STUDY ON THE APPLICATION OF ADDITIVE SYSTEMS IN POLYMERIC LUBRICATING GREASES

By

RAVI KUMAR DIXENA

INDIAN OIL RESEARCH AND DEVELOPMENT CENTRE

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CONTENTS

Chapter I: Introduction and Literature Review

Chapter II: Selection of thickeners

Chapter III: Oil Bleed tendency and Rheological studies of PP and mPP thickened greases by incorporating recycled and virgin HDPE

Chapter IV: A study on Tribological behavior of ZDDP in Polymer thickened lubricating greases

Chapter V: Study on Tribological behavior of Polymeric Greases with Inorganic Fullerene like functionalized Nano WS_2 additive

Chapter VI: “Structure – Property” Correlation of Polymeric Greases

DECLARATION CERTIFICATE

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, where except due acknowledge has been made in text.

(Ravi Kumar Dixena)

Indian Oil Corporation Ltd.,
Research and Development Centre
Faridabad-121007
Haryana, India
Date:

THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled **“STUDY ON THE APPLICATION OF ADDITIVE SYSTEMS IN POLYMERIC LUBRICATING GREASES”** submitted by Mr. Ravi Kumar Dixena to University of Petroleum and Energy Studies, Dehradun for the award of the degree of Doctor of Philosophy is a bona fide record of the research work carried out by his under my supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for award of any other degree or diploma.

8/10/2015

(Dr. E. Sayanna)
General Manager (Grease & HSE)
Indian Oil Corp. Ltd.
Research & Development Centre,
Faridabad-121007
Haryana, India

R.P. Badoni
12/10/2015

(Dr. R. P. Badoni)
Distinguished Professor
University of Petroleum &
Energy Studies,
Dehradun-248007
Uttarakhand, India

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EXECUTIVE SUMMARY

Over 80 percent of bearings are grease lubricated world over due to many advantages and ease of application. It is a semisolid lubricant which offers the advantages of two lubricating groups viz. lubricating oils and solid lubricants. Lubricating greases are intermediate in their properties between liquid lubricants (oils) and solid lubricants. Grease can be defined as "A solid to semi fluid product of dispersion of a thickening agent in a liquid lubricant. Other ingredients imparting special properties may be incorporated" (ASTM D 288, Standard Definitions of Terms Relating to Petroleum). Greases are thixotropic materials under normal conditions. Owing to their semisolid nature and are not thrown out of open lubrication points by centrifugal forces, and thus can be applied to unsealed lubrication points. However, when the load is increased and a critical value has been reached, the grease gets deformed and may start flowing like ordinary lubricating oils. Mechanical stable greases used in goos sealed bearings do not leak out even reaching near critical loaded conditions. Grease is often expected to perform as a seal, corrosion inhibitor, shock absorber, water resistance and a noise suppressant.

The main advantages of greases over oils are their ability to hold on in unsealed lubrication points, higher corrosion protection properties, serviceability in contact with water and other corrosive media and a higher economical efficiency of application.

In the simplest case the grease can be considered as two component system consisting of a liquid dispersion medium and a solid dispersed phase. The dispersion

medium, which accounts for 75-95% of the grease composition, can be either petroleum or synthetic oils or other lubricating liquids. The dispersed phase (5-25%) can consist of salts of high molecular weight carboxylic acids (soaps), inorganic and organic solid hydrocarbons (silica gel, bentonites, lyophilic graphite, carbon black, pigments, polymers, urea derivatives, etc.) as well as other highly dispersible substances with a high enough specific surface, capable of getting in non-aqueous media, such as siloxane greases thickened with carbon black, pigments and polymers.

Currently, the most commonly used thickeners in grease manufacturing worldwide is the Lithium hydroxystearate followed by other thickeners such as soaps based on Sodium, Calcium, Polyurea, Aluminium complex, Calcium sulphonate etc,. Soap based thickeners specially Lithium hydroxystearate gives desired properties such as good mechanical and thermal stability, and water tolerance and is therefore globally used in highest volumes for grease manufacturing in large volumes. However, drawback of Lithium grease includes its availability and cost, as demand for Lithium batteries has been growing at about 25 percent a year, outpacing the 4 percent to 5 percent overall gain in Lithium [Riseborough, Jesse. "IPad Boom Strains Lithium Supplies After Prices Triple". Businessweek. Retrieved 1 May 2013.]. [On June 9, 2014, the Financialist publication, produced by the Credit Suisse company, stated that demand for lithium is growing at more than 12 percent a year; according to Credit Suisse, this rate exceeds projected availability by 25 percent] . This poses a challenge before grease industry to find alternate thickeners for greases manufacturing. However, no existing known thickeners can replace Lithium soap thickeners completely. There are many possible and plausible combinations of greases developed as alternates to Lithium base greases. In view of the foregoing discussion, polymeric thickeners specially Polypropylene are most suitable due to their availability, low cost, wide variety of grades and over all easy manufacturing processing and low processing cost.

One of the major draw backs of polypropylene thickened grease are their high oil bleed tendency. Oil bleed tendency of lubricating grease is a very crucial parameter, which directly affects the lubrication performance of lubricating greases and consequently the service life of bearings. In present research work, in one set of experiments, polymer grease was prepared with virgin and recycled high density polyethylene, which not only improved oil bleed performance but rheological properties too. The work thus opens a new route for the recycling of used HDPE in making lubricating grease which may help in alleviating a major environmental problem and disposal of waste HDPE polymer on a large scale.

One of the most important techniques of upgrading the performance characteristics of lubricants, including lubricating greases, is the incorporation of various additives and fillers into their compositions. The solubility in oils and surface activity of additives under certain conditions significantly affects the process of structurization and the rheological characteristics of greases. It is this fact that complicates the use of additives in greases as compared to their use in oils. It has been established by researchers that the performance of an additive in lubricating grease depends on the property and structure of thickener. The additive that performed well with one thickener may or may not perform well with other thickeners. Literature search indicates that the performance assessment of polymers in lubricating grease was purely based on the rheological modification and thickening/gelling tendency with oil to produce grease. No work has been reported on the study of performance of additives in polymeric greases. Hence, another set of experiments was undertaken where ZDDP was used as an antiwear additive and its performance with various polymeric thickeners was evaluated.

The present dissertation work reports that to achieve satisfactory results with conventional sulphur phosphorus containing additives like ZDDP certain alteration/modification are required with Polypropylene type thickeners. To strengthen this approach, tribological study on polymeric greases was carried out with functionalized nano WS_2 in comparison to the conventional additives, and it was found that functionalized nano WS_2 performs very well irrespective of thickener type.

LIST OF SYMBOLS

G'	Storage Modulus
G"	Loss Modulus
ω	Angular frequency
rad/S	Radian per second (unit of angular frequency)
13C	Carbon 13 NMR
1H	Proton NMR
ppm	Parts per million
cSt	Centistokes
g	Gram
MFI	Melt flow index
g/cc	Gram/cubic centimetre
M_w	Weight average molecular weight
M_n	Number average molecular weight
T_m	Melting temperature
ΔH_f	Enthalpy of fusion
Ra	Surface roughness

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
DIN	Deutsche Industrienorm
BIS	Bureau of Indian Standards
IS	Indian Standard
GPC	Gel Permeation Chromatograph
SEM	Scanning Electron Microscopy
EDAX	Energy-dispersive X-ray Spectroscopy
NMR	Nuclear Magnetic Resonance
TGA	Thermo Gravimetric Analysis
PDSC	Pressure Differential Scanning Calorimetry
DSC	Differential Scanning Calorimetric
PP	Polypropylene
mPP	Maleated Polypropylene
HDPE	High Density Polyethylene
rHDPE	Recycled High Density Polyethylene
WSD	Wear Scar Diameter
WL	Weld Load

LIST OF FIGURES

LIST OF TABLES

CHAPTER-I

INTRODUCTION
AND
LITERATURE REVIEW

INTRODUCTION AND LITERATURE REVIEW

1.5 LUBRICANTS: OVERVIEW

Industry is the back bone of economy and their growth goes hand in hand. Almost all the industries use machines to increase their productivity, minimize the production cost and save time but, the cost of production and health of an industry depends on the cost of operation and machines life. In 1966 P. Jost in his survey conducted in U.K. region [1] demonstrated the enormous waste that occurred due to wear and related causes. Later in 1990 the author [2] defined the potential savings as a percentage of the Gross Domestic Product (GDP) and shown that 0.4% of GDP could be saved in terms of energy with proper application of lubrication science to the lubricated process. The above study was a clear indication of growing importance of lubricants in industries for healthier economy. The impact of lubricant to the industry and economy is so enormous that the consumption of lubricant is now a days taken as a bench mark for GDP of a country.

The first use of lubricant was reported 1400 BC [3] in the very basic form as animal (water, gypsum, and animal fats) fat or tar. Over the years robust growth in industries has taken place and with modernization of industries more sophisticated and highly efficient equipments are coming up which demands for high performance lubricants. To cater the need of these industries, over the time enormous change has taken place in the lubricant technology. Today we have innumerable grades of lubricants available in the market [4], [5].

The basic function of lubricant is to reduce friction and wear of any machine as a result service life of machines is increased. The main cause of wear is friction and heat generated due to contact between metal parts moving against one another. The severity of wear depends on many factors such as metallurgy, equipment design and operating conditions (load, speed, temperature etc.). Friction and wear is the least when contact between two contacting metal surfaces is minimum and vice-versa. A lubricant acts as a barrier and prevents direct contact between the moving metal surfaces and thus, reduces friction and wear. Other than lubrication, lubricant has many diverse role such as, heat transfer (cooling), cleaning, suspending the contaminants, transfer of power, protection from oxidation, corrosion, and wear, etc.

1.6 TYPE OF LUBRICANTS

Every equipment/machine has special design features that require specific type of lubricant for lubrication. Same equipment but different OEM or different OEM's but same equipment may not necessary need same type of lubricant. Apart from the design features of machines, geographical location and climatic operating conditions of any region calls for special types of lubricants for that region. The same lubricant cannot be used everywhere in all lubrication regimes. Hence, there are a number of lubricants available in the market to meet the diverse equipment requirements. Every lubricant has its own specification which is designed to meet the lubrication requirement. And which defines the limit of conditions within which lubricant can be used for smooth functioning of machine.

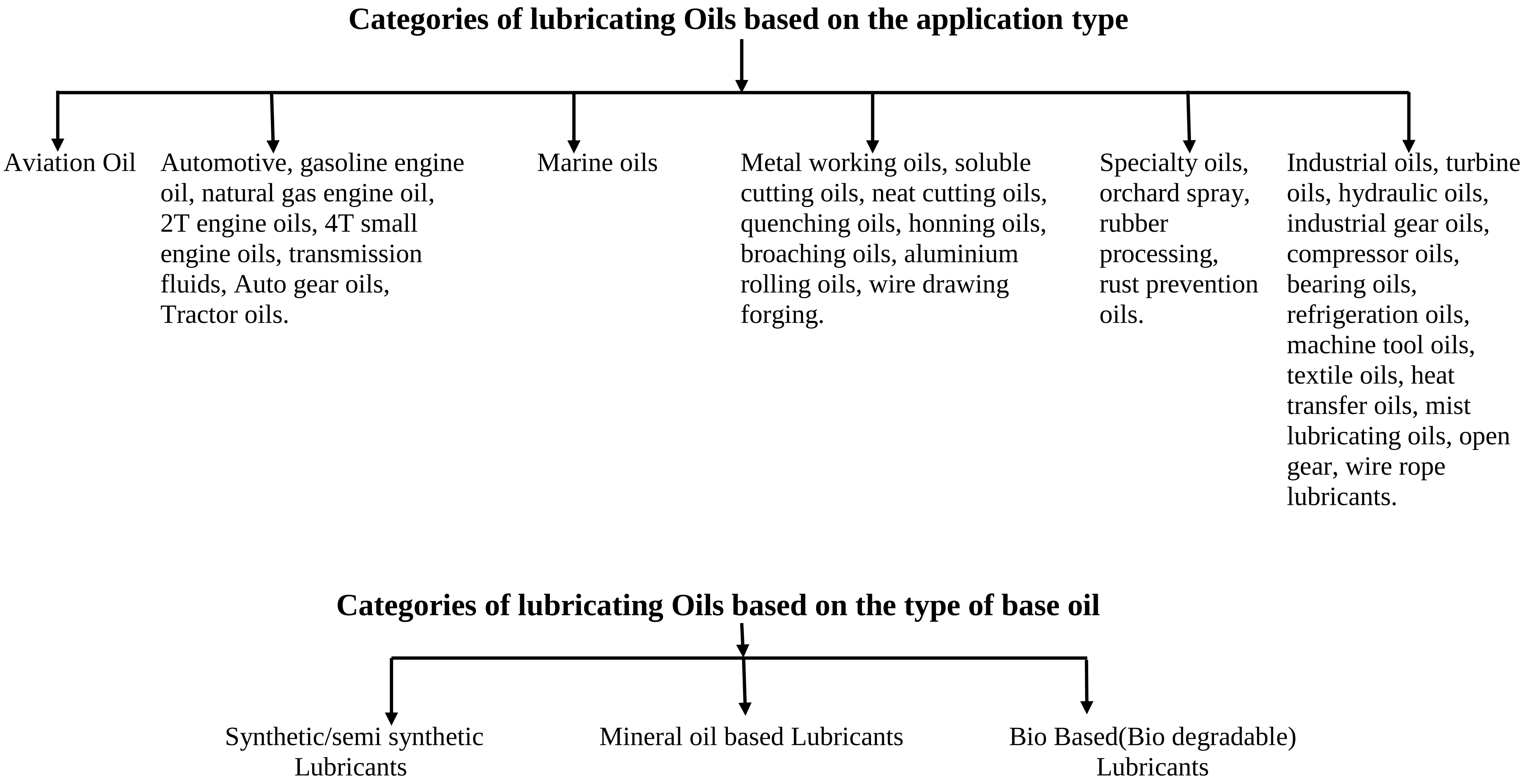

Fig. 1.1: Classification of lubricating oils

Lubricants can be broadly classified as Solid lubricants (MoS_2, Graphite, etc.), Semi solid lubricants (Lubricating Greases, pastes and gels) and liquid lubricants (hydraulic oils, engine oils etc.). According to the applications and type of base oils, lubricating oils have been further sub divided into the categories shown in Fig. 1.1 [6].

Lubricating greases: The classifications of lubricating greases are discussed in detailed in later section.

1.7 LUBRICATING GREASES: INTRODUCTION AND DEFINITIONS

Whilst most of the lubricants are fluids suitable for high speed closed gear systems, lubricating greases are semi fluid to semi solid in nature. They are formulated for distinctive applications mainly for bearing lubrication and high load low speed operations. Grease is a combination of lubricating oil thickened with thickening agents to give desired consistency. According to ASTM D-288 (American Society for Testing and Materials, 1916 race Street, Philadelphia, PA 19103) lubricating grease was defined as “a solid-to-semi fluid product of dispersion of a thickening agent in a liquid lubricant. Other ingredients imparting special properties may be incorporated”. The above definition does not cover all the aspects of lubricating greases hence, such definitions no longer appear in the book of ASTM standards. Lubricating grease is an exceptionally complex product and no single definition is sufficient to define all its attributes. Grease is neither solid nor liquid rather undergoes a phase transition under certain conditions and behaves both as a solid and liquid. Sinister [7] defined grease based upon rheology, which is a function of physical condition of stress, temperature, etc. and according to him grease is defined as:

A lubricant which under certain loads and within its range of temperature application, exhibits the properties of a solid body, undergoes plastic strain and starts to flow like a liquid should the load reach the critical point, and regains solid like properties after removal of the stress

Later Hamnelid, L [8] defined lubrication grease based on its very purpose of use as DESSSS, a ‘dynamic energy saving, shearable, surface separator’. And finally Chang [9], defined lubricating grease simply as:

> *“lubricating grease is what grease makers make”*

1.7.1 History and Development

Lubricating grease has witnessed a long and continuous transformation from its very basic form of raw animal fats, vegetable oils and water to the modern lubricating greases. Archeological reports suggest that the art of making grease was known to the mankind since 4000 years ago [3]. Historically, the first soap used to thicken grease was hydrated calcium soap [10]. Although it has very low dropping point, calcium soap grease ruled the market for almost 50 years. Aluminium and Sodium soap greases were also developed in between 1880 to 1940. Each of these greases has one or more inherent drawbacks like low drop point, high water solvency etc.

The introduction of Lithium soap-thickened grease in 1940s by Clarence Earle [11] was a major turnaround for grease industry. Grease prepared from 12-hydroxystearic acid, exhibits superior overall properties than the greases made from the other fatty acids or esters. Lithium grease due their superior thermal stability and water tolerance became very popular as multipurpose grease and captured a big portion of global grease market soon after its inception. A lot of other greases like complex-soaps, non-soap based greases, some specialty greases like fluorinated greases were developed after 1940, but nothing could replace Lithium thickener. Even today, Lithium grease constitutes about 70-80% of total grease market world over. A time based lubricating grease development trend is shown in Fig. 1.2 [12].

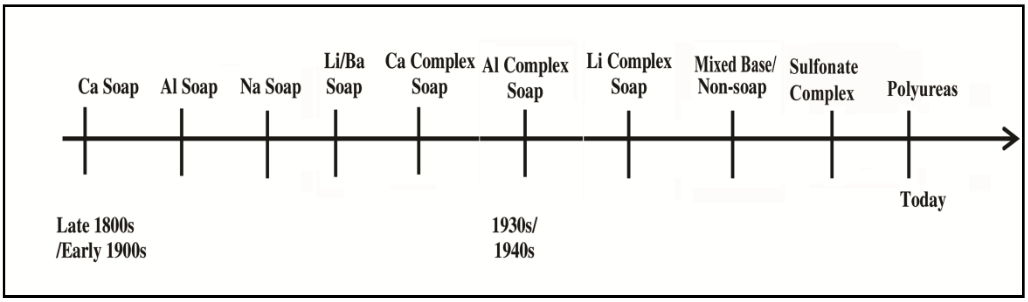

Fig. 1.2: Time based lubricating grease development

1.7.2 Composition

Lubricating grease is nothing but thickened lubricant. A typical lubricating oil contains base fluid and performance additives and a lubricating greases contains one additional component i.e. thickener. The percentage composition of base oil, thickener and performance additives is 70-90%, 5-10 % and 0-10% respectively. But majority of the greases comprise of 80-90% base oil, 10-15% thickener and 0-10% of performance additives. Standard grease product contains all the three components but the percentage composition varies product to product.

Base Oil

- Mineral
- Synthetic
- Bio-based/Vegetable oils

Thickener

- Soap
- Non Soap (Comprises of all the thickeners other than soaps like clay, polyurea, dues, waxes, etc.)

Additives

- Oxidation Inhibitors
- Antiwear additives
- Extreme Pressure additives
- Rust and corrosion Inhibitors
- Friction modifiers
- Tackifiers
- Structure Modifiers

1.7.3 Classification of Lubricating Greases

Lubricating Greases may be arranged according to the following classification methods:

- Classification of greases by application: Antifriction, Multipurpose, Industrial, Automotive, Low temperature. Biodegradable (Wheel bearing, Chassis etc.)

- Classification of greases by additives: EP greases (extreme pressure grease) or graphited grease.
- Classification of greases by NLGI according to consistency: NLGI Classification of greases is based on the consistency as measured by worked penetration values at 25 °C as given in Table 1.1.
- Classification of greases by type of base-oil used: Synthetic, semi-synthetic, mineral-oil based or bio-degradable greases.
- Classification of greases according to thickeners: Lubricating greases are also categorized based on the chemical composition of thickeners as shown below;

Soap based:

- **Simple Soap:** Li-Soap, Al-Soap, Ca-Soap, Na-Soap.
- **Mixed Soap:** Li-Ca, Ca-Li.
- **Complex Soap:** Li-Complex, Al-Complex, Ca-Complex.

Non-Soap based:

- Polymers (eg. Polyurea, PP, PTFE, etc.), Organo Clay, Pigments, Fumed Silica, etc.

1.7.4 Application, Function and Properties

Application and Function

There is fundamental difference between lubricating fluids, solid lubricants and intermediate product-greases. Although, the basic functions of all the lubricants remains similar, The function of lubricating grease differs substantially from fluid and solid lubricants. Greases are thixotropic in nature they flow and release oils for lubrication under shearing forces and regains its original structure when the force is removed. The following are some of the important functions of lubricating grease which differentiate it from liquid and solid lubricants [13]–[19]. Lubricating grease are semisolid in nature and once applied are not thrown out of open lubrication points by centrifugal forces, and thus can be applied to unsealed lubrication points. Simple Plummer box is sufficient to incorporate the grease for the bearing lubrication whereas, for the lubrication of multiple grease points, a central lubrication system can be applied. It incorporates a pump with dual pipeline and metering devices. Online filters are also installed for ensuring contaminant free grease to the bearing. Whereas, for lubricating oils a special sump, circulating pump, pipelines, filter, cooling/heating device (optional) will be required for liquid for similar application.

- As a sealant it prevents contaminants like gases, liquids or solids from entering into the lubricated points.
- Grease is very poor conductor of heat
- Resist leakage and dripping-off from the lubricated surface.
- Some specially formulated grease provides satisfactory lubrication even after absorbing considerable amount of water.
- Grease matrix acts as a reservoir and grease lubricated surface has long relubrication intervals. It is suitable for filled for life applications,

- Grease has higher temperature and load carrying capacities than lubricating oils because of the higher dynamic viscosity and elasticity provided by thickener system.
- Grease matrix is a good carrier for wide range of solid additives and Nano particles. Stable dispersion and solvency is a common problem encountered working with lubricating fluid and solid additives. These additives can be evenly dispersed in greases to improve specific performance capabilities. However, the performance of nano additives in grease formulation is not well studied due to limited availability of the additives at the mating/rubbing surfaces.

As stated above lubricating grease has several advantages over fluid lubricant but it fall short in some cases such as, it has poor heat transfer properties hence, cannot be used as a coolant. It cannot be used as a brake fluid or in power transmission since it is highly elastic.

Properties

Lubricating grease has to meet certain properties specific to the grease lubricated equipment for satisfactory performance. The property and specification of greases differs from product to product. In order to test the performance of greases, a large number of physico-chemical, mechanical and analytical tests are carried out. These tests are designed simulating actual field conditions. However, the laboratory performance does not necessary mean the products actual field performance. There are many standards of testing followed throughout the world. Some commonly followed standards are ASTM: in North America, IP (Institute of Petroleum): in Europe, DIN: in Germany, JIS: in Japan, IS (Indian Standards): in India and GOST: in Russia.

One of the most important features of lubricating grease is its consistency. It is a measure of the relative hardness of lubricating grease and classified in to 9 different grades by NLGI classification (National Lubricating Grease Institute) [Table 1.1]. Hence, it is also termed as NLGI grades. Consistency is usually measured by ASTM Cone Penetration Test, ASTM D-217 and D-1403 [20], [21]. Unit of measurement of penetration value is recorded in tenths of a millimeter.

Table 1.1: NLGI classification system for penetration of greases.

NLGI Grade	ASTM worked (60 double stroke) penetration Range @25^oC	Appearance
000	445-475	Fluid
00	400-430	Semi-fluid
0	335-385	Very soft
1	310-340	Soft
2	265-295	Normal grease
3	220-250	Semi solid
4	175-205	Very firm
5	130-160	Hard
6	85-115	Very Hard

The maximum operating temperature of lubricating grease is indicated by its dropping point. The hardness of grease is function of temperature. Greases retain their hardness only to a point, and then at some temperature, they become fluid. Dropping point of lubricating grease is determined by IP-396, ASTM D-566, or ASTM D-2265 [22]–[24] methods. To summarize all the properties of lubricating grease is beyond the scope of this write-up however, some important test/properties of grease are listed in Table 1.2.

Table 1.2: Some common standard test methods of lubricating greases.

S. No.	Characteristics	test methods	Significance
1	Penetration	ASTM D:217 and 1403	It is a measure of hardness of grease. Used to determine the consistency and NLGI grade
	Mechanical stability	ASTM D:217, ten thousand and one lac double strokes.	It is a measure to test the grease's stability to retain its consistency when subjected to high mechanical shear or high loading condition in application. Highly stable grease is preferable because a large change in consistency can cause grease either to run out of the lubricating area or will not flow properly and fail to provide proper lubrication.
2	Drop Point	D:566, D:2265, IP:396, P:52, IP:132	It is used to test the maximum usable temperature of greases however the results have limited significance with respect to the service performance because the test is held under static conditions.
3	Oil Separation	D:6184, D:1742	Nearly all greases separate oil during storage and application. Excessive oil Separation from lubricating grease may affect the consistency and low oil separation invariably affects the lubricity of greases. ASTM D:1742 test method is used to test oil separation during storage at 25o C and ASTM D:6184 is tested at 100o C. These procedures do not predict oil separation under dynamic conditions. They are used for specification and quality control
4	Roll stability	D:1831	In this test grease is sheared by rotating a cylinder containing 5kg roller at 165 rpm for 2 hours or as per specification. The change in penetration is measured at the end of the test. The results show a directional change in consistency that occurs in service. Simulating the rolling condition in the bearings.
5	Water wash out	D:1264	This test is used to measure the resistance of grease to washout with water under prescribed laboratory conditions. The grease packed ball bearing in housing is rotated at 600 rpm. The housing is subjected to jet of water at a specified temperature and flow rate. The results obtained with this test method may not correlate with those in service because of housing or seal design.
6	Water Spray-off	D:4049	The aim of this test method is to test the water resistance of greases but in a more severe laboratory conditions than water washout test.

			A thin layer of grease over a standard steel plate is impinged with a jet of water at 40 psi pressure for 5 minutes at specified test temperature. The plate after test is dried in oven and loss of grease is measured.
7	Corrosion Copper corrosion Rust prevention Emcor	D:4048, IP:112,P:51 D:1743 IP:220, D:6138	Copper corrosion test measures the corrosive tendency of grease toward copper metal under laboratory conditions. This test does not consider other factors affecting the corrosion other than the grease itself. In this test a tapered roller bearing filled with grease is kept in a 100% relative humidity condition for 48hrs at 52O C. A pass or fail result is reported on completion of the test. This test indicates the ability of grease to prevent rust in static conditions. The correlation of this test with static service condition is considered to be quite good. Emcor test is more severe than the above tests and carried out with distilled or synthetic sea water in dynamic wet conditions.
9	Oxidation stability Oxygen bomb method PDSC	D:942 IP:142 D:5483	The intent to design this test was to predict shelf/storage life of prepacked bearings. It has little correlation with the stability of greases in the bearings or in actual applications. It is useful for comparative study of same type of greases, primarily for quality control to indicate batch-to-batch uniformity. In this test 2-10 mg of sample taken in Aluminium pans and placed in a chamber, which is pressurized to 500 psi with oxygen for 2hours or till an exothermic reaction occurs. The oxidation induction time determined by this method is considerably faster than D 942. However, like D942, no correlation has been determined between test and service performance. Its significance is limited to product development and quality control.
10	Low temperature torque	D:1478, IP:186	Bearing encounters resistance when thick or highly viscous lubricant is used than free flowing fluid lubricant. Additional energy is needed to overcome the torque generated by the lubricant. The effect is pronounced in colder regions and sub-zero temperatures. The test is useful for developing greases for devices which operates at low temperature particularly for aerospace applications.
11	Weld Load	D:2596	This test method is used to determine load-carrying properties of greases. Load-wear index or Mean-Hertz load, Weld point and

			nonseizure load are determined. Samples can be differentiated as low, medium, or high extreme pressure properties in a very short time. The test results may not correlate with service performance due to change in parameters. It is widely used for sspecification purpose.
12	Wear Scar	D:2266	A relative wear preventive characteristic is determined under steel-on-steel contacts. This test is widely used in grease specifications and development. Significance is very limited when conditions are changed.

