Macromolecules and their Multiphase Polymer Systems

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Edited by

Hanna J. Maria, Sabu Thomas and Reeba Mary Cherian

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CHAPTER ONE

ROLE OF BIO-BASED GREENER LUBRICANT ADDITIVES TOWARDS SUSTAINABLE DEVELOPMENT: PRESENT SCENARIO AND FUTURE PERSPECTIVES

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Abstract

Lubricants are used to reduce friction and wear between interacting surfaces and to assist mechanical motion. They comprise of base oil doped with certain amount of additives which enhance or sometimes suppress the existing properties of base oil according to requirement for a particular application. Traditionally petroleum-based lubricant additives had been utilized in almost every single application in automobile industry. However, in the present scenario, need for biodegradable, eco-friendly, greener lubricant additive is on the rise. The present chapter is concerned with the synthesis and performance evaluation of chemically modified vegetable oils as additive and their potentiality as alternate lubricant additive. Performance evaluation of these chemically modified vegetable oils revealed that they can be a replacement for mineral lube. Studies have proved that these biodegradable additives are quite similar or in some cases better viscosity index improver (VII) and pour point depressant

(PPD) than the traditional petroleum-based additives. Their performance as antiwear additive, friction modifier, corrosion inhibitor excels in various applications. Several research groups have been employed to overcome the problems associated with high production cost of these greener additives in comparison to the conventional ones.

Keywords: Lubricants, Additives, Viscosity Index Improver, Pour Point Depressant, Anti-wear

1. Introduction

Utilization of greener additives for lubrication purposes especially in the automotive industry is on the rise. Greener additives, prepared from bio–based renewable sources such as vegetables, animals, plants or trees, are in general characterized as biodegradable and environment friendly. Vegetable oils are mostly used for the preparation of eco–friendly additives due to the following characteristics. Natural vegetable oils or plant oils offer many inherently advantageous properties when used as lubricants, such as high viscosity indices (VI) because of their high molecular weights. Presence of triglyceride structure (**Figure 1**) enables these oil molecules to cling to metal surfaces via physical bonding and provide better boundary lubricity than non–polar petroleum–based mineral oils. Besides, the triglyceride part makes the vegetable oils stable enough over a wide range of temperature as well. [1] Reasonably lower vapour pressure renders high flash point of these lubricants and hence accounts for their safer and hazard-free application. Additionally, bio–based oils have superior compatibility with additive molecules. [2]

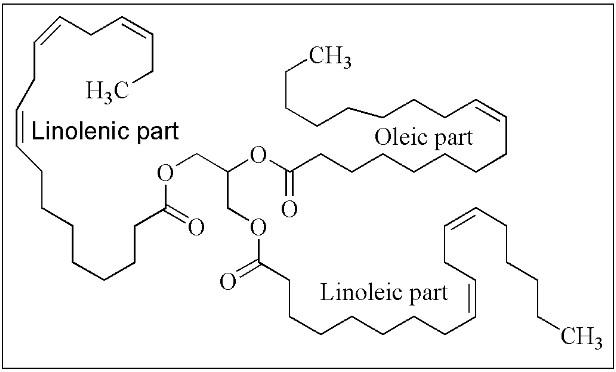

Figure 1: General structure of triglyceride found in vegetable oils

However, they also have inherent limitations when compared with mineral or synthetic oils. As a result, there are vegetable oil derivatives such as simple and complex esters, estolides, and an array of other chemically modified oils that offer base oils for versatile applications. A thorough understanding of the properties of the base oil along with an evaluation of the performance requirements of the end use is essential for preparing a superior bio-based lubricant. Vegetable oils are often chemically modified, mixed together or extracted from genetically enhanced seed oils with higher inherent stability. This field is ever exploring with the advents of new development every now and then towards achieving a greener and safer world. As for example, Patrick A. Bonnaud et al. very recently have applied molecular simulation method to carry out a thorough investigation on the effect of base oils over the properties of eco-friendly amine-based additives and their results have successfully established these additives as efficient anti-wear additives. [3]

2. What are lubricant additives?

Lubricant additives are those substances which satisfy the required or desired properties of lubricating oil by rendering some specific properties or enhancing the existing ones or even sometimes resisting some. Typically, they consist of a polar head group and a non–polar hydrocarbon chain.

