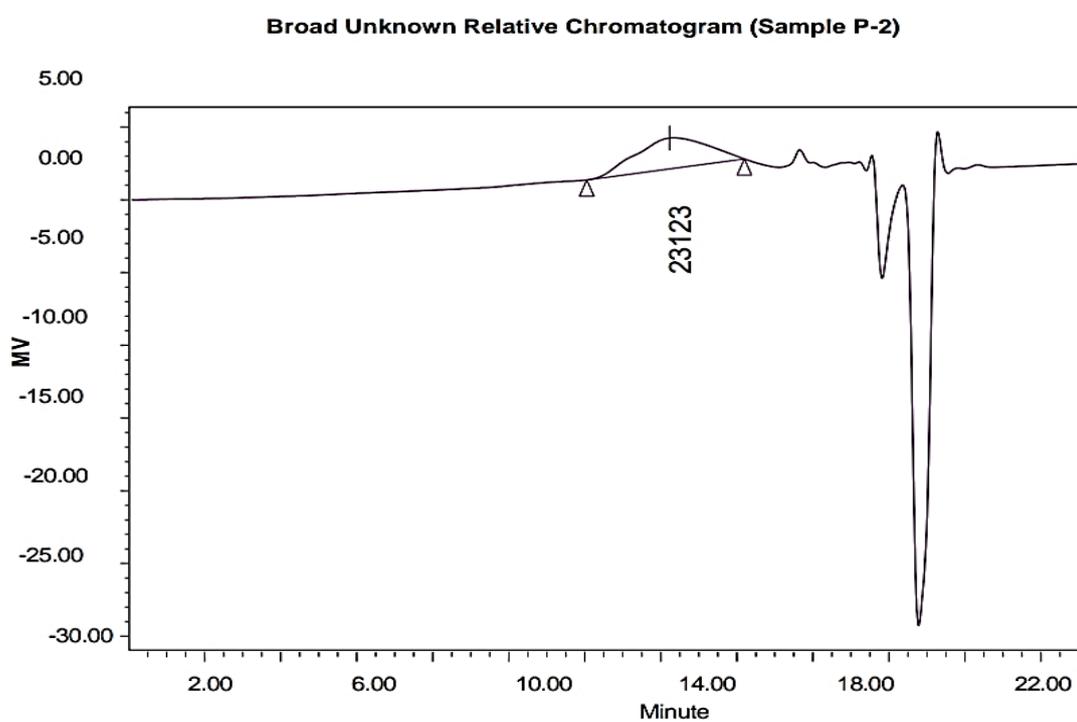


Figure 2.2.5: GPC chromatogram of the copolymer P-2

Broad Unknown Relative Chromatogram (Sample P-3)

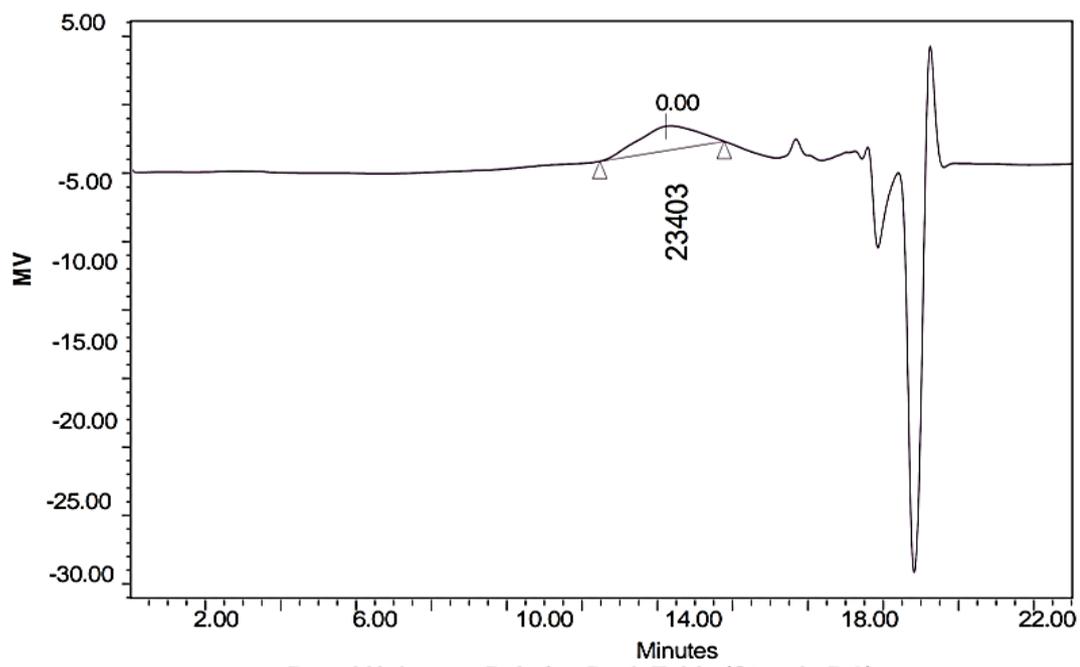


Figure 2.2.6: GPC chromatogram of the copolymer P-3

Broad Unknown Relative Chromatogram (Sample P- 4)

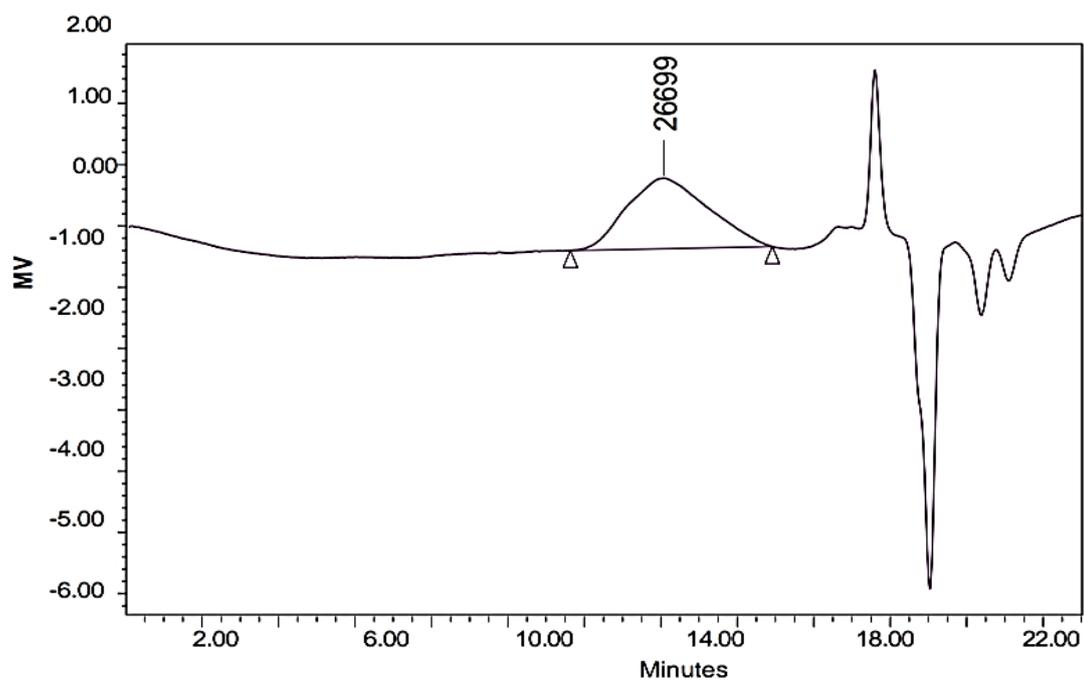


Figure 2.2.7: GPC chromatogram of the copolymer P-4

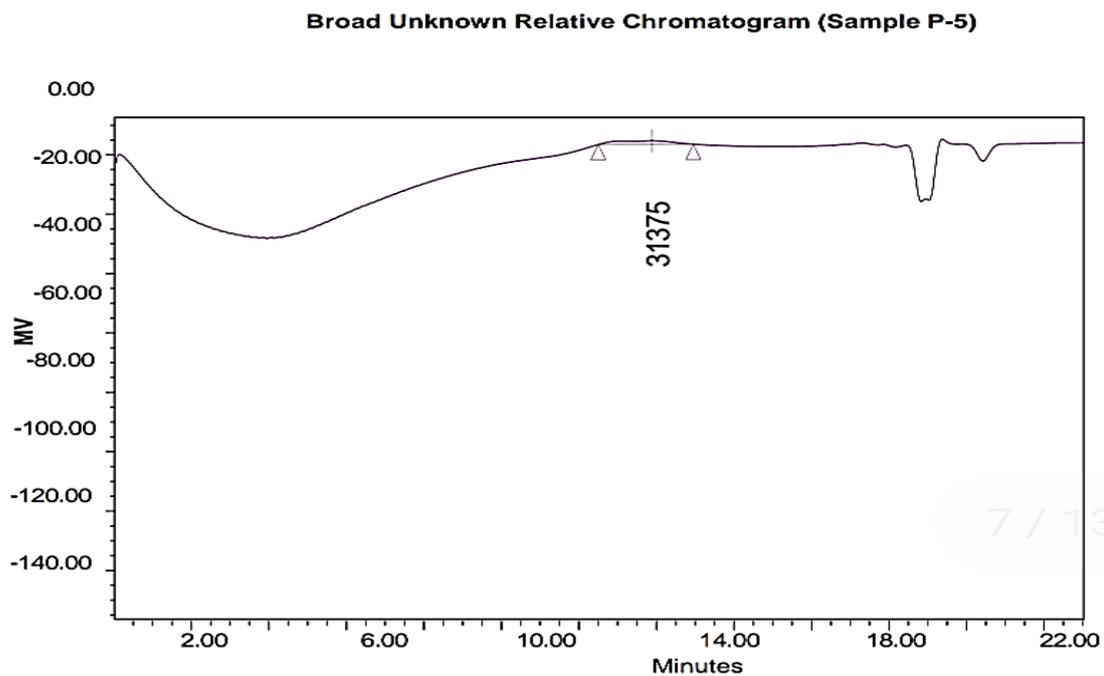


Figure 2.2.8: GPC chromatogram of the copolymer P-5

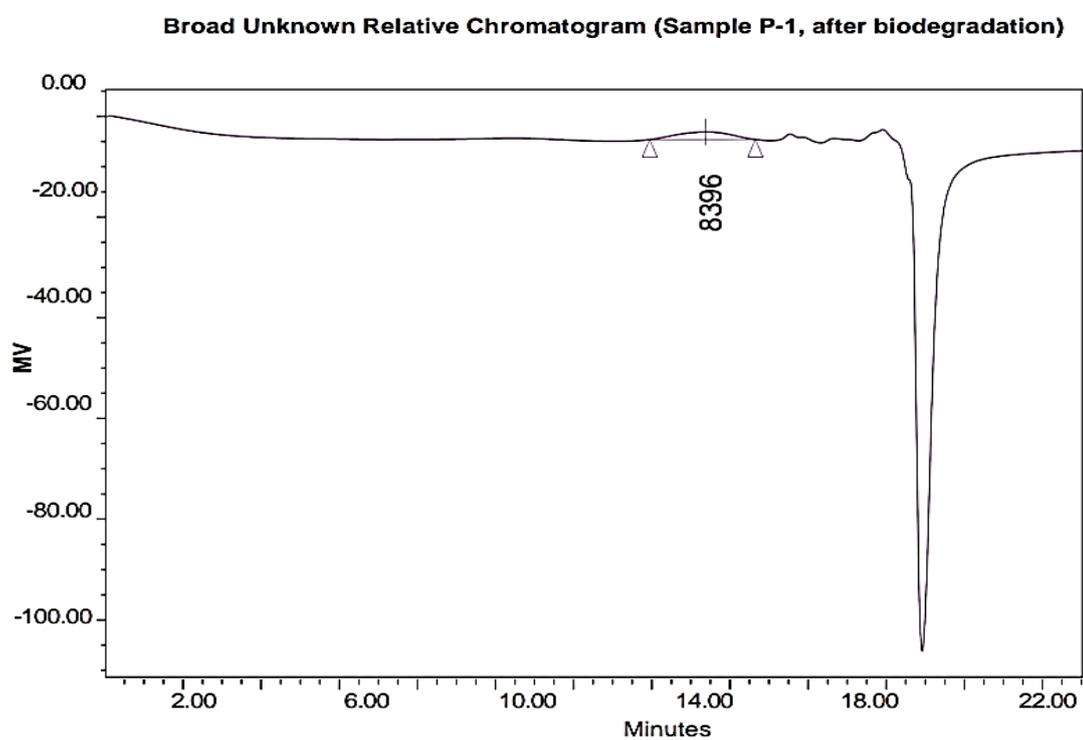


Figure 2.2.9: GPC chromatogram of the copolymer P-1, after biodegradation

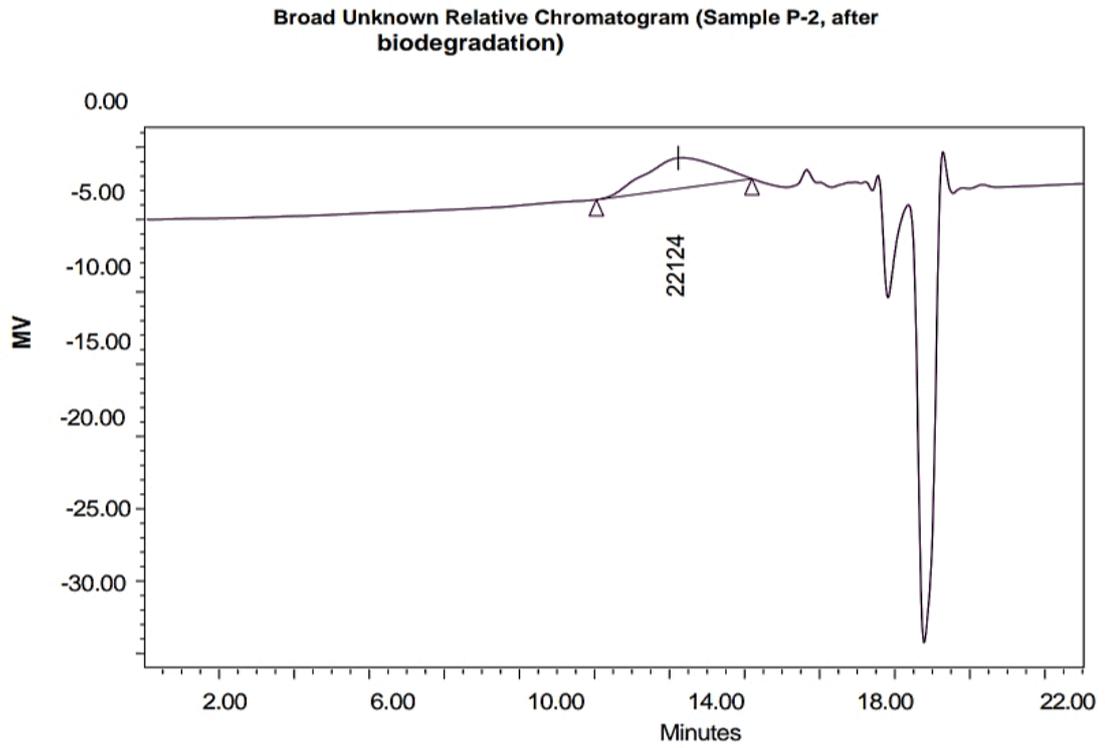


Figure 2.2.10: GPC chromatogram of the copolymer P-2, after biodegradation

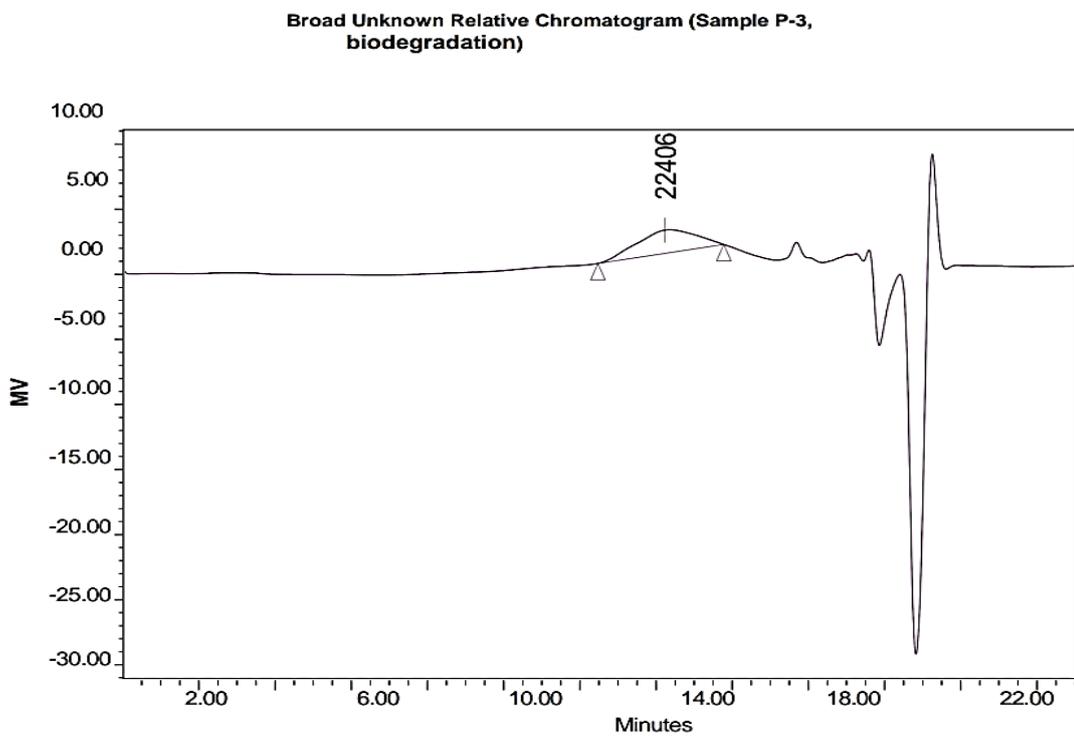


Figure 2.2.11: GPC chromatogram of the copolymer P-3, after biodegradation

Broad Unknown Relative Chromatogram (Sample P-4, after biodegradation)