1.8 LUBRICATING GREASE THICKENERS

The primary role of a thickener is to provide the characteristic semi-solid structure/body to the grease; the thickener holds the oil within its micro structural network and provides varying resistance to flow. Many grease characteristics such as water resistance, high temperature properties, mechanical stability, compatibility with other greases, synergism with additives, etc. are clearly defined by the thickeners. Any alteration in thickener property would eventually affect several other characteristics of a grease. Hence, selecting a right thickener is very crucial and critical and perhaps this is the reason that most of the researches on lubricating greases were thickener oriented so far and major developmental milestones were achieved with the invention of new thickeners [11], [25]–[27]. Brief description of grease properties associated with thickeners is given in Table 1.3.

NLGI production survey report 2013 (Fig. 1.3) clearly indicates that soap based thickeners are the most preferred in industries. Among soap-based greases lithium constitute around 77 % of the total grease production world over. Calcium soap grease comprises 6.5 and non soap greases which include polyurea, organo clay etc, is accounted for about 9%. Lithium greases is a better choice for customers due to its low cost and reasonably good overall properties than other costly non soap products.

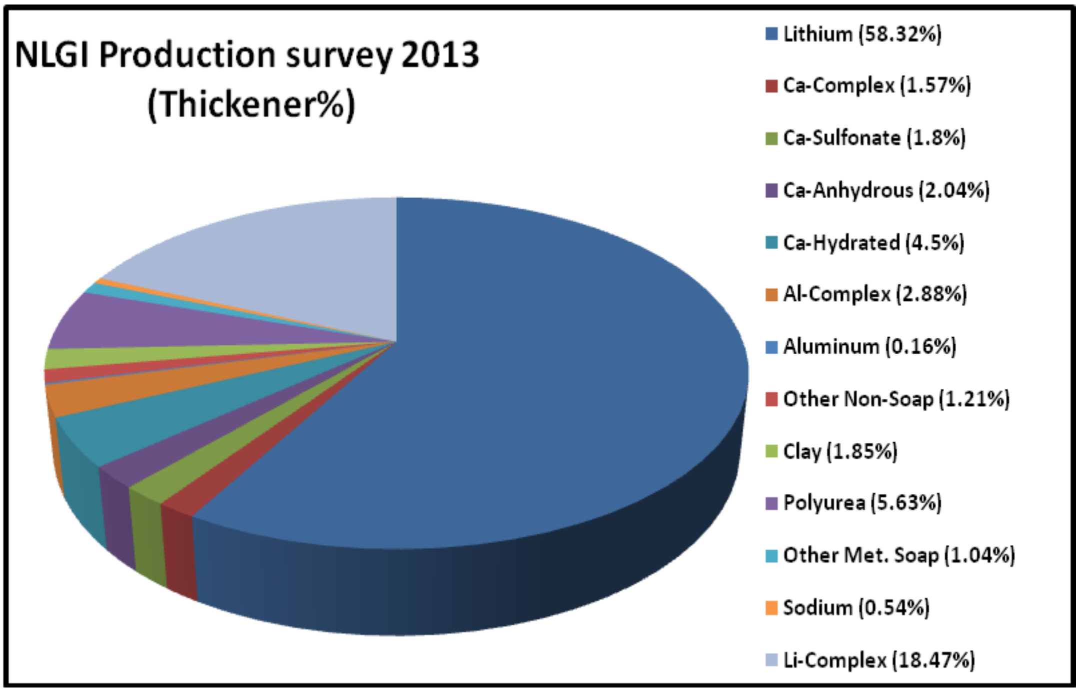

Fig. 1.3: NLGI Production Survey 2013

Table 1.3: Lubricating Grease characteristics based on type of thickeners [28]

Thickener Type	Texture/ Appearance	Dropping Point (^{o}C)	Water Resistance	Mechanical stability	Other properties
Lithium	Smooth, buttery	175-200	Moderate	Excellent	Good heat resistance, good pumpability, good oxidation stability
Calcium (hydrated & unhydrous)	Smooth, buttery	140-150	Good	Good	Good pumpability
Aluminum	Smooth, buttery gel like	90-110	Good	Fair to Poor	Excellent oxidation stability
Sodium	Rough, fibrous	175-200	Poor	Fair	Good heat resistance
Lithium Complex	Smooth, buttery	260-300	Moderate	Excellent	Good heat resistance, good pumpability, good oxidation stability
Calcium Complex	Smooth, buttery	260-300	Good	Excellent	Good heat resistance
Aluminum Complex	Smooth, buttery, gel like	240-270	Good	Good to excellent	Good heat resistance, Excellent oxidation stability
Polyurea	Buttery	240-300	Good	Good to Excellent	Excellent heat resistance, good oxidation stability
Organo clay	Buttery	>300	Good	Fair to Excellent	Excellent heat resistance, good pumpability, good oxidation stability

1.8.1 A comparative overview of soap based thickeners particularly lithium-soap and polymeric thickeners

The volumes of polymer thickened greases are negligible out of total grease market. On the other hand soap based thickeners despite some disadvantage over polymeric and other non-soap thickeners are entirely dominating. The preference of soap based greases over non-soap greases is also reflected in the research articles published over the years. A noticeable shift towards the research in polymers as a thickener and rheology modifiers can be seen in the research articles published in recent past [29]–[33]. The main focus of these researches are either to replace thickeners (mainly Lithium) content partly and modify the rheological property by incorporating polymer content in to the thickener system. A comparative point by point discussion of soap based and non-soap based grease with special emphasis on lithium thickener and polymeric thickener is given below:

Process: Batch process manufacturing of soap based grease is by far the most widely used method [34]. This involves charging of base oil and stoichiometric mixture of fatty acid and alkali, heating the components up-to the melting temperature of fatty acids, saponification, dispersion of soaps, dehydration, cut-back with remaining base oils and finally additization and homogenization/milling. The saponification reaction (Fig. 1.4) is greatly affected by temperature, pressure strength of the alkali, composition of fatty acids, concentration of reactants, and intimate contact of reacting ingredients [35]. Hence, a precise control of process parameters is very crucial for desired product output. Incomplete reaction leaves behind free acid and alkali which may adversely affect the anticorrosion/antirust and antioxidant property of the finished grease including the yield.

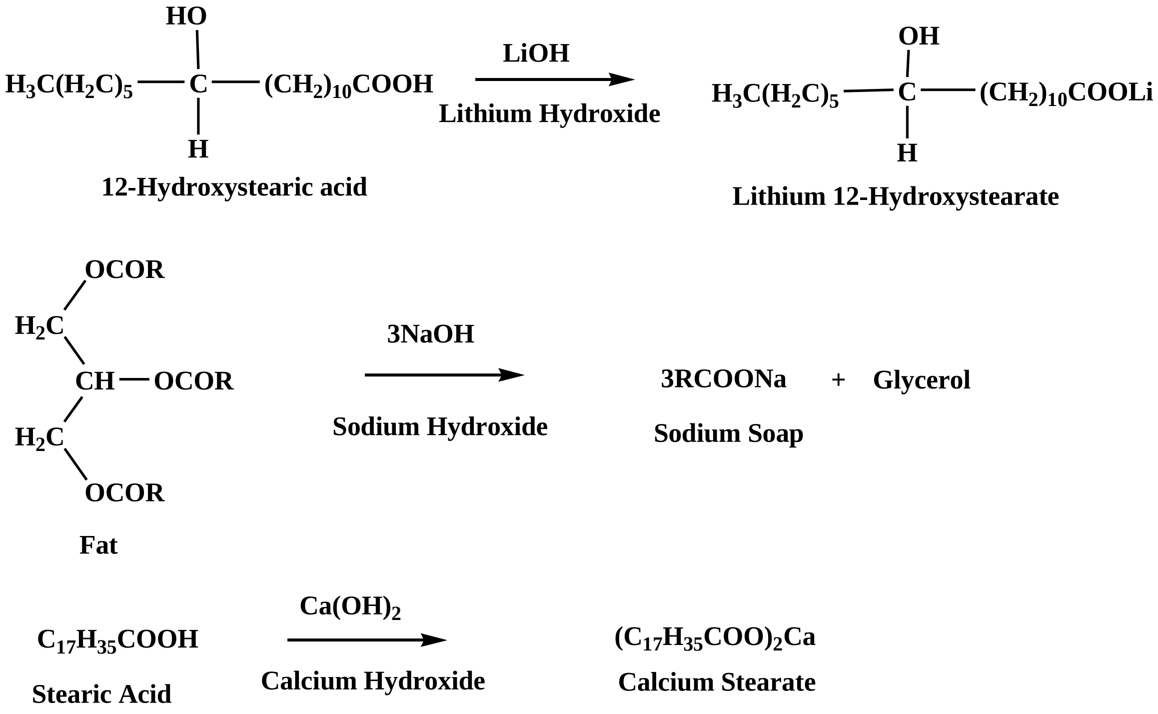

Fig. 1.4: Some common saponification reactions

Processing of polymeric greases specially Polyethylene and Polypropylene is very simple and does not involve complex chemical reactions [36], [37]. So there is no issue of free acid or free base left out after process. Polymers are dispersed in to the base oil by heating them above its melting temperature and then quenched and milled to obtain base grease. Process parameters are better controlled due to less critical parameters. Final yield is better than soap based greases.

Cost and availability: Polymeric greases have advantage of low cost over soap based greases. Comparatively the overall costs of polymeric (PE and PP type) greases are lower than soap based greases. Be it sophisticated equipment, components (Fatty acids and alkali), or cost of labor involved in manufacturing, polymeric greases win by distinct margin. For example a typical manufacturing cycle of soap based greases are around 8-12 Hrs whereas, it is 2-4 Hrs in PE and PP type greases. Around 4 Hrs time saving in process can be achieved in polymeric greases. Cost of polymeric greases can be further lowered by the use of recycled or waste polymers.

Looking into the abundance of Lithium mineral one could hardly think of its shortage. But a major shift has been noticed in recent years due to the mobile phone revolution and raising trend of EVM'S globally, where lithium batteries are used as a power source. The demand of lithium has sky-rocketed and grease manufacturers are the most affected. There is mixed view about the projected shortage of lithium in near to long term [38]–[40]. Even if we agree to the view of Yasik and Pizarro the projected increasing cost cannot be overlooked as demand for Lithium batteries has been growing at about 25 percent a year, outspacing the 4 percent to 5 percent overall gain in Lithium [39], [40]. Any increase in LiOH cost would eventually increase the cost of Lithium grease.

Toxicity: Polypropylene and polyethylene are non-toxic to living beings; they are extensively used in food grade applications. The toxicity of Lithium grease is however not yet reported and it is supposed to be safe but due to the presence of metal its toxicity still questionable.

Environmental factors: Disposal of waste polymer is a big concern and challenge throughout the world [41], [42]. Use of Recycled polymers as an additive to enhance the performance of lubricating greases or as a thickener would open up a new and cost effective method for disposal of waste polymers in bulk.

Others: Science behind the additives interaction with thickener and its chemical and physical behavior is very complex subject and without any experimental evidence it is not fair to comment precisely how additive will respond to any thickener. However, it is generally believed that a non ionic thickener does not compete with ionic additive to adhere to the available surface and thus additives response is better in non ionic environment [43]. Hence, it can be supposed that polar additives like ZDDPs and ionic liquids would give better results in PE and PP thickeners as compared to the metallic soap thickeners or other polar thickeners. So, it can be conceived that the dosage of additives will be comparatively less over soap based greases to achieve a given EP/AW/AO property.

Compatibility is a major issue in re-lubrication of industrial bearings with the greases other than previously used. A compatibility chart is shown in Table 1.4. The structural stability of some of the greases like aluminium, clay and sulphonate complex greases are very sensitive towards other greases. Proper cleaning of bearing and bearing elements is very essential before such lubrication. In case of polymeric grease compatibility is not a big issue as polymers are generally used to improve tackiness and water resistance of greases and failure due to incompatibility is not yet reported.

Table 1.4: Compatibility chart of lubricating greases.

Compatibility of thickeners **C=compatible** **I=Incompatible** **B=Boarder line compatible** **NA=data not available**	**Aluminium Complex**	**Barium**	**Calcium**	**Calcium 12-Hydroxystearate**	**Calcium Complex**	**Clay**	**Lithium**	**Lithium 12-hydroxyst**	**Lithium Complex**	**Polyurea**	**Sodium**	**Calcium Sulphonate**
Aluminium Complex	X	I	I	C	I	I	I	I	C	I	I	I
Barium	I	X	I	C	I	I	I	I	I	I	I	B
Calcium	I	I	X	C	I	C	C	B	C	I	I	NA
Calcium 12-Hydroxy	C	C	C	X	B	C	C	C	C	I	I	NA
Calcium Complex	I	I	I	B	X	I	I	I	C	C	I	C
Clay	I	I	C	C	I	X	I	I	I	I	I	I
Lithium	I	I	C	C	I	I	X	C	C	I	I	C
Lithium 12-hydroxystearate	I	I	B	C	I	I	C	X	C	I	I	C
Lithium Complex	C	I	C	C	C	I	C	C	X	I	I	C
Polyurea	I	I	I	I	C	I	I	I	I	X	I	I
Sodium	I	I	I	I	I	I	I	I	I	I	X	I
Calcium Sulphonate	I	B	NA	NA	C	I	C	C	C	I	I	X

Soap based greases decompose in the presence of acids/bases. Polymers are less reactive as compared to metal salts and are very much inert in nature. This could be best suited to the applications where acid/alkali/salt resistance grease is required. The fluorinated polymers and perfluoropolyalkylethers are being used in space applications as a lubricant or additive due to their low volatility and inertness.[44], [45]. The other applications where polymer based greases are suitable is paper and pulp industry.

1.8.2 Polymers as a lubricating grease component

The following section presents exhaustive literature review on the use of the polymers as a thickener/sdditives in lubricating greases -

The soap free acid resistant grease having good metal adherence was claimed by Averson [46]. Polymerized product of isobutylene with boron tetra fluoride having mol wt. of at least 1000 was used as a thickener in mineral base oil. Finely divided asbestos was also added to give body to grease.

A product of high melting chlorinated paraffin wax and naphthalene which may be further mixed with oil, wax or asbestos. The author claimed the grease to have anti rust property useful for plug valve applications [47]

The polymers having at least two double bonds in the molecules and which are capable of polymerization when heated with mineral oil form elastic gel like structure. According to the author the product was stable non-fusible elastic gel suitable for lubricating purpose. The reactant contains 80% of mineral oil and 1% catalyst (benzoyl peroxide) and rest synthetic polymer having at least two double bonds such as acrylic acid, alpha substituted acrylic acid or a derivative of acrylic acid. The mixture is then heated to polymerize at 50 ^{o}C for 24hrs followed by 75 ^{o}C for another 24hrs [48].

Tetrafluoro-ethylene/monoolefine hydrocarbon copolymers are pyrolised by heating to 200-370 ^{o}C to form unsaturated fluorine containing low molecular weight product ranging from thin liquid like consistency to hard waxes [49]. Another stable and inert grease composition comprising of fluorinated oil and surface esterified silica gel was reported by Peterson [50] the grease composition was useful for under water applications as well as under extreme corrosive conditions.

Hineline [51] prepared lubricating grease having E.P. properties, 10% of isobutylene-isoprene (or any diolefin) co-polymer having molecular weight in the range 15000 to 250000 was treated with an excess of sulphur compounds (sulphur chloride, tetramethylthiuram sulfide, etc.) at room temperature in 10% of paraffinic oil as solvent. The removal of unreacted portion was carried out by blowing CO_2. Fontana and Kidder [52] proposed method to obtain polymers of 1-olefins having high thickening power by varying reaction parameters such as catalyst vs reactant mole ratio, rate of addition of reactant and reaction temperatures etc.

Murrey and Rohner[53] substituted part of soap of lubricating grease by water dispersible polyvinyl alcohol or phenol formaldehyde resin as a reinforcing agent.The said grease was stable under severe operating conditions.

The thermosetting phenol-formaldehyde resins which has only A stage of polymerization in a mixture 2-20% with 90 - 80% of either tri-o-cresyl phosphate, trioctyl phosphate or tributyl phosphate was further polymerised by heating to above 232 °C to obtain grease. The composition containing 1% or more such resin produces grease like structure usable over a temperature range from 21 to 205 °C [54].

Zajac and Whiting [55] prepared lithium soap polymer grease with zero soap content and without using any volatile solvent. The silicon polymers ranging from light liquid to polymer resins were used. The resultant product has high temperature stability and high dropping point. Similarly grease prepared from straight chain or cross linked polymethyl polysiloxane thickener and phenylmethyl silicon oil were reported to have high temperature stability and high dropping point [56]

Mitacek and Graham [57] prepared lubricating grease using high density polyethylene having density above 0.94/cm^3. The soap concentration was greatly reduced and could even be eliminated completely by increasing HDPE concentrations. The mechanical stability of the grease was best when the milling temperature was controlled in between 80 to 90 °C. Blending of polyethylene in base oil and saponification reaction were carried out separately and they are mixed before milling. The author claimed the grease to have excellent working stability and good lubricity. Dodson et al [58] claimed that grease prepared from polyethylene having density higher than 0.94 tend to have grainy structure. The problem can be eliminated by using low molecular weight polyethylene and using a mixture of polyethylene and atactic polypropylene.

Polymerization of ethylene or propylene by catalyst such as mixture of aluminium monohalides with titanium tetrachloride, aluminium trialkyls with titanium tetrachlorides, etc. in inert liquid diluent at temperature 40 - 120 °C were carried out to produce powdered lubricant [59]. The dry powder thus produced can be used to thicken lubricating oil to produce lubricating greases. advantage of this invention is that off specification polymer from regular manufacturing can be used.

Messina and Gisser [60] disclosed stable grease compositions having excellent low torque characteristics, suitable for low temperature applications. The grease was composed of polysiloxane, polytetrafluoroethylene having a mol. wt. of 10000-50000 and percentage particle size less than 30 microns in diameter. Dispersion of PTFE was prepared in trichlorotrifluoroethane solvent the solvent was then gradually evaporated by heating and simultaneously polysiloxanes were added in to the composition. The grease was cooled to room temperature and milled and subjected to low temperature treatment prior to use.

Mayers and Mirada [61] prepared aluminum complex grease with high soap content (5-30%) in low viscosity paraffin oil by reacting aromatic carboxylic acid then with a higher fatty acid. The grease was then blended with isobutylene polymer having molecular weight in the range 9000-25000. The author claimed that the grease was excellent in structural stability, having low oil bleeding, water resistant, cohesive, usable over high temperature and was compatible with other soap greases.

Fukui et al. [62] obtained patent for fluorine containing grease composition having good chemical and heat resistance. Halogen containing polyether was used as base oil and fluororesin such as PTFE, chlorotrifluoroethylene, etc. as a thickener. Smaller the size of resin higher is the thickening tendency with better properties. The content of the resin in formulation ranges from 0.5 to 60 %. Grease can be either prepared by direct blending and milling or by using solvent like trichlorotrifluoroethane.

Shear modulus and critical yield stress is very important characteristics of lubricating greases used as cable filling materials. Such greases are prone to high oil bleed/syneresis due to thin consistency. Levy et al. [63] incorporated rubber polymer in the composition to minimize syneresis and to reduce colloidal particle content of the grease composition.

Olov and Herman[36] proposed polymeric greases for quiet running applications. The grease having good mechanical stability also possesses improved oil bleeding at low temperature. Co or homo polymer of polypropylene having molecular weight >200000 and 50000 - 100000 were used as a thickener. The ration of high to low average molecular weight was preferably 1:19.

In most of the earlier works related to polymer thickened greases [58], [64] and in some recent work [65], 5-35% of metallic soap thickeners was used as an essential component. Polymeric (especially polypropylene type) greases without soap content discussed above were not suitable for high temperature applications above 140 °C. Meizer and Lankamp [66] claimed lubricating grease having dropping point in the range 180-220 °C. High melting (>235 °C) methylpentene polymer up to 75-55 by wt. % was used in the grease composition to enhance dropping point.

Meijer and Muller [67] recently obtained patent on polymer thickened greases for off-shore and wind turbine applications. Apart from the polymer thickeners the grease composition contains an acid component having a pKa in the range 2-7 and metal salt.

The polyolefin grease composition discussed above particularly in the reference [36] contains a low molecular weight and high molecular weight polymers in the ration preferably 1:20. Meijer and Pasaribu [68] incorporated a third component "polar wax" in the ration 1:20 by wt %. The grease displays excellent low friction behavior. The polar wax used in this invention includes; polypropylene wax (Maleated polypropylene), polyethylene wax, polar derivative of montanic wax, saponified montanic acid, ester or oxidized polyethylene wax etc. The effect of presence of polymer (polyethylene) on wear property of lube oil is also discussed by Bercea et al. [69].

Ali et al. [70] found that polymeric powder can be used in lithium greases to prevent three body abrasive wear. HDPE, LDPE, Polyamide (PA6), polyvinylchloride (PVC) and polymethylmethacrylate (PMMA) were added individually in lithium base grease in powder form. Wear scar measurements and coefficient of friction tests were carried out. It was concluded that abrasive wear due to contaminant can be reduced by addition of polymer powder having particle size greater than the size of contaminant. Antiwear action can also be regulated by controlling particle size and concentration of polymer powder.

Caporiccio [71] invented grease composition containing fluorinated polymer (PTFE), hexagonal lattice boron nitride powder having particle size 2-50 and 0.01 – 1 µm, and fluorinated polymer oils. The grease prepared thus was reported to have exceptionally good lubricity property even under severe operating conditions.

Mortin et al [72] studied applicabilibity of virgin LDPE (Molecular weight; 2.07x105, Density; 0.924 gm/cm^3) as an additive for rheological modification of lithium 12-hydroxystearate lubricating grease. It was concluded that apparent viscosity and linear viscoelastic function of modified grease can be significantly increased by incorporating LDPE. In another set of experiments[31] similar studies were carried out by the authors with recycled LDPE and concluded that recycled LDPE can be used as an additive for rheological modifications of lithium greases. In both the experiments LDPE oil blend was prepared by keeping LDPE in oil for a period of 12 Hrs to induce swelling of polymer, at a temperature above polymer melting point. The blend was then added in to the grease at the beginning of cooling stage.

Moreno et al [73] modified rheological and morphological characteristics of Lithium stearate grease by adding PBTDI [poly(1,4 butanediol) tolylene 2,4-diisocyanate] terminated polymer. The polymer was added at different stage of manufacturing process. It was found that highest modification in the said property was observed when polymer was added at cooling stage.

Polyolefins crystallinity and vinyl acetate content of ethylene-vinyl acetate polymers are the two parameters exerting most influence on rheological property of lithium lubricating grease modified with these polymers. Compared to the base grease higher viscoelastic function and viscosity was observed in formulations containing HDPE, LDPE and PP. Mechanical stability of grease containin polymer additive was better than base grease and no change in coefficient of friction was observed[30].

An increase in linear viscoelastic function was observed when lithium thickener was partly replaced by virgin or recycled polyolefins (PP and HDPE). HDPE shows different small amplitude oscillatory shear (SAOS) functions-frequency dependence due to its linear structure. The rheological properties of the modified grease were also influenced by thermo-mechanical processing variables. Coefficient of friction of modified blends was slightly higher than that of lithium grease [32].

The applicability of amorphous/recycled PP as a thickening agent for lubricating grease in mineral oil was investigated by Martin-Alfonso et al[33]. Influence of amorphous/recycled polypropylene (PP) on rheology, lubricant performance and thermal properties was studied. The evolution of SAOS functions of recycled PP at intermediate temperatures (25-50^{o}C) and higher polymer concentration was very similar to those found in other commercial lubricating greases. The formulations exhibited low values of friction coefficient and poor mechanical stability than lithium lubricating greases.

Biodegradable gel like dispersion of ethylated cellulose pulp in castor oil has similar rheological behavior as that of kraft cellulose pulp. Ethyl cellulose with low degree of substitution (DS) form relatively strong gel than ethyl cellulose with high DS. 25-60% of DS is suitable for better rheological response. The influence of molecular weight of ethyl cellulose, derivative concentration, and derivative property on thermo mechanical response, rheological response and mechanical properties were also studied [74].

Many more articles/patents are available discussing polymer’s applications to enhance lubricating grease property [75]–[79]. Other than as a thickener they are used to improve bleed tendency, water resistance/ tackiness, thixotropy, etc. in soap/non-soap greases [29], [80], [81].

1.9 AW/EP ADDITIVES FOR GREASES

When grease is to be used under more severe conditions of load and wear, antiwear and extreme pressure additives are incorporated in to the grease. Additives for fluid lubricants and lubricating greases are similar except solid additives. Conventional AW/EP additives usually contain elements which are capable of forming chemical/physical protective film over the metal surface applied. These compounds include; Sulphur, Phosphorus, Zinc, Nitrogen, Boron, etc in various organic/inorganic chemical forms single or in combinations [82]–[94]. Thiophosphates, Dithiophosphate especially zinc dialkyldithiophosphates are the most widely preferred due to their multifunctional characteristics [95]–[97].

Over the last decade nano materials have been extensively explored for their applicability as an additive for lubricants. Solid/semisolid consistency of lubricating grease provides better stability of nano dispersion. Several metal oxides, carbonates, borates are being used to improve tribological performance of lubricating greases[98]–[103]. Carbon compounds such carbon nano tubes, fullerene like carbon compounds, Inorganic fullerene like WS_2 have shown better performance than conventional additives [104].

Another class of non conventional additives is Ionic liquids. They are highly polar salts of organic compounds having melting point close to or below room temperature. Due to high polarity they tend to adsorb preferentially to the applied surface and creates strong film over the surface.

They are highly effective in reducing coefficient of friction and wear. They also contain phosphorus, sulphur etc. elements in the compounds which are very well known for their AW/EP actions [105]–[112].

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CHAPTER-II

SELECTION OF THICKENERS

SELECTION OF THICKENERS

2.1 INTRODUCTION:

Use of soap based thickeners for lubricating greases is very common since ages [1–3]. Arveson [4] tried an unconventional approach and used PIB as a thickener to produce soap free grease. No doubt, the invention of Lithium soap in 1942 [1] was a major breakthrough for grease industry, the journey to find alternate/new thickeners still continued. The reason behind this is already discussed in detail in “Chapter 1” of this dissertation work.

Since 1940 to till date one can find a series of patents and publications highlighting the applicability of polymers as a thickener or as a performance additive to improve water resistance, tackiness, bleed, etc. of lubricating greases [5–7]. Polymer used as thickeners, can be broadly categorized in two categories; 1. Containing PTFE, fluoroethers, polyorganosiloxanes and functionalized polymers used for especial application as these materials are very costly 2. Containing polyolefin type polymers particularly polypropylene and polyethylene intended for use in general purpose applications [8–12]. Mortein et al [13] found that the microstructural network of polypropylene thickened grease closely resembles commercial Lithium lubricating greases and moreover, the rheological response was also similar. Other polyolefins (PE, HDPE, EVA etc.) were also found useful to enhance rheological response of Lithium soap grease [12].

