

Synthesis and performance evaluation of organic polymeric additives for lube and crude oils

A Thesis submitted to the University of North Bengal

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In
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December-2019

DECLARATION

I declare that the thesis entitled “**Synthesis and performance evaluation of organic polymeric additives for lube and crude oils**” has been prepared by me under the guidance of Prof. Pranab Ghosh, Department of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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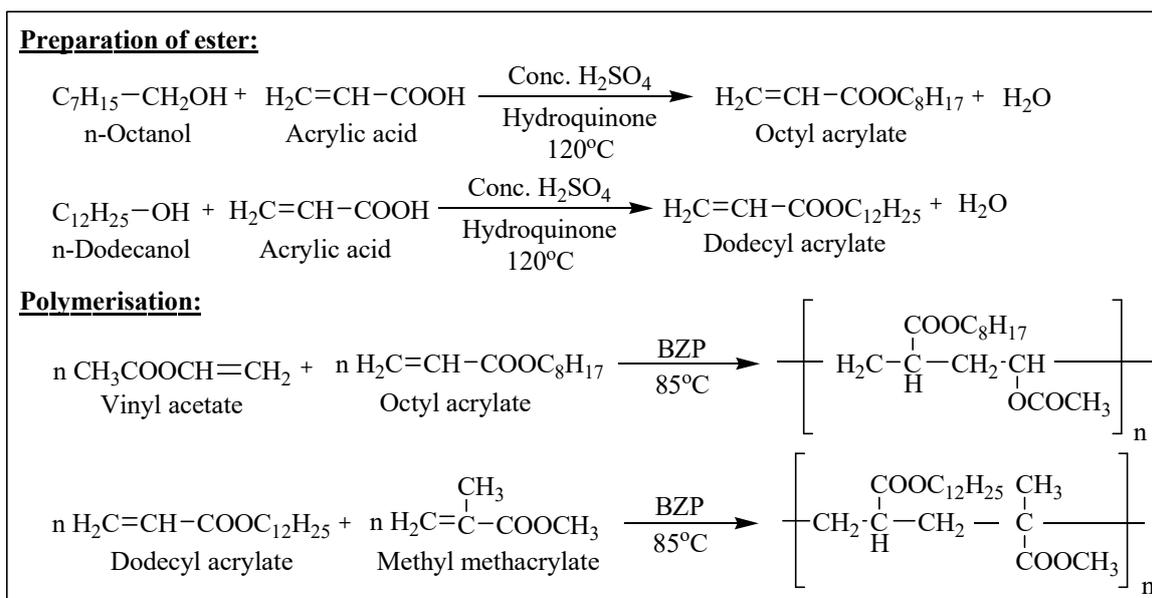
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ABSTRACT

The research works in this thesis entitled “**Synthesis and performance evaluation of organic polymeric additives for lube and crude oils**” begun from August’ 2015. The main focus was on developing multifunctional polymeric additives for lube oil and crude oil as well. Development of multifunctional additive has been a vast area of research in modern automotive industry. An introduction about the whole research work, its background and objective has been provided in **Chapter I**.

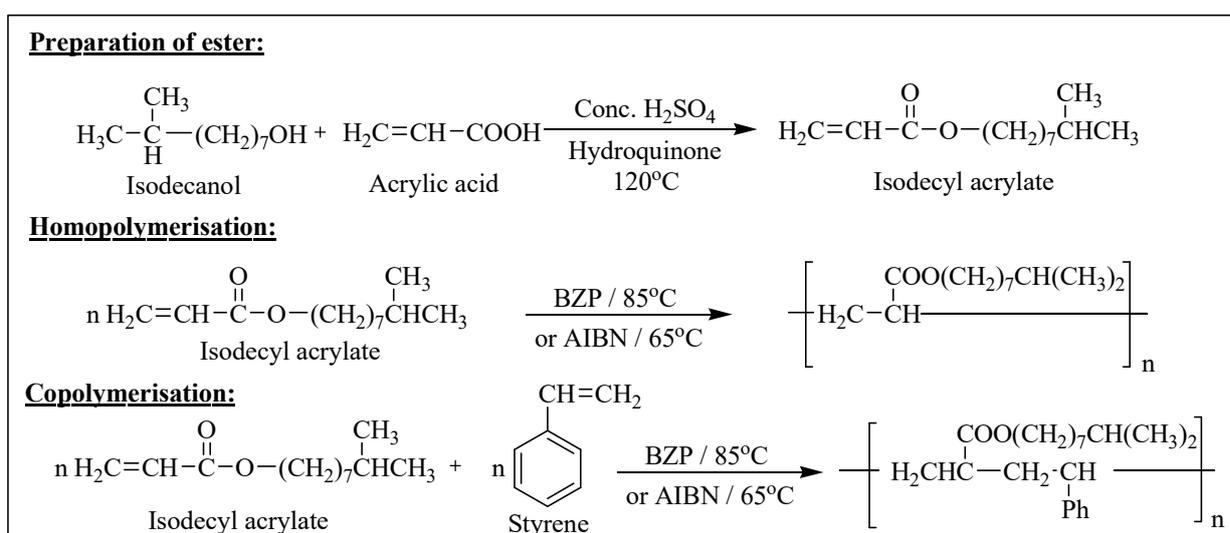
In **Chapter II**, performance of some polymeric additives were evaluated in lube oil, special emphasis was given to draw a line of relation between their preparatory method and performance. In **Chapter II.A**, polymer blending method was utilised to develop a new polymeric additive. Polymer blending has attracted much attention as an easy, cost-effective and less time-consuming method for developing new polymeric materials enriched with versatile commercial application. In addition, polymer blends are supposed to carry better thermal and mechanical properties compared to their parent polymers. Here in this work, a polymer blend of two copolymers – one of vinyl acetate and octyl acrylate and another of methyl methacrylate and dodecyl acrylate were prepared and characterised by FT-IR and NMR spectroscopy.



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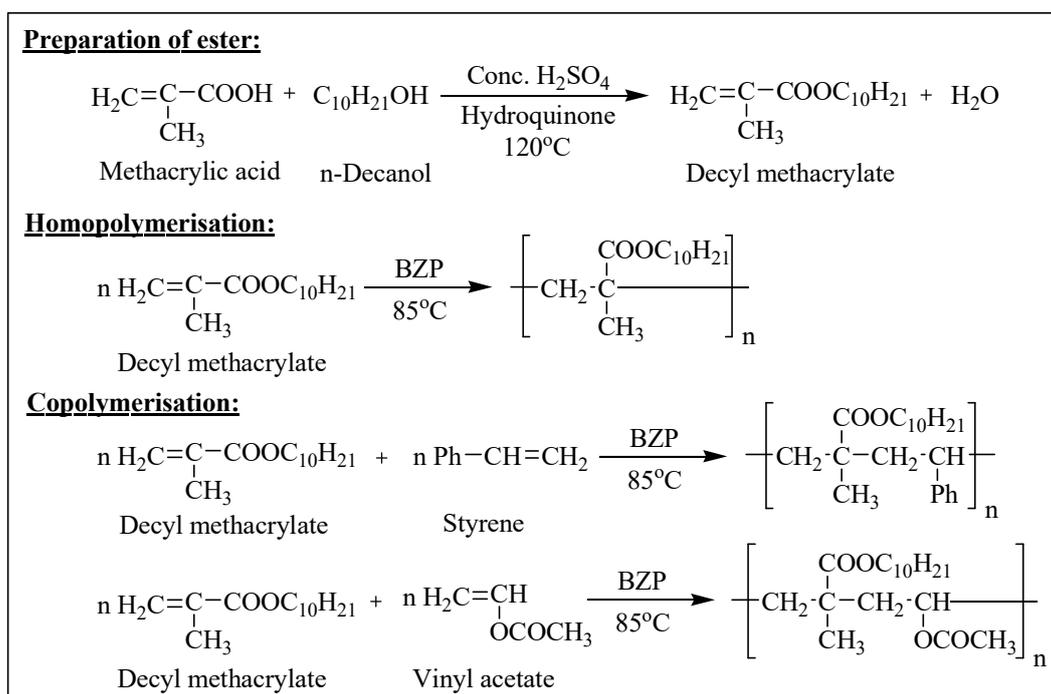
The molecular weight was determined by Gel Permeation Chromatography (GPC). A comparative study between the blend and its parent copolymers, in terms of their mechanical property as well as their performance as flow improver in lube oil has been provided here.

In **Chapter II.B**, the amount of initiators used in polymerisation processes and its effect on the performance of prepared polymers has been highlighted. Here, homopolymers of isodecyl acrylate and its copolymers with styrene have been prepared using various percentages of the initiator whether BZP or AIBN following free radical polymerisation process. The performance of the prepared polymers in lube oil as pour point depressant (PPD), viscosity index improver (VII) and also their shear stability have been evaluated to draw a comparison between the performance of the polymers prepared using different percentages of initiator whether BZP or AIBN.



Chapter III deals with crude oil, its handling problems and effective remedial methods using polymeric additives. Crude oil, basically the unprocessed oil, consists of mainly paraffin, aromatic hydrocarbons, asphaltenes, sulphur and various heavy metals may be present in it depending upon the geological background. But storage and transportation of crude suffer a lot of trouble due to its high viscosity and wax deposition especially at low temperature. Deposited wax gradually immobilizes the oil. Despite such problems, heavy and even extra heavy crude oil has attracted much attention to satisfy the ever increasing demand of energy all over the world. To overcome the problems, a number of flow improvers (FI) or pour point depressants (PPD) have been prepared. But still it is a challenging aspect of this

research area to find out the perfect dosage of the additives with minimum cost and improve the efficiency of the conventional additives. In **Chapter III.A**, homo polymer of decyl methacrylate and its copolymers with styrene and vinyl acetate separately at different percentage composition in the presence of benzoyl peroxide (BZP) as initiator have been prepared. All the prepared polymers are characterised by FT-IR and NMR. The molecular weight was determined by Gel Permeation Chromatography (GPC). The performance of the prepared additives in crude oil was evaluated as flow improver (FI) or pour point depressant (PPD).



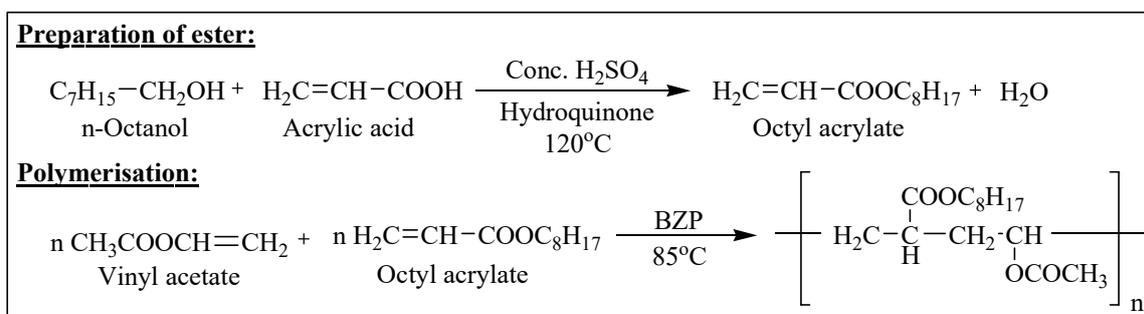
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Another work has been performed on the crude oil using polymer blend this time depicted in **Chapter III.B**. Since polymer blending process has been emerged as an economic and easy process to develop better polymeric materials with higher thermal and mechanical stability, polymer blend has been evaluated here as flow improver and viscosity modifier for crude oil in comparison to its parent copolymers. In addition, shear stability was also measured to for both the blend and its parent copolymers in the crude oil to establish better mechanical stability against stress of the former.

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In **Chapter IV**, ionic liquids (ILs) have been evaluated as additives for both the lube oil and crude oil. ILs have come out as a promising lubricant additive in base oil during the past few years especially due to their low volatility, non-flammability, thermal stability, moisture stability and miscibility with organic compounds. Anti-wear and anti-corrosion activities of ILs were extensively explored in various studies.

Chapter IV.A investigates whether the flow improvement property and shear stability of a polymeric additive can be affected when blended with an IL. A comparative study is given here on the properties as pour point depressant (PPD), viscosity index improver (VII) and shear stability in terms of PSSI values of the acetate-based polymer, imidazolium-based IL and their blend separately when added to a base oil.



In crude oil extraction and transportation also, ILs are the new addition which has got enough potential to be emerged out as an effective, environment friendly multifunctional additive. On the other hand polymers have already gained a prominent position in this field with tremendous applicability over the years whether as PPDs, viscosity index improvers (VIIs) or as additives with high shear stability. In **Chapter IV.B**, an IL doped polymeric additive has been developed for crude oil to evaluate its performance as PPD, VII and also its shear stability in comparison to the individual performance of its parent polymer and the IL in the same crude oil.

PREFACE

The petroleum and automotive industries are developing technologies and materials for the supply of better than better service products for engines and motor vehicles in this ever growing and fast moving world. Increasing consumer demands and economic pressures have converted the internal combustion engines more and more sophisticated ones. As a result, engine oils are becoming more stressed, giving rise to a need for new multifunctional additives. Hence new lubricants are developed to meet the changes required. For example, a new engine design configuration may require improved lubricant performance and on the other hand, a different service application or lubricant drain interval may require changes in lubricant performance. A vast group of research scientists have been engaged to identify these changes and to develop new lubricant additives or enhance the performance of the existing ones by simple modification to satisfy the requirements.

Base oils or synthetic base stocks alone cannot provide all the engine lubricant functions required by a modern gasoline or diesel engine. Over the last eighty years a number of chemical additives have been developed to enhance base stock properties, overcome their deficiencies and provide the new performance levels required by the technological evolution of engines or by new regulations. But no single additive component can do everything. Several additive components are needed to deliver the performance required. Performance requirements change as engine design, operating conditions, legislation, and source of supply and processing methods of the base oil change. Several additive components of different chemistry are used, at concentrations from 0.005% to more than 10% as is required.

The present thesis deals with the development of some effective polymeric additives for both the lube oil and crude oil. All the prepared additives were characterised by FT-IR and NMR spectroscopy. Their molecular weights were determined by Gel Permeation Chromatography (GPC) method. **Chapter II.A** demonstrates the utilisation of polymer blend as lube oil additive. Polymer blend has been an easy and economic polymer modification process to generate new polymeric material with better performance, at least in terms of mechanical and thermal stability. Hence a comparative study has been provided here between the performance of the blend and its parent copolymer a lube oil additive.

The succeeding work embodied in **Chapter II.B** provides an investigation about the effect of percentage of initiator used in the polymerisation process, on the performance of the polymers prepared. Here number of homopolymers and copolymers were prepared via free radical polymerisation process using different percentages of initiator either BZP or AIBN. Then these polymers were evaluated as pour point depressant and viscosity index improver in lube oil. In addition, their shear stability in lube oil was also evaluated. A visible effect of amount of initiator has been marked on the performance of the polymers prepared.

Chapter III.A demonstrates the efficiency polymeric additives for crude oil. High viscosity and wax deposition at low temperature are main barriers against crude oil extraction, transportation via pipeline and even storage in reservoirs. Varieties of remedial methods have been applied to overcome such obstacles over the decades. In this chapter some methacrylate-based polymeric additives have been prepared and employed as pour point depressants for crude oil.

Subsequent work in **Chapter III.B** deals with utilisation of polymer blend as flow improver as well as viscosity modifier for crude oil. Since polymer blends are supposed to be mechanically more stable than its parent polymers, their shear stability in crude oil also measured to check whether they are strong enough maintain their activity even under severe stress such as may be experienced during turbulent flow of crude oil.

In addition, ionic liquids (ILs) also have attracted much attention as a promising candidate with lots of capabilities in this lubrication. Especially their low volatility, non-flammability, thermal stability, moisture stability and miscibility with organic compounds have been the point of attraction to be explored in the world of petroleum science. But ILs are comparatively much more expensive than the traditional lube oils. Hence it wouldn't be economical to replace the mineral base oils with ILs, rather the later can be added to the lube oil in very small quantity as an additive to formulate a better lubricating package. The **Chapter IV** cites the application of ILs as lube oil and crude oil additives. **Chapter IV.A** in particular, has investigated here whether ionic liquids can enhance the performance of a polymeric additive in lube oil. Besides, a number of studies have established that ILs are quite good at viscosity reduction of crude oil. On the other hand polymers are also proved to

do the same quite effectively. **Chapter IV.B** shows whether ionic liquid–doped additives can do it better and whether they are more resistant against mechanical shear.

TABLE OF CONTENTS

Abstract	i–iv
Preface	v–vii
List of Schemes	xv
List of Tables	xvi–xvii
List of Figures	xviii–xix
List of Appendices	xx–xxi
Appendix A: List of Publications	xx
Appendix B: List of Paper Presentations	xxi
Abbreviations	xxii–xxiii

CHAPTER I. Lubricant Industry: Application of additives specially, polymers and ionic liquids 1–22

I.A. GENERAL INTRODUCTION	2–7
I.A.1. Additives	3–7
I.A.1.a. Pour Point Depressants (PPD)	3–4
I.A.1.b. Viscosity index improver (VII)	4–6
I.A.1.c. Extreme pressure (EP) additives	6
I.A.1.d. Friction modifiers	6
I.A.1.e. Anti–wear additives	7
I.A.1.f. Detergents and dispersants	7
I.A.1.g. Corrosion and rust inhibitor	7
I.B. LUBE OIL	8–10
I.B.1. Lube oil from crude oil	8–9
I.B.2. Dependence of additives on base stocks and vice versa	9–10
I.B.3. Problems when different additives are added together	10
I.C. CRUDE OIL	11–18
I.C.1. Composition of crude oil	11–12
I.C.1.a. Hydrocarbons	11–12
I.C.1.b. Non–hydrocarbons	12
I.C.2. Handling problems of crude oil	12–13

I.C.3. Remedies	13–18
I.C.3.a. Mechanical method: pipeline “pigging”	14
I.C.3.b. Injection of naphtha or CO ₂	14
I.C.3.c. Thermal treatment	14
I.C.3.d. Dilution method	15
I.C.3.e. Annular flow of crude oil	15
I.C.3.f. Preventive method	15–18
I.C.3.f.1. Ethylene–Vinyl Acetate (EVA) copolymer	16
I.C.3.f.2. Alkyl Acrylate copolymer	16–17
I.C.3.f.3. Maleic Anhydrides copolymer	17
I.C.3.f.4. Other Type of Additives	17–18
I.D. IONIC LIQUID	19–22
I.D.1. Properties	19
I.D.2. Applications of ILs in automotive industry	19–21
I.D.3. Imidazolium based ILs	21–22
I.E. REFERENCES	22
CHAPTER II. Additives for lubricating (lube) oil	23–63
CHAPTER II.A. Synthesis of polymeric blend of vinyl acetate and acrylate–based copolymers and its performance evaluation in lubricating oil	24–39
II.A.1. INTRODUCTION	24–25
II.A.2. BACKGROUND & OBJECTIVES	26–27
II.A.3. EXPERIMENTAL SECTION	27–29
II.A.3.a. Materials	27–28
II.A.3.b. Preparation of esters and their purification	28–29
II.A.3.c. Preparation of copolymers and blend	29
II.A.4. MEASUREMENTS	29–31
II.A.4.a. Molecular weight determination	29
II.A.4.b. Spectroscopic Measurements	30
II.A.4.c. Performance evaluation as pour point depressants in lube oil	30

II.A.4.d. Performance evaluation as viscosity index improver (VII)	30
II.A.4.e. Shear stability measurement	30–31
II.A.5. RESULTS AND DISCUSSION	31–39
II.A.5.a. Molecular Weight Analysis	31
II.A.5.b. Spectroscopic analysis	31–34
II.A.5.c. Performance evaluation as pour point depressant	34–35
II.A.5.d. Performance evaluation as viscosity index improver	36–37
II.A.5.e. Shear stability index analysis	38–39
II.A.6. CONCLUSION	39
II.A.7. REFERENCES	39

CHAPTER II.B. Effect of percentage of initiator used in the polymerisation process on the performance of the prepared additives: A comparative study 40–63

II.B.1. INTRODUCTION	40–41
II.B.2. BACKGROUND & OBJECTIVES	41–43
II.B.3. EXPERIMENTAL SECTION	43–44
II.B.3.a. Materials	43–44
II.B.3.b. Preparation of esters and their purification	44
II.B.3.c. Preparation of polymers	44
II.B.4. MEASUREMENTS	44–46
II.B.4.a. Molecular weight determination	44
II.B.4.b. Spectroscopic Measurements	45
II.B.4.c. Performance evaluation as pour point depressants in lube oil	45
II.B.4.d. Performance evaluation as viscosity index improver (VII)	45
II.B.4.e. Shear stability measurement	46
II.B.5. RESULTS AND DISCUSSION	46–63
II.B.5.a. Molecular Weight Analysis	46–47
II.B.5.b. Spectroscopic analysis	48–50
II.B.5.c. Performance evaluation as pour point depressant	51–52
II.B.5.d. Performance evaluation as viscosity index improver	52–58
II.B.5.e. Shear stability index analysis	58–63
II.B.6. CONCLUSION	63

II.B.7: REFERENCES	63
--------------------	----

CHAPTER III. Additives for crude oil	64–88
---	--------------

CHAPTER III.A. Development of methacrylate based polymeric additives for crude oil	64–77
---	--------------

III.A.1. INTRODUCTION	65–66
-----------------------	-------

III.A.2. BACKGROUND AND OBJECTIVE	66–67
-----------------------------------	-------

III.A.3. EXPERIMENTAL SECTION	67–68
-------------------------------	-------

III.A.3.a. Materials	67–68
----------------------	-------

III.A.3.b. Purification of ester and its purification	68
---	----

III.A.3.c. Preparation of polymers	68
------------------------------------	----

III.A.4. MEASUREMENTS	69
-----------------------	----

III.A.4.a. Molecular weight determination	69
---	----

III.A.4.b. Spectroscopic Measurements	69
---------------------------------------	----

III.A.4.c. Performance evaluation as pour point depressants in crude oil	69
--	----

III.A.5. RESULTS AND DISCUSSION	69–76
---------------------------------	-------

III.A.5.a. Molecular Weight Analysis	69–70
--------------------------------------	-------

III.A.5.b. Spectroscopic analysis	70–75
-----------------------------------	-------

III.A.5.c. Analysis of pour point values	75–76
--	-------

III.A.6. CONCLUSION	77
---------------------	----

III.A.7. REFERENCES	77
---------------------	----

CHAPTER III.B. Polymer blend: A new approach towards flow improvement of crude oil	78–88
---	--------------

III.B.1. INTRODUCTION	78–79
-----------------------	-------

III.B.2. BACKGROUND AND OBJECTIVES	79–81
------------------------------------	-------

III.B.3. EXPERIMENTAL SECTION	81
-------------------------------	----

III.B.3.a. Materials	81
----------------------	----

III.B.3.b. Preparation and purification of esters	81
---	----

III.B.3.c. Preparation of copolymers and blend	81
--	----

III.B.4. MEASUREMENTS	82
III.B.4.a. Molecular weight determination	82
III.B.4.b. Spectroscopic Measurements	82
III.B.4.c. Performance evaluation as pour point depressants in crude oil	82
III.B.4.d. Performance evaluation as viscosity index improver (VII)	82
III.B.4.e. Shear stability measurement	82
III.B.5. RESULTS AND DISCUSSION	83–87
III.B.5.a. Molecular Weight Analysis	83
III.B.5.b. Spectroscopic analysis	83
III.B.5.c. Performance evaluation as pour point depressant	83–84
III.B.5.d. Performance evaluation as viscosity index improver	85–86
III.B.5.e. Shear stability index analysis	86–87
III.B.6. CONCLUSION	88
III.B.7: REFERENCES	88
CHAPTER IV. Ionic liquid doped polymeric additive in lubricating oil	89–113
CHAPTER IV.A. An investigative approach towards the flow improvement property of ionic liquid doped polymeric additive in lubricating oil	90–101
IV.A.1. INTRODUCTION	90–91
IV.A.2. BACKGROUND AND OBJECTIVES	91–93
IV.A.3. EXPERIMENTAL SECTION	93
IV.A.3.a. Materials	93
IV.A.3.b. Prepration of ester and its purification	93
IV.A.3.c. Preparation of polymer and its blend with IL	93
IV.A.4. MEASUREMENTS	94
IV.A.4.a. Molecular weight determination	94
IV.A.4.b. Spectroscopic Measurements	94
IV.A.4.c. Performance evaluation as pour point depressants in base oil	94
IV.A.4.d. Performance evaluation as viscosity index improver (VII)	94
IV.A.4.e. Shear stability measurement	94
IV.A.5. RESULTS AND DISCUSSION	95–100

IV.A.5.a. Molecular Weight Analysis	95
IV.A.5.b. Spectroscopic analysis	95
IV.A.5.c. Performance evaluation as pour point depressant	95–96
IV.A.5.d. Performance evaluation as viscosity index improver	96–98
IV.A.5.e. Shear stability index analysis	98–100
IV.A.6. CONCLUSION	100–101
IV.A.7: REFERENCES	101
CHAPTER IV.B. Enhancement of additive properties in crude oil through introduction of ionic liquid	102–113
IV.B.1. INTRODUCTION	102–103
IV.B.2. BACKGROUND AND OBJECTIVES	103–105
IV.B.3. EXPERIMENTAL SECTION	105
IV.B.3.a. Materials	105
IV.B.3.b. Preparation and purification of esters	105
IV.B.3.c. Preparation of copolymers and its blend with the IL	105
IV.B.4. MEASUREMENTS	106–107
IV.B.4.a. Molecular weight determination	106
IV.B.4.b. Spectroscopic Measurements	106
IV.B.4.c. Performance evaluation as pour point depressants in crude oil	106
IV.B.4.d. Performance evaluation as viscosity index improver (VII)	106
IV.B.4.e. Shear stability measurement	106–107
IV.B.5. RESULTS AND DISCUSSION	107–112
IV.B.5.a. Molecular Weight Analysis	107
IV.B.5.b. Spectroscopic analysis	107
IV.B.5.c. Performance evaluation as pour point depressant	107–109
IV.B.5.d. Performance evaluation as viscosity index improver	109–111
IV.B.5.e. Shear stability index analysis	111–112
IV.B.6. CONCLUSION	112–113
IV.B.7: REFERENCES	113

BIBLIOGRAPHY	114–144
References for Chapter I	114–124
References for Chapter II.A	125–126
References for Chapter II.B	127–130
References for Chapter III.A	131–133
References for Chapter III.B	134–136
References for Chapter IV.A	137–140
References for Chapter IV.B	141–144
INDEX	145–146

LIST OF SCHEMES

CHAPTER II.A

Scheme II.A: Preparation of octyl acrylate and its subsequent polymerization with vinyl acetate; Preparation of dodecyl acrylate and its subsequent polymerization with methyl methacrylate 27

CHAPTER II.B

Scheme II.B: Preparation of isodecyl acrylate; its subsequent homopolymerisation and copolymerization with styrene 43

CHAPTER III.A

Scheme III.A: Preparation of decyl methacrylate; its homopolymerisation and copolymerization with styrene and vinyl acetate separately 67

CHAPTER III.B

Scheme III.B: Polymerisation of vinyl acetate with octyl acrylate and dodecyl acrylate with methyl methacrylate; blending of prepared polymers 80

CHAPTER IV.A

Scheme IV.A: Preparation of octyl acrylate and its copolymerization with vinyl acetate 92

LIST OF TABLES

CHAPTER II.A

Table II.A.1: Base Oil (BO) Properties	28
Table II.A.2: Molecular weight and polydispersity index data	31
Table II.A.3: Pour point data with respect to the different concentrations of the additives in base oil (BO)	35
Table II.A.4: Viscosity Index (VI) data with respect to the different concentrations of the additives in base oil 1 (BO1)	36
Table II.A.5: Viscosity Index data with respect to the different concentrations of the additives in base oil 2 (BO2)	37
Table II.A.6: PVL & PSSI data with respect to the different concentrations of the additives in base oil (BO)	38

CHAPTER II.B

Table II.B.1: Percentage of initiator used during polymerisation and molecular weight data	46–47
Table II.B.2: Pour point (PP) data (°C) with respect to the different concentrations (% w/w) of the additives in BO	51–52
Table II.B.3: Kinematic viscosities (KV) with respect to the different concentrations of the additives in BO1	53–54
Table II.B.4: Kinematic viscosities (KV) with respect to the different concentrations of the additives in BO2	54–55
Table II.B.5: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO	55–56
Table II.B.6: Kinematic viscosity after shear at 100 °C (^s KV ₂) and PVL data with respect to the different concentrations of the additives in BO1	57–58
Table II.B.7: Kinematic viscosity after shear at 100 °C (^s KV ₂) and PVL data with respect to the different concentrations of the additives in BO2	59–60
Table II.B.8: PSSI data with respect to the different concentrations of the additives in BO	60–61

CHAPTER III.A

Table III.A.1: Specification of the crude oil	68
Table III.A.2: Percentage composition, M_n , M_w and PDI values of polymers (P_1 to P_9)	70
Table III.A.3: Pour point data with respect to the different concentrations of the additives in crude oil	75

CHAPTER III.B

Table III.B.1: Molecular weight and Pour point data ($^{\circ}\text{C}$)	84
Table III.B.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in crude oil	85
Table III.B.3: PVL & PSSI data with respect to the different concentrations of the additives in crude oil	87

CHAPTER IV.A

Table IV.A.1: Pour point data with respect to the different concentrations of the additives in base oil (BO)	95
Table IV.A.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in base oil 1 (BO1)	97
Table IV.A.3: Viscosity Index data with respect to the different concentrations of the additives in base oil 2 (BO2)	97–98
Table IV.A.4: PVL & PSSI data with respect to the different concentrations of the additives in base oil (BO)	99

CHAPTER IV.B

Table IV.B.1: Pour point data ($^{\circ}\text{C}$) with respect to the different concentrations (% w/w) of the additives in crude oil	108
Table IV.B.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in crude oil	109
Table IV.B.3: PVL & PSSI data with respect to the different concentrations of the additives in crude oil	111

LIST OF FIGURES

CHAPTER I

Figure I.A: Diagram showing how PPD/FI works	4
--	---

CHAPTER II.A

Figure II.A.1: FT–IR spectrum of polymer P ₁	32
Figure II.A.2: FT–IR spectrum of polymer P ₂	32
Figure II.A.3: ¹ H NMR spectrum of P ₁	32
Figure II.A.4: ¹³ C NMR spectrum of P ₁	33
Figure II.A.5: ¹ H NMR spectrum of P ₂	33
Figure II.A.6: ¹³ C NMR spectrum of P ₂	34
Figure II.A.7: PP (°C) at different concentrations (% w/w) of additive	35
Figure II.A.8: Variation of viscosity index with respect to the different concentrations of the additives	37
Figure II.A.9: Variation of PSSI with respect to the different concentrations of the additives	39

CHAPTER II.B

Figure II.B.1: FT–IR spectrum of P ₁	48
Figure II.B.2: FT–IR spectrum of P ₁₁	48
Figure II.B.3: ¹ H NMR spectrum of P ₁	49
Figure II.B.4: ¹³ C NMR spectrum of P ₁	49
Figure II.B.5: ¹ H NMR spectrum of P ₁₁	50
Figure II.B.6: ¹³ C NMR spectrum of P ₁₁	50
Figure II.B.7: Variation of viscosity index with respect to the different concentrations of the additives in BO1	57
Figure II.B.8: Variation of viscosity index with respect to the different concentrations of the additives in BO2	57
Figure II.B.9: Variation of PSSI with respect to the different concentrations of the additives in BO1	62
Figure II.B.10: Variation of PSSI with respect to the different concentrations of the additives in BO2	62

CHAPTER III.A

Figure III.A.1: FT–IR spectrum of P ₁	71
Figure III.A.2: FT–IR spectrum of P ₃	71
Figure III.A.3: FT–IR spectrum of P ₇	71
Figure III.A.4: ¹ H NMR spectrum of P ₁	72
Figure III.A.5: ¹³ C NMR spectrum of P ₁	72
Figure III.A.6: ¹ H NMR spectrum of P ₃	73
Figure III.A.7: ¹³ C NMR spectrum of P ₃	73
Figure III.A.8: ¹ H NMR spectrum of P ₇	74
Figure III.A.9: ¹³ C NMR spectrum of P ₇	74
Figure III.A.10: Variation of pour point with respect to the different concentrations of the additives in crude oil	76

CHAPTER III.B

Figure III.B.1: Variation of pour point at different concentrations of the additives	84
Figure III.B.2: Variation of viscosity index at different concentrations of the additives	86
Figure III.B.3: Variation of PSSI at different concentrations of the additives	87

CHAPTER IV.A

Figure IV.A.1: Variation of Pour point with respect to the different concentrations of the additives	96
Figure IV.A.2: Variation of viscosity index with respect to the different concentrations of the additives	98
Figure IV.A.3: Variation of PSSI with respect to the different concentrations of the additives	100

CHAPTER IV.B

Figure IV.B.1: Variation of pour point with respect to the different concentrations of the additives	108
Figure IV.B.2: Variation of viscosity index with respect to the different concentrations of the additives	110
Figure IV.B.3: Variation of PSSI with respect to the different concentrations of the additives	112

LIST OF APPENDICES

APPENDIX A: List of Publications

1. Ghosh, P. and **Yeasmin, S.** (2019). Performance evaluation of polymeric blend of vinyl acetate and acrylate-based copolymers in lubricating oil. *Pet. Sci. Technol*, 37:845.
2. Ghosh, P. and **Yeasmin, S.** (2019). Polymer blend: a new approach towards flow improvement of crude oil. *Pet. Sci. Technol*, doi: 10.1080/10916466.2019.1697287.
3. **Yeasmin, S.**, Hoque, M. and Ghosh, P. (2018). Synthesis and Characterization of Methacrylate Based Polymeric Additives for Crude Petroleum Oil. *Chem. J.*, 3:333.

(Not related to the Thesis)

1. Castor Oil Based Multifunctional Greener Additives for Lubricating Oil Author(s): Ghosh, P., Hoque, M., Karmakar, G. and **Yeasmin, S.** (2017). *Curr. Environ. Eng.*, 4:197.

Appendix B: List of Paper Presentations

1. **Sultana Yeasmin**, Mainul Hoque and Pranab Ghosh, “Performance–based designing of flow improvers for waxy crude oil”. Poster presentation at International seminar on “Frontiers in Chemistry 2018”, dated August 27, 2018, Department of Chemistry, University of North Bengal, India.
2. **Sultana Yeasmin**, “Polymeric additives for crude oil”. Oral presentation at National seminar on “Frontiers in Chemistry 2017”, dated February 20–21, 2017, Department of Chemistry, University of North Bengal, India.

ABBREVIATIONS

ABS	Acrylonitrile–Butadiene–Styrene
AIBN	Azobisisobutyronitrile
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATRP	Atom Transfer Radical Polymerisation
BO	Base Oil
BZP	Benzoyl Peroxide
DDA	Dodecyl Acrylate
DEA	Diethanolamine
DMA	Decyl Methacrylate
EOR	Enhanced Oil Recovery
EP	Extreme Pressure
EVA	Ethylene–Vinyl Acetate
FT–IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HPLC	High Performance Liquid Chromatography
IDA	Isodecylacrylate
IL	Ionic Liquid
KV	Kinematic Viscosity
MEM	Micro–electromechanical machines
MMA	Methyl Methacrylate
MTBE	Methyl tert–Butyl Ether
MW	Molecular Weight
MWD	Molecular Weight Distribution
NMR	Nuclear Magnetic Resonance Spectroscopy

OA	Octyl Acrylate
PAH	Poly-crosslinked Aromatic Hydrocarbons
PDI	Polydispersity Index
PEG	Polyethylene Glycol
PFPE	Perfluoropolyether
PIL	Protic Ionic Liquid
PP	Pour Point
PPD	Pour Point Depressant
PPM	Parts Per Million
PS	Polystyrene
PSSI	Permanent Shear Stability Index
PVL	Permanent Viscosity Loss
RTIL	Room Temperature Ionic Liquid
TAME	tert-Amyl Methyl Ether
THF	Tetrahydrofuran
TMS	Tetramethylsilane
TVL	Temporary Viscosity Loss
VA	Vinyl Acetate
VI	Viscosity Index
VII	Viscosity Index Improver
WAT	Wax Appearance Temperature
ZDDP	Zincdialkyldithiophosphate

CHAPTER I

**Lubricant Industry: Application of additives specially, polymers
and ionic liquids**

I.A. GENERAL INTRODUCTION

Lubrication means improving the smoothness of movement of one surface over another and the materials, having such capability of lubrication, are called lubricants or lubricating agents. Lubricants are usually liquids or semi-liquids but may be solids, gases, or any combination of solids, liquids, and gases [1]. The applications of lubricants are:

- (a) It reduces the friction between the surfaces of mated moving parts and therefore lowers energy loss due to friction.
- (b) It slows down the wear of parts by changing the type of friction, removes heat from parts, when they tend to get hot during operation and keeps grit out of the clearances between parts.
- (c) It protects parts from corrosion.
- (d) It reduces shocks between mated parts.