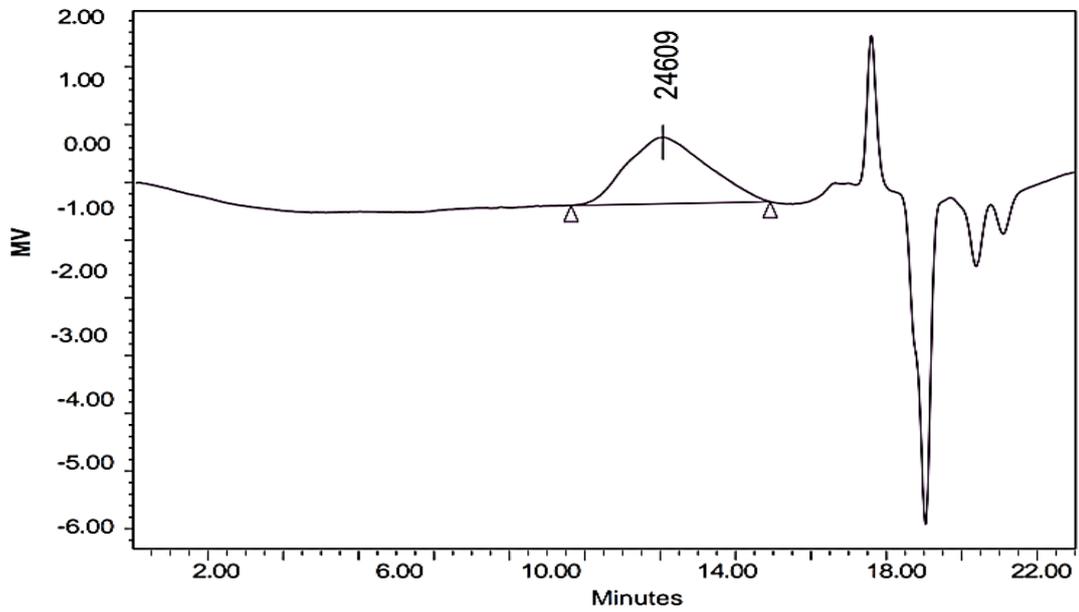


Figure 2.2.12: GPC chromatogram of the copolymer P-4, after biodegradation

Broad Unknown Relative Chromatogram(Sample P-5, after biodegradation)

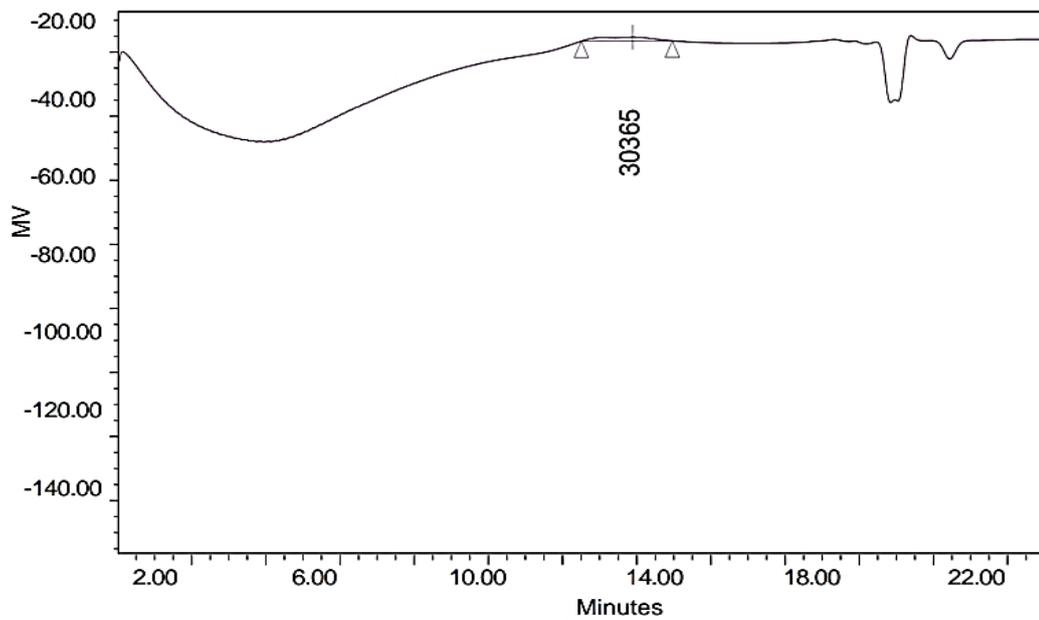


Figure 2.2.13: GPC chromatogram of the copolymer P-5, after biodegradation

Chapter III

A Greener Lubricant Formulation using Rapeseed Oil Based Eco-Friendly Lube Oil Additives

2.3.1 Introduction

The origin of base oil is usually petroleum and it is a complex mixture of aromatic, paraffinic, and naphthenic hydrocarbons and its main function is to lubricate the engine components. For the smooth functioning of a modern engine, it is essential to add additives to the base oil. Lubricants i.e. the suitable formulated product of lube oil and additives are generally liquids or semiliquids and are used for the longevity and better performances of automotive engines. The main functions of a lubricant are to keep moving parts apart, protect against wear, reduce friction, transfer heat, prevent rust and corrosion, as antioxidants, detergents/dispersants, etc. Although, the petroleum-based lubricating oil exhibit satisfactory performance but they are not environmentally friendly. Because they are eco-toxicity and non-biodegradability. Therefore, currently, strict regulations are being imposed in various countries on lube oil-based lubricants and their non-biodegradable toxic wastes materials [1]. This increasing environmental awareness made the researchers search for some new, environmentally benign, multifunctional additives. In this regard, easily available vegetable oils have been considered as a potential substance. Moreover, they show excellent antiwear properties [2], enhanced extreme pressure (EP) additive performance, exhibited high viscosity index [3] and low volatility [4]. There are lots of research papers where chemically modified vegetable oils have been used as additives for base oil or base stocks in the formulation of bio-lubricant [5]. Rapeseed oil (RO) is very interesting for its richness of mono-unsaturated fatty acids, and its low content of saturated fatty acids in comparison to other edible oils. Rapeseed oil is also used in blends with other vegetable oils (sunflower, soybean, corn, etc.) to increase the fatty acid profile of the vegetable oils. It has huge applications in the field of nutritional and health claims. Apart from its above utilities, its unique composition and proven thermal stability over

the other edible vegetable oils, points towards the additive properties of its suitably prepared polymers. However, research articles regarding the application of RO as a green multifunctional lube oil additive are not yet reported. Therefore, in this work, we have synthesized homopolymer of RO (HRO) and the copolymer of it with styrene in different percentage ratios to get thermally stable, cost-effective as well as eco-friendly multifunctional lubricant additives. The Performance evaluation like viscosity index improver, pour point depressant and antiwear of the prepared polymeric additives was carried out according to the respective ASTM method.

2.3.2 Experimental Section

2.3.2.1 Materials

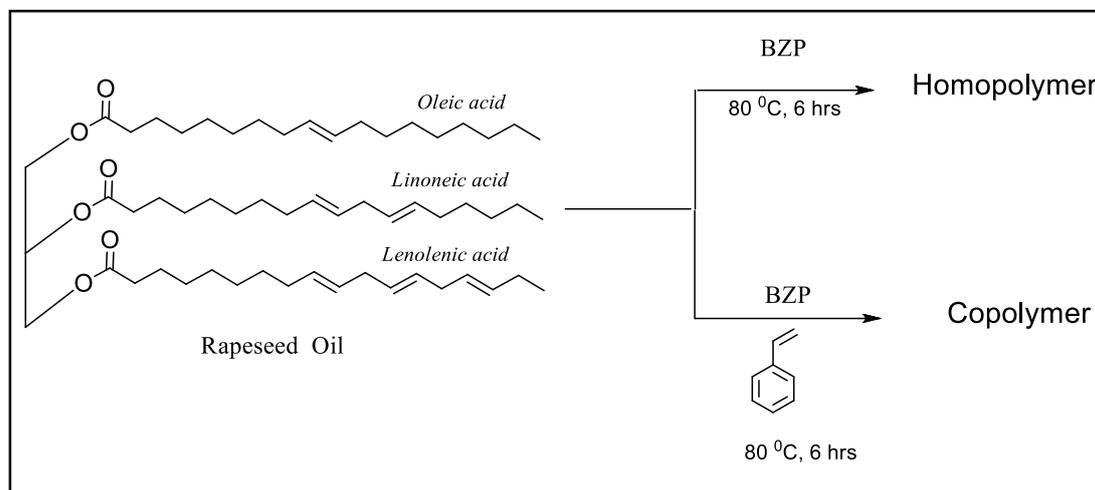
Rapeseed oil (about 90% unsaturation) was collected from a local grocer's shop. Toluene was obtained from Merck Specialties Pvt. Ltd., (India). Benzoyl peroxide (LOBA Chemie, India) was used after recrystallization from a chloroform-methanol mixture. Styrene (GC 99.8%, Thomas Baker Chemicals Pvt. Ltd., India). The mineral base oil (SN150) was collected from IOCL, Dhakuria, West Bengal, India. The physical properties of the rapeseed oil and base oil are shown in **Table 2.3.1**. Fungal specimens were collected from the Department of Microbiology, North Bengal University, West Bengal, India for determining the biodegradability of the polymers.

2.3.2.2 Synthesis of the Polymers

The copolymers were prepared by taking the monomers, RO, and styrene at different ratios (**Table 2.3.2**) in presence of BZP initiator by free radical polymerization method using toluene as solvent. The polymerization was done in a three-necked round bottom flask on a magnetic stirrer. A thermometer, condenser, and an inlet for nitrogen were in the three necks. In the flask, a definite amount of rapeseed oil and styrene was heated to 80°C and maintained for 20 minutes. Initiator BZP (0.5% w/w, with respect to the

total monomer) was then added and refluxed for 6 hours. The detailed procedure was followed from our previous publication [3].

Scheme 2.3.1 Reactions for the preparation of homopolymer of rapeseed oil and copolymer with styrene



2.3.3 Measurements

2.3.3.1 Spectroscopic Measurements

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

2.3.3.2 Molecular Weight Determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at room temperature at a flow rate of 1mL/min.

2.3.3.3 Thermo Gravimetric Analysis (TGA)

TGA data were measured on the Shimadzu TGA-50 system, at a heating rate of 10⁰ C / min.

2.3.3.4 Evaluation of Viscosity Index

Viscosity index (VI) was calculated according to ASTM D 2270-10. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40°C and 100°C. The effect of additive concentration on VI was investigated by using different concentrations ranging from 1% - 5% (w/w).

2.3.3.5 Evaluation of Pour Point

The ASTM D 97-09 method was used to determine the pour point of the additive blended lube oil using the cloud and pour point tester model WIL-471 (India).

2.3.3.6 Evaluation of Anti Wear Performance

The anti-wear performance of the additive doped lube oil in terms of wear scar diameter (WSD) was determined by Four-ball wear test apparatus (FBWT) using the ASTM D 4172-94 method. In this experiment, 392 N (40 Kg) load at 75°C for 60 min was applied to measure the wear scar diameter. The rotating speed and diameter of the ball were 1200 rpm and 12.7 mm respectively.

2.3.3.7 Biodegradability Test

Vegetable oil-based additives are inherently biodegradable compared to synthetic additives. In the present investigation, biodegradability was tested by (a) the soil burial degradation test, and (b) the disc diffusion method against fungal pathogens [6].

2.3.3.8 Disc Diffusion (DD) Method

In this method, the biodegradability of the prepared additives was tested using four different fungal pathogens, (viz. *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA) and *Colletotrichum gloeosporioides* (CG)) in an incubator (Sigma Scientific Instruments Pvt. Ltd., India) and the culture media for the fungal strain was prepared by mixing potato extract, agar powder, and dextrose, in a 10:1:1 proportion by weight. 1.0 g of each of the polymeric vegetable oil-based additives were placed in Petri dishes with 2 g of the culture media and incubated at 40°C for 30 days with the different fungal pathogens. The change of colour from

yellow to blackish confirmed fungal growth. After 30 days, the additive samples were collected from the fungal media and washed with chloroform, purified, and dried. Finally, the weight loss for each of the samples was calculated.

2.3.3.9 Soil Burial Degradation Test (SBD Test)

In this method, the microorganisms attack the surface of the polymer film [7]. 1.0 g of each of the polymeric additive was taken to prepare the polymer films. The films so obtained were then buried in the soil (containing the microorganisms) in an incubator. The soil was placed in a tray, the relative humidity was maintained to 50–60% with the help of a humidity chamber and the temperature was set at 30⁰C. The soil used in this investigation was taken from the campus of the North Bengal University (West Bengal, India) and have pH 7.3 and moisture content of 25%. The buried polymer films were collected at regular intervals of 15 days up to 3 months. After the biodegradation test, recovered films were washed with CHCl₃, filtered with the help of Whatman grade 41 filtration paper, and dried in a vacuum oven at 53⁰C. The recovered polymer so obtained was purified by precipitation of their hexane solution by methanol and dried in a vacuum oven at 53⁰C to constant weight. The test was carried as per ISO 846:1997 [8], [9]. The extent of degradation of the polymeric additives in the tests was determined by measuring the percent of weight loss (PWL) of the samples. The PWL was determined by the equation,

$$PWL = [(M0 - M1)/M0] \times 100 \quad \text{Eq.(1)}$$

Where M0 is the initial mass and M1 is the remaining mass after the test and subsequent drying until constant weight. The degradation of the polymeric additives was also established by observing the shift in the IR absorption frequency of the ester carbonyls after the biodegradability test.

2.3.4 Result and Discussion

2.3.4.1 Spectroscopic Data Analysis

The spectroscopic data of all the prepared polymers were analyzed to confirm the predicted structure of the additives. In the case of a copolymer, the characteristic IR absorption peak at 1743cm^{-1} was for the ester carbonyl group of the rapeseed oil part along with other peaks in the range 2857cm^{-1} to 2931cm^{-1} . The peaks at 810cm^{-1} , 756cm^{-1} , 724cm^{-1} , and 695cm^{-1} were assigned to the phenyl group of styrene. A peak at around 3000cm^{-1} was due to the stretching of C-H bond of the aromatic ring (**Figure 2.3.1**). In the ^1H NMR, the methyl protons appear in the range of 0.87 - 0.89 ppm, the methylene protons in the range of 1.28 - 1.62 ppm and the methine protons appeared in the range of 2.03 - 2.29 ppm for the alkyl chains. A peak at 4.08 ppm indicates the protons of $-\text{OCH}_2$ group. The peaks in the range of 4.10 - 4.14 ppm indicate the protons of $-\text{COOCH}_2$ group of rapeseed oil. A broad peak in the range of 6.80 - 7.64 ppm indicates the protons of the aromatic ring of styrene (**Figure 2.3.2**). In the ^{13}C NMR of the copolymer, the peaks in the range of 14.14 - 41.03 ppm were due to carbons of all CH_3 and CH_2 groups. The peaks at 58.13 ppm indicate the methine carbons of $-\text{CH}-$ of $-\text{COCH}$ group. The peaks in the range of 60 - 62.08 ppm represent the carbons of $-\text{OCH}_2$ groups. The $-\text{CH}_2$ carbons of $-\text{OCOCH}_2-$ group of rapeseed oil showed peaks in the range of 64.61 - 68.99 ppm. The aromatic carbons appear in the range of 127.93 - 130.88 ppm. The peaks in the range of 165.65 - 173.00 ppm confirm the carbons of ester carbonyl groups (**Figure 2.3.3**). In the case of the homopolymer of rapeseed oil, the IR absorption band at 1741cm^{-1} (**Figure 2.3.4**) showed the presence of the ester carbonyl group. In the ^1H NMR spectra of the homopolymer of rapeseed oil (**Figure 2.3.5**), the peaks in the range of 4.12- 4.33 ppm indicate the protons of $-\text{COOCH}_2$ group of rapeseed oil, the methyl protons appear in the range of 0.86 - 0.90

ppm, the methylene protons in the range of 1.26 - 1.62 ppm and the methine protons appeared in the range of 2.29 - 2.34 ppm for the alkyl chains (**Figure 2.3.6**). In the ^{13}C NMR spectra of the homopolymer of rapeseed oil, the ester carbonyl group appears at 173.98ppm, the carbons of $-\text{OOCCH}_2$ group appears at 62.07 - 68.91 ppm (**Figure 2.3.7**).

2.3.4.2 Molecular Weight Data Analysis

The experimental values of number average molecular weights (M_n) and weight average molecular weights (M_w) of the prepared polymers (P-1 to P-5) are given in **Table 2.3.3**. From the experimental data, it is seen that among the five polymers, P-5 has the highest molecular weight. Moreover, it is also observed that with increasing the percentage of styrene in the backbone of rapeseed oil, the molecular weight increases. Therefore, the percentage of styrene has a significant role during polymerization.

2.3.4.3 Analysis of TGA Data

The TGA values of the five polymers are given in **Table 2.3.2**. From the table, it is clear that the thermal degradation of polymer P-1 is higher than the other polymers which signifies that P-1 is thermally less stable. The thermal degradation of polymers P-3, P-4, and P-5 are almost similar. In the case of polymer P- 1, major decomposition starts at 160°C with about 30% weight loss. For polymers P-3, P-4, and P-5, major decomposition starts approximately at 268°C with 18% weight loss. Due to the copolymerization of rapeseed oil with styrene, the thermal stability increases. Therefore, copolymerization with styrene has significant importance to improve thermal stability.

2.3.4.4 Analysis of Viscosity Index Values

VI was calculated at different concentrations ranging from 1% to 5% (w/w) to the base oil. The experimental values of VI are given in **Table 2.3.4**. From the table, it is found that VI values increase with increasing the concentration of polymers in the base oil. The viscosity of lubricating oil decreases with increasing temperature but the expansion of polymer molecules takes place with increasing temperature and due to this, the size of the micelle increases. This increased in micelle size interfere with the reduction of the viscosity of the lubricant [10]. Moreover, increasing the concentration of polymer in lubricating oil leads to an increase in the total volume of polymer micelle in lube oil and improves the VI property [11]. It has been observed that the VI value increases by the incorporation of styrene in the backbone of the homopolymer of rapeseed oil. This may be due to the higher crosslink density of the copolymers. The copolymer P-5 has the highest effect on VI increments followed by P-4, P-3, P-2, and P-1. The higher values VI in the case of P-5 containing the maximum percentage of styrene in the feed, are due to greater volume of the solvated additive molecule i.e. micelle compared to others which may be associated with its higher average molecular weights and lower PDI value.

2.3.4.5 Analysis of Pour Point Values

The pour point of the lubricants prepared by blending the polymers at different concentration levels ranging from 1%–5% (w/w) are shown in **Table 2.3.5**. All the polymers are effective as PPD and the efficiency as pour point increases with increasing the concentration of polymers up to a certain limit (4% concentration). This indicates that at this concentration, the polymer interacts with the paraffinic wax of base oil effectively and decreases the size of crystals of the paraffinic wax [12]. Among the prepared five polymers, P-4 showed better performance as PPD.