2.2 AIM OF THE PRESENT WORK

The aim of the work is to find out suitable polymers available commercially that can be used as potential thickeners for making lubricating greases. From the vast variety of synthetic polymers available, only a few are suitable as grease thickeners. Present work will be focused upon the study of polyolefin type polymers. Particularly polypropylene, Maleated polypropylene, polyethylene and Maleated polyethylene. The outline of work methodology is as follows;

1. Commercial Polypropylene, Maleated polypropylene, polyethylene and Maleated polyethylene will be used individually as a thickener to prepare grease in mineral oil.
2. Thickener concentration of all the greases will be optimized to get NLGI Grade 2 consistencies as it is the most preferred consistency for majority of industrial applications.
3. The combination of high molecular weight, low molecular weight and polymers of different category will be studied to get better grease structure and properties.
4. The effect of various thickener compositions on drop point, penetration and oil bleed tendency will be studied.

5. The dropping points of polyolefin thickened greases are generally lower than simple Lithium soap and complex soap based greases. So, another objective of this study is to improve dropping point of polymeric greases by incorporating suitable additives.

2.3 EXPERIMENTAL

2.3.1 **Materials and Methods**

Paraffinic mineral lubricating oils (Kinematic Viscosity 160 cSt at 40 ^{o}C) supplied by Indian Oil Corporation Ltd, India was used to prepare lubricating grease samples, physical properties of the base oil is given in Table 2.1. Polypropylene (PP), Maleated Polypropylene (mPP), Maleated Polyethylene (mPE) and high molecular weight (avg. mol wt. $\approx 4x10^{5}$) polypropylene (PP_{hm}) was supplied by Pluss Polymers Pvt. Ltd., Faridabad and linear low density polyethylene, a product of Reliance Industries India, supplied by a local supplier were used as thickeners. Raffia grade virgin high density polyethylene from Indian Oil Corporation Ltd. and recycled cream colored high density polyethylene from plastic scrap available with the same trade name was used as an additive, which was supplied by a local supplier. MFI and Density of polymers are given in Table 2.2. Lithium 12-hydroxystearate and polyurea thickeners were prepared using in house methods and techniques (not disclosed).

Table 2.1: Melt flow index (MFI g/10 min) and Density of polymers. (* supplied by manufacturer).

Sample	**MFI* (g/10 min)**	**Density***
Polypropylene (PP)	1700	0.903.
Polypropylene$_{HM}$	25	n.a.
Maleated Polypropylene	120	0.908
Polyethylene	4.5	0.936
Maleated Polyethylene	120	0.932
HDPE	1.2	0.954
HDPE$_{raffia}$	0.9	0.952

Table 2.2: Physico-Chemical properties of base oil (provided by supplier)

Base Oil Properties	
Colour	Brown
Kinematic Viscosity (cSt)	
@40 ^{o}C	169.9
@100 ^{o}C	16
Viscosity Index	96.8
Aromatic Content	7.8
Paraffinic content	65.3
Naphthenic Content	26.9
Density	0.897
Aniline Point	107.6
Flash Point	285

2.3.2 Grease Manufacturing

The process of making greases from polyolefin polymers are not mentioned precisely in public domain. Most of the reports are patents and processes are discussed in broader perspective [14]. Some authors [15] prepared dispersion of polymers by keeping oil and polymer mixture at elevated temperature for a period of at least 12 hrs to induce swelling of polymers. This method is suitable only when the polymers are used as an additive for other greases but not when it is used as a thickener.

In our study, Sotelem reactor model RMP 5005 was used to process the batches of size 1.5-2 kg. All the contents were charged at once in full quantity in to the kettle then the materials were heated up to 200^o – 210 ^{o}C under nitrogen atmosphere for a period of 1hr. Materials were transferred to a 10 kg capacity wide mouth steel container then cooled suddenly by pouring dry ice powder or by employing ice salt mixture externally as mentioned in each batch. Milling parameters are very crucial in manufacturing polymeric greases. In US Patent No “3392119”, mentioned that to get better structure of greases, milling has to be carried out preferably between 70 - 90 $^{\circ}$C. It is observed that such a precise temperature control is very difficult by normal means and methods because the temperature inside the chamber increases continuously due to friction between the plates of milling machine. Hence, to control the heating affect we carried out milling operation in small lots preferably 250 gms in each pass and allow the machine to cool down to room temperature before milling next lot or employed circulation of tap water externally to cool down the milling chamber.

2.3.3 Heat Stability Test

ASTM D-6184 test method was followed to study the heat stability property in terms of oil bleed tendency for all the grease samples at temperature 100 °C. 10±2 gms of sample was weighed in a conical sieve and hanged over a standard 100 ml beaker by means of cover lid. The samples were kept in an oven capable of maintaining up to 150 ±0.5 °C. Test was conducted in duplicate for 30 hours and average of two results was reported.

2.3.4 Cone Penetration Test

Cone penetration test is the basic test in the grease evaluations. It helps in knowing the consistency (hardness & softness) of the grease. To determine the unworked, worked (60 double stroke) penetration and mechanical stability (10^5 double strokes) of the lubricating grease, cone penetration test was performed using Seta penetrometer model 17500-0 for all the samples as per the ASTM D-217 (Full cone geometry) or as per ASTM D-1403 (half cone geometry). The samples were kept in incubator/water bath at 25 °C for a period of 2-3 hrs before doing penetration test

2.4 **RESULTS AND DISCUSSIONS**

Experiment: 1

Table 2.3 shows the penetration data and other observation of the polypropylene grease processed under varying cooling and milling conditions. The process was the same as mentioned in section 2.3.4 and two different batches were taken. First batch was cooled rapidly by pouring dry ice powder and second batch was cooled externally with the help of NaCl-Ice mixture. Half (50/50) of the quantity of both the batches were milled under controlled temperature and other half quantity was milled without controlling milling temperature. The batch cooled suddenly with dry ice powder showed better thickening and was harder in consistency as measured by unworked and worked penetration than the batch cooled externally with the help of NaCl-Ice mixture.

The effect of temperature controlled milling results in smooth and greasy structure of grease. In Uncontrolled milling, a Cake like material was formed when the material was cooled to room temperature after milling was completed. Therefore, cooling with dry ice along with controlled temperature milling was adopted for further research work.

Table 2.3: Effect of cooling and milling on the penetration of finished grease

<table>
<tr><td colspan="3">Contents</td><td colspan="2">Percentage composition</td></tr>
<tr><td colspan="3">Polypropylene</td><td colspan="2">11.22</td></tr>
<tr><td colspan="3">Polypropylene$_{hm}$</td><td colspan="2">0.58</td></tr>
<tr><td colspan="3">Base Oil</td><td colspan="2">88.2</td></tr>
<tr><td colspan="5">Penetration as per ASTM D-217 test method</td></tr>
<tr><td></td><td colspan="2">Sudden cooling by pouring dry ice powder</td><td colspan="2">Cooled externally by NaCl-ice mixture</td></tr>
<tr><td></td><td>Milled at controlled temp.</td><td>Milled without temp. control</td><td>Milled at controlled temp.</td><td>Milled without temp. control</td></tr>
<tr><td>Unworked</td><td>351</td><td>Melted during milling and becomes cake after cooling</td><td>365</td><td>Melted during milling and becomes cake after cooling</td></tr>
<tr><td>Worked</td><td>354</td><td>-do-</td><td>375</td><td>-do-</td></tr>
</table>

Table 2.4: Effect on structure and penetration without high mol. wt. content polymer

<table>
<tr><td colspan="2">Contents</td><td colspan="2">Percentage composition</td></tr>
<tr><td colspan="2">Polypropylene</td><td colspan="2">12</td></tr>
<tr><td colspan="2">Polypropylene (high mol wt.)</td><td colspan="2">-Nil-</td></tr>
<tr><td colspan="2">Base Oil</td><td colspan="2">88</td></tr>
<tr><td colspan="4">Penetration as per ASTM D-217 test method</td></tr>
<tr><td></td><td colspan="2">Sudden cooling by pouring dry ice powder</td><td rowspan="2">Appearance</td></tr>
<tr><td></td><td colspan="2">Milled at controlled temperature</td></tr>
<tr><td>Unworked</td><td colspan="2">355</td><td rowspan="2">Homogeneous, smooth and soft</td></tr>
<tr><td>Worked</td><td colspan="2">378</td></tr>
</table>

Experiment: 2

It is mentioned in the literature [16] that use of mixture of high molecular weight and low molecular weight content of polymeric thickeners in a ratio preferably 1:20 is suitable. However, in experiment no. 2, when the grease was prepared by such composition some grainy substance was observed. But when the grease was prepared with low molecular weight polymer alone (Table 2.4), the appearance was smooth and no change in penetration was found. One can easily speculate that all the polymers have a molecular weight distribution i.e. it contains a range of low to high molecular weight content and so, there is always some quantity of high molecular weight polymer present in low mol. wt. product. And if the polydispersity of low molecular weight polymer is high then the need to add high molecular weight content in thickener composition can be eliminated. Polydispersity and other characterization data of selective polymers are given in subsequent chapter.

Table 2.5: Thickener percentage and penetration values

Type of thickener	Thickener Percentage	Penetration as per ASTM D-217		Dropping Point as per D-566/2265
Polypropylene	14	293	337	143
-do-	16	279	303	
-do-	18	242	283	
-do-	20	201	237	
Maleated Polypropylene	11.5	313	345	143
-do-	13.5	275	315	
-do-	15.5	231	287	
-do-	18	n. a.	n. a.	
Polyethylene	8	265	288	117
-do-	9	260	270	
-do-	10	231	241	
Maleated Polyethylene	8	285	325	116
-do-	9	270	300	
-do-	10	246	273	

Experiment: 3

This experiment was carried out to optimize thickener content of various thickeners to get desired consistency of NLGI grade 2. Table 2.5 lists the penetration data for all the samples having different thickener content. NLGI grade 2 consistency was obtained at 18, 15.5, 9 and 9 % of thickener concentration for polypropylene, maleated polypropylene, polyethylene and maleated polyethylene respectively.

Experiment: 4

Oil bleed tendency of grease is an indirect assessment of the thickener structure stability. To assess this, heat stability test of all the samples was carried out as per ASTM D-6184 (test method for oil separation from lubricating grease). It was observed (Table 2.5) that PP and mPP yield NLGI grade 2 consistencies at 18 % and 15.5% thickener concentration. Hence, the heat stability test was carried out with the samples containing the same thickener content i.e. 15.5 in both the samples. Bleed of polypropylene grease was found to be much higher and maleated polypropylene was better than polypropylene where as polyethylene and Maleated polyethylene show least oil bleed. Olov et al [16] also reported that polypropylene greases show high oil bleed tendencies even at low temperatures.

In an effort to improve oil bleed of PP and mPP, further study (Table 2.7) was carried out with mixed thickener composition of PP and mPP, over all thickener content was always maintained at 18 (PP), 15.5 (mPP) and 9 % (PE and mPE). Another study was carried by incorporating 1% of HDPE’s in both PP and mPP grease. HDPE was added in to the composition during initial charging along with other thickener.

It is evident from the table that no improvement in oil bleed was observed in the mixed thickener composition containing PP and mPP. Out of the two HDPEs the raffia grade HDPE i.e. HDPE$_{raffia}$ effectively reduced the oil bleed tendency of both the PP and mPP greases. Further elaborative study of oil bleed tendency and method of improvement is discussed in subsequent chapter.

Table 2.6: Heat stability of PP, mPP and PE greases having grade NLGI 2 consistency

Penetration			**Dropping Point**	**Heat Stability (%)**
	Unworked	**Worked**		
Polypropylene	285	312	143	10.6
Maleated polypropylene	231	287	143	8.2
Polyethylene	260	270	117	3.8
Maleated polyethylene	265	277	116	3.9

Table 2.7: Heat stability of greases having mixture of two different thickeners.

Thickener type	Composition	Heat Stability
PP + mPP	50:25	No improvement
PP + mPP	50:50	No improvement
PP + HDPE	1%	No improvement
PP + HDPE$_{raffia}$	1%	Improved
mPP + HDPE	1%	No improvement
mPP + HDPE$_{raffia}$	1%	Improved

Table 2.8: Dropping point of greases additized with lithium 12-hydroxystearate and polyurea.

Thickener % of PP	% of additive	Dropping point as per ASTM D-566/2265
PP + Lithium 12-hydroxystearate	0.5	160 (not repeatable)
	1	192
	2	195
PP with polyurea	0.5	no change
	1	no change
	2	no change
mPP + Lithium 12-hydroxy stearate	0.5	162 (not repeatable)
	1	191
	2	192
mPP + polyurea	0.5	no change
	1	no change
	2	no change
PE + Lithium 12-hydroxystearate	0.5	145 (not repeatable)
	1	190
	2	193
PE + Polyurea	0.5	no change
	1	no change
	2	no change

Experiment: 5

Dropping point of lubricating greases is very crucial to decide its application temperature range. Low dropping point grease cannot be used for higher temperature operations. Drop point was determined as per ASTM D 566/2265 test methods. PP type greases in our study drops at 143 ^{o}C and PE type greases at around 116 °C. One drawback of the past [17] studies carried out to improve dropping point of polymeric greases by using TPX (methylpentene) polymers, is use of polymer which higher processing temperature and yield very hard product which is very difficult to mill under normal conditions.

In this experiment we have used preformed Lithium 12-hydroxystearate and polyurea as an additive for polymeric greases. 0.5, 1 and 2% of the additives were taken and charged along with the polymeric thickener. Results are shown in Table no 2.8. It is found that Lithium 12-hydroxy stearate was able to improve dropping point of all the greases even at very low concentration of 1% on the other hand polyurea was not effective to improve the dropping point of any grease at the concentration studied.

2.5 **CONCLUSIONS**

From the various experimental findings it can be concluded that

- Controlled temperature during milling operation is very important to get better property of the polymer based finished greases.
- Processing temperature should be much higher than the melting point of polymer for proper dispersion in mineral oil.
- Rapid cooling with the help of dry ice powder produces grease having harder consistency and good mechanical stability. Slow cooling adversely effects the consistency and mechanical stability of finished product.
- It is not always necessary to have combination low molecular weight and high molecular weight component in thickener to get better grease. A low

molecular weight polymer (mol. wt. ≈ 1×10^5) with high polydispersity can be used alone as a thickener.

- Oil bleed tendency for PP and mPP greases is higher than Polyethylene type greases.
- Heat stability of PP and mPP grease can be improved by incorporating selective category of HDPE.
- Dropping point of polymeric greases can be improved significantly by using Lithium 12-hydroxy stearate as an additive.

Detailed study on oil bleed tendency of pp and mpp thickened grease is proposed for further work. As one of the HDPE was very effective in controlling the oil bleed of pp and mpp grease in this work.

Physical and Chemical properties of polymeric thickeners are different and not comparable with other soap and non-soap based thickeners. Hence, the behavior of polymers in grease and its compatibility with performance additives are unpredictable and needs of thorough investigation.

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CHAPTER III

OIL BLEED TENDENCY AND RHEOLOGICAL STUDIES OF PP AND mPP THICKENED GREASES

OIL BLEED TENDENCY AND RHEOLOGICAL STUDIES OF PP AND mPP THICKENED GREASES

3.1 INTRODUCTION

Lubricating grease is a three component system i.e. thickener, base oil and performance additive, used predominantly for the lubrication of bearing elements and low speed gear systems [1]. Grease consistency is an important measure for selection of grease for specific applications [2]. Proportion and type of base oil and thickener in lubricating greases influence a number of properties including consistency and rheology [3, 4]. Lubricating grease serves as a reservoir for lubricating oil and an optimum release of lubricating oil during operation is desirable for good lubrication performance. Oil release from lubricating greases is induced by mechanical forces and temperature. Insufficient oil release or excessive loss of oil from lubricating grease causes lubricant starvation and may lead to bearing failure [5, 6]. Oil bleeding rate directly affects the useful service life and performance of the bearing, thus it is apparent that oil bleed characteristics of lubricating grease have a role in performance assessment of lubricating greases. Hence due significance has been given by various researchers to study and improve oil bleed characteristics of various types of lubricating greases [4,7-9]. There are several research papers published focusing on other aspects of polymer thickened greases [10-15], but oil bleed tendency at high temperatures and methods of improvement has hardly been studied in detail [16]. Polymers are grafted with some functional groups to further improve the existing properties or to incorporate additional properties in the field of concern [17-19] such as flow, oil bleed, etc. Recycled polymers are cheaper material sources and are easily available with a wide range of grades from single recycled to non reusable waste. Attempts were made by researchers in the recent past to study application potential of different types of recycled polymers in lubricating greases [12, 15]. This research work aims to study the effect of recycled and virgin HDPE on bleeding tendency of PP and mPP thickened greases over a wide temperature range and any change in rheological properties therein.

3.2 AIM OF THE PRESENT WORK

Oil bleed in lubricating greases is a common phenomenon. It is highly temperature dependent and during application it is desirable to the extent it helps in lubrication performance. PP type greases are reported to have excessive oil bleed tendency and PE type greases are more stable towards oil bleed as compared to PP grease. The scope of present work is to study the oil bleed tendency of PP and mPP thickened lubricating greases by conical sieve method and to make a comparative assessment of both the greases.

Another objective of this work is to investigate the oil bleed performance of PP and mPP type greases by incorporating different grades of HDPE and to find out optimum percentage composition of thickeners with minimum oil bleed tendency.

The above study will be carried out in various temperature segments ranging from 60-120 °C to investigate the effect of temperature on the said property.

The safe disposal of waste polymer is a common severe problem world over. They are readily available almost everywhere and are cheaper than virgin polymers. Another objective of the study is to find use of recycled/waste polymer as a lubricating grease additive to improve oil bleed performance and to compare its effectiveness vis-a-vis virgin polymers of the same grade.

Rheology is a very crucial property of lubricating grease. It is important for grease to have thick consistency to remain intact in contact zone. But at the same time it should flow when stress is applied and regain its original structure when stress is removed. This type of physical behavior is a function of the interaction between the components of lubricating greases. An alteration in grease composition may reflect in rheological property of the greases. Since this property is the most important for actual service behavior of lubricating grease, it is necessary to study the effect in rheological response of lubricating grease after any change in the composition. Another effort would be to study the modification in grease matrix through rheological studies of PP and mPP thickened grease on incorporating virgin and recycled HDPE polymers.

3.3 EXPERIMENTAL

3.3.1. Materials

A mixture of group I and group II paraffinic mineral lubricating oils (Kinematic Viscosity 160 cSt at 40 °C) supplied by Indian Oil Corporation Ltd, India was used to prepare lubricating grease samples. Polypropylene and Maleated

Polypropylene, supplied by Pluss Polymers Pvt. Ltd. were used as thickeners. Raffia grade virgin high density polyethylene from Indian Oil Corporation Ltd. and recycled cream colored high density polyethylene from plastic scrap available with the same trade name was used as an additive, which was supplied by a local supplier. Melting temperature (Tm), fusion enthalpy (ΔHf) and other physical properties of polymers are given in Table 3.1.

Table 3.1: Weight average molecular weight (Mw), number average molecular weight (Mn), polydispersity (Mw/Mn), melting temperature (Tm) and fusion enthalpy (ΔHf) of polymers. * Density data of the polymer samples are arranged by manufacturer.

Sample	MFI* (g/10 min)	Density*	M_w	M_n	M_w/M_n	T_m	ΔH_f
PP	1700	0.903	1.20×10^5	3.8×10^4	3.2	161.5	102
mPP	120	0.908	1.42×10^5	5.1×10^4	2.8	160	109
HDPE	0.9	0.952	5.73×10^5	4.6×10^4	12	132	237
rHDPE	1.55	n. a.	3.95×10^5	3.3×10^4	11.9	131.5	219

3.3.2 Grease Manufacturing

Gel like dispersion of polymers was prepared using Sotelem reactor model RMP 5005 through batch process under nitrogen atmosphere. The contents were heated up to 200-210 ^{o}C with constant stirring at 150 rpm. After 1 hour the material was poured into 20 liter steel container and quenched with dry ice to 70 - 90 ^{o}C. The material was then milled in Frigmaires Colloid Mill (Model JC 100) to obtain grease. The processing and milling parameters for all the samples were kept identical. With the same percentage composition, both PP and mPP have different thickening tendencies. Hence thickener proportion was adjusted to obtain target consistency (worked cone penetration of 270 to 300). 18% PP and 15.5% mPP gave desired consistency. 26 greases with different PP, mPP and HDPE (virgin and recycled) concentrations were studied; detailed compositions are given in Table 3.2.

Table 3.2: Percentage composition of polymers in greases.

Sample	% of PP	% of HDPE	% of rHDPE
PP18	18	nil	nil
PP17.5	17.5	nil	nil
PP17	17	nil	nil
PP16	16	nil	nil
PP14	14	nil	nil
PP+ HDPE0.5	17.5	0.5	nil
PP+HDPE1	17	1	nil
PP+HDPE2	16	2	nil
PP+HDPE4	14	4	nil
PP+rHDPE0.5	17.5	nil	0.5
PP+rHDPE1	17	nil	1
PP+rHDPE2	16	nil	2
PP+rHDPE4	14	nil	4
mpp15.5	15.5	nil	nil
mPP15	15	nil	nil
mPP14.5	14.5	nil	nil
mPP13.5	13.5	nil	nil
mPP11.5	11.5	nil	nil
mPP+HDPE0.5	15	0.5	nil
mPP+HDPE1	14.5	1	nil
mPP+HDPE2	13.5	2	nil
mPP+HDPE4	11.5	4	nil
mPP+rHDPE0.5	15	nil	0.5
mPP+rHDPE1	14.5	nil	1
mPP+rHDPE2	13.5	nil	2
mPP+rHDPE4	11.5	nil	4

3.3.3 Gel Permeation Chromatography

High temperature gel permeation chromatography (HT-GPC) analysis of all the polymers was carried out on PLGPC 220 HTGPC equipment fitted with Refractive Index (RI) measurement facility. The oven compartment is fitted with an injection valve, GPC columns and Differential Refractive Index (DRI) detector. The weight-average molecular weight, ($M_{w)}$, number-average molecular weight, (M_n), and poly-dispersity, (M_w/M_n), values are listed in Table 3.1.

3.3.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed with a Mettler Toledo DSC 1 Instrument. Each test sample was weighed to about 10±2 mg, sealed in standard aluminium pans and subjected to heating cycles from 25 to 200 ^{o}C, 200 to 25 ^{o}C, 25 to 200 ^{o}C at a heating rate of 20 ^{o}C/min in first heating cycle and 10 ^{o}C/min in second heating cycle; with nitrogen flow rate of 50 ml/min. The heat flow curve of the second heating cycle was taken for study.

3.3.5 Heat Stability Test

ASTM D-6184 test method was followed to study the heat stability property in terms of oil bleed tendency for all the grease samples at temperatures 60, 80, 100, and 120 $^{\circ}$C. Oven capable of maintaining up to 150 ±0.5 $^{\circ}$C was used for study. Test was conducted in duplicate for 30 Hrs for study in each temperature and average of two results was reported.

3.3.6 Cone Penetration Test

To determine the unworked and worked (60 double stroke) penetration of the lubricating grease, cone penetration test was performed using Seta Penetrometer model 17500-0 for all the samples as per the ASTM D-1403 (half scale geometry) and values obtained were converted into the full scale cone penetration values applying the factor as per ASTM D-217.

3.3.7 Rheological Studies

Rheological measurements were carried out in controlled strain rheometer(Anton Paar Physica MCR 301). All samples having the same thermal history (during grease manufacturing) were subjected to strain sweep test at a frequency of 1Hz to determine the linear viscoelastic region. SAOS (small amplitude oscillatory sweep) measurements were carried out inside linear viscoelastic region using a 25mm, Plate-on-Plate geometry at 1mm gap in a frequency range between 10^{-2} and 10^{2} rad/s at 25 ^{o}C.

3.3.8 Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^{1}H /^{13}C NMR spectra were recorded on an Agilent 500 MHz DD2 NMR spectrometer equipped with a 10 mm dual probe at 130 ± 0.1^{o}C. Temperature was calibrated by replacing the NMR sample tube with a tube containing 80% ethylene glycol and 20% DMSO-d_6 at the same sample height as the polymer solution. N_2 gas was used for temperature control and to flush the probe. NMR spectra were obtained without sample spinning because sample spinning did not significantly affect the ^{13}C NMR lineshape in the polymer spectra [3]. For a good line shape the magnet was carefully shimmed. At high temperature stability of ^{1}H (decoupler nuclei) tuning and matching was not stable. To avoid this condition experiment was started after two hours of the temperature reaching at the desired point and an extra N_2 gas tube placed into the magnet bore at the top of the magnet to avoid temp gradient. Prior to data acquisition, the observed pulse widths were verified for both the ^{13}C and ^{1}H channels by determination of the 90^o pulse widths.

^{1}H NMR: Acquisitions experimental conditions used for ^{1}H NMR are: spectral width = 1543.2 Hz, spectral size = 32K, 90° pulse = 18.1 μs, relaxation delay = 10 s and number of scans = 32. All ^{1}H NMR spectra reference with 1,1,2,2-tetrachloroethane peak at 5.98 ppm.

^{13}C NMR: Acquisitions experimental conditions used for ^{13}C NMR are: spectral width = 20161 Hz, spectral size = 64K, 90° pulse = 14.35 μs, relaxation delay = 14 s acquisition time =1.625 s, and number of scans = 3000-4000 for data averaging. The center of the spectrum was set at 65.9 ppm with spectrum width set at 160.4 ppm.

Sample Preparation

^{1}H NMR: The sample for ^{1}H NMR was prepared in pure 1,1,2,2-tetrachloroethane-d2. Approximately 0.080 g of the polymer sample was weighed into a 10 mm NMR tube and 3.0 mL of 1,1,2,2-tetrachloroethane-d2 containing hexamethyldisiloxane as an internal reference.

^{13}C NMR: Approximately 0.350 g of the polymer sample is weighed into a 10 mm NMR tube and 3.0 mL of 1,1,2,2-tetrachloroethane-d2/ortho-dichlorobenzene (TCE-d2/ODCB) (w:w, 1:1). Oxygen was reduced by a nitrogen purge via an inserted pipette for ca. 2 min. The tube was capped and placed in an aluminum heating block of sample preparation unit for high temperature at 150°C for ca. 4 hours. The sample was periodically checked for homogeneity and mixed manually as necessary. A homogeneous mixture was evident by visualization of the uniform distribution of the polymer in solution with no apparent areas of high solvent concentration or air pockets.

3.4 POLYMER CHARACTERIZATION THROUGH DSC AND NMR TECHNIQUES

3.4.1 Differential Scanning Calorimetry

A DSC measurements was carried out for all polymer samples and the thermograms of samples corresponding to the second heating cycle are displayed in Fig. 3.1. Single endothermic peak appears at 132 °C and 131.5 °C for virgin HDPE and recycled HDPE respectively, which can be attributed to their characteristic melting temperatures, the fusion endotherm of PP and mPP shows the characteristic melting peaks at 161.5 °C and 160 °C respectively.

