ABSTRACT

Lubricants are materials that are used for a specific purpose to reduce friction and wear between interacting surfaces and to assist mechanical motion. Lubricants usually contain base oil base lube oil with doping of a certain amount of additives. Additives are generally polymeric substances. The additives either improve the already existing property of the base oil or introduce some new feature into it.

The present research work is entitled "***MODIFICATION OF VEGETABLE OILS AS A POTENTIAL BASE OIL AND A MULTIFUNCTIONAL LUBE OIL ADDITIVE***", concerned with the synthesis, characterization, and performance evaluation of some multifunctional organic compounds as an additive to lube oil and to evaluate the performance of chemically modified vegetable oils as additive as well as to assess their potential as alternate lubricant base stock. The additives explored in this study are typically based on Polymers made from methacrylate and vinyl acetate. Biodegradable multifunctional lube oil additives based on vegetable oils (Homo and copolymer of castor oil, rapeseed oil, rice bran oil, linseed oil with acrylate, styrene,1 decene, α- pinene, etc) have also been prepared and investigated. The additives that were synthesized involved a free radical mechanistic pathway by thermal irradiation. Azobisisobutyronitrile (AIBN) or benzoyl peroxide (BZP) were used as free-radical initiators. Another part of this study was to synthesize epoxidized vegetable oils(Linseed oil, Castor oil, Olive oil, Soyabean oil, Sunflower oil) and subsequent epoxy ring-opening with different alcohols (2-ethyl hexanol, dodecanol, n-octanol,1-decanol, isodecanol). Performance evaluation of these chemically modified vegetable oils revealed that they can be a replacement for mineral lube. The additives, as well as modified vegetable oils, were characterized by spectral techniques (^{1}H-NMR, ^{13}C-NMR, and FT-IR), followed by molecular weight determination by Gel Permeation

Chromatography (GPC) and finally, their thermal stability was assessed by Thermo Gravimetric Analysis (TGA). The additives doped in mineral oil and modified vegetable oils were investigated for their performances as Pour Point Depressant (PPD) and Viscosity Index Improver (VII) as per the standard ASTM (American society for testing and materials) methods. Antiwear properties were ascertained by the Four-Ball Wear test (FBWT). Biodegradability analyses were also conducted for the vegetable oil-based additives by Soil Burial Method (SBT) and Disc Diffusion method (DD) to test their biocompatible nature.

The detailed research work has been divided into **PART-1, PART-2, and PART-3.**

PART-1, entitled "**Methacrylate based polymers as lube oil additive**" is then divided into two chapters, Chapter-1, Chapter-2,

Chapter-1, of Part-1, describes the **background and objective** of this study, the research, and developments made on acrylate and methacrylate-based polymers as a lube oil additive.

Chapter-2 of Part-1, describes the **synthesis, characterization, and performance evaluation of the homopolymers of Dodecyl methacrylate (DDMA) and its copolymers with vinyl acetate**. Homo-polymer of DDMA and four copolymers of dodecyl methacrylate(DDMA) and vinyl acetate (VA) at different molar ratios were synthesized by thermal free radical polymerization method using BZP as radical initiator. All the polymers were characterized by spectral studies, their molecular weights were determined by GPC and they were assessed for their performances as low-temperature flow improvers and viscosity modifiers in the base oil when doped. The results showed that the copolymers have better viscosity modification properties, better low-temperature flow, and an increase in thermal

stability. It is also observed that the viscosity modification and the pour point performance of the additives depend on the concentration of the additives in the base fluid.

The work has been published: Ghosh P, Roy D,& Paul S,(2020), IJANS 9(6):29-36.

PART-2 entitled "**Biodegradable multifunctional lube oil additives using modified vegetable oils.**" is again divided into four chapters, Chapter-1, Chapter-2, Chapter-3, and Chapter-4.

Chapter-1, of Part-2, contains the **background and objective** of the present study i.e. the research and development made so far in this area.

Chapter-2 of Part-2, deals with **biodegradable lube oil additives obtained from the homopolymer of castor oil and its copolymers with acrylates**. The polymers were characterized by FT-IR and NMR spectroscopy, their molecular weights were measured by GPC and their thermal stability was determined by TGA. The experimental results showed that the prepared copolymers are better additives than homopolymers. A biodegradability test of all the polymers was carried out by the Disc Diffusion method. From the above study, it was found that the homopolymer and copolymer of castor oil were effective additives in terms of Viscosity Index Improver and Pour Point Depressant, copolymers were more effective than homopolymer. Thermal stability and average molecular weight of copolymers increase with increasing the alkyl chain length of acrylate moiety. Due to the presence of a biodegradable backbone, the polymeric additives were environmentally benign also.

This work has been published: Ghosh P, Hoque M, Roy D (2020) J Sci Ind Res,79:537-543.

Chapter-3 of Part-2, explores the potential of **polymers synthesized from styrene(STY) and Rapeseed oil to act as an environment-friendly multifunctional lubricant oil additive**. A detailed study in this area involved the Synthesis of the homopolymer of rapeseed oil and its copolymer with styrene using thermal irradiation and BZP as free radical initiator. Characterization of the polymer was carried out by spectral (FT-IR, NMR), GPC, and TGA. Biocompatibility and multifunctional performances (Viscosity Index Improver, Pour Point Depressant, and Antiwear) in lube oil compared to conventional additives was investigated using standard ASTM methods. Biodegradability was determined by DD and SBT degradation method. From the above study, it was found that the copolymers were found more effective than the homopolymer as Viscosity Index Improver, Pour Point Depressant, and Antiwear additive for base oil. On the other hand, the presence of rapeseed oil in the additive composition introduces excellent biodegradability too, in the additive.

This work has been published: Ghosh P, Paul S, Roy D (2020) IJPPE 6(3):29-37.

Chapter-4, of Part-2, explores the **performance of homopolymer of rice bran oil (RBO) and copolymers with decyl acrylate and α-pinene as multifunctional lube oil additives** at different percentages ratios using thermal irradiation and involve free radical mechanistic pathway. Characterization of the polymers was recorded by spectral technique (FT-IR and NMR spectroscopy). The Gel Permeation Chromatography method (GPC) was used to determine the average molecular weight of the prepared polymers. The Thermo Gravimetric analysis (TGA) method was used to study the thermal stability of the prepared polymers at high temperatures. Standard ASTM methods were used to investigate the performance of all the prepared polymers in two types of base oil as Viscosity Index Improver (VII)

and Pour Point depressant (PPD). The biodegradability of all the polymers was tested by the disc diffusion method and soil burial method. It was found that the average molecular weight of copolymers of RBO with DA is better than RBO with α-pinene. The viscosity index value of the homopolymer of RBO was lower than copolymers and the viscosity index value increases with increasing the percentage of DA or α-pinene in copolymers. The pour point of the lubricant compositions was found to be better for the copolymers of RBO with DA than the copolymers of RBO with α-pinene and the values decreased with the increasing concentration of the lubricant composition. The homopolymer of RBO and copolymers of RBO with α-pinene showed significant biodegradability than copolymers of RBO with DA.

This work has been published: Ghosh P, Roy D, Hoque M (2020) J.Indian Chem.Soc:97:1-5.

PART-3 explores the potential of **" Modification of vegetable oils as multifunctional lube oil additives and a potential base stock".** This part is again divided into three chapters, Chapter-1, Chapter-2, and Chapter-3.

Chapter-1 of Part-3, deals with the **background and objective** of this study i.e. the research and development in this area so far.

Chapter-2, of Part-3, describes **the opportunity of using linseed oil homo and co-polymers as multifunctional additives to lube oil**. Linseed oil-based biodegradable polymeric additives were prepared and their effectiveness as Pour Point Depressant, Viscosity Index Improver, and their Shear Stability in terms of Permanent Shear Stability Index (PSSI) were evaluated in lube oil. Polymers were proved to act as a good Pour Point Depressant, Viscosity Index Improver, and Shear Stability Improver as well. The copolymers acted like better PPDs than the homopolymer whereas the latter showed better VI improving the property. Keeping in view the environmental issue, the results were quite inspiring. Apart from being

biodegradable and eco–friendly, the linseed oil-based additives might be considered to be potential candidates to replace the traditional harmful organic chemical-based polymeric additives depending on the evaluated parameters. All the additives synthesized in this research illustrated excellent additive performances and, therefore, the outcome of this study can give a new dimension in the field of multifunctional additive research.

This work has been published: Ghosh P, Roy D, Paul S, Yesmin S (2021) Journal of Macromolecular Science, Part A,58(1):2-7.

Chapter-3 of Part-3, deals with the "**Synthesis characterization and performance evaluation of chemically modified vegetable oil to be used as lubricant base stock".** Linseed oil(LO), Castor oil(CO), Olive oil (OLO), Soyabean oil (SBO), Sunflower oil(SFO) epoxide were prepared and are characterized by FTIR and NMR spectroscopy. The reaction of epoxidized linseed oil with 2 ethyl hexanol, dodecanol,n octanol,1 decanol, and isodecanol in the presence of a catalytic amount of sulfuric acid gave rise to open-ringed products. Oxirene ring-opened products of linseed oil exhibit better low-temperature flow and high viscosity index. Ring opened product with isodecanol and 2 ethyl hexanol showed better results compared to others. ECO, EOLO, ESBO, ESFO rings were also opened through the same procedure using isodecanol and the product exhibited high Viscosity Index and excellent low-temperature flow in this case also. Ring opened product displayed better Thermo Oxidative Stability compared to those vegetable oils from which they are synthesized. Better pour point, high viscosity index, better Thermal-Oxidative stability, and better antiwear property compared to conventional mineral lube make these products an alternative to the latter and more environmentally benign.