3. Different types of additives

Different kinds of additives can be blended with the lubricating oil to fulfill the required aspects of various fields of applications. They may be classified as

1. PPDs (Pour Point Depressants)
2. Viscosity index improvers (VIIs)
3. Friction Modifiers
4. Rust Inhibitors
5. Corrosion Inhibitors etc.

4. Traditional additives vs Greener additives

From the very beginning organic polymeric substances consisting of a non-polar long hydrocarbon chain of 14 to 25 carbon atoms and a polar head group typically acrylates or acetates are commercially available as effective lubricant additives such as vinyl acetate copolymers, methacrylate–based copolymers, modified maleic anhydride copolymers etc. Basically the traditional additives are derived from petroleum feedstocks and hence their application is quite harmful to the environment. Hence bio-based lubricant additives have attracted so much attention over the decades.

However, untreated bio–based lubricant additives suffer from several disadvantages mainly poor oxidative stability, poor low temperature properties, low thermal stability, and comparatively high wear rate. Typical plant oils cannot fully meet the performance criteria for most lubricants. [2] Hence to compete with vastly used and highly qualified mineral base stocks, bio–based lubricants need to be modified.

At elevated temperature vegetable oils get oxidized in the presence of water following the free radical mechanism at a faster rate compared to the mineral oils. During this oxidization process, it undergoes a complex chemical reaction, producing acid and sludge that polymerizes to a plastic consistency. Sludge may settle in critical areas of the equipment and interfere with the lubrication and cooling functionalities of the fluid. The oxidized oil also corrodes equipment. The key factor behind this faster oxidation of plant oils is the presence of polyunsaturated fatty acids such as linoleic and linolenic acids. The double bonds in the alkenyl chains easily react with oxygen to form free radicals which then degrade to form peroxides and acids followed by polymerization and fragmentation. Thus, a higher degree of unsaturation leads to higher rate of oxidation. According to Gryglewicz et al. rapeseed oil, which is rich in polyunsaturated fatty acids, is less resistant to the action of oxygen as well as high temperature. [4] The poor oxidation stability of soybeanoil (soya oil) occurs due to the presence of higher amounts of linoleic (having two double bonds) and linolenic (having three double bonds) parts. Genetic plant modification, chemical modification andchemical additives all can increase oxidation stability.

Another big factor is pour point which is the lowest temperature at which the oil can retain its fluidity. Like mineral oils vegetable oils also tend to form macro–crystalline structures at low temperatures where uniform stacking of the 'bend' triglyceride backbone restricts the flow at lower temperature. [5] In fact the cold flow properties of unmodified bio–based lubricants are inferior to mineral oil–based and synthetic lubricants. The pour point of mineral oil–based lubricants ranges from–18°C to –30°C whereas that for canola and rapeseed oil is around –9°C and for unmodified soybean oil about –2°C. Modifiedvegetable–based lubricants can have pour points as low as –40°C. As the number of double bond increases the pour point of vegetable oils decreases which has been supported by the study of Jayadas and Nair. [6] According to their report the fatty acid chains in a bent configuration prevents close packing of the molecules at lower temperature and hence vegetable oils withhigh percentage of unsaturated fatty acid chains exhibit lower pour points. It was supported by another study [4] where rapeseed oil exhibited lower pour point (−21°C) compared to olive oil (−15°C) which is clearly due to the high unsaturated fatty acidcontent of rapeseed oil. Thus, the pour point problem can be solved withchemical additives or blending with other fluids such assynthetic oils with lower pour points.

Different modern technological approaches have been adopted to solve the problems associated with the application of plant oils in formulation of bio–based lubricants. Some of the techniques include chemical modification such as internal esterification, transesterification, epoxidation, blending with synthetic esters, blending with additives, enzymatic synthesis and some other novel methods have been employed to eliminate or minimize the drawbacks of raw vegetable oil towards the formulation of bio–based lubricant additives.