In automotive industry for modern engines and high-speed machinery demand of lubricants is increasing day by day and hence a great amount of research body has been engaged to develop high performance lubricating agents [2]. Especially during the last decades the demands of oils and lubricants have increased vastly [3]. Modern lubricants are formulated from a wide range of base fluids and chemical additives. It is the base fluid that provides a fluid layer between the moving surfaces to keep them apart from each other which resist the friction. It minimizes the heat evolved during operation and eliminates the wear particles. The development of modern engine and transmission technology would have been impossible without advanced lubricant additives chemistry and lubricant formulation. Modern engine oils contain a wide range of additives, which are blended with base oils to form a complete package capable of meeting demanding performance requirements [4]. Additives for the future lubricants are required to maintain oil consumption under control over the service life of the equipment and at the same time, they have to provide a high level of thermal stability with enhanced low-temperature fluidity. They are required to reduce the oxidative or thermal degradation and wear of the oil, minimize rust and corrosion, lessen the deposition of harmful deposits on lubricated parts, and

prevent destructive metal to metal contact. Many types of additives have been developed to satisfy special lubrication needs. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes such as oxidative or any other degradations, take place in the product during its service life [5]. Today, practically all types of lubricating oil contain at least one additive, and some oils contain additives of several different types as a combination [6]. Different types of lube oil additives are used such as detergents-dispersants [7], antioxidants [8], corrosion inhibitors [9], extreme pressure agents [10], viscosity index improvers [11] and pour point depressants [12]. Before going into the details about the lubricants some terms associated with lubrication and its requirement need to be discussed first here.

I.A.1. Additives

Additives are those substances which fulfill the desired properties of lubricating oil by adding some specific properties or enhancing the existing properties or sometimes resisting some. Typically they are chemical substances mostly, with a polar head group and a nonpolar hydrocarbon chain. According to requirement different types of additives are blended with the lubricating oil as stated below.

I.A.1.a. Pour Point Depressants (PPD)

The pour point of a fluid is the lowest temperature at which it will pour or flow when it is chilled without disturbance under prescribed conditions. Most mineral oils contain some dissolved wax and when the temperature decreases, this wax begins to separate out as crystal from the liquid state and gradually as the temperature lowers further it develops a 3-D wax matrix which entraps the oil and ceases its fluidity [13]. Certain high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures [14–20]. The chemical additives are synonymously referred to as pour point depressants, flow improvers, paraffin inhibitors, or wax modifiers. Pour point depressants have no effect on the crystallization temperature or the number of crystals formed. Their most widely accepted mechanisms of action include adsorption, co-crystallization, nucleation, and improved wax solubility [14, 21–24] as shown in the **Figure I.A.**

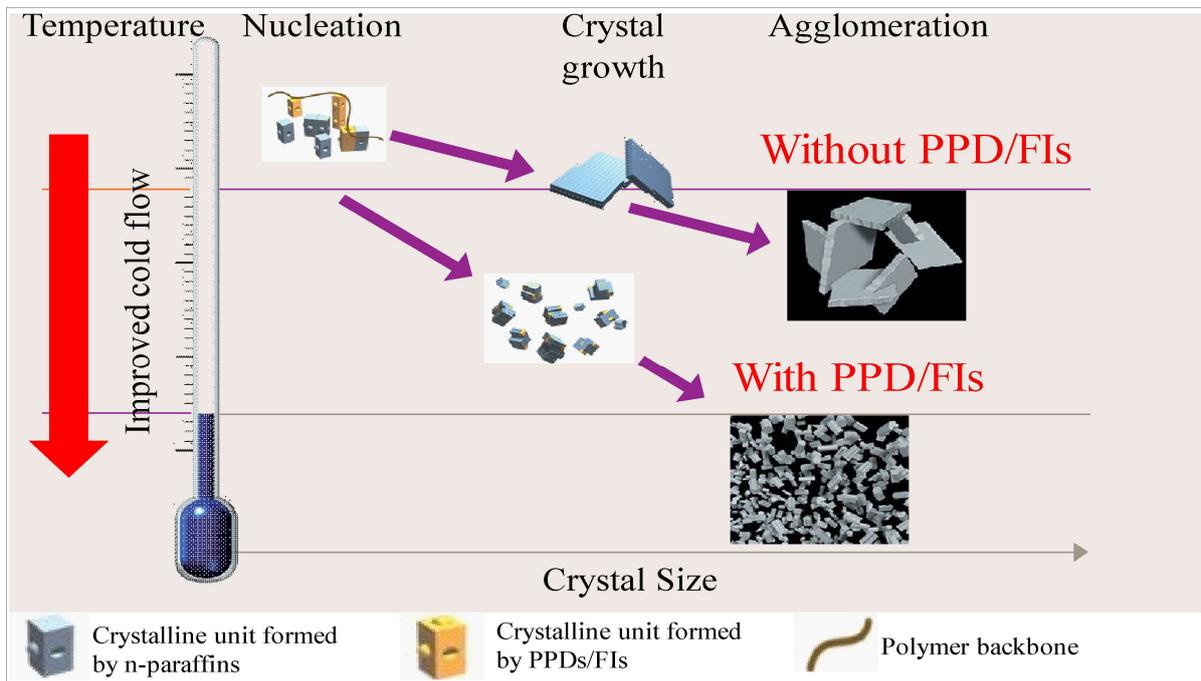


Figure I.A: Diagram showing how PPD/FI works

The effectiveness of a pour point depressant depends on the chemical composition of the polymer, its structural characteristics and the length of the alkyl side chains [25–27]. Although the removal of the last traces of wax from oils is difficult and expensive, pour point depressants provide an economical and of course effective means of facilitating the proper flow of the oil in an engine at low temperatures [28–30].

I.A.1.b. Viscosity index improver (VII)

Viscosity is one of the most important parameters of a lubricant and must be kept under limits to act accordingly. Addition of oils with lower viscosity, contamination by fuel and solvents or any lubricant degradation may cause reduction in a lubricant viscosity. On the other hand, presence of insoluble contaminants, pronounced oxidation and water contamination may increase the viscosity of a lubricant [31]. The rate at which viscosity changes with temperature is known as the viscosity index (VI) of a fluid [32]. The higher the VI, the more constant is its viscosity. In general with increase in temperature viscosity of the oil decreases but viscosity index improvers (VIIs) are those substances which when added to the oil in small amount, actually reverse this

general phenomenon which may be explained taking examples of polymers, widely used as VIIs. When polymers added in small quantity to the oil in normal temperature, they are supposed to exist as tight coils in the oil and held in colloidal suspension so that their effect on viscosity is minimized. As the temperature increases the solubility of the polymers also increases and these coils unfold themselves into open chain configuration which has larger volume and hence higher viscosity is observed at higher temperature [4, 33 & 34]. Viscosity modifiers are a key ingredient in modern lubricants. They modify the flow characteristics of lubricants and are required for most multi-grade fluids. They enable the oil to be used over an extended temperature range eliminating the need for seasonal oil changes. Performance of viscosity index improvers depends on the behavior of the polymer molecules in the oil, polymer solubility, molecular weight and their resistance to shear degradation [35].

Stability of viscosity modifiers plays a key role which is expressed in terms of **shear stability index**. Stability against mechanical shear or stress is termed as shear stability. When polymers are subjected to a high shear stress in equipment such as between piston rings and a cylinder wall, between gear teeth or across the pressure relief valve of a hydraulic system, the random coil configuration the polymer is severely distorted. In extreme cases, bond energies can be exceeded, and the polymer breaks down. Thus the polymer loses its effectiveness under shearing conditions. Resistance against such distortion at severe mechanical shear is called shear stability of a particular additive. Distortion or breaking of a polymer is associated with loss of its properties most importantly viscosity loss. When a polymer in base oil undergoes degradation two kinds of viscosity loss is observed such as permanent viscosity loss (**PVL**) and temporary viscosity loss (**TVL**), the former being mostly used for shear stability measurement and expressed as –

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

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

V_i = KV of the oil after addition of polymer

V_s = KV of the oil doped with polymer after shearing]

Shear stability is expressed in terms of permanent shear stability index (**PSSI**) which is expressed as –

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

[V_o = KV of the oil before addition of polymer and others represent same parameters as above.]

Shear stability under particular shearing condition depends on various factors starting from the structure, molecular weight of the polymer to its concentration in the base oil and even on the base oil used also. Some other factors also play important role here. Various studies have suggested that increasing molecular weight of the polymer also increases the polymer volume in an oil solution [36] and consequently, a polymer with higher molecular weight will impart higher viscosity index than a polymer of the same type with lower molecular weight [37]. Further, the amount of branching can also be critical to the polymer behavior. A disadvantage of long-chain branching is that it reduces the thickening efficiency and shear stability lubricating oil, relative to simple copolymer of similar molecular weight and composition [34]. On the other hand, the viscosity index increases with increase in the chain length when the degree of branching is fixed. In addition, it has been seen that the pour point decreases with increase in the degree of branching [38].

I.A.1.c. Extreme pressure (EP) additives

These are a special class of boundary lubrication additives which react with the metal surface to form compounds with lower shear strength than the metal. This low-shear compound provides the lubrication.

I.A.1.d. Friction modifiers

They can either adsorb or react with the surface to reduce friction by forming a very low shear-strength film. Without a friction modifier, the friction coefficient in the transmission would increase at low-sliding velocity where surface asperities make contact which would result in rough shifting and high-transmission in vehicles.

I.A.1.e. Anti-wear additives

In sliding contacts, physical loss of material occurs which is called wear. It occurs due to highly stressed interfacial zones where a local mechanical loss happens influenced by environmental factors. Additives which resist such loss are called anti-wear additives. Zinc dialkyldithiophosphate (ZDDP) has been widely utilised as anti-wear additives.

I.A.1.f. Detergents and dispersants

To prevent carburettor fouling and engine deposits detergent additives are required and on the other hand dispersant additives are required to combat sludge in crankcase engine oils. Polybutenyl succinimide is one of the mostly used detergent and dispersant additives. Dispersants in general are expected to be beneficial for wear protection and it has been demonstrated that succinimide dispersants can partially remove films formed by ZDDP under rubbing conditions [39]. The benefit of dispersants of different molecular weight and functionality can be seen from a number of studies but many of them are complicated by neglecting the influence of dispersant upon viscosity and hence oil film thickness.

I.A.1.g. Corrosion and rust inhibitor

Environmental effect, excessive friction between the surfaces or presence of impurities may lead to corrosion. The chemical substances which can decrease the rate of such corrosion are called corrosion inhibitors. It is assumed that the inhibitors form a coating between the corrosive substance and the metal and thus surround the metal or related object. Corrosion inhibitors are commonly found in the form of spray in combination with lubricant. Rust inhibitor is also another form of corrosion inhibitor. It has been designed to slow down the oxidization process in metals which have been exposed to oxygen and water and begun to rust. It is also obtained as anti-rust sprays in the market which can be applied to metal surfaces to stop rust from forming and create a protective barrier that lubricates the surface and prevents further rust.

I.B. LUBE OIL

During the process of crude oil refining, after removal of gas oils and lighter fractions by distillation, the remaining more viscous portion produces the base fluids of lubricating oil or lube oil. Refined petroleum base oils are the major source for formulation of lubricating oil due to easy availability, excellent performance and cheaper price. There is another class of base fluid called non-petroleum base fluid, used in special cases where petroleum base oils are in short supply or where substitution by natural products is practicable or desirable.

I.B.1. Lube oil from crude oil

To prepare the base fluids, first of all proper selection of crude oil is required since every crude oil varies from each other in terms of content, composition ratios, boiling range distribution of their components etc. Hence according to requirement thorough study is required to obtain much needed physical and chemical properties in the base fluid essential to formulate lubricant. In the refinery base oil extraction from crude involves a number of steps such as:

1. **Distillation:** To separate the desirable lube components from the bulk of the crude oil distillation is required where both the components of too low boiling point and too high boiling point are removed leaving the lubricant boiling range distillates.
2. **Removal of aromatics:** To obtain oil with better VI and stability, aromatic components are removed and the oil is made rich in saturated hydrocarbons.
3. **De-waxing:** To control low temperature properties of the base oil wax is removed as far as possible.
4. **Finishing:** To improve the colour and stability of the base oil, traces of polar components are removed.

The yield of base oil after these processes depends on the amount of desirable components in the lubricant boiling range. After obtaining an appropriate quality lubricant base stock, lubricating oil is formulated by blending required additives with it. But modern automotive engine oils and transmission fluids require additives as a package that meets certain industry-

specified testing criteria whereas in other cases, such as metalworking fluids and greases individual additives are furnished to the base stock [40]. It may be mentioned here also that lubricant additives are chemical substances mostly organic or organometallics which are added to oils or base stocks in quantities of a few weight percent to improve the lubricating capacity and durability of the oil. Lubricant additives fulfill some specific purposes such as resisting wear, improving the oxidation resistance, controlling corrosion and contamination by reaction products, reducing excessive decrease of lubricant viscosity at high temperatures, and enhancing lubricant characteristics by reducing the pour point and inhibiting the generation of foam [41]. But to meet the expectation of latest technology, multifunctional additives are in high demand which can satisfy multiple requirement single handedly.

I.B.2. Dependence of additives on base stocks and vice versa

Just like lube oils require additives to act as good lubricant, the additives also require a quality grade lube oil to act appropriately. Lubricant base stocks influence additive performance through two main functions; solubility and response. For example, performance of surface active additives depends largely on their ability to get adsorbed on the machine surface at the proper time and place. Base stocks with poor solubility characteristics may allow these additives to separate before they can fulfill their intended functions. Conversely, base stocks with very high-solubility characteristics may keep the additives in solution, not allowing them to get adsorbed on machine surface. Additive response depends on base stock composition. Natural sulfur, nitrogen, and phenolic inhibitors are removed along with undesirable materials during base stock refining. Removal of these natural inhibitors often results in reduced oxidation inhibition relative to unrefined stocks. However, the natural inhibitors, as well as the undesirable materials removed during base stock refining, often interfere with additive performance. Synthetic base oils, depending on their chemical structure, exhibit very specific solubility characteristics, additive response, and additive compatibility that are sometimes different from mineral oils. The most common synthetic base oils are synthetic hydrocarbons, such as poly-alpha olefins, and esters, such as adipate, azelate and pentaerythritol esters. Synthetic hydrocarbons exhibit excellent additive response but are poor additive solvents.

Esters vary in additive response and are excellent solvents except for additives with which they react to form precipitates. Synthetic oils can be blended with each other or with mineral oil to provide the optimum balance of solubility and additive response.

I.B.3. Problems when different additives are added together

Most modern lubricants require more than one additive to meet all performance demands. In some cases, individual additives are blended directly into the base oil. In other cases, a group of additives are blended into an additive package, which is subsequently blended into the base oil. Since most additives are active chemicals, they can interact in the package or in the lubricant to form new compounds. These interactions can decrease additive effectiveness and lead to insoluble or otherwise undesirable by-products. Additive functionalities frequently depend on their limited solubility in the lubricant. As for example, many lubricants require both an anti-wear additive like zinc dialkyl dithiophosphate (ZDDP) and a dispersant together. To act accordingly, ZDDP must be able to leave the bulk of the lubricant and adhere to the machine surface to function as a wear inhibitor. But in presence of a dispersant in the same lubricant, the action of ZDDP is prevented since the dispersant can hold the ZDDP in solution rather letting it go to the surface. Surface active additives can also compete with each other such as both wear inhibitors and some rust inhibitors function by adsorbing on metal surfaces and they compete for the same surface. The wear inhibitor can displace the rust inhibitor on the surface and be detrimental to rust inhibition. Likewise, the rust inhibitor can displace the wear inhibitor.

I.C. CRUDE OIL

Crude oil is supposed to be the biggest source of energy all over the world due to its higher and cheaper availability compared to other energy resources. In general, if the crude oil has an API (American Petroleum Institute) gravity equal to or less than 20, it is considered as heavy and if the API is 10 or less than 10 the oil is termed as extra-heavy crude oil or bitumen. Heavy crude oil and bitumen resources are considered to be more than double the conventional light oil reserves throughout the globe. Abrupt increase in population and constant industrialization result in higher demand of energy consumption which on the other hand results in declining source of lighter oil and increasing demand of the higher crude.

I.C.1. Composition of crude oil

Crude oil is basically the result of a complex combination of chemical and physical processing on the buried remains of plants and animals over millions of years. Depending on the geological background, the composition of crude oil varies a lot which reflects in its properties.

I.C.1.a. Hydrocarbons

Basically crude oil is a complex mixture of various hydrocarbons as given below:

1. **Alkanes:** Saturated linear or branched-chain aliphatic hydrocarbons known as paraffins with the general formula C_nH_{2n+2} . When $n = 13-60$, paraffins exist as solids. When the $n = 13-36$ ($C_{13}-C_{36}$), softmushy waxes are observed. This is also called paraffinic hydrocarbons or macrocrystalline waxes. Hard crystalline waxes have 30-60 or more carbons ($C_{30}-C_{60}$) in the chain. It is also called naphthenic hydrocarbons or micro-crystalline waxes. Paraffin is generally assumed to be in solution
2. **Alkenes:** Unsaturated hydrocarbons known as olefins but comparatively rare in crude oils. Certain refining processes produce large amounts of alkenes by cracking or dehydrogenation process.
3. **Alicyclics:** Saturated cyclic structures based on five and six-membered rings, known as naphthenes.

4. **Aromatics:** Cyclic structures with conjugated double bonds, mainly based on the six-membered benzene ring.

I.C.1.b. Non-hydrocarbons

Many organic compounds in crude oil incorporate other elements such as S, N, O etc, sometimes within ring structures or as functional groups attached to a hydrocarbon structure. Organosulphur compounds are generally much more prevalent than nitrogen or oxygen containing molecules. The principal oxygen containing molecules are carboxylic acids as either saturated aliphatic acids or cycloalkanoic acids (naphthenic acids). Traces of phenols and furans may also occur.

Besides heavy crudes have complex components of high molecular weight and high polarity, called asphaltenes. Asphaltenes are usually referred as the heaviest, most aromatic part of crude oil. It comprises the active surface area of crude oil [42–44], which is insoluble in light paraffin such as n-pentane, n-hexane, and n-heptane, but soluble in light aromatic compounds such as benzene, Toluene or pyridine. The structure of asphaltene is really complex. It is assumed that they have a nucleus composed of one or more poly-crosslinked aromatic hydrocarbons (PAH) attached to aliphatic chains. Asphaltenes have heteroatoms such as nitrogen, sulfur and oxygen indicating the presence of functional groups such as carboxyl, ketones, aldehydes, benzothiophenes, dibenzothiophenes, naphthenobenzothiophenes, alkyl sulphides, alkyl aryl sulphides and aryl sulphides. Some metals such as vanadium, iron, and nickel are also present there [45–47]. Presence of highly strong C=S bonds drastically increases the viscosity of the crude [48, 49]. In addition, asphaltenes are amphiphilic in nature and hence they tend to self-associate and form large aggregates which also increase the viscosity of heavy crude.

I.C.2. Handling problems of crude oil

Although heavy and even extra heavy crude oil have been considered to be the biggest source of energy required globally, their production is a bit challenging area. Especially high pour point and high viscosity are the main barriers against their high production and even transportation via pipeline to various refineries. In normal conditions paraffins are soluble in the crude, but changes

in temperature and/or pressure, loss of volatile components, etc., paraffin precipitates out as wax and adheres to the surfaces in the surrounding environment [50]. As the temperature decreases, the higher molecular weight wax becomes less soluble, solidifies, and separates out from the liquid phase. The temperature at which wax begins to precipitate out from the crude oil is called the wax appearance temperature (WAT) [51]. If sufficient wax is deposited over time, portions of the production system such as wellbores and flow lines can become partially or totally blocked thus having a significant production loss. Studies have suggested that under the most favorable conditions, the waxes form an orthorhombic lattice, but changes in conditions bring about a mixture of orthorhombic and hexagonal lattices also. In the pipelines also, wax deposition occurs as a result of lateral transport by diffusion, shear dispersion, and Brownian diffusion [52] where the temperature is very low or becomes very low seasonally.

From preheat exchangers to crude oil unit heaters, and distillation columns there occurs significant economic and operating cost penalties. Apart from increasing the cost of processing and the maintenance such problems also limit the flexibility of processing different types of crude oils. Presence of undesirable components such as asphaltenes, heavy metals and sulphur also contribute to the high viscosity of crude oil which account for the extremely low mobility of the crude in reservoir. Also in the pipelines which are the most convenient ways to transport crude oil from the production field to the refineries, moving heavy crude oil and bitumen is extremely challenging because of their inability to flow freely since high viscosity causes huge pressure drop in the pipeline and to overcome it huge energy i.e. high pumping power is required which results in increase in cost and at the same time huge production loss every year.

I.C.3. Remedies

Previously when there were enough sources of easily extractible lighter oils, heavy crude was supposed to be uneconomical to produce and process. But constant industrialization and growing demand of energy have forced the mankind to pay attention to the heavy and even extra heavy crude reserves since ever decreasing and limited source of lighter oils alone cannot quench the ever increasing thirst for energy globally. Hence variety of remedial treatments has been

employed to overcome the challenges associated with crude oil from production to transportation.

I.C.3.a. Mechanical method: pipeline “pigging”

Pigging refers to scouring action of a device to remove the wax deposited on the wall inside the pipelines. But to carry out the process, the system needs to be shut down for 1 to 3 operating days which causes severe production loss [53].

I.C.3.b. Injection of naphtha or CO₂

It is a very common and well known technique for viscosity reduction to improve the production of heavy and extra-heavy oil both at the site and at the surface [54–56]. However, these techniques may lead to precipitation of asphaltenes and their deposition in porous media through the production system [54, 55] which in turn may reduce the porosity and permeability of the system. As a result a kind of permanent damage occurs there at the reservoir condition which reflects in huge production loss in the long run.

I.C.3.c. Thermal treatment

After long period of shut down, to start up the pumps and carry the oil to the refineries thermal treatment is required by hot fluid or electric heating to remove wax for short flowlines and downhole. Having a good thermal insulator along the pipeline is required to maintain the temperature of the system above cloud point of the crude. But since it is a kind of local treatment its effectiveness is less. Besides this method is economically very costly, when large distances are to be transported [57, 58].

Catalytic cracking method may also be mentioned here under the thermal treatment for viscosity reduction. Since asphaltenes and resins are believed to be the main reason behind high viscosity of heavy crude, Yufeng et al. [59] investigated the catalytic cracking of asphaltenes and resins by converting them into lighter molecules using nickel and iron catalysts. However, each thermal process demands high amounts of energy and the use of costly agents necessary to carry out the reactions typical of each process.

I.C.3.d. Dilution method

Dilution method is probably the oldest and the most common method for viscosity reduction on surface since 1930's [54]. This method requires addition of light hydrocarbons, organic solvents like methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME), etc or alcohols like pentanol, hexanol etc, gasoline and middle distillates like kerosene in the ratio of 0–20% for heavy crude oil and 25 to 50% for bitumen [60]. But this process comes with its own drawbacks. To carry the diluents along with the crude, there requires another parallel pipeline which itself is a cost worthy process and after the use, oil recovery is another ordeal. Moreover, determining perfect dosage of suitable diluents for a particular crude oil is essential since any mismatch with the quantity may result further deposition of asphaltene and paraffin in the pipeline. Hence hard study is needed to determine the required ratio of oil to diluents for a particular crude oil after full analysis of its composition and large variety of parameters associated with its nature. It means dilution method is not as simple as an arbitrary mixing process.

Natural gas condensates were also used as diluents, but their lower production compared to higher requirement for heavy crude production is a barrier against their use. Besides, asphaltenes are not totally soluble in these condensates and as a result flocculation occurs in the pipeline which leads to partial plugging.

I.C.3.e. Annular flow of crude oil

Another way to improve crude oil production apart from viscosity reduction is reducing pressure drop in pipelines by introducing annular flow. Isaacs and Speed [61] first reported this technique where the possibility of the channeling of viscous fluids through the lubrication of the walls of the tube with water required in the range 10–30% was cited [62, 63]. However, this technique also comes with some limitations which include the formation of waves that are created at the interface of the water and the oil and thus hinders the flow [61, 64].

I.C.3.f. Preventive method

Sometimes it is more preferable to prevent a problem or trouble before its occurrence than to find a solution after it gets happened. Hence the causes and pattern of the problems associated with

storage or transportation of crude oil have been thoroughly investigated and some preventive methods have been utilised to resist or diminish the barriers as far as possible. Some of these methods have been discussed below.

Application of additives

Versatile application of chemicals such as surfactants, scavengers, emulsion breakers, polymers, nanoparticles and other chemical additives as wax modifier and viscosity reducer for crude oil has been studied extensively [65]. So far polymers have gained prominent position among these all in this field. It has been proved in various studies that polymers having long alkyl chain and high molecular weight are good flow improvers for crude oil. Some common polymeric additives are discussed below.

I.C.3.f.1. Ethylene–Vinyl Acetate (EVA) copolymer

Ethylene–vinyl acetate (EVA) copolymer is a linear chain polymer of ethylene and vinyl acetate which has been widely used because of its ability to control the size of the wax crystals [66, 67]. Various studies have been reported about the effect of chain length of EVA on the flow properties of crude oil. As for example, according to Ashbaugh et al. [68] the efficiency of the additive to improve flow ability decreases with the carbon number of the wax crystals. Some studies have also shown the effect of addition of other active systems like methyl methacrylate (MMA), diethanolamine (DEA) etc. on the flow improvement ability of EVA [69, 70].

I.C.3.f.2. Alkyl Acrylate copolymer

Alkyl acrylate copolymers are explored extensively as pour point depressant for waxy crude oils [71]. It contains various sets of alkyl group with carbon number ranging from C₁₄ to C₂₆. Various studies have suggested that the efficiency is influenced by the alkyl chain length and the polarity of the polymer [72]. Again number of studies utilised different combinations of alkyl acrylate with the other co–monomers for further reduction of pour point of crude oil than using only alkyl acrylate polymer [73]. In another study organic nano–clay particles with polyoctadecylacrylate were utilised by Yao et al. [74] which revealed that the pour point of the Changqing waxy crude

oil was reduced by 9°C and viscosity was decreased by 33.8% at 800 mg polyoctadecylacrylate per kg of clay.

I.C.3.f.3. Maleic Anhydride copolymer

Maleic anhydride is known as one of the most active polymerising agents. Its copolymer with styrene or any alkyl esters such as acrylates and acetates have been extensively studied as effective flow improver for waxy crude oil [75–77]. Studies have suggested that longer the chain of the fatty acid in the ester higher will be the effectiveness of the copolymer for viscosity reduction of crude oil which was attributed to the fact that solubility of paraffin wax increased with increasing length of the alkyl chain [75]. Various studies have proved that apart from the alkyl chain length of the polymer, presence of polar group, molecular weight and composition of the polymer are the determining factors for its ability to act as flow improver of crude oil.

I.C.3.f.4. Other Type of Additives

Terpolymers are comparatively newer addition in this field of additives. Castro et al. reported that the viscosity of Mexican crude oil was reduced using the terpolymer consisting of high percentage of styrene and low percentage of n-butylacrylate and vinyl acetate [78]. Another copolymer, synthesized by amination of terpolymer containing monomers of octadecyl acrylate, vinyl acetate and maleic anhydride was reported to depress the pour point of Shengli crude oil by 11°C [79]. Another study suggested that incorporation of the hydrophobic part in the polymer could be effective in enhancing its viscosity reducing property due to the intermolecular association [80]. Nanotechnology also appears as a promising remedial technique in this field. It emerges as a complementary technique capable of competing in both economic and technical ground because of its high potential in improving the mobility of heavy crude by reducing the viscosity through the interaction of minute particles with asphaltenes present in the crude. In addition, the nanometric size of the particles does not represent a problem to plug the pore grooves of conventional crude oil deposits. Its surface has high affinity for the asphaltenes present in the crude, much larger than the affinity between own asphaltene aggregates and thus considerable reduction of viscosity is obtained. Several studies have reported some well designed nanoparticles as efficient viscosity reducers of heavy crude oil [61, 81]. Olusegun Peter

Akinyemi et al. successfully investigated the influence of cheaper natural chemicals, obtained from plant seeds (jatropha, rubber and castor) on the rheological properties and wax deposition tendencies of Nigerian waxy crude oil [82]. An environmentally friendly and cost effective additive for light and heavy crude oils of Oman was reported by Salam K. Al-Dawery and Saleh K. Al-Shereiqi [83]. They used waste bio materials such as fiber of palm tree, date palm kernel and walnut shell materials as viscosity reducing agents on light and heavy crude oils of Oman. In another study by Manojkumar Gudala it was found that addition of 2000 ppm potato starch to the 85% heavy crude oil and 15% water mixture at 40°C decreased viscosity of the crude by 80.24% which is an excellent and very inspiring result [84].

I.D. IONIC LIQUID

Ionic liquids are molten salts composed of large, asymmetric organic cations and usually an inorganic anion having melting point less than 100°C. Usually they are classified based on their cationic part, such as ammonium, imidazolium, pyridinium, and phosphonium [85]. The anionic part commonly consists of chloride [Cl]⁻, bromide [Br]⁻, iodide [I]⁻, hexafluorophosphate [PF₆]⁻, tetrafluoroborate [BF₄]⁻, methanesulfonate [CH₃SO₃]⁻, bis(trifluoromethanesulfonyl)imide [(CF₃SO₂)₂N]⁻, and nitrate [NO₃]⁻ [85, 86]. The physical and chemical properties of the ILs can be modified utilising varied range of cationic and anionic combinations [87].

I.D.1. Properties

Due to large shape, the charges on the ions in ILs usually remain in diffused state and hence the electrostatic force between the ions is highly diminished which accounts for its failure to acquire a regular crystalline shape and opting for the liquid state at room temperature. ILs are unique to exhibit versatile properties such as low volatility, non-flammability, thermal stability, moisture stability, miscibility with organic compounds, good electronic and ionic conductivity and its broad application in electrochemical field [88]. They are often referred to as ‘designer solvents’ due to their ability to dissolve a variety of organic, inorganic and organometallic compounds by simply choosing the proper combination of cations and anions. Some ILs possess amphiphilic structure consisting of both hydrophobic tail groups and hydrophilic head groups with surface activity. Imidazolium-based ionic liquids containing hydrophobic chain longer than four carbon atoms exhibit such behaviour. In addition ILs are considered to be more environmentally friendly in comparison to current alternative solvents and electrolytes [89] and hence are treated as green solvents [90]. Most importantly, availability of various combinations of cation and anion enriched with unique properties, ILs have attained enormous attention over the decade [91] and today variety of ILs are explored with versatile application.

I.D.2. Applications of ILs in automotive industry

Such a promising range of properties along with their potential for controlled reactivity and also their low evaporation, researchers are provoked to explore their application in corrosion

protection [92, 93] and tribology. Especially their extremely low vapor pressure, non flammability and thermal stability even upto temperatures above 200°C are accounting for their capability of lubricating even at increased temperatures and pressure. So far most of the IL based lubricants were investigated at a more fundamental level, but some studies have explored their applications such as in engine lubrication [94–97] and micro–electromechanical machines (MEMs) [98–100]. M. Anand et al have explored the high miscibility and no corrosive behaviour of two phosphonium based ILs i.e. trihexyltetradecylphosphoniumbis(2,4,4-trimethylpentyl)phosphinate and trihexyltetradecylphosphoniumbis(2-ethylhexyl)phosphate and used them successfully as additive in the fully formulated diesel engine lubricants [101]. This study provided a pathway for the used lubricants to recover their tribological performance for further use at the end of service life. Patrick Rohlmann et al. evaluated phosphonium orthoborate ionic liquid as a wear reducing additive in biodegradable oils at steel–steel surfaces in the boundary lubrication regime [102]. Again 1,4-bis(2-ethylhexyl)sulfosuccinate anion–based ILs containing different cation–imidazolium and organoammonium were synthesized and characterized as candidate lubricant additives in synthetic ester oils by Zeyun Wang [103]. Tribological tests on these synthesized ILs which were fully miscible with synthetic ester oil and noncorrosive to steel, revealed effective friction reduction and antiwear functionality. In addition, they worked well with the other typical additives, such as viscosity improver, antioxidant, pour point depressant etc. In another work, three phosphonate ionic liquids such as 1-butyl-3-methylimidazolium *O*-butylphosphonate, *N,N*-dibutylammonium *O*-butyl phosphonate and *N,N*-dibutylammonium *O*-ethyl phosphonate were used as additives in polyethylene glycol (PEG) for steel/steel contact by Yunyan Han et al. and their characterization showed that these ionic liquids improved the tribological performances of the base oil significantly owing to the competitive adsorption between the base oils and the additives and also the chemical reactions between the ionic liquids and the metal substrate [104]. V Pejakovic et al. studied the influence of temperature on tribological behaviour of a sulfate–based ionic liquid with a pyrrolidinium cation as neat lubricant and as additive for glycerol in lubrication of steel–steel contacts and showed that the ionic liquid played an important role in the friction and wear reduction, as well as in the smoothening of the worn surface [105]. Shuyan Yang et al. investigated the tribological performance of IL additives in the mixed lubrication and the

elastohydrodynamic lubrication regimes and evaluated that IL additives could reduce friction and metal wear compared to pure PEG in mild conditions [106]. In another study, ionic liquids were investigated as a possible base oil of next-generation space grease to solve mainly temperature related issues and compatibility with space environment [107]. The newly synthesized perfluoropolyether (PFPE) ionic liquid whose terminal group is an ammonium salt with a carboxylic acid has better frictional properties and has been used for magnetic tapes for about a quarter century because of their good lubricity [108]. Ammonium-based protic ionic liquids (PILs) were tested as lubricant fluids for aluminum-steel contacts by Maria Rita Ortega Vega et al. and they showed that the increase of the anion carbon chain length in the PIL structure reduced significantly the coefficient of friction value [109]. Jun Qu et al. evaluated the anti-wear behavior of an oil-miscible ionic liquid i.e. trihexyltetradecylphosphoniumbis(2-ethylhexyl)phosphate in a base oil at 1.0 wt% concentration under both room and elevated temperatures and reported that the IL and the conventional anti-wear additive, zinc dialkyl-dithiophosphate (ZDDP) worked equally well to prevent scuffing and reduce wear in the room temperature tests, but the IL significantly outperformed ZDDP in the tests performed at 100°C [110]. Patrícia M. Amorim et al. tested imidazolium-based ILs as additives to the base oil PEG to lubricate Si surfaces and found that almost all the additives (2 wt%) led to a decrease in friction coefficient as well as an increase in viscosity [111].