2.3.4.6 Analysis of Anti-wear Properties

The tribological properties of the lubricant compositions were determined by measuring WSD through FBWT apparatus applying 392 N load and values are given in **Table 2.3.6**. The antiwear performance of the lube oil is significantly improved when the polymers are blended with it and is reflected in the lower WSD values of the lubricant compositions. The copolymers showed better results compared to the homopolymer. The polymer P-5 at 5% concentration showed the highest reduction in WSD values compared to the other polymers. This indicates that the film formed by the lubricant between the two moving metal surfaces is very strong. It may be due to higher molecular weight and hence higher number of polar side chains of the ester carbonyl groups and hydroxyl groups present in rapeseed oil [13], [14]. The contribution of the higher percentage of styrene in the polymer feed has also played a significant role in it with its aromatic ring structure.

2.3.4.7 Analysis of Biodegradability Test

Biodegradability test results (**Table 2.3.7**) with the homo (P-1) and copolymers (P-2 to P-5) showed significant biodegradability against the fungal pathogens, *Calletotricheme camellia*, and *Alternaria alternata*, though the result is, as expected, better for the homopolymer of rapeseed oil. A close observation of the test results showed considerable biodegradation for all the samples. The analysis of the SBD tests indicated that the degradation of the polymeric additives increased continuously with the increasing number of days. Further, both the homo and copolymer showed significant weight losses against the fungal pathogens, especially against *Alternaria alternate* (AA), in the DD test. Moreover, as expected for zero styrene content and owing to the presence of the natural monomer unit, the HRO (P-1) showed the highest biodegradability among all the additives in both of the tests. The FT- IR peaks of the

polymer P-1 showed a shift in the peak positions and a considerable decrease in peak height and intensity after the DD test. The biodegradable nature of the prepared polymers was confirmed by the shift of IR peak and the decrease in the IR peak intensities of the polymers before and after the biodegradation tests and also with the PWL of the polymers [14].

2.3.5 Conclusion

From the above study, it was found that the copolymer of rapeseed oil with styrene showed excellent multifunctional performance for base oil. As a viscosity index improver, pour point depressant, and antiwear additive, the copolymers are found more effective than the homopolymer. In addition, the presence of rapeseed oil in the additive composition introduces excellent biodegradability too, in the additive. The average molecular weight and thermal stability of the copolymers increase with the increase in the percentage of styrene. Therefore, the above study is definitely a potential approach to formulate a greener lubricant composition with excellent multifunctional additive properties for lube oil.

2.3.6 Reference

References are given in *BIBLIOGRAPHY* under “Chapter II of Part III” (Page No.147-148).

2.3.7 Tables and Figures

Table 2.3.1: Properties of Rapeseed oil and Base oil

<i>Rapeseed Oil</i>		<i>Base Oil</i>	
<i>Properties</i>	<i>Values</i>	<i>Properties</i>	<i>Values</i>
Saponification index (mg/g)	167-74	Density at 313K, Kg.m ⁻³	868.03
Iodine index 9mg/g)	97-100	Viscosity at 313K	20.31x10
Refractive index at 50 °C	1.462	Viscosity at 373K	3.25x10
Density (g/ml)	0.916	Viscosity index	85
Saturated fatty acid (%)	7.36	Pour point (°C)	-6
Monounsaturated fatty acid (%)	63.27	Cloud point (°C)	-8
Polyunsaturated fatty acid (%)	28.14	-	-
Oleic acid(g)	61.744	-	-
Linoleic acid ω-6 (g)	19.005	-	-
α-Linoleic acid ω-3 (g)	9.137	-	-

Table 2.3.2: Percentage composition and TGA values of the prepared polymers

<i>Polymer Code</i>	<i>% Composition of monomer (w/w) in the feed</i>		<i>TGA values</i>	
	<i>RO</i>	<i>Sty</i>	<i>Decom. Temp.</i>	<i>PWL</i>
P-1	100	0	160/320	28/78
P-2	98	2	210/355	24/85
P-3	96	4	266/382	17/80
P-4	94	6	268/382	19/81
P-5	92	8	268/384	18/79

RO=Rapeseed Oil, Sty= Styrene, Decom. Temp.= Decomposition temperature, PWL= Percentage Weight Loss,

Table 2.3.3: Molecular weight of the prepared polymers

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

Table 2.3.4: Viscosity index (VI) values of polymer blended base oil

<i>Polymer Code</i>	<i>VI of polymer blended base oil at different concentrations (w/w)</i>					
	0%	1%	2%	3%	4%	5%
P-1	85	89	95	104	112	118
P-2	85	94	98	112	115	128
P-3	85	96	104	114	123	131
P-4	85	101	106	116	124	133
P-5	85	103.5	111	125	135	145

Table 2.3.5: Pour point values of polymer blended base oil and its graphical representation

Polymer Code	Pour point ($^{\circ}$ C) base oil at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	-6	-9	-12	-12	-15	-16
P-2	-6	-10	-12	-16	-18	-16
P-3	-6	-10	-12	-16	-20	-18
P-4	-6	-12	-15	-18	-22	-24
P-5	-6	-10	-15	-18	-18	-22

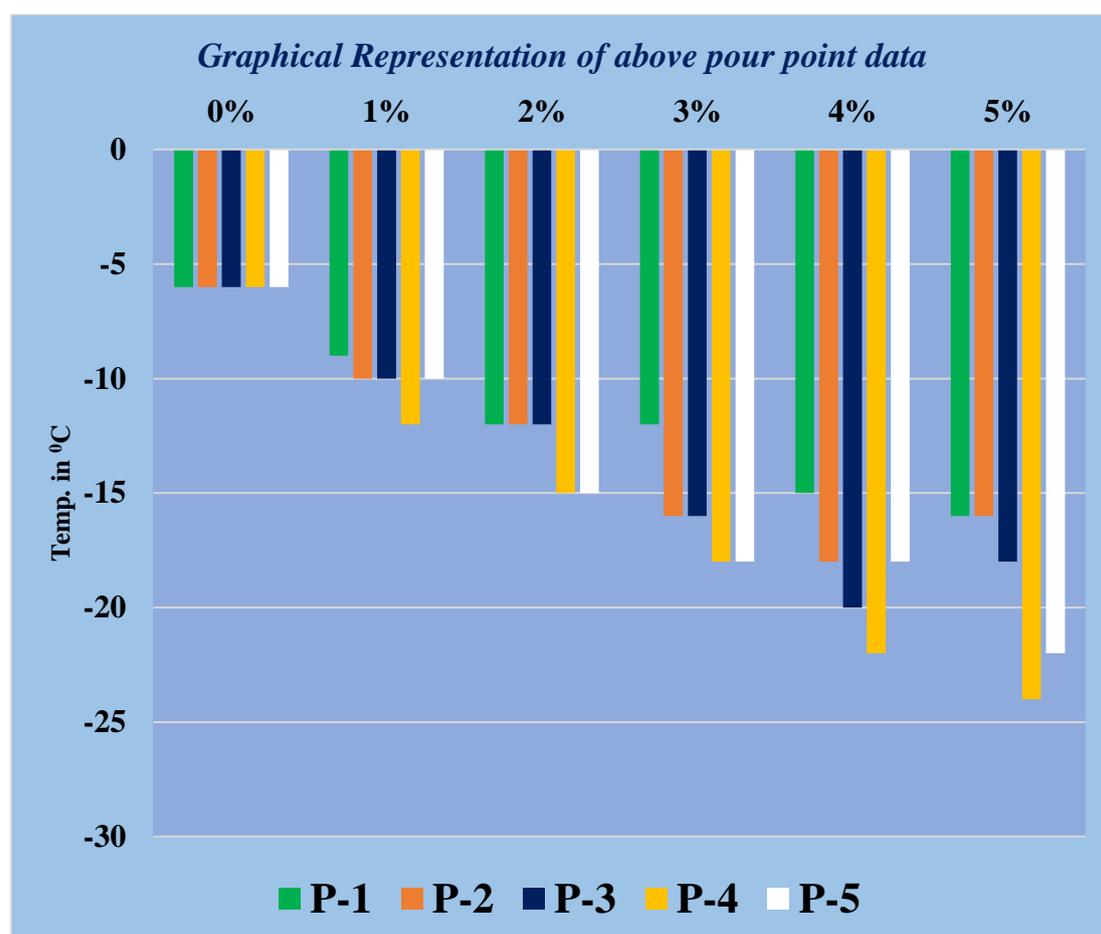


Table 2.3.6: Anti-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant compositions and its graphical representation

Polymer code	WSD of lubricant (in mm) at different polymer concentration (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	1.116	1.067	1.044	1.025	1.007	0.964
P-2	1.116	1.065	1.037	1.023	1.003	0.957
P-3	1.116	1.06	1.028	1.018	0.992	0.955
P-4	1.116	1.052	1.022	1.002	0.958	0.931
P-5	1.116	1.031	1.013	0.992	0.943	0.911

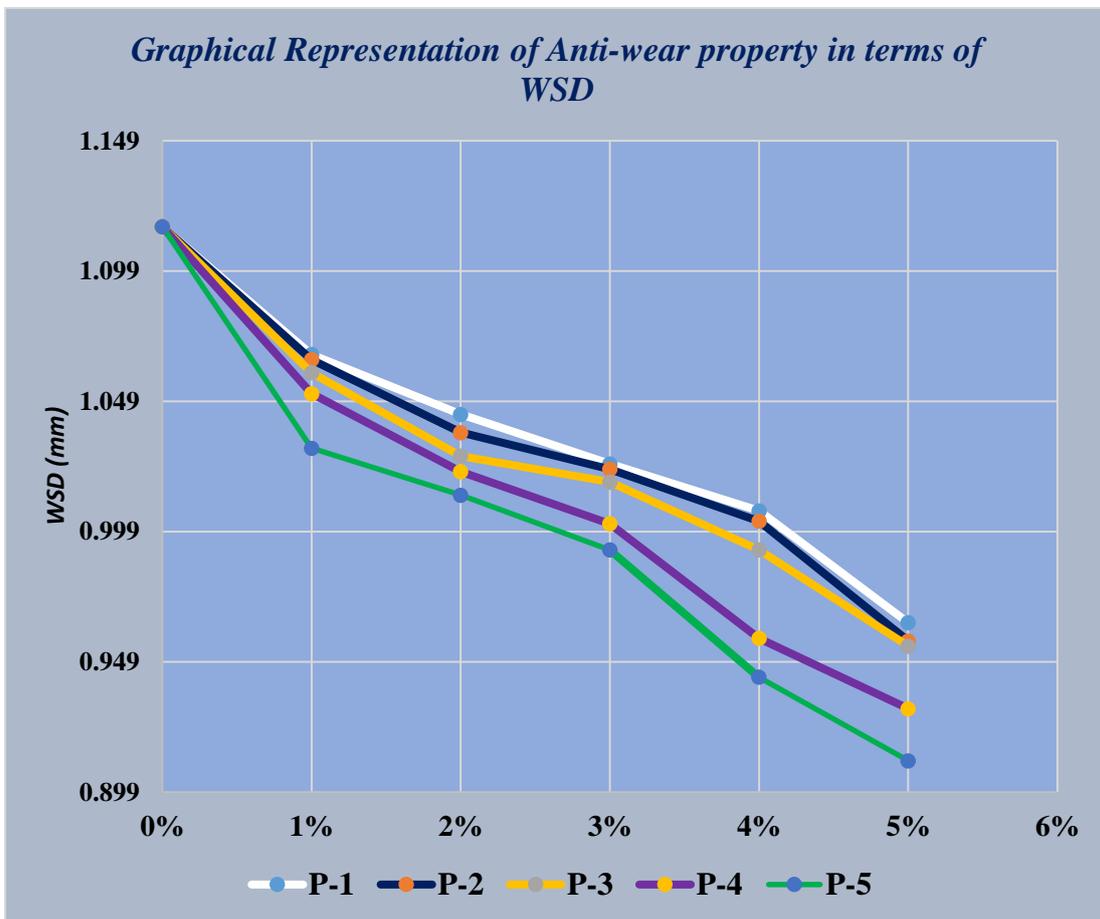


Table 2.3.7: Result of biodegradability test by the disc diffusion method and soil burial degradation

Sample	Weight loss in disc diffusion method (g) [Pathogens used]					Weight loss in soil burial degradation (g)
	[CC]	[FE]	[AA]	[CG]	[CE]	
P-1	0.45	0	0.62	0	0	0.47
P-2	0.38	0	0.54	0	0	0.35
P-3	0.3	0	0.48	0	0	0.3
P-4	0.26	0	0.39	0	0	0.25
P-5	0.22	0	0.35	0	0	0.19

CC=Calletotricheme camellia, FE= Fussarium equisitae, AA=Alternaria alternata, CG=Colletrichum gleosporoides, CE=Curvularia eragrostidies

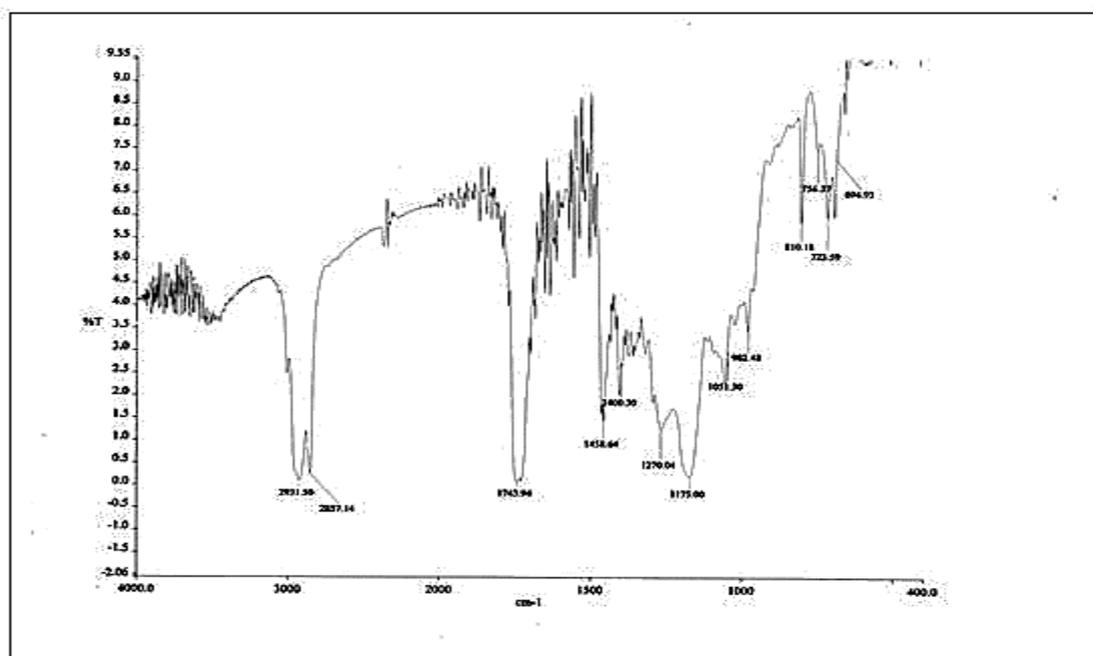


Figure 2.3.1: A representative FT-IR spectra of the rapeseed oil – styrene copolymer

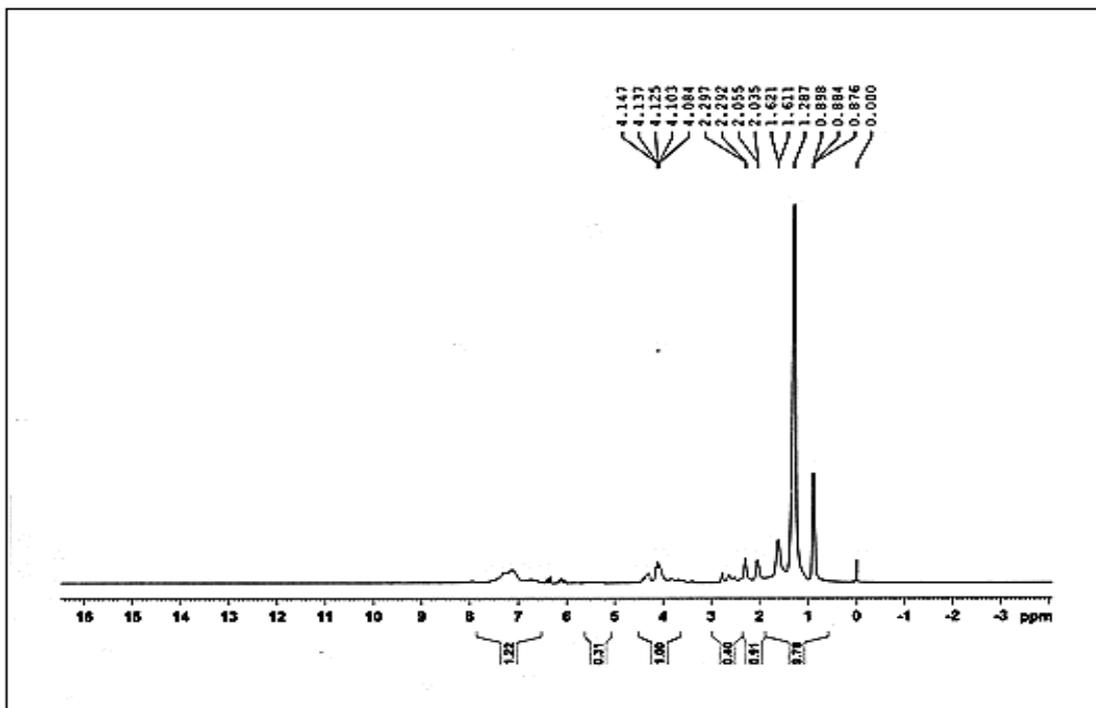


Figure 2.3.2: A representative ^1H NMR spectra of rapeseed oil – styrene copolymer