5. Preparation of bio-based greener additives

Studies have shown that chemically modified vegetable oil–based biolubricants exhibit excellent oxidation stability and cold flow properties. Chemically functionalized esters are formulated for high performance lubrication from relatively pure raw materials. The undesirable impurities present in conventional petroleum base oils are absent in synthetic esters. Besides synthetic esters have better thermo-oxidative stability and high viscosity index (VI).

5.1. Chemical modifications

The performance limitations of plant oil or vegetable oil base stocks can be overcome through chemical modification. Special attention has been given toward improving the thermal and low–temperature stability of plant oils by chemical modification. The molecular structures of plant oils have some potential sites for chemical modification, mainly at the double bonds. Several studies have proved that one double bond will increase the viscosity, but two or more double bonds will decrease the viscosity of the lubricant, besides introduction of branched or aromatic hydrocarbon molecules with high molecular weight can generally reduce the pour point of vegetable oils by preventing molecule packing at lower temperature. [6, 7] In general, a high degree of unsaturation is favourable for low-temperature properties of the lubricant whereas it is unfavourable for the oxidation stability. Modification of vegetable oils renders lots of advantages such as increasing stability of the lubricant over a wide range of temperature as well as excellent wear and friction characteristics.

5.1.1. Transesterification

Transesterification of vegetable oil is known to enhance lubricity and hence can better coat the surface of metal against wear. [8] This is one of the widely used chemical modification process where the triglyceride moleculeof vegetable oil conventionally reacts with three moles of methanol in the presence of an acid or basecatalyst, resulting in glycerol and mixtures of fatty acid methyl esters, as shown in **Figure 2**.

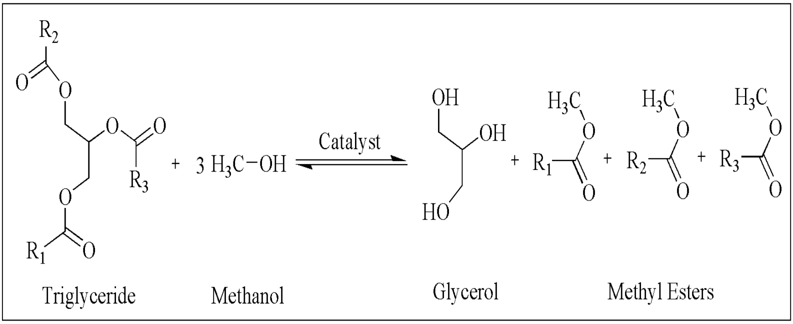

Figure 2: General transesterification process

The hydrogen atoms in position β relative to the hydroxyl group in the glycerol molecule can be replaced through transesterification process where glycerol is replaced with polyol which does not contain β–hydrogen atoms, such as neopentyl glycol (NPG), trimethylolpropane (TMP) or pentaerythritol (PE). [9] The structure of these polyols has been shown in **Figure 3.** This process prevents theself–polymerization and thus thermal stability of the lubricant at high temperatures is increased. [9] In general polyol esters contain more ester groups compared to others and hence are more polar. Due to this higher polarity volatilityof the lubricant is reduced whereaslubricity is enhanced.

Usually, the functionality of the polyols affects the viscosity of ester–based lubricants. The viscosity of vegetable oil–based TMP esters is higher than that of equivalent NPG esters [4], which may be due to the presence of three acid groups in the structure of TMP esters and the existence of only two groups in the molecules of NPG esters. It has been shown that TMP esters have better thermo–oxidative stability compared to NPG esters, which is evident by the increase in acid number and viscosity. [4] TMP esters as bio–based lubricants have been widely studied in metalworking fluid, aircraft turbine oils and engine oils.

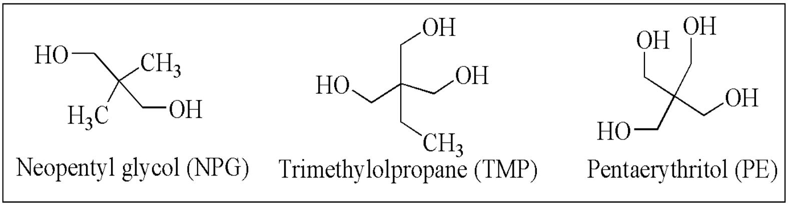

Figure 3: Structures of neopentyl glycol (NPG), trimethylolpropane (TMP) or pentaerythritol (PE) polyol esters.