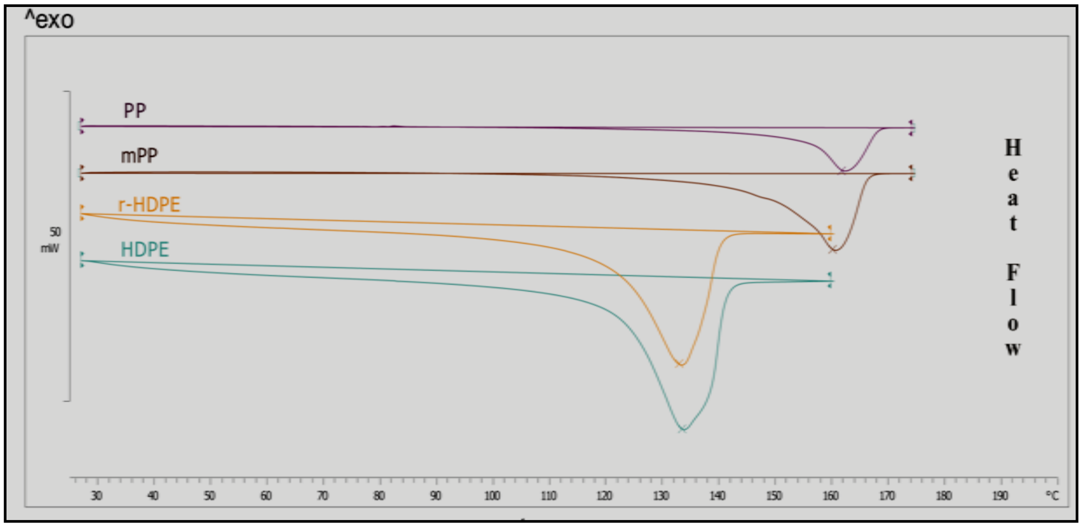


Fig. 3.1: DSC heat flow curves of PP, mPP, HDPE and rHDPE

3.4.2 NMR Studies

HDPE and rHDPE (^{13}C): In contrast to all the other analytical methods discussed, nuclear magnetic resonance (NMR), in particular ^{13}C NMR provided quantitative results regarding branch contents without external calibration. This is due to the area of the observed peak being directly proportional to the number of nuclear spins contributing to that peak. More importantly, through the use of the bulk CH_2 peak as an internal standard, absolute degrees of branching can be determined by simple spectral integration. For these reasons ^{13}C NMR, with its large chemical shift range, has become the standard method for comonomer content and sequence determination in polyolefins [25-26]. The ^{13}C NMR spectrum of virgin HDPE and recycled HDPE are given in Fig. 3.2 and 3.3 respectively. The chemical shifts assigned to different groups for both the HDPEs are give in Table 3.3 followed the Randall and Pooter [25-26].

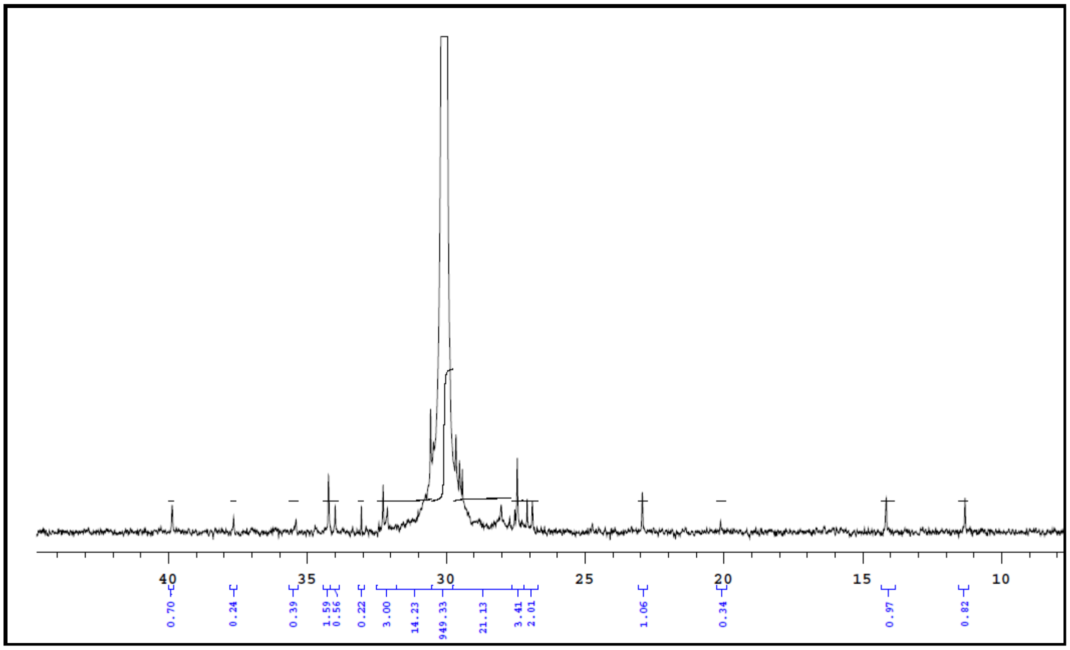


Fig. 3.2: NMR spectra of virgin HDPE

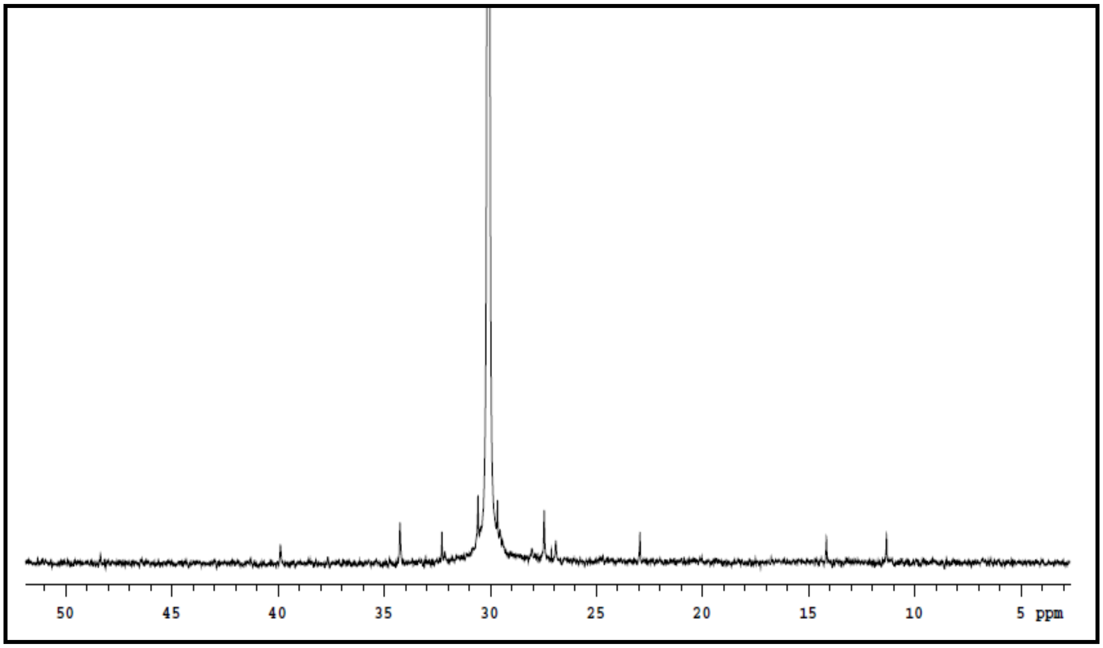


Fig. 3.3: NMR spectra of rHDPE

Table 3.3: Peak assignment in ^{13}C NMR spectrum of HDPE

Peaks	Chemical shift (ppm)
1S	14.1
2S	22.7
3S	31.0
-CH3 of ethyl	11.2
-CH3 of methyl	20.1
brC of methyl	33.3
brC of ethyl	39.8
brC of LCB	38.2
αCH2 of Methyl	37.6
αCH2 of ethyl	34.2
αCH2 of LCB	34.6
βCH2 of all branch	27.3
γ CH2 of all branch	30.5
Δ CH2 of all branch	30.0

PP (^{13}C): The ^{13}C-NMR spectrum is very sensitive to various configurations of PP and exhibit signals at different chemical shift values depending upon the tacticity of PP. The characteristic ^{13}C-NMR signals in an Isotactic PP are:

Isotactic PP

CH_3 = 21.8 ppm (mmmm)

CH = 28.7 ppm

CH_2 = 46.6 ppm

^{13}C-NMR spectra of PP sample shown in Fig. 3.4 exhibit sharp signals at 21.9 ppm (CH_3), 29 ppm (CH) and 46.8 ppm (CH_2) carbon and indicate that the sample has isotactic configuration.

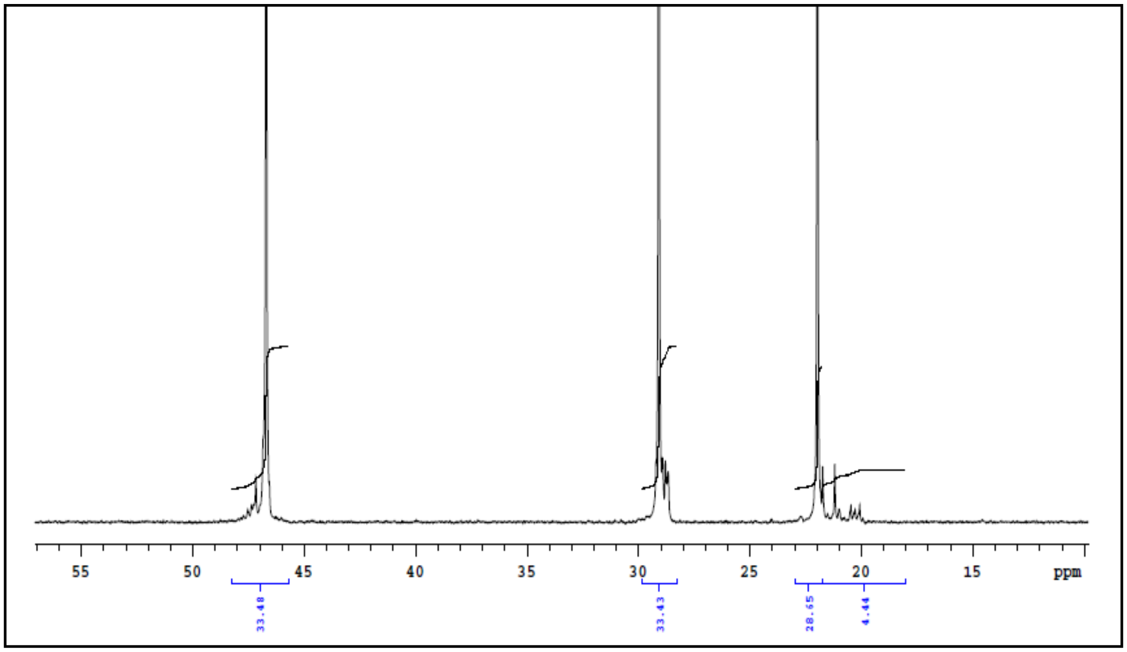


Fig. 3.4: ^{13}C NMR spectra of PP

mPP (^{1}H): ^{1}H NMR spectrum of Polypropylene shows three characterstics signals at 1.9 ppm for methine protons (CH), 1.5 ppm for methylene (CH2) and 1.1 ppm for methyl (CH3) protons. mPP spectrum shows additional peaks at 2.1 and 2.3 ppm for CH protons of Maleic anhydride ring (as given below) which confirmed the Maleic anhydride grafting on PP. ^{1}H NMR spectrum of Maleic anhydride grafted polypropylene (mPP) given in Fig. 3.6.

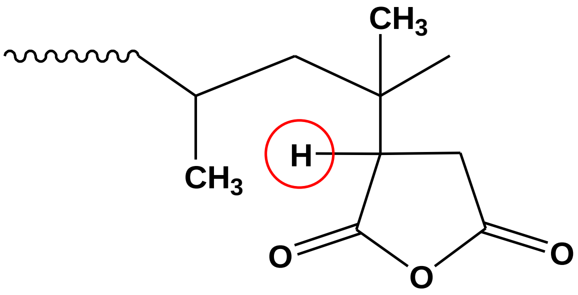


Fig. 3.5: Structure of mPP

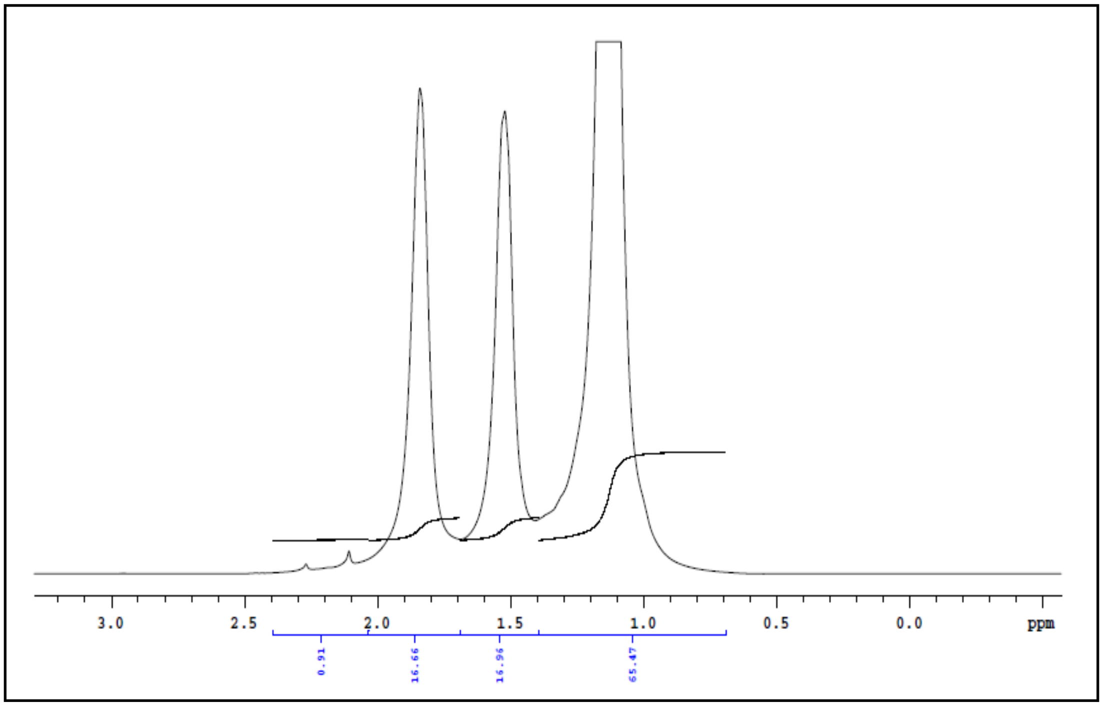


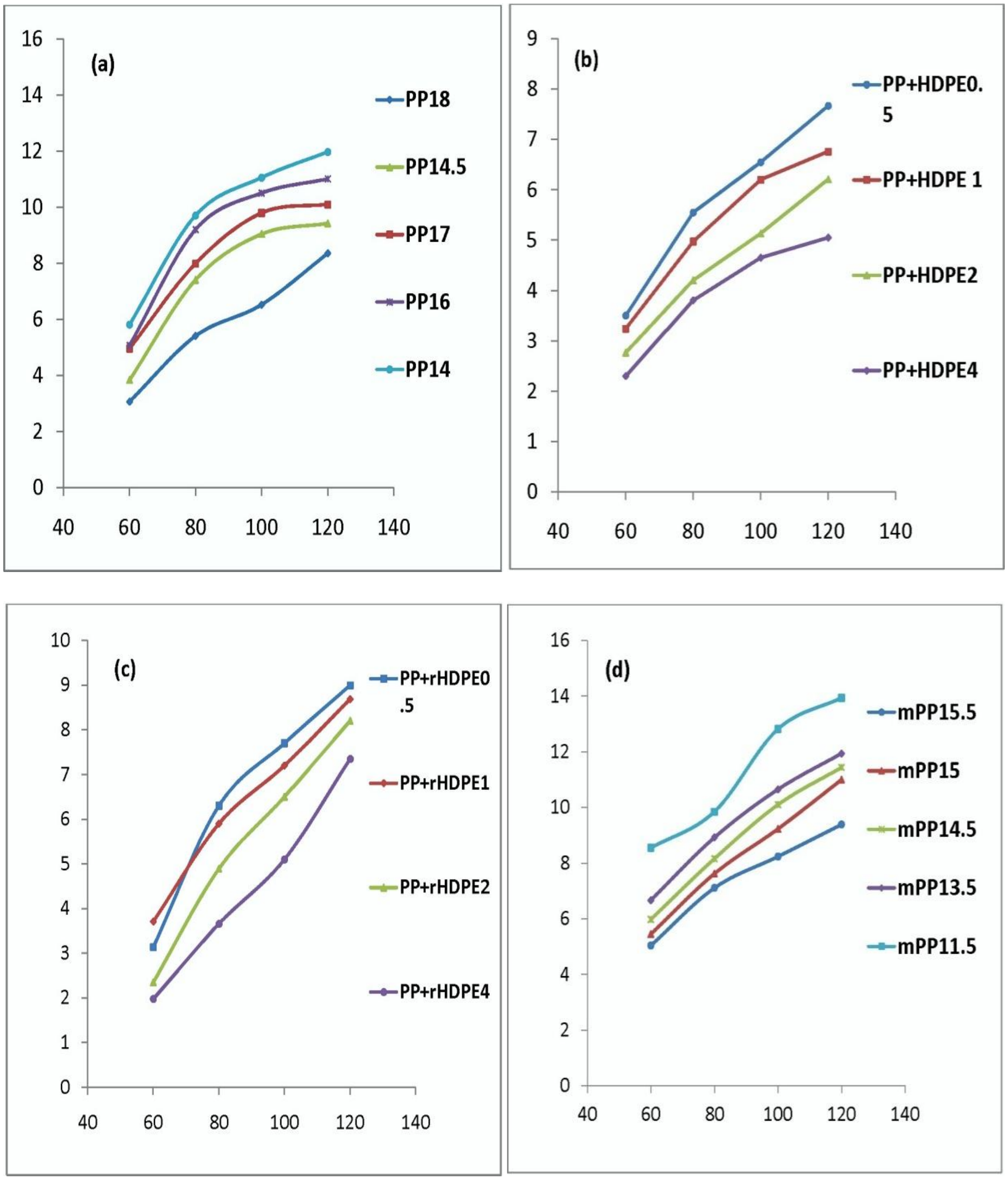
Fig. 3.6: ^{1}H NMR Spectra of mPP

3.5 RESULTS AND DISCUSSIONS

3.5.1 Heat Stability

Heat stability (Oil bleed tendency) of greases PP, mPP & their compositions modified with virgin HDPE and rHDPE were studied at temperatures 60, 80, 100 & 120 °C following ASTM D-6184 standard method. Fig. 3.7 shows plots of heat stability versus temperature for all the samples studied. The trend is similar in all the plots i.e. minimum at low temperature and maximum at high temperature, irrespective of thickener type. An increase in oil bleed tendency was observed with decrease in thickener content and vice versa in both the thickener types PP and mPP over entire temperature range studied [Fig. 3.7. (a) and (d)]. Similar observation was reported by Cann, P.M. [20] with lithium hydroxystearate thickener. Fig. 3.7 (b) & (c) represent the oil bleed performance of PP and mPP thickened greases modified with HDPE. An improvement in oil bleed performance was observed which increases with the HDPE content in thickener, there was a marginal improvement noticed with PP+HDPE 0.5 and PP+Rhdpe 0.5 i.e. with 0.5% HDPE content. Improvement more than 60% was observed with 4% HDPE content both with PP and mPP thickened greases. A gradual and consistent improvement in oil bleed performance was noticed above 0.5% HDPE content. The performance of recycled HDPE was quite similar to virgin HDPE's performance.

In general the oil retention ability of PP grease is better than HDPE grease due to its well formed microstructural network in oil medium, similar to lithium lubricating grease where as HDPE remains coiled and dispersed with poor oil retention capacity [15]. As reported by J.E. Martin-Alfonso et al HDPE acts as filler in lithium lubricating grease, thereby improving grease structure. However, it is speculated that the portion of HDPE soluble in base oil increases viscosity [21]. Hence when grease was blended with PP an improvement in oil bleed performance was noticed due to influence on base oil viscosity. Oil bleed tendency of PP grease is highly temperature sensitive and abrupt increase of oil bleed with temperature is observed [22] (Fig. 3.7). On the other hand PP+HDPE blend was more stable than pure PP grease over a wide temperature range. This may be as a result of increased oil retention capacity by HDPE due to uncoiling of chain with increasing temperature. (There are other physico-chemical properties like base oil and thickener interaction, base oil viscosity [20] which actuates the release of base oil from grease when the temperature is raised). Nevertheless addition of HDPE (virgin and recycled) improves oil bleed tendency compared to pure PP & mPP grease, the oil bleed tendency at high temperature remains always higher than oil bleed tendency at low temperature due to the aforementioned counter phenomenon.


(a)
16
14
12
10
8
6
4
2
0
40
60
80
100
120
140
PP18
PP14.5
PP17
PP16
PP14
(b)
9
8
7
6
5
4
3
2
1
0
40
60
80
100
120
140
PP+HDPE0.5
PP+HDPE 1
PP+HDPE2
PP+HDPE4
(c)
10
9
8
7
6
5
4
3
2
1
0
40
60
80
100
120
140
PP+rHDPE0.5
PP+rHDPE1
PP+rHDPE2
PP+rHDPE4
(d)
16
14
12
10
8
6
4
2
0
40
60
80
100
120
140
mPP15.5
mPP15
mPP14.5
mPP13.5
mPP11.5

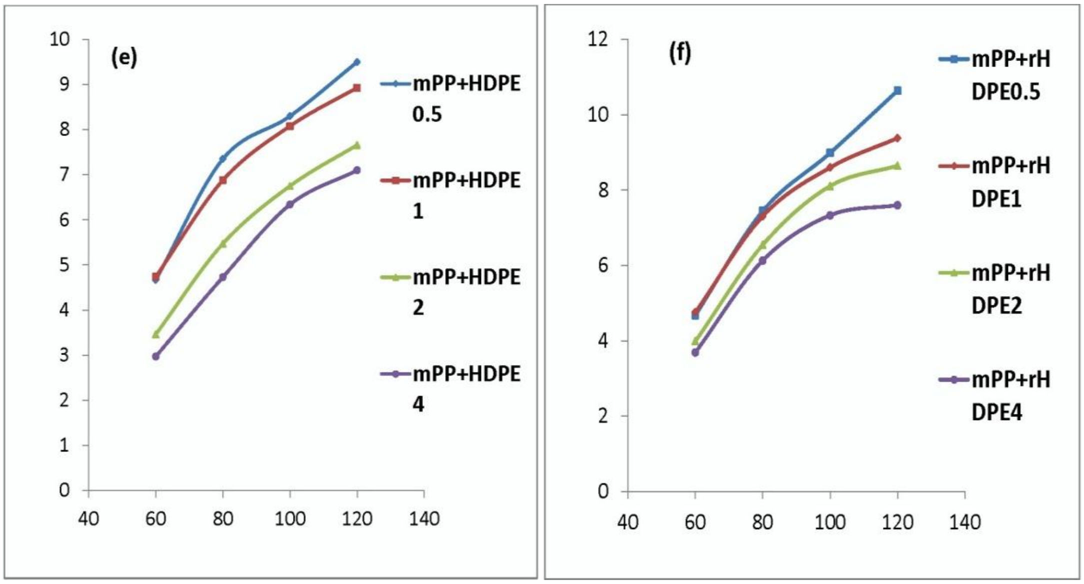


Fig. 3.7: Oil bleed tendency in percentage (y axis) versus Temperature in ^{o}C (x axis), PP grease with varying thickener content(a), PP grease modified with virgin HDPE(b), PP grease modified with recycled HDPE(c), mPP grease with varying thickener content(d), mPP modified with virgin HDPE(e), mPP modified with rHDPE(f).

3.5.2 Cone Penetration test

Unworked and worked cone penetration values of all the samples are shown in Table 3.4. The penetration values of grease samples increases with decreasing thickener content which is quite obvious. All the polymers have different thickening capacity with the same thickener content; the order of thickening tendency is HDPE >mPP>PP. Both virgin and recycled HDPE show higher thickening capacity than other polymers, therefore replacing PP and mPP with more than 2 percent HDPE (virgin and recycled) shows low unworked and worked penetration values. The differences between unworked and worked penetration values of polymeric greases are highly dependent on milling conditions and processing parameters. Slight change of a parameter like milling time and temperature may result in significant change in unworked and worked penetration values. So, care has been taken to keep the process and milling conditions identical.

Table 3.4: Unworked and Worked cone penetration and G_N^0 values of grease samples.

Sample	Unworked Penetration	Worked Penetration	G_N^0
PP18	217	269	86700
PP17.5	235	279	71500
PP17	259	291	56300
PP16	279	303	52700
PP14	293	337	17266
PP+ HDPE0.5	217	271	78833
PP+HDPE1	241	277	78166
PP+HDPE2	237	275	87920
PP+HDPE4	225	263	115666
PP+rHDPE0.5	231	281	83100
PP+rHDPE1	235	279	81300
PP+rHDPE2	219	277	89100
PP+rHDPE4	207	253	124000
mpp15.5	231	287	81300
mPP15	257	303	57400
mPP14.5	265	311	56100
mPP13.5	275	315	40900
mPP11.5	315	345	15700
mPP+HDPE0.5	243	293	52950
mPP+HDPR1	253	289	59620
mPP+HDPE2	243	285	77250
mPP+HDPE4	211	269	122000
mPP+rHDPE0.5	243	295	58100
mPP+rHDPE1	243	291	58725
mPP+rHDPE2	227	273	87600
mPP+rHDPE4	227	267	97300

3.5.3. Rheological Studies

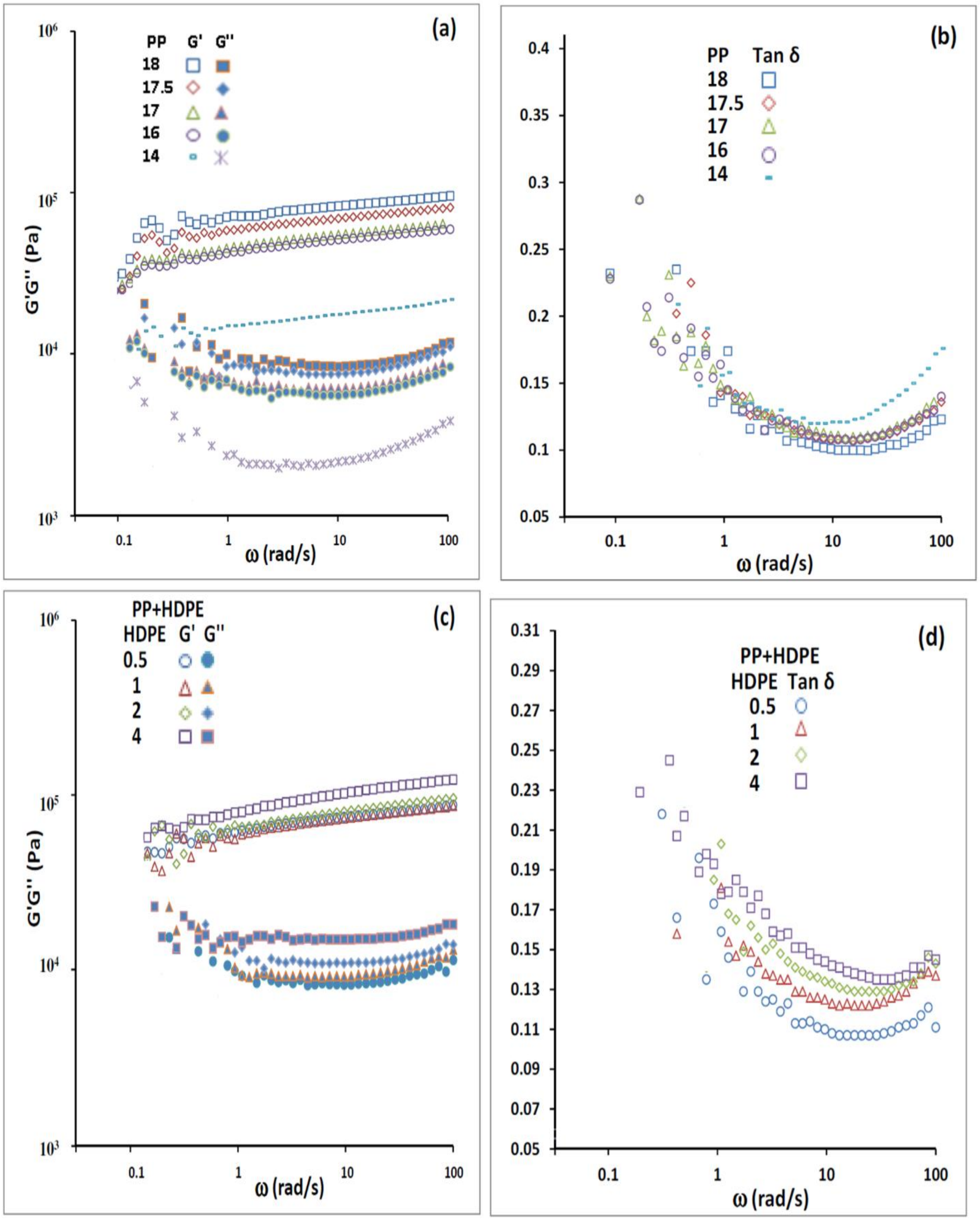
Fig. 3.8 shows the viscoelastic response of PP and mPP grease with frequency as a function of thickener concentration and HDPE (virgin and recycled) concentration in the linear viscoelastic range. It was observed that the frequency dependence of all the samples studied was similar to that found with other lubricating greases as reported in the past [15]. As is evident from Fig. 3, the SAOS response of PP and mPP thickened greases are very similar. Moreover, the SAOS response as a function of thickener content is also similar and hence only pp thickened system will be quoted for further discussion. A high G" than G' was reported for polypropylene (amorphous and recycled) thickener system with ≤ 9% thickener content in a previous study [23]. The present study shows a high storage modulus for all the samples studied. This is a consequence of high thickener content (≤18% for PP and ≤ 15.5 % for mPP). All greases are more elastic than viscous in nature and hence, loss tangent values are below zero.