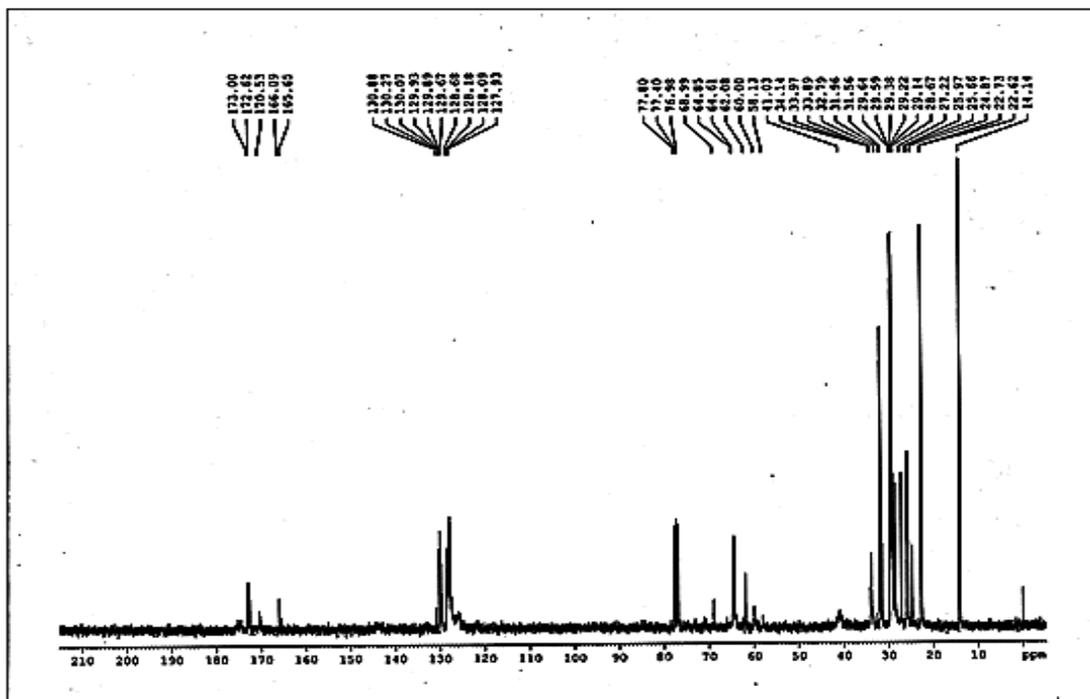


Figure 2.3.3: A representative ^{13}C NMR spectra of rapeseed oil- styrene copolymer

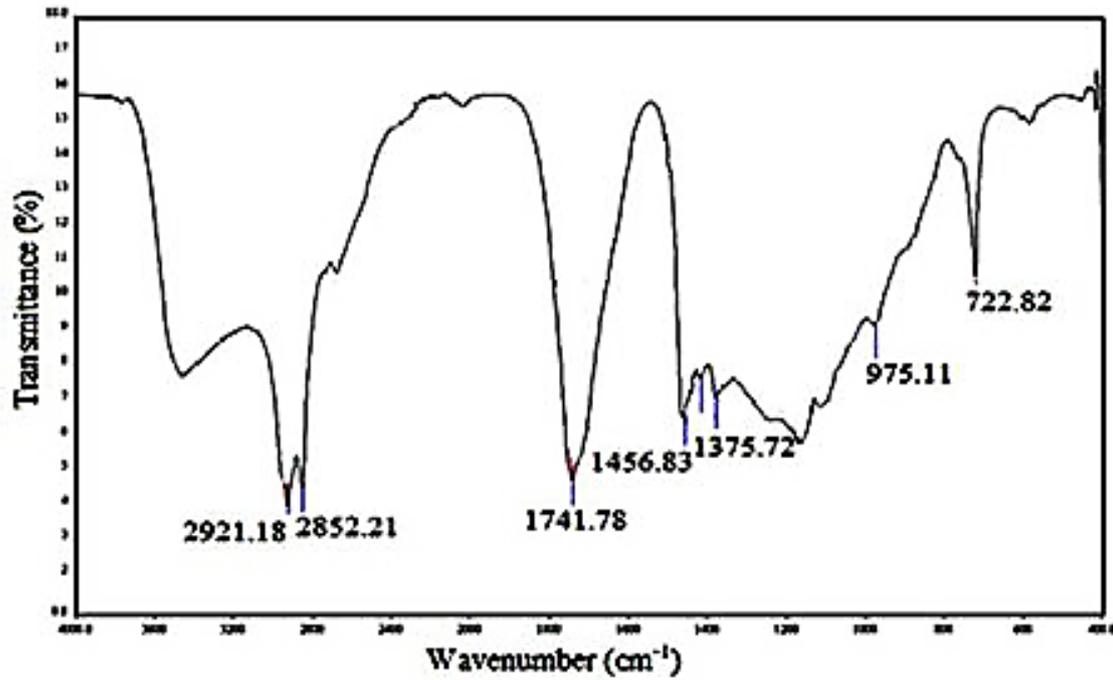


Figure 2.3.4: FT-IR spectra of the homo polymer of rapeseed oil

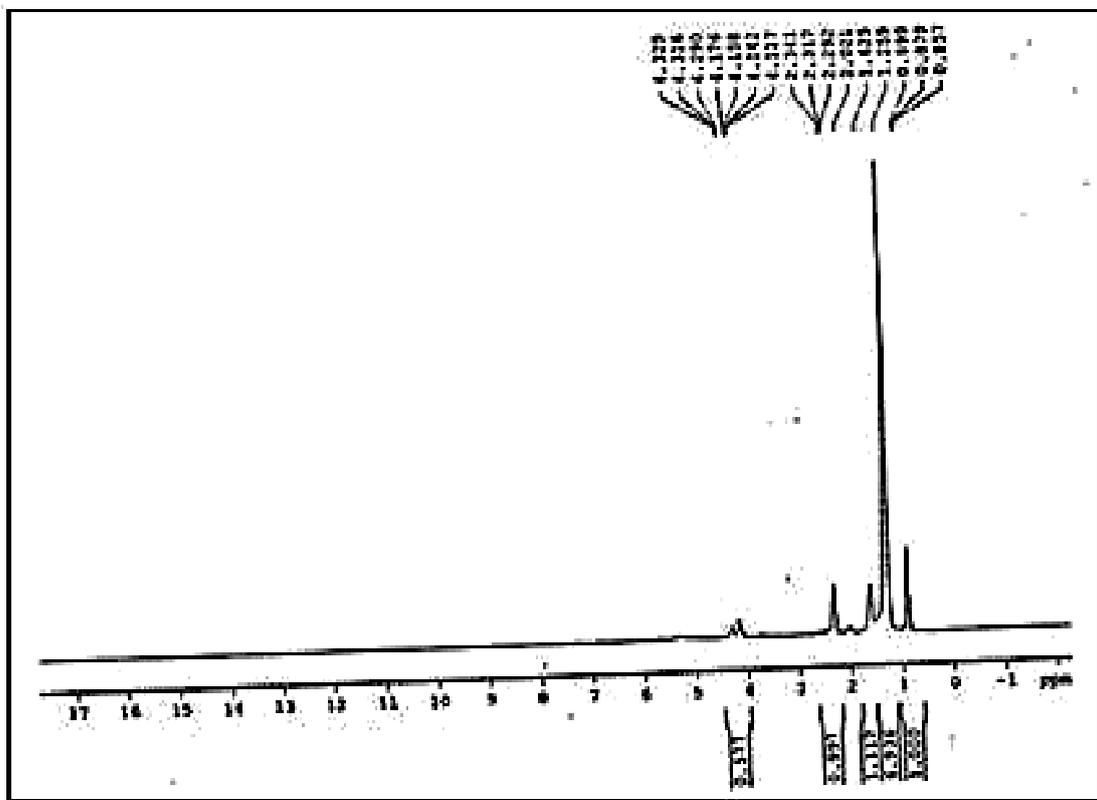


Figure 2.3.5: ¹H NMR spectra of homo polymer of rapeseed oil

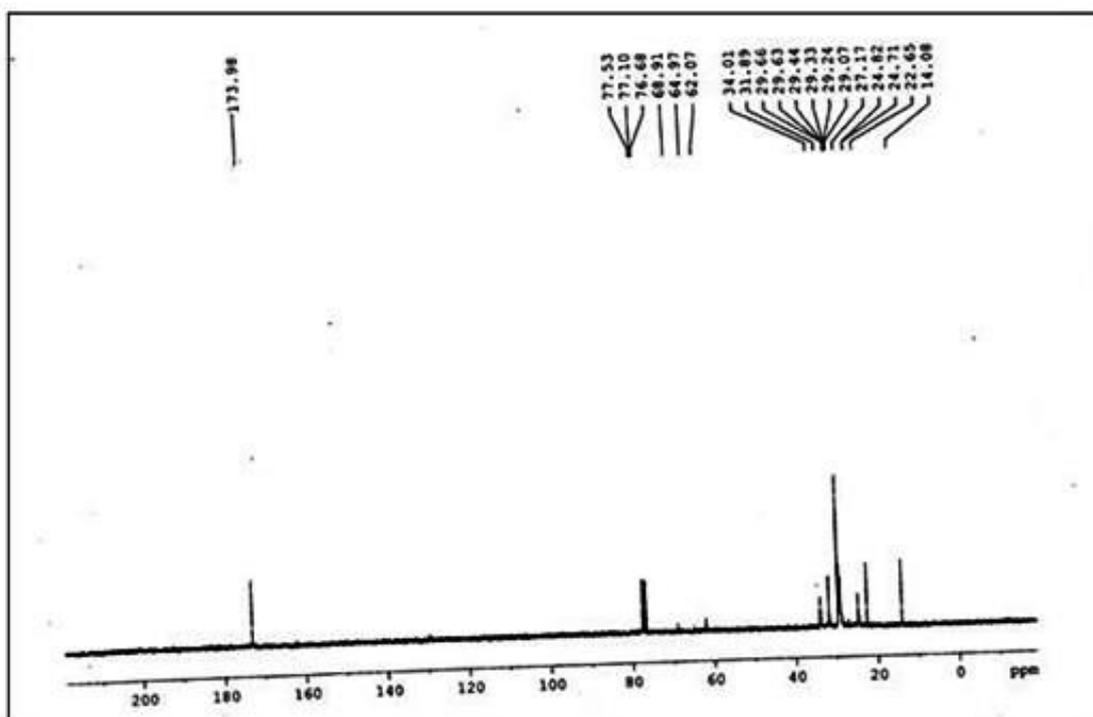


Figure 2.3.6: ^{13}C spectra of homo polymer of rapeseed oil

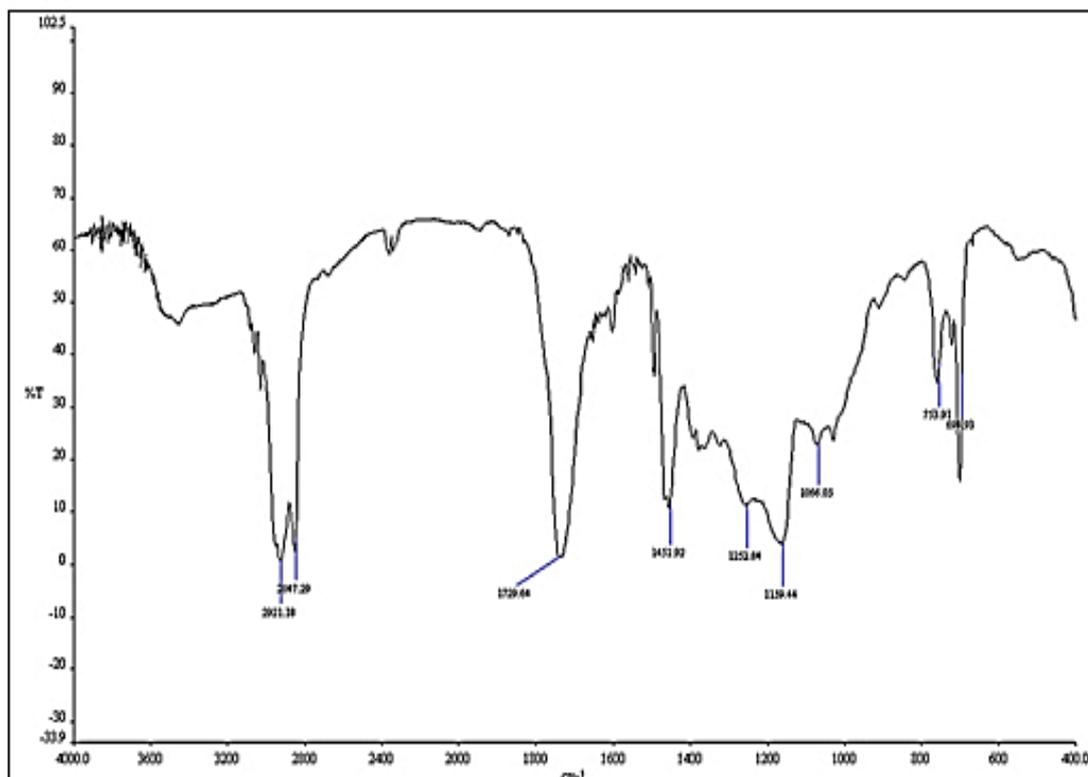


Figure 2.3.7: A representative FT-IR spectra of the copolymer after biodegradability test

References

General Introduction

1. 24 - Lubricants, Editor(s): W.F. Gale, T.C. Totemeier, Smithells Metals Reference Book (Eighth Edition), Butterworth-Heinemann, 2004, Pages 24-1-24-15, ISBN 9780750675093
2. I. Mangas, M.A. Sogorb, E. Vilanova, Lubricating Oils, Editor(s): Philip Wexler, Encyclopedia of Toxicology (Third Edition), Academic Press, 2014, Pages 670-676, ISBN 9780123864550
3. Vasishth, A., Kuchhal, P., & Anand, G. (2014). Study of rheological properties of industrial lubricants. In Conference papers in science (Vol. 2014). Hindawi.
4. A.M. Al-Sabagh, M.W. Sabaa, G.R. Saad, T.T. Khidr, T.M. Khalil, Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties, Egyptian Journal of Petroleum, Volume 21, Issue 1, 2012, Pages 19-30
5. Miller Arnold, The chemistry of lubricating oil additives, 1956, Journal of Chemical Education, 33(7), 308
6. Rudnick, L. R. Lubricant additives: Chemistry and Application, CRC press, 2003
7. Rizvi, S. Q. A. A comprehensive review of lubricant chemistry, technology, selection and design. ASTM international, West Conshohocken, PA., 2009, 100-112.
8. Soni, H. P.; Kiranbala; Bharambe, D. P. Performance- based on designing of wax crystal growth inhibitors. Energy Fuels 2008, 22, 3930-3938
9. Castro, L. V.; Vazquez, F. Copolymers as flow improvers for Mexican crude oil. Energy Fuels 2008, 22, 4006-4011

10. Denis, J. Pour point depressants in lubricating oils. *Lubr. Sci.* 1989, 1(2), 131-147.
11. Florea, M.; Catrinoiu, D.; Luca, P.; Ballius, S. The chemical composition on the pour point depressant properties of methacrylate copolymers used as additives for lubricating oils. *Lubr. Sci.* 1999, 12(1), 31-44.
12. Garcia, M. C; Carbognani, L.; Urbina, A.; Orea, M. Paraffin deposition in oil production.oil composition and paraffin inhibitors activity. *Pet. Sci. Technol.* 1998, 16, 1001-1021.
13. Al-Shafy, H. I.; Ismail, E. A. Studies on the influence of polymeric additives as flow improvers for waxy crude oil. *IOSR J. Eng.* 2014, 4, 54-61.
14. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* 2012, 21, 19-30.
15. El-Gamal, I. M.; Atta, A. M.; Al- Sabbagh, A. M. Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* 1997, 76, 1471-1478.
16. Ghosh, P.; Hoque, M. Synthesis and performance evaluation of vinyl acetate-maleic anhydride based polymeric additives for lube oil. *Pet. Sci. Technol.* 2015, 33, 1182-1189.
17. Onyeji, L. I.; Aboje, A. A. The effect of additive on the viscosity index of lubricating oil (engine oil). *Int. J. Eng. Sci. Tech.* 2011, 3(3), 1864-1869.
18. Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. Synthesis and evaluation of acrylate polymers in lubricating oil. *J. Chem. Eng. Data* 2011, 56, 3752-3758.
19. Ghosh, P.; Upadhyay, M.; Das, M. K. Studies on the additive performance of liquid crystal blended polyacrylate in lubricating oil. *Liq. Cryst.* 2014, 41(1), 30-35.
20. Masabumi, M.; Hiroyasu, S.; Akihito, S.; Osamu, K. Prevention of oxidative degradation of ZnDTP by microcapsulation and verification of its antiwear performance. *Tribol. Int.* 2008, 41, 197-204.

21. Ahmed, N. S.; Nassar, A. M.; Abdel-Azim, A. A. A. Synthesis and evaluation of some detergents/dispersant additives for lube oil. *Int. J. Polym. Mater.* 2008, 57, 114-124.
22. Smalheer, C. V.; Smith, R. K. — “Lubricant Additives” Cleveland, Lensing-Hiles Co. 1967.
23. Ghosh, P.; Hoque, M. Mannich bases and phosphosulphurized Mannich bases: Synthesis characterization and performance evaluation as potential lube oil additives. *J. Sci. Ind. Res.* 2015, 74, 150-154.
24. Alema-Vazquez, L. O.; Villagomez-Ibarra, J. R. Polyisobutenylsuccinimides as detergents and dispersants in fuel: infrared spectroscopy application. *Fuel*, 2001, 80, 965-968.
25. Abdel-Azim, A.; Nasser, A. M.; Ahmed, N. S.; Kamal, R. S. Multifunctional lube oil additives based on octadecene-maleic anhydride copolymer. *Pet. Sci. Technol.* 2011, 29, 97–107.
26. Forbes, E. S.; Neustadter, E. L. The mechanism of action of polyisobutenyl succinimide lubricating oil additives. *Tribol. Int.* 1972, 5(2), 72-77.
27. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Tech.* 2006, 13, 398-403.
28. Changqiao, Z.; Congcong, G.; Fengfeng, G.; Jian, W.; Dawei, Z.; Yan, W.; Dawei, X. Synthesis of comb bipolymers and their pour point depressing properties. *J. Pet. Sci.* 2014, 11, 155-160.
29. Latyshev, V. N.; Novikov, V. V.; Syrbu, S. A.; Kolbashov, M. A. Tribological properties of some cholesterical liquid-crystal additives. *J. Frict. Wear.* 2009, 30(6), 411–414.
30. Ahmed, N. S.; Nassar, A. M.; Nasser, R. M.; Khattab, A. F.; Abdel-Azim, A. A. Synthesis and evaluation of some polymers as lubricating oil additives. *J. Dis. Sci. Technol.* 2012, 33, 668-675.
31. Cai, G.; Zhang, L.; Ma, L.; Eli, W. Synthesis and characterization of polybutylacrylate viscosity index improver with anti-wear function. *Lubr. Sci.* 2015, 27(4), 209-216.