S. K. Tulashie et al. have provided a formulation of biolubricant from castor, palm kernel and coconut oils via transesterification followed by additionof some additives such as pour point depressant, viscosity modifier, and antioxidant. [10] According to this study, transesterification process was performed for the removal of glycerol from the vegetable oils to produce a biodiesel since glycerol may produce highly toxic acrolein during thermal decomposition. The prepared biodiesel was further modified into the bio-basedlubricants that would be environment friendly. The obtained bio–based lubricant was evaluated in comparison to commercial engine oils and the results were quite promising.

5.1.2. Hydrogenation

Hydrogenation is another useful process to reduce the unsaturation of vegetable oil. In this process hydrogen is added to the C=C bonds in the triglycerides of an oil molecule followed by geometric and positional isomerization. To prevent degradation of the low–temperature properties of the lubricant such as the pour point, partial hydrogenation is conducted to form monoenes only without reducing to full saturation. [11] Via selective hydrogenation, linolenic acid is first hydrogenated followed by linoleic acid and oleic acid. In industrial processes Raney Ni catalyst is most commonly used to conduct selective hydrogenation. However, due to toxicity problems associated with this catalyst, Pd is preferred which has higher catalytic activity over Ni and can be used in softer conditions also. [12]

5.1.3. Epoxidation

Epoxidation is one of the most important and popular chemical modifications of vegetable oils since a wide range of products can be produced from the epoxide groups or oxirane ring performing versatile reactions under moderate conditions. For example, the conversion of epoxidized vegetable oils to diesters results in excellent properties at low temperatures due to the branching effect. [13] Conventionally, epoxidation process is carried out by peroxy acids (**Figure 4**) including acid ion exchange resins, enzymesand metal catalystfollowedby ring-opening of the epoxidized oil and esterification process as well.

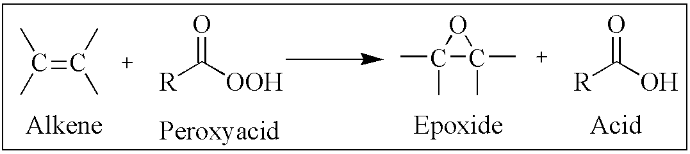

Figure 4: Reaction of double bonds with peracids.

A series of bio–based polyols were produced from olive, canola, grape seed, linseed, and castor oil via epoxidation with formic acid and hydrogen peroxide, followed byring–opening reaction. [14] The resulting polyols and polyurethane showed better thermal and mechanical stability due to crosslinking density.

5.1.4. Polymerization

Polymerization of vegetable oil is one of the easiest and economic processes to reduce the degree of unsaturation in vegetable oil towards formulation of superior quality bio–based lubricants. Biolubricants can be prepared through homopolymerization of vegetable oils or fatty esters or their epoxy derivatives and copolymerization with suitable co–monomers via cationic, free radical, ring opening, and condensation polymerization. Free radical polymerization process was carried out on various vegetableoils towards formulation of eco–friendly lubricant additives. [15] Polymer nano–composites, prepared from polymerization of vegetable oil or its derivatives with different organic or inorganic nanofillers, are widely employed in the automotive industry, especially as an antiwear additive in lubricants. [16]

5.1.5. Conversion into cyclic carbonates, fatty amines, amides and alcohols

5.1.5.1. Cyclic carbonates

The olefinic group present in the triglycerides can be converted to various other functional groups via simple chemical reactions which are quite useful towards the formulation of bio–based lubricants. Cyclic carbonates can easily be prepared via coupling reaction between carbon dioxide and epoxy fatty acid derivatives or epoxidized oils. These carbonates are non–toxic and biodegradable and hence may be referred as green intermediates. Simple alkali halides in combination with a phase transfer catalyst were successfully employed to prepare bis–carbonate from the reaction between epoxidized methyl linoleate and CO_2. [17]

