Abstract

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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