32. Nassar, A. M.; Ahmed, N. S.; Abdel –Aziz, K. I.; El-Kafrawy, A. F.; Abdel-Azim, A. A. A. Synthesis and evaluation of detergent/dispersant additives from polyisobutylene succinimides. *Int. J. Polym. Mater.* 2006, 55, 703–713.
33. Regueira, T.; Lugo, L.; Fandino, O.; Lopez, E. R.; Fernandez, J. Compressibilities and viscosities of reference and vegetable oils for their use as hydraulic fluids and lubricants. *Green Chem.* 2011, 13, 1293-1302.
34. Ertugrul, D.; Filiz, K. Using cotton seed oil as an environmentally accepted lubricant additive. *Energy Sources.* 2004, 26, 611-625.
35. Maleque, M. A.; Masjuki, H. H.; Sapuan, S. M. Vegetable based biodegradable Lubricating oil additive. *Ind. Lubr. Tribol.* 2003, 55(3), 137-143.
36. Gobinda Karmakar and Pranab Ghosh, Atom Transfer Radical Polymerization of Soybean Oil and Its Evaluation as a Biodegradable Multifunctional Additive in the Formulation of Eco-Friendly Lubricant, *ACS Sustainable Chemistry & Engineering* 2016 4 (3), 775-781

Part I

Chapter I

1. Pirro, D. M.; Wessol, A. A. *Lubricants Fundamentals*. New York: Marcel Dekker, 2001, 37-43.
2. Santos, J. C. O.; Santos, I. M. G.; Souza, A. G.; Sobrinho, E. V.; Fernandes V. J.; Silva, Jr. A. J. N. Thermoanalytical and rheological characterization of automotive mineral lubricants after thermal degradation. *Fuel* 2004, 83, 2393-2399.
3. Wu, C.; Zang, J.; Li, W.; Wu, N. Molecular dynamics simulation guiding the improvement of EVA-type pour point depressant. *Fuel* 2005, 84, 2039-2047.
4. Kajdas, C.; Majzner, M. Effectiveness of selected CHO compounds as antiwear additives to white mineral oils. *Tribol. Transac.* 2005, 48, 93-99.

5. Xiangqiong, Z.; Heyang, S.; Wenqi, R.; Zhongyi, H.; Tianhui, R. Tribological study of trioctylthiotriazine derivative as lubricating oil additive. *Wear* 2005, 258, 800-805.
6. Aleman-Vazquez, L. O.; Villagomez-Ibarra, J. R. Polyisobutenylsuccinimides as detergents and dispersants in fuel: infrared spectroscopy application. *Fuel* 2001, 80, 965-968.
7. Zhongyi, H.; Jinliang, L.; Xiangqiong, Z. Study of the tribological behaviours of S, P-containing triazine derivatives as additives in rapeseed oil. *Wear* 2004, 257, 389-394.
8. Barnes, A. M.; Bartel, K. D.; Thibon, V. R. A. A review of zinc dialkyldithiophosphates (ZDDPS): Characterization and role in lubricating oil. *Tribol. Int.* 2001, 34, 389-395.
9. N. S. Ahmed, A. M. Nassar, R. M. Nasser, A. F. Khattab & A.-A. A. Abdel-Azim, Synthesis and Evaluation of Some Polymeric Compounds as Pour Point Depressants and Viscosity Index Improvers for Lube Oil, *Petroleum Science and Technology*, 2008, 26(12), 1390-1402
10. Abdel-Azim, A. A.; Huglin, M. B. Proceedings of the second Egyptian conference of chemical engineering, Cairo, Egypt, 1984, March 18–20, 117–123.
11. Eckert, R. J. A.; Covey, D. F. Developments in the field of hydrogenated diene copolymers as viscosity index improvers. *Lubr. Sci.* 1988, 1, 65–80.
12. Garcia, M. C.; Carbognani, L.; Urbina, A.; Orea, M. Paraffin deposition in oil production, oil composition and paraffin inhibitors activity. *Pet. Sci. Technol.* 1998, 16, 1001-1021.
13. Huiyang, Z.; Weibang, Z.; Zhuomei, L. Synthesis of polymers with long side chain of N-alkyl esters and their effects on pour-point depression of oil. *J. Appl. Polym. Sci.* 1991, 43, 919-924.
14. Wuhua, C.; Zongchang, Z.; Caoyong, Y. The interaction of waxes with pour point depressants. *Fuel* 2010, 89, 1127-1132.
15. Ghosh, P.; Das, T.; Nandi, D. Shear stability and thickening properties of homo and copolymer of methyl methacrylate. *American J. of polym. Sc.* 2011, 1, 1-5.

16. Florea, M.; Catrinoiu, D.; Luca, P.; Balliu, S. The influence of chemical composition on the pour-point depressant properties of methacrylate copolymers used as additives for lubricating oil. *Lubr. Sci.* 1999, 12, 31-44.
17. Ghosh, P.; Das, T.; Das, M. Evaluation of poly (acrylates) and their copolymer as viscosity modifiers. *Res. J. Chem. Sci.* 2011, 1, 18-25.
18. Ghosh, P.; Das, M. Study of the influence of some polymeric additives as viscosity index improvers and pour point depressants – synthesis and characterization. *J. Pet. Sci. Eng.* 2014, 119, 79–84.

Chapter II

1. Ghosh, P., Pantar, A.V., Rao, U. S., & Sarma, A. S. (1998). α - Olefin Copolymers as Viscosity Modifier Additives in Lubricating Oil. *Ind. J. Chem. Technol.*, 5, 309-314.
2. Mohamed, M. M., Hamdi, H. A., & Mohamed, F. E. J. (1994). Multi-functional viscosity index improvers. *Chem. Tech. Biotechnol.*, 60, 283-289.
3. Ghosh, P., Das, T., & Nandi, D. (2011). Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate. *American Journal of Polymer Science*, 1(1), 1-5.
4. Abdel-Azim, A. A. A., Nassar, A. M., Ahmed, N. S., & Kamal, R. S. (2006). Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. *Pet. Sci. Technol.*, 24, 887–894.
5. Rein, S. W., Alexander, D. L., Cryvoff, S. A., & Dahlstrom, M. A. (1987). Investigation of engine oil shears stability in laboratory test and road test. SAE paper No. 872047.
6. Ghosh, P., & Karmakar, G. (2012). Synthesis and Characterization of Polymyrystyl Acrylate as a Potential Additive for Lubricating Oil. *American Journal of Polymer Science*, 2(1), 1-6.
7. Karmakar, G., & Ghosh, P. (2013). Green additives for lubricating oil. *ACS Sustainable Chem Eng.*, 1, 1364–1370.
8. Tanveer, S., & Prasad, R. (2006). Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.*, 13, 398–403.

9. Al-Sabagh, A. M., Sabaa, M. W., Saad, G. R., Khidr, T. T., & Khalil, T. M. (2012). Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egyptian Journal of Petroleum*, 21, 19-30.
10. Chen, W. H., Zhao, Z. C., & Yin C. Y. (2010). The interaction of waxes with pour point depressants. *Fuel*, 89, 1127-1132.
11. Dodecyl Acrylate and its Copolymer with Styrene and 1-Decene: A Study of Shear Stability, Thickening and Viscosity Index Properties P. Ghosh, S. Paul and M. Hoque, *International Journal of Research and Analytical Reviews*, 2020, 7(2), 772-779.

Chapter III

1. Torimoto, T., Tsuda, T., Okazaki, K., Kuwabata, S. (2010). New frontiers in materials science opened by ionic liquids. *Adv. Mater.* 22: 1196–1221.
2. Ye, C., Liu, W., Chen, Y., Yu, L. (2001). Room-temperature ionic liquids: a novel versatile lubricant. *Chem. Commun.* 2244–2245.
3. Feng, Z., Yongmin, L., Weimin, L. (2009). Ionic liquid lubricants: designed chemistry for engineering applications. *Chemical Society Reviews*. 9(38): 2590-2599.
4. Pensado, A.S., Comunas M.J.P., Fernandez J. (2008). The pressure-viscosity coefficient of several ionic liquids. *Tribology Letters*. 31(2): 107-118.
5. Somers, A., Howlett, P., MacFarlane, D., Forsyth, M. (2013). A Review of Ionic Liquid Lubricants. *Lubricants*. 1: 3–21.
6. Viesca, J.L., García, A., Hernández-Battez, A., González, R., Monge, R., Fernández-González, A. et al. (2013). FAP- anion ionic liquids used in the lubrication of a steel-steel contact. *TribolLett.* 52: 431–437.
7. Wang, H., Lu, Q., Ye, C., Liu, W., Cui, Z. (2004). Friction and wear behaviors of ionic liquid of alkyl imidazolium hexafluorophosphates as lubricants for steel/steel contact. *Wear*. 256: 44–48.
8. Otero, I., López, E.R., Reichelt, M., Villanueva, M., Salgado, J., Fernández, J. (2014). Ionic liquids based on phosphonium cations as neat lubricants or lubricant additives for a steel/steel contact. *ACS Appl Mater Interfaces*. 6(13): 115–128.

9. Palacio, M., Bhushan, B. (2010). A review of ionic liquids for green molecular lubrication in nanotechnology. *TribolLett.* 40: 247–68.
10. Qu, J., Blau, P.J., Dai, S., Luo, H., Meyer, H.M. (2009). Ionic Liquids as Novel Lubricants and Additives for Diesel Engine Applications. *TribolLett.* 35:181–189.
11. Plechkova, N.V., Seddon, K.R. (2008). Applications of ionic liquids in the chemical industry. *Chem.Soc.Rev.*37: 123–150.
12. Ghosh, P., Das, T., Nandi, D. (2011). Synthesis Characterization and Viscosity Studies of Homopolymer of Methyl Methacrylate and Copolymer of Methyl Methacrylate and Styrene. *J Solution Chem.* 40: 67–78.
13. Upadhyay, M., Dey, K., and Ghosh, P. (2016). Biodegradable multifunctional additives for lube oil – synthesis and characterization. *Pet Sci Technol* 34: 1255–1262.
14. Tanveer, S., and Prasad, R. (2006). Enhancement of viscosity index of mineral base oils. *Ind J Chem. Technol.* 13: 398-403.

Chapter IV

1. Roy, M.; Mortier, M. R.; Fox, F. M.; Orszulik, T. S. *Chemistry and Technology of Lubricants*. 3rd ed., Springer, Heidelberg, USA, 2010. DOI: 10.1023/b105569.
2. Singh, R. K.; Kukrety, A.; Kumar, A; Chouhan, A.; Saxena, R. C.; Ray, S. S.; Jain, S. L. Synthesis, characterization and performance evaluation of N,N–Dimethylacrylamide–alkyl acrylate co–polymers as novel multi–functional additives for lube oil. *Adv. Polym. Technol.* 2018, 37, 1695–1702. DOI: 10.1002/adv.21826.
3. Al-Sabagh, M. A.; Noor El-Din, R. M.; Morsi, E. R.; Elsabee, Z. M. Styrene–maleic anhydride copolymer esters as flow improvers of waxy crude oil. *J. Petrol. Sci. Eng.*, 2009, 65, 139–146. DOI: 10.1016/j.petrol.2008.12.022.
4. Wu, Y.; Ni, G.; Yang, F.; Li, C.; Dong, G. Modified Maleic Anhydride Co–polymers as Pour–Point Depressants and Their Effects on Waxy Crude Oil Rheology. *Energy & Fuels*, 2012, 26, 995–1001. DOI: 10.1021/ef201444b.

5. Liu, T.; Fang, L.; Liu, X.; Zhang, X. Preparation of a kind of reactive pour point depressant and its action mechanism, *Fuel*, 2015, 143, 448–454. DOI: 10.1016/j.fuel.2014.11.094.
6. Cao, K.; Zhu, Q.; Wei, X.; Yao, Z. Study on the Influence of the Imidization Degree of Poly(styrene-co-octadecyl maleimide) as a Flow Improver in Waxy Crude Oils with Asphaltenes. *Energy & Fuels*, 2015, 29, 993–1000. DOI: 10.1021/ef501281u.
7. Lu, Y.; Zhang, X.; Yao, G. Exploration of the Function of Diesel Fuel Additives Influencing Flow. *Energy & Fuels*, 2011, 25, 2115–2118. DOI: 10.1021/ef200127q.
8. Mishra, M. K.; Saxton, R. G. U.S. Pat., 1998, 5,834,408.
9. Elganidi, I.; Elarbe, S. B.; Abdullah, N.; Ridzuan, N. Characterization of a novel terpolymer containing maleic anhydride-co-stearyl methacrylate-co-benhely acrylate for wax inhibition application. *Mater. Sci. Eng.*, 2019, 702, 012027. DOI: 10.1088/1757-899X/702/1/012027.
10. Jang, J.; Kim, B. S. Studies of crosslinked styrene-alkyl acrylate copolymers for oil absorbency application. II. Effects of polymerization conditions on oil absorbency. *J. Appl. Polym. Sci.* 2000, 77, 903–913. DOI: 10.1002/(SICI)1097-4628(20000725)77.
11. Huiyang, Z.; Weibang, Z.; Zhuomei, L. Synthesis of polymers with long side chain of N-alkyl esters and their affects on pour-point depression of oil. *J. Appl. Polym. Sci.*, 1991, 43, 919 – 924. DOI: 10.1002/app.1991.070430509.
12. Baruah, D. S.; Laskar, C. N.; Subrahmanyam, B. Experimental investigation on high conversion free-radical polymerization of behenyl acrylate. *J. Appl. Polym. Sci.*, 1994, 51, 1701–1707. DOI: 10.1002/app.1994.070511002.
13. Subrahmanyam, B.; Baruah, D. S.; Rahman, M.; Laskar, C. N.; Mazumder, K. R. Studies on high conversion polymerization of n-alkyl acrylates. *Polymer*, 1994, 35, 862–865. DOI: 10.1016/0032-3861(94)90887-7.
14. Sarmah, D.; Baruah, D. S. Synthesis, characterization, and thermal properties of copolymers of behenyl acrylate and behenyl fumarate. *J. Appl. Polym. Sci.*, 2003, 90, 2721–2726. DOI: 10.1002/app.12927.
15. Machado, A. L.; Lucas, E. F.; Gonzalez, G. Poly (ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: oil viscosity, pour point and

- phase behaviour of organic solutions. *J. Pet. Sci. Eng.*, 2001, 32, 159–165. DOI: 10.1016/S0920–4105(01)00158–9.
16. Schwahn, D.; Richter, D.; Lin, M.; Fetters, L. J. Cocrystallization of a poly (ethylene–butene) random copolymer with C24 in n–decane. *Macromolecules*, 2002, 35, 3762–3768. DOI: 10.1002/app.35268.
17. Jung, K. M.; Chun, B. H.; Park, S. H.; Lee, C. H.; Kim, S. H. Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricant oil. *J. Appl. Polym. Sci.*, 2011, 120, 2579–2586. DOI: 10.1002/app.33330.
18. Chen, Z.; Wang, X.; Zhang, H.; Yang, C.; Shan, H. A study on the interaction of crude oil waxes with polyacrylate pour point depressants by Monte Carlo Simulation. *Pet. Sci. Technol.*, 2014, 32, 2151–2157. DOI: 10.1080/10916466.2013.769571.
19. Kumar, M. N. S. Review on polymeric and copolymeric pour point depressants for waxy crude oils and studies on Bombay high crude oil. *Quart J. Technol.*, 1989, 15, 47–62.
20. Castro, L. V.; Flores, E. A.; Vazquez, F. Terpolymers as flow improvers for Mexican crude oils. *Energy & Fuels*, 2011, 25, 539–544. DOI: 10.1021/ef101074m.
21. Fuchs, M. The world lubricants market, current situation and outlook. 12th International colloquim on Tribology, 2000.
22. Than, D.; Chuong, T.; Tuy, D. *AIP Conf.Proc.*, 2017, 1878, 020002.
23. Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. Synthesis and evaluation of acrylate polymers in lubricating oil. *J. Chem. Eng. Data.*, 2011, 56, 3752–3758. DOI: 10.1021/je2003435.
24. Amal, N. M.; Nehal, A. S.; Rasha, K. S.; Abdel–Azim, A. A.; El–Nagdy, I. E. Preparation and evaluation of acrylate polymers as viscosity index improvers for lube oil. *Petrol. Sci. Technol.*, 2005, 23, 537. DOI: 10.1081/LFT–200031097.
25. Hipeaux, C. J.; Born, M.; Durand, P. J.; Claudy, P.; Letoffe, M. J. Physico–chemical characterization of base stocks and thermal analysis by differential scanning calorimetry and thermomicroscopy at low temperature. *Thermochim. Acta.*, 2000, 348, 147–159. PII: S 0040–6031(02)00180–6.

26. Nassar, A. M. The behaviour of polymers as viscosity index improvers. *Petrol. Sci. Technol.*, 2008, 26, 514–522. DOI: 10.1080/10916460600806101

Chapter V

1. Stephen M.H. *Tribol. Int.* 2004, 37(7):537-545.
2. Shakvorostov D., Pohlmann K., Sherge M. *Wear* 2004, 257(1/2):124-130.
3. Qin M., Chen G., Gao Y. J. *Synth. Lubr.* 2001, 2001(4):9-14 (in Chinese).
4. Cao M., Zheng S., Zhang H. J. *West. Chong. Inst.* 2003, 2 (4):15-18.
5. Zhou M., Zhu H., Jiao Y. J. *Phys. Chem. C.* 2009, 113(20):8945-8947.
6. Soares J.W., Whitten J.E., Oblas D.W. *Langmuir*, 2008, 24(2):371-374.
7. Han M., Zhao K. J. *Phys. Chem. C.* 2008, 112:9192-9202.
8. Stomenov P.K., K.R.L., Manchin G.L., Klabunde K.J. *Langmuir*, 2002, 18:6679-6686.
9. Battez A.H., Gonzdez R., Felgueroso D. *Wear*, 2007, 263:1568-1574.
10. Zhou J.F., Wu Z.S., Zhang Z.J. *Wear*, 2001, 249:333- 337.
11. Ou Z., Liu W., Xu B.: China Patent, 011244442.9 [P]. 2003 (in Chinese).
12. Tang E.J., Cheng G.X., Ma X.L. *Appl. Surf. Sci.* 2006, 252:5227-5232.
13. Chen S., Li N., Liu W. J. *Jil. Inst. Chem. Technol.* 2002, 19(3):4-6. (in Chinese)
14. Abdel A., Amal M.N., Nehal S.A., Rasha S.K., Ei Nagdy E.I. *Pet. Sci. Tech.* 2005, 23:537-546.
15. Ghosh P., Das T., Das M. *Res. J. Chem. Sci.* 2011, 1(3):18-25.
16. Bataille P., Sharifi-Sanjani N., Evin E. J. *Sol. Chem.* 1994, 23(2):325-338.
17. Florea M., Catrinoiu D., Luca P., Balliu S. *Lub. Sci.* 1999, 12(1):31-44.
18. Dey K., Karmakar G., Upadhyay M., Ghosh P. *Sci. Rep.* 2020, 10:1-10
19. Upadhyay M., Das M.K., Dabrowski R., Ghosh P. *Asian J. Nanosci. Mater.* 2019, 2:257-270
20. Jyoti M., Vijay D., Radha S. *Inter. J. Sci. Res. Pub.* 2013, 3(11):1-5.
21. Tanveer S., Prasad R. *Ind. J. Chem. Technol.* 2006, 13:398–403.
22. Kumar G.S., Balamurugan A., Vinu S., Radhakrishnan M., Senthilprabhu G. *J. Sci. Ind. Res.* 2012, 71:562–565.
23. Karmakar G., Ghosh P. *ACS Sustain. Chem. Eng.* 2015, 3:19–25.
24. Zlovar A.A., Orel Z.C., Kogej K., Zigon M. *J. Nanometer.* 2012, 9.

25. Talam S., Karumuri S.R., Gunnam N. *ISRN Nanotechnology*, 2012, doi: 10.5402/2012/372505.
26. Dumontel B., Canta M., Engelke H., Chiodoni A., Racca L., Ancona A., Limongi T., Canavese G., Cauda V. *J. Mater. Chem B*. 2017, 5:8799-8813
27. Sato M., Yamaguchi I. *Eur. Polym. J.* 2008, 44:3430-3438.
28. Battez A.H., Rodriguez R.G., Viesca J.L., Fernandez J.E. *Wear*, 2008, 265:422-428.
29. Koushik Dey, Sujan Paul, Pranab Ghosh. Multifunctional additive properties of acrylate based ZnO Nano composite for lubricating oil. *Asian Journal of Nanoscience and Materials*, 4(2) 2021, 159-170.

Part II

Chapter I

1. Zeng, X.; Li, J.; Wu, X.; Ren, T.; Liu, W. The tribological behaviors of hydroxyl containing dithiocarbamate- triazine derivatives as additives in rapeseed oil. *Tribol. Int.* 2007, 40 (3), 560–566.
2. Zeng, X.; Wu, H.; Yi, H.; Ren, T. Tribological behavior of three novel triazine derivatives as additives in rapeseed oil. *Wear* 2007, 262 (5–6), 718–726.
3. Erhan, S. Z.; Sharma, B. K.; Liu, Z.; Adhvaryu, A. Lubricant base stock potential of Chemically modified vegetable oils. *J. Agri. Food. Chem.* 2008, 56 (19), 8919–8925.
4. Erhan, S. Z.; Asadauskas, S. Lubricant base stocks from vegetable oils. *Ind. Crop. Prod.* 2000, 11 (2–3), 277–282.
5. Karmakar, G.; Ghosh, P. Soybean oil as a biocompatible multifunctional additive for lubricating oil. *ACS Sustainable Chem. Eng.* 2015, 3, 19–25.
6. Singh, A. K. Development of Biodegradable Lubricant Chemical Business (ISSN 970-3136) 22 (4) April 2008, 53-55.
7. Rizvi, S. Q. A. Additive chemistry and technology, *Tribology data hand book*. Booser, E. R. (Ed.), New York: CRC Press, 1997, 1, 117-137.
8. Ertugrul, D.; Filiz, K. Using cotton seed oil as environmentally accepted lubricant additive. *Energ. sources* 2004, 26, 611-625.

9. Guner, F. S.; Yagci, Y.; Erciyes, A. T. Polymer from triglycerides oils. *Prog. Polym. Sci.* 2006, 31, 633-670.
10. Mofijur, M.; Masjuki, H. H.; Kalam, M. A.; Shahabuddin, M.; Hazrat, M. A.; Liaquat A. M. Palm Oil methyl ester and its emulsions effect on lubricant performance and engine components wear. *Energ. Procedia* 2012, 14, 1748–1753
11. Fox, N. J.; Stachowiak, G. W. Vegetable oil-based lubricants—a review of oxidation. *Tribol. Int.* 2007, 40, 1035–1046.
12. Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Oxidation, Friction reducing, and low temperature properties of epoxy fatty acid methyl esters. *Green Chem.* 2007, 9 (5), 469–474.
13. Vinci, D.; Kersbulck, J.; Greaves, M. R.; Khelidj, N. High performance renewable base fluids derived from castor oil for industrial applications, solving friction problems. *Synopsis 17th International Colloquium, Tribol.* 2010, 88.
14. Regueira, T.; Lugo, L.; Fandino, O.; Lopez, E. R.; Fernandez, J. Compressibilities and viscosities of reference and vegetable oils for their use as hydraulic fluids and lubricants. *Green Chem.* 2011, 13, 1293–1302.
15. Joseph, P. V.; Sharma, D. K., Improvement of thermo-oxidative stability of non – edible vegetable oil of Indian origin for biodegradable lubricant application. *Lubr. Sci.*, 2010, 22, 149–161.
16. Maleque, M. A.; Masjuki, H. H.; Sapuan, S. M. Vegetable based biodegradable lubricating oil additives. *Ind. Lubr. Tribol.* 2003, 55, 137-143.
17. Ghosh, P.; Das, T.; Karmakar, G.; Das, M. Evaluation of acrylate-sunflower oil copolymer as viscosity index improvers for lube oils. *J. Chem. Pharm. Res.* 2011, 3, 547–556.
18. Li, W.; Jiang, C.; Chao, M.; Wang, X. Natural garlic oil as a high performance, environmentally friendly, extreme pressure additive in lubricating oils. *ACS Sustainable Chem. Eng.* 2014, 2, 798–803.
19. Quinchia, L. A.; Delgado, M. A.; Valencia, C.; Franco, J. M.; Gallos, C. Viscosity modification of high oleic sunflower oil with polymeric additives for the design of new biolubricant formulations. *Environ. Sci. Technol.* 2009, 43, 2060-2065.

20. Nassar, A. M.; Ahmed, N. S.; Nasser, R. M. Jojoba polymers as lubricating oil additives. *Petroleum & Coal* 2015, 57, 120-129.
21. Bisht, R. P. S.; Sivasankaran, G. A.; Bhatia, V. K. Additive properties of Jojoba oil for lubricating formulations. *Wear* 1993, 161, 193-197.
22. Karmakar, G.; Ghosh, P. Green additives for lubricating oil. *ACS Sustainable Chem. Eng.* 2013, 1, 1364-1370.
23. Ghosh, P.; Das, T.; Karmakar, G.; Das, M. Evaluation of acrylate-sunflower oil copolymer as viscosity index improvers for lube oils. *J. Chem. Pharm. Res.* 2011, 3, 547-556.
24. Ghosh, P.; Karmakar, G. Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int. J. Ind. Chem.* 2014, 5, 7-17.

Chapter II

1. Shanta, S. M.; Molina, G. J.; Soloiu, V. Tribological Effects of Mineral–Oil Lubricant Contamination with Biofuels: A Pin–on–Disk Tribometry and Wear Study. *Adv. Tribol.* 2011. DOI: 10.1155/2011/820795.
2. Li, W.; Jiang, C.; Chao, M.; Wang, X. Natural Garlic Oil as a High–Performance, Environmentally Friendly, Extreme Pressure Additive in Lubricating Oils. *ACS Sustainable Chem. Eng.* 2014, 2, 798–803. DOI: 10.1021/sc400462n.
3. Saha, D. K.; Ghosh, P. Naturally derived green bio–additives. *J. Macromol. Sci. A.* 2018, 55, 384–392. DOI: 10.1080/10601325.2018.1444419.
4. Sharma, B. K.; Adhvaryu, A.; Erhan, S. Z. Friction and wear behavior of thioether hydroxy vegetable oil. *Wear* 2009, 42, 353–358. DOI: 10.1016/j.triboint.2008.07.004.
5. Karmakar, G.; Ghosh, P. Soybean Oil as a Biocompatible Multifunctional Additive for Lubricating Oil. *ACS Sustain. Chem. Eng.* 2015, 3, 19–25. DOI: 10.1021/sc500685r.
6. Ghosh, P.; Hoque, M.; Karmakar, G. Castor Oil as Potential Multifunctional Additive in the Formulation of Eco–Friendly Lubricant. *Polym. Bull.* 2018, 75, 501–514. DOI: 10.1007/s00289–017–2047–6.

7. Mutlu, H.; Meier, M. A. R. Castor oil as a renewable resource for the chemical industry. *Eur. J. Lipid Sci. Technol.* 2010, 112, 10–30. DOI: 10.1002/ejlt.200900138.
8. Singh, A. K. Castor oil–based lubricant reduces smoke emission in two–stroke engines. *Indian crops. prod.* 2011, 33, 287–295. DOI: 10.1016/j.indcrop.2010.12.014.
9. Chinchkar, D. S.; Satpute, S.T.; Kumbhar, N. R. Castor Oil as Green Lubricant–A Review. *Int. J. Eng. Res. Technol.* 2012, 1, 1–3.
10. Tanveer, S.; Sharma, U. C.; Prasad, R. Rheology of multigrade engine oils. *Indian J. Chem. Technol.* 2006, 13, 180–184.
11. Karmakar, G., and Ghosh, P. Green Additives for Lubricating Oil. *ACS Sustain. Chem. Eng.* 2013, 1, 1364–1370. DOI: 10.1021/sc400181g.
12. El–Gamal, I. M.; Atta, A. M.; Al–Sabbagh, A. M. Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* 1997, 76, 1471–1478. DOI: 10.1016/S0016–2361(97)00062–8.
13. Masjuki, H. H.; Maleque, M. A. Investigation of the anti–wear characteristics of palm oil methyl ester using a four–ball tribometer test. *Wear* 1997, 206, 179–186.
14. Castor oil based eco-friendly lubricating oil additives. M. Hoque, S. Paul and P. Ghosh, *Journal of Macromolecular Science, Part A, Pure and Applied Chemistry*, 2021, 58(5), 329-335.

Chapter III

1. Betton CI (2010) *Lubricants and Their Environmental Impact*. In: *Chemistry and Technology of Lubricants*, Eds. Mortier RM, Fox MF, Orszulik ST, Springer, The Netherlands, pp. 435-457.
2. Shanta, S. M., Molina, G. J., and Soloiu, V. (2011). Tribological effects of mineral-oil lubricant contamination with biofuels: A pin-on-disk tribometry and wear study. *Adv. Tribol.* doi:10.1155/2011/820795.
3. Ghosh, P., Hoque, M., and Karmakar. G. (2018). Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant. *Polym. Bull.* 75:501-514

4. Sharma, B. K., Adhvaryu, A., and Erhan, S. Z. (2009). Friction and wear behavior of thioether hydroxyl vegetable oil. *Wear* 42:353–358.
5. Karmakar, G., and Ghosh, P. (2015). Soybean oil as a biocompatible multifunctional additive for lubricating oil. *ACS Sustainable Chem. Eng.* 3: 19–25.
6. Ghosh P, Das T, Nandi D, Karmakar G, Mandal A (2010) Synthesis and characterization of biodegradable polymer: Used as a pour point depressant for lubricating oil. *Int J Polym Mater* 59: 1008–1017.
7. Liu M, Huang Z, Yang Y (2010) Analysis of biodegradability of three biodegradable mulching films. *J Polym Environ* 18: 148–154.
8. Chandure AS, Umare SS (2007) Synthesis, Characterization and Biodegradation Study of Low Molecular Weight Polyesters. *Int J Polym Mater* 56: 339–353.
9. Ghosh P, Karmakar G (2014) Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int J Ind Chem* 5: 7.
10. Tanveer, S., Sharma, U. C., and Prasad, R. (2006). Rheology of multigrade engine oils. *Indian J. Chem. Technol.* 13:180–184.
11. Karmakar, G., and Ghosh, P. (2013). Green additives for lubricating oil. *ACS Sustainable Chem. Eng.* 1:1364–1370.
12. El-Gamal, I.M., Atta, A. M., and Al-Sabbagh, A. M. (1997). Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* 76:1471–1478.
13. Masjuki, H. H., Maleque, M. A. (1997). Investigation of the anti-wear characteristics of palm oil methyl ester using a four-ball tribometer test. *Wear* 206: 179 –186.
14. Greener Lubricant Formulation: Rapeseed Oil Based Eco-Friendly Lube Oil Additives. P. Ghosh, S. Paul and D. Roy, *International Journal of Petroleum and Petrochemical Engineering*, 2020, 6(3), 29-37.

INDEX

A

Acrylic acid, 35, 36, 52, 53, 70

Additive, 1, 2, 19, 50, 74, 78, 122

AIBN, 20, 51

Alternaria alternate, 118, 123

Antioxidant, 2, 9, 19, 50, 91, 115

Anti-wear, 6, 7, 14, 16, 34, 38, 40, 50, 69, 75, 94, 97, 100

B

Base oil, 1, 11, 21, 24, 35, 36, 39, 48, 50, 55, 58, 70, 74, 78, 91, 94, 95, 99, 115, 116

Behenyl acrylate, 16, 51, 53, 54, 56, 57, 58

Behenyl alcohol, 52, 53

Biodegradability, 2, 10, 11, 90, 92, 94, 97, 101, 115, 118, 119, 123, 124

BZP, 35, 53, 54, 70, 72, 95, 116

C

Copolymer, 3, 4, 8, 15, 16, 19, 23, 25, 51, 54, 57, 91, 94, 98, 116, 120, 122, 124

Corrosion inhibitors, 50

Castor oil, 10, 90, 92, 93, 94, 95, 98, 100

D

1-Decene, 16, 17, 18, 20, 52, 54, 56, 58, 92

Detergent, 2, 7, 10, 14, 50, 94, 115

Disc diffusion method, 11, 97, 118,

Dispersant, 2, 7, 8, 10, 14, 19, 50, 70, 94, 115

Dodecyl acrylate, 10, 16, 18, 19, 20, 71, 72, 73, 75

E

Esterification, 36, 53, 71

Extreme pressure, 2, 14, 19, 69, 94, 115

F

Fatty acid, 5, 91, 95, 102, 115, 125

Four Ball Wear Test, 38, 75, 97, 118

Friction modifier, 2, 5, 6

Fungal pathogens, 11, 107, 118, 123

G

Graphite, 69

GPC, 11, 21, 37, 48, 55, 74, 96, 101, 117

H

Homopolymer, 16, 19, 20, 21, 36, 41, 51, 54, 56, 57, 72, 74, 92, 95, 96, 98, 100, 116

Hydroquinone, 35, 42, 53, 70, 71

I

Ionic liquid, 10, 16, 17, 33, 34, 38, 49, 41

Isodecyl acrylate, 10, 16, 19, 52, 53, 59

J

Ojoba oil, 91, 92

K

Kinematic viscosity, 16, 22, 37, 55

L

Liquid crystal, 70

Lubricant, 1, 3, 4, 6, 14, 19, 21, 24, 34, 50, 58, 75, 78, 90, 94, 100, 114, 115, 122

Lubricating oil, 1, 11, 17, 33, 51, 68, 69, 80, 90, 94, 99, 115

M

Mahua oil, 90

Maleic anhydride, 3, 8, 51

Mannich base, 8

N

Nanoparticle, 17, 69, 70, 72, 73, 76, 77, 78, 79

Number average molecular weight, 23, 26, 37, 55, 74,

P

Percent weight loss, 26, 47, 56, 58, 64

PDI, 26, 43, 56, 58, 60

Polyisobutylene, 8

Polymethacrylate, 51

Pour point, 2

Pour point depressant, 2, 3, 10, 14, 19, 20, 25, 50, 55, 57, 70, 74, 78, 92, 100, 116

Photo micrographic image, 48

R

Radical polymerization, 54, 95

Rapeseed oil, 10, 90,

Ricinoleic acid, 94, 102

S

Shear Stability Index, 16, 22, 40, 44

Soil burial test, 11

Soya bean oil, 90

Sunflower oil, 90, 91, 92

T

Thermogravimetric analysis, 21, 39, 56, 74, 77, 79, 96

Thickening effect, 5, 15

TMS, 37, 55, 73, 96, 117

Triglyceride, 90

V

Vegetable oil, 3, 4, 7, 10, 88, 90, 91, 94, 115

Vinyl acetate, 51, 91

Viscosity index, 1, 4, 11, 14, 16, 18, 19, 20, 22, 24, 37, 50, 55, 58, 64, 70, 74, 78, 90
91

Viscosity modifier, 2, 4, 10, 16, 41, 74, 78, 79, 91

W

Wear scar diameter, 40, 75, 97, 118

Weight average molecular weight, 23, 26, 55, 58, 74, 96, 98, 117

X

XRD, 11, 73, 76, 77, 79, 85

Z

Zinc dialkyl dithiophosphate, 7, 10

Zinc dithiophosphate, 7

Greener Lubricant Formulation: Rapeseed Oil Based Eco-Friendly Lube Oil Additives

Sujan Paul, Dibakar Roy, Pranab Ghosh*

Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India

***Corresponding Author:** Pranab Ghosh, Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India

Abstract: Growing environmental issues over the use of mineral oil based lubricants in automobile sectors have led to an increased attention towards the use of greener environmentally benign bio-lubricants. Working in this direction, the present report describes the synthesis of homopolymer of rapeseed oil and its copolymer with styrene. Characterization of the polymer was carried out by spectral (FT-IR, NMR), GPC and thermo gravimetric analysis. Biocompatibility and multifunctional performances [viscosity index improver, pour point depressant and antiwear] in lube oil compared to conventional additives was investigated using standard ASTM methods. Biodegradability was determined by disc diffusion and soil burial degradation method.

Keywords: Rapeseed oil, styrene, viscosity index improver, pour point depressant, antiwear, biodegradability.

1. INTRODUCTION

The base oil or the lubricating oils is usually of petroleum origin. It is a complex mixture of paraffinic, aromatic and naphthenic hydrocarbons and the main function of it is to lubricate the engine components. The addition of additives to lubricating oil is very essential for smooth functioning of modern engines. Lubricants i.e. the suitable formulated product of lube oil and additives are generally liquids or semi-liquids and are used for the longevity and better performances of automotive engines. The key functions of a lubricant are to keep moving parts apart, reduce friction, protect against wear, transfer heat, prevent rust and corrosion, as antioxidant, as detergents/dispersants etc.

Although, the petroleum based lubricants exhibit satisfactory performance but they are not environmental benign due to their eco-toxicity and non-biodegradability. Strict regulations are, therefore, currently being imposed in a number of countries on lube oil-based lubricants together with their non-biodegradable toxic wastes materials (Betton et al., 2010). This increasing environmental awareness has provided researchers with the impetus to search for some new, environmentally benign, multifunctional additives. In this hunt, easily available vegetable oils have been considered as a potential candidate.

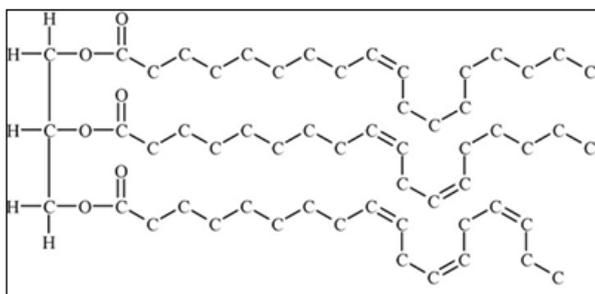
Moreover, they show excellent antiwear properties (Shanta et al., 2011), enhanced extreme pressure (EP) additive performance, exhibited high viscosity index (Ghosh et al., 2018) and low volatility (Sharma et al., 2009). There are lots of research papers where chemically modified vegetable oils have been used as additive for base oil or base stocks in the formulation of bio-lubricant (Karmakar et al., 2015).

Rapeseed oil (RO) is interesting for its richness in mono-unsaturated fatty acids, and for its low content in saturated fatty acids in comparison to other edible oils. Rapeseed oil is also frequently used in blends of vegetable oils (sunflower, soybean, corn, etc.) to improve the fatty acid profile of the vegetable oils. It has tremendous application in the field of nutritional and health claims. Apart from its above utilities, its unique composition and proven thermal stability over the other edible vegetable oils, points towards the additive properties of its suitably prepared polymers.

However research articles regarding such an application of RO as green multifunctional additive for lubricant are not yet reported.

Therefore, in this work we have synthesized homopolymer of RO (HRO) and copolymer of it with styrene in different percentage ratios to get thermally stable, cost effective as well as eco-friendly

multifunctional lubricant additives. Performance evaluation of the prepared polymeric additives was carried out as viscosity index improver, pour point depressant and antiwear according to respective ASTM method.



Molecular structure of rapeseed oil

2. EXPERIMENTAL SECTION

2.1. Materials

Rapeseed oil (about 90% unsaturation) was collected from a local grocer's shop. Toluene (GC 99.5%) was obtained from Merck Specialties Pvt. Ltd., (India). Benzoyl peroxide (LOBA chemie, India) was used after recrystallisation from chloroform- methanol mixture. Styrene (GC 99.8%, Thomas Baker Chemicals Pvt. Ltd., India) and the mineral base oil SN150 was collected from IOCL, Dhakuria, West Bengal, India. The physical properties of the rapeseed oil and base oil are shown in table 1. Fungal specimens were collected from the sister Department, Department of Microbiology, North Bengal University, West Bengal, India for testing the biodegradability of the polymers.

Table1. Properties of Rapeseed oil and Base oil

Rapeseed oil		Base oil	
Properties	Values	Properties	Values
Saponification index(mg/g)	167-74	Density at 313 K, kg.m ⁻³	868.03
Iodine index(mg/g)	97-100	Viscosity at 313 K	20.31×10
Refractive index at 50°C	1.462	Viscosity at 373 K	3.25 ×10
Density(g/ml)	0.916	Viscosity index	85
Saturated fatty acid (%)	7.36	Pour point (°C)	-6
Mono unsaturated fatty acid (%)	63.27	Cloud point (°C)	-8
Polyunsaturated fatty acid(%)	28.14	-	-
Oleic acid(g)	61.744	-	-
Linoleic acid ω-6(g)	19.005	-	-
α-Linoleic acid ω-3(g)	9.137	-	-

2.2. Synthesis of the Polymers

The copolymers were prepared by taking the monomers, RO and styrene at different ratios (table 2) in presence of BZP initiator by free radical polymerization method using toluene as solvent. The polymerization was accomplished in a three necked round bottom flask fitted with a magnetic stirrer, thermometer, condenser and an inlet for the introduction of nitrogen. In the flask, definite amount of rapeseed oil and styrene was heated to 80 °C and maintained for 20 minutes. Initiator BZP (0.5% w/w, with respect to the total monomer) was then added and refluxed for 6 hour. The detail procedure is mentioned in our previous publication (Ghosh et al., 2018).

Table2. Percentage composition and TGA values of the prepared polymers

Polymer Code	% Composition of monomers(w/w) in the feed		TGA values	
	RO	Sty	Decom. Temp.	PWL
P-1	100	0	160/320	28/78
P-2	98	2	210/355	24/85
P-3	96	4	266/382	17/80
P-4	94	6	268/382	19/81
P-5	92	8	268/384	18/79

RO = Rapeseed oil; Sty = Styrene; Decom. Temp.=Decomposition temperature; PWL= Percentage Weight loss.

2.3. Spectroscopic Measurements

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

2.4. Molecular Weight Determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at room temperature at a flow rate of 1mL/min.

2.5. Thermo Gravimetric Analysis (TGA)

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

3. PERFORMANCE EVALUATION

3.1. Evaluation of Viscosity Index

The change of viscosity of the lubricant with increasing temperature is expressed in terms of a parameter called Viscosity index (VI). It was calculated according to ASTM D 2270-10. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40 °C and 100 °C. The effect of additive concentration on VI was investigated by using different concentrations ranging from 1% - 5% (w/w).

3.2. Evaluation of Pour Point

Pour point of the additive blended lube oil was determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India).

3.3. Evaluation of Anti Wear Performance

The antiwear performance of the lubricant compositions in terms of wear scar diameter (WSD) was determined by Four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method. In this experiment 392 N (40 Kg) load at 75 °C for 60 min was applied to measure the wear scar diameter. The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm respectively.

3.4. Biodegradability Test [dks]

Several tests have been devised for measuring the biodegradability of vegetable oil based additives, as they have an inherent biodegradability compared to the synthetic additives. In the present investigation it was tested by (a) the disc diffusion method against fungal pathogens (Ghosh et al., 2010) and (b) the soil burial degradation test.

3.5. Disc Diffusion (DD) Method

In this method, biodegradation of the prepared additives were tested against four different fungal pathogens, viz. *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA) and *Colletotrichum gloeosporioides* (CG) in a bacteriological incubator (Sigma Scientific Instruments Pvt. Ltd., India). Culture media for the fungal strains were prepared by mixing potato extract, dextrose, and agar powder in a 10:1:1 proportion by weight. 1.0 g of each of the polymeric additives were placed in Petri dishes with 2 g of the culture media and incubated at 310 K for 30 days with the different fungal pathogens. The fungal growth was confirmed by a change of colour from yellow to blackish. After 30 days, the additive samples were recovered from the fungal media and washed with chloroform, purified and dried. Finally, the weight loss for each of the samples was calculated.

3.6. Soil Burial Degradation Test (SBD Test)

In this test method the microorganisms attacks the surface of the polymer film (Liu et al., 2010). 1.0 g of each of the polymeric additive was taken to produce the polymer films. The films so obtained were then buried in soil (containing the microorganisms) in a bacteriological incubator. The soil was placed in a tray, the relative humidity was maintained to 50–60% with the help of a humidity chamber and the temperature was set at 303 K. The soil used in this study was taken from the campus of the North Bengal University (West Bengal, India) with pH 7.3 and moisture content of 25%. The buried polymer films

In the ^{13}C NMR of the copolymer, the peaks in the range of 14.14 - 41.03 ppm were due to carbons of all CH_3 and CH_2 groups. The peaks at 58.13 ppm indicate the methine carbons of $-\text{CH}-$ of $-\text{COCH}-$ group. The peaks in the range of 60 - 62.08 ppm represent the carbons of $-\text{OCH}_2$ groups. The $-\text{CH}_2$ carbons of $-\text{OCOCH}_2-$ group of rapeseed oil showed peaks in the range of 64.61– 68.99 ppm. The aromatic carbons appear in the range of 127.93 -130.88 ppm. The peaks in the range of 165.65 - 173.00ppm confirms the carbons of ester carbonyl groups (**figure 3**).

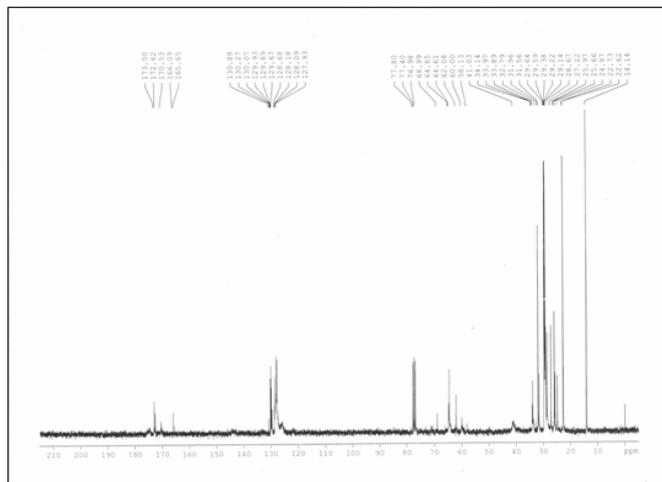


Figure3. A representative ^{13}C NMR spectra of rapeseed oil-styrene copolymer

In case of homopolymer of rapeseed oil, the IR absorption band at 1741 cm^{-1} (**figure 4**) showed the presence of ester carbonyl group. In the ^1H NMR spectra of homopolymer of rapeseed oil (**figure 5**), the peaks in the range of 4.12- 4.33 ppm indicate the protons of $-\text{COOCH}_2$ group of rapeseed oil, the methyl protons appear in the range of 0.86 - 0.90 ppm, the methylene protons in the range of 1.26 - 1.62 ppm and the methine protons appeared in the range of 2.29 - 2.34 ppm for the alkyl chains (**figure 5**). In the ^{13}C NMR spectra of homopolymer of rapeseed oil, the ester carbonyl group appears at 173.98 ppm, the carbons of $-\text{OOCH}_2$ group of appears at 62.07 – 68.91 ppm (**figure 6**).

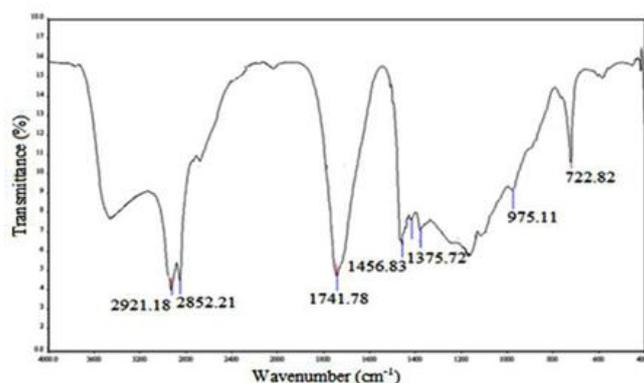


Figure4. FT-IR spectra of the homopolymer of rapeseed oil

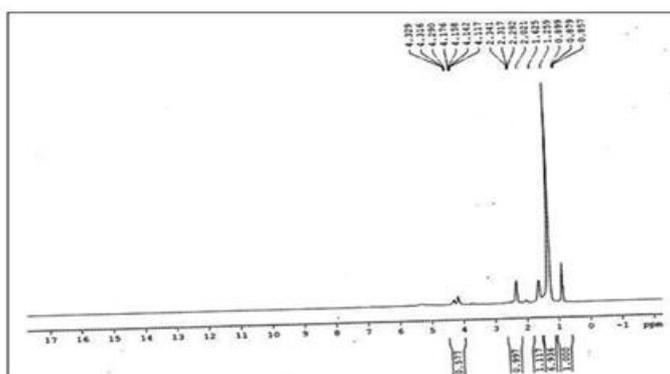


Figure5. ^1H - NMR spectra of homopolymer of rapeseed oil

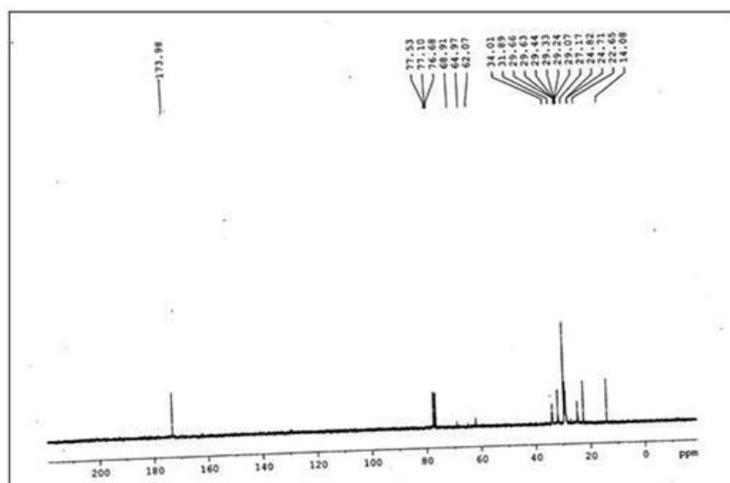


Figure6. ^{13}C - NMR spectra of homopolymer of rapeseed oil

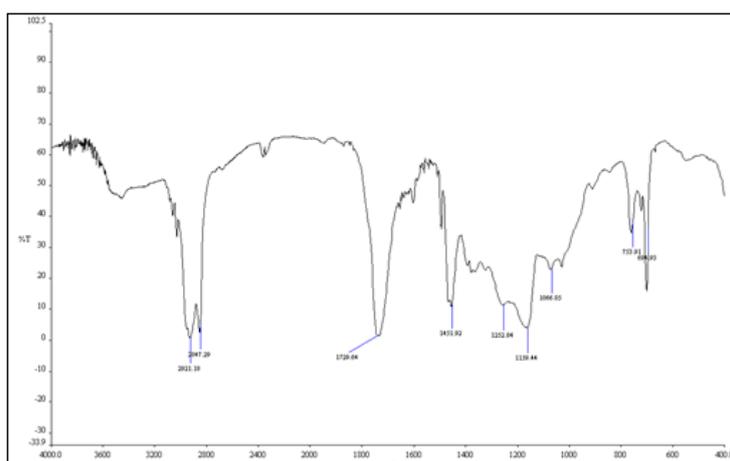


Figure7. A representative FT-IR spectrum of the copolymer after biodegradability test

4.2. Molecular Weight Data Analysis

The experimental values of number average molecular weights (M_n) and weight average molecular weights (M_w) of the prepared polymers (P-1 to P-5) are given in table 3. From the experimental data, it is seen that among the five polymers, P-5 has highest molecular weight. Moreover, it is also observed that with increasing the percentage of styrene in the backbone of rapeseed oil, the molecular weight increases. Therefore, percentage of styrene has a significant role during polymerization.

Table3. Molecular weight of the prepared polymers

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

4.3. Analysis of TGA Data

The TGA values of the five polymers are given in table 2. From the table, it is clear that the thermal degradation of polymer P-1 is higher than the other polymers which signify that P-1 is thermally less stable. The thermal degradation of polymers P-3, P-4 and P-5 are almost similar. In case of polymer P-1, major decomposition starts at 160 °C with about 30% weight loss. For polymers P-3, P-4 and P-5, major decomposition starts approximately at 268 °C with 18% weight loss. Due to copolymerization of rapeseed oil with styrene, the thermal stability increases. Therefore, copolymerization with styrene has a significant importance to improve the thermal stability.

4.4. Analysis of Viscosity Index Values

VI was calculated at different concentrations ranging from 1% to 5% (w/w) to the base oil. The experimental values of VI are given in table 4. From the table, it is found that VI values increase with increasing the concentration of polymers in base oil. The viscosity of lubricating oil decreases with increasing temperature but expansion of polymer molecules take place with increasing temperature and due to this, the size of micelle increases. This increased in micelle size interfere the reduction of the viscosity of the lubricant (Tanveer et al., 2006). Moreover, with increasing the concentration of polymer in lubricating oil leads to an increase in the total volume of polymer micelle in lube oil and improves the VI property (Karmakar et al., 2013). It has been observed that VI value increases by incorporation of styrene in the backbone of homopolymer of rapeseed oil. This may be due to higher crosslink density of the copolymers. The copolymer P-5 has highest effect on VI increment followed by P-4, P-3, P-2 and P-1. The higher values VI in case of P-5 containing maximum percentage of styrene in the feed, are due to greater volume of the solvated additive molecule i.e. micelle compared to others which may be associated with its higher average molecular weights and lower PDI value.

Table4. Viscosity index (VI) values of polymer blended base oil

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

4.5. Analysis of Pour Point Values

The pour points of the lubricants prepared by blending the polymers at different concentration levels ranging from 1%–5% (w/w) are shown in table 5. All the polymers are effective as PPD and the efficiency as pour point increases with increasing the concentration of polymers up to certain limit (4% concentration). This indicates that at this concentration, the polymer interacts with the paraffinic wax of base oil effectively and decreases the size of crystals of the paraffinic wax (El-Gamal et al., 1997). Among the prepared five polymers, P-4 showed better performance as PPD.

Table5. Pour point values of polymer blended base oil

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

4.6. Analysis of Anti Wear Properties

The tribological properties of the lubricant compositions were determined by measuring WSD through FBWT apparatus applying 392 N load and values are given in table 6. The anti wear performance of the lube oil is significantly improved when the polymers are blended with it and is reflected in the lower WSD values of the lubricant compositions. The copolymers showed better result compared to the homopolymer. The polymer P-5 at 5% concentration showed highest reduction in WSD values compared to the other polymers. This indicates that the film formed by the lubricant between the two moving metal surfaces is very strong. It may be due to higher molecular weight and hence higher number of polar side chains of the ester carbonyl groups and hydroxyl groups present in rapeseed oil (Masjuki et al., 1997). The contribution of higher percentage of styrene in the polymer feed has also played a significant role in it with its aromatic ring structure.

Table6. Antiwear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition

Polymer Code	WSD of lubricant (in mm) at different polymer concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	1.116	1.067	1.044	1.025	1.007	0.964
P-2	1.116	1.065	1.037	1.023	1.003	0.957

P-3	1.116	1.060	1.028	1.018	0.992	0.955
P-4	1.116	1.052	1.022	1.002	0.958	0.931
P-5	1.116	1.031	1.013	0.992	0.943	0.911

4.7. Analysis of Biodegradability Test

Biodegradability test results (table 7) with the homo (P-1) and copolymers (P-2 to P-5) showed significant biodegradability against the fungal pathogens, *Calletotricheme camellia* and *Alternaria alternata*, though the result is, as expected, better for the homopolymer of rapseed oil. A close observation of the test results showed considerable biodegradation for all the samples. The analysis of the SBD tests indicated that the degradation of the additives studied increased continuously with the increasing number of days. Further, both the homo and copolymer of showed significant weight losses against the fungal pathogens, especially against *Alternaria alternate* (AA), in the DD test. Moreover, as expected for zero styrene content and owing to the presence of the natural monomer unit, the HRO (P-1) showed the highest biodegradability among all the additives in both of the tests. The FT- IR peaks of the polymer P-1 showed shift in the peak positions and considerable decrease in peak height and intensity after the DD test. The shift and the decrease in the IR peak intensities of the polymers before and after the biodegradation tests together with the PWL of the polymers confirmed the biodegradable nature of the prepared polymers.

Table7. Result of biodegradability test by the disc diffusion method and soil burial degradation.

Sample	Weight loss in disc diffusion method(g) [Pathogens used]					Weight loss in soil burial degradation (g)
	[CC]	[FE]	[AA]	[CG]	[CE]	
P-1	0.45	0	0.62	0	0	0.47
P-2	0.38	0	0.54	0	0	0.35
P-3	0.30	0	0.48	0	0	0.30
P-4	0.26	0	0.39	0	0	0.25
P-5	0.22	0	0.35	0	0	0.19

CC = *Calletotricheme camellia*; FE = *Fussarium equisetae*; AA = *Alternaria alternata*; CG = *Colletrichum gleosporides*; CE= *Curvularia eragrostidies*.

5. CONCLUSION

From the above study it was found that the copolymer of rapeseed oil with styrene showed excellent multifunctional performance for base oil. As a viscosity index improver, pour point depressant and antiwear additive, the copolymers are found more effective than the homopolymer. In addition, the presence of rapseed oil in the additive composition introduces excellent biodegradability too, in the additive. Average molecular weight and thermal stability of the copolymers increases with the increase in the percentage of styrene. Therefore, the above study is definitely a potential approach to formulate a greener lubricant composition with excellent multifunctional additive properties for lube oil.

ACKNOWLEDGEMENT

The authors thank to UGC, New Delhi for financial support. Special thanks to IOCL, India for providing the base oil.

REFERENCES

- [1] Betton CI (2010) Lubricants and Their Environmental Impact. In: Chemistry and Technology of Lubricants, Eds. Mortier RM, Fox MF, Orszulik ST, Springer, The Netherlands, pp. 435-457.
- [2] Chandure AS, Umare SS (2007) Synthesis, Characterization and Biodegradation Study of Low Molecular Weight Polyesters. *Int J Polym Mater* 56: 339–353.
- [3] El-Gamal, I.M., Atta, A. M., and Al-Sabbagh, A. M. (1997). Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* 76:1471–1478.
- [4] Ghosh, P., Hoque, M., and Karmakar. G. (2018). Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant. *Polym. Bull.* 75:501-514
- [5] Ghosh P, Das T, Nandi D, Karmakar G, Mandal A (2010) Synthesis and characterization of biodegradable polymer: Used as a pour point depressant for lubricating oil. *Int J Polym Mater* 59: 1008–1017
- [6] Karmakar, G., and Ghosh, P. (2013). Green additives for lubricating oil. *ACS Sustainable Chem. Eng.* 1:1364–1370.

- [7] Karmakar, G., and Ghosh, P. (2015). Soybean oil as a biocompatible multifunctional additive for lubricating oil. *ACS Sustainable Chem. Eng.* 3: 19–25.
- [8] Ghosh P, Karmakar G (2014) Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int J Ind Chem* 5: 7
- [9] Liu M, Huang Z, Yang Y (2010) Analysis of biodegradability of three biodegradable mulching films. *J Polym Environ* 18: 148–154.
- [10] Masjuki, H. H., Maleque, M. A. (1997). Investigation of the anti-wear characteristics of palm oil methyl ester using a four-ball tribometer test. *Wear* 206: 179 –186.
- [11] Shanta, S. M., Molina, G. J., and Soloiu, V. (2011). Tribological effects of mineral-oil lubricant contamination with biofuels: A pin-on-disk tribometry and wear study. *Adv. Tribol.* doi:10.1155/2011/820795.
- [12] Sharma, B. K., Adhvaryu, A., and Erhan, S. Z. (2009). Friction and wear behavior of thioether hydroxyl vegetable oil. *Wear* 42:353–358.
- [13] Tanveer, S., Sharma, U. C., and Prasad, R. (2006). Rheology of multigrade engine oils. *Indian J. Chem. Technol.* 13:180–184.

Citation: *Sujan Paul, Dibakar Roy, Pranab Ghosh, “Greener Lubricant Formulation: Rapeseed Oil Based Eco-Friendly Lube Oil Additives”, International Journal of Petroleum and Petrochemical Engineering, 6(3), pp. 29-37. DOI: [https:// doi.org/10.20431/2454-7980.0603004](https://doi.org/10.20431/2454-7980.0603004)*

Copyright: © 2020 Authors, this is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Dodecyl Acrylate and its Copolymer With Styrene and 1-Decene: A Study of Shear Stability, Thickening and Viscosity Index Properties

^aSujan Paul, ^bMainul Hoque, ^aPranab Ghosh*

^aNatural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling-734013, India

^bDepartment of Chemistry, Kokrajhar Govt. College, Kokrajhar- 783370, Assam, India

Abstract: Homo polymer of dodecylacrylate (DDA) and two copolymers with styrene and 1-decene by using azobisisobutyronitrile (AIBN) as initiator were synthesised. All the prepared polymers were characterised by FT-IR and NMR. Gel Permeation Chromatography (GPC) method was used to determine the molecular weight. The degradation stability towards mechanical shearing (shear stability) of the homo polymer and copolymers at different concentration level has been investigated. With a view to understanding the relationship between the shear stability of the polymer and thickening effect, the thickening abilities of the polymer were also determined and compared. Viscosity index and pour point properties of the homo polymer and copolymers were also determined in base oil.

Key words: Homo polymer, copolymer, shear stability, thickening effect, pour point

Introduction

Modern lubricants are composed of a base fluid and a package of chemical additives. When additives are added to the base fluid, they can improve the properties already present or add some new properties (Ghosh et al., 1998). The most important additives which are commonly added to the base fluid are viscosity index improver (VII), pour point depressant (PPD), antiwear, antioxidant, dispersant, extreme pressure additives etc.

The viscosity index is an indicator which indicates the change in viscosity at high temperature. A higher viscosity index indicates the small change in viscosity at higher temperature. Viscosity index improvers are long chain, high molecular weight polymeric additives. They function by increasing the relative viscosity of base fluid more at high temperatures than at low temperatures (Mohamed et al., 1994). Oil thickening property of the additives is a direct measure of percent increase in the viscosity of the base fluid for addition of unit amount of

additive. This property indicates extent of interaction of the additive with the base fluid. Greater is the thickening property; greater is the extent of interaction. Shear stability is one of the important criteria that determine the suitability of a viscosity index improver in a lubricant composition which is an indicator to indicate the amount of viscosity of oil, may lose during operation (Ghosh et al., 2011).

The pour point is the lowest temperature at which the base fluid stops its flowing. The base fluid contains some dissolved paraffinic wax. At low temperature, the wax crystallizes to form a rigid structure and trap the oil molecules. As a result, the oil will lose its capability to flow. To overcome this problem, some polymeric additives are used as pour point depressant (PPD). The PPD functions by inhibiting the formation of a wax crystal structure that occurs at low temperature (Abdel-Azim et al., 2006).

In this article, we have prepared homo polymer of dodecylacrylate and two copolymers with styrene (10%, w/w) and 1-decene (10%, w/w) by using AIBN as initiator and investigated the efficiency of the additives as viscosity index improver and pour point depressant in base fluid. Shear stability and thickening property of each additive in base fluid have also been investigated and reported here.

EXPERIMENTAL SECTION

Synthesis of the polymers: The copolymers were prepared by taking the monomers of DDA (90%, w/w) and styrene or 1-decene (10%, w/w) in presence of AIBN initiator without any solvent. The polymerization was completed in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. The mixture of monomers was heated to 85 °C and then AIBN (0.5% w/w, with respect to the total monomer) was added and continuously heated for 5 hour keeping the temperature constant at 85°C. After the completion of reaction time, the product was poured into methanol. A precipitate appeared which was filtered off and dried. The homo polymer of DDA was also prepared in the similar procedure. The prepared homo polymer and two copolymers with styrene and 1-decene were designated as P-1, P-2 and P-3 respectively.

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

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

Thermo gravimetric analysis (TGA): The thermo gravimetric analysis was carried out on a mettler TA – 3000 system, at a heating rate of 10°C / min.

Determination of shear stability: Shear stability of a lubricant is one of the essential criteria that determine the suitability of the additive in a lubricant formulation. The loss of viscosity of a lubricant under shearing condition can be expressed in terms of permanent viscosity loss (PVL) or permanent shear stability index (PSSI). The PVL/PSSI value was determined as per ASTM D-3945 method by the following relation (Ghosh et al., 2011).

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

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

Where V_i = Kinematic viscosity of lubricant before shearing at 100 ° C

V_s = Kinematic viscosity of lubricant after shearing at 100 ° C

V_o = Kinematic viscosity of lube oil at 100 ° C

Higher the PVL/PSSI value, lower is the shear stability of the polymer.

Evaluation of Thickening Property

Kinematic viscosity of the lube oil and that of additive blended lube oil were evaluated at 40° C and 100° C. Thickening power of the lubricant was determined by calculating the percent increase in viscosity of the lubricant composition by the addition of unit amount of additive.

Determination of viscosity index (VI): VI of the lubricant composition was determined according to ASTM D 2270-10 method. The kinematic viscosity of the lubricant composition was determined at 40° C and 100° C. Different concentrations of additives ranging from 1% - 5% (w/w)] were used to study the effect of additive concentration on VI.

Determination of pour point: Pour point of the lubricant composition was determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different concentrations ranging from 1%- 5% (w/w).

RESULTS AND DISCUSSION

Spectroscopic analysis: The homopolymer of DDA (P-1) exhibited IR absorption band at 1736.6 cm^{-1} for the ester carbonyl group. The two peaks at 2858.5 cm^{-1} and 2922 cm^{-1} were due to the characteristic of CH_3CH_2 -group. The peaks at 1464.8, 1400.2, 1229, 1214 and 1150.5 cm^{-1} due to CO stretching vibration and absorption bands at 1064.2, 710.4 and 690 cm^{-1} were due to bending of C-H bond. In the ^1H NMR of homopolymer, methyl and methylene protons appeared in the range of 0.890 to 1.936 ppm. A broad peak at 3.938 ppm confirmed the

protons of $-\text{OCH}_2$ group. There is no any peak in the range of 5-6 ppm, indicated that polymerisation was completed successfully. In the ^{13}C NMR of homopolymer, the peaks at 176.54 – 177.82 ppm indicated the presence of ester carbon. There was no any peak in the range of 120-150 ppm and it confirmed the polymerization.

In the IR spectrum of copolymer (P-3), the ester carbonyl group appeared at 1730.4 cm^{-1} . Peaks at 746.3 cm^{-1} and 706 cm^{-1} indicated the C-H bond of the phenyl group of styrene. In the ^1H NMR, multiplet peak in the range of 3.904 - 4.225 ppm indicated the protons of $-\text{OCH}_2$. A broad peak in the range of 7.018 - 7.322 ppm indicated the protons of phenyl group. No peak in the range of 5-6 ppm indicated the confirmation of polymerisation. In the ^{13}C NMR, the peaks in the range of 176.2 - 177.74 ppm confirmed the presence of ester carbons. The carbons in the phenyl group appeared in the range of 125.00 - 128.52 ppm. All the spectroscopic data of copolymer P-2 was found approximately same with the homo polymer, P-1.

Analysis of Molecular weight and TGA: The experimental value of number average molecular weight (M_n), weight average molecular weight (M_w) and TGA values of the prepared additives (P-1 to P-3) are given in table 1. From the data, it is observed that the copolymer P-3 have the highest molecular weight followed by homo polymer P-1. From the TGA values, it is observed that the additive P-3 is thermally more stable than P-2 and P-1. It may be due to presence of styrene moiety in P-3 which supports in thermally stability.

Analysis of shear stability: PVL and PSSI values were calculated in additive doped lube oil at different concentration ranging from 1% - 5% (w/w) at 100°C . The experimental values are listed in table 2. From the values, it is found that copolymers are more stable under shear (lower PVL/PSSI value) than homo polymer. Among the three additives, the order of stability under shear is $\text{P-3} > \text{P-2} > \text{P-1}$. Moreover, it is also observed that with increasing the concentration of additive to the base oil, the shear stability decreases (higher PVL/PSSI value) (Rein et al., 1987).

Analysis of thickening Property

Thickening power of both homo polymer and copolymers are depicted in table 3 which indicated a gradual decrease with the increase in concentration of the additive. This may be because of the fact that the additive molecules are assumed to be a coiled like aggregation with increase in concentration to the base oil (Ghosh and Karmakar, 2012). From the results, it was observed that the thickening power of the additive P-1 was higher than that of additives P-2 and P-3. This indicated that from the point view of fuel economy, the additive P-1 is better than additives P-2 and P-3.

Analysis of viscosity index (VI) values: VI values of the prepared additives in base oil listed in table 4. The viscosity of base oil without any additive decreases with increasing temperature but when additives are added to the base oil, the decrement of viscosity does not occur. At high temperature, additive molecules in base oil medium swell up and as a result, the size of micelle enhances. This enhanced in micelle size resists the reduction of the viscosity of the lubricant composition and hence improves VI. It was also found that at higher concentration of the lubricant composition, the VI values are higher. This is because at higher concentration, the micelle size increases and hence improves the VI property (Karmakar and Ghosh, 2013; Tanveer and Prasad, 2006). The copolymer P-3 has better VI property than P-2 and P-1. It may be due to higher molecular weight of P-3.

Analysis of Pour point (PP) values: The pour points of the base oil as well as base oil containing different additives at different concentration levels [1%–5% (w/w)] are given in table 5. From the experimental values, it is observed that base oil containing additives have lower PP than base oil and hence the prepared additives can be used as PPD. Moreover, it is observed that the efficiency as PPD increases with increasing concentration. The reason behind it may be, at higher concentration, the interaction between the additive and paraffinic wax present in base oil is more effective (Al-Sabagh et al., 2012; Chen et al., 2010). All the three prepared additives are approximately equally effective as PPD. The additive P-3 showed slightly higher performance as PPD than the others two additives.

Conclusions

The study indicated that the copolymers are more stable under shear than homo polymer but the thickening property of homo polymer is greater than copolymers. This study also indicated that the efficiency of the prepared additives as viscosity index improver and pour point depressant increases with increasing concentration of the additives in base oil. Viscosity index property of the additives is directly proportional to the average molecular weight but there is no any correlation between pour point and average molecular weight.

Acknowledgement

The authors thank to UGC, New Delhi for financial support and thank also to IOCL, India for providing the base oil.

References

- Abdel-Azim, A. A. A., Nassar, A. M., Ahmed, N. S., & Kamal, R. S. (2006). Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. *Pet. Sci. Technol.*, 24, 887–894.
- Al-Sabagh, A. M., Sabaa, M. W., Saad, G. R., Khidr, T. T., & Khalil, T. M. (2012). Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egyptian Journal of Petroleum*, 21, 19-30.
- Chen, W. H., Zhao, Z. C., & Yin C. Y. (2010). The interaction of waxes with pour point depressants. *Fuel*, 89, 1127-1132.
- Ghosh, P., & Karmakar, G. (2012). Synthesis and Characterization of Polymyristyl Acrylate as a Potential Additive for Lubricating Oil. *American Journal of Polymer Science*, 2(1), 1-6.
- Ghosh, P., Das, T., & Nandi, D. (2011). Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate. *American Journal of Polymer Science*, 1(1), 1-5.
- Ghosh, P., Pantar, A.V., Rao, U. S., & Sarma, A. S. (1998). α - Olefin Copolymers as Viscosity Modifier Additives in Lubricating Oil. *Ind. J. Chem. Technol.*, 5, 309-314.
- Karmakar, G., & Ghosh, P. (2013). Green additives for lubricating oil. *ACS Sustainable Chem Eng.*, 1, 1364–1370.
- Mohamed, M. M., Hamdi, H. A., & Mohamed, F. E. J. (1994). Multi-functional viscosity index improvers. *Chem. Tech. Biotechnol.*, 60, 283-289.
- Rein, S. W., Alexander, D. L., Cryvoff, S. A., & Dahlstrom, M. A. (1987). Investigation of engine oil shears stability in laboratory test and road test. *SAE paper No. 872047*.
- Tanveer, S., & Prasad, R. (2006). Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.*, 13, 398–403.

Table 1: Average molecular weight and TGA values of the prepared polymers

Polymer code	Molecular weight			TGA value	
	M _n	M _w	PDI	Decom. Tem.	PWL
P-1	7731	14155	1.83	172/350	26/84
P-2	6016	8638	1.44	170/320	22/90
P-3	13958	23737	1.70	245/420	20/78

M_n = Number average molecular weight; M_w = Weight average molecular weight; PDI = Polydispersity index; Decom.Tem.=Decomposition temperature; PWL=Percent weight loss

Table 2: PVL and PSSI Values of the Additives Doped Base Oil

Mass fraction	KV (at 373K)						PVL			PSSI		
	before shear			after shear			P-1	P-2	P-3	P-1	P-2	P-3
	P-1	P-2	P-3	P-1	P-2	P-3						
0.000	3.68	3.68	3.68	3.68	3.68	3.68	0.00	0.00	0.00	0.00	0.00	0.00
0.010	3.84	3.82	3.80	3.83	3.81	3.80	0.23	0.18	0.13	5.76	5.10	4.03
0.020	3.95	3.93	3.92	3.93	3.91	3.90	0.53	0.43	0.38	7.77	6.80	6.35
0.030	4.16	4.14	4.12	4.11	4.10	4.09	1.03	0.84	0.77	9.01	7.67	7.25
0.040	4.29	4.26	4.25	4.22	4.20	4.19	1.67	1.35	1.27	11.84	10.00	9.54
0.050	4.49	4.47	4.46	4.39	4.38	4.37	2.24	2.07	1.97	12.40	11.78	11.34

Table 3: Thickening power (THK) of the Additives Doped Base Oil

mass fraction of the additive	THK(at 313K)			THK(at 373K)		
	P-1	P-2	P-3	P-1	P-2	P-3
0.010	3.07	2.97	2.92	4.23	3.71	3.36
0.020	2.21	2.14	2.12	3.66	3.39	3.20
0.030	1.90	1.87	1.86	3.31	3.12	2.98
0.040	1.74	1.72	1.71	3.12	2.93	2.83
0.050	1.66	1.64	1.63	2.41	2.28	2.21

Table 4: VI values of the Additives Doped Base Oil

mass fraction of the additive	VI		
	P-1	P-2	P-3
0.000	82	82	82
0.010	90	90	99
0.020	99	98	102
0.030	108	107	110
0.040	112	110	118
0.050	118	115	126

Table 5: Pour Point (PP) of the Additives Doped in Base Oil

mass fraction of the additive	Pour Point (°C) of base oils in presence of		
	P-1	P-2	P-3
0.000	-6	-6	-6
0.010	-9.5	-9.1	-8.8
0.020	-10.3	-10.1	-9.7
0.030	-11.4	-11.0	-10.7
0.040	-12.8	-12.1	-11.9
0.050	-13.2	-12.9	-12.3