5.1.5.2. Fatty amines

When fatty acids or fatty acid alkyl esters are treated with ammoniaat a high temperature in the presence of a dehydration catalyst, fatty nitriles are obtained which are further hydrogenated by a metal catalyst to form fatty amines. Fatty amines are very much useful as friction modifier in engine oils [18] and are supposed to be better than the commercial ZDDP type antiwear additives. Stearyl amine with almost 96%yield was obtained when oleic acid reacted with excess ammoniaat 408 K and 35 bar to produce oleonitrile followed by catalytic hydrogenation at 413 K. [19] In internal combustion engine or a gearboxpartially neutralized fatty amine salt can be used as an excellent friction modifier. [20]

5.1.5.3. Fatty amides

Another class of compound namely fatty amideisprepared by base catalyzed aminolysis of fatty acids or esters using ammonia, primary or secondary amine such as dimethylamine, ethanolamine, isopropanolamine, or diethanolamine. Fatty amides obtained using diethanolamine have versatile application as active ingredients to manufacture dry cleaning soaps, fuel oil additives, rust inhibitors, textile scouring, dye levelinwoolen cloths. [21] Fatty amides also help to increase lubricity of fuels.Fatty amides derived fromsaturated fatty acid triglyceride with a deficiency of dialkanolamine can be used as improved friction modifier or antiwear additive to crankcase oils. [22]

5.1.5.4. Fatty alcohols

Polyunsaturated fatty alcohols can beeasily obtained from fatty esters of vegetable oils or natural fatsvia selective reduction by a metal–basedsolid hydrogenation catalyst under high pressure and temperature. Fatty alcohols or their derivatives can be used for the production of differentindustrially useful materials such as biolubricants, plasticizers, surfactants, etc. Generally, the larger chain alcohols are suitable for producing biofuels. Mueller et al. [23] have reported theapplication of linear and branched fatty alcohols consisting of at least 12 carbon atoms or mixturesof such fatty alcohols with carboxylic acid esters as a lubricating additive in water–based drilling fluids for geological exploration. These fatty alcohols are also used as an antifoam additive for lubricants.

5.1.6. Metathesis: A new approach with considerable potential

Metathesis is a bimolecular process involving the exchange of bonds between the two reacting chemical species providing the products with similar or identical bonding affiliations. As for example AB and CD after metathesis would produce AD and CB. Elevance Renewable Science has come up with the idea of applying this novel metathesis chemistry to improve the stability of vegetable oil by opting out the undesirable part from the oil under consideration. Recently acyclic diene metathesis polymerization and ring–opening metathesis polymerization of functionalized fatty alcohols have been employed to synthesize vegetable oil–based polymers. It is believed that this chemistry could hold great promise for future modified soybean oils. But still there remains an unresolved question on the biodegradability of the new potential products.

5.2. Genetic modification

Genetic modification of various vegetable oils has opened a new horizon towards the development of bio–based lubricants with industrial application. A major research group is engaged in tackling the problems associated with low oxidation stability and poor cold flow properties from its root level mainly by reducing both saturated and polyunsaturated fatty acids of vegetable oils. DuPont and Monsanto are two major pioneering companies in this field. DuPont has introduced genetically modified soya oil with transgenic high oleic acid content (>80%) and less than

3%linolenicacid content which has been commercially evaluated also. Monsanto also reporteda transgenic variety of soya oil with high oleicacid (73%) content and less than 3% each ofsaturates and linolenic acid content. These reductions of saturated fats and linolenic acid are made up by the substantial increase inthe oleic acid component. These genetically modified oil varieties have been successfully evaluated in industrial applications as high temperature engine oils and hydraulicfluids.