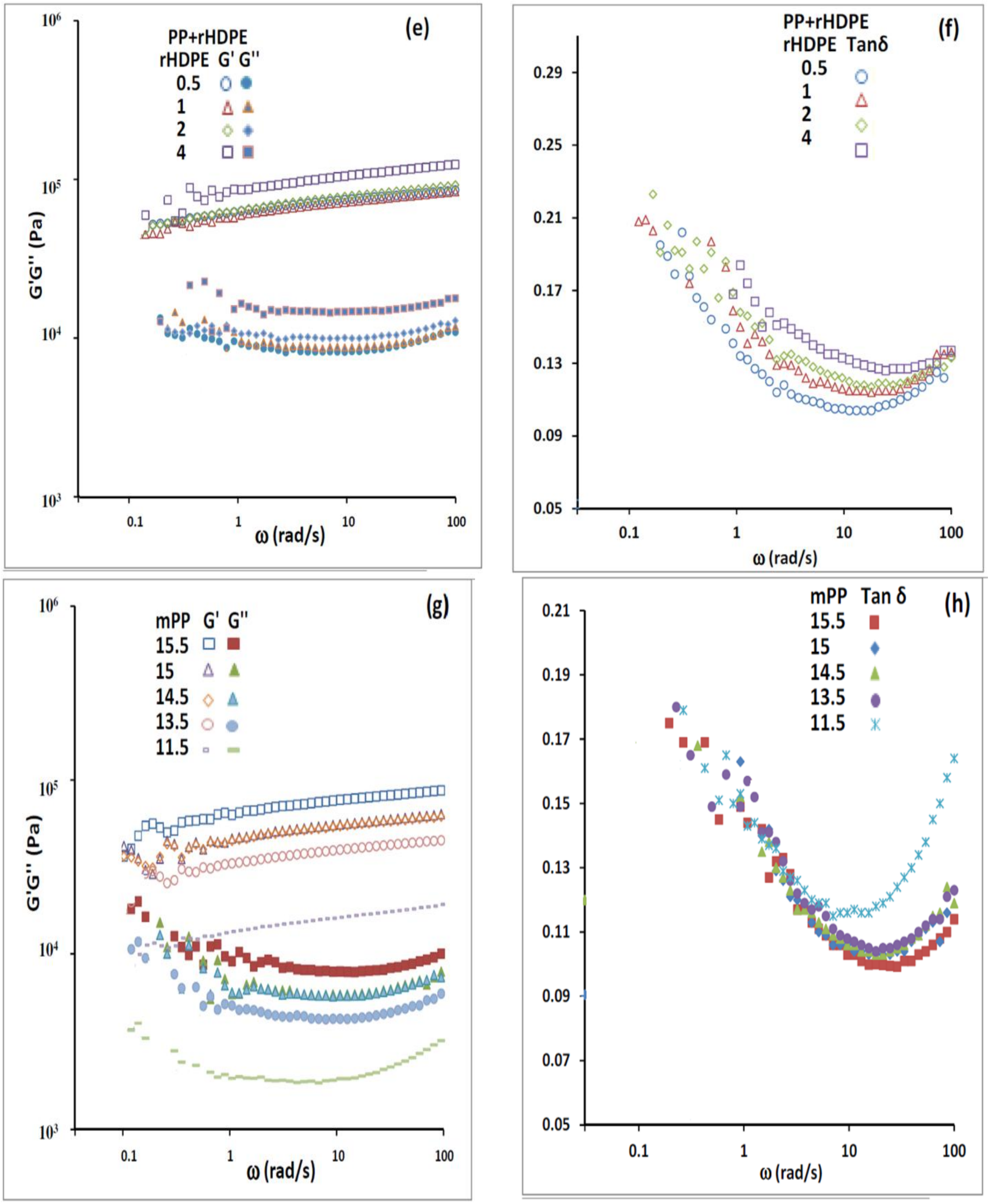
Fig. 3.8 (a) and (g) shows variation of G' and G" as a function of thickener concentration. The values of SAOS function decrease with decreasing thickener concentration and the decrease in storage modulus is more prominent than storage modulus. A dominance of viscous response over elastic response was observed with decrease in thickener concentration. Reduction in thickener concentration results in to a less compact microstructural network with fewer entanglements between network fibers, as is evident from Fig. 3.8 (b) and (h). Correspondingly Fig. 3.8 (a and h) shows high tangent values from intermediate to high frequency range as reported earlier [24] for systems with highly entangled structural network.

The plateau modulus G_N^0 (Table 3.4) is a characteristic parameter of the highly structured polymeric system, having interchain contact points, here it is estimated as,

$$G_N^0 = [G']_{\tan\delta \rightarrow \min}$$

Although all the samples show a characteristic plateau region at intermediate to high frequencies (Fig. 3.8) an increase in plateau modulus was observed with increase in PP/ HDPE ratio. Moreover the plateau region shifted to higher frequency range with increase in HDPE content. The grease with high HDPE content shows higher viscoelastic response than grease with low or no HDPE content in relation to the grease with similar overall thickener content. For polymers of the same molecular weight, the degree of branching is a crucial parameter to influence rheological properties of a given solvent. A linear polymer shows more viscous response than branched polymer of the same molecular weight [21] and as expected, a relatively high modification on viscous response was observed than elastic response on partially replacing PP by HDPE. From the foregoing discussion, it can be anticipated that the more viscous structure (high G") would mean more oil bleed at high temperatures, whereas more elastic structures (high G') would result in less oil bleed or compact structure.


(a)
PP G' G''
18
17.5
17
16
14
G'G'' (Pa)
10⁶
10⁵
10⁴
10³
0.1
1
10
100
ω (rad/s)
(b)
PP Tan δ
18
17.5
17
16
14
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0.1
1
10
100
ω (rad/s)
(c)
PP+HDPE
HDPE G' G''
0.5
1
2
4
G'G'' (Pa)
10⁶
10⁵
10⁴
10³
0.1
1
10
100
ω (rad/s)
(d)
PP+HDPE
HDPE Tan δ
0.5
1
2
4
0.31
0.29
0.27
0.25
0.23
0.21
0.19
0.17
0.15
0.13
0.11
0.09
0.07
0.05
0.1
1
10
100
ω (rad/s)


(e)
PP+rHDPE
rHDPE G' G''
0.5
1
2
4
G'G'' (Pa)
10⁶
10⁵
10⁴
10³
0.1
1
10
100
ω (rad/s)
(f)
PP+rHDPE
rHDPE Tanδ
0.5
1
2
4
0.29
0.25
0.21
0.17
0.13
0.09
0.05
0.1
1
10
100
ω (rad/s)
(g)
mPP G' G''
15.5
15
14.5
13.5
11.5
G'G'' (Pa)
10⁶
10⁵
10⁴
10³
0.1
1
10
100
ω (rad/s)
(h)
mPP Tan δ
15.5
15
14.5
13.5
11.5
0.21
0.19
0.17
0.15
0.13
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0.07
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1
10
100
ω (rad/s)

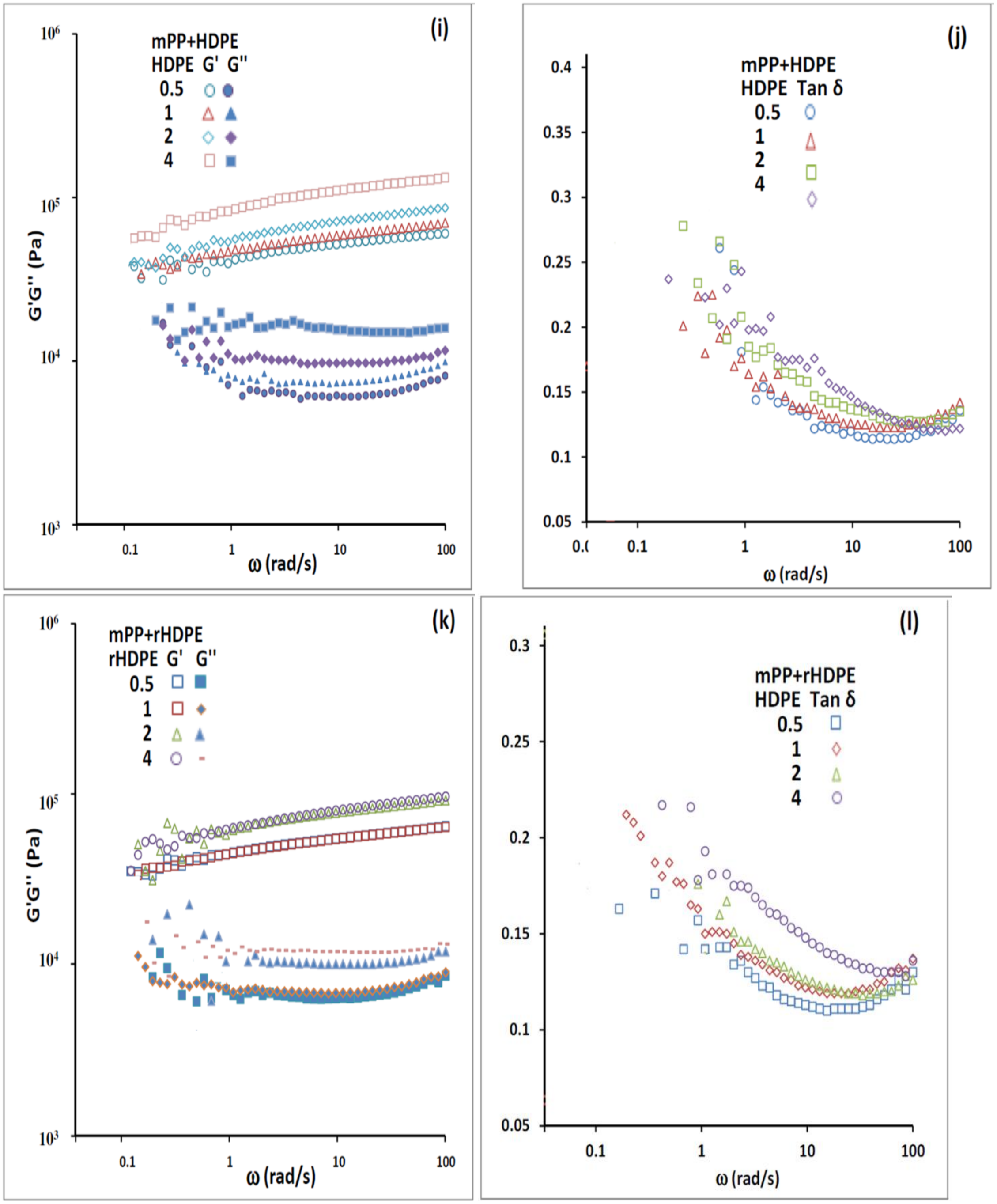

Fig. 3.8: Evolution of storage modulus (G') and loss modulus (G'') and loss tangent (tan δ) with frequency for PP and mPP greases with different PP/mPP concentrations(a,b,g,h), PP and mPP modified with HDPE (c,d,i,j), PP and mPP modified rHDPE (e,f,k,l).

3.6 CONCLUSIONS

Oil bleed performance of pure PP and mPP grease and modified with virgin and recycled HDPE was studied. Based on experimental results obtained it can be concluded that

- Both PP and mPP exhibit similar oil bleed tendencies. However mPP shows slightly high thickening tendency with same thickener concentration over PP.
- HDPE increased G’ and G” values of PP and mPP greases thereby inhibiting oil bleed tendency.
- The oil bleed inhibiting tendency of these modified greases is sensitive to temperature, HDPE content and overall thickener content.
- Oil bleed tendency of greases varies from thickener to thickener but grease with same thickener type tends to bleed more oil which has comparatively higher viscous response (high G") than elastic (low G').

  In future work exhaustive microscopy analysis will be done to look into the microstructure of polymers and correlation with oil bleed tendency.

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CHAPTER IV

A STUDY ON TRIBOLOGICAL BEHAVIOR OF ZDDP IN POLYMER THICKENED LUBRICATING GREASES

A STUDY ON TRIBOLOGICAL BEHAVIOR OF ZDDP IN POLYMER THICKENED LUBRICATING GREASES

4.1 INTRODUCTION

Polymers find a number of applications in lubricating grease industry. They have been widely used as additives to improve water resistance, tackiness, bleed tendency and drop point of lubricating greases [1]. Recent studies on a number of virgin and recycled polymers confer them as an excellent rheology modifiers and a potential thickening agent for lubricating greases [2–5]. It is pertinent to mention that other than thickening efficiency and rheology properties, several other performance characteristics of finished grease are to be met for actual field applications such as antiwear, antiscuffing, etc. Additives are added in to grease to impart these additional properties hitherto not present in the grease. Studies have shown that performance of the additives depends on the presence of the other components in the lubricant, which may have synergistic or adverse effects [6–8].

Grease lubrication depends on grease components including additives and their concentration. Thickener type and its structure in grease are important factors which affect physical properties and tribological behavior of the base grease and fully formulated grease. Atsushi et al. [9] studied affect on friction, wear and rheology of Lithium soap grease with different soap fiber lengths prepared in ester base oil and found that the grease with longer soap fibers had a lower coefficient of friction than the grease with shorter soap fibers. More work on the influence of thickener and thickener structure on grease performance can be found in references, [10–12]. Physico-chemical properties and microstructural network of polymeric greases are different from the conventional Lithium base greases and other soap based thickeners [5]. Conventional soap thickeners are polar whereas polymers like polypropylene and polyethylene are non polar and retractable in nature. Most of the conventional S and P containing additives show synergism with conventional thickeners but the performance and tribological behavior of these additives with polymeric greases are little known and very scanty literature is available on the study and performance of these additives with lubricating grease containing polymers or polymeric thickeners.

S and P containing additive particularly Zinc Dialkyl Dithiophosphates (ZDDPs) are undoubtedly the most successful and widely used multifunctional additives for lubricating oils and greases. A plethora of research has been conducted which focuses on the understanding of characteristic, tribological behavior and application of ZDDP in lubricants [13–18]. It is expected that the interaction between oil, thickener and additive at the contact point between two mating metal surfaces determines the friction and wear performance of the additive in lubricating greases. This study aims to investigate the performance of S and P containing additive particularly ZDDP as a tribological additive in PP, mPP and PE thickened lubricating greases in comparison to Lithium grease.

4.2 AIM OF THE PRESENT WORK

Antiwear (AW) and extreme pressure (EP) characteristics are a part of the specifications of many industrial and automotive greases. It is necessary for a grease operating at high load and severe wear conditions to have good AW and EP characteristics. Base greases are doped with additives to impart AW and EP property. There are several classes of additives but Sulphur, Phosphorus containing conventional additives are the most commonly used. The scope of this study is to find suitable conventional commercial additives and to study their AW and EP performance in polymeric greases. To study all the conventional commercial additives is beyond the scope of this work hence, a few common selective additives will be worked upon and the best among them will be further studied. Another objective of this endeavour is to study the effect of additive in anti friction performance by SRV method.

In continuation to this study the correlation of additives AW/EP response with thickener content will be further explored. Wear profile and worn surface analysis will be carried out with the help of SEM analysis. SEM (EDX) will be employed to study elemental distribution over worn surface. Reasoning and justification of the finding will be based upon SEM analysis and earlier published research articles. The study will thus conclude whether the conventional additives are as effective for polymeric greases as they are for lithium greases. This study is an effort to provide a suggestive approach to get best result out of conventional additives in polymeric greases.

4.3 EXPERIMENTAL SECTION

4.3.1 Materials

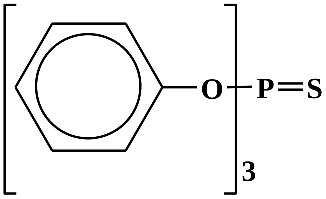
Group I paraffinic mineral lubricating oils (Kinematic Viscosity 160 cSt at 40 ^{o}C) supplied by Indian Oil Corporation Ltd, India was used to prepare lubricating grease samples. Polypropylene(PP) and Maleated Polypropylene (mPP) were supplied by M/s. Pluss Polymers Pvt. Ltd., Faridabad India and linear low density polyethylene (PE), a product of Reliance Industries India, supplied by a local supplier were used as thickeners. MFI, Density, Molecular weight (M_w, $M_{n)}$, Polydispersity (M_w/M_n), Melting temperature (Tm) and fusion enthalpy (ΔHf) of polymers are given in Table 4.1. Triphenyl phosphorothionate, Dialkyl Dithiophosphate ester and ZDDP are sourced from commercial additive suppliers. Structures of the compounds and some typical physical and chemical properties provided by the suppliers are given in Fig. 4.1 and Table 4.2 respectively.

Table 4.1: Molecular weight ($M_{w,}$ M_n), polydispersity (M_w/M_n), melting temperatue; (T_m) and heat of fusion (ΔH_f) of polymers.

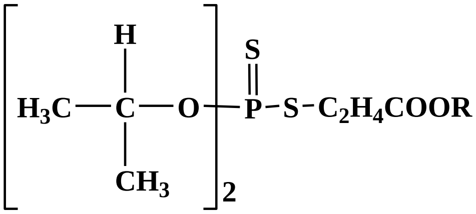
Sample	MFI* (g/10 min)	Density*	M_w	M_n	M_w/M_n	T_m	ΔH_f
PP	1700	0.903	1.20×10^5	3.8×10^4	3.2	161.5	102
mPP	120	0.908	1.42×10^5	5.1×10^4	2.8	160	109
LLDPE	4.5	0.936	2.73×10^5	5.1×10^4	5.3	126	237

Table 4.2: Physical and chemical properties of additives used.

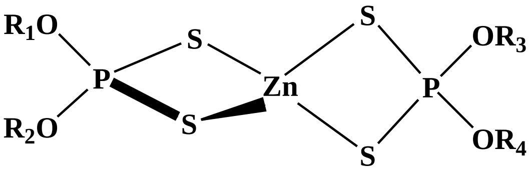
	Dialkyl Dithiophosphate ester	Triphenyl Phosphorothionate	ZDDP
Appearance	Clear, Slightly yellow liquid	Crystalline white flakes	
Viscosity @40 °C (cSt)	5	n.a.	320
Melting Point (°C)	n.a.	52	n.a.
Density (g/cm^3)	1.1	1.19	n.a.
Flash point (°C) (Pensky-martens)	114	>200	n.a.
Elements (%)			
Phosphorus	9.7	8.9	9.3
Sulphur	21.5	9.3	19.0
Zinc	nil	nil	10.0



triphenyl phosphorothionate



dithiophosphate



R= alkyl

Zinc dialkyl dithiophosphate

Fig. 4.1: Structure of the additives

4.3.2 Grease Manufacture

Gel like dispersion of polymers was prepared using Sotelem Reactor model RMP 5005 through batch process under nitrogen atmosphere. The contents were heated up to 200-210 ^{o}C with constant stirring at 150 rpm. After 1 Hr the material was poured into 20 liters size steel container and quenched with dry ice to 70-90 $^{\circ}$C. The material was then milled in Frigmaires Colloid Mill to obtain grease. The processing and milling parameters for all the polymeric samples were kept identical. With the same percentage composition, all the thickeners have different thickening tendencies. Hence, thickener proportion in the grease was adjusted to obtain target consistency (worked cone penetration) of 270 to 300. Four greases with different thickener proportions were prepared, detailed composition are given in Table 4.3. Lithium grease was prepared using in house processing method of Indian Oil Corporation Limited, which is not disclosed here.

Table 4.3: Composition of greases, penetration (ASTM D-217) values (mm/10) and drop point (ASTM D-566)

Grease	Thickener %	Unworked penetration	Worked penetration	Drop Point **(^{o}C)**
PP	18	217	270	143
mPP	15.5	231	287	143
LLDPE	9	260	270	115

4.3.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed with a Mettler Toledo Instrument. Each test sample was weighed to about 10±2 mg, sealed in standard aluminium pans was subjected to heating cycles from 25 to 200 °C, 200 to 25 °C, 25 to 200 °C at a heating rate of 20 °C/min in first heating cycle and 10 °C/min in second heating cycle; with nitrogen flow rate of 50 ml/min. The heat flow curve of the second heating cycle was taken for study.

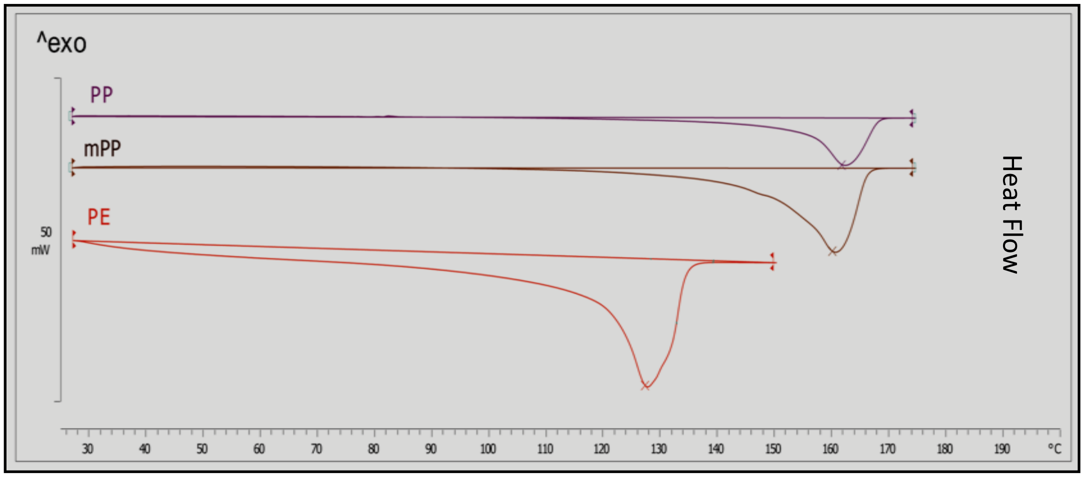


Fig. 4.2: DSC heat flow chart of PP, mPP and PE polymers.

4.3.4 Tribological performance

The tribological behavior of all the greases was evaluated under steel/steel contact using three test methods viz. Four Ball EP test, Four Ball Wear test & SRV Friction test and at least two replicates for each sample were performed.

IP-239 test method was followed to study EP performance on a Stanhope-seta Four Ball EP test machine at ambient temperature using AISI E 52100 steel balls of 12.7 mm diameter, Surface roughness (Ra) of 0.035 µm and hardness RC 65-66 against three ball configurations in rotary motion at 1450 rpm.

Wear test was carried out as per ASTM D 4172 test method on Falex Four Ball wear tester under similar configuration as Four Ball EP tester in rotary motion with 1200 rpm at 75 °C for a test duration of 60 minutes, in sliding contact under lighter loads (392 N) than those used in the 4-Ball EP Tester. Averages of wear scar diameter (WSD) of the three stationary balls were taken. A microscope with an accuracy of ±0.01 mm was used to measure the WSD of the balls.

Coefficient of friction was determined using Optimol SRV-III tester [(AISI 52100 steel ball, 10 mm diameter) against lower stationary block (AISI 52100 cylindrical steel block, 24 mm ×7.9 mm; Ra of the block 0.08 µm)] in reciprocating sliding motion at temperature 70 °C, at a Frequency 50 of Hz, a stroke length of 1 mm, under a step load of 50, 100, 150, 200, 250, 300, 350 and 400 N at a test duration of 5 minutes under each load.

4.3.5 SEM EDAX study

After the Four Ball Wear test, the lower steel balls were collected and cleaned in petroleum spirit (60-80 °C boiling range). HITACHI S-3400N scanning electron microscope was used for SEM and EDAX studies on cleaned balls.

4.3.6 NMR Study

Instruments and experimental methods are described in chapter III

4.4 POLYMER CHARACTERIZATION

4.4.1 NMR

Characterizations of polymer samples were carried through NMR and DSC techniques. Characterization of PP and mPP is given in chapter III.

LLDPE: ^{13}C NMR spectrum of the LLDPE sample is shown in Fig. 4.4 LLDPE is a substantially linear polymer, with significant numbers of short branches, commonly introduced by copolymerization of ethylene with longer-chain olefins like 1-butene, 1-hexene or 1-octene comonomers. The spectrum shows the signals at chemical shift values matching with the presence of an ethyl branched structure.