I.D.3. Imidazolium based ILs

Imidazolium based ILs were studied extensively owing to their higher stability than a conventional synthetic oil at 200°C [112], easy adsorption onto a surface, such as phosphonyls and esters [113, 114] and easy variation of alkyl chain length to tune up wear and friction [115–117] according to requirement. From various studies it was determined that the longer the alkyl chain length in the imidazolium group, the lower the wear [118]. Again number of studies suggested that ILs having highly fluorinated anions possess higher thermal stability. Thus imidazolium tetrafluoroborates were hugely utilised due to their ability to exhibit lower friction and wear than traditional lubricants for a number of systems [119, 120]. But ILs are very much expensive compared to mineral base oils and synthetic base oils and hence they cannot be used solely in large volume. On the other hand, they may be used as a lubricant additive where a small

amount of IL is doped into base oil, but provides a large difference to the friction and wear [121]. But there comes a problem with solubility of the IL in base oil. Generally ILs due to their polarity, are not so easily soluble in non polar base oils [122, 123] but it is seen that longer the alkyl chain length on the imidazolium group, higher is the solubility of IL in base oils [124].

I.E. REFERENCES

References for chapter I are given in bibliography section (page 114–124).

CHAPTER II

Additives for lubricating (lube) oil

CHAPTER II.A

Synthesis of polymeric blend of vinyl acetate and acrylate–based copolymers and its performance evaluation in lubricating oil

II.A.1. INTRODUCTION

Polymer blending is a kind of polymer modification process that has attracted much attention as an easy, cost–effective and less time–consuming method for developing new polymeric materials enriched with versatile application at commercial sector. A polymer blend is analogous to metal alloys. It is a mixture of two or more polymers, blended together to form a new material with different physical properties. Generally, there are five main types of polymer blend: thermoplastic–thermoplastic blends; thermoplastic–rubber blends; thermoplastic–thermosetting blends; rubber–thermosetting blends; and polymer–filler blends. In general, preparation of polymers by traditional method using some suitable raw materials which are easy to polymerise and then commercialization of new polymer requires many years and the whole process is very expensive too. But polymer blending process may reduce both cost and time for the development and commercialization of new polymeric material to perhaps two to three years [1]. A study revealed that the production of polymer blends replacing traditional polymers represents half of all plastics produced in 2010 [2].

The most important and interesting thing about polymer blends is that the properties of the blends can be manipulated as per its requirement, by suitable selection of the component polymers [3]. Today’s highly sophisticated polymer industry is equipped with ultra–high–performance injection moulding machines and extruders which easily allow phase–separations and via which viscosity changes also can be effectively detected or manipulated during the processing stages [4]. Although such modern and sophisticated blending technology has greatly enhanced the performance capabilities of polymer blends, it has to face a huge challenge every now and then to come up to the increasing market expectation. To satisfy market pressure, for specific applications polymer blends must perform under some specified mechanical, chemical, thermal or electrical condition. Hence thorough study of the properties and performance of polymer blends is essential to determine the maximum limit of performance of a particular blend.

Recently a data-based approach to the development of industrial polymer blends with specified final properties was presented by John F. MacGregor et al [5].

The performance of polymer blends depends on the properties of each polymer in the blend, their content and morphology. The cost of the blend depends on the material, compounding method and blend morphology. Most blends have been developed for the improvement of a specific property such as impact strength and the process or recycling facility. Polymer blends can be classified as:

1. Immiscible Polymer Blends: These blends have large size domains of dispersed phase and poor adhesion between them. If the blend is formed by two polymers, two glass transition temperatures will be observed. Poly(propylene)-poly(styrene) and poly(propylene)-poly(ethylene) are immiscible blends.
2. Miscible Polymer Blends: These are homogeneous blends with a single-phase structure. In this case, one glass transition temperature will be observed. For example, poly(styrene)-poly(phenylene oxide) and poly(styrene-acrylonitrile)-poly (methyl methacrylate) are miscible blends.
3. Compatible Polymer Blends: These are immiscible polymer blends but exhibit uniform physical properties due to strong interface interactions between the polymer blend components.
4. Compatibilized Polymer Blends: These are also immiscible blends whose physical properties can be stabilized by adding surface-active species called compatibilizers. These compatibilizers influence various morphological processes.

The properties of a polymer blend depend on the final morphology. Hence various research groups have recently undertaken extensive studies of the miscibility and phase behaviour of polymer blends. In practice, the physical properties of interest are found either by miscible pairs or by a heterogeneous system, depending on the type of application. The mixing is exothermic only when strong specific interactions occur between the blend components. The most common specific interactions found in polymer blends are hydrogen bonding [6].

II.A.2. BACKGROUND & OBJECTIVES

Various studies have been performed with polymer blends which establish its effectiveness. Blends of polystyrene (PS) and Acrylonitrile–Butadiene–Styrene (ABS) were prepared in different ratios by melt blending technique by Buthaina A. et al. and the results from their work showed that the mechanical properties for blend system were better than those of pure polymers [7].

Rajendran et al. Successfully Prepared polymer electrolyte membranes comprising of poly(ethyl methacrylate)/ poly(vinyl chloride) with propylene carbonate as plasticizer and LiClO_4 as salt by solvent casting technique [8].

The green blends of an ionic liquid, 1–ethyl–3–propylimidazolium bis(trifluoromethanesulfonyl)imide {[EPrI][TFSI]} and a biodegradable polymer, poly(3–hydroxybutyrate), were investigated by Li–Ting Lee and Chun–Ting Yang to explore the effect of ILs on the crystallization behaviours of the biodegradable polymers [9].

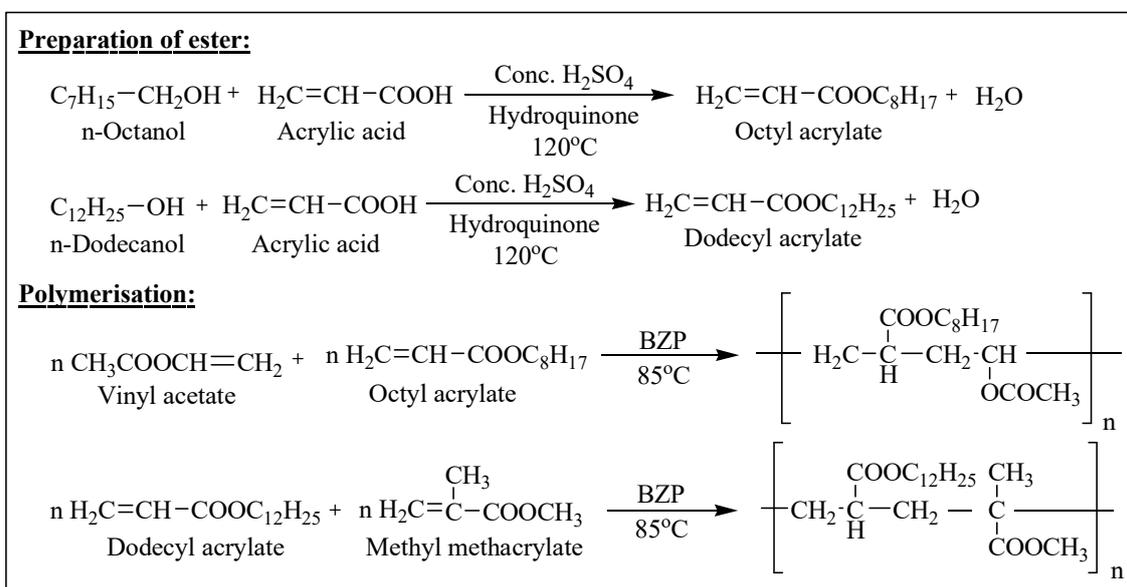
The effect of soybean lecithin and acrylated epoxidized soybean oil as biomass–based compatibilizer agents was studied successfully by Eksiler et al. for the purpose of enhancing the compatibility of environmentally friendly thermoplastic blend of poly (lactic acid) and synthetic rubber [10].

In the area of drug delivery systems, chitosan blends have been widely used for drugs control because of their various advantages such as non–toxicity, biocompatibility, biodegradability and availability of terminal functional groups [11].

The versatility and unique characteristics, such as hydrophilicity, film–forming ability, biodegradability, biocompatibility, antibacterial activity and non–toxicity of chitosan has contributed to the successful development of various blends for medical, pharmaceutical, agricultural and environmental applications [12]. Biodegradable compatibilized polymer blends

have acquired widespread application in packaging industry replacing non-biodegradable materials to satisfy the demands in environmental safety and sustainability [13].

In view of the versatility of polymer blends we have prepared two copolymers—one P₁ of vinyl acetate (VA) and octyl acrylate (OA) and another P₂ of dodecyl acrylate (DDA) and methyl methacrylate (MMA) and then prepared their blend. We characterised them via FT-IR, ¹H NMR and ¹³C NMR spectroscopy. We further evaluated their performance as flow improver for lubricating oil and also investigated their mechanical strength in terms of shear stability index.



Scheme II.A: Preparation of octyl acrylate and its subsequent polymerization with vinyl acetate; Preparation of dodecyl acrylate and its subsequent polymerization with methyl methacrylate

II.A.3. EXPERIMENTAL SECTION

II.A.3.a. Materials

Dodecyl alcohol, octyl alcohol, methyl methacrylate (MMA), Acrylic acid, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. Properties of the mineral base oils used are tabulated in **Table II.A.1**.

Table II.A.1: Base Oil (BO) Properties

Physical Property	BO1	BO2
Density (gcm⁻³ at 40°C)	0.83	0.95
Viscosity at 40°C in cSt	6.698	24.211
Viscosity at 100°C in cSt	2.02	4.47
Viscosity Index (VI)	81.13	89.87
Pour Point (PP in °C)	-3	-6
Cloud Point (°C)	-10	-8

BO1, BO2 collected from IOCL, Dhakuria, West Bengal

II.A.3.b. Preparation of esters and their purification

The ester (dodecyl acrylate, DDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of dodecyl alcohol in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. Another ester (octyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol. The process was carried out in a resin kettle which was heated gradually from room temperature to 130°C using a well-controlled thermostat under a slow stream of deoxygenated nitrogen. The extent of esterification was monitored by the amount of liberated water [14].

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

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

II.A.3.c. Preparation of copolymers and blend

The copolymers were prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). We have prepared two copolymers – one of vinyl acetate (VA) and octyl acrylate (OA) designated as P₁ and another of dodecyl acrylate (DDA) and methyl methacrylate (MMA) designated as P₂.

The polymerization process was carried out in a four-necked round bottom flask fitted with stirrer, condenser, thermometer and an inlet for the introduction of nitrogen along with a dropping funnel. The monomers were taken in equimolar amount and the initiator BZP was added in 0.5% amount of the total mass. Toluene was added as solvent. The reaction temperature was fixed at 85°C for 6h. At the end of the reaction, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 40°C. The two prepared and purified copolymers were further mixed together via mechanical blending process at a magnetic stirrer at 60°C to get a homogeneous blend.

II.A.4. MEASUREMENTS

II.A.4.a. Molecular weight determination

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

II.A.4.b. Spectroscopic Measurements

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

II.A.4.c. Performance evaluation as pour point depressants in lube oil

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

II.A.4.d. Performance evaluation as viscosity index improver (VII)

Viscometric properties were determined at 40°C in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at six different concentrations of the sample solutions. The time of flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2%. Precautions regarding prevention of evaporation of solvent were taken in all the cases. Kinematic viscosity (KV) data at 40°C, 100°C and viscosity index (VI) data are given in **Table II.A.4 and II.A.5**.

II.A.4.e. Shear stability measurement

Shear stability of a polymer is a measurement of its ability to sustain its viscosity under shearing conditions. Viscosity loss under shearing conditions may be of two kind's viz. Temporary Viscosity Loss (TVL) and Permanent Viscosity Loss (PVL) [15]. The latter occurs due to mechanical degradation of polymer molecules and is often expressed in terms of Permanent Shear Stability Index (PSSI). PSSI data is obtained following the equations expressed in chapter I (**I.A.1.b**). The PVL and PSSI values are measured here preparing 1%–6% solutions of the

prepared copolymers and their blend in BO1 and BO2 as per ASTM D-3945 method and are given in **Table II.A.6**.

II.A.5. RESULTS AND DISCUSSION

II.A.5.a. 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 (P_1 , P_2) and their blend are given in **Table II.A.2**. From the experimental data, it was found that blend had higher number average and weight average molecular weight than the copolymers. This result also indicates a fine blending of P_1 and P_2 . Again in terms of polydispersity index (PDI) the polymer blend is less poly-dispersed than the copolymers (P_1 and P_2) which indicates better uniformity in the blend. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the M_w values decrease but PDI value increases.

Table II.A.2: Molecular weight and polydispersity index data

Additive	M_n	M_w	PDI
P_1	25339	53374	2.11
P_2	13644	31166	2.28
Blend	34110	58693	1.72

II.A.5.b. Spectroscopic analysis

IR spectrum for copolymer P_1 (**Figure II.A.1**) showed clear peak around 1739 cm^{-1} and 1685 cm^{-1} indicating the presence of ester carbonyl group. Strong peak around 1107 cm^{-1} accounted for the presence of C–O stretching frequency for ester group. Similar IR spectrum is obtained for the polymer P_2 (**Figure II.A.2**). Here peak at 1732 cm^{-1} indicates the presence of ester carbonyl group and peak around 1165 cm^{-1} appeared for the carbonyl C–O stretching. In both cases no

peak has been observed around 3100 cm^{-1} associated with alkenyl C–H stretching. This observation actually supported the complete polymerization in both the polymers.

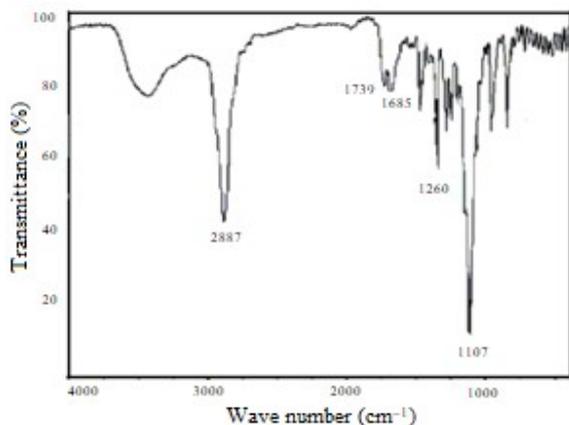


Figure II.A.1: FT-IR spectrum of polymer P₁

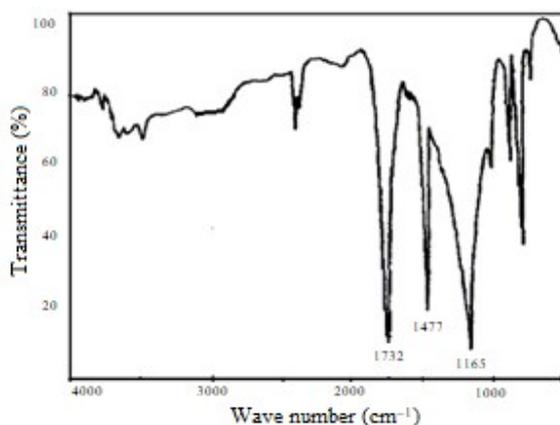


Figure II.A.2: FT-IR spectrum of polymer P₂

¹H NMR spectroscopy for the polymer P₁ produced the following result (**Figure II.A.3**). Here, peaks in the range of 3.36–3.58 ppm indicated the presence of –OCH₂– protons and peaks in the range of 1.53–1.69 ppm accounted for the presence of –CH₂– and –CH₃ protons attached with carbonyl carbon. Peaks in the range of 0.90–1.27 ppm indicated the presence of other methyl or methylene protons. Absence of peaks around 6 ppm indicated absence of unsaturation and hence supports total polymerisation.

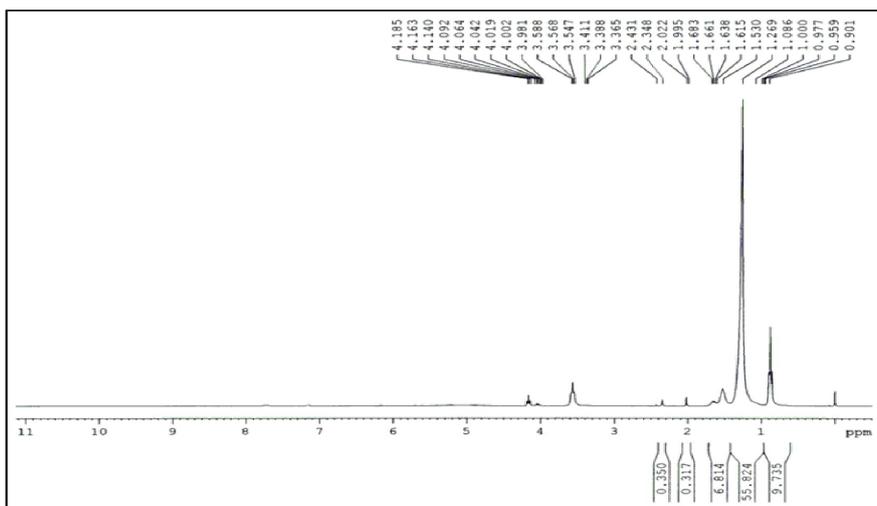


Figure II.A.3: ¹H NMR spectrum of P₁

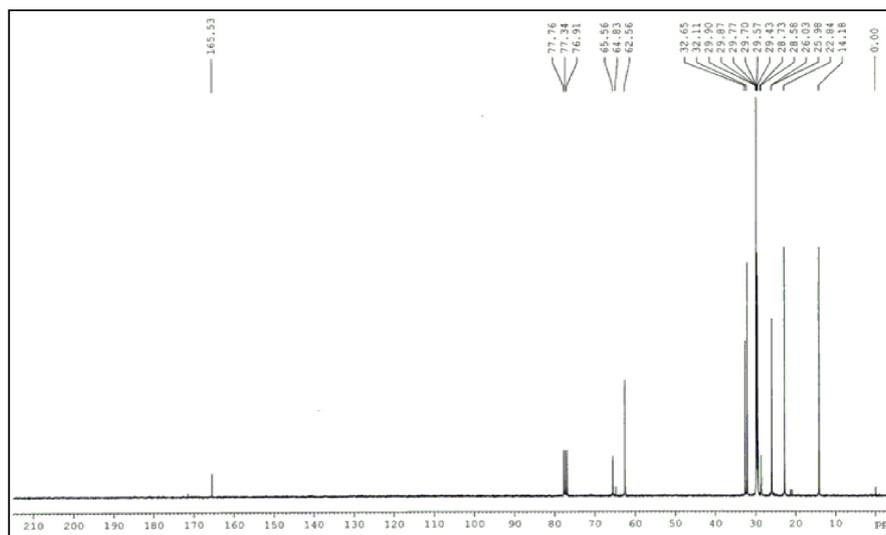


Figure II.A.4: ¹³C NMR spectrum of P₁

In ¹³C NMR of the polymer P₁ (**Figure II.A.4**), the peak around 165.5 ppm indicated the presence of ester carbonyl carbon. The peaks at 62.6–65.6 ppm corresponded to the –OCH₂– carbons and peaks ranging from 14.2–32.4 ppm for all other sp³ carbons. Again no peak in the range of 120–150 ppm indicated the absence of sp² carbons and confirmed the successful polymerization.

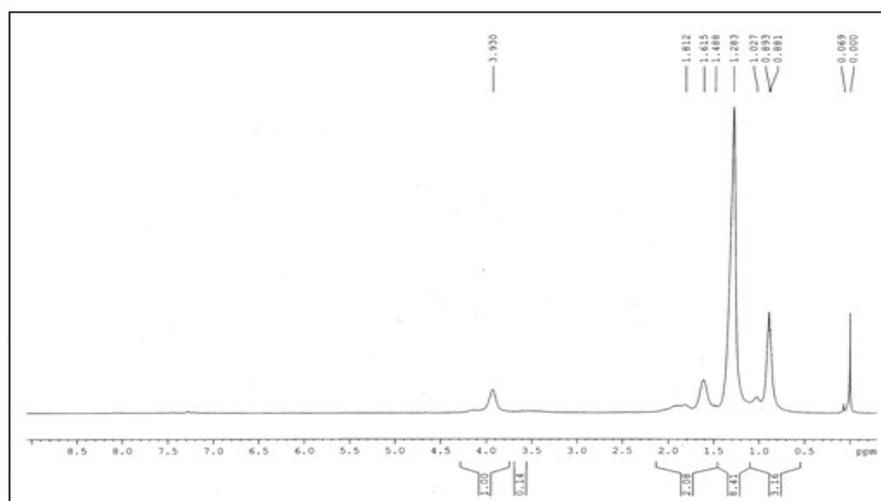


Figure II.A.5: ¹H NMR spectrum of P₂

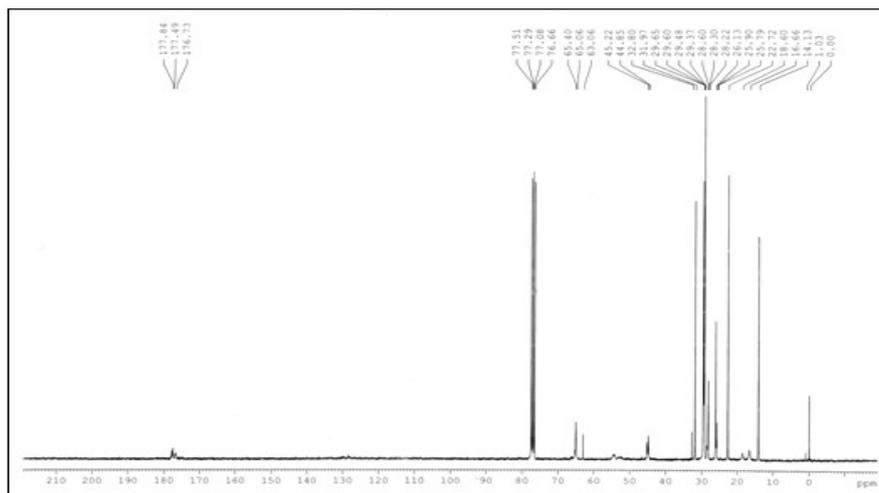


Figure II.A.6: ^{13}C NMR spectrum of P_2

^1H NMR spectroscopy for the polymer P_2 (Figure II.A.5) also showed almost similar values. Here peaks around 3.93 ppm indicated the presence of $-\text{OCH}_2-$ protons and peaks in the range 0.88–1.61 ppm appeared for other methyl and methylene protons. In ^{13}C NMR of the polymer P_2 , (Figure II.A.6) ester carbonyl peak appeared at 174.7–177.8 ppm and $-\text{OCH}_2-$ carbons appeared in the range of 63.06–65.40 ppm. Here also no peak appeared around 120–150 ppm corresponding to unsaturated carbons.

II.A.5.c. Performance evaluation as pour point depressant

Analysing the pour point data given in Table II.A.3, it may be said that both the prepared copolymers and their blend acted as good flow improvers and among them all the copolymer P_2 i.e. copolymer of methyl methacrylate and dodecyl acrylate was proved to be the best one. The graphical representation of the pour point data (Figure II.A.7) makes the comparison clearer.

The pour point depression at higher concentrations nearly reaches to constant or almost no change is observed at higher concentration which may be due to lower solubility of the polymers at higher concentration. The longer alkyl chain length of the ester in P_2 actually accounts for its better effectiveness as PPD which was supported by earlier reports [16]. In case of the blend lower solubility in the base oil might retard its property as flow improver at higher

concentration. The best result was obtained for the copolymer P₂ at 3% concentration in the base oil 2 (BO2).

Table II.A.3: Pour point data with respect to the different concentrations of the additives in base oil (BO)

Additive	BO	PP (°C) at different concentrations (% w/w) of additive						
		0%	1%	2%	3%	4%	5%	6%
P ₁	BO1	-3	-10.0	-10.9	-11.5	-11.9	-11.0	-10.5
	BO2	-6	-12.0	-12.5	-13.2	-11.9	-10.8	-10.7
P ₂	BO1	-3	-11.5	-12.0	-12.8	-12.5	-11.9	-11.0
	BO2	-6	-13.5	-14.4	-15.2	-14.9	-13.0	-12.9
Blend	BO1	-3	-10.5	-11.2	-11.0	-10.3	-10.0	-9.5
	BO2	-6	-12.0	-12.5	-13.1	-13.0	-12.4	-11.9

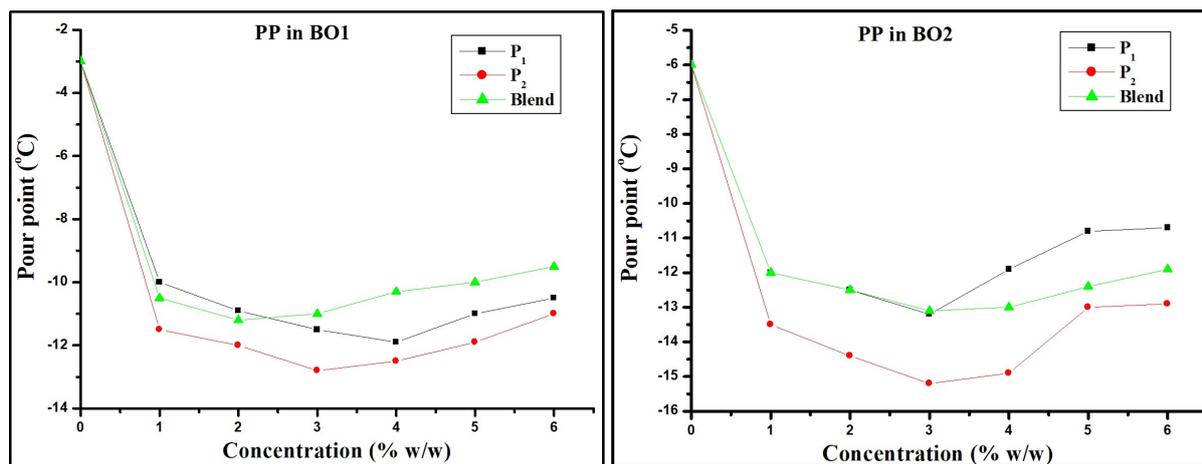


Figure II.A.7: PP (°C) at different concentrations (% w/w) of additive

II.A.5.d. Performance evaluation as viscosity index improver

Among the copolymers, P₁ i.e. copolymer of vinyl acetate and octyl acrylate showed better result (Table II.A.4 and II.A.5) as viscosity index improver which may be attributed to its lower alkyl chain length in the ester and also its higher molecular weight than P₂.

Table II.A.4: Viscosity Index (VI) data with respect to the different concentrations of the additives in base oil 1 (BO1)

Conc ⁿ	P ₁			P ₂			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	6.705	2.120	113	6.701	2.100	106	6.710	2.160	128
2	6.714	2.160	127	6.709	2.130	111	6.724	2.190	135
3	6.727	2.200	141	6.717	2.180	132	6.740	2.240	153
4	6.750	2.250	157	6.123	2.210	144	6.770	2.280	164
5	6.780	2.300	170	6.741	2.250	155	6.800	2.310	172
6	6.810	2.340	184	6.760	2.290	171	6.830	2.350	185

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

Interestingly here blend of P₁ and P₂ acted as the best viscosity index improver may be due to its higher molecular weight. Irrespective of all the polymers and base oil, viscosity index gradually increased with increasing concentration (Figure II.A.8) of the added polymers which may be due to an increase in the total volume of the polymer micelles in the oil solutions [17].

Table II.A.5: Viscosity Index data with respect to the different concentrations of the additives in base oil 2 (BO2)

Conc ⁿ	P ₁			P ₂			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	24.320	4.850	122	24.250	4.710	111	24.380	5.050	137
2	24.340	5.000	134	24.280	4.860	123	24.430	5.180	147
3	24.390	5.250	153	24.330	5.040	137	24.550	5.470	168
4	24.480	5.370	161	24.410	5.200	149	24.590	5.590	176
5	24.570	5.560	174	24.490	5.370	161	24.640	5.710	184
6	24.650	5.780	189	24.560	5.640	180	24.700	5.820	191

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

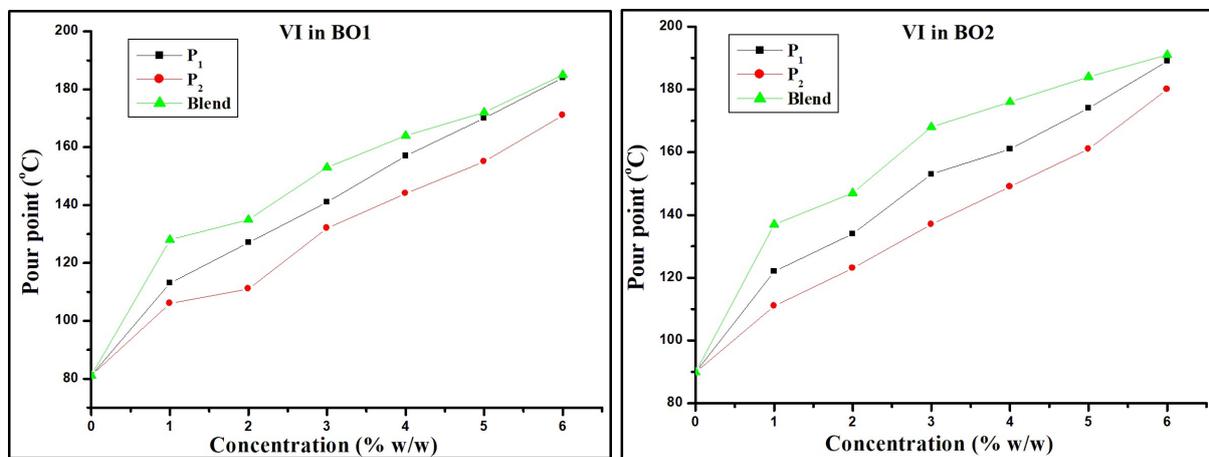


Figure II.A.8: Variation of viscosity index with respect to the different concentrations of the additives

II.A.5.e. Shear stability index analysis

As expected polymer blend of the prepared copolymers showed highest stability against mechanical shear at all concentrations, which clearly supports its better mechanical and thermal property in both the base oils (**Table II.A.6**).

Table II.A.6: PVL & PSSI data with respect to the different concentrations of the additives in base oil (BO)

Base Oil	Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
		P ₁	P ₂	Blend	P ₁	P ₂	Blend	P ₁	P ₂	Blend
BO1	1	2.081	2.016	2.110	1.84	1.86	2.32	39.00	48.75	35.71
	2	2.100	2.083	2.125	2.78	2.21	2.97	42.86	52.22	38.23
	3	2.120	2.080	2.150	3.64	4.59	4.02	44.44	62.50	40.91
	4	2.140	2.090	2.173	4.89	5.43	4.69	47.83	63.16	41.15
	5	2.150	2.100	2.190	6.52	6.67	5.19	53.57	65.22	41.38
	6	2.160	2.100	2.220	7.69	8.29	5.53	56.25	70.37	39.39
BO2	1	4.655	4.560	4.965	4.02	3.18	1.68	51.32	62.50	47.22
	2	4.710	4.610	5.020	5.80	5.14	3.09	54.72	64.10	51.61
	3	4.800	4.660	5.493	8.57	7.54	1.11	57.69	66.67	60.70
	4	4.837	4.710	4.880	9.93	9.42	12.70	59.22	67.12	63.39
	5	4.890	4.730	4.920	12.05	11.92	13.83	61.47	71.11	63.71
	6	4.930	4.820	4.930	14.71	14.54	15.29	64.89	74.07	65.93

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100°C.

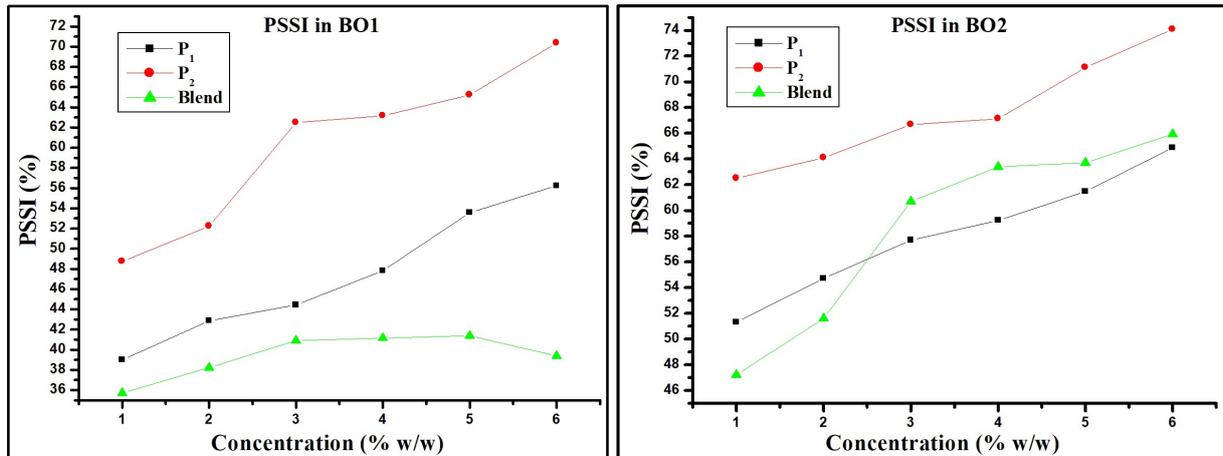


Figure II.A.9: Variation of PSSI with respect to the different concentrations of the additives

Another important observation was that irrespective of both the copolymers and their blend, moderately higher PSSI value was obtained in case of the base oil with higher viscosity (BO2). It is believed that polymer molecules are more tightly bound in high viscous base oil and hence the mobility of the polymer chain is reduced which makes the polymer molecule more susceptible to bond rupture i.e. mechanical degradation. Hence in base oil with higher viscosity, shear stability of the additives decreases [18] which was evident from our result more clearly shown in **Figure II.A.9**. Higher the concentration of the additive higher was the PSSI and hence PSSI value. But the relationship between the concentration of the polymer and shear stability index was not linear since various other factors like molecular weight of the polymer, composition of the base oil might play different role on shear stability.

II.A.6. CONCLUSION

Thus it may be concluded that all the prepared polymers including the blend were proved to be a good flow improver for lubricating oil. When it comes to mechanical stability the polymer blend of the prepared copolymers excels. It may be because of its higher molecular weight and lower polydispersity index. The blend was also proved to a better viscosity modifier at all concentrations in the base oil.

II.A.7. REFERENCES

References for chapter II.A are given in bibliography section (page 125–126).

CHAPTER II.B

Effect of percentage of initiator used in the polymerisation process on the performance of the prepared additives: A comparative study

II.B.1. INTRODUCTION

High performance lubricating oil is a major exploring area in automotive industry. It is the lubricant which keeps the moving surfaces away from each other and protects them from corrosion and rust and thus enhances engine's durability and performance [1]. Modern lubricants are formulated from wide variety of mineral base oils blended together with some appropriate chemical additives [2]. The additives play very important role to optimize the properties of lubricants such as pour point depressants [3, 4], viscosity index improvers [5, 6], extreme pressure additives [7] etc. Polymers have conquered a special and major place in this aspect to be explored as additives. A number of research groups have been engaged in this field to synthesize multifunctional polymeric additive. But still there is a quest to find out the most suitable cost effective additive with minimum dosage but maximum effect.

Free radical polymerisation has been considered to be one of the most favourite processes for the production of polymers. Free radical polymerisation process proceeds via three steps; mainly initiation, propagation and termination. Free radical polymerisation processes are really very hard to control. But today some advanced techniques have made it possible to control free radical polymerization reactions especially by suppressing termination and transfer processes which has gained enough attention, even if their share in the total polymer production is still rather small [8].

Peroxy compounds may be the oldest initiating agents in technical polymerization processes since about 100 years. Either singly or in combination with other promoting agent, benzoyl peroxide (BZP) has been utilised vastly in free radical polymerisation processes. Berger et al. delivered a kinetic study on BZP initiated polymerisation of styrene in bulk at 30 to 80°C [9]. The rates and degrees of polymerisation of styrene using various concentration of BZP initiator at 60°C was determined by Mayo et al where contribution to the average degree of

polymerisation of chain transfer of the polymer radical with the monomer and peroxide was evaluated [10]. They reported that chain transfer with the initiator, the efficiency of benzoyl peroxide in initiating chains in styrene and the relative importance of disproportionation and coupling in the termination reaction are closely related. Kinetic study of polymerisation of styrene in benzene at 60°C initiated by BZP was reported by P.C. Deb and G. Meyerhoff [11].