6. Current examples of bio-based lubricant additives and their application in automotive industry

6.1. Soybean oil

Soya oil is one of the most abundant andinexpensive renewable resources towards the formulation of high molecular weight polymers. It consists of poly–unsaturated fatty acids with the main component being linoleic acid (ca. 50 wt%). Hydroxylated soya oil has been vastly investigated due to their versatile application towards various synthetic routes such as in the preparation of the water borne polyurethanes in aqueous dispersions which are widely used as adhesives and coatings ofvarious materials like textiles, metals, plastics, and wood. [24] G. Karmakar et al. [25] have synthesized homopolymers of soybean oil and its copolymers withmethyl acrylate, 1–decene and styrene by a thermal method using azobisisobutyronitrile (AIBN) as a radical initiator to produce a cost–effective and eco–friendly lubricant composition.The prepared polymers acted as efficient VII, antiwear and PPD additive for the base fluids.It was also shown that polymerization increased the thermo–oxidativestability of soybean oil. In another study they compared the homopolymer of soybean oil with itsmethyl acrylate–basedand methyl methacrylate–based copolymers and concluded that the copolymers outweigh the homopolymer in all respect such as antiwear additive, PPD and VII [26]. Hwang and Erhan [27] have reported that oxidation stability of soya oil can be improved and at the same time pour point can be reduced via introduction of branching. They have utilized sulphuric acid as catalyst for the ring–opening reaction of epoxidized soybean with various linear and branched alcohols and further esterification process was carried out on the resulting hydroxyl group with acid anhydride.

6.2. Olive oil

P. Ghosh et al. [28] synthesized copolymers of isodecyl acrylate with olive oil by thermal method using BZP (benzoyl peroxide) asradical initiator. Performance evaluation of the prepared polymers under standard ASTM methods established them as an efficient PPD and VII for mineral base oils. These olive oil based multifunctional additives also exhibited excellent biodegradability when tested against fungal pathogens and microorganisms bydisc diffusion (DD) method and by soil burial test (SBT) method. Their thermal stability also was good enough. Another comparative study between olive oil and rapeseed oil was conducted where both the oils were transesterified to produce NPG and TMP esters using calciummethoxide as catalyst. [29] The oliveoil-based esters exhibited higher thermo–oxidative stability compared to the rapeseed oil based esters which was accounted by the low content polyunsaturated acids in the former.

6.3. Neem Oil

Neem is a native tree to Indian–subcontinent. Inspite of enormous application of Neem and its derivatives in various sectors starting from pesticides, self–healing coat to antiwear agent, neem oil was hardly explored with tribological propertiesas bio–lubricant. B. Suresha et al. [30] have investigated the role of graphene nano platelets (GNPs) in neem oil on its viscosity, friction, wear and on seizure load as well. These all are essential parameters for the proper selection of lubricant in differentsliding components of food processing machines. The results showed that 1 wt.% of GNPs in neem oil exhibitedthe least coefficient of friction and smoother wear whereas seizure load of neem oil was greatly improved by 0.5 wt.% of GNPs as compared to pure neem oil. Further this study proved that neem oil has enough potential to be explored for the formulation of bio–based lubricants and its abundance may lower the cost of production also which is a serious drawback for bio-based lubricants.

6.4. Sunflower oil

P. Ghosh et al. have conducted several studies on sunflower oil- based biolubricants and additives. [31–33] A comparative study was presented on the tribological properties of the homopolymer of sunflower oil synthesized under different conditions – one by microwaveirradiation method and another by thermal method using benzoylperoxide (BZP) as initiator. [31] According to this study the homopolymer prepared under microwave irradiation are better PPD and VII in mineral base oils when tested under standard ASTM method. This study has provided a microwave–assistedand cost–effective greener approachfor synthesis of biodegradable lube oil additive.In other study copolymers of sunflower oil with methyl methacrylate, decyl acrylate and styrene were prepared and compared with the homopolymer of sunflower oil. [32] The results showed that the copolymers were thermally more stable. Most importantly the extent ofmonomer incorporation was directly proportional to the thermal stability of thecopolymers. The cold flow properties also improved in case of the copolymers.

The selective hydrogenation of ethyl esters of sunflower oilat low temperatures was studied in the presence of a supported catalyst containing Pd, Pt and Ru [34] where the Pd catalyst exhibited the best catalyticperformance. The modification of Pd catalysts using copper and lead orby the addition of amines into the reaction medium can improve the selectivity. The use of various oxidesupports (α–Al_2O_3, γ–Al_2O_3, TiO_2, MgO, ZnO, CeO_2, $CeZrO_2$) does notenhance the selectivity of the reaction towards the cis C18:1 in the Pd catalyst. [34]