Introduction of 1-butene units among contiguous ethylene repeat units leads to the presence of an ethyl branch on the polymer backbone, having the following structure (Fig. 4.3):

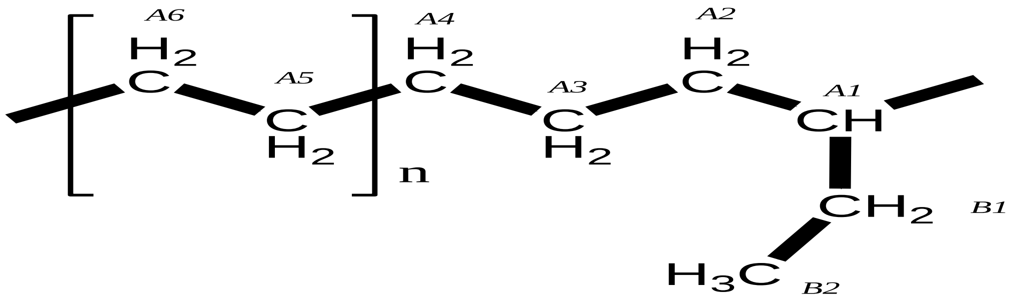


Fig. 4.3 Structure of LLDPE showing ethyl branch on polymer backbone

Contiguous 1-butene sequence shall lead to ethyl branches. It is clear from the spectrum that there is significant contiguous 1-butene sequence as well as other short branches in the LLDPE sample

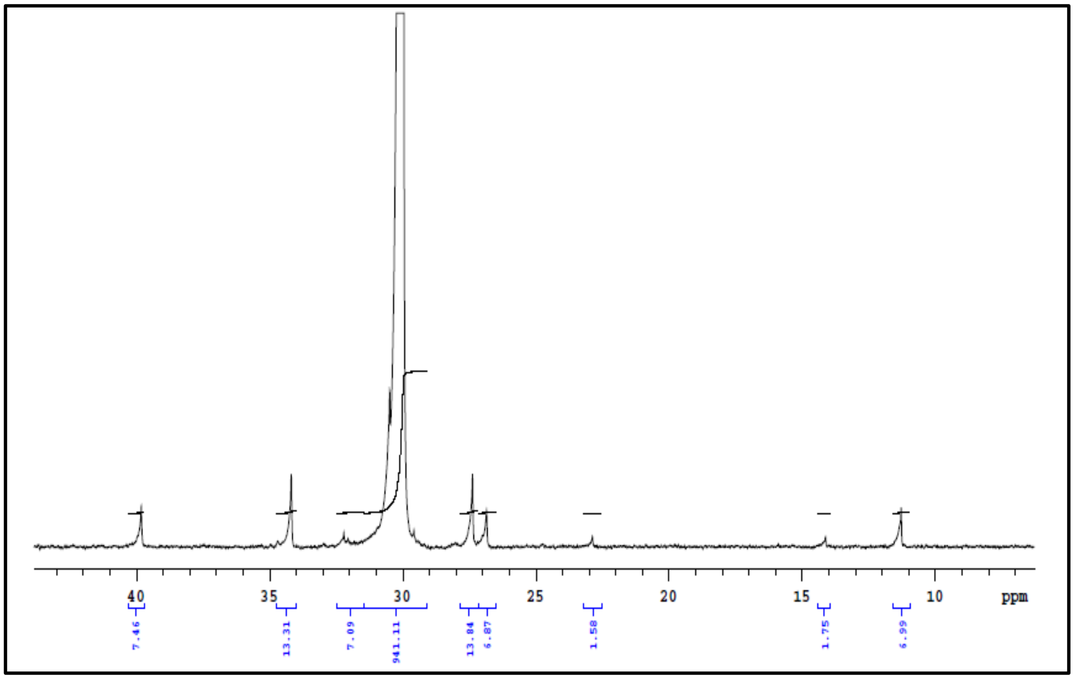


Fig. 4.4: NMR Spectra of LLDPE

4.4.2 DSC

A DSC measurement was carried out for all polymer samples. The thermograms corresponding to the second heating cycle were recorded and analyzed. Single endothermic peak appears at 132 °C for LLDPE, which can be attributed to its characteristic melting temperature, the fusion endotherm of PP and mPP shows the characteristic melting peaks at 161.5 °C and 160 °C respectively.

4.5 RESULTS AND DISCUSSIONS

4.5.1 Anti Wear Performance

Table 4.4 shows the weld load and wear scar dia results of the samples additised with one percent of triphenyl phosphorothionate, Dialkyl Dithiophosphate ester and ZDDP additives. The results show that the antiwear properties of all the additives are comparable but antiscuffing performance of triphenyl phosphorothionate is inferior to other additives. The antiwear and antiscuffing performance of ZDDP is marginally better than the other two additives. Further elaborative tribological studies of polymeric greases were carried out with ZDDP.

Table 4.4: weld load and wear scar diameters of greases additised with Triphenyl phosphorothionate, Dithiophosphate and ZDDP additives.

	ZDDP		Triphenyl phosphorothionate		Dithiophosphate	
	Weld Load (kg)	Wear Scar Dia (mm)	Weld Load (kg)	Wear Scar Dia (mm)	Weld Load (kg)	Wear Scar Dia (mm)
PP	180	1.0	140	1.0	160	1.0
mPP	200	0.65	140	0.7	180	0.65
PE	200	0.7	140	0.7	180	0.7
Li	200	0.65	140	0.65	180	0.65

Two sets of experiments were further carried out with greases additised with ZDDP. One set having the same consistency of NLGI 2 and the other keeping same thickener concentration for all the greases, irrespective of the consistency of the greases. Fig. 4.5 (a) shows the wear scar diameter with varying percentage of additives in different greases. The result indicates that under a constant load of 392 N, the wear performance of additive free grease depends on the type and content of the thickener in the greases. Amongst the three polymeric thickeners, PP and mPP showed high WSD and WSD of PE was similar to conventional Lithium lubricating grease. Moreover, the wear scar diameter of PP and mPP grease is also higher than the WSD of base oil itself (1.1>0.9), whereas the WSD of PE and Lithium grease is same as that of the base oil (0.9 and 0.9). This shows that the PP and mPP as a thickener in base oil behaves as a pro-wear component. Performance of Lithium grease is consistent with earlier findings [19]. The probable reasons for poor performance by PP and mPP thickener are discussed in subsequent paragraphs.

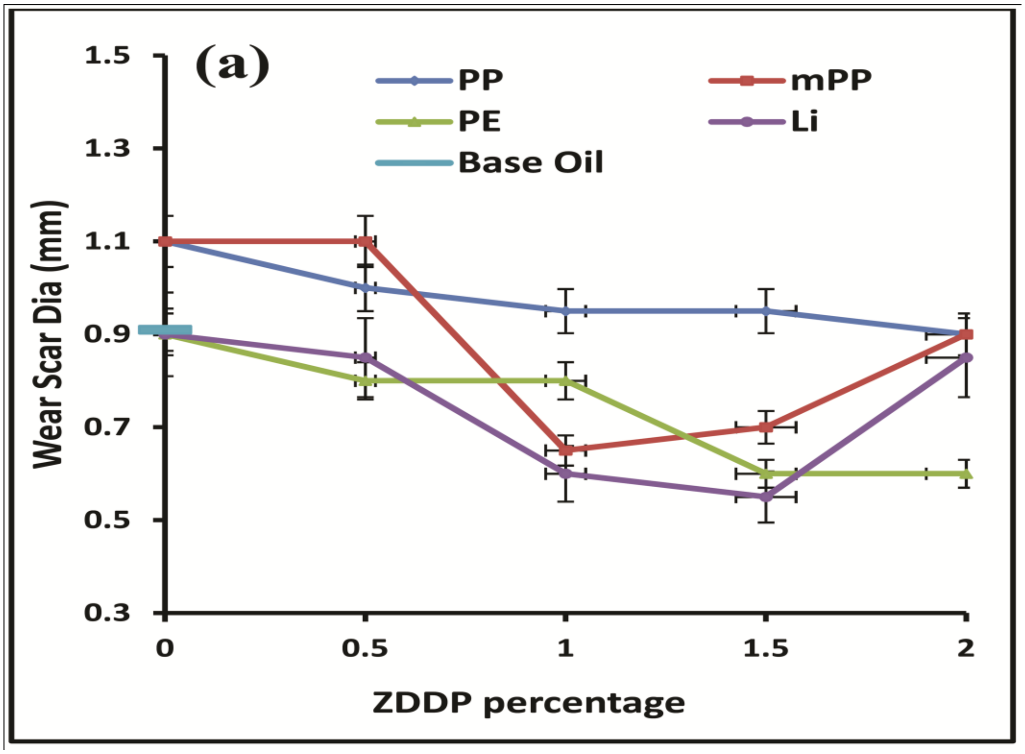
The variation of WSD with concentration of ZDDP for mPP and Lithium grease is similar to earlier reported values in base oil [20], low WSD at optimum concentration (%) and a sudden increase in WSD when concentration is increased to 2%. PP grease does not show any improvement in wear scar diameter with ZDDP, within the concentration range studied. On the other hand, for PE grease the WSD decreases initially up to 1% concentration and then remains constant throughout the concentration range studied. The consistency of all the above greases studied fall under same NLGI grade. From these results it can be inferred that the consistency of the grease does not directly influence the performance of the additive in polymeric greases.

ZDDP works by forming protective tribo and antifriction film over the surface. In base oil protective film formation is facilitated without hindrance due to free mobility of additive, but presence of thickener creates competitiveness for adsorption and film formation between additive and thickeners. In addition to the above factors, percentage of polymer in the lubricating grease is supposed to influence ZDDP effectiveness. Since the thickener content in PP is very high (18%) it shows poor wear scar property as compared to mPP, PE and Lithium greases having thickener content 15.5, 9 and 9% respectively.. Poor performance of additives with higher thickener concentration is earlier reported by T. Kazutoshi et al [21]. Another observation is that the antiwear response of additive is better in the grease containing higher percentage of base oil [91% (Li) = 91% (PE) > 84.5% (mPP) > 82% (PP)].

In order to study the effect of thickener content and polarity on the performance of ZDDP, a further study was carried out with varying thickener concentration. Fig. 4.5 (b) shows the result of wear scar diameter with varying thickener composition for Lithium and PP grease. Data of mPP and PE thickened grease is not shown for the reason that PP and mPP grease show similar results whereas preparation of PE grease with higher PE content is difficult by normal procedure as the product becomes rubbery and cannot be milled to obtain grease. It is clear from the Fig. 4.5 (b) that for polymeric thickener there is a critical thickener concentration beyond which additives response is affected. The critical thickener concentration for good additive response in case of PP and mPP thickener is below 15-16 percent. Performance of the additive in Lithium grease is not affected by thickener concentration. However, a similar study could not be performed for PE thickener for above mentioned reason.

A. Naveira Suarez et al [22] in a study with base oil of different polarity reported that the film formation and antiwear activity of ZDDP depends on the polarity of the components present in the lubricant. The non polar component present in the lubricant do not hinder the access of additive molecule to the surface whereas polar component due to its higher affinity competes with the additive molecule to adhere to the surface and therefore, restricts antiwear film formation by the additive molecules. Contrary to the above, Lithium grease shows better performance than the other polymeric thickeners. mPP grease does not show similar performance as Lithium grease, may be due to low percentage of grafting, which may not be sufficient enough to influence highly polar additive for the antiwear performance.

The above finding is difficult to understand and explain as per general belief that presence of polar component in lubricant adversely affects the tribological performance of ZDDP [22]. In that context additized PP and PE grease would have shown similar or better results than Lithium grease and increasing thickener content in Lithium grease would have adverse effect on wear performance. Similarly, an increase in PP content would have resulted in better wear performance or no effect at its worst. Following is the reasoning and explanation proposed by H.B. Silver et al. [12]. A study of clay and graphite thickened greases and additive seems most justified in this case also. Authors discussed that a polar thickener interacts with polar additive molecules and acts as a carrier for the additive to bring it to the metal surface. Hence, increase in polar thickener concentration should not adversely affect the performance of polar additives. On the other hand non polar thickener does not interact with additive molecules and presence of such thickener is deterrent to the additive's performance and an increase in such thickener concentration is less beneficial. In the present study polymer are non-polar/less polar compared to Lithium soap thickener. Therefore, in line with the explanations provided in reference 13, the AW performance of polymeric greases with ZDDP will be either equivalent or poor to Lithium grease.



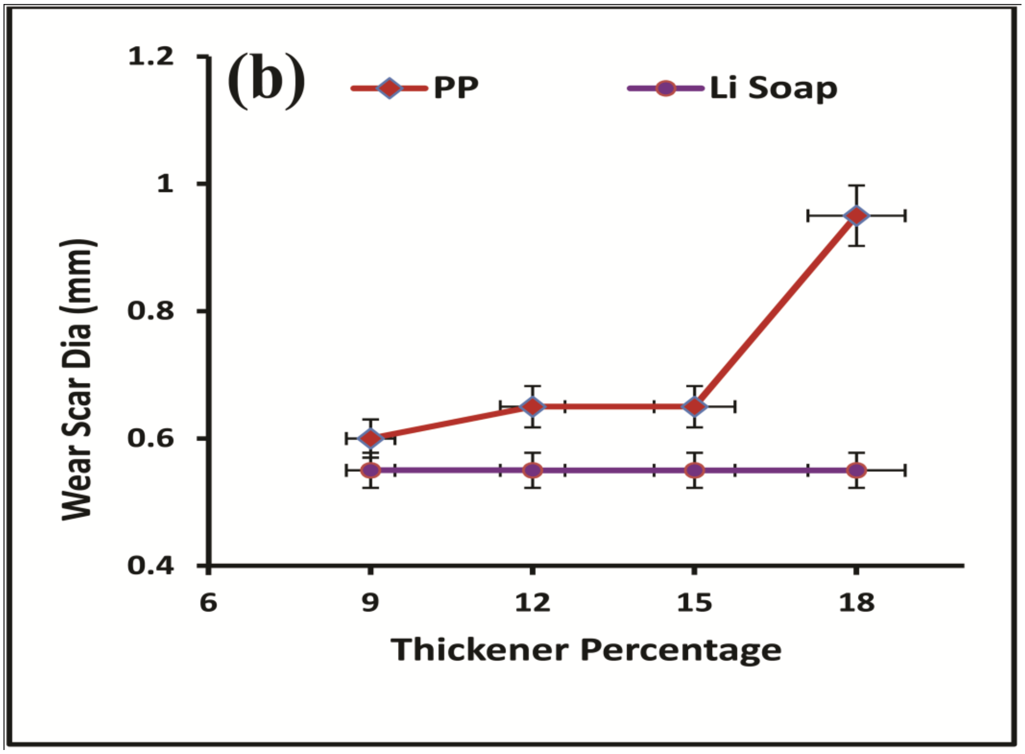


Fig. 4.5: (a) Wear scar diameter of the greases with varying ZDDP composition. (b) Wear scar diameter of PP and Li grease with varying thickener content and 1.5 percent of ZDDP.

4.5.2 Load-carrying Capacity

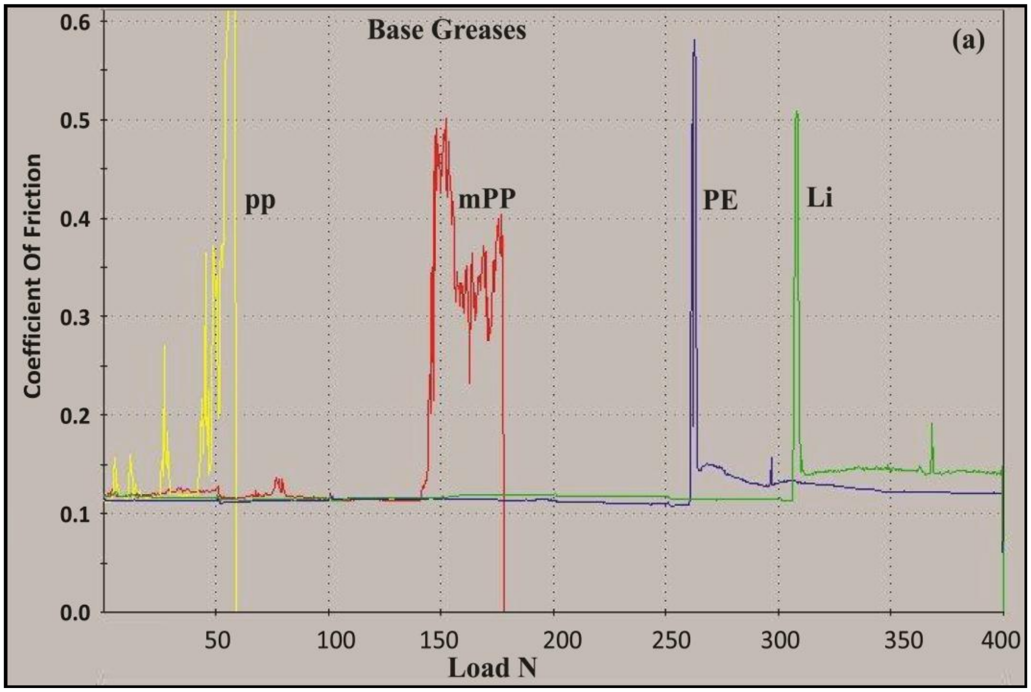
ZDDPs are reported to enhance the load carrying property of the lubricants also [23]. Load carrying capacity (L_W values) of base greases and with 1.5% ZDDP are shown in Table 4.5. It can be seen that the L_W value of PP and mPP; PE and Lithium base grease are same i.e. 160 and 180 kg. The load carrying capacity of PE and Lithium base grease are 12.5 % higher than PP and mPP base grease. The L_W values of the greases containing 1.5% ZDDP is in the following order-Lithium (280) = PE (280) = mPP (280) > PP (250). Although the load carrying capacity of PP and mPP base grease is identical, the improvement in load carrying capacity with 1.5% additive for mPP grease is 12% higher. The response to load carrying capacity of PE and Lithium grease are same and they show at least 55 % improvement than that of the base grease. It is evident from the table that although the L_W values of mPP, PE and Lithium grease with additive are identical (280 kg), the order of additive effect is still mPP>PE=Lithium. We suppose that this may be due to the following reasons: grease with high thickener content show poor response to additive which can be seen from the result that grease with higher thickener content (PP grease, having 18% thickener) show least improvement in EP property than grease with lower thickener content (mPP, PE and Lithium, having 16.5, 8 and 9% thickener respectively). The SEM image (Fig. 4.8) of worn surface of balls also reveals that in PP thickened sample does not show phosphorus and zinc film. Only scanty Sulphur film was observed as compared to other samples.

Table 4.5: Load carrying capacity (L_W) of base greases (in kg); with 1.5 % additive and wear scar diameter of different greases without additive (in mm)

grease	**L_W** Without additive (Kg)	L_W with Additive(Kg)	WSD without additive (mm)
PP	160	250	1.1
mPP	160	280	1.1
PE	180	280	0.9
Lithium	180	280	0.9

4.5.3 Friction Reducing Performance

The friction data of base grease and greases additized with ZDDP are given in Fig. 4.6. Poor antifriction behavior was observed in case of PP and mPP grease whereas PE and Li base greases were better. The order of antifriction behavior for all the base greases is Li>PE>mPP>PP (Fig. 4.6 a). However, ZDDP is mainly used as an antiwear and antioxidant additive, SRV result shows that ZDDP significantly influences the scuffing load of the greases. PP, mPP, PE and Li greases scuffed at 50, 150, 200 and 250N loads respectively without ZDDP. In presence of the additive all the greases sustained up to 400N load (Fig. 4.6 b). However very high coefficient of friction was observed in case of PP and mPP at intermediate loads, and at higher loads (above 300N) all greases behaved similarly. The high friction coefficient observed at intermediate load in case of PP additized and mPP additized was as expected due to poor film forming property by ZDDP in PP type thickeners as discussed in earlier section.



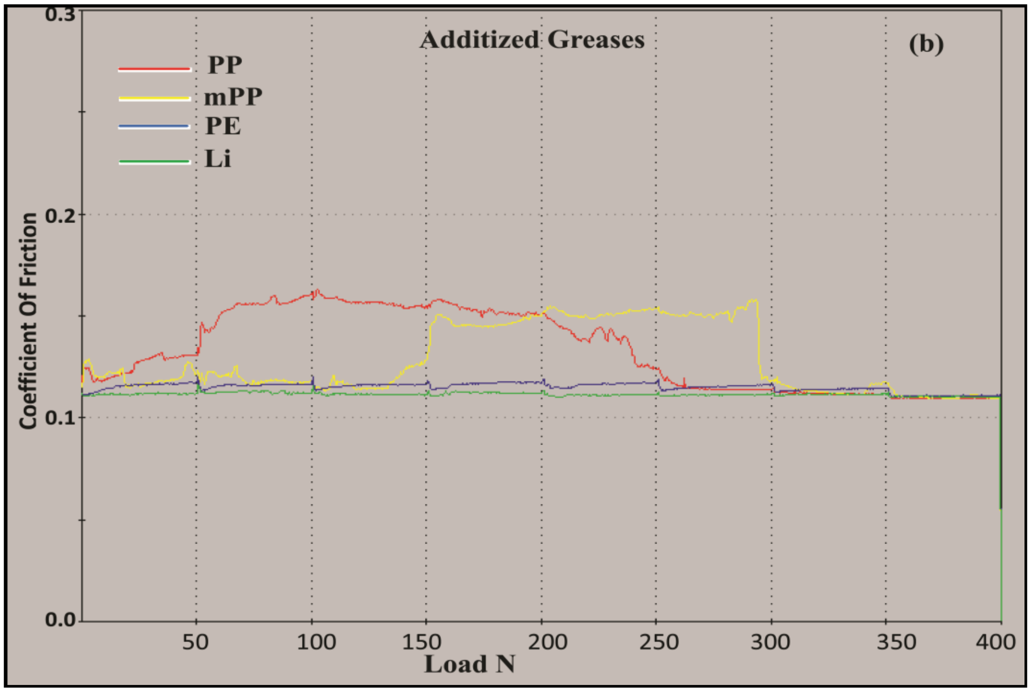
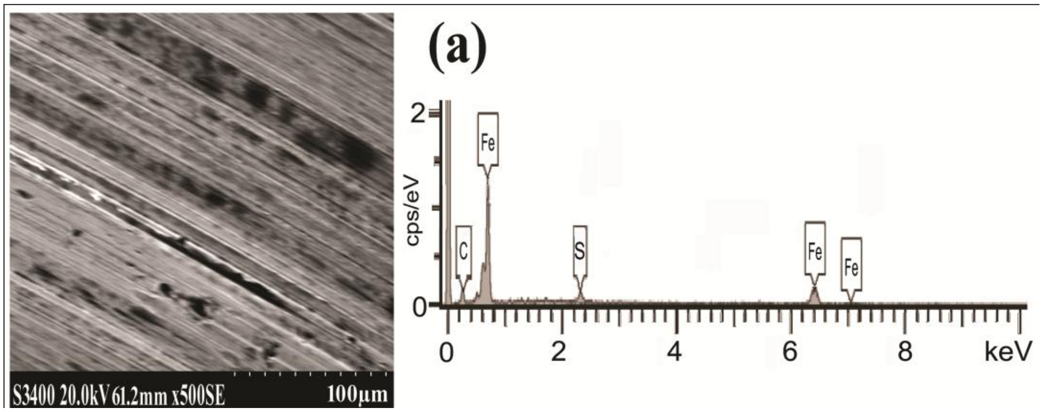


Fig. 4.6: Coefficient of friction by SRV at 50°C. Base greases (a) and additized greases (b)

4.5.4 Surface Analysis

SEM EDAX was carried out on the worn surface of steel balls after Falex Four Ball Wear test. The SEM images of worn surface lubricated with different lubricating greases containing 1.5% ZDDP are shown in Fig. 4.7. It clearly shows that the tribofilm of mPP and PE (Fig. 4.7 b & c) are quite different from PP and Li greases (Fig. 4.7 a & d). Worn surface lubricated by PP grease shows some scuffing sign and abrasive wear. Contrary to the above, abrasive wear was not observed in mPP, PE and Li grease lubricated surfaces. Scarred surface lubricated with mPP and Lithium greases were uniform and smoother than PP lubricated surface and shows signs of existence of good surface protective film. Though the surface lubricated with PE grease shows deep wear marks but the wear scar diameter and EP property was similar to mPP and Li greases. Energy-dispersive spectroscopy (EDAX) shows that the content (low intensity peak) of sulphur element on PP lubricated scarred surface is lowest than that of other greases. Moreover, no phosphorus and zinc elemental peaks are observed in case of PP lubricated film. ZDDP's antifriction mechanism is facilitated by phosphate film formation, absence of phosphorus and zinc confirms that the PP as a thickener hinders the phosphate film formation by ZDDP. As a result high wear scar diameter was observed with PP grease lubricated surface. Contrary to the above good and evenly distributed sulphur, phosphorus & zinc (Fig. 4.8) film and more intense sulphur peak were observed in worn surfaces lubricated with mPP, PE and Lithium greases.



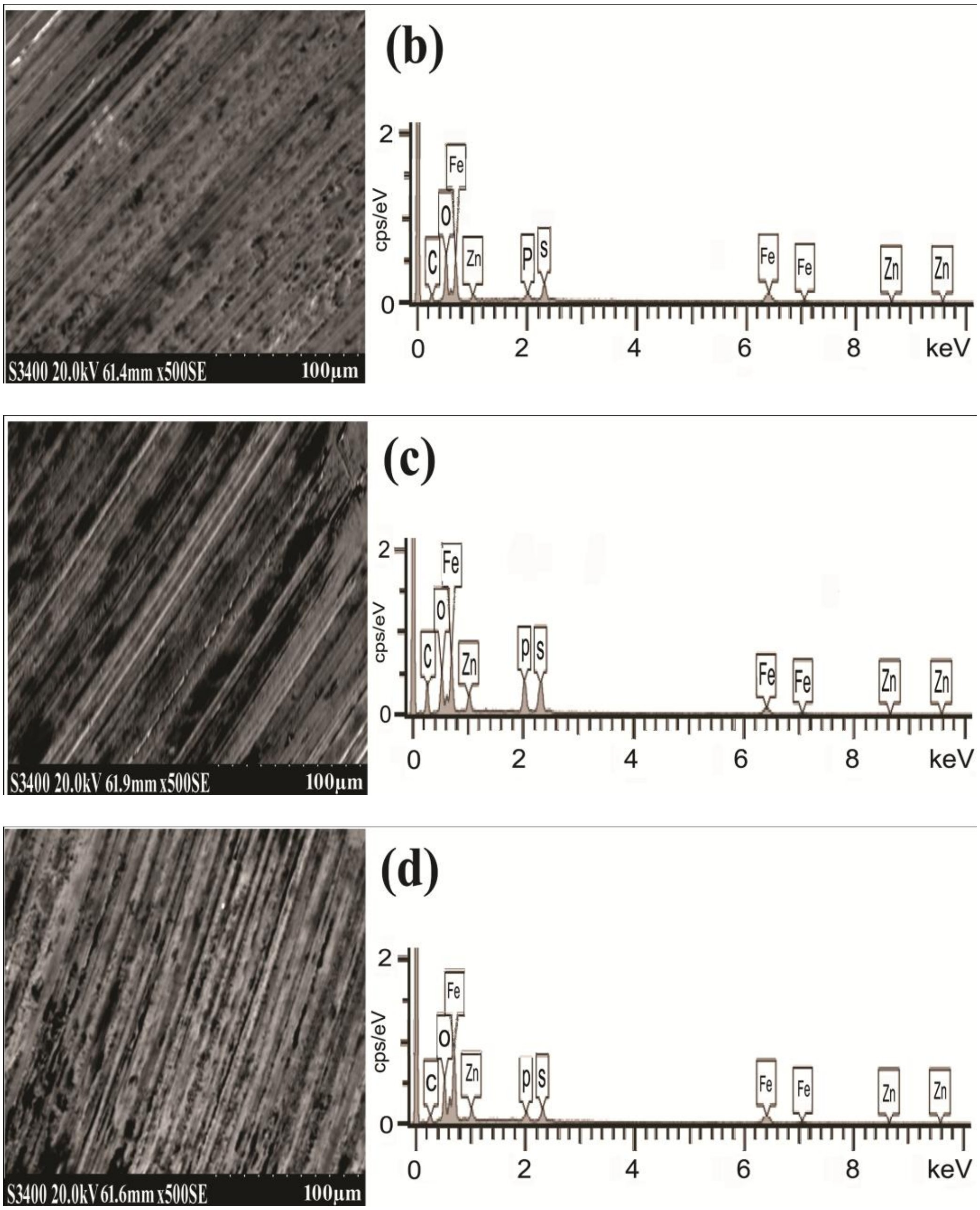
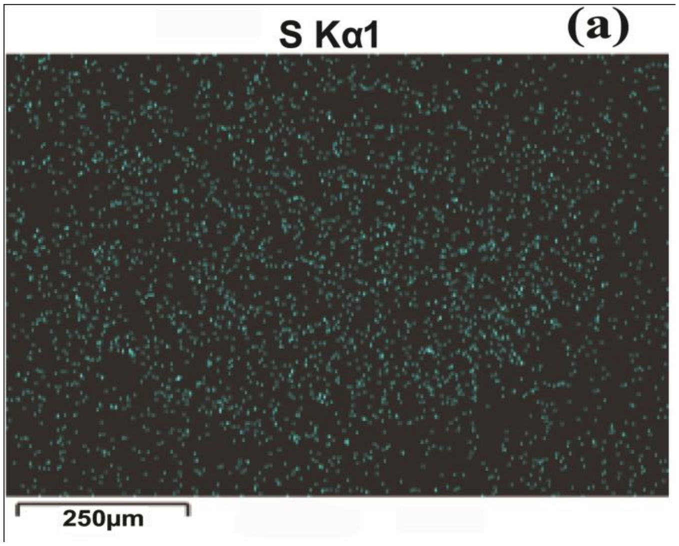
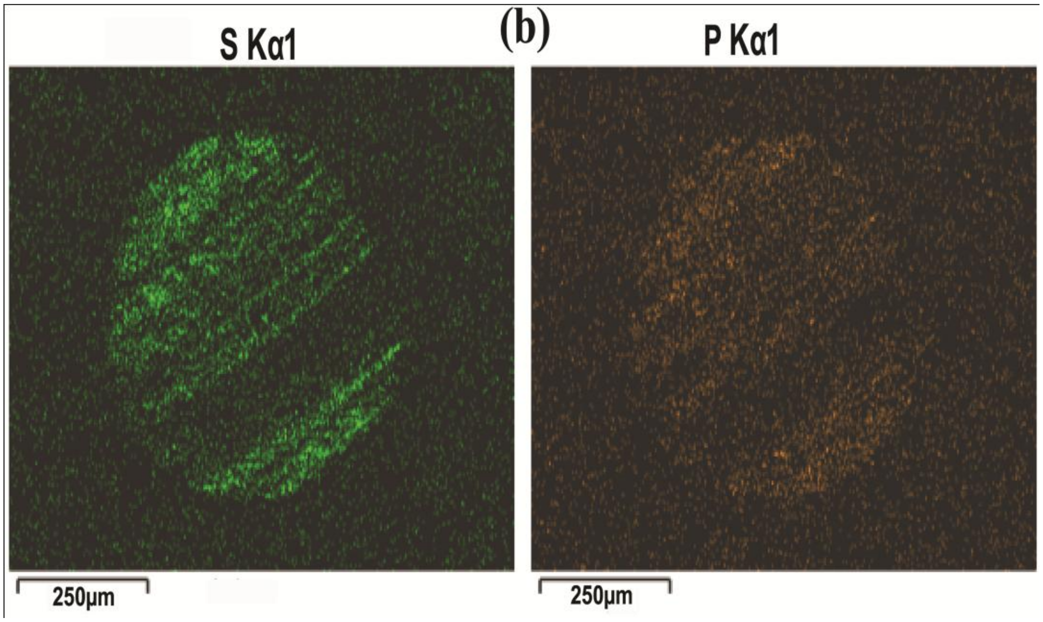


Fig. 4.7: SEM image and elemental peaks of worn surface. Additized PP grease (a), additized mPP grease (b), additized PE grease (c) and additized Li grease (d).


S Kα1
(a)
250µm


(b)
S Kα1
P Kα1
250µm
250µm

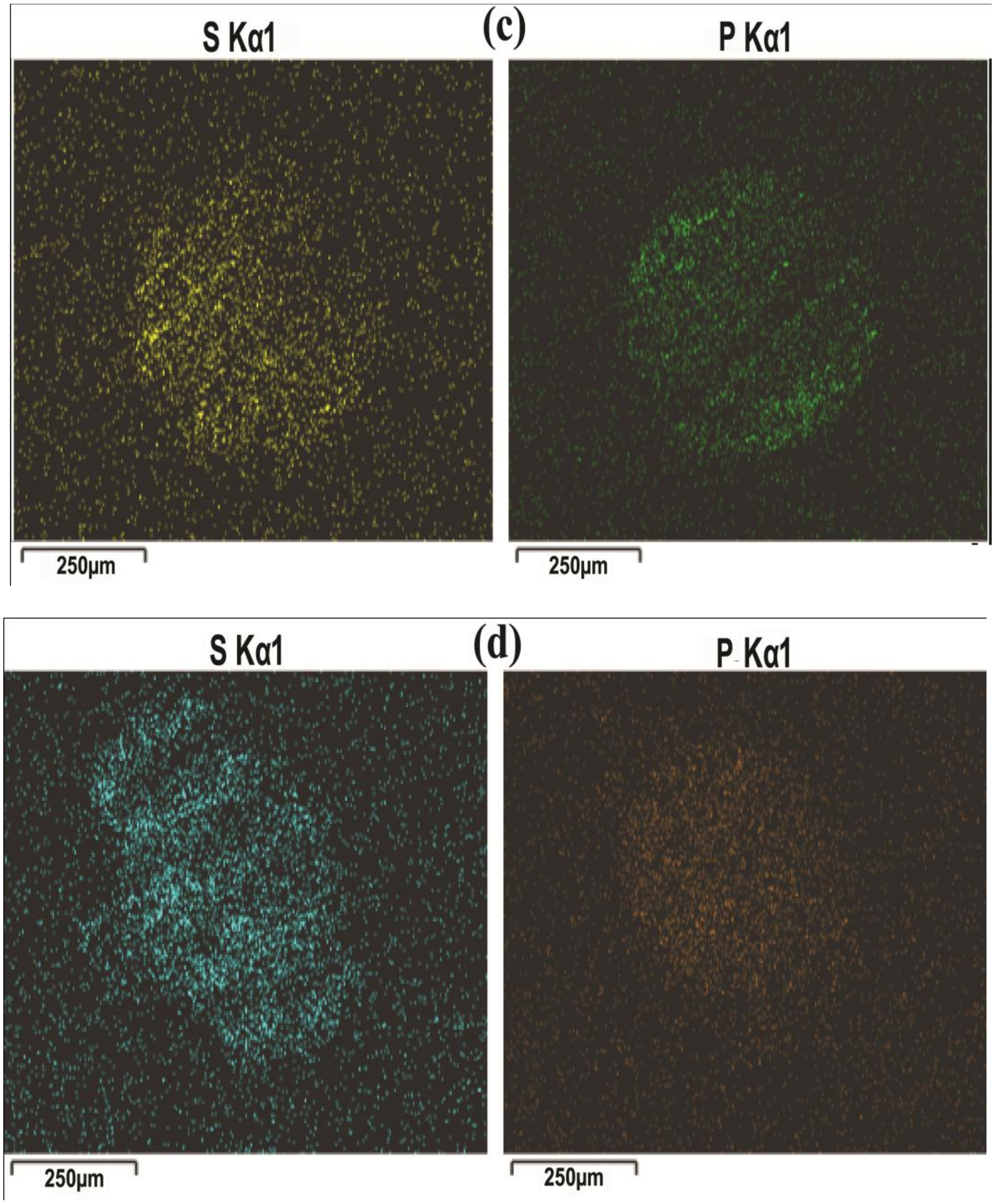


Fig. 4.8: Distribution of elements in SEM image of worn surface of steel balls. Additized PP grease (a), additized mPP grease (b), additized PE grease (c) and additized Li grease (d).

4.6 CONCLUSIONS

From the above experimental work and results, the following conclusions can be drawn:

- Under boundary lubrication condition, the performance of ZDDP depends on the type and percentage of thickener present in polymeric lubricating grease.
- Antiwear, EP and antifriction performance of ZDDP in mPP, PE type thickener was similar to Lithium lubricating grease.
- With ZDDP additive PP thickener can be used only up to an optimum concentration for better additive response.
- In PP type thickener the antifriction and antiwear performance of ZDDP was poor but EP property was not much affected.
- ZDDP is an effective antiwear additive for Lithium base greases and can be applied to polymeric type greases as well, except for the PP thickened lubricating grease.

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CHAPTER V

STUDY ON TRIBOLOGICAL BEHAVIOR OF POLYMER GREASES WITH FULLERENE LIKE FUNCTIONALIZED NANO WS_2

STUDY ON TRIBOLOGICAL BEHAVIOR OF POLYMER GREASES WITH FULLERENE LIKE FUNCTIONALIZED NANO WS_2

5.1 INTRODUCTION

Polymers have proven to be excellent thickeners and Rheology modifiers for lubricating greases [1]–[5], but comparative high wear rate than lithium and lithium complex grease is the biggest setback for polymer thickened lubricating greases, specially polypropylene (PP) and mah-g polypropylene (mPP) thickened lubricating grease [Table 5.2]. The conventional additive S and P containing additive such as ZDDP which perform very well with lithium and lithium complex greases is not as effective in polypropylene greases. Function of conventional tribological additive involves complex physical and chemical reactions over the contact surface. During the friction process a protective film is formed by physisorption, chemisorption and tribochemical reactions on the tribological contact, which is highly influenced by the interactions/synergism of additive with the other components present in the system [6]–[8].

Plethora of published research work is available on nano particles to investigate their effect on friction or wear property in tribological contacts [9]–[13]. Inorganic fullerene-like metal dichalcogenides such as WS_2 present better tribological performance than carbon based fullerenes [14], [15]. As an additive they significantly improve the tribological performance of lubricant [16]–[21], apart from that they are inert, non toxic, non-magnetic and highly resistant to oxidative and thermal degradation [22]. unlike the S and P containing additives they do not involve complex tribochemical reaction, rather these particles are supposed to roll over the contact area and thus acting as a spacer which eliminates metal to metal contact between two mating metal surfaces. More over their spherical shape confers them chemical inertness thus, unlike ZDDPs selectiveness to thickener type these compounds can be supposed to perform well in a multi-component system like greases irrespective of the nature of the thickener. Another class of compounds which can be used as antiwear additives are ionic liquids, these compounds have shown remarkable antiwear and antifriction performances [23]–[26].

The aim of this work is to study the tribological performance of fullerene like nano WS_2 particle functionalized with sodium metaphosphate and tetrabutylphosphonium methanesulfonate ionic liquid under boundary lubrication as an additive in polymeric lubricating greases. In this work the antiwear and antiscuffing efficiency of functionalized nano WS_2 and ionic liquid was compared and the better performing additive was further studied in severe friction condition with different polymer thickened greases. Coefficient of friction, four ball weld load and four ball wear machine was used for tribological tests, Scanning Electron

Microscopy-Energy Dispersive Spectroscopy (SEM-EDAX) was used for analysis of worn surface after four ball wear test.

5.2 AIM OF THE PRESENT WORK

Compounds containing any one, two or all the three from Sulphur, phosphorus and zinc are widely used as an additives to enhance AW and EP characteristics of lubricants and lubricating greases. Much work has been published concerning the role of these additives and there has been continual effort to further improve the performance potential of these additives. No doubt these additives have served the industries very long at their best, they have some performance limitations and it is high time to look beyond these conventional additives to get further performance enhancements. Nano additives and recently ionic liquid additives has gathered the attention of researchers as they have broken the established performance barriers and shown excellent tribological performance. And yet another class of additives is nano particles functionalized with some active tribological compounds.

In previous chapter it was observed that conventional additives are selective towards thickener in their performance. The current work is focused to study the tribological performance of non conventional additives in polyolefin thickened greases. In this work two different class of additives viz. functionalized nano WS_2 and ionic liquid will be studied. The additive with best result in AW/EP will be selected for further study.

- Functionalized nano WS_2, and Ionic liquid (Tetrabutyl phosphonium methane sulfonate) are selected for the study.
- These two additives will be doped in to the polymeric and lithium grease individually and will be tested for antiwear and EP properties by four ball test methods.
- The additive with best antiwear and EP result will be further tested in all the greases in various concentrations.
- The worn surface of the steel balls after four ball wear test will be investigated with SEM image and SEM EDAX.
- Coefficient of friction test of the selected grease will also be carried out with SRV testing machine.
- For ambiguous result in SRV test further investigation with SEM image or SEM EDAX will be carried out.

5.3 EXPERIMENTAL SECTION

Materials, methods used for characterization of physical and chemical properties of all the polymer samples used as a thickener are given in previous chapters. Some physical properties of additives and structure of ionic liquid as provided by supplier is given in Table 5.1 and Fig. 5.1.

Table 5.1: Physical properties of additives used

	Functionalized WS_2	Tetrabutylphosphonium methanesulfonate
Appearance	Dark paste	Crystalline white solid
Density, g/cm^3	1.30-1.60	n.a.
Melting point ^oC	n.a.	59-62
Penetration(P_{60}), 0.1 mm	330-370	n.a.
Concentration on nano powder in paste, %	50-80	n.a.
Phosphates/sodium hexametaphosphate content	70-95%	n.a.

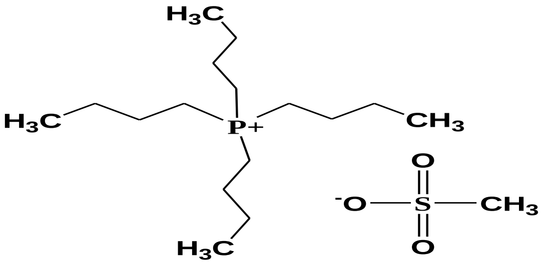


Fig. 5.1: Structure of ionic liquid

5.4. RESULTS AND DISCUSSIONS

5.4.1 Tribological properties

Blends of polymeric greases and lithium grease were prepared containing 0.5, 1.0 and 2.0% of Ionic liquid. Weld Load and WSD were measured for all the samples but no improvement in WL and WSD was observed. Further studies were carried out with functionalized nano WS_2. The wear scar property of additized and additive free greases are shown in Fig. 5.2. The results indicate that the wear performance of additive free grease depends on the thickener type in the greases. Among all two polymeric thickeners PP and mPP shows high wear scar diameter and WSD of PE is similar to conventional Lithium lubricating grease. Moreover, the wear scar diameter of PP and mPP grease is also higher than the WSD of base oil itself (1.1>0.9), where as the WSD of PE and Lithium grease is same as that of the base oil (0.9 and 0.9). Performance of Lithium grease is consistent with earlier findings. PP and mPP in base oil behave as pro-wear components. Author hypothesized that under pressure polymers flattens and oil is squeezed out of the contact zone and polymers retract and shrink back when pressure is released leaving starved surface and high Wear Scar Diameter.

In order to find optimum concentration for obtaining best tribological performance, several percentage compositions (1, 3, 5 and 7 wt%) of nano WS_2 were tested for four ball wear. Fig. 5.2 shows that addition of 5% or more nano additive is required to produce reduction in wear scar diameter as compared to base greases. Only PE grease shows improvement in wear property at minimum additive concentration i.e. 1% and shows consistent improvement in wear scar diameter with increasing additive concentration. Best results of additive were obtained in PE and Li greases. It has been shown that PP and mPP thickened grease show marginal improvement with low additive concentration. Above 5%

additive concentration PP and mPP grease show good improvement in wear property but comparatively less improvement than PE and Li greases.

In the present study the antiwear performance of all the thickeners including Li soap are very good with the functionalized nano WS_2 additive. Performance was not similar in all the thickeners quantitatively but was substantially good as compared to ZDDP. Unlike S and P containing additives which involve complex tribochemical reactions to produce tribofilm to prevent wear between the rubbing metal surfaces, nano additives present between the metal surfaces prevent the direct contact between them and thus prevent wear by acting as nano bearings [27]. The nano additives are more effective for the thickeners which interfere in the tribochemical reactions thus inhibiting the antiwear activity of the additives. On the other hand the lubrication mechanism of nano additive largely based on physical phenomena. Thus polymer thickened greases like PP and mPP which show least antiwear property with S and P containing additive show good antiwear response with functionalized WS_2 additive.

Table 5.2: Load carrying capacity (L_W) of base greases (in kg); with 7 % additive and wear scar diameter of different greases without additive (in mm)

grease	L_W Without additive (Kg)	L_W with additive(Kg)	WSD without additive (mm)
Polypropylene	160	800	1.1
Mah-g Polypropylene	160	800	1.1
Polyethylene	180	700	0.9
Lithium	180	800	0.9

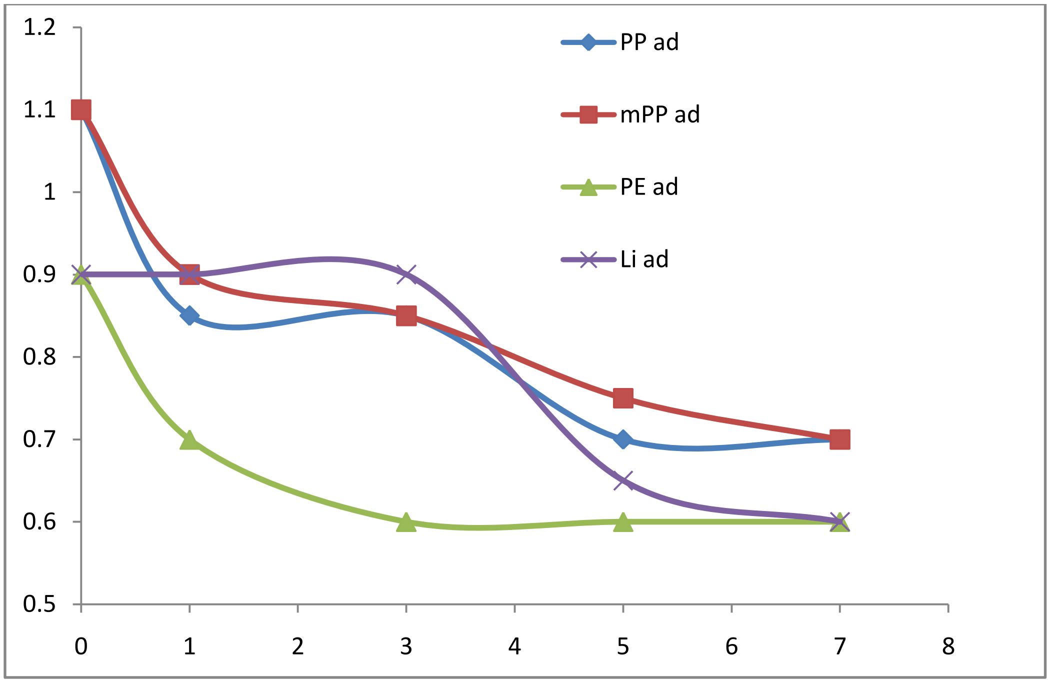
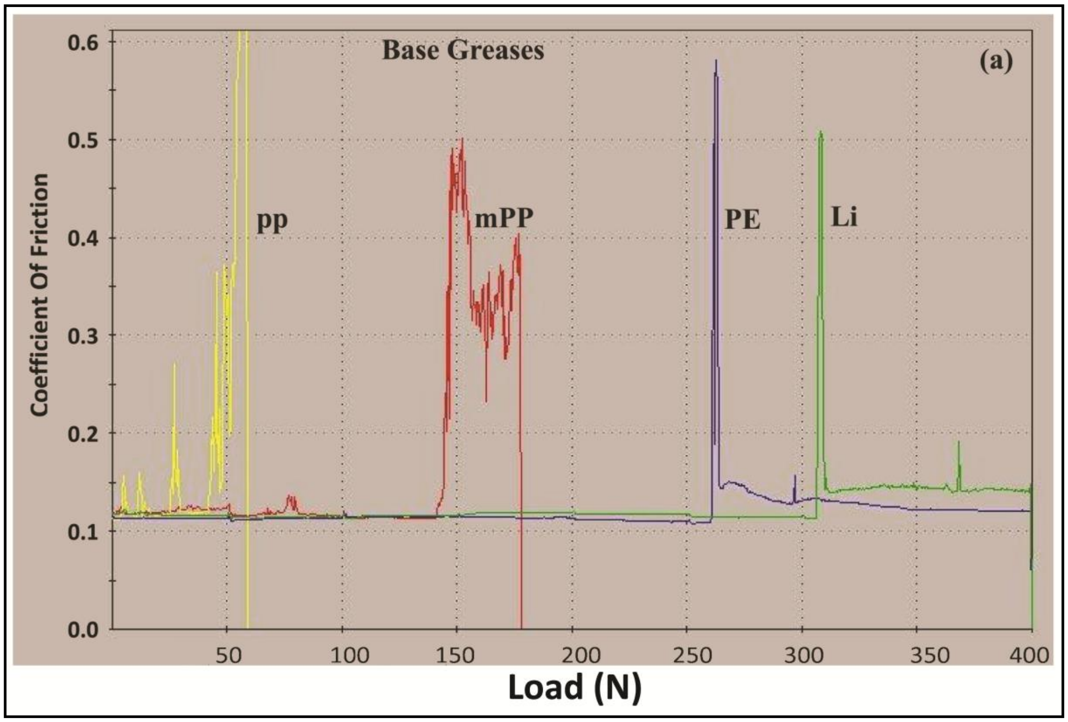


Fig. 5.2: Wear Scar Diameter (X-axis) of the samples after four ball wear test with respect to additive concentration (Y-axis).

5.4.2 Coefficient of friction and Four Ball Weld Load

Fig. 5.3 (a) shows the coefficient of friction of all the base greases and Fig. 5.3 (b) shows the coefficient of friction of the greases additized with 5% functionalized nano WS_2. It is evident from the Fig. 5.3 that the base greases show variable and very poor friction coefficient even at very low load of 50N. PP thickened base grease could not sustain even 50N load and failed, mPP, PE and Li grease failed at 150, 300 and 350 respectively. Lithium base grease is better among all the base greases studied. On addition of 5% nano additive frictional performance of all the greases except PE grease was improved substantially and did not fail even at higher load of 400N. PE thickened lubricating grease shows unexpected performance and failed at a load of 400N. The carbon residue found over the SRV disc (Fig. 5.6e) indicates the degradation of PE thickener component and it is speculated that the temperature of the contacting metal surface lubricated with additized PE grease rises >300 ^oC causing thickener and additive degradation. L Rapoport [28] in a study of Fullerene like nano WS_2 in lubricating oil reported that the performance of additive diminished when the temperature of the contacting metal surface rises above 320 ^oC or above the oxidation temperature of the nano additive However, more work is required to strengthen this hypothesis. Similar performance trend was observed in antiscuffing properties of all the greases. PP, mPP and Lithium greases show highest improvement in scuffing load i.e from 160/180 to 800 kg. PE grease shows slightly lower improvement in scuffing load i.e. from 180 to 700 kg.



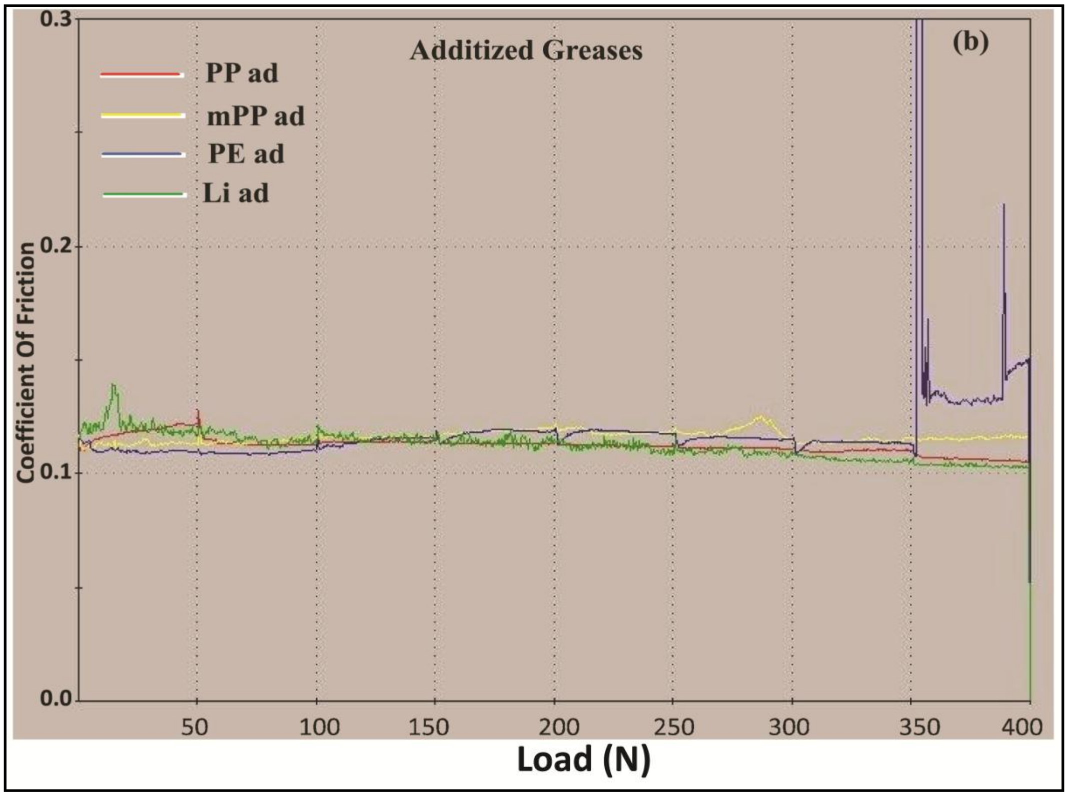


Fig. 5.3: Coefficient of friction by SRV at 50°C. Base greases (a) and additised greases (b)

5.4.3 SEM (EDAX)

The SEM images of worn surface after four ball wear test as well as after frictional test are shown in Fig. 5.4 to 5.6. From Fig. 5.4 it is clearly visible that the wear profile of the balls directly corresponds to the antiwear performance of the grease under study. The greases (PE and Li) having low wear have comparatively smooth wear track and low wear marks on the worn surfaces of steel balls after four ball wear test, on the other hand greases (PP and mPP) with high wear have deep wear tracks and more wear marks on the worn surface.

Smoothest wear mark was observed with PE lubricated surface which has minimum wear scar diameter.

SEM images of ball and disc after frictional test was also carried out for all the four samples. In the Fig. 5.5 and 5.6 it can be clearly seen that the samples having low coefficient of friction have smooth wear marks on balls as well as discs. The disc and balls lubricated with additized PE grease which failed in friction test at 400N, shows patches of deep wear marks on the ball and very rough and cracked wear surface on the disc. All the other discs and balls have similar wear marks over the surface (wear marks on Lithium lubricated balls could not be located hence not shown in the images).

SEM image of all the samples after four ball wear test were also carried out to study elemental distribution on the wear surface. Tungsten was not found in any of the worn surfaces as expected since it was not involved in tribochemical reaction and rather it worked as a spacer between two mating metal surfaces. Only some sulphur and phosphorus films were observed which could arrive from the functional group “sodium metaphosphate” attached with the WS_2.

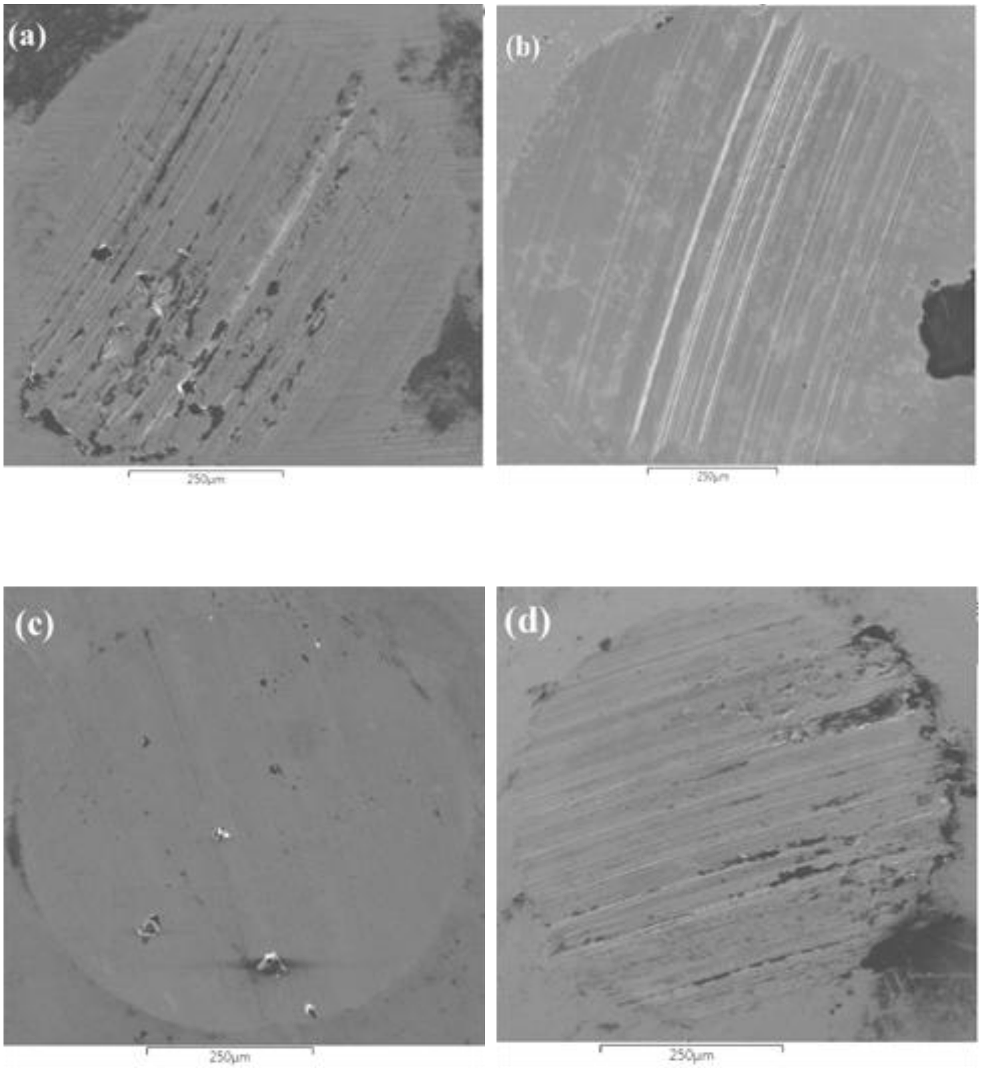


Fig. 5.4: SEM image of worn surface after four ball wear test. Additized PP grease (a), additized mPP grease (b), additized PE grease (c) and additized Li grease (d).

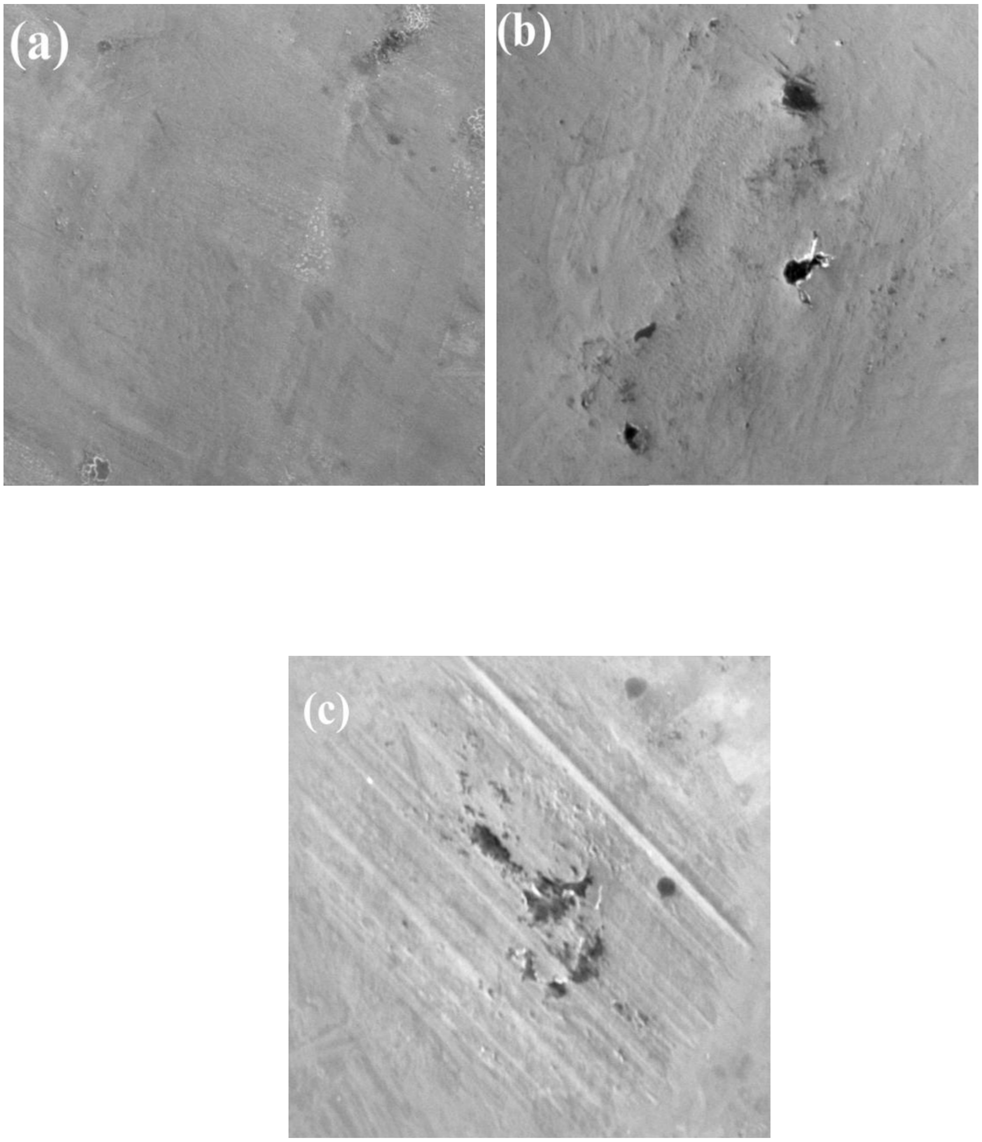


Fig. 5.5: SEM image of worn surface of balls after srv test . Additized PP grease (a), additized mPP grease (b) and additized PE grease (c).

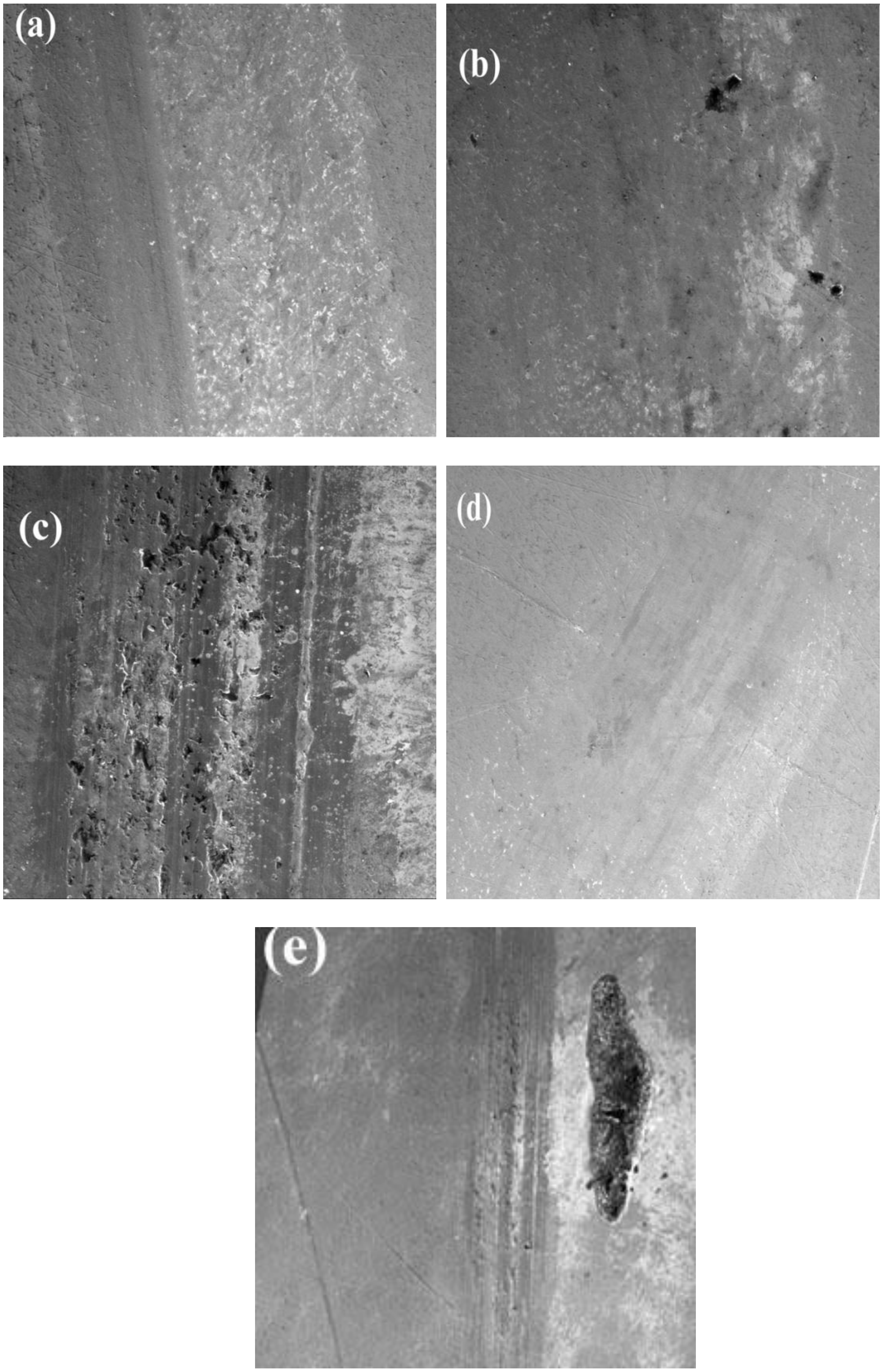


Fig. 5.6: SEM image of worn surface of disc after srv test . Additized PP grease(a), additized mPP grease(b), additized PE grease(c), additized Li grease (d) and carbon residue over disc of additized PE (e).

5.5 CONCLUSIONS

- Response of functionalized WS_2 depends on the type of thickener in the lubricating greases.
- WS_2 is equally effective to improve antiwear property of all the greases but PE thickener responds even at very low additive concentration.
- Good antifriction and antiscuffing property was obtained in additized PE grease then the base grease. However the improvement was quantitatively poor as compared to the other greases.
- Functionalized nano WS_2 was found to be a better additive for polymeric thickened greases.

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CHAPTER VI

“STRUCTURE – PROPERTY” CORRELATION OF POLYMERIC GREASES

“STRUCTURE – PROPERTY” CORRELATION OF POLYMERIC GREASES

6.1 INTRODUCTION

Polymeric greases have many advantages over the soap based greases such as ease of manufacturing, less manufacturing time, lower process temperature better response of performance additives , etc.[1-3]. But on the other hand, polymeric greases suffer from the drawbacks of specific manufacturing requirements, high bleed tendency, low dropping point, etc. [4]. In nut-shell, selection of polymeric grease for industrial applications would be a trade-off between its positives and negatives.

It is an established fact that the polymeric grease exhibit better thermal stability. Al-Sammerrai studied thermal stability of polypropylene and polyethylene base grease by TGA and DSC techniques and concluded that PP and PE base greases are better in thermal stability than the lithium base grease [5]. In previous chapters manufacturing procedures, oil bleed tendency, rheological response and tribological studies of polymeric greases with conventional and nano additives were studied in detailed individually. This chapter deals with the thermo-oxidative characteristics of polymeric base greases and greases additised with conventional and nano EP/AW additives in comparison to lithium grease.

6.2 AIM OF THE PRESENT WORK

Polymer thickened greases have great potential as industrial lubricants. However, most of the industrial applications demand lubricant to work at high temperature, speed and loads. Suitability of the polymeric greases for such applications can be assessed through determination of various physico-chemical properties such as dropping point, oil bleed and oxidation & thermal stability. These properties in turn depend on the composition and manufacturing process of the polymeric grease. Present study focuses on the manufacturing process and ‘structure-property’ correlation study of various polymeric greases in comparison to commercial Lithium grease. Polypropylene (PP), maleated-PP (mPP) and Linear Low Density Polyethylene (PE) prepared in mineral base oil were studied. Effect on dropping point, oxidation stability, thermal stability and oil bleed of both polymeric and Lithium greases containing conventional EP/AW additive i.e. Zinc di-alkyl di-thiophosphate (ZDDP) and a functionalized nano WS_2 EP additive was also studied. In addition to their physico-chemcial properties, greases were also analysed by Pressure Differential Scanning Calorimetry (PDSC), Scanning Electron Microscopy (SEM), Thermo-Gravimetric Analysis (TGA).

Effect of thickener and additives on greases structure was considered for explanation of the results obtained.

6.3 EXPERIMENTAL

6.3.1 Materials used, Grease Manufacturing procedure, Grease Testing and Scanning Electron Microscope (SEM) study are described in previous chapters.

6.3.2 Pressure Differential Scanning Calorimetry (PDSC) analysis

Oxidation onset temperature of the lubricating grease at desired test temperature was determined as per ASTM D 5483 test method using Q20P Pressure Differential Scanning Calorimeter from M/s TA Instruments.

6.3.3 Thermo-Gravimetric Analysis (TGA)

Thermal degradation of grease samples in the temperature range 0° to 800° C, both in air and inert atmosphere(Nitrogen) was determined by Universal V2.4F equipment of M/s TA instruments, UK.

6.4 RESULTS AND DISCUSSION

Three different polymeric greases with and without additives in NLGI grade 2 consistency were prepared with PP, mPP and PE respectively. NLGI grade of the commercially procured Lithium EP grease was also 2. Physico-chemcial test data generated on all four greases is compiled in Table 6.1 & 6.2.

Table 6.1: Physico-chemcial test data of different base greases

S. No.	Property	PP	mPP	PE	Li
1.	NLGI grade	2	2	2	2
2.	Additives	None	None	None	None
3.	Dropping point, °C	143	141	116	201
4.	Oil separation, %	6.5	8.2	3.8	1.9
6.	Oxidation stability (D 942) Pressure drop, psi, 100hrs	3.5	2.1	2.0	5.0
5.	Oxidation stability (PDSC)				
	i)Onset Temperature, °C	245.8	246.8	250.9	191.1
	ii) Peak max, ° C	278.2	277.8	283.9	229.3

Table 6.2: Physico-chemical test data of greases dosed with EP additives

S. No.	Property	PP		mPP		PE		Li	
1.	NLGI grade	2		2		2		2	
2.	EP/AW additive	ZDDP	WS_2	ZDDP	WS_2	ZDDP	WS_2	ZDDP	WS_2
3.	Dropping point, °C	144	143	143	143	116	116	202	201
4.	Oil separation, %	6.6	7.2	8.2	9.0	6.1	10.0	3.3	7.4
6.	Oxidation stability (D 942) Pressure drop, psi, 100HRS	3.5	3.5	4.0	3.0	2.7	3.1	3.3	2.5
5.	Oxidation stability (PDSC)								
	i) Onset Temperature, °C	256.5	216.6	252.3	220.0	254.7	216.6	221.6	211.9
	ii) Peak max, ° C	286.6	281.1	284.6	286.8	288.7	286.1	244.7	280.5

As expected, Table 6.1 shows that the dropping point of commercial Lithium EP grease (Li) is maximum. Dropping point of soap based grease is essentially dependent on melting temperature of the thickener salt [6]. For most of the Lithium base greases dropping point is generally in the range of 190–205 °C coinciding the melting of Lithium-12 hydroxystearate. Among the polymeric greases dropping point of PP thickened grease is the highest i.e. 143 °C. This dropping point is suitable for most of the general industrial applications and is in the range of Sodium and anhydrous Calcium base greases. Table 6.2 shows that addition of ZDDP or functionalized nano WS_2 did not affect the dropping point of greases.

From the application point of view, mild oil bleed is considered good for the lubrication purpose. A close look at the oil separation data of greases given in Table 6.1 shows that polymeric greases bleed excessively in comparison to Lithium grease. Oil bleed is a direct indicator of the stability of thickener gel structure which in turn depends on thickener concentration. Greases with higher NLGI grade are shown to bleed less in comparison to the greases with lower consistency [7][8]. As expected, Lithium grease forms a stable dense fibrous network of the thickener, leading to better immobilization of mineral oil in comparison to the polymeric greases [SEM pictures of polymeric and Lithium greases]. SEM micrographs of all greases are shown in Fig 1 (PP), (mPP), (PE) & (Li). Higher bleed of mPP grease can be explained as follows – To obtain the same NLGI grade polymeric grease, around 3-5% less mPP thickener was required in comparison to PP or PE. Therefore, a weak, less-dense polymeric thickener structure is expected in mPP grease leading to higher values of oil bleed [7].

From Table 6.2 it can be noted that the addition of either ZDDP or WS_2 significantly increased oil bleed of all greases. Polar additives are known to affect the thickener structure adversely which may result in the higher oil bleed tendency [9-10]. The effect is more pronounced with WS_2. In the current study a paste comprising of dispersed WS_2 powder was used. The WS_2 was functionalized with Sodium hexameta-phosphate and other inorganic phosphates (not disclosed by supplier).

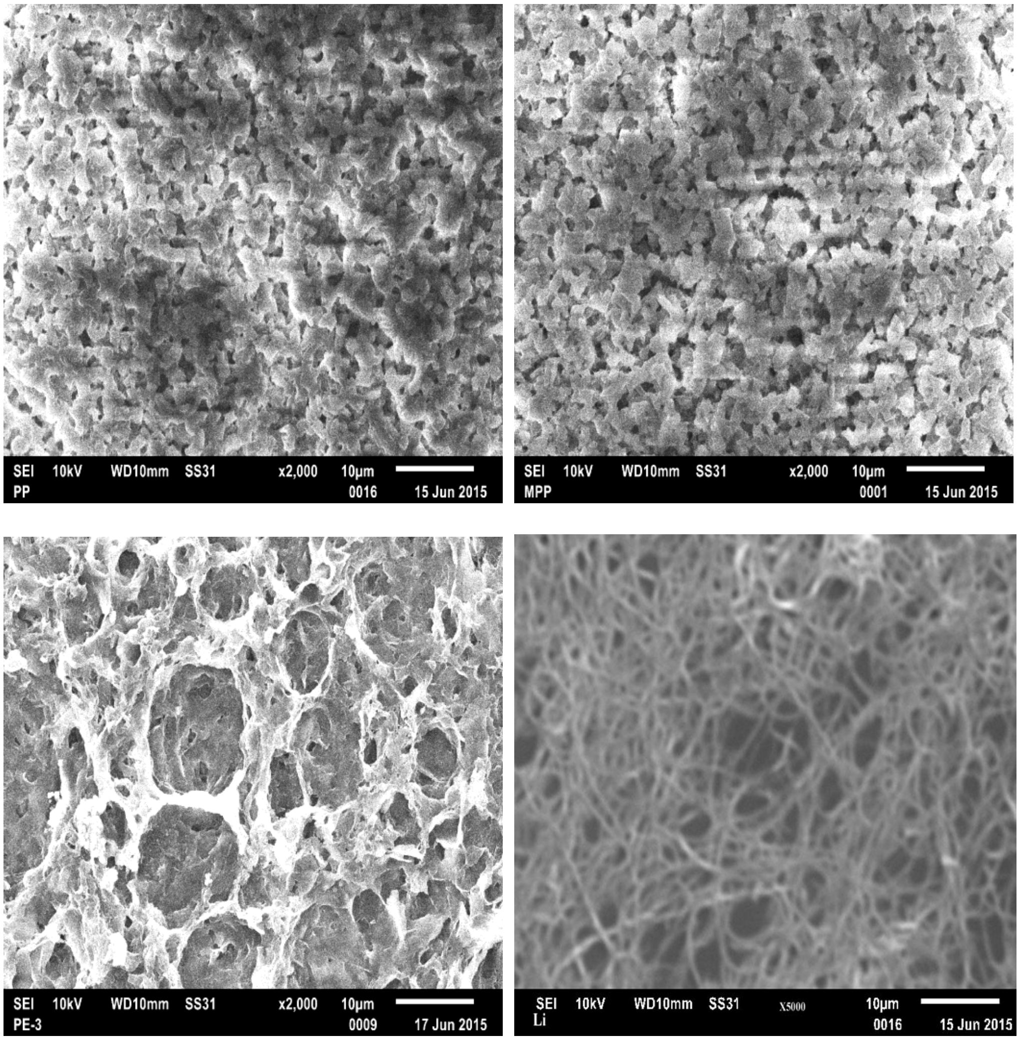

Fig. 6.1: SEM images of PP, mPP, PE and Lithium grease thickeners.

Base oil and thickener type are considered while discussing the oxidation stability of the greases. In static oxidation stability test ASTM D-942, oxygen pressure drop in polymeric greases was far less than the Lithium grease, even though the oil bleed tendency of polymeric greases is higher. The reason for this finding may be that the Lithium grease soap is metal based and metal is known to catalyze the oxidation process. Among the polymeric greases the oxidation stability of mPP and PE were comparable and that of the PP grease was the worst. To further investigate oxidation stability data obtained from the PDSC study given in Table 6 is considered. It can be readily seen that due to the presence of the metal soap oxidation of the Lithium EP grease starts at lower temperature i.e. 191 °C compared to polymeric greases, 245 – 250 °C. It can also be noted form Table 6.1 that the peak max for all greases is within the temperature range of 35 – 40 °C from onset, indicating similar type of base oil present in all greases and absence of any anti-oxidant additive.

Table 6.2 shows the effect of addition of ZDDP and WS_2 on oxidation stability. Consumption of the oxygen in ASTM D 942 test for Lithium EP grease has come down whereas for polymeric greases it is rather unchanged or there is marginal increase. From PDSC data of Table 6.2 it can be observed that for all grasses the temperature range between oxidation onset and peak max is unchanged (35-40 °C) with ZDDP addition. However, with WS_2 the temperature range has increased to 60-70 °C. This observation is not well understood at the moment, the authors speculate that the WS_2 functionalized with phosphates act as an anti-oxidant.

Thermo gravimetric data for all greases is compiled in Table 6.3. For greases without additives, it can be noted that under Air or Nitrogen atmosphere temperature corresponding to 1% wt. loss is comparable for mPP and Lithium greases whereas for both PP and PE greases it is significantly lower. The initial decomposition temperature generally coincides with the melting of thickener molecules. Decomposition at 600 °C shows that there is considerable residue left by Lithium grease. This is due the presence of metal in grease or additives which ultimately leads to the formation of metal oxide [5][11]. mPP grease left minimum residue and PP, PE greases left residue <1.0%. This property of polymeric greases is useful in industrial applications where sludge formation is a concern. For additized greases similar trend was observed, though the amount of residue left was much higher due to the metal from additives.

Table 6.3: Thermo gravimetric analysis data of greases

S. No.	**Property**	**PP**		**mPP**		**PE**		**Li**	
1.	T° C, (1%)								
	Nitrogen	157.7		183.0		157.3		186.9	
	Air	156.1		180.6		151.9		181.1	
2.	W^{600} (%)								
	Nitrogen	0.45		0.61		0.87		3.86	
	Air	0.32		0.28		0.42		2.03	
		ZDDP	WS_2	ZDDP	WS_2	ZDDP	WS_2	ZDDP	WS_2
3.	T° C, (1%)								
	Nitrogen	208.9	154.6	207.6	179.7	208.9	191.3	216.4	185.6
	Air	206.0	140.8	191.7	164.2	204.5	168.6	212.5	161.7
4.	W^{600} (%)								
	Nitrogen	1.32	3.69	1.18	3.92	1.10	4.57	2.39	4.15
	Air	0.76	3.48	0.74	3.85	0.51	3.79	2.09	4.02

6.5 CONCLUSIONS

- Composition of polymeric grease plays a crucial role in deciding its physico-chemical properties.
- Grease based on mPP thickener was overall winner, as it required relatively low thickener concentration to give identical high temperature properties such as oil bleed, oxidation stability and thermal stability like Lithium EP grease. Thus, it was considered as a suitable choice for industrial applications.
- Role of additive was found thickener dependent.
- Functionalized WS_2 was also found to improve oxidation behavior of polymeric and Lithium EP greases.
- Polymeric greases were found to have comparable thermal stability to Lithium grease with an advantage of producing very less residue at high temperatures compared to Lithium grease.

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APPENDIX

APPENDIX A

RHEOLOGY:

Rheology is the study of the flow of matter, generally accounts for the behavior of non-Newtonian fluids, by characterizing the minimum number of functions that are needed to correlate stresses with rate of change of strain or strain rates

Shear stress (σ) = Force / Area (Nm^{-2} or Pascal, Pa).

Shear strain = Change of length/ Initial length (Simple ratio and so No units).

Hooke's law relates the strain to the stress via a material constant known as the MODULUS, G. (G = stress / strain)

Complex Modulus:

In the oscillation test the value of 'viscoelastic G', obtained from the ratio of the stress amplitude to the strain amplitude is referred to as the materials complex modulus. This modulus is the 'sum' of the elastic component called the "STORAGE MODULUS" (G'), and the viscous component called the "LOSS MODULUS" (G").

We define the complex modulus as: G* = G' + i x G"

By measuring the ratio of the stress to the strain (G*) as well as the phase difference between the two (delta, δ) we can define G' and G" in terms of sine and cosine functions as follows:

$G' = G^* \cos \delta$

$G'' = G^* \sin \delta$

Since G* is essentially Stress/strain, G' and G" have units of Pascal (Nm^{-2}).

Loss tangent: $\tan \delta = G''/G'$ (measure of damping)

Oscillatory Shear measurements:

By subjecting a specimen to an oscillatory stress (σ) and determining the response, both the elastic and viscous or damping characteristics can be obtained.

Linear Viscoelasticity:

When oscillatory shear measurements are performed in the linear viscoelastic regime, the storage modulus G' (elastic response) and loss modulus G" (viscous behavior) are independent of the strain amplitude. Viscosity experiments are carried out in the zero-shear-rate Newtonian plateau (low shear rate).

COEFFICIENT OF FRICTION

The coefficient of friction is shown by;

$f = \mu F_n$

Where, f is the frictional force, μ is the coefficient of friction, and F_n is the normal force.

The friction force is the force exerted by a surface when an object moves across it - or makes an effort to move across it.

The frictional force can be expressed as

$Ff = \mu N$ (1)

Where,

Ff = frictional force (N, lb)

μ = static (μs) or kinetic (μk) frictional coefficient

N = normal force (N, lb)

LIST OF PUBLICATIONS

- Dixena, R., Sayanna, E., & Badoni, R. (2014). ***Recycled and Virgin HDPEs as Bleed Inhibitors and Their Rheological Influences on Lubricating Greases Thickened with PP and mPP***. Lubricants, 2(4), 237-248.
- R.K. Dixena, E. Sayanna, and R.P. Badoni - ***A Study on Tribological Behaviors of ZDDP in Polymer Thickened Lubricating Greases***. Accepted for publication in the journal "Lubrication Science", Wiley.
- R.K. Dixena, N. K. Pokhriyal, E. Sayanna, and R.P. Badoni. ***Study of tribological behaviors of polymer greases with fullerene like functionalized*** WS_2. Submitted to NLGI Spokesman, NLGI.
- R.K. Dixena, N. K. Pokhriyal, E. Sayanna, and R.P. Badoni. ***"Structure – property" correlation of polymeric greases*.** Submitted to Euro grease journal, ELGI.