On the other hand, azobisisobutyronitrile (AIBN) is the first and up to now mostly used aliphatic azo initiator. It was discovered by Thiele and Heuser in 1896 [12]. Several studies proved that AIBN yields initiating radicals at the same rate irrespective of different series of solvents [13, 14]. But presence of cyano group makes it susceptible to cause toxic side products during thermal decomposition which is a drawback of this initiator.

II.B.2. BACKGROUND & OBJECTIVES

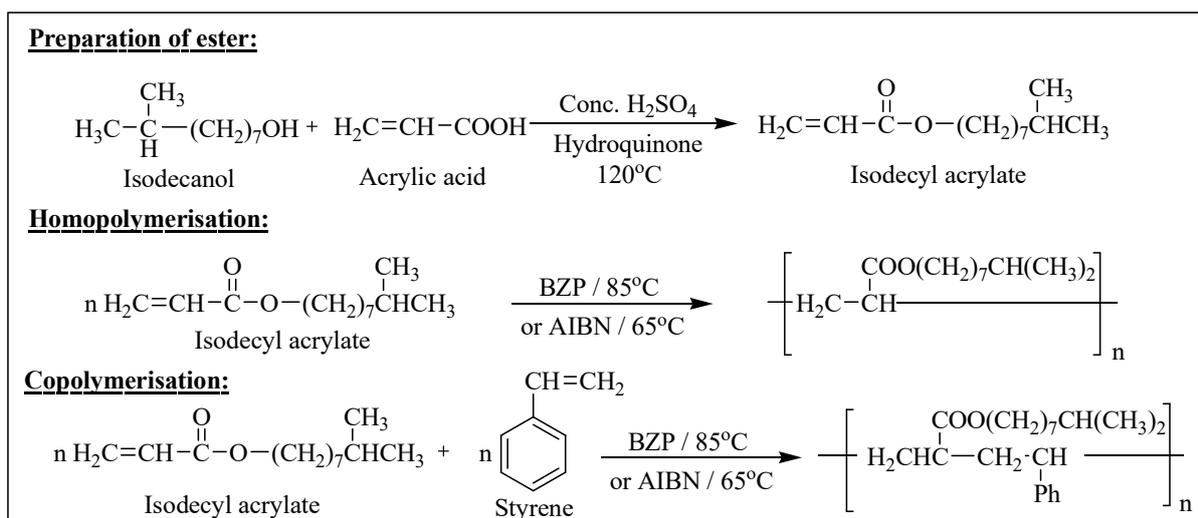
Several kinetic investigations of polymerisation under binary initiator system like BZP–amine system have been reported [15]. S. N. Trubitsyna et al. delivered a report on the interaction of benzoyl peroxide with the polymeric emulsifier, aminated polystyrene [16]. Cationic emulsifiers of the quaternary ammonium salt form an efficient initiating system with benzoyl peroxide. In alkaline conditions, the quaternary ammonium salt isomerises to a carbinolbase which interacts with the peroxide via peroxide–amine mechanism leading to formation of the benzoate radical, which initiates polymerization. The free radical homopolymerization of bis–phenol–A–bis(glycidyl methacrylate), a urethane dimethacrylate and triethylene glycol dimethacrylate induced by a benzoyl peroxide–amine redox couple was studied by Sideridou et al using differential scanning calorimetry [17]. This study revealed that amines with electron donating para–substituents are efficient co–initiators for polymerization at 37°C whereas amines with the electron–withdrawing para–substituent could not initiate polymerization at 37°C, but only at higher temperatures. Polymerization of methyl methacrylate in the presence of binary systems containing benzoylperoxide and activators 4–(4–dimethylaminostyryl)pyridine, 4–(4–dimethylaminostyryl)pyridine–N–oxide in chlorobenzene at 30°C was studied by N. A. Turovskii et al. The rate constants of decomposition of benzoyl peroxide in the presence of

activators, initial polymerization rates, initiation rates, and initiation efficiencies at 30°C were determined [18].

Different kinetic studies have been reported on AIBN-initiated polymerisation. The kinetic rate constants of AIBN initiated polymerisation of styrene at 60°C were determined by Braks and Huang [19]. Burnett and Loan observed that the rate of polymerization of methyl methacrylate, methyl acrylate, and vinyl acetate in benzene decreases with the increase in solvent concentration [20]. The AIBN-initiated polymerization of methylmethacrylate in pyridine at 50°C proceeds to higher conversion than that carried out in bulk. The increased values of the overall rate constant are due to the increased values of the initiation rate constant. Another report showed that polymerization of vinyl acetate in benzene experienced low polymerisation rate which was explained by the formation of a complex between the growing radical and benzene [21]. This complex remains comparatively inactive in the propagation reaction. Same case of retardation was observed also in the AIBN-initiated polymerization of styrene in carbon tetrabromide [22]. Burnett and co-workers found that the polymerization rate of methylmethacrylate in halogenated benzenes and in naphthalene at 60°C in presence of AIBN was higher than in cases when the solvent acts as an inert diluents. They suggested that three macroradical species might contribute to propagation in methylmethacrylate polymerization: an uncomplexed species, a species complexed with solvent, and a species complexed with monomer [20]. Recently AIBN in combination with (SiMes)Ru(PPh₃)IndCl₂ catalytic system was investigated for controlled radical polymerisation of methylmethacrylate in solution and various factors such as aging time of the initiator, concentration of the monomer, polymerisation time, temperature and nature of solvent were examined [23]. Kinetic study of AIBN initiated polymerisation of methylmethacrylate in pyridine at 50°C, done by Kaloforov revealed that the overall rate constant increases with increasing initiation rate constant [24]. Another investigation estimated the retarding effect of acetophenone in the polymerization of methylmethacrylate initiated by AIBN in the temperature range of 50 to 80°C where the effects of varying concentrations of substrate, monomer, initiator, and salts were also investigated by Manjushree Senapati et al [25]. A comparative study between homopolymer of decyl methacrylate and its copolymer with different concentration of styrene using AIBN and BZP initiator was presented

by Ghosh et al. [26]. Another comparative study between homogeneous reverse atom transfer radical polymerisation (ATRP) of styrene using BZP in presence of CuBr/ CuBr₂ complexed by 4,4'-di(5-nonyl)-2,2'-bipyridine and the same polymerisation using AIBN and CuBr₂/2dNbpy was reported [27].

As we can see lot of studies have done on the kinetic investigations of the AIBN or BZP-initiated polymerisation processes. But few studies have reported providing their proper comparison. In this present context, we have delivered a comparative study over the effect of percentage of the initiator either BZP or AIBN, used during the homopolymerisation of isodecyl acrylate and its copolymerisation with styrene, on the molecular weights of the prepared polymers and on their performance as PPDs, VIIs and extreme pressure additives.



Scheme II.B: Preparation of isodecyl acrylate; its subsequent homopolymerisation and copolymerization with styrene

II.B.3. EXPERIMENTAL SECTION

II.B.3.a. Materials

Isodecyl alcohol, acrylic acid and styrene (99%, Sigma–Aldrich) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. AIBN (GC 98%), obtained from Spectrochem Pvt. Ltd. Mumbai (India) was recrystallized from CHCl_3 -MeOH before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd.) was used as received. Properties of the mineral base oils used are previously mentioned in Chapter II.A.

II.B.3.b. Preparation of esters and their purification

The ester (isodecylacrylate, IDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of isodecyl alcohol in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in Chapter II.A [28].

II.B.3.c. Preparation of polymers

The homo polymer of isodecylacrylate and its copolymer with styrene were prepared via free radical polymerisation using varied percentage of either BZP or AIBN. Homopolymers P_1 to P_5 and copolymers P_{11} to P_{15} were prepared using BZP whereas homopolymers P_6 to P_{10} and copolymers P_{16} to P_{20} were prepared using AIBN. The percentages of the added initiator with respect to total weight of monomer during polymerisation are mentioned in **Table II.B.1**. The process of polymerization and purification of polymer was carried out by the procedure as reported in Chapter II.A [28].

II.B.4. MEASUREMENTS

II.B.4.a. Molecular weight determination

The average molecular weights of the prepared polymers were measured by 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 number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) data are given in **Table II.B.1**.

II.B.4.b. Spectroscopic Measurements

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

II.B.4.c. Performance evaluation as pour point depressants in lube oil

The lowest temperature at which movement of the oil sample can be noticed when the sample container is tilted, is called pour point of that oil [29]. To achieve high performance lube oil its pour point must be lowered with perfect dosage of perfect additives called pour point depressants. The performance of our prepared polymers as ppds in the mineral base oils (BO1 and BO2) was tested according to the ASTM D 97-09 method. Solutions were prepared using different doping concentrations ranging from 1% to 5% (w/w) for each of the prepared polymer and the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India). The values are given in **Table II.B.2**.

II.B.4.d. Performance evaluation as viscosity index improver (VII)

Viscometric properties of the prepared polymers were determined at 40°C in toluene solution, using an Ubbelohde OB viscometer. For each polymer five solutions were prepared from 1% to 5% (w/w) concentration in both the base oils. The time of flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2%. Precautions regarding prevention of evaporation of solvent were taken in all the cases. Kinematic viscosity (KV) data at 40°C, 100°C and viscosity index (VI) data in BO1 and BO2 are given in **Table II.B.3**, **II.B.4** and **II.B.5**.

II.B.4.e. Shear stability measurement

Shear stability of a polymer is one of the most important parameters to judge its acceptability as a chemical additive. It is a measurement of ability to sustain viscosity under shearing conditions. The required equations for shear stability measurement are discussed in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured here preparing 1%–5% solutions of the prepared polymers in BO1 and BO2 as per ASTM D-3945 method and are given in **Table II.B.6**, **II.B.7** and **II.B.8**.

II.B.5. RESULTS AND DISCUSSION

II.B.5.a. 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 (P_1 to P_{20}) are given in **Table II.B.1**. It is evident from the molecular weight data that the homopolymers have higher molecular weight than the copolymers irrespective of the initiators used during polymerisation. But the homopolymers prepared using BZP initiator, have higher molecular weight than those prepared using AIBN initiator. On the other hand copolymers prepared using AIBN initiator, have higher molecular weight than those prepared using BZP initiator. But PDI values are more or less same in all the cases. Comparing all the molecular weight data it may be said that the homopolymer P_2 prepared using 0.5% BZP showed highest molecular weight among all whereas polymerisation using 1.0% AIBN showed better result among polymers prepared using AIBN initiator.

Table II.B.1: Percentage of initiator used during polymerisation and molecular weight data

Polymer	BZP (%)	AIBN (%)	M_n	M_w	PDI
P_1	0.1	–	14059	32540	2.31
P_2	0.5	–	14544	33121	2.28
P_3	1.0	–	14100	32699	2.32

P₄	1.5	–	13812	30611	2.22
P₅	2.0	–	13514	30219	2.24
P₆	–	0.1	13000	28900	2.22
P₇	–	0.5	13109	30100	2.30
P₈	–	1.0	13777	30127	2.29
P₉	–	1.5	13549	29903	2.21
P₁₀	–	2.0	13400	30000	2.24
P₁₁	0.1	–	12511	28400	2.27
P₁₂	0.5	–	12914	28854	2.23
P₁₃	1.0	–	12814	28103	2.19
P₁₄	1.5	–	12611	28004	2.22
P₁₅	2.0	–	12031	27899	2.32
P₁₆	–	0.1	12006	29910	2.49
P₁₇	–	0.5	12870	30059	2.34
P₁₈	–	1.0	13048	30101	2.31
P₁₉	–	1.5	13005	30000	2.31
P₂₀	–	2.0	12954	29801	2.30

P₁ to P₁₀ and P₁₁ to P₂₀ represent homopolymer of isodecyl acrylate and copolymers of isodecyl acrylate with styrene respectively

II.B.5.b. Spectroscopic analysis

The IR spectrum of all the prepared homopolymers and copolymers showed clear peak ranging from $1730\text{ cm}^{-1} - 1737\text{ cm}^{-1}$ corresponding to ester carbonyl. For example, the IR spectrum of one of the homopolymers (P_1) and one of the copolymers (P_{11}) have been shown below (**Figure II.B.1 & Figure II.B.2**). In case of the homopolymer peak at 1734 cm^{-1} corresponded to ester carbonyl group whereas in case of the copolymer, ester carbonyl stretching frequency appeared around 1733 cm^{-1} . Here, peaks around 2990 cm^{-1} corresponded to aromatic C=C of styrene present in the copolymers. No peak is obtained above 3000 cm^{-1} which indicates absence of C=C unsaturation and supports complete polymerisation in all the cases.

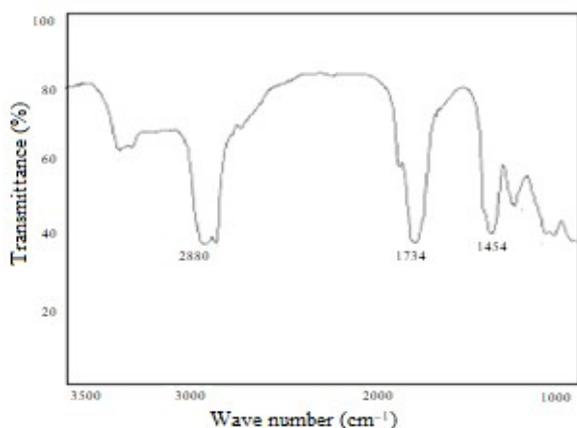


Figure II.B.1: FT-IR spectrum of P_1

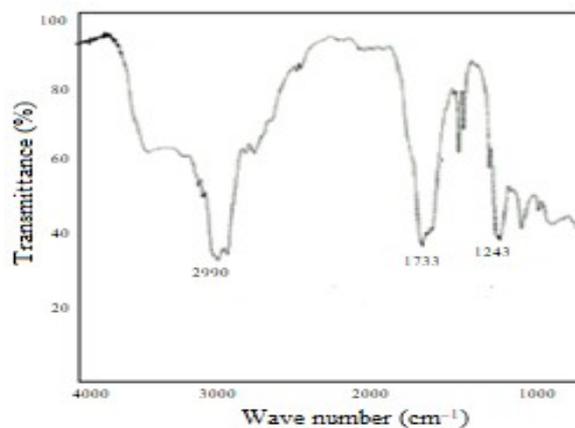


Figure II.B.2: FT-IR spectrum of P_{11}

The results obtained in ^1H NMR and ^{13}C NMR spectroscopy of the homopolymer P_1 are given in **Figure II.B.3** and **Figure II.B.4** respectively. In ^1H NMR spectrum, peaks appeared at 3.92–4.15 ppm due to presence of $-\text{OCH}_2-$ protons and other protons appeared at 0.92–1.69 ppm. In the ^{13}C NMR spectra ester carbonyl carbon produced peak around at 174.3 ppm and $-\text{OCH}_2-$ carbons appeared in the range from 59.8–65.9. The $-\text{CH}_2-$ carbons attached to the ester group appeared around 40 ppm and the rest sp^3 carbons appeared below upto 13.9 ppm.

121.7–133.3 ppm accounted for the presence of aromatic moiety styrene. Peaks in the range 62.7–66.2 ppm appeared for $-OCH_2-$ carbons. Other carbons attached with ester group produced peaks in the range 28.5–32.5 ppm. The rests accounted for other methyl and methylene carbons in the range 14.1–26.2 ppm.

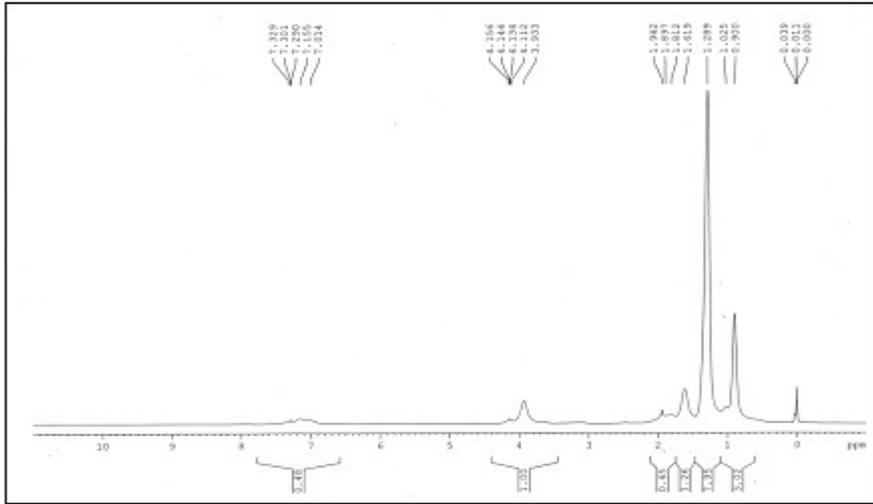


Figure II.B.5: $^1\text{H-NMR}$ spectrum of P_{11}

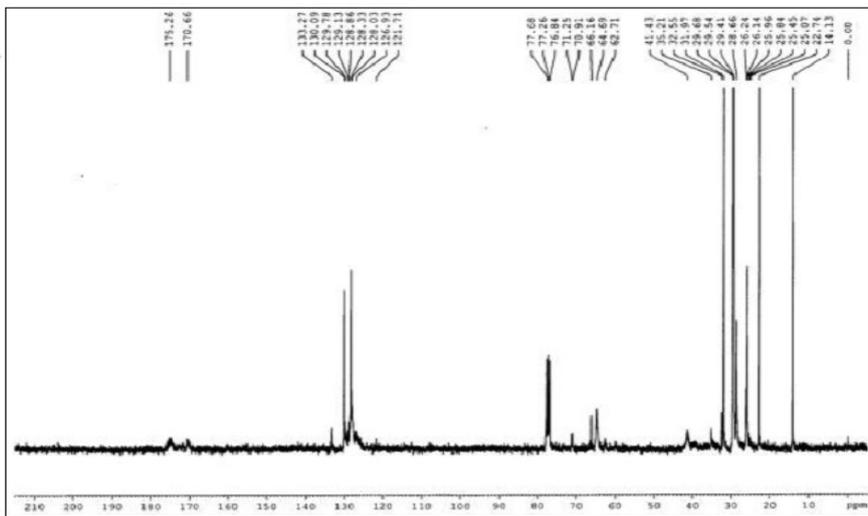


Figure II.B.6: $^{13}\text{C-NMR}$ spectrum of P_{11}

II.B.5.c. Performance evaluation as pour point depressant

When the temperature decreases and reaches towards pour point wax crystals come out of the base oil and gradually gets bigger in shape and finally form a 3-D network of wax crystal which entraps the liquid and at some point immobilises the oil. Pour point depressants do not in any way affect the temperature at which the wax crystals grow or the amount of wax precipitates out, rather they modify the growing pattern of the waxes [31]. With decreasing temperature PPDs also come out of the solution as crystals along with the wax crystals and form a PPD backbone on the wax crystals. Due to this PPD backbone there plays a steric hindrance which keeps the wax crystals far apart and prevents the formation of 3-D network of wax crystal. Thus PPDs improve the flow property of base oil. Generally polymers with long alkyl chain, high molecular weight are good enough in this field [32].

Table II.B.2: Pour point (PP) data (°C) with respect to the different concentrations (% w/w) of the additives in BO

Conc ⁿ	PP data in BO1					PP data in BO2				
	1%	2%	3%	4%	5%	1%	2%	3%	4%	5%
P₁	-8.9	-9.1	-9.4	-9.4	-9.2	-11.7	-11.9	-12.3	-12.6	-12.6
P₂	-9.0	-9.2	-9.5	-9.7	-10.0	-12.2	-12.4	-12.7	-12.9	-12.8
P₃	-8.8	-9.0	-9.3	-9.5	-9.7	-12.0	-12.3	-12.8	-12.7	-12.7
P₄	-8.9	-9.3	-9.6	-9.6	-9.4	-12.2	-12.4	-12.7	-12.6	-12.3
P₅	-8.7	-9.1	-9.3	-9.7	-9.6	-11.9	-12.5	-12.6	-12.5	-12.2
P₆	-8.4	-8.7	-9.0	-9.2	-9.4	-11.4	-11.7	-11.9	-11.9	-11.8
P₇	-8.4	-8.8	-9.1	-9.4	-9.4	-11.0	-11.2	-11.5	-11.8	-11.8
P₈	-8.6	-8.9	-9.2	-9.5	-9.6	-11.3	-11.6	-11.8	-12.0	-12.0
P₉	-8.5	-8.8	-9.0	-9.3	-9.4	-11.2	-11.4	-11.5	-11.7	-11.5

P₁₀	-8.6	-8.9	-9.1	-9.5	-9.4	-11.1	-11.3	-11.6	-11.8	-11.8
P₁₁	-10.7	-10.9	-11.2	-11.4	-11.3	-13.2	-13.6	-13.9	-14.1	-14.2
P₁₂	-10.9	-11.0	-11.3	-11.5	-11.5	-13.4	-13.9	-14.0	-13.8	-13.8
P₁₃	-10.9	-11.1	-11.4	-11.4	-11.2	-13.0	-13.3	-13.6	-14.0	-14.1
P₁₄	-10.8	-11.0	-11.2	-11.2	-10.9	-13.3	-13.5	-13.7	-14.0	-14.0
P₁₅	-10.7	-10.9	-11.1	-11.3	-11.4	-13.1	-13.5	-13.8	-14.2	-14.0
P₁₆	-11.0	-11.3	-11.5	-11.8	-11.8	-14.3	-14.7	-15.1	-15.0	-14.9
P₁₇	-11.1	-11.4	-11.6	-11.7	-11.6	-14.2	-14.8	-15.0	-14.8	-14.6
P₁₈	-11.1	-11.4	-11.6	-11.9	-11.9	-14.5	-14.9	-15.5	-15.9	-15.8
P₁₉	-10.9	-11.3	-11.6	-11.6	-11.5	-14.1	-14.6	-15.2	-15.0	-15.0
P₂₀	-11.0	-11.2	-11.5	-11.7	-11.7	-14.2	-14.6	-14.9	-15.2	-15.2

Concⁿ represents concentrations (% w/w) of the additives in base oil (BO)

Analysing the pour point data given in **Table II.B.2**, it may be said that all the prepared polymers acted as good flow improvers. But the copolymers are proved to be better PPDs than the homopolymers. Styrene incorporation in additive is well known to form an effective pour point depressant. This is also supported by our results. Among all P₁₈ copolymer prepared using 1.0% AIBN, showed highest pour point depression in both the base oils (BO1 and BO2). Homopolymers may be because of their higher molecular weight are less soluble in the base oil and hence are lesser effective as pour point depressant than the copolymers.

II.B.5.d. Performance evaluation as viscosity index improver

Solubility of the polymer, its molecular weight and composition play important role on its performance as viscosity index improver [33]. It is said that polymers exist as random coils in base oil solutions. As the temperature increases 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 decrease in viscosity with increase in temperature [34].

Table II.B.3: Kinematic viscosities (KV) with respect to the different concentrations of the additives in BO1

Conc ⁿ	1%		2%		3%		4%		5%	
	KV ₁	KV ₂								
P₁	6.713	2.101	6.736	2.130	6.749	2.172	6.763	2.201	6.785	2.243
P₂	6.721	2.123	6.747	2.140	6.768	2.193	6.787	2.241	6.821	2.315
P₃	6.718	2.113	6.741	2.140	6.762	2.184	6.779	2.220	6.803	2.261
P₄	6.712	2.103	6.734	2.121	6.739	2.164	6.755	2.181	6.771	2.210
P₅	6.710	2.091	6.728	2.101	6.735	2.142	6.751	2.172	6.761	2.190
P₆	6.704	2.041	6.711	2.062	6.723	2.091	6.738	2.102	6.747	2.131
P₇	6.709	2.071	6.723	2.090	6.731	2.112	6.744	2.131	6.753	2.151
P₈	6.710	2.081	6.725	2.102	6.736	2.142	6.749	2.163	6.762	2.181
P₉	6.704	2.061	6.710	2.071	6.722	2.101	6.739	2.123	6.743	2.140
P₁₀	6.705	2.061	6.712	2.083	6.724	2.112	6.743	2.148	6.747	2.165
P₁₁	6.703	2.042	6.708	2.066	6.719	2.089	6.734	2.101	6.739	2.125
P₁₂	6.702	2.041	6.706	2.059	6.716	2.081	6.729	2.101	6.738	2.125
P₁₃	6.703	2.033	6.707	2.051	6.718	2.083	6.734	2.103	6.740	2.121
P₁₄	6.701	2.035	6.704	2.051	6.713	2.071	6.726	2.092	6.734	2.125

P₁₅	6.701	2.031	6.705	2.052	6.713	2.078	6.727	2.101	6.735	2.123
P₁₆	6.704	2.052	6.711	2.072	6.723	2.101	6.739	2.121	6.743	2.152
P₁₇	6.708	2.072	6.721	2.092	6.729	2.110	6.741	2.140	6.750	2.171
P₁₈	6.709	2.073	6.723	2.091	6.730	2.121	6.743	2.143	6.754	2.182
P₁₉	6.705	2.063	6.711	2.085	6.724	2.113	6.742	2.149	6.748	2.162
P₂₀	6.704	2.051	6.712	2.060	6.722	2.091	6.740	2.113	6.745	2.135

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

Table II.B.4: Kinematic viscosities (KV) with respect to the different concentrations of the additives in BO2

Conc ⁿ	1%		2%		3%		4%		5%	
	KV ₁	KV ₂								
P₁	24.371	4.810	24.423	4.961	24.503	5.152	24.569	5.340	24.643	5.505
P₂	24.382	4.861	24.457	5.082	24.541	5.292	24.622	5.484	24.711	5.720
P₃	24.376	4.821	24.432	4.990	24.519	5.191	24.593	5.390	24.667	5.561
P₄	24.363	4.770	24.408	4.873	24.479	5.025	24.523	5.142	24.618	5.270
P₅	24.352	4.730	24.393	4.821	24.447	4.933	24.502	5.051	24.586	5.182
P₆	24.337	4.651	24.360	4.723	24.418	4.810	24.464	4.912	24.558	5.029
P₇	24.350	4.722	24.371	4.802	24.438	4.900	24.482	5.019	24.571	5.161
P₈	24.353	4.735	24.388	4.818	24.441	4.950	24.497	5.061	24.573	5.211
P₉	24.339	4.702	24.365	4.763	24.423	4.851	24.469	4.965	24.561	5.089

P₁₀	24.342	4.723	24.373	4.789	24.432	4.891	24.478	5.025	24.567	5.137
P₁₁	24.332	4.629	24.355	4.691	24.413	4.789	24.460	4.878	24.554	5.009
P₁₂	24.335	4.642	24.359	4.709	24.415	4.802	24.462	4.889	24.556	5.023
P₁₃	24.330	4.621	24.353	4.678	24.410	4.769	24.458	4.869	24.551	4.989
P₁₄	24.328	4.601	24.350	4.667	24.408	4.759	24.456	4.859	24.550	4.981
P₁₅	24.327	4.591	24.347	4.649	24.407	4.752	24.453	4.838	24.548	4.969
P₁₆	24.341	4.732	24.368	4.789	24.425	4.901	24.472	5.001	24.575	5.109
P₁₇	24.353	4.731	24.391	4.820	24.438	4.981	24.492	5.108	24.563	5.283
P₁₈	24.353	4.738	24.375	4.818	24.440	4.943	24.491	5.058	24.575	5.252
P₁₉	24.340	4.701	24.374	4.802	24.435	4.918	24.479	5.029	24.569	5.148
P₂₀	24.338	4.678	24.362	4.729	24.420	4.838	24.465	4.931	24.560	5.039

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

Table II.B.5: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO

Concⁿ	VI data in BO1					VI data in BO2				
	1%	2%	3%	4%	5%	1%	2%	3%	4%	5%
P₁	107	115	128	137	149	118	130	144	158	169
P₂	113	119	133	151	170	122	139	154	168	184
P₃	109	117	131	143	155	119	132	147	161	173
P₄	105	112	126	132	141	115	123	134	143	152

P₅	102	107	119	127	133	112	119	127	136	145
P₆	89	94	101	106	113	106	111	118	125	134
P₇	98	103	108	115	121	111	117	125	133	144
P₈	101	107	118	126	132	112	118	129	137	148
P₉	93	98	106	111	118	110	114	121	129	138
P₁₀	95	101	109	117	124	111	116	124	134	142
P₁₁	87	93	99	104	111	104	109	116	123	132
P₁₂	87	92	100	105	112	105	110	117	124	133
P₁₃	86	92	99	104	112	103	108	115	122	131
P₁₄	85	91	97	103	111	102	107	114	121	130
P₁₅	85	92	97	104	110	101	106	113	120	129
P₁₆	92	97	106	113	121	112	117	125	132	140
P₁₇	96	101	109	117	128	112	119	131	140	153
P₁₈	98	103	112	119	131	113	119	128	137	151
P₁₉	95	101	109	117	123	110	117	126	135	143
P₂₀	90	94	102	107	114	108	112	120	127	135

Concⁿ represents concentration in % w/w

It is seen from the **Table II.B.3** and **II.B.4** that the homopolymers exhibited better kinematic viscosity at all concentrations compared to the copolymers. Higher molecular weight of the homopolymers may be the reason behind it since higher the molecular weight of the polymer higher is the volume it exposed in the solution and hence higher viscosity is observed.

Comparing all the data from **Table II.B.5** and the figures, P₂ homopolymer has been proved to be the best viscosity index improver among all the prepared polymers. The homopolymers are also associated with higher viscosity index values again due to their higher molecular weight [35]. The comparison among the homopolymers is well understood from the **Figure II.B.7**. Among the homopolymers, P₂ i.e. the homopolymer of isodecylacrylate having highest molecular weight prepared using 0.5% BZP showed highest kinematic viscosity values at all concentrations in both the base oils.

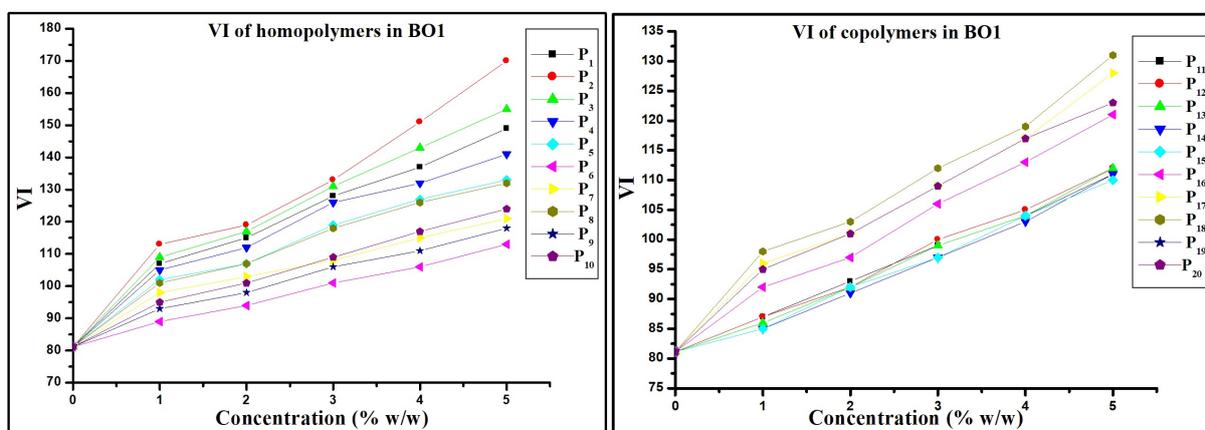


Figure II.B.7: Variation of viscosity index with respect to the different concentrations of the additives in BO1

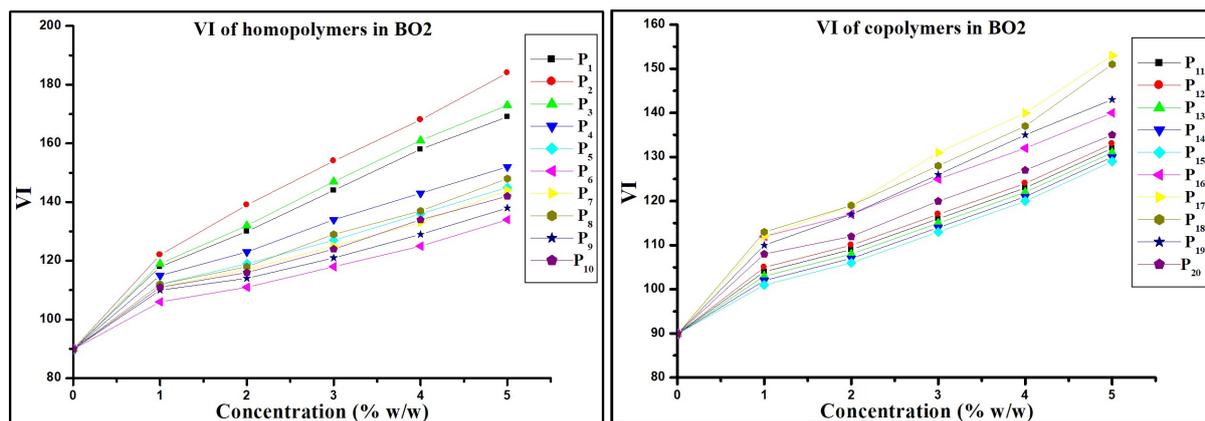


Figure II.B.8: Variation of viscosity index with respect to the different concentrations of the additives in BO2

Graphical representation of VI data of the copolymers (**Figure II.B.8**) shows clear comparison between their viscometric properties. Among the copolymers, P₁₈ i.e. the copolymer of isodecyl acrylate and styrene prepared using 1% AIBN, exhibited better result as viscosity index improver than all the copolymers. Overall it may be said that homopolymers prepared using BZP initiator are proved to be better viscosity index improver. With increasing concentration of the polymer in the base oil, total volume of the polymer micelle increases and hence the viscosity index data also increases with increasing concentration of the polymer in base oil [36].

II.B.5.e. Shear stability index analysis

PSSI and PVL data (**Table II.B.6, II.B.7 and II.B.8**) provide a clear picture about acceptability of polymer as a shear stable additive.

Table II.B.6: Kinematic viscosity after shear at 100°C (^sKV₂) and PVL data with respect to the different concentrations of the additives in BO1

Conc ⁿ	1%		2%		3%		4%		5%	
	^s KV ₂	PVL								
P₁	2.071	1.43	2.081	2.35	2.101	3.22	2.112	4.09	2.131	4.91
P₂	2.093	1.42	2.101	1.87	2.135	2.74	2.157	3.57	2.012	4.76
P₃	2.085	1.42	2.088	2.34	2.112	3.21	2.132	4.05	2.159	4.87
P₄	2.077	1.43	2.079	1.89	2.103	2.78	2.113	3.21	2.131	3.62
P₅	2.062	1.44	2.057	1.90	2.069	3.27	2.076	4.15	2.089	4.57
P₆	2.055	1.20	2.059	1.90	2.068	3.27	2.079	3.70	2.078	4.59
P₇	2.051	0.97	2.058	1.44	2.071	1.89	2.080	2.35	2.087	2.79
P₈	2.029	0.54	2.035	1.21	2.046	2.11	2.045	2.62	2.051	3.71
P₉	2.041	0.92	2.044	1.26	2.056	2.09	2.062	2.74	2.068	3.36

P₁₀	2.043	0.82	2.052	1.35	2.067	2.04	2.081	2.76	2.091	3.19
P₁₁	2.031	0.46	2.039	1.02	2.046	1.63	2.053	2.24	2.061	2.78
P₁₂	2.029	0.54	2.031	0.93	2.041	1.87	2.044	2.67	2.049	3.35
P₁₃	1.981	2.41	2.034	0.78	2.045	1.68	2.051	2.33	2.057	2.97
P₁₄	1.983	2.32	2.035	0.73	2.041	1.40	2.046	2.11	2.056	3.02
P₁₅	1.986	2.14	2.036	0.68	2.047	1.11	2.061	1.86	2.066	2.54
P₁₆	2.036	0.86	2.046	1.16	2.058	2.00	2.067	2.50	2.076	3.44
P₁₇	2.048	1.06	2.058	1.53	2.068	1.99	2.083	2.66	2.097	3.36
P₁₈	2.049	1.01	2.058	1.53	2.072	2.26	2.079	2.85	2.097	3.81
P₁₉	2.039	1.02	2.047	1.59	2.057	2.51	2.067	3.41	2.074	3.98
P₂₀	2.036	0.68	2.037	1.12	2.049	1.96	2.056	2.56	2.063	3.14

Concⁿ represents concentration in % w/w

Table II.B.7: Kinematic viscosity after shear at 100°C (^sKV₂) and PVL data with respect to the different concentrations of the additives in BO2

Conc ⁿ	1%		2%		3%		4%		5%	
	^s KV ₂	PVL								
P₁	4.749	1.25	4.868	1.81	5.019	2.52	5.159	3.37	5.249	4.54
P₂	4.810	1.03	4.990	1.77	5.172	2.27	5.320	2.92	5.510	3.67
P₃	4.756	1.24	4.901	1.80	5.038	2.89	5.178	3.89	5.278	5.04
P₄	4.701	1.47	4.762	2.26	4.851	3.39	4.891	4.86	4.960	5.88

P₅	4.652	1.68	4.708	2.28	4.760	3.45	4.843	5.15	4.844	6.56
P₆	4.531	2.58	4.551	3.60	4.569	4.99	4.590	6.52	4.619	8.15
P₇	4.612	1.91	4.668	2.70	4.712	3.88	4.758	4.99	4.833	6.39
P₈	4.639	1.90	4.681	2.70	4.748	4.04	4.790	5.34	4.828	7.29
P₉	4.578	2.55	4.602	3.36	4.629	4.54	4.651	6.25	4.690	7.68
P₁₀	4.609	2.33	4.629	3.14	4.673	4.49	4.722	5.98	4.762	7.21
P₁₁	4.512	2.59	4.523	3.62	4.541	5.22	4.549	6.76	4.575	8.78
P₁₂	4.519	2.59	4.531	3.82	4.649	5.21	4.570	6.54	4.590	8.56
P₁₃	4.513	2.39	4.562	2.56	4.520	5.24	4.533	6.98	4.543	9.01
P₁₄	4.502	2.17	4.511	3.43	4.522	5.04	4.532	6.79	4.542	8.83
P₁₅	4.489	2.18	4.487	3.44	4.501	5.26	4.501	7.02	4.509	9.26
P₁₆	4.609	2.54	4.642	3.13	4.689	4.29	4.708	5.80	4.753	7.05
P₁₇	4.628	2.11	4.678	2.90	4.768	4.22	4.807	5.69	4.900	7.19
P₁₈	4.650	1.89	4.689	2.69	4.748	3.85	4.812	4.94	4.911	6.48
P₁₉	4.601	2.13	4.655	3.13	4.709	4.27	4.754	5.57	4.802	6.79
P₂₀	4.549	2.78	4.561	3.59	4.591	5.17	4.609	6.49	4.644	7.94

Concⁿ represents concentration in % w/w

Table II.B.8: PSSI data with respect to the different concentrations of the additives in BO

Conc ⁿ	PSSI (%) data in BO1					PSSI (%) data in BO2				
	1%	2%	3%	4%	5%	1%	2%	3%	4%	5%

P₁	37.50	45.45	46.67	50.00	50.00	17.65	18.37	19.12	20.69	24.27
P₂	30.00	33.33	35.29	36.36	37.93	12.82	13.43	14.63	15.84	16.80
P₃	33.33	41.67	43.75	45.00	45.83	17.14	17.31	20.83	22.83	25.69
P₄	37.50	40.00	42.86	43.75	42.11	23.33	27.50	30.91	37.31	38.75
P₅	42.86	50.00	58.33	60.00	58.82	26.67	31.43	36.96	44.83	47.89
P₆	41.67	50.00	58.33	57.14	62.50	66.67	68.00	70.59	72.73	73.21
P₇	40.00	42.86	44.44	45.45	46.15	36.00	39.39	44.19	46.29	47.83
P₈	55.00	62.50	62.86	68.75	71.82	34.62	38.23	41.67	45.76	51.35
P₉	47.50	52.00	55.00	58.00	60.00	52.17	55.17	57.89	63.26	63.93
P₁₀	42.50	46.67	47.78	49.17	49.28	44.00	48.39	52.38	54.55	56.06
P₁₁	47.50	52.50	56.67	58.75	59.00	75.00	77.27	78.13	80.49	81.48
P₁₂	55.00	63.33	65.00	70.00	71.00	70.59	75.00	75.76	76.19	78.18
P₁₃	49.00	53.33	58.33	61.25	63.00	73.33	80.00	83.33	85.00	86.54
P₁₄	47.00	50.00	58.00	62.86	64.00	76.92	80.00	82.76	84.62	86.27
P₁₅	43.50	46.67	46.00	48.75	53.75	83.33	88.89	89.28	91.89	92.00
P₁₆	46.67	48.00	52.50	53.00	56.92	46.15	46.88	48.83	54.72	56.25
P₁₇	44.00	45.71	46.67	47.50	48.67	38.46	40.00	41.18	46.03	46.91
P₁₈	42.00	45.71	48.00	50.83	51.88	33.33	37.14	40.43	42.37	43.59
P₁₉	52.50	55.00	58.89	60.83	61.43	43.48	45.45	46.67	50.00	51.47
P₂₀	46.67	57.50	58.57	60.00	60.91	61.90	65.38	67.57	69.57	70.17

Concⁿ represents concentration in % w/w

Modern additives are required to facilitate the engine oil getting strong enough against severe mechanical shear. Basically under extreme pressure, additive in lube oil solution undergoes molecular degradation and loses its viscosity improvement property. Hence to be recommended as a good additive for multi-grade engine oil, it must be less prone towards molecular degradation against mechanical stress. Analysing all the data obtained from **Table II.B.6, II.B.7 and II.B.8** it may be concluded that P₂ homopolymer exhibited higher stability against mechanical shear at all concentrations in both the base oil. It implies that viscosity loss after shear in case of P₂ is least among all the prepared polymers.

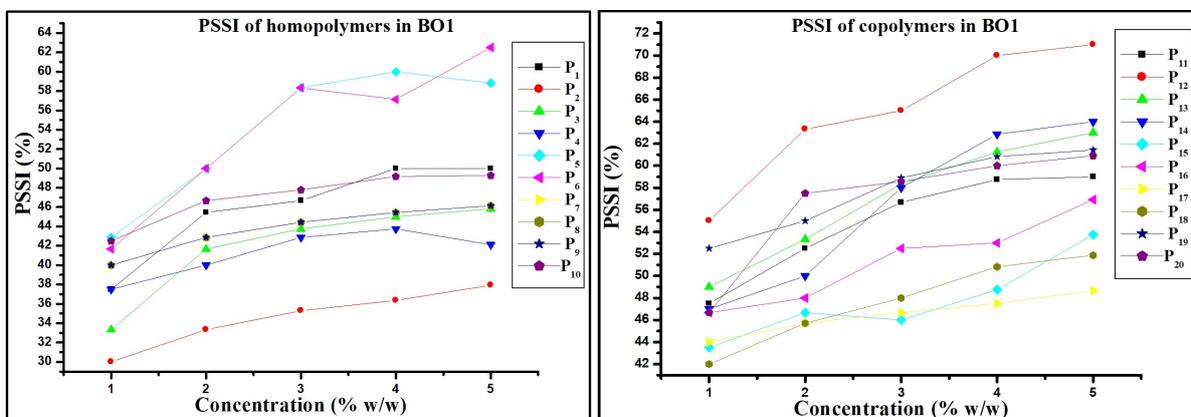


Figure II.B.9: Variation of PSSI with respect to the different concentrations of the additives in BO1

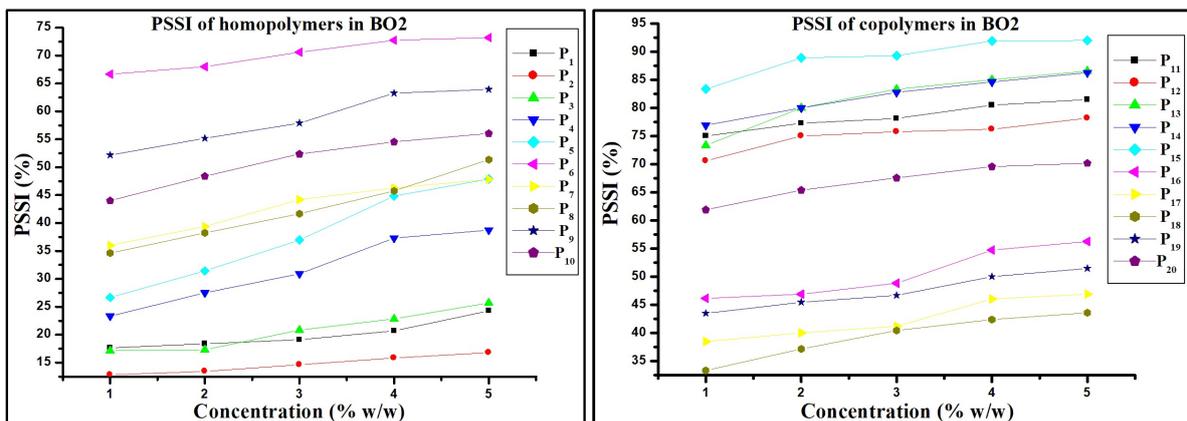


Figure II.B.10: Variation of PSSI with respect to the different concentrations of the additives in BO2

It is also seen that the homopolymers prepared using BZP initiator are comparatively better shear stable. Styrene inclusion in additive generally makes it more susceptible towards molecular degradation under shear. As a result, our prepared copolymers are associated with higher PSSI values. Among the copolymers, P₁₈ i.e. the copolymer prepared using 1% AIBN is more shear stable. Again higher the concentration of the additive in the lube oil solution higher is PVL and PSSI values. This observation is more evident from the graphical representations (**Figure II.B.9 & Figure II.B.10**).

II.B.6. Conclusion

This comparative study reveals that percentage of the initiator either BZP or AIBN used during the polymerisation process does play an important role in determining the properties from molecular weight to viscometric properties of the additives in lube oil. Data obtained from GPC summarises that homopolymers of isodecyl acrylate prepared using BZP are associated with higher molecular weight than those prepared using AIBN whereas reverse observation was obtained in case of copolymers with styrene. The homopolymer prepared using 0.5% BZP showed highest molecular weight among all the prepared polymers. This homopolymer is also proved to be better viscosity modifier and better extreme pressure additive. But the copolymers are better pour point depressants than the homopolymers. Among all the polymers the copolymer prepared using 1% AIBN showed highest pour point depression. Thus the above study may help us to choose proper dosage of initiator while polymerisation to prepare a polymeric additive as per our required property.

II.B.7: REFERENCES

References for chapter II.B are given in bibliography section (page 127–130).

CHAPTER III

Additives for crude oil

CHAPTER III.A

Development of methacrylate based polymeric additives for crude oil

III.A.1. INTRODUCTION

Crude oil is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins [1]. When the temperature decreases paraffin precipitates out from the crude oil and forms wax crystals. With additional wax precipitation, the crystals grow into plates and finally, if the temperature is decreased far enough, the plates will grow together to form a three-dimensional network which traps the oil molecules and deteriorate the flow properties of the oil i.e. immobilizes the oil [2]. The lowest temperature at which the flow property of fluid is ceased, called the pour point. Other constituents of crude oil such as asphaltenes also play important role while ascertaining the behaviour of crude oil. These large heterogeneous molecules with condensed aromatic nuclei may associate to form colloidal sized particles that strongly influence the viscosity of the oil medium and affect the crystallization of the wax [3–6]. Hence waxy crude oil causes many problems during storage and transportation mainly because of this crystallization and deposition of paraffin wax crystals in the flow line causing a number of handling problems as well in regions where the service temperatures are or become seasonally very low [7].

Pour point depressants do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates. When wax crystals form, pour point depressants co-crystallize along with the wax species present in the oil and modify the growing pattern of wax crystal structures. Additionally, the wax crystals are kept apart from each other by the PPD backbone, and as a result of this steric hindrance, the wax crystals are no longer able to form three-dimensional structures with each other that inhibited the flow property. Some commercially available properly designed polymeric flow improvers are poly (ethylene-co-vinyl acetate) (EVA) [8], poly (ethylene-butene) [9], polymethacrylates [10, 11], and modified maleic anhydride copolymers [12, 13]. Basically these polymeric wax inhibitors consist of a non polar long hydrocarbon chain of 14 to 25 carbon atoms in addition with a polar segment typically

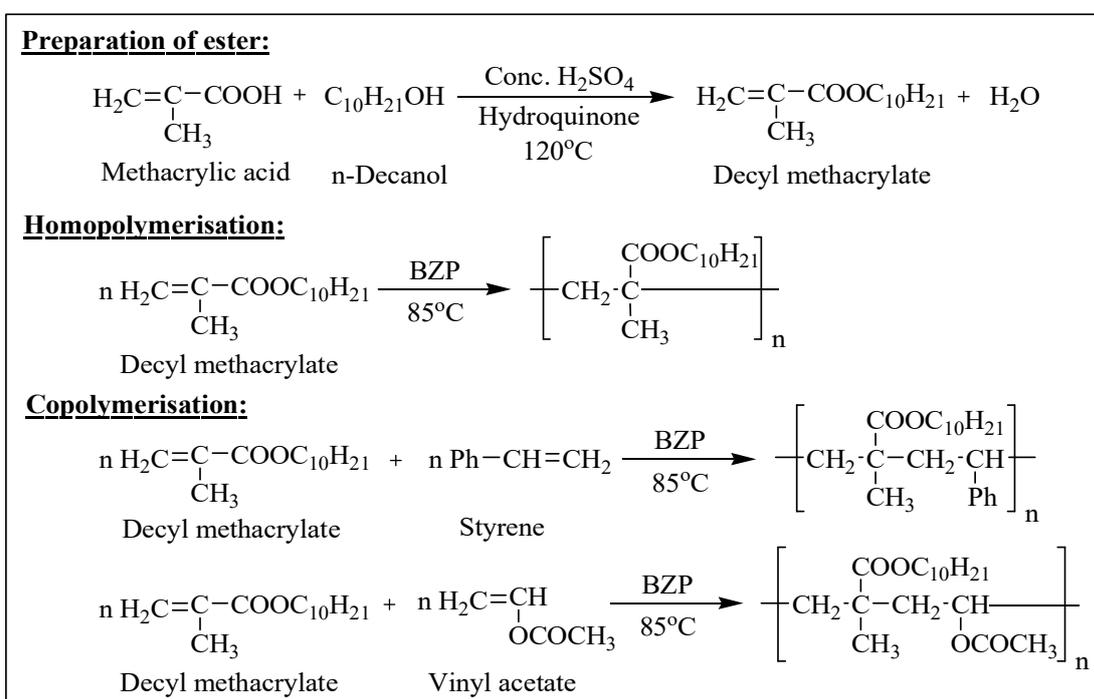
acrylates or acetates. The hydrocarbon part is responsible for the interaction between the additive and paraffin of the oil while the polar part limits the degree of co-crystallization and thus inhibits the aggregation stage.

III.A.2. BACKGROUND AND OBJECTIVE

Recently Chen et al. investigated the interaction of crude oil waxes with polyacrylate pour point depressants (PPDs) bearing different structures and reported that polyacrylate polymers with polar building blocks interacted more easily with the paraffin content which would effectively inhibit wax-crystal precipitation and improve crude oil low-temperature fluidity [14]. Another study supports that an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer having pendant hydrocarbon chain groups [15]. 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 for crude oil [16, 17]. For example, polybehenyl acrylate with a lower MW exhibited better efficacy as a flow improver for asphaltene-rich crude oil [18] and acrylate/methacrylate polymer additives with a lower range of MWs achieved the optimum effectiveness for waxy crude oils [19]. According to Kuzmic et al., polymeric additives of alkyl acrylate with styrene, acrylic acid, and 1-vinyl-2-pyrrolidone with MWs below 20000 were not efficient for crude oils from Croatian oil fields [20] while in another study by Taraneh et al., it was reported that ethylene vinyl acetate copolymer with a higher MW was the better additive for crude oils with low asphaltene contents [21]. T. J. Behbahani had investigated the influence of different concentrations of polymeric flow improver such as dodecylpolymethacrylate and tetradodecylpolymethacrylate on pour point of waxy oils and found that the higher molecular weight flow improver (tetradodecylpolymethacrylate) had better efficiency on pour point of waxy oils [22]. Moreover the performance of a flow improver is also related to the wax and asphaltene composition in the crude oil [15–17, 20]. Hence it can be summarized that the performance of a polymeric flow improver is dependent upon both the structure of the flow improver and the oil composition [23].

Vinyl acetate copolymer, acrylate copolymer and their derivatives [24, 25] are broadly applicable to improve the flow ability of very waxy crude oil, diesel fuel and other base oils at

low temperature. Vinyl acetate copolymers satisfy most of the properties which a good additive must possess. On the other hand methacrylate polymers, the first of the polymeric pour point depressants, continue to be viewed as the best chemistry available today due to the molecular structure of the polymers and the tremendous flexibility in chemical structure. In the present context, we have prepared homopolymer of decyl methacrylate and its copolymers with styrene and vinyl acetate separately at different percentage compositions and evaluated them as flow improver for crude oil collected from Oil India Ltd, Duliajan, Assam (India).



Scheme III.A: Preparation of decyl methacrylate; its homopolymerisation and copolymerization with styrene and vinyl acetate separately

III.A.3. EXPERIMENTAL SECTION

III.A.3.a. Materials

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), Styrene (99%, Sigma–Aldrich), Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), Decyl alcohol (DA, 98%, SRL Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine

Cheme 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. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. Crude oil was collected from Oil India Ltd, Duliajan, Assam (India). Before experiment the crude oil was tested for pour point and was found 24°C. The properties of the crude oil are listed in **Table III.A.1**.

Table III.A.1: Specification of the crude oil

Source	Duliajan, Assam
Pour point	24°C
Density	900 Kg/m ³
Plastic viscosity	5.2 mPa.S at 27°C
Yield value	10 dy/cm ² at 30°C
Wax content	>10%

III.A.3.b. Preparation of ester and its purification

The ester (decyl methacrylate, DMA) was prepared by reacting 1.1 mol of methacrylic acid with 1 mol of decyl alcohol in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in Chapter II.A [26].

III.A.3.c. Preparation of polymers

The polymers (homo and copolymers) were prepared by free radical polymerization (**Scheme III.A.**) at different percentage composition of monomers (**III.A.2**) in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of polymer was carried out by the procedure as reported in Chapter II.A [26].

III.A.4. MEASUREMENTS

III.A.4.a. 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 (0.4%, w/v) in the same manner as mentioned in Chapter IIA.

III.A.4.b. Spectroscopic Measurements

FT-IR and NMR data were obtained following the same procedure as mentioned in Chapter IIA.

III.A.4.c. Performance evaluation as pour point depressants in crude oil

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

III.A.5. RESULTS AND DISCUSSION

III.A.5.a. Molecular Weight Analysis

The experimental values of M_n , M_w and PDI (polydispersity index) of the prepared polymers are tabulated in **Table III.A.2**. Molecular weight is one of the most important factors to determine the flow improvement property of a polymer. From this table, it can be stated that on increasing the percentage of styrene or vinyl acetate both the number average molecular weight and weight average molecular weight gradually increases. But the copolymers of vinyl acetate are less poly-dispersed than those of styrene based copolymers.

Table III.A.2: Percentage composition, M_n , M_w and PDI values of polymers (P₁ to P₉)

Polymer code	% of DMA	% of Sty.	% of VA	M_n	M_w	PDI
P ₁	100.0	–	–	20482	49682	2.42
P ₂	97.5	2.5	–	21592	58982	2.73
P ₃	95.0	5.0	–	27457	77688	2.83
P ₄	92.5	7.5	–	28946	81556	2.82
P ₅	90.0	10.0	–	30345	93842	3.09
P ₆	97.5	–	2.5	21575	33018	1.53
P ₇	95.0	–	5.0	24013	35842	1.49
P ₈	92.5	–	7.5	56866	66210	1.16
P ₉	90.0	–	10.0	61990	81219	1.31

DMA = Decyl methacrylate, Sty. = Styrene, VA = Vinyl acetate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

III.A.5.b. Spectroscopic analysis

The homopolymer of decyl methacrylate, P₁ shows IR absorption band at 1735 cm⁻¹ (**Figure III.A.1**) corresponding to the ester carbonyl group. Due to the presence of –CH₂CH₃ group the peak at 2854 cm⁻¹ and 2924 cm⁻¹ appeared and for the CO stretching vibration the peak at 1465 cm⁻¹ appeared. The IR spectra of copolymers of decyl methacrylate with styrene (P₂ to P₅) are similar and exhibited the following results: The absorption band for ester carbonyl group at 1735 cm⁻¹ shifted to 1728 cm⁻¹ in the copolymer. For example, IR spectrum of P₃ has been shown in **Figure III.A.2**.

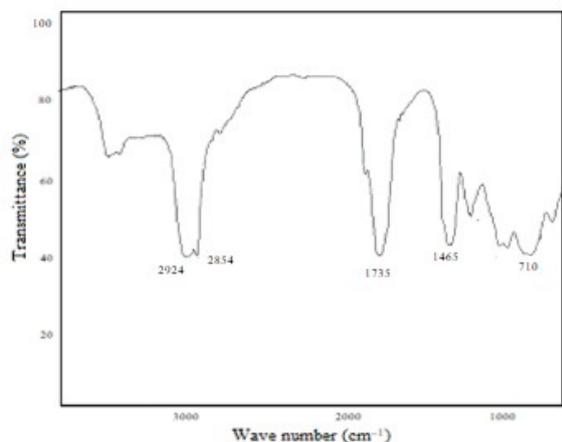


Figure III.A.1: FT-IR spectrum of P₁

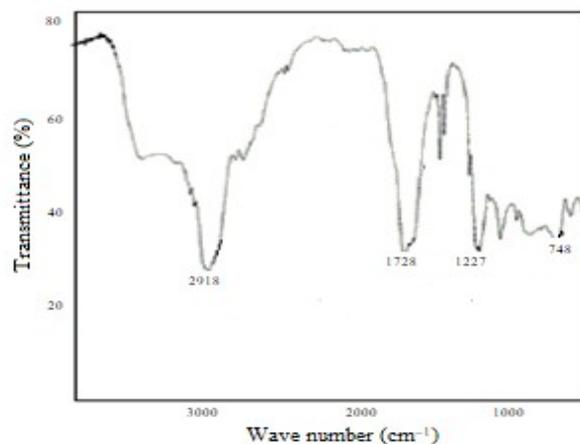


Figure III.A.2: FT-IR spectrum of P₃

For the copolymers of decyl methacrylate and vinyl acetate (P₆ to P₉) the IR spectra are similar and showed the following results: Peaks at 1733 cm⁻¹ and 1717 cm⁻¹ indicate the presence of ester carbonyl groups and the peak at 2922 cm⁻¹ is for the -CH₂CH₃ group. IR spectrum of P₇ is given for instance (**Figure III.A.3**).

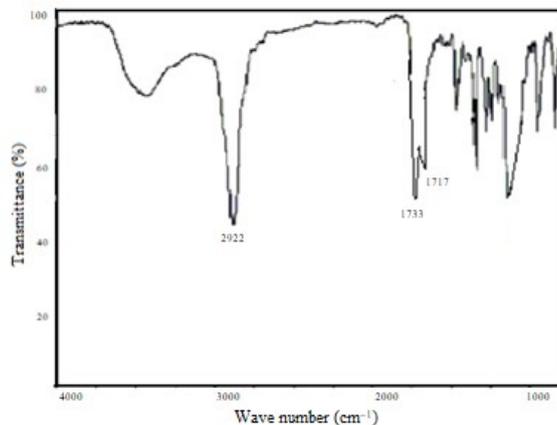


Figure III.A.3: FT-IR spectrum of P₇

In the ¹H NMR spectrum of the homopolymer, P₁ (**Figure III.A.4**), the methyl and methylene protons appeared in the range of 0.89 to 1.93 ppm for all alkyl groups and a broad peak at 3.93 ppm for the protons of -OCH₂- group. Absence of any peak in the range of 5–6 ppm corresponds to sp² carbon confirms the polymerisation. In ¹³C NMR spectrum of the homopolymer (**Figure III.A.5**), the peaks at 177.5 ppm indicated the presence of ester carbon.

The peaks at 65.0 ppm and 64.9 ppm confirmed the presence of $-\text{OCH}_2-$ carbon and peaks in the range of 14.2–45.1 ppm accounted for all sp^3 carbon atoms of alkyl groups. Absence of sp^2 carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120–150 ppm.

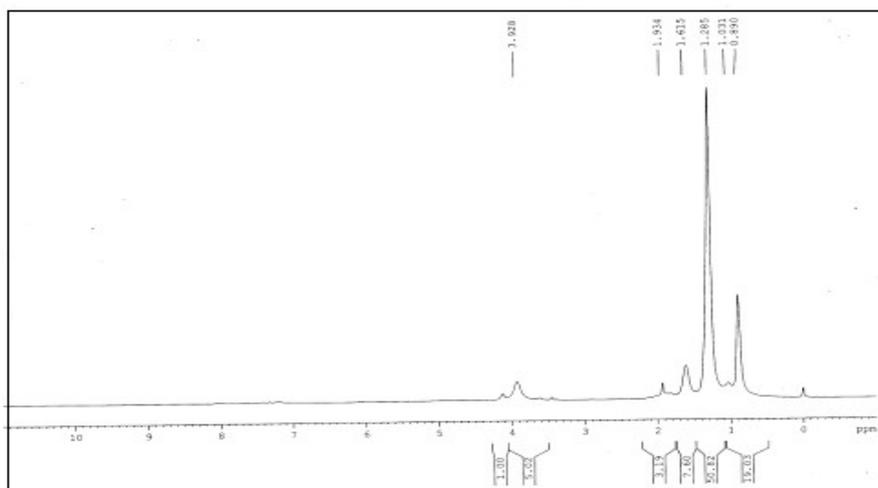


Figure III.A.4: ^1H NMR spectrum of P_1

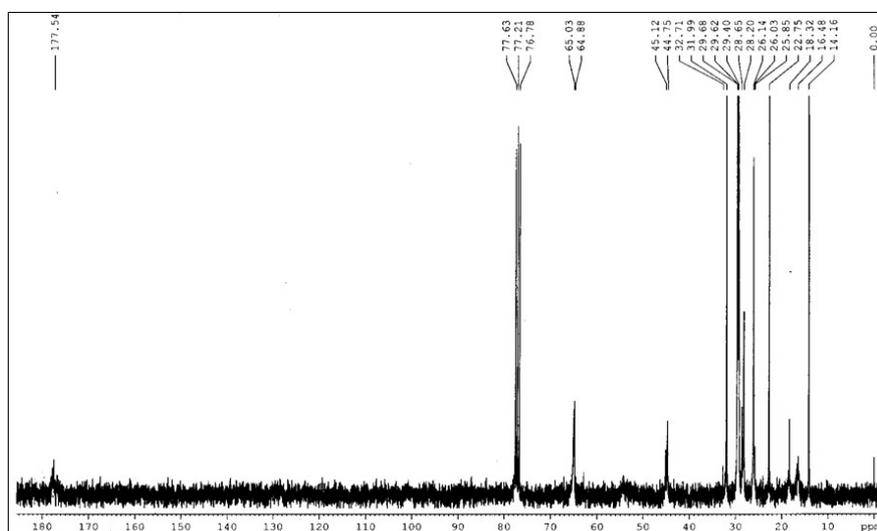


Figure III.A.5: ^{13}C NMR spectrum of P_1

In the ^1H NMR spectrum of the copolymers of styrene, a broad peak at 7.01–7.33 ppm appeared for the protons of phenyl group. As for example ^1H NMR spectrum of P_3 is given in

In the ^1H NMR spectrum of P_7 , one of the copolymers of vinyl acetate (**Figure III.A.8**), a broad peak at 3.93–4.16 ppm indicated the protons of $-\text{OCH}_2-$ groups. The hydrogen atoms attached to sp^3 carbons appeared in the range of 0.86 ppm to 2.64 ppm. Absence of any peak in the range of 5–6 ppm confirmed the polymerisation successfully.

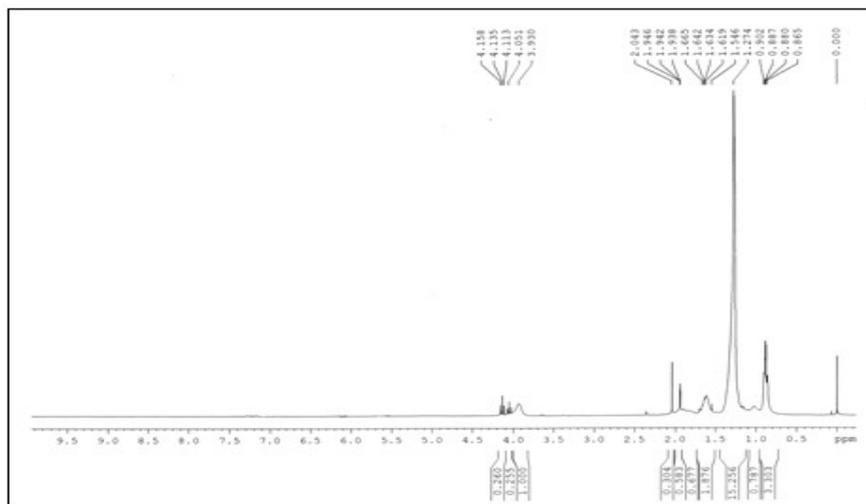


Figure III.A.8: ^1H NMR spectrum of P_7

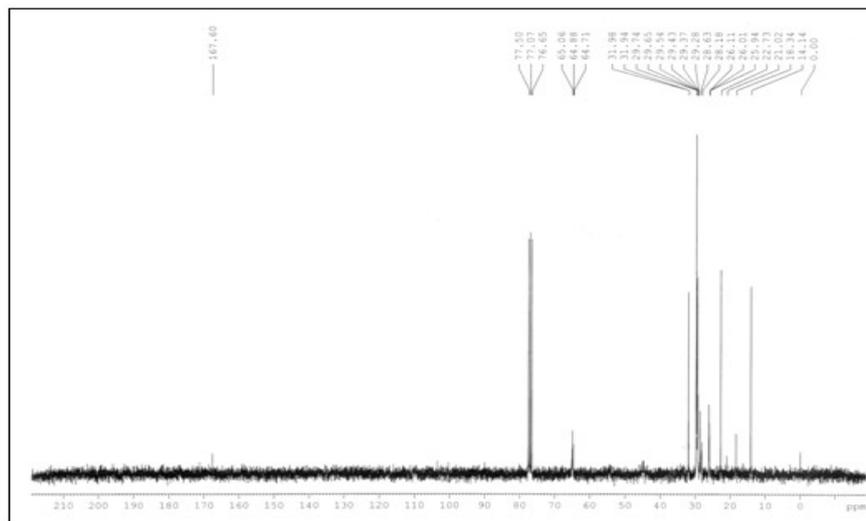


Figure III.A.9: ^{13}C NMR spectrum of P_7

In ^{13}C NMR spectrum of this copolymer (**Figure III.A.9**), the peaks at δ 176.7–176.8 ppm were due to the presence of ester carbonyl group. The peaks at 64.7–65.4 ppm corresponded to the $-\text{COCH}_3$ methyl carbon and $-\text{OCH}_2-$ carbons, peaks ranging from 14.1–45.1 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.

III.A.5.c. Analysis of pour point values

The experimental values of pour point are given in **Table III.A.3**. The values suggest that all the prepared polymers (P_1 to P_9) can be used effectively as pour point depressants (PPD) or flow improvers (FI) for Duliajan crude oil.

Table III.A.3. Pour point data with respect to the different concentrations of the additives in crude oil

Polymer code	Pour point ($^{\circ}\text{C}$) of additives doped crude oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P₁	24	13.5	12.9	12.2	11.5	10	10.3
P₂	24	10.5	10.1	9.8	9.0	8.1	8.5
P₃	24	10.7	10.4	9.5	10.9	11.1	12.0
P₄	24	10.8	10.1	9.5	11.2	12.5	13.0
P₅	24	13.8	14.1	14.9	15.0	15.5	16.1
P₆	24	8.0	7.8	7.5	8.1	9.2	10.0
P₇	24	7.9	6.8	6.1	5.9	4.2	4.5
P₈	24	8.5	8.0	7.5	8.1	8.6	9.0
P₉	24	10.1	10.8	11.9	12.5	13.0	13.8

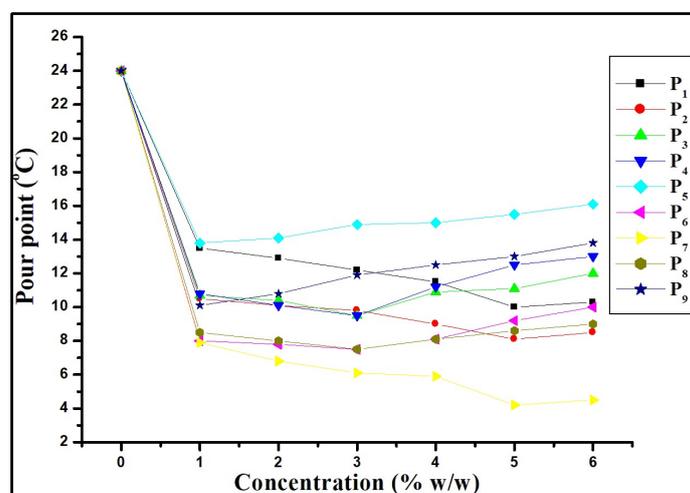


Figure III.A.10: Variation of pour point with respect to the different concentrations of the additives in crude oil

The obtained result is better represented in the above **Figure III.A.10**, where a sharp decrease in pour point of the crude oil is observed in presence of the additives. The copolymers (P₂ to P₉) are better than the homopolymer (P₁) as FI. But with varying concentration, the pour point values do not linearly co-relate. In case of the copolymers of decylmethacrylate and styrene (P₂ to P₅), P₂ copolymer with the lowest percentage of styrene (2.5%) acts as the better FI than the others and using 5% (w/w) solution of this polymer we get the lowest pour point of 8.1°C. Increase in the percentage of styrene results in increasing the phenyl content in the additive. Hence it may be the reason behind that P₃ to P₅ copolymers with higher percentage of styrene gradually showed higher pour point and at 6% (w/w) solution P₅ copolymer with highest percentage of styrene (10%, w/w) shows highest pour point of 16.1°C. The vinyl acetate copolymers (P₆ to P₉) showed better results than the copolymers of styrene. These polymers are better FI and may be due to absence of phenyl group which reduces the adsorption of the polymer molecule on the wax crystals that happened in case of styrene copolymers. The P₇ copolymer having 5% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers. At 5% concentration this polymer showed lowest pour point of 4.2°C. Polymers with higher molecular weights especially P₅ and P₉ showed comparatively poor results. It may be because of their low solubility in the crude oil.

III.A.6. CONCLUSION

From the above study it is found that homopolymer of decyl methacrylate and its copolymer with styrene and vinyl acetate are effective as flow improver for the crude oil. The vinyl acetate based copolymers are better flow improver than styrene based copolymers. Moreover, it was also found that copolymers with lower molecular weight are more effective as flow improver than copolymers with higher molecular weight. Therefore, molecular weight of polymer has a significant role in relation to the performance of the polymers as flow improvers for crude oil.

III.A.7. REFERENCES

References for chapter III.A are given in bibliography section (page 131–133).

CHAPTER III.B

Polymer blend: A new approach towards flow improvement of crude oil

III.B.1. INTRODUCTION

Constant industrialization and considerable increase in energy consumption have increased the demand for oil which is supposed to be the main energy source all over the World [1, 2]. To meet the global requirement heavy and even extra heavy crude oil are getting enough attention due to limited and declining source of light or medium crude reserves. But storage and transportation of crude oil through pipelines is one of the challenging issues especially at cold areas or where the temperature becomes seasonally very low. The composition of crude oil, its density, viscosity and ambient temperature conditions are key factors behind such problem.

Crude oil, basically a form of unprocessed oil, is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins [3] and other heavy metal may be present in it depending on the geological background [4]. As the temperature decreases, paraffins in the crude crystallize out forming a three dimensional matrix of wax crystals which begin to trap the molecules of liquid hydrocarbon until the oil ceases to flow [5–8]. Thus Paraffin deposition diminishes oil production and its removal from the pipeline is also a high cost issue. Pour point depressants (PPDs) or flow improvers (FIs) are substances which modify the growing pattern of the wax crystals and limit their aggregation and thus enhance the flow even at low temperature. An efficient PPD should be a linear polymer or copolymer having pendant hydrocarbon groups in the polymeric backbone [9]. Several polymers have been evaluated as wax crystal modifiers and among them poly(ethylene-co-vinyl-acetate) copolymers are vastly used since they possess good efficiency as crude oil flow modifiers and wax deposition inhibitor [10, 11]. Hemant P. Soni synthesized copolymers of maleic anhydride and esters of n-alkyl alcohols with oleic acid and methacrylic acid and evaluated them as efficient pour point depressants and flow improvers for crude oil from Gandhar oil field, Gujarat, India [5]. Another study was conducted on Algerian crude oil by D. Djemiat et al where the

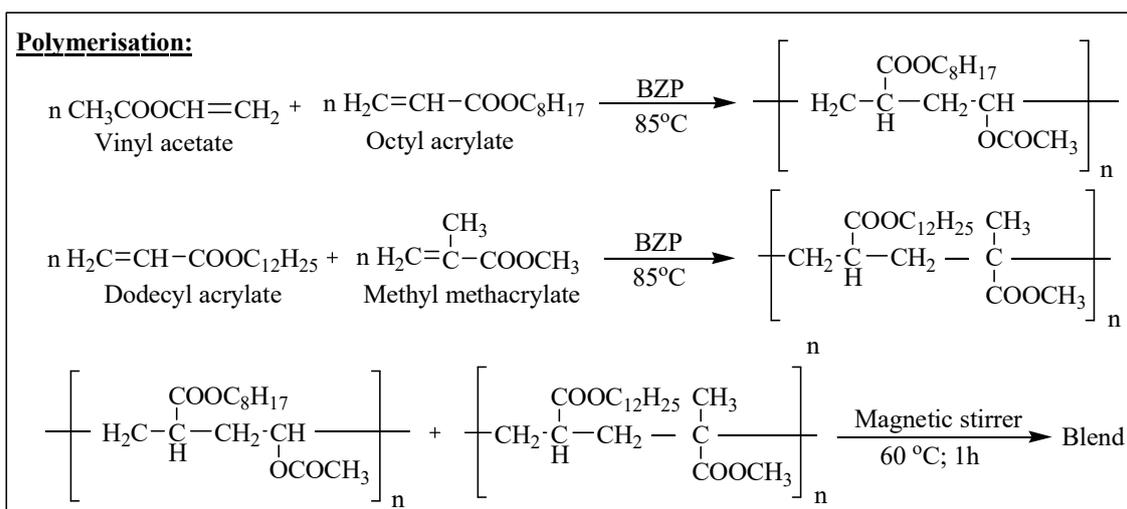
addition of the copolymer, poly(ethylene-co-vinyl-acetate) containing 12% of vinyl acetate, improved the rheological parameters and hence the flow property of crude oil [12].

While considering the flow property of crude oil viscosity is another important parameter which is strongly influenced by the presence of asphaltenes, very large heterogeneous molecules with condensed aromatic nuclei containing heteroatoms such as nitrogen, sulfur and oxygen, and metals such as vanadium, iron, and nickel [13–15]. Presence of strong bonds like C=S drastically increases the viscosity of the crude [16, 17]. Asphaltenes themselves also may associate to form colloidal sized particles leading to large aggregates and thus increase the viscosity of heavy crude [18–20]. Thus during storage or transportation of crude oil, these asphaltenes and paraffins precipitate out forming multiphase flow leading to large pressure drops, increased pumping costs, blocked pipelines and hence huge production loss ranging up to millions of dollars every year [21].

III.B.2. BACKGROUND AND OBJECTIVES

Various preventive methods such as mechanical methods, thermal treatment and chemical methods are commonly employed to overcome the troubles associated with crude oil extraction, storage and transportation. The oldest and the most popular one is dilution of crude with light hydrocarbons, organic solvents like methyl tert-butyl ether, tert-amyl methyl ether, etc, alcohols like pentanol, hexanol, etc, gasoline and middle distillates like kerosene [22]. These diluents reduce the viscosity of crude oil thereby facilitating its transportation through pipelines. But this process requires another well maintained pipeline for carrying the solvent which is itself a cost increasing factor, again identifying proper diluent to oil ratio for different crude oil depending upon its composition and finally recovery of the oil from diluent are not less than an ordeal [23]. Several studies have utilised chemicals such as surfactants, scavengers, emulsion breakers, polymers, nanoparticles and other chemical additives as wax modifier and viscosity reducer in crude oil application [24]. Castro et al. reported that the viscosity of Mexican crude oil was reduced using the terpolymer consisting of high percentage of styrene and low percentage of n-butylacrylate and vinyl acetate [7]. Joonaki et al. developed an ionic additive named IRAN91 which reduced viscosity up to 64% of heavy oil collected from Marun oil field, Bangestan

reservoir [25]. Several studies have reported some well designed nanoparticles as efficient viscosity reducers of heavy crude oil [26, 27]. Olusegun Peter Akinyemi et al. successfully investigated the influence of cheaper natural chemicals, obtained from plant seeds (jatropha, rubber and castor) on the rheological properties and wax deposition tendencies of Nigerian waxy crude oil [28]. An environmentally friendly and cost effective additive for light and heavy crude oils of Oman was reported by Salam K. Al-Dawery and Saleh K. Al-Shereiqi [29]. They used waste bio materials such as fiber of palm tree, date palm kernel and walnut shell materials as viscosity reducing agents on light and heavy crude oils of Oman. In another study by Manojkumar Gudala it was found that addition of 2000 ppm potato starch to the 85% Heavy crude oil and 15% water mixture at 40°C decreased viscosity of the crude by 80.24% which is an excellent and very inspiring result [30].



Scheme III.B: Polymerisation of vinyl acetate with octyl acrylate and dodecyl acrylate with methyl methacrylate; blending of prepared polymers

Today polymer blending has attracted much attention as an easy and economic method for developing new polymeric materials with huge and versatile applications in commercial sector. In our previous work we investigated the properties of polymeric blend in comparison of its parent copolymers and established that the polymeric blend possessed much better mechanical and thermal stability when treated in lubricating oil as additive [31]. Now since for crude oil extraction and transportation we require mechanically and thermally stable additives so that they

do not undergo easy degradation under severe mechanical stress, we tried to evaluate the polymer blend as flow improver for crude oil. We prepared the blend following the above **Scheme III.B.**

III.B.3. EXPERIMENTAL SECTION

III.B.3.a. Materials

Dodecyl alcohol, octyl alcohol, methyl methacrylate (MMA), Acrylic acid, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. The crude oil was collected from IOCL, Assam having pour point of 27°C and densities of 0.851 and 0.808 g/cc at 40°C and 100°C respectively.

III.B.3.b. Preparation and purification of esters

The esters dodecyl acrylate (DDA) and octyl acrylate (OA) were prepared and purified as per the procedure mentioned earlier in Chapter II.A.

III.B.3.c. Preparation of copolymers and blend

Two copolymers – one of vinyl acetate (VA) and octyl acrylate (OA) designated as P₁ and another of dodecyl acrylate (DDA) and methyl methacrylate (MMA) designated as P₂, were prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer) following the same procedure as reported in Chapter II.A [32]. The process of blending is mentioned in Chapter II.A [31].

III.B.4. MEASUREMENTS

III.B.4.a. 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) following the same procedure as mentioned in Chapter II.A. The values are given in **Table III.B.1**.

III.B.4.b. Spectroscopic Measurements

FT-IR and NMR data were obtained following the same procedure as mentioned in Chapter IIA.

III.B.4.c. Performance evaluation as pour point depressants in crude oil

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

III.B.4.d. Performance evaluation as viscosity index improver (VII)

Viscometric parameters were determined according to ASTM D 2270-10. The kinematic viscosity of the crude oil containing the copolymers and the blend was determined at 40°C and 100°C. Different concentrations of the polymers in the crude (% w/w) from 1% to 6% were used to study the effect of concentration on VI of the additive-doped crude oil. All of the experimental data, given in **Table III.B.2** were noted by taking an average of three experimental results under identical conditions in each case.

III.B.4.e. Shear stability measurement

Shear stability of a polymer is a measurement of its mechanical stability against shearing condition. It is measured following the equations provide in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured here preparing 1%-6% solutions (% w/w) of the prepared copolymers and their blend in the crude oil as per ASTM D-3945 method and are given in **Table III.B.3**.

III.B.5. RESULTS AND DISCUSSION

III.B.5.a. 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 (P_1 , P_2) and their blend are given in Table 1. Analysing the experimental data, it was found that blend had higher number average and weight average molecular weight than the copolymers. This result also indicates a fine blending of P_1 and P_2 . Again in terms of polydispersity index (PDI) the polymer blend is less poly-dispersed than the copolymers (P_1 and P_2) which indicates better uniformity in the blend. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the M_w values decrease but PDI value increases.

III.B.5.b. Spectroscopic analysis

Spectral data along with analysis for the prepared polymers are given previously in **Chapter II.A.**

III.B.5.c. Performance evaluation as pour point depressant

The pour point data given in **Table III.B.1** clearly prove that both the prepared copolymers (P_1 and P_2) and their blend are good pour point depressants for the crude oil. Among them all, P_2 copolymer i.e. copolymer of dodecyl acrylate and methyl methacrylate gave the best result as ppd. Longer alkyl chain of this copolymer might play better role in the co-crystallisation process in crude oil [34]. At 4% concentration (% w/w) in the crude oil this copolymer exhibited highest depression in pour point from 27°C (untreated crude) to 4.1°C. At higher concentrations the polymers, especially the blend which is of higher molecular weight became less effective due to lower solubility. It implies that solubility is a major factor while considering flow improvement of crude oil. Graphical representation (**Figure III.B.1**) clearly indicates that a distinct decrease in pour point is obtained when the prepared additives were added to the crude oil.

Table III.B.1: Molecular weight and Pour point data (°C)

		P ₁	P ₂	Blend
Molecular weight and polydispersity index data	M_n	25339	13644	34110
	M_w	53374	31166	58693
	PDI	2.11	2.28	1.72
Pour point data (°C) with respect to the different concentrations (% w/w) of the additives in crude oil	0	27	27	27
	1	6.5	5.9	6.1
	2	6.2	5.1	5.8
	3	5.7	4.6	5.3
	4	4.9	4.1	5.1
	5	4.4	4.1	5.6
	6	4.4	4.3	6.3

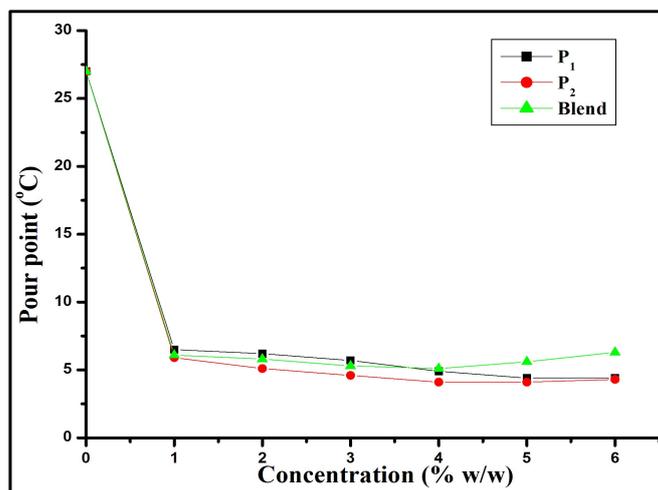


Figure III.B.1: Variation of pour point at different concentrations of the additives

III.B.5.d. Performance evaluation as viscosity index improver

Viscosity is another important parameter when dealing with crude oil. It may be mentioned here that the measured kinematic viscosities at 40°C and 100°C of the untreated crude oil are 11.243 and 2.926 cSt respectively. While analysing the data obtained from viscometric measurements (Table III.B.2 and Figure III.B.2), it is evident that the prepared copolymers and their blend are effective viscosity reducers for the crude oil under consideration. Interestingly, here the polymeric blend showed highest reduction in kinematic viscosity of the crude oil. At 3% concentration in crude oil this polymer blend showed highest reduction in kinematic viscosity which is over 50%. Its comparatively higher molecular weight might be the reason behind this better efficiency.

Table III.B.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in crude oil

Conc ⁿ	P ₁			P ₂			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	5.953	2.217	233	7.358	2.327	142	5.877	2.213	242
2	5.861	2.230	239	7.147	2.317	153	5.728	2.193	254
3	5.673	2.193	262	6.735	2.237	158	5.496	2.165	277
4	5.513	2.176	280	6.724	2.231	157	5.473	2.157	276
5	5.507	2.171	278	6.722	2.229	157	5.465	2.153	276
6	5.504	2.167	276	6.717	2.227	156	5.462	2.151	275

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

It is noted that at 40°C, the effect of the additives in reduction of kinematic viscosity is prominent, but at 100°C the effect is very little since at this higher temperature the viscosity the untreated crude oil itself is highly diminished. At higher concentrations the efficiency of the

polymers was reduced due to lower solubility which fact again cites the importance of solubility factor for effectiveness of additives in crude oil.

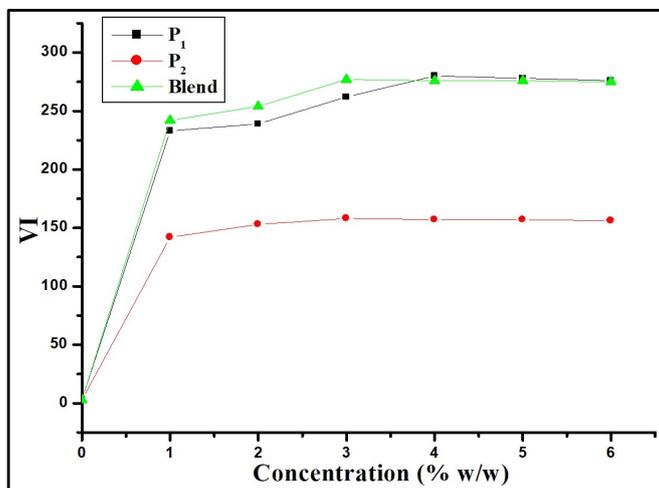


Figure III.B.2: Variation of viscosity index at different concentrations of the additives

III.B.5.e. Shear stability index analysis

Analysing the PVL and PSSI data given in **Table III.B.3**, we found that polymeric blend showed lowest PVL and PSSI values at all concentrations simply indicating highest stability against mechanical shear. This result really inspired us the most towards improvement of flow properties of crude oil. In crude oil extraction or transportation, stability factor of the additive must be taken into account against severe shear experienced during the turbulent flow of crude oil. Hence crude oil additives must be stable enough and must not lose their activity undergoing easy degradation.

So our prepared polymer blend may be a good candidate to be nominated as an efficient flow improver for the crude oil under consideration. The graphical representation (**Figure III.B.3**) better shows the comparison. It is evident from here that the polymer blend is better shear stable than the copolymers. Variation of shear stability with concentration is also clearly marked from the graphical representation.

Table III.B.3: PVL & PSSI data with respect to the different concentrations of the additives in crude oil

Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
	P ₁	P ₂	Blend	P ₁	P ₂	Blend	P ₁	P ₂	Blend
1	2.475	2.600	2.406	11.64	11.73	8.72	36.39	45.58	27.07
2	2.481	2.608	2.401	12.62	12.56	9.48	38.45	47.78	28.38
3	2.486	2.618	2.394	13.36	17.03	10.58	39.97	55.29	30.53
4	2.487	2.638	2.412	14.29	18.24	11.82	41.47	58.56	31.60
5	2.518	2.652	2.440	15.98	18.98	13.33	45.96	60.69	37.13
6	2.534	2.668	2.458	16.94	19.80	14.27	48.35	63.09	39.61

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100°C.

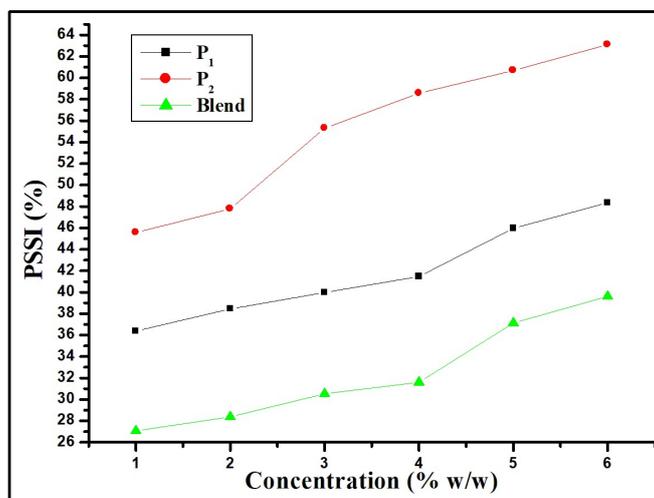


Figure III.B.3: Variation of PSSI at different concentrations of the additives

Copolymer of dodecyl acrylate and methyl methacrylate (P₂) exhibited highest PSSI value which indicates that this copolymer is more prone to mechanical degradation under shear than others. With increasing concentration of the polymers in the crude oil, PVL values as well as PSSI values increase.

III.B.6. CONCLUSION

The above study may be summarised as follows. Both the copolymers and their blend can act as efficient flow improvers for crude oil collected from Assam. Methacrylate-based copolymer was proved to be the better one as pour point depressant due to its longer alkyl chain. But in case of viscosity reduction vinyl acetate-based copolymer and the blend exhibited better performance. Most importantly the polymer blend in crude oil showed highest stability against mechanical shear. But further study is needed to ensure its efficiency in other crude oils also. However, since polymer blending is a cheaper and less time consuming process compared to preparation and characterization of new polymeric material, the above study may open a new horizon of flow improver for crude oil where polymer blend may occupy the prominent position as an efficient and stable flow improver.

III.B.7: REFERENCES

References for chapter III.B are given in bibliography section (page 134–136).

CHAPTER IV

Ionic liquid doped polymeric additive

CHAPTER IV.A

An investigative approach towards the flow improvement property of ionic liquid doped polymeric additive in lubricating oil

IV.A.1. INTRODUCTION

Automotive industry is getting flourished day by day with new inventions and applications of lubrication science which is itself an ever exploring area of research. In general, a typical lubricant is composed of mineral base oils doped with different categories of additives such as antioxidants, detergents, dispersants, friction modifiers, pour point depressants (PPDs), antiwear additives, extreme–pressure additives, and viscosity modifiers as per requirement [1]. Recent advances with ionic liquids (ILs) have provoked a lot of studies on the application of ILs in the lubrication industry.

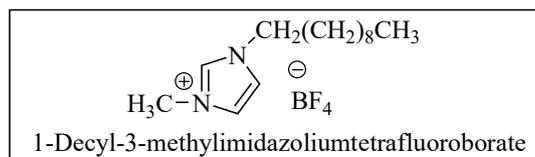
Ionic liquids are molten salts composed of large, asymmetric organic cations like imidazolium, ammonium, phosphonium etc and usually an inorganic anion such as tetrafluoroborate, hexafluorophosphate etc. The electrostatic force between the ions is highly diminished since the charges on the ions are usually diffuse over the large molecule and hence they fail to acquire a regular crystalline shape, rather they opt for the liquid state at room temperature mostly. ILs are unique to exhibit versatile properties such as low volatility, non–flammability, thermal stability, moisture stability, miscibility with organic compounds, good electronic and ionic conductivity and its broad application in electrochemical field [2]. They are often referred to as ‘designer solvents’ due to their ability to dissolve a variety of organic, inorganic and organometallic compounds by simply choosing the proper combination of cations and anions. In addition ILs are considered to be more environmentally friendly in comparison to current alternative solvents and electrolytes [3] and hence are treated as green solvents [4]. Most importantly, availability of various combinations of cation and anion enriched with unique properties, ILs have attained enormous attention over the decade [5] and today variety of ILs are explored with versatile application.

Such a promising range of properties along with their potential for controlled reactivity and also their low evaporation, researchers are provoked to explore their application in corrosion protection [6, 7] and tribology. Especially their extremely low vapor pressure, non flammability and thermal stability even upto temperatures above 200°C are accounting for their capability of lubricating even at increased temperatures and pressure.

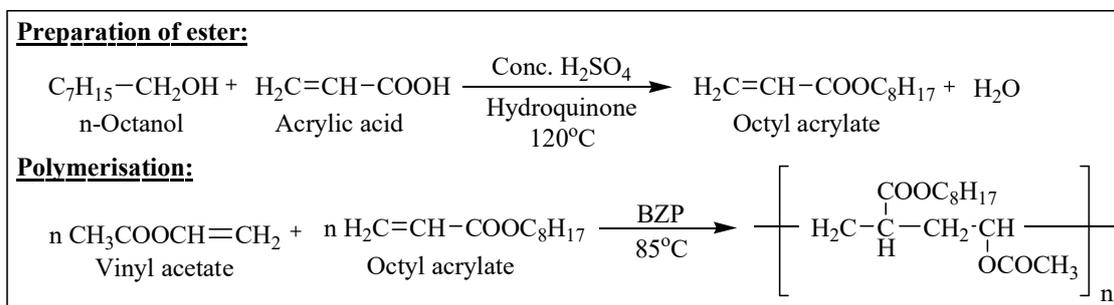
IV.A.2. BACKGROUND AND OBJECTIVES

Various studies have explored the versatile behavior of ILs in engine lubrication [8–11], micro–electromechanical machines (MEMs) [12–14], in the fully formulated diesel engine lubricants [15] etc. Phosphonium orthoborate ionic liquid was evaluated as a wear reducing additive in biodegradable oils at steel–steel surfaces in the boundary lubrication regime [16]. Tribological tests on 1,4–bis(2–ethylhexyl)sulfosuccinate anion–based ILs containing different cation–imidazolium and organoammonium revealed effective friction reduction and antiwear functionality [17]. Again phosphonate ionic liquids were used as additives in polyethylene glycol (PEG) for steel/steel contact by Yunyan Han et al. and their characterization showed that these ionic liquids improved the tribological performances of the base oil significantly [18]. Sulfate–based ionic liquid with a pyrrolidinium cation as neat lubricant and as additive for glycerol in lubrication of steel–steel contacts played an important role in the friction and wear reduction, as well as in the smoothing of the worn surface [19]. In other studies ILs were utilized in the mixed lubrication and the elastohydrodynamic lubrication regimes [20], in the possible base oil of next–generation space grease [21], in magnetic tapes [22] etc. Ammonium–based protic ionic liquids (PILs) showed that the increase of the anion carbon chain length in the PIL structure reduced significantly the coefficient of friction value [23]. Trihexyltetradecylphosphoniumbis(2–ethylhexyl)phosphate was evaluated as anti–wear additive which performed equally with the conventional anti–wear additive, zinc dialkyl–dithiophosphate (ZDDP) at room temperature and even at higher temperature 100°C the former outperformed the later [24]. Imidazolium–based ILs were utilized as additives in the base oil PEG to decrease the friction coefficient and improve the viscometric properties [25].

Imidazolium based ILs provide versatile application owing to their higher stability than a conventional synthetic oil at 200°C [26], easy adsorption onto a surface, such as phosphonyls and esters [27, 28] and easy variation of alkyl chain length to tune up wear and friction [29–32]. Imidazolium tetrafluoroborates are supposed to exhibit lower friction and wear than traditional lubricants for a number of systems [4, 33]. These immense applications of imidazolium tetrafluoroborates have initiated us to utilise it in our present work. But due to higher expense compared to mineral base oils and synthetic base oils, ILs cannot be used solely in large volume. But they may be used as a lubricant additive where a small amount of IL is doped into base oil [34]. To solve the solubility problem in non polar base oils [10, 35] longer alkyl chain is preferred as longer the alkyl chain length on the imidazolium group, higher is the solubility of IL in base oils [1]. Hence we opted for 1-decyl-3-methylimidazolium tetrafluoroborate for this present work.



Here we have prepared a copolymer of vinyl acetate and octyl acrylate and blended it with the said IL (**Scheme IV.A**). Vinyl acetate and acrylate-based polymers are broadly applicable to improve the flow ability of even very waxy crude oil, diesel fuel to other base oils at low temperature [36, 37].



Scheme IV.A: Preparation of octyl acrylate and its copolymerization with vinyl acetate

Vinyl acetate copolymers satisfy most of the properties, a good additive must possess. This reason actually prompted us to explore it in this present study where we have investigated the effect of the IL under consideration on the flow improvement properties of acetate–acrylate based copolymer.

IV.A.3. EXPERIMENTAL SECTION

IV.A.3.a. Materials

Octyl alcohol, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), Acrylic acid were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. The preferred IL 1–decyl–3–methylimidazolium tetrafluoroborate was obtained from TCI Chemicals (India) Pvt. Ltd. Properties of the mineral base oils used are mentioned in earlier Chapter II.A..

IV.A.3.b. Preparation of ester and its purification

The ester (octyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol in presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in Chapter II.A [38].

IV.A.3.c. Preparation of polymer and its blend with IL

The copolymer of vinyl acetate and octyl acrylate was prepared by free radical polymerisation in presence of BZP as initiator (0.5% w/w, with respect to the total monomer) following the same process as described in Chapter II.A [38]. The prepared and purified copolymer was blended with the ionic liquid in 1:1 ratio via mechanical blending process in a magnetic stirrer at 60°C to obtain a homogeneous blend.

IV.A.4. MEASUREMENTS

IV.A.4.a. Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by GPC method (Water 2414, polystyrene calibration) as described in Chapter II.A.

IV.A.4.b. Spectroscopic Measurements

Spectral data were obtained following the same procedure as in Chapter II.A.

IV.A.4.c. Performance evaluation as pour point depressants in base oil

The effect of additive concentration on pour point of the base oils was tested by using different doping concentrations ranging from 1% to 6% (w/w) for each of the prepared copolymer, IL and their blend. 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).

IV.A.4.d. Performance evaluation as viscosity index improver (VII)

According to ASTM D 2270–10 method viscometric parameters were determined at 313 and 373 K using different doping concentrations (% w/w) from 1% to 6% of the additives in the base oils. All of the experimental data, given in **Table IV.A.2 & IV.A.3** were noted by taking an average of three experimental results under identical conditions in each case.

IV.A.4.e. Shear stability measurement

Stability against mechanical shear is expressed in terms of shear stability index or PSSI values. It is basically measurement of viscosity loss under shearing condition which may be of two kinds such as Temporary Viscosity Loss (TVL) and Permanent Viscosity Loss (PVL) [39] discussed in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured for the solutions prepared using 1% – 6% (% w/w) doping concentration of the prepared copolymer, IL and their blend in the base oils as per ASTM D–3945 method and are given in **Table IV.A.4**.

IV.A.5. RESULTS AND DISCUSSION

IV.A.5.a. Molecular Weight Analysis

The obtained values of M_n , M_w and PDI of the prepared copolymer are 25339, 53374 and 2.11 respectively. In general, these values are kind of a proof for a successful polymerisation.

IV.A.5.b. Spectroscopic analysis

Spectral data with analysis of the prepared polymer have already been discussed in **Chapter II.A.**

IV.A.5.c. Performance evaluation as pour point depressant

Pour point data obtained from **Table IV.A.1** implies that the copolymer and its blend with IL are effective pour point depressant in both the base oils.

Table IV.A.1: Pour point data with respect to the different concentrations of the additives in base oil (BO)

Additive	BO	PP (°C) at different concentrations (% w/w) of additive						
		0%	1%	2%	3%	4%	5%	6%
Polymer	BO1	-3	-10.0	-10.9	-11.5	-11.9	-11.0	-10.5
	BO2	-6	-12.0	-12.5	-13.2	-12.9	-12.4	-11.9
IL	BO1	-3	-7.0	-7.5	-9.0	-8.4	-8.1	-7.0
	BO2	-6	-8.1	-9.3	-9.5	-10.2	-10.1	-10.1
Blend	BO1	-3	-10.7	-11.1	-11.7	-12.1	-11.9	-11.8
	BO2	-6	-12.4	-12.8	-13.3	-13.7	-13.6	-13.5

Concⁿ represents concentration in % w/w

High molecular weight of the polymer accounts for its effectiveness as pour point depressant. But the IL alone is hardly effective as PPD for the base oils. Since a polymeric backbone is a vital condition to be an effective pour point depressant the IL is lacking behind in this case. But due to the presence of a hydrophobic long alkyl chain which may interact with the wax coming out at reduced temperature from the base oil, a little change is observed in the pour point of the base oils. With increasing concentration the depression slightly enhances and gets fixed at some point due to lower solubility at higher concentrations as clearly shown in **Figure IV.A.1**. Better interaction is observed in case of the blend of the polymer and the IL. Comparing the data for the polymer and its blend with the IL, it is observed that they are more or less equally active as PPD, but the blend is slightly better which may be attributed to the fact that the IL under consideration also possessed a long alkyl chain which enhances the activity of the polymer.

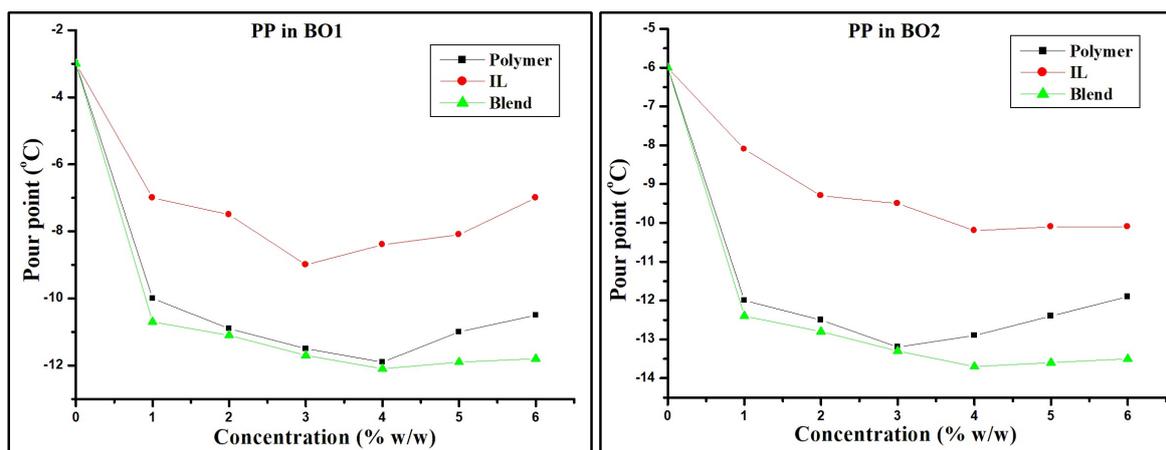


Figure IV.A.1: Variation of Pour point with respect to the different concentrations of the additives

IV.A.5.d. Performance evaluation as viscosity index improver

From the viscometric data (**Table IV.A.2 & IV.A.3**), it was observed that all the additives i.e. the copolymer, IL and their blend acted as moderate to good viscosity index improvers in both the base oils. If compared between IL and the copolymer of octyl acrylate and vinyl acetate, the later actually outweighs the IL. The obvious reason behind this is that the polymers exist as a coil in the base oil at normal temperature, but at elevated temperature this coil unfolds itself into a chain structure with higher volume and hence higher surface area that is responsible for higher

viscosity index of doped base oil. Thus temperature effect is reversed in case of polymers and as a result polymers act as better viscosity index improver in base oil.

Table IV.A.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in base oil 1 (BO1)

Conc ⁿ	Polymer			IL			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	6.705	2.120	113	6.700	2.033	86	6.721	2.181	135
2	6.714	2.160	127	6.706	2.051	91	6.737	2.223	147
3	6.727	2.200	141	6.712	2.072	98	6.763	2.274	162
4	6.750	2.250	157	6.720	2.094	104	6.792	2.325	176
5	6.780	2.300	170	6.729	2.125	113	6.822	2.355	184
6	6.810	2.340	184	6.738	2.143	118	6.841	2.391	197

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

Table IV.A.3: Viscosity Index data with respect to the different concentrations of the additives in base oil 2 (BO2)

Conc ⁿ	Polymer			IL			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	24.320	4.850	122	24.235	4.512	94	24.388	5.113	142
2	24.340	5.000	134	24.244	4.593	102	24.442	5.234	151
3	24.390	5.250	153	24.257	4.714	111	24.563	5.502	170

4	24.480	5.370	161	24.269	4.875	124	24.601	5.686	183
5	24.570	5.560	174	24.281	4.983	133	24.655	5.782	189
6	24.650	5.780	189	24.291	5.107	142	24.712	5.891	196

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

Comparing all the data (Figure IV.A.2) it was observed that IL and the polymer blend acted as the best viscosity index improver among all three. It simply suggested that the IL under consideration actually enhanced the viscometric property of the polymer. The observation is not in any contrary to the other base oil also. Irrespective of all the additives and base oil, viscosity index gradually increased with increasing concentration of the additive which may be due to an increase in the total volume of the micelles in the oil solutions [40].

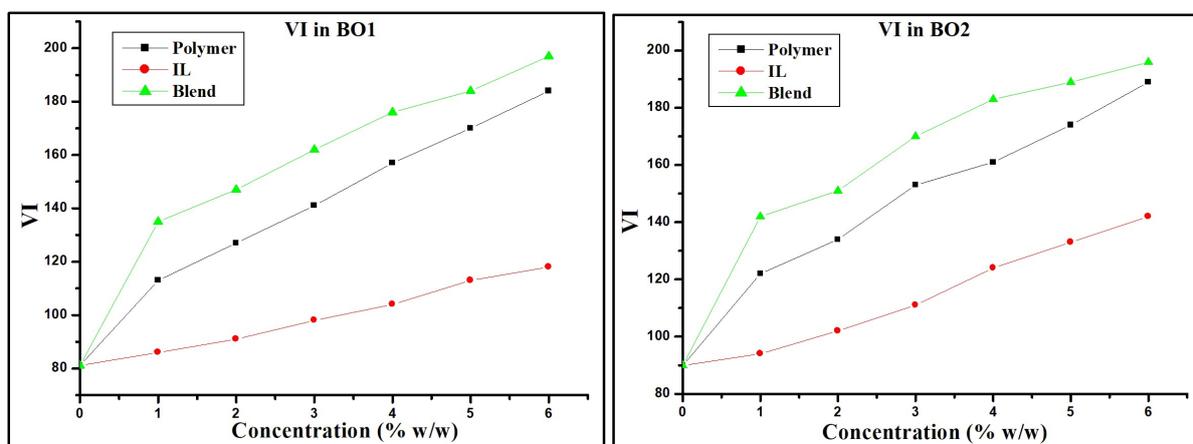


Figure IV.A.2: Variation of viscosity index with respect to the different concentrations of the additives

IV.A.5.e. Shear stability index analysis

The polymer–IL blend showed highest stability against mechanical shear at all concentrations, which clearly supports its better mechanical and thermal property in both the base oils (Table IV.A.4).

Table IV.A.4: PVL & PSSI data with respect to the different concentrations of the additives in base oil (BO)

Base Oil	Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
		Polymer	IL	Blend	Polymer	IL	Blend	Polymer	IL	Blend
BO1	1	2.081	2.022	2.142	1.84	0.54	1.79	39.00	84.61	24.22
	2	2.100	2.022	2.176	2.78	1.41	2.11	42.86	93.55	23.15
	3	2.120	2.031	2.215	3.64	1.98	2.59	44.44	78.85	23.23
	4	2.140	2.042	2.252	4.89	2.48	3.14	47.83	70.27	23.93
	5	2.150	2.047	2.271	6.52	3.67	3.57	53.57	74.28	25.07
	6	2.160	2.055	2.295	7.69	4.11	4.02	56.25	71.54	25.88
BO2	1	4.655	4.476	5.032	4.02	0.79	1.58	51.32	85.71	14.15
	2	4.710	4.492	5.137	5.80	2.19	1.85	54.72	82.11	12.69
	3	4.800	4.502	5.380	8.57	4.48	2.21	57.69	86.88	11.82
	4	4.837	4.528	5.545	9.93	7.12	2.48	59.22	85.68	12.84
	5	4.890	4.565	5.614	12.05	8.39	2.91	61.47	81.48	12.80
	6	4.930	4.635	5.709	14.71	9.24	3.09	64.89	74.09	12.81

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100°C.

The PSSI data also suggested that the polymer is itself a good shear stable additive. But when blended with the IL under consideration, the mechanical stability is enhanced much more. It implies that the blend undergoes molecular degradation under mechanical shear at much lower rate compared to the polymer and the IL alone. Higher the concentration of the additive in the

base oil, higher is the volume exposed to the mechanical shear and hence the PSSI values increase with increasing concentration of the additive in both the base oils, but this relationship is not totally linear since some other factors also come into play under severe mechanical shear like molecular weight of the polymer, composition of the base oil etc.

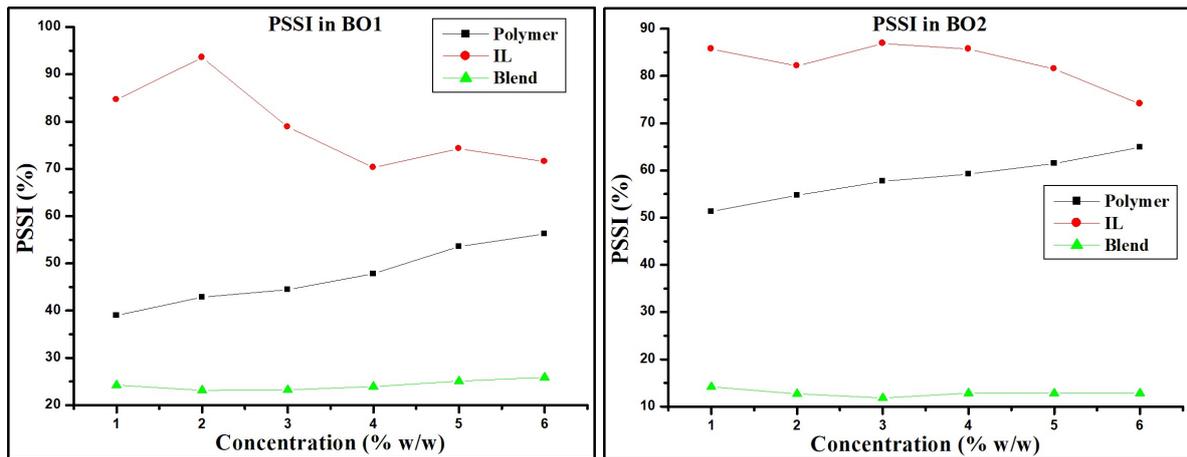


Figure IV.A.3: Variation of PSSI with respect to the different concentrations of the additives

Graphical representation (**Figure IV.A.3**) provides clear comparison of shear stability among the additives. It clearly shows that IL alone is comparatively poor shear stable than the polymer and the blend. The blend of the polymer and the IL here has been proved to possess better mechanical stability.

IV.A.6. CONCLUSION

From the above study, it may be concluded that the IL under consideration does play an effective role when blended with acetate–acrylate copolymer. The polymer is itself a good pour point depressant, viscosity index improver and at the same time it is quite stable against mechanical shear under severe condition. The IL alone is not as effective as the polymer in terms of pour point depressant, but its viscometric properties are moderate. Above all, blend of the polymer and the IL predominates in every property i.e. pour point depression, viscosity index and shear stability. Though IL has been proved to be a promising lubricating agent, its high cost retards its solo application. When blended with proper polymer, lower amount of IL is required which

lowers the cost to a considerable amount and at the same time the blend exhibits better property than even the parent polymer also.

IV.A.7: REFERENCES

References for chapter IV.A are given in bibliography section (page 137–140).

CHAPTER IV.B

Enhancement of additive properties in crude oil through introduction of ionic liquid

IV.B.1. INTRODUCTION

Crude oil, whether heavy, medium or lighter, is probably the biggest source of energy around the globe [1]. But crude oil extraction, transportation via pipeline or its storage require a lot of struggle basically due to its composition, high viscosity, high pour point and some other factors also. Crude oil is originally a form of unprocessed oil which is a complex mixture of hydrocarbons, particularly saturates, aromatics, resins and asphaltenes [2] and depending on the geological background, other heavy metal may be present in it [3]. At lower temperature n-paraffins precipitate out forming wax crystals and when the temperature decreases more, these crystals get bigger in size to form a 3-D network which finally immobilizes the oil. Thus transportation of crude via pipeline to the refineries or else becomes a hurdle at low temperature. High viscosity of crude oil is another barrier against its production and transportation as well since huge energy is required to dig out the oil from reservoir and the process gets worsened due to large pressure drop which in turn results in huge production loss [4]. Despite such drawbacks, heavy and even extra heavy crude oil is getting enough attention as the main energy source due to limited and decreasing source of medium or light oil. Hence petrochemical industry is exploring continuously new strategies to defeat the obstacles faced throughout the crude oil displacement from reservoir to production facilities and further into the refinery process up to conversion into various petrochemical products of higher commercial value [5].

To tackle these barriers, number of methods have been utilized viz. mechanical methods, thermal treatment, dilution of crude with light hydrocarbons, alcohols like pentanol, hexanol, etc, gasoline and middle distillates like kerosene [6] and chemical methods like treatment with surfactants, scavengers, emulsion breakers, polymers, nanoparticles and other chemical additives as wax modifier and viscosity reducer [7]. More or less all these processes come with their own drawbacks whether high cost in some cases or recovery of oil after treatment [8]. Application of

chemical additives like polymers have conquered much advanced place among these methods, but still it is a challenging area to find out a perfect multifunctional additive with maximum effect at minimum dosage.

Ionic liquids have emerged out as a promising candidate in this field with lots of potential. Basically ionic liquids are molten salts consisting of large, asymmetric organic cations like imidazolium, ammonium, phosphonium etc and usually an inorganic anion such as tetrafluoroborate, hexafluorophosphate etc. The most interesting feature of ILs is that variety of combination of cation and anion is available each with unique properties and hence versatile application of ILs is available in the industry [9]. ILs are enriched with low volatility, non-flammability, thermal stability, moisture stability, miscibility with organic compounds, good electronic and ionic conductivity which promoted its application in versatile studies such as in magnetic tapes [10], in electrochemical fields [11], in corrosion protection [12, 13], in engine lubrication [14] and micro-electromechanical machines (MEMs) [15–17]. Recently, many room temperatures ILs or RTILs are developed as potential “green” solvents due to their environment friendly and renewable characteristics [18]. Lots of studies have been performed promoting successful application of ILs in tribology [19–21]. Owing to high thermal stability, ionic liquids were investigated even as a possible base oil of next-generation space grease to solve mainly temperature related issues and compatibility with space environment [22].

IV.B.2. BACKGROUND AND OBJECTIVES

Due to such versatile applications, number of studies have been performed over the applicability of ILs in crude oil also, such as in enhanced oil recovery, asphaltene degradation, bitumen recovery, desulphurization, interfacial tension reduction in crude oil–water system etc [23, 24]. According to Nares et al. some ILs are capable of altering the viscosity of heavy crude [25]. ILs are well capable of preventing the precipitation of asphaltene during enhanced oil recovery (EOR) process by effectively breaking the asphaltene association [26]. Again some surface-active ILs can also be used as demulsification agents to break water/oil emulsion during oil refining process [27]. Sivabalan Sakthivel et al has investigated the enhancement of solubility of heavy crude oil in solvent and imidazolium-based IL mixture and reported almost 60% increase

in solubility compared to the blank solvent without IL [5]. According to their report, the ILs were successful in reducing the surface tension and interfacial tension between solvent and crude oil and hence this study provides an efficient pathway for the recovery of entrapped oil from exhausted reservoirs. Ali Alarbah et al. proved in their study with 1-ethyl-3-methyl-imidazolium acetate IL that the potential of injecting a slug of the IL and brine is much better than that of introducing a slug of alkali and brine in case of medium oil recovery [28]. Again, Mabkhot Bin Dahbag et al reported ammonium sulfate based IL as an efficient environment friendly substitute for surfactants in enhanced oil recovery (EOR) [29]. Another study by Zeeshan Rashid et al. suggested that ILs with hydrophobic anions can be used to prevent asphaltene deposition which is actually responsible for high viscosity of crude oil [30]. Imidazolium, pyridinium, and thiazolium based ILs were investigated as viscosity reducers for Mexican heavy oil and Canadian and Venezuelan bitumens by Deepa Subramanian et al and the study revealed that ILs with higher alkyl chain length at the cationic group are better viscosity reducer [31]. According to a study done by Watheq Kareem Salih, there is a clear relation between the molecular weight of ionic liquids and their efficiency in the demulsification process for crude oil emulsions viz. higher the molecular weight higher is the efficiency [32]. Thus ILs have lots of applications as viscosity reducer [33], surfactants [34] and demulsifiers [35] in petrochemical industry.

But ILs are comparatively much expensive than mineral base oils and synthetic base oils and hence they cannot be used solely in large volume. On the other hand, they may be used as a lubricant additive where a small amount of IL is doped into base oil to provide a large difference to the friction and wear [36]. In the present context, we have evaluated the performance of an imidazolium based IL in combination with acrylate-acetate copolymer in wax modification, viscosity modification and also evaluated their shear stability in crude oil. To tackle solubility issue we have opted for a long alkyl chain on the imidazolium group and since ILs having highly fluorinated anions possesses higher thermal stability, we preferred tetrafluoroborate as the anion part. On the other hand, vinyl acetate and acrylate-based polymers are broadly applicable to improve the flow ability of even very waxy crude oil, diesel fuel to other base oils at low temperature [37]. The aim of our present work is to find out whether the IL under consideration

can enhance the activity of the polymer when blended together in comparison of their solo application in crude oil. We have followed here the same scheme as we followed in the previous chapter (Chapter IV.A).

IV.B.3. EXPERIMENTAL SECTION

IV.B.3.a. Materials

Octyl alcohol, Acrylic acid, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. The crude oil was collected from IOCL, Assam having pour point of 27°C and densities of 0.851 and 0.808 g/cc at 40°C and 100°C respectively. The IL 1-decyl-3-methylimidazolium tetrafluoroborate was provided by TCI Chemicals (India) Pvt. Ltd. and was used as obtained.

IV.B.3.b. Preparation and purification of esters

The ester (octyl acrylate, OA) was prepared and purified following the same procedure as described in Chapter II.A.

IV.B.3.c. Preparation of copolymers and its blend with the IL

The copolymer of vinyl acetate (VA) and octyl acrylate (OA) was prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer) following the same procedure as reported in Chapter II.A [38]. The prepared polymer was mixed with the IL in 1:1 ratio at a magnetic stirrer and heated at 60°C to obtain a homogeneous blend.

IV.B.4. MEASUREMENTS

IV.B.4.a. Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) of the prepared copolymer were measured by GPC method as described in Chapter II.A.

IV.B.4.b. Spectroscopic Measurements

Spectroscopic measurements were done as per the procedure mentioned in Chapter II.A.

IV.B.4.c. Performance evaluation as pour point depressants in crude oil

The effect of additive concentration on pour point of the crude oil was tested by using different doping concentrations ranging from 1% to 6% (% w/w) for the prepared copolymer, IL and their blend separately. 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). The obtained result is given in **Table IV.B.1**.

IV.B.4.d. Performance evaluation as viscosity index improver (VII)

Viscometric parameters were determined according to ASTM D 2270–10. The kinematic viscosity of the crude oil containing the copolymers and the blend was determined at 40°C and 100°C. Different concentrations of the polymers in the crude (% w/w) from 1% to 6% were used to study the effect of concentration on VI of the additive–doped crude oil. All of the experimental data, given in **Table IV.B.2** were noted by taking an average of three experimental results under identical conditions in each case.

IV.B.4.e. Shear stability measurement

Under severe mechanical stress an additive experiences molecular degradation and hence loses its activity as a VII. The more the degradation the more will be activity loss. Thus mechanical stability against shearing condition is measured in terms of shear stability index which is discussed earlier in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured here

preparing 1%–6% solutions (% w/w) of the prepared copolymers and their blend in the crude oil as per ASTM D–3945 method and are given in **Table IV.B.3**.

IV.B.5. RESULTS AND DISCUSSION

IV.B.5.a. Molecular Weight Analysis

Molecular weight is one of the key indicators of a proper polymerization process. The prepared copolymer exhibited number average molecular weight of 25339 and weight average molecular weight of 53374 in GPC. Such high value of molecular weight is very helpful towards its application as PPD or VII. Besides its PDI value was 2.11 which imply that the copolymer is highly polydispersed.

IV.B.5.b. Spectroscopic analysis

Spectral data with analysis of the prepared polymer have already been discussed in **Chapter II.A**.

IV.B.5.c. Performance evaluation as pour point depressant

It is evident from various studies that polymers with higher alkyl chain length are more effective flow improver [40]. Our prepared copolymer of octyl acrylate and vinyl acetate has been proved to be no exception in this case. From the pour point data (**Table IV.B.1**), it has been seen that this copolymer is really an effective PPD for the crude oil under consideration.

The graphical representation (**Figure IV.B.1**) cites the result better where a sharp decrease in pour point of the crude oil is observed when the polymeric additive was added. But the IL alone has hardly any effect on the pour point of the crude oil. A little variation in pour point of the crude is observed when doped with IL alone which is indicative for some possible interaction between the long alkyl chain on the imidazolium group and the paraffin waxes of the crude.

Table IV.B.1: Pour point data (°C) with respect to the different concentrations (% w/w) of the additives in crude oil

concentration	Polymer	IL	Blend
0%	27	27	27
1%	6.5	24.0	5.8
2%	6.2	22.6	5.5
3%	5.7	22.0	5.1
4%	4.9	22.3	4.5
5%	4.4	23.0	4.2
6%	4.4	23.6	4.3

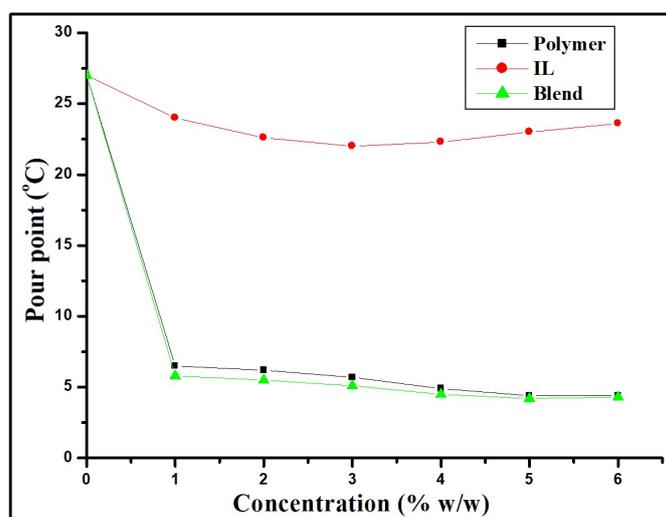


Figure IV.B.1: Variation of pour point with respect to the different concentrations of the additives

The blend of the copolymer and the IL virtually predominates over others as PPD. It simply suggests that the IL actually enhances the effectiveness of the copolymer. Presence of acrylate and acetate groups in the polymer makes it really active to interact with the IL which itself is unique to possess a complex mixture of interactions like ionic interaction, covalent

interaction, van der Waals interaction and even hydrogen bonding. At higher doping concentrations of the additives in the crude oil, the pour point just ceased to change due to less solubility which clearly supports the fact that the effectiveness of PPDs depends very much on their solubility.

IV.B.5.d. Performance evaluation as viscosity index improver

Asphaltene aggregation is a major factor for high viscosity of crude oil [41]. Besides presence of strong bonds like C=S drastically increases the viscosity of the crude [42]. Hence any interaction with the asphaltenes via pi-pi, aliphatic, acid-base, or charge-transfer interactions may result in viscosity change. Ionic liquids are well capable of exhibiting aromatic, aliphatic, acid-base, and charge-transfer interactions [43]. It may be mentioned here that the measured kinematic viscosities at 40°C and 100°C of the untreated crude oil under consideration are 11.243 and 2.926 cSt respectively.

Table IV.B.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in crude oil

Conc ⁿ	Polymer			IL			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	5.953	2.217	233	5.532	2.112	235	5.413	2.091	243
2	5.861	2.230	239	5.465	2.105	241	5.327	2.087	250
3	5.673	2.193	262	5.343	2.093	252	5.234	2.065	258
4	5.513	2.176	280	5.217	2.072	263	5.148	2.054	267
5	5.507	2.171	278	5.112	2.051	272	5.033	2.027	275
6	5.504	2.167	276	5.021	2.034	281	4.934	2.013	284

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

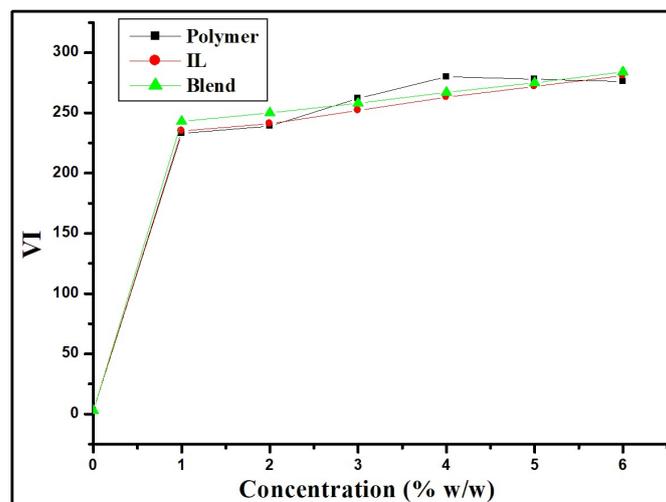


Figure IV.B.2: Variation of viscosity index with respect to the different concentrations of the additives

From the viscometric data obtained from **Table IV.B.2**, it is obvious that our chosen IL is really an effective viscosity reducer for the crude oil. Asphaltenes are reported to be strong H-bond receivers and ILs have the capability to act as strong H-bond donor [30]. Hence ILs can act as asphaltene stabilizer. Besides dispersing properties of ionic liquids along with solvating properties make them suitable candidate for treating asphaltene rich crude oil. Our chosen IL fulfills all the criteria required for possible interaction with asphaltenes and also with the paraffins of the crude oil. Presence of long alkyl chain on the imidazolium group accounts for some aliphatic interaction as well along with other interactions. In case of doping with the copolymer also, definite viscosity reduction is observed though comparatively little but distinct. Presence of acrylate and acetate functionality in the polymer may be the reason behind some interaction to reduce viscosity. But dramatic reduction is observed when doped with the copolymer-IL blend. The result is better represented in **Figure IV.B.2**.

With increasing concentration of the additive in the crude oil viscosity index has been increased, but at higher concentrations this change has almost vanished due to lower solubility which means solubility of the additive does play an important role for viscosity modification. Another noticeable thing is that at 40°C the effect of the additives in reduction of kinematic

viscosity is prominent, but at 100°C the effect is very little since at this higher temperature the viscosity the untreated crude oil itself is highly diminished.

IV.B.5.e. Shear stability index analysis

Shear stability index is an important parameter for a multifunctional additive since from production to refining a crude oil has to undergo a lot of processing stages which may involve severe mechanical shear also. To maintain the activity, an appropriate multifunctional additive for the crude oil must be shear stable also. In this view our obtained result is really an optimistic one.

Table IV.B.3: PVL & PSSI data with respect to the different concentrations of the additives in crude oil

Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
	Polymer	IL	Blend	Polymer	IL	Blend	Polymer	IL	Blend
1	2.475	2.217	2.156	11.64	4.97	3.11	36.39	12.90	7.78
2	2.481	2.211	2.152	12.62	5.04	3.11	38.45	12.91	7.75
3	2.486	2.207	2.147	13.36	5.45	3.97	39.97	13.69	9.52
4	2.487	2.203	2.143	14.29	6.32	4.33	41.47	15.34	10.21
5	2.518	2.198	2.140	15.98	7.17	5.57	45.96	16.80	12.57
6	2.534	2.193	2.136	16.94	7.17	5.95	48.35	17.83	13.19

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100°C.

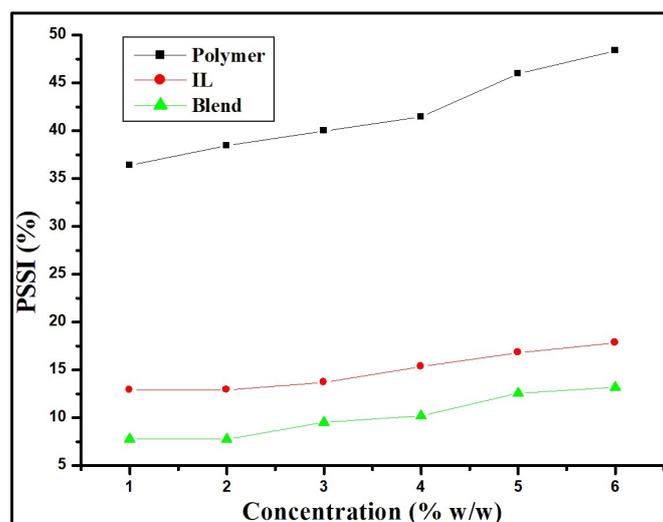


Figure IV.B.3: Variation of PSSI with respect to the different concentrations of the additives

Analyzing all the data (**Table IV.B.3**) it may be said the copolymer and the blend are very much shear stable in the crude oil under consideration. In case when the crude oil is treated with the IL alone, change in viscosity after shear is high which implies that the IL undergoes molecular degradation fast under mechanical shear which is better represented in **Figure IV.B.3**. In case of the polymer doped crude oil viscosity change is low. Most interesting result has been obtained in case of the blend. The result clearly showed that this blend of the copolymer and the IL is comparatively much more resistant against degradation under mechanical shear. When blended together there has been arisen number of possible interaction between to copolymer and the IL due to presence of variety of functionality in both the system and thus a better mechanically stable system of blend has been obtained. Again effect of concentration also has played an important role. With increasing concentration of the additive PSSI value increases, but not linearly since some other factors also may have a role here.

IV.B.6. CONCLUSION

In summary it may be said that an imidazolium-based IL doped polymeric additive has been developed which has been proved to be a better pour point depressant, a good viscosity reducer of asphaltene rich crude oil and at the same time possessed better shear stability in comparison to its parent copolymer and the IL. It was evident that the IL under consideration actually promoted

the activity of the copolymer which is itself a good PPD and VII. The IL had the capability to interact well with the asphaltene of the crude oil and hence could play an efficient viscosity reducer. This study provides a way to explore ionic liquids in enhancement of performance of polymeric additives. Since solo application of IL is a costly one, this doping method where little amount of IL is required, a cost effective approach has also been developed here for treatment of crude oil.

IV.B.7: REFERENCES

References for chapter IV.B are given in bibliography section (page 141–144).

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INDEX

A

Additive	3
AIBN	2
Alkyl Acrylate Copolymer	16–17
Anti-wear additives	7

B

Base oil	8, 28
BZP	29

C

Corrosion and rust inhibitor	7
Crude oil	11, 68

D

Detergents and dispersants	7
----------------------------	---

E

Ethylene–Vinyl Acetate	16
Extreme pressure additives	6

F

Free radical polymerization	40
Friction modifiers	6

I

Imidazolium based ILs	21–22
Ionic liquid	19

L

Lube oil	8
Lubricant	2

M

Maleic Anhydrides Copolymer	17
-----------------------------	----

P

Polymer blend	24
Pour Point Depressants	3–4

S

Shear stability	5–6
-----------------	-----

T

Terpolymer	17
------------	----

V

Viscosity index improver	4–6
--------------------------	-----



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Performance evaluation of polymeric blend of vinyl acetate and acrylate-based copolymers in lubricating oil

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ABSTRACT

Polymer modification processes like blending has attracted much attention as an easy, cost-effective and less time-consuming method for developing new polymeric materials enriched with versatile commercial application. Polymer blends are supposed to carry better thermal and mechanical properties compared to their parent polymers. In this view we have prepared a polymer blend of two copolymers— one of vinyl acetate and octyl acrylate and another of methyl methacrylate and dodecyl acrylate and characterized them by FT-IR and NMR spectroscopy. The molecular weight was determined by Gel Permeation Chromatography (GPC). We represented here a comparative study of their mechanical property as well as their performance as flow improver.

KEYWORDS

copolymers; gel permeation chromatography; mechanical property; polymer blends; vinyl acetate

1. Introduction

A polymer blend, analogous to metal alloys is a mixture of two or more polymers blended together to form a new material with different physical properties. Generally, there are five main types of polymer blend: thermoplastic–thermoplastic blends; thermoplastic–rubber blends; thermoplastic–thermosetting blends; rubber–thermosetting blends; and polymer–filler blends, all of which have been extensively studied. By traditional method using some suitable raw materials which are easy to polymerize, preparation and then commercialization of new polymer usually requires many years and is very expensive too. But polymer blending process may reduce both cost and time for development and commercialization of new polymeric material to perhaps 2–3 years (Scobbo and Goettler 2003). Hence polymer blending has attracted much attention as an easy and economic method for developing polymeric materials with huge and versatile applications in commercial sector. As for example, the production of polymer blends replacing traditional polymers represents half of all plastics produced in 2010 (Parameswaranpillai, Thomas, and Grohens 2015).

The properties of the blends can be manipulated as per its requirement, by suitable selection of the component polymers (Paul 1989). Today the polymer industry has become highly sophisticated, equipped with ultra-high-performance injection molding machines and extruders which easily allow phase-separations and via which viscosity changes also can be effectively detected or manipulated during the processing stages (White and Bumm 2011). Although such modern and sophisticated blending technology has greatly enhanced the performance capabilities of polymer blends, there originates a huge challenge to come up to the market expectation. To satisfy market pressure, for specific applications polymer blends must perform under some specified mechanical, chemical, thermal or electrical condition. Hence thorough study of the properties and performance of polymer blends is

essential to determine the maximum limit of performance of a particular blend. Recently a data-based approach to the development of industrial polymer blends with specified final properties was presented by John F. MacGregor et al. using building partial least-squares (PLS) models that combined databases on previously made blends and databases on the properties of the component materials used in these blends. (Muteki, MacGregor, and Ueda 2006).

The performance of polymer blends depends on the properties of each polymer in the blend, their content and morphology. The cost of the blend depends on the material, compounding method and blend morphology, which can be reduced for a specific application. Most blends have been developed for the improvement of a specific property such as impact strength and the process or recycling facility. Polymer blends can be classified as:

1. **Immiscible Polymer Blends:** These blends have large size domains of dispersed phase and poor adhesion between them. If the blend is formed by two polymers, two glass transition temperatures will be observed. Poly(propylene) (PP)–poly(styrene) (PS) and poly(propylene)–poly(ethylene) (PE) are immiscible blends.
2. **Miscible Polymer Blends:** These are homogeneous blends with a single-phase structure. In this case, one glass transition temperature will be observed. For example, poly(styrene) (PS)–poly(phenylene oxide) (PPO) and poly(styrene–acrylonitrile) (SAN)–poly (methyl methacrylate) (PMMA) are miscible blends.
3. **Compatible Polymer Blends:** These are immiscible polymer blends but exhibit uniform physical properties due to strong interface interactions between the polymer blend components.
4. **Compatibilized Polymer Blends:** These are also immiscible blends whose physical properties can be stabilized by adding surface-active species called compatibilizers. These compatibilizers influence various morphological processes.

The properties of a polymer blend depend on the final morphology. Hence various research groups have recently undertaken extensive studies of the miscibility and phase behavior of polymer blends. In practice, the physical properties of interest are found either by miscible pairs or by a heterogeneous system, depending on the type of application. The mixing is exothermic only when strong specific interactions occur between the blend components. The most common specific interactions found in polymer blends are hydrogen bonding, (Bourara et al. 2014).

Rajendran et al. Successfully Prepared polymer electrolyte membranes comprising of poly (ethyl methacrylate)/poly (vinyl chloride) with propylene carbonate (PC) as plasticizer and LiClO_4 as salt by solvent casting technique (Rajendran et al. 2008).

The green blends of an ionic liquid, 1-ethyl-3-propylimidazolium bis(trifluoromethanesulfonyl) imide {[EPrI][TFSI]} and a biodegradable polymer, poly(3-hydroxybutyrate) (PHB), were investigated by Li-Ting Lee and Chun-Ting Yang to explore the effect of ILs on the crystallization behaviors of the biodegradable polymers (Lee and Yang 2016).

Blends of polystyrene (PS) and Acrylonitrile–Butadiene–Styrene (ABS) were prepared in different ratios by melt blending technique by Buthaina et al. and the results from their work showed that the mechanical properties for blend system were better than those of pure polymers. (Buthaina and Karrer 2010).

The effect of soybean lecithin (SOLE) and acrylated epoxidized soybean oil (AESO) as biomass-based compatibilizer agents was studied successfully by Yoshito Andou et al. for the purpose of enhancing the compatibility of environmentally friendly thermoplastic blend of poly (lactic acid) (PLA) and synthetic rubber (PI) (Eksiler et al. 2017).

In the area of drug delivery systems, chitosan blends have been widely used for drugs control because of their various advantages such as non-toxicity, biocompatibility, biodegradability and availability of terminal functional groups (Chandy and Sharma 2009).

Table 1. Base Oil (BO) properties

Physical property	BO1	BO2
Density (gcm ⁻³ at 40 °C)	0.83	0.95
Viscosity at 40 °C in cSt	6.698	24.211
Viscosity at 100 °C in cSt	2.02	4.47
Viscosity Index (VI)	81.13	89.87
Pour Point (PP in °C)	-3	-6
Cloud Point (°C)	-10	-8

BO1, BO2 collected from IOCL, Dhakuria, West Bengal.

The versatility and unique characteristics, such as hydrophilicity, film-forming ability, biodegradability, biocompatibility, antibacterial activity and non-toxicity of chitosan has contributed to the successful development of various blends for medical, pharmaceutical, agricultural and environmental applications (El-Hefian et al. 2014). Biodegradable compatibilized polymer blends have acquired widespread application in packaging industry replacing non-biodegradable materials to satisfy the demands in environmental safety and sustainability (Muthuraj et al. 2017).

In view of the versatility of polymer blends we have prepared two copolymers—one P₁ of vinyl acetate (VA) and octyl acrylate(OA) and another P₂ of dodecyl acrylate (DDA) and methyl methacrylate (MMA) and then prepared their blend. We characterized them via FT-IR, ¹H-NMR and ¹³C-NMR spectroscopy. We further evaluated their performance as flow improver for lubricating oil and also investigated their mechanical strength in terms of shear stability index.

Experimental section

Materials

Dodecyl alcohol, octyl alcohol, methyl methacrylate (MMA), Acrylic acid, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. Properties of the mineral base oils used are tabulated in Table 1.

Preparation of esters and their purification

The ester (dodecyl acrylate, DDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of dodecyl alcohol in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. Another ester (octyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol. The method of esterification and its purification were carried out by the process as reported in the earlier publication (Ghosh et al. 2011).

Preparation of copolymers and blend

The copolymers were prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of polymer was carried out by the procedure as reported in our earlier publication (Ghosh et al. 2011). We have prepared two copolymers– one of vinyl acetate (VA) and octyl acrylate (OA) designated as P₁ and another of dodecyl acrylate (DDA) and methyl methacrylate (MMA) designated

Table 2. Molecular weight and polydispersity index data

Additive	M_n	M_w	PDI
P ₁	25339	53374	2.106410
P ₂	13644	31166	2.284337
Blend	34110	58693	1.720705

as P₂. The two prepared and purified copolymers were further mixed together via mechanical blending process at a magnetic stirrer at 60 °C to get a homogeneous blend.

Measurements

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 (0.4%, w/v) at 308 K temperature at a flow rate of 1 mL/min. The values are given in Table 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 wave number range (400–4000 cm⁻¹). NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl₃ was used as solvent and tetramethylsilane (TMS) as reference material.

Performance evaluation as pour point depressants in lube oil

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

Performance evaluation as viscosity index improver (VII)

Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at least nine different concentration of the sample solutions. The time of flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2%. Precautions regarding prevention of evaporation of solvent were taken in all the cases. Kinematic viscosity (KV) data at 40 °C, 100 °C and viscosity index (VI) data are given in Tables 4 and 5.

Shear stability measurement

Shear stability of a polymer is a measurement of its ability to sustain its viscosity under shearing conditions. Viscosity loss under shearing conditions may be of two kinds viz. Temporary Viscosity Loss (TVL) and Permanent Viscosity Loss (PVL) (Ghosh et al. 1998). The latter occurs due to mechanical degradation of polymer molecules and is often expressed in terms of Permanent Shear Stability Index (PSSI) using the equations,

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

Additive	BO	PP (°C) at different concentrations (% w/w) of additive						
		0%	1%	2%	3%	4%	5%	6%
P ₁	BO1	-3	-10	-10.9	-11.5	-11.9	-11	-10.5
	BO2	-6	-12	-12.5	-13.2	-11.9	-10.8	-10.7
P ₂	BO1	-3	-11.5	-12	-12.8	-12.5	-11.9	-11
	BO2	-6	-13.5	-14.4	-15.2	-14.9	-13	-12.9
Blend	BO1	-3	-10.5	-11.2	-11	-10.3	-10	-9.5
	BO2	-6	-12	-12.5	-13.1	-13	-12.4	-11.9

Table 4. Viscosity Index (VI) data with respect to the different concentrations of the additives in base oil 1 (BO1)

Conc ⁿ	P ₁			P ₂			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	6.705	2.120	113	6.701	2.100	106	6.710	2.160	128
2	6.714	2.160	127	6.709	2.130	11	6.724	2.190	135
3	6.727	2.200	141	6.717	2.180	132	6.740	2.240	153
4	6.750	2.250	157	6.123	2.210	144	6.770	2.280	164
5	6.780	2.300	170	6.741	2.250	155	6.800	2.310	172
6	6.810	2.340	184	6.760	2.290	171	6.830	2.350	185

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

Table 5. Viscosity Index data with respect to the different concentrations of the additives in base oil 2 (BO2)

Conc ⁿ	P ₁			P ₂			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	24.320	4.850	122	24.250	4.710	111	24.380	5.050	137
2	24.340	5.000	134	24.280	4.860	123	24.430	5.180	147
3	24.390	5.250	153	24.330	5.040	137	24.550	5.470	168
4	24.480	5.370	161	24.410	5.200	149	24.590	5.590	176
5	24.570	5.560	174	24.490	5.370	161	24.640	5.710	184
6	24.650	5.780	189	24.560	5.640	180	24.700	5.820	191

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

Table 6. PVL & PSSI data with respect to the different concentrations of the additives in base oil (BO)

Base Oil	Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
		P ₁	P ₂	Blend	P ₁	P ₂	Blend	P ₁	P ₂	Blend
BO1	1	2.081	2.016	2.110	1.84	1.86	2.32	39.00	48.75	35.71
	2	2.100	2.083	2.125	2.78	2.21	2.97	42.86	52.22	38.23
	3	2.120	2.080	2.150	3.64	4.59	4.02	44.44	62.50	40.91
	4	2.140	2.090	2.173	4.89	5.43	4.69	47.83	63.16	41.15
	5	2.150	2.100	2.190	6.52	6.67	5.19	53.57	65.22	41.38
	6	2.160	2.100	2.220	7.69	8.29	5.53	56.25	70.37	39.39
BO2	1	4.655	4.560	4.965	4.02	3.18	1.68	51.32	62.50	47.22
	2	4.710	4.610	5.020	5.80	5.14	3.09	54.72	64.10	51.61
	3	4.800	4.660	5.493	8.57	7.54	1.11	57.69	66.67	60.70
	4	4.837	4.710	4.880	9.93	9.42	12.70	59.22	67.12	63.39
	5	4.890	4.730	4.920	12.05	11.92	13.83	61.47	71.11	63.71
	6	4.930	4.820	4.930	14.71	14.54	15.29	64.89	74.07	65.93

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100 °C.

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

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

V_o = KV of the oil before addition of polymer

V_i = KV of the oil after addition of polymer

V_s = KV of the oil doped with polymer after shearing

The PVL and PSSI values are measured here preparing 1–6% solutions of the prepared copolymers and their blend in BO1 and BO2 as per ASTM D-3945 method and are given in Table 6.

Results and discussion

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 (P_1 , P_2) and their blend are given in Table 2. From the experimental data, it was found that blend had higher number average and weight average molecular weight than the copolymers. This result also indicates a fine blending of P_1 and P_2 . Again in terms of polydispersity index (PDI) the polymer blend is less poly-dispersed than the copolymers (P_1 and P_2) which indicates better uniformity in the blend. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the M_w values decrease but PDI value increases.

Spectroscopic analysis

In IR spectra for both the copolymers (P_1 and P_2) peaks around $1732\text{--}1734\text{ cm}^{-1}$ clearly indicates the presence of ester carbonyl group. But for the blend this peak for ester carbonyl group shifted to around 1710 cm^{-1} which may be due to interaction between the copolymers like hydrogen bonding while blending. Absence of peaks above 3000 cm^{-1} indicates absence of $\text{C}=\text{C}$ unsaturation and supports complete polymerization in all the cases.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data also support the above result. The peaks appeared in the range of $3.933\text{--}4.15\text{ ppm}$ indicated the presence of $-\text{OCH}_2-$ protons. Here again the absence of peaks around 6 ppm indicated total polymerization. In $^{13}\text{C-NMR}$ the peak around 176 ppm indicated the presence of ester carbonyl carbon. The peaks at $64.66\text{--}65.06\text{ ppm}$ corresponded to the $-\text{OCH}_2$ carbons, peaks ranging from $14.08\text{--}45.09\text{ ppm}$ for all other sp^3 carbons. Again no peak in the range of $120\text{--}150\text{ ppm}$ indicated the absence of sp^2 carbons and confirmed the polymerization.

Performance evaluation as pour point depressant

Analysing the pour point data given in Table 3, it may be said that both the prepared copolymers and their blend acted as good flow improvers and among them all the copolymer P_2 i.e. copolymer of methyl methacrylate and dodecyl acrylate was proved to be better than P_1 and the blend. It may be because of the longer alkyl chain length of the ester in P_2 which was supported by earlier reports (Behbahani 2014). In case of the blend lower solubility in the base oil might retard its property as flow improver at higher concentration. The best result was obtained for the copolymer P_2 at 3% concentration in the base oil 2 (BO2).

Performance evaluation as viscosity index improver

Among the copolymers, P_1 i.e. copolymer of vinyl acetate and octyl acrylate showed better result (Tables 4 and 5) as viscosity index improver which may be attributed to its lower alkyl chain length in the ester and also its higher molecular weight than P_2 . Interestingly here blend of P_1 and P_2 acted as the best viscosity index improver may be due to its higher molecular weight. Irrespective of all the polymers and base oil, viscosity index gradually increased with increasing concentration of the added polymers which may be due to an increase in the total volume of the polymer micelles in the oil solutions (Nassar 2008).

Shear stability index analysis

As expected polymer blend of the prepared copolymers showed highest stability against mechanical shear at all concentrations, which clearly supports its better mechanical and thermal property in both the base oils (Table 6). Another important observation was that irrespective of both the copolymers and their blend, moderately higher PSSI value was obtained in case of the base oil with higher viscosity (BO2). It is believed that polymer molecules are more tightly bound in high viscous base oil and hence the mobility of the polymer chain is reduced which makes the polymer molecule more susceptible to bond rupture i.e. mechanical degradation. Hence in base oil with higher viscosity shear stability of the additives decreases (Alexander et al. 1989) which was evident from our result. Higher the concentration of the additive higher was the PVL and hence PSSI value. But the relationship between the concentration of the polymer and shear stability index was not linear since various other factors like molecular weight of the polymer, composition of the base oil might play different role on shear stability.

Conclusion

Thus, it may be concluded that all the prepared polymers including the blend were proved to be a good flow improver for lubricating oil. When it comes to mechanical stability the polymer blend of the prepared copolymers excels. It may be because of its higher molecular weight and lower polydispersity index. The blend was also proved to a better viscosity modifier at all concentrations in the base oil.

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Polymer blend: a new approach towards flow improvement of crude oil

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Polymer blend: a new approach towards flow improvement of crude oil

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ABSTRACT

Crude oil extraction, transportation and even its storage require a lot of struggle due to its high density, high viscosity and high pour point. To overcome these problems, polymers have attracted much attention as efficient chemical additive. Moreover polymer blending is an economic and easy process to develop better polymeric materials with higher thermal and mechanical stability. In this context, we evaluated a polymer blend of two copolymers viz. vinyl acetate-octyl acrylate and dodecyl acrylate-methyl methacrylate, as flow improver by measuring viscometric parameters, pour point and shear stability index in crude oil.

KEYWORDS

crude oil; pour point; additive; polymer blending; shear stability index

1. Introduction

Constant industrialization and considerable increase in energy consumption have increased the demand for oil which is supposed to be the main energy source all over the World (Chen et al. 2010; Ranalli 1995). To meet the global requirement heavy and even extra heavy crude oil are getting enough attention due to limited and declining source of light or medium crude reserves. But storage and transportation of crude oil through pipelines is one of the challenging issues especially at cold areas or where the temperature becomes seasonally very low. The composition of crude oil, its density, viscosity and ambient temperature conditions are key factors behind such problem.

Crude oil, basically a form of unprocessed oil, is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins (Huang et al. 2011) and other heavy metal may be present in it depending on the geological background (Olutoye 2005). As the temperature decreases, paraffins in the crude crystallize out forming a three dimensional matrix of wax crystals which begin to trap the molecules of liquid hydrocarbon until the oil ceases to flow (Soni and Bharambe 2006; Garcia et al. 1998; Castro, Flores, and Vazquez 2011; Soldi et al. 2007). Thus Paraffin deposition diminishes oil production and its removal from the pipeline is also a high cost issue. Pour point depressants (PPDs) or flow improvers (FIs) are substances which modify the growing pattern of the wax crystals and limit their aggregation and thus enhance the flow even at low temperature. An efficient PPD should be a linear polymer or copolymer having pendant hydrocarbon groups in the polymeric backbone (Kumar 1989). Several polymers have been evaluated as wax crystal modifiers and among them poly(ethylene-co-vinyl-acetate) copolymers are vastly used since they possess good efficiency as crude oil flow modifiers and wax deposition inhibitor (Andre et al. 2001; Shafey et al. 2014). Hemant P. Soni synthesized copolymers of maleic anhydride and esters of n-alkyl alcohols with oleic acid and methacrylic acid and evaluated them as efficient pour

point depressants and flow improvers for crude oil from Gandhar oil field, Gujarat, India (Soni and Bhambe 2006). Another study was conducted on Algerian crude oil by D. Djemiat et al where the addition of the copolymer, poly (ethylene-co-vinyl-acetate) containing 12% of vinyl acetate, improved the rheological parameters and hence the flow property of crude oil (Djemiat, Safri, and Benmounah 2017).

While considering the flow property Crude oil viscosity is another important parameter which is strongly influenced by the presence of asphaltenes, very large heterogeneous molecules with condensed aromatic nuclei containing heteroatoms such as nitrogen, sulfur and oxygen, and metals such as vanadium, iron, and nickel (Groenzin and Mullins 1999; Mullins et al. 2012; Speight 2014). Presence of strong bonds like C=S drastically increases the viscosity of the crude (Chuan et al. 2010; Ghanavati, Shojaei, and A. R 2013). Asphaltenes themselves also may associate to form colloidal sized particles leading to large aggregates and thus increase the viscosity of heavy crude (Xu et al. 2011; Frohlich and Rice 2005; Atta, Al-Shafy, and Ismail 2011; Shafey et al. 2011). Thus during storage or transportation of crude oil, these asphaltenes and paraffins precipitate out forming multiphase flow leading to large pressure drops, increased pumping costs, blocked pipelines and hence huge production loss ranging up to millions of dollars every year (Freiner, Zainuddin, and Venkatesan 2010).

Various preventive methods such as mechanical methods, thermal treatment and chemical methods are commonly employed to overcome these problems. The oldest and the most popular one is dilution of crude with light hydrocarbons, organic solvents like methyl tert-butyl ether, tert-amyl methyl ether, etc, alcohols like pentanol, hexanol, etc, gasoline and middle distillates like kerosene (Maamari and Buckley 2003). These diluents reduce the viscosity of crude oil thereby facilitating its transportation through pipelines. But this process requires another well maintained pipeline for carrying the solvent which is itself a cost increasing factor, again identifying proper diluent to oil ratio for different crude oil depending upon its composition and finally recovery of the oil from diluent are not less than an ordeal (Kulkarni and Wani 2016).

Several studies have utilized chemicals such as surfactants, scavengers, emulsion breakers, polymers, nanoparticles and other chemical additives as wax modifier and viscosity reducer in crude oil application (Anisuzzaman, Fong, and Madsah 2018). Castro et al. reported that the viscosity of Mexican crude oil was reduced using the terpolymer consisting of high percentage of styrene and low percentage of n-butylacrylate and vinyl acetate (Castro, Flores, and Vazquez 2011). Joonaki et al. developed an ionic additive named IRAN91 which reduced viscosity up to 64% of heavy oil collected from Marun oil field, Bangestan reservoir (Joonaki, Ghanaatian, and Zargar 2012). Several studies have reported some well designed nanoparticles as efficient viscosity reducers of heavy crude oil (Chen et al. 2009; Greff and Babadagli 2012). Olusegun Peter Akinyemi et al. successfully investigated the influence of cheaper natural chemicals, obtained from plant seeds (jatropha, rubber and castor) on the rheological properties and wax deposition tendencies of Nigerian waxy crude oil (Akinyemi et al. 2016). An environmentally friendly and cost effective additive for light and heavy crude oils of Oman was reported by Salam K. Al-Dawery and Saleh K. Al-Shereiqi (Bello et al. 2005). They used waste bio materials such as fiber of palm tree, date palm kernel and walnut shell materials as viscosity reducing agents on light and heavy crude oils of Oman. In another study by Manojkumar Gudala it was found that addition of 2000 ppm potato starch to the 85% Heavy crude oil and 15% water mixture at 40 °C decreased viscosity of the crude by 80.24% which is an excellent and very inspiring result (Gudala et al. 2018).

Today polymer blending has attracted much attention as an easy and economic method for developing new polymeric materials with huge and versatile applications in commercial sector. In our previous work we investigated the properties of polymeric blend in comparison of its parent copolymers and established that the polymeric blend possessed much better mechanical and thermal stability when treated in lubricating oil as additive (Ghosh and Yeasmin 2019). Now since for crude oil extraction and transportation we require mechanically and thermally stable additives

so that they do not undergo easy degradation under severe mechanical stress, we tried to evaluate the polymer blend as flow improver for crude oil.

2. Experimental section

2.1. Materials

Dodecyl alcohol, octyl alcohol, methyl methacrylate (MMA), Acrylic acid, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd.) was used as received. The crude oil was collected from IOCL, Assam having pour point of 27°C and densities of 0.851 and 0.808 g/cc at 40°C and 100°C respectively.

2.2. Preparation of esters

The ester (dodecyl acrylate, DDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of dodecyl alcohol. The reactants were mixed with toluene along with few drops of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor in a resin kettle and heated gradually from room temperature to 403 K 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 (octyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol following the same procedure.

2.3. Purification of prepared esters

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

2.4. Preparation of copolymers and blend

Two copolymers—one of vinyl acetate (VA) and octyl acrylate (OA) designated as P_1 and another of dodecyl acrylate (DDA) and methyl methacrylate (MMA) designated as P_2 , were prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer) following the same procedure as reported in our earlier publication (Ghosh et al. 2011). The process of blending is mentioned in our previous publication (Ghosh and Yeasmin 2019).

3. Measurements

3.1. 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 (0.4%, w/v) at 308 K temperature at a flow rate of 1 mL/min. The values are given in Table 1.

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 wave number 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.

3.3. Performance evaluation as pour point depressants in crude oil

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

3.4. Performance evaluation as viscosity index improver (VII)

Viscometric parameters were determined according to ASTM D 2270-10. The kinematic viscosity of the crude oil containing the copolymers and the blend was determined at 313 and 373 K. Different concentrations of the polymers in the crude (% w/w) from 1% to 6% were used to study the effect of concentration on VI of the additive-doped crude oil. All of the experimental data, given in Table 2 were noted by taking an average of three experimental results under identical conditions in each case.

3.5. Shear stability measurement

Shear stability of a polymer is a measurement of its mechanical stability against shearing condition. Viscosity loss under shearing conditions may be of two kind viz. Temporary Viscosity Loss (TVL) and Permanent Viscosity Loss (PVL) (Ghosh, Pantar, and Sarma 1998). The latter occurs due to mechanical degradation of polymer molecules and is often expressed in terms of Permanent Shear Stability Index (PSSI) using the following equations,

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

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

V_o = KV of the oil before addition of polymer

V_i = KV of the oil after addition of polymer

V_s = KV of the oil doped with polymer after shearing

The PVL and PSSI values are measured here preparing 1%–6% solutions (% w/w) of the prepared copolymers and their blend in the crude oil as per ASTM D-3945 method and are given in Table 3.

Table 1. Molecular weight and pour point data (°C).

		P ₁	P ₂	Blend
Molecular weight and polydispersity index data	M _n	25339	13644	34110
	M _w	53374	31166	58693
	PDI	2.106410	2.284337	1.720705
Pour point data (°C) with respect to the different concentrations (% w/w) of the additives in crude oil	0	27	27	27
	1	6.5	5.9	6.1
	2	6.2	5.1	5.8
	3	5.7	4.6	5.3
	4	4.9	4.1	5.1
	5	4.4	4.1	5.6
	6	4.4	4.3	6.3

Table 2. Viscosity index (VI) data with respect to the different concentrations of the additives in crude oil.

Conc ⁿ	P ₁			P ₂			Blend		
	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI	KV ₁	KV ₂	VI
1	5.953	2.217	233	7.358	2.327	142	5.877	2.213	242
2	5.861	2.230	239	7.147	2.317	153	5.728	2.193	254
3	5.673	2.193	262	6.735	2.237	158	5.496	2.165	277
4	5.513	2.176	280	6.724	2.231	157	5.473	2.157	276
5	5.507	2.171	278	6.722	2.229	157	5.465	2.153	276
6	5.504	2.167	276	6.717	2.227	156	5.462	2.151	275

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

Table 3. PVL & PSSI data with respect to the different concentrations of the additives in crude oil.

Conc ⁿ	KV ₂ after shear			PVL (%)			PSSI (%)		
	P ₁	P ₂	Blend	P ₁	P ₂	Blend	P ₁	P ₂	Blend
1	2.475	2.600	2.406	11.6373	11.7318	8.7212	36.3892	45.5759	27.0687
2	2.481	2.608	2.401	12.6191	12.5593	9.4847	38.4508	47.7832	28.3765
3	2.486	2.618	2.394	13.3607	17.0317	10.5773	39.9727	55.2975	30.5333
4	2.487	2.638	2.412	14.2923	18.2429	11.8219	41.4666	58.5611	31.5994
5	2.518	2.652	2.440	15.9834	18.9771	13.3302	45.9602	60.6886	37.1280
6	2.534	2.668	2.458	16.9358	19.8024	14.2724	48.3530	63.0901	39.6129

Concⁿ represents concentration in % w/w; KV₂ represents kinematic viscosity at 100 °C.

4. Results and discussion

4.1. Molecular weight analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity index data (PDI) of the prepared polymers (P₁, P₂) and their blend are given in Table 1. Analyzing the experimental data, it was found that blend had higher number average and weight average molecular weight than the copolymers. This result also indicates a fine blending of P₁ and P₂. Again in terms of polydispersity index (PDI) the polymer blend is less poly-dispersed than the copolymers (P₁ and P₂) which indicates better uniformity in the blend. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the M_w values decrease but PDI value increases.

4.2. Spectroscopic analysis

In IR spectra absence of peaks above 3000 cm⁻¹ indicates absence of C=C unsaturation which supports complete polymerization in all the cases. For both the copolymers (P₁ and P₂) peaks around 1732–1734 cm⁻¹ clearly indicate the presence of ester carbonyl group. But for the blend this peak for ester carbonyl group shifted to around 1710 cm⁻¹ which may be due to interaction between the copolymers like hydrogen bonding while blending.

In ¹H-NMR spectra peaks appeared in the range of 3.933–4.15 ppm clearly indicate the presence of -OCH₂- protons. Here again the absence of peaks around 6 ppm indicate absence of C=C unsaturation and hence total polymerization. In ¹³C-NMR spectra, peak at 176 ppm indicates the presence of ester carbonyl carbon. The peaks at 64.66–65.06 ppm corresponded to the -OCH₂ carbons, peaks ranging from 14.08–45.09 ppm for all other sp³ carbons. Again no peak in the range of 120–150 ppm indicated the absence of sp² carbons and confirmed the polymerization.

4.3. Performance evaluation as pour point depressant

The pour point data given in Table 1 clearly prove that both the prepared copolymers (P₁ and P₂) and their blend are good pour point depressants for the crude oil. Among them all, P₂

copolymer i.e., copolymer of dodecyl acrylate and methyl methacrylate gave the best result as ppd. Longer alkyl chain of this copolymer might play better role in the co-crystallisation process in crude oil (Behbahani 2014). At 4% concentration (% w/w) in the crude oil this copolymer exhibited highest depression in pour point from 27 °C (untreated crude) to 4.1 °C. At higher concentrations the polymers, especially the blend which is of higher molecular weight became less effective due to lower solubility. It implies that solubility is a major factor while considering flow improvement of crude oil.

4.4. Performance evaluation as viscosity index improver

Viscosity is another important parameter when dealing with crude oil. It may be mentioned here that the measured kinematic viscosities at 40 °C and 100 °C of the untreated crude oil are 11.243 and 2.926 cst respectively. While analyzing the data obtained from viscometric measurements (Table 2), it is evident that the prepared copolymers and their blend are effective viscosity reducers for the crude oil under consideration. Interestingly, here the polymeric blend showed highest reduction in kinematic viscosity of the crude oil. At 3% concentration in crude oil this polymer blend showed highest reduction in kinematic viscosity which is over 50%. Its comparatively higher molecular weight might be the reason behind this better efficiency. It is noted that at 40 °C, the effect of the additives in reduction of kinematic viscosity is prominent, but at 100 °C the effect is very little since at this higher temperature the viscosity the untreated crude oil itself is highly diminished. At higher concentrations the efficiency of the polymers was reduced due to lower solubility which fact again cites the importance of solubility factor for effectiveness of additives in crude oil.

4.5. Shear stability index analysis

Analyzing the PVL and PSSI data given in Table 3, we found that polymeric blend showed lowest PVL and PSSI values at all concentrations simply indicating highest stability against mechanical shear. This result really inspired us the most towards improvement of flow properties of crude oil. In crude oil extraction or transportation, stability factor of the additive must be taken into account against severe shear experienced during the turbulent flow of crude oil. Hence crude oil additives must be stable enough and must not lose their activity undergoing easy degradation. So our prepared polymer blend may be a good candidate to be nominated as an efficient flow improver for the crude oil under consideration. Copolymer of dodecyl acrylate and methyl methacrylate (P₂) exhibited highest PSSI value which indicates that this copolymer is more prone to mechanical degradation under shear than others. With increasing concentration of the polymers in the crude oil, PVL values as well as PSSI values increase.

5. Conclusion

The above study may be summarized as follows. Both the copolymers and their blend can act as efficient flow improvers for crude oil collected from Assam. Methacrylate-based copolymer was proved to be the better one as pour point depressant due to its longer alkyl chain. But in case of viscosity reduction vinyl acetate-based copolymer and the blend exhibited better performance. Most importantly the polymer blend in crude oil showed highest stability against mechanical shear. But further study is needed to ensure its efficiency in other crude oils also. However, since polymer blending is a cheaper and less time consuming process compared to preparation and characterization of new polymeric material, the above study may open a new horizon of flow improver for crude oil where polymer blend may occupy the prominent position as an efficient and stable flow improver.

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Synthesis and Characterization of Methacrylate Based Polymeric Additives for Crude Petroleum Oil

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Abstract:

Wax deposition in crude oil especially at low temperature causes serious problem during its storage and transportation since this deposited wax gradually immobilizes the oil. Thus, waxy crude oils have high pour point resulting lots of handling problems. To solve this problem, a number of flow improvers (FI) or pour point depressants (PPD) have been prepared. But still it is a challenging aspect of this research area to find out the perfect chemistry with an improved efficiency and cost-effective additives over the conventional one. In this context and in continuation of our effort for the development of additive systems for lube and crude oils, homo polymer of decyl methacrylate and its copolymers with styrene and vinyl acetate at different percentage composition in the presence of benzoyl peroxide (BPO) as initiator have been prepared. All the prepared polymers are characterised by FT-IR, NMR and Gel Permeation Chromatography (GPC). The prepared additives showed excellent performance as flow improver (FI) or pour point depressant (PPD) in crude oil.

Keywords: Crude oil, additives, flow improver, wax crystal network, homopolymer, copolymer.

Introduction

Crude oil is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins (Huang et al., 2011). When the temperature decreases paraffin precipitates out from the crude oil and forms wax crystals network. Their presence causes many problems (Guo et al., 2006) during storage and transportation mainly because of the crystallization and deposition of paraffin wax crystals in the flow line causing a number of handling problems as well in regions where the service temperatures (Xu et al., 2011; Frohlich et al., 2005; Atta et al., 2011; Al-Shafey et al., 2011) are or become seasonally very low (Song et al., 2005; Huiyang et al., 1991).

Pour point depressants do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates. When wax crystals form, pour point depressants co-crystallize along with the wax species present in the oil and modify the growing pattern of wax crystal structures. Additionally, the wax crystals are kept apart from each other by the PPD backbone, and as a result of this steric hindrance, the wax crystals are no longer able to form three-dimensional structures with each other that inhibited the flow property.

Some commercially available properly designed polymeric flow improvers are poly (ethylene-co-vinyl acetate) (EVA) (Machado et al., 2001), poly(ethylene-butene) (PEB) (Schwahn et al., 2002), polymethacrylates (Soldi et al., 2007; Jung et al., 2011), and modified maleic anhydride copolymers (Wu et al, 2012; Xu et al., 2011; Deshmukh and Baramde, 2011). Basically, these polymeric wax inhibitors consist of a non-polar long hydrocarbon chain of 14 to 25 carbon atoms in addition with a polar segment typically acrylates or acetates. The hydrocarbon part is responsible for the interaction between the additive and paraffin of the oil while the polar part limits the degree of co-crystallization and thus inhibits the aggregation stage. Recently Chen et al. investigated the interaction of crude oil waxes with polyacrylate pour point depressants (PPDs) bearing different structures and reported that polyacrylate polymers with polar building blocks interacted more easily with the paraffin content which would effectively inhibit wax-crystal precipitation and improve crude oil low-temperature fluidity (Chen et al., 2014). Another study supports that an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer having pendant hydrocarbon chain groups (Kumar, 1989). 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 for crude oil (Borthakur et al., 1996; Castro et al., 2011). For example, polybehenyl acrylate with a lower MW exhibited better efficacy as a flow improver for asphaltene-rich crude oil (Chanda et al., 1998) and acrylate/methacrylate polymer additives with a lower range of MWs achieved the optimum effectiveness for waxy crude oils (El-Gamal et al., 1994). According to Kuzmic et al., polymeric additives of alkyl acrylate with styrene, acrylic acid, and 1-vinyl-2-pyrrolidone with MWs below 20000 were not efficient for crude oils from Croatian oil fields (Ercegkuzmic et al., 2008) while in another study by Taraneh et al., it was reported that ethylene vinyl acetate copolymer with a higher MW was the better additive for crude oils with low asphaltene contents (Taraneh et al., 2008). T. J. Behbahani had investigated the influence of different concentrations of polymeric flow improver such as dodecylpolymethacrylate and tetradodecylpolymethacrylate on pour point of waxy oils and found that the higher molecular weight flow improver (tetradodecylpolymethacrylate) had better efficiency on pour point of waxy oils (Behbahani, 2014). Moreover, the performance of a flow improver is also related to the wax and asphaltene composition in the crude oil (Kumar, 1989; Borthakur et al., 1996; Ercegkuzmic et al., 2008; Castro et al., 2011). Hence it can be summarized that the performance of a polymeric flow improver is dependent upon both the structure of the flow improver and the oil composition (El-Gamal et al., 1992).

Vinyl acetate copolymer, acrylate copolymer and their derivatives (Qian et al., 1996; Jordan et al., 1978) are broadly applicable to improve the flow ability of very waxy crude oil, diesel fuel and other base oils at low temperature. Vinyl acetate copolymers satisfy most of the properties which a good additive must possess. On the other hand, methacrylate polymers, the first of the polymeric pour point depressants, continue to be viewed as the best chemistry available today due to the molecular structure of the polymers and the tremendous flexibility in chemical structure. In the present context, we have prepared homopolymer of decyl methacrylate and its copolymers with styrene and vinyl acetate separately at different percentage compositions and evaluated them as flow improver for crude oil collected from Oil India Ltd, Duliagan, Assam (India). The properties of the crude oil are listed in table 1.

Experimental Section

Materials

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), Styrene (99%, Sigma-Aldrich), Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), Decyl alcohol (DA, 98%, SRL Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. Crude oil was collected from Oil India Ltd, Duliagan, Assam (India). Before experiment the crude oil was tested for pour point and was found 24 ° C.

Preparation of the monomer and its purification

The monomer (decyl methacrylate, DMA) was prepared by reacting 1.1 mol of methacrylic acid with 1 mol of decyl alcohol in the presence of concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in the earlier publication (Ghosh et al., 2011).

Preparation of polymers:

The polymers (homo and copolymers) were prepared by free radical polymerization (scheme1) at different percentage composition of monomers (table 2) in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of polymer was carried out by the procedure as reported in our earlier publication (Ghosh et al., 2011). (Please insert scheme 1 here)

Measurements

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 (0.4%, w/v) at 308K temperature at a flow rate of 1mL/min.

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 (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.

Performance evaluation as pour point depressants/flow improvers in crude oil

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

Results and Discussion

Molecular Weight Analysis:

The experimental values of M_n , M_w and PDI (polydispersity index) of the prepared polymers are tabulated in table 2. From table 2, it can be stated that on increasing the percentage of styrene or vinyl acetate both the number average molecular weight and weight average molecular weight gradually increases. But the copolymers of vinyl acetate are less poly-dispersed than those of styrene-based copolymers. (Please insert table 2 here)

Spectroscopic analysis:

The homopolymer of decyl methacrylate shows IR absorption band at 1735.8 cm^{-1} corresponds to the ester carbonyl group and those at 1064.6, 710 and 690 cm^{-1} are due the bending of C–H bond. Due to the presence of $-\text{CH}_2\text{CH}_3$ group the peak at 2854.5 cm^{-1} and 2924 cm^{-1} appeared and for the CO stretching vibration the peaks at 1465.8, 1404, 1229, 1211 and 1149.5 cm^{-1} appeared. The IR spectrum of copolymers of decyl methacrylate with styrene (P-2 to P-5) are similar and exhibited the following results: The absorption band for ester carbonyl group at 1735.8 cm^{-1} shifted to 1728.1 cm^{-1} in the copolymer and the peaks at 748.3 cm^{-1} and 702 cm^{-1} were due to the C-H bond of the phenyl group of styrene. For the copolymers of decyl methacrylate and vinyl acetate (P-6 to P-9) the IR spectrum are similar and showed the following results: Peaks at 1732.9 cm^{-1} and 1716.5 cm^{-1} indicate the presence of ester carbonyl groups and the peaks at 2853.6 cm^{-1} and 2922.9 cm^{-1} are for the $-\text{CH}_2\text{CH}_3$ group. The peaks at 1456.2 cm^{-1} , 1377.1 cm^{-1} , 1368.4 cm^{-1} , 1321.1 cm^{-1} , 1296.1 cm^{-1} , 1238.2 cm^{-1} , 1163.0 cm^{-1} , 1065.5 cm^{-1} and 1011.6 cm^{-1} were due to CO stretching vibration and absorption bands at 814.9 and 721.3 cm^{-1} were for bending of C-H bond.

In the ^1H NMR data of the homopolymer, the methyl and methylene protons appeared in the range of 0.890 to 1.934 ppm for all alkyl groups and a broad peak at 3.928 ppm for the protons of $-\text{OCH}_2$ group. Absence of any peak in the range of 5-6 ppm corresponds to sp^2 carbon confirms the polymerisation. In the ^1H NMR of the copolymers of styrene, a broad peak at 7.014-7.329 ppm appeared for the protons of phenyl group. The peaks appeared in the range of 3.933-4.15 ppm indicated the presence of $-\text{OCH}_2$ protons. All the sp^3 protons appeared in the range of 0.9-1.942 ppm. Here again the absence of peaks in the range of 5-6 ppm indicated

total polymerisation. In the ^1H NMR of copolymers of vinyl acetate a broad peak at 3.926-4.158 ppm indicated the protons of $-\text{OCH}_2$ and $-\text{OCH}_3$ groups. The hydrogen atoms attached to sp^3 carbons appeared in the range of 0.858 ppm to 2.637 ppm. Absence of any peak in the range of 5-6 ppm confirmed the polymerisation successfully.

In ^{13}C NMR of the homopolymer, the peaks at 177.54 ppm indicated the presence of ester carbon. The peaks at 65.03 ppm and 64.88 ppm confirmed the presence of $-\text{OCH}_2$ carbon and peaks in the range of 14.16–45.12 ppm accounted for all sp^3 carbon atoms of alkyl groups. Absence of sp^2 carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120-150 ppm. In the ^{13}C NMR of the copolymers of styrene, the peaks in the range of 176.8-177.79 ppm indicated the ester carbons. The phenyl carbons appeared in the range of 125.04-128.56 ppm. Peaks appearing at 64.86 ppm and 65.02 ppm indicated the $-\text{OCH}_2$ carbon whereas peaks in the range of 14.12-54.41 ppm corresponded to all the sp^3 carbons.

In ^{13}C NMR of the copolymers of vinyl acetate the peaks at δ 176.60 -176.70 ppm were due to the presence of ester carbonyl group. The peaks at 64.66 - 65.06 ppm corresponded to the $-\text{COCH}_3$ methyl carbon and $-\text{OCH}_2$ carbons, peaks ranging from 14.08–45.09 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.

Analysis of pour point values

The experimental values of pour point are given in table 3. The values suggest that all the prepared polymers (P-1 to P-9) can be used effectively as pour point depressants (PPD) or flow improvers (FI) for Duliajan crude oil. The copolymers (P-2 to P-9) are better than the homopolymer (P-1) as FI. But with varying concentration, the pour point values do not linearly co-relate. In case of the copolymers of decylmethacrylate and styrene (P-2 to P-5), P-2 copolymer with the lowest percentage of styrene (2.5%) acts as the better FI than the others and using 5% (w/w) solution of this polymer we get the lowest pour point of 8.1°C. Increase in the percentage of styrene results in increasing the phenyl content in the additive. Hence it may be the reason behind that P-3 to P-5 copolymers with higher percentage of styrene gradually showed higher pour point and at 6% (w/w) solution P-5 copolymer with highest percentage of styrene (10%, w/w) shows highest pour point of 16.1°C. The vinyl acetate copolymers (P-6 to P-9) showed better results than the copolymers of styrene. These polymers are better FI and may be due to absence of phenyl group which reduces the adsorption of the polymer molecule on the wax crystals (Abdel-Azim et al., 2006) that happened in case of styrene copolymers. The P-7 copolymer having 5% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers. At 5% concentration this polymer showed lowest pour point of 4.2 ° C. Polymers with higher molecular weights especially P-5 and P-9 showed comparatively poor results. It may be because of their low solubility in the crude oil. (Please insert table 3 here)

Conclusion

From the above study it is found that homopolymer of decyl methacrylate and its copolymer with styrene and vinyl acetate are effective as flow improver for the crude oil. The vinyl acetate-based copolymers are better as flow improver than styrene based copolymers. Moreover, it was also found that copolymers with lower molecular weight are more effective as flow improver than copolymers with higher molecular weight. Therefore, molecular weight and the chemistry of polymer chain have a significant role in relation to the performance of the additives as flow improvers for crude oil.

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Scheme 1

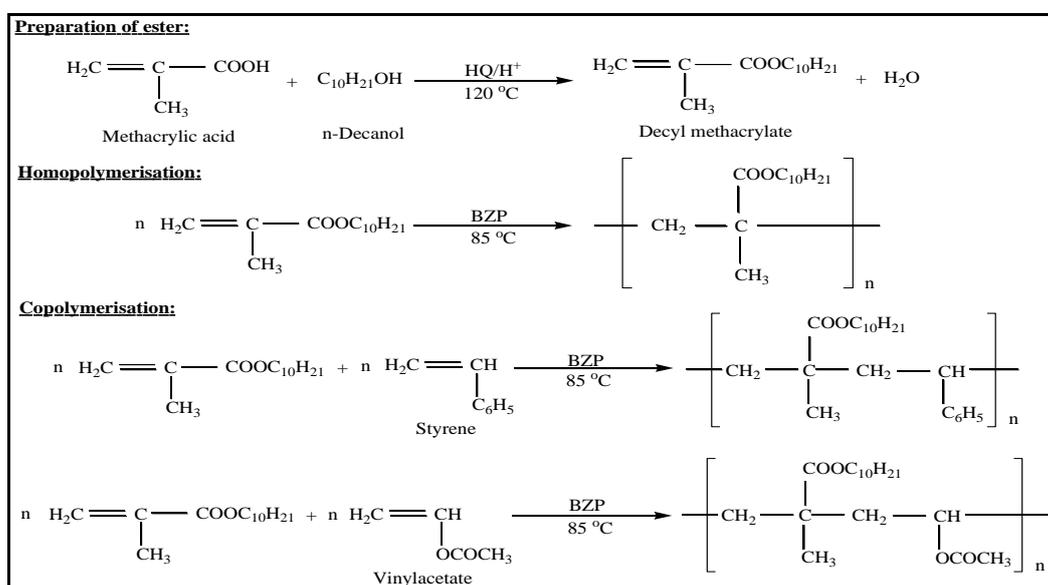


Table 1: Specification of the crude oil

Source	Duliajan, Assam
Pour point	24°C
Density	900 Kg/m ³
Plastic viscosity	5.2 mPa.S at 27°C
Yield value	10 dy/cm ² at 30°C
Wax content	>10%

Table 2: Percentage composition, M_n , M_w and PDI values of polymers (P-1 to P-9)

Polymer code	% of DMA	% of Sty.	% of VA	M_n	M_w	PDI
P-1	100	-	-	20482	49682	2.4256
P-2	97.5	2.5	-	21592	58982	2.7316
P-3	95	5	-	27457	77688	2.8294
P-4	92.5	7.5	-	28946	81556	2.8175
P-5	90	10	-	30345	93842	3.0925
P-6	97.5	-	2.5	21575	33018	1.5300
P-7	95	-	5	24013	35842	1.4920
P-8	92.5	-	7.5	56866	66210	1.1640
P-9	90	-	10	61990	81219	1.3100

DMA = Decyl methacrylate, Sty. = Styrene, VA = Vinyl acetate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

Table 3: Pour point data with respect to the different concentrations of the additives in crude oil

Polymer code	Pour point (°C) of additives doped crude oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	24	13.5	12.9	12.2	11.5	10	10.3
P-2	24	10.5	10.1	9.8	9	8.1	8.5
P-3	24	10.7	10.4	9.5	10.9	11.1	12
P-4	24	10.8	10.1	9.5	11.2	12.5	13
P-5	24	13.8	14.1	14.9	15	15.5	16.1
P-6	24	8	7.8	7.5	8.1	9.2	10
P-7	24	7.9	6.8	6.1	5.9	4.2	4.5
P-8	24	8.5	8	7.5	8.1	8.6	9
P-9	24	10.1	10.8	11.9	12.5	13	13.8

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