6.5. Castor oil

Castor oil exhibits higher viscosity index compared to the super–refined mineral oils due to the presence of hydroxyl monounsaturated triglycerides which via hydrogen bonding raises the viscosity to a very good level. P. Ghosh et al. [35] prepared the homopolymer of castor oil and its four copolymers with methyl methacrylate, dodecyl acrylate, 1–decene and styrenevia free radical polymerization using azobisisobutyronitrile (AIBN) as initiator. The prepared polymers were evaluated as biodegradable multifunctional additives towards the formation of eco–friendly lubricant and the results showed that the copolymer of Castor oil and styreneexhibited highestmolecular weight and highest VI value followed by the copolymer of Castor oil and methyl methacrylate whereas the acrylate copolymers were more efficient as PPD and antiwear additive compared to others and showed higher thermal stability also. All the polymers showed significant biodegradability when tested through soil burial test (SBT) method.

6.6. Linseed oil

Linseed oil (LSO) is colorless or somewhat yellowish oilobtained from the dried and ripened seeds of the flax plant (Linumusitatissimum). Due to high rate of production in India, LSO can be acceptable as a resource for the formulation of bio–based lubricant from economic point of view. D. Roy et al. [36] have successfully utilized LSO toward the formulation of bio–based lubricant additive. In this study homopolymer of LSO and its four copolymers with styrene, 1–decene, isodecyl acrylate and octyl acrylate, respectively, were synthesized in presence of benzoyl peroxide (BZP) initiator. Their performance evaluation showed that the copolymers were better PPDs than the homopolymer whereasthe homopolymer of linseed oil excelled as VII which is attributed to the higher molecular weight of the later. Moreover, the mechanical stability of all the prepared polymers was good enough.

6.7. Palm oil

Palm Oil can be extracted from the fruit of palm tree (*ElaeisGuineensis).* This oil contains large amount of oleic acidand palmitic acids. H. Fernandes et al. [37] carried out ring opening metathesis polymerization (ROMP) on red palm olein (RPO) oil derived from crude Palm oil with the novel monomer ofnorbornene (NBE) towards the development of simple, cost effectivevalue–addedraw material for industrial use.

6.8. Rapeseed oil

Rapeseed oil is richin erucic acid (~ 45%). It also contains several minor constituents for lubricatingapplications such as free fatty acids, phosphatides (gum), enzymes (particularly myrosinase) and glucosinolate. [38] In a study, Rapeseed oil was epoxidized using the conventional epoxidationmethod where carboxylicacid was reacted with concentrated hydrogen peroxide. [39] The study revealed that the oxidation stability of the epoxidized rapeseed oil was enhancedsignificantly in the presence of antioxidants. Also, the epoxidizedrapeseed oil had better friction–reducing characteristics and extremepressure capabilities compared to the untreated oil which is attributed to theformation of a polyester or polyether material film by the three–member ring of oxirane created by tribo–polymerization.

6.9. Canola oil

Canola oil has attained enough attention mainly because of its nutritional quality. In terms of composition, it is almost similar to rapeseedoils except the fact that erucic acid (monosaturated omega–9 fatty acid) in canola oil is nearly negligible (< 1%). [40] Bio–based lubricant produced from canolaoil has a high VI due to the polyunsaturated fattyacid chains present in it. [41] Synthesized bio–based lubricants from methyl oleate and canola biodiesel were prepared by Sripada et al. [41] via transesterification process with TMP using sodium methoxide as catalyst. The prepared bio–based lubricants derived from methyl oleate biodiesel and canola biodiesel showed excellent pour point of –51°C and –66°C respectivelydueto the high degree of unsaturation and polyunsaturation. A single step process towards formulation of bio–based lubricant from epoxidized canolaoil was developed through simultaneous epoxy ring–opening and esterification in the presence of acetic anhydride and sulphated Ti–SBA–15 catalyst. [42] The prepared biolubricants possessed better tribological properties.

6.10. Chaulmoogra oil

Chaulmoogra oil is inedible oil which is extracted from seeds of chaulmoogra tree (Hydnocarpuswightianus) that grows in the wastelands of India and other countries. Presence of long–chain cyclic fatty acids (41%) like chaulmoogric acid, hydnocarpic acid and gorlic acid distinguishes chaulmoogra oil from other oils. Research on how cyclic fatty acids influence the properties of vegetable oils and affect their efficacy as base oils for lubricants is scarce in theliterature. S. Salaji et al. [43] has presented a preliminary evaluation of the physicochemical, viscometric, oxidative and tribological properties of chaulmoogra oil as a lubricant base stock. The results obtained from this study can be summarized as follows: The VI for chaulmoogra oil is significantlybetter than the commercial oil of its comparable viscosity grade; Cold flow properties are close to the saturated coconut oil; the cyclic fatty acid composition of chaulmoograoil gives it better friction properties which can be improved in presence of ZDDP. Thus, chaulmoogra oil has lots of potential to be utilized with appropriate additives as a green lubricant with minimum ecological impact.

6.11. Jatropha curcasseed oil

Jatropha oil extracted fromJatropha seedby solvent extraction method has been employed for the production of biolubricant via transesterification process for light gear applications. [44] At first methyl ester of the oil was produced which was transesterified with ethylene glycol to produce the biolubricant with similar properties of commercial base oil having viscosity grade of 46. Trimethylolpropane (TMP) esters derived from jatropha oil are biodegradable and have high lubricity properties. [45] In addition, it was shown that the oxidation stabilityof TMP ester (Jatropha) increases by 100% compared to Jatrophaoil due to the elimination of β–CH groups. The introduction ofbranching into methyl ester reduces the pour point by disturbing thealignment and stacking of hydrocarbon chains. This allows the oil tosolidify at lower temperatures.

6.12. Coconut oil

Coconut oil is rich in saturatedfatty acids (91%) and therefore, it does not oxidize easily. Coconutoil has been widely used as a lubricant in rickshaws and scootersin Southern India. This oil has been shown to improve vehicle mileage; engine pick up and operations. [46] In addition coconut oil produces comparatively lesser smoke when burnt. [47]

6.13. Calophylluminophyllum L

Calophylluminophyllum L., commonly known as polanga or honne,is abundantin the seashores of Philippines. This plant is nativetotropical Asia. The seeds of Calophylluminophyllum L. containa high percentage of oil (65–75%) which is mainly used for medicinal purposes and as hair grease. However, this oil has also found its application in the production of biodiesel with suitable physicochemical properties.

6.14. Desert date oil

Desert date oil which is available in abundant amount may be referred as potential alternative to the mineral oil. It contains a high amount of free fatty acid which can be reduced by two–step acid–base transesterification process followed by addition of trimethylolpropane. [48] In this study nanoparticles were added in different amounts to the modified desert date oil to improve its tribological properties and the results revealed that 0.9% concentration of the copper nanoparticles showed a significant improvement in term of reducing coefficient of friction (COF),wear rate, mean wear scar diameter and improved worn surface morphology was obtained with comparison tothe mineral oil. Thus, the modified desert date oil with an application of 0.9%copper nanoparticles could be considered as a suitable alternative to the mineral oil while considering environmentalconcern and energy saving.

7. Challenges and Future perspectives

Although the natural resources are abundant, their proper utilization is still not in vogue mostly because of ignorance among mass level and lack of guidance strong initiatives from regulatory bodies. Hence, still bio–based lubricant additives are treated as second fiddle in most of the bigger or smaller automotive industries. But people have become more and more aware and influenced by the continuous and effective advents by the huge research bodies in this field.

Other than utilization of the bio-based additives as much as possible, the automotive industry is also checking out the emerging technologies that are being developed to further lessenthe environmental impact of lubricants such as the application of nanotechnology to create self-healing lubricants that can repair small cracks andscratches in equipment, helping to extend the lifespan of equipment and reduce waste. Besides, ionic liquids (ILs) are also emerging as the promising greener additive as well. These substitutive technologies are conquering the industry day by day which not only reduces the environmental impact of petroleum-based additives but also promotes more sustainable industrial culture. Overall, green lubricant additives are potential candidates to play an important role in mitigating climate change. Proper awareness among mass level and stern regulatory implementations on both the customers and marketers are indeed the biggest requirement to fulfill the necessities towards sustainable application of greener lubricant additives.

8. Conclusions

Over the past decade enormous research has been conducted towards improvement in vegetable oil base stocks including low–erucicacid containing rapeseed oils, high oleic soya and rapeseed oils, castor oil with improved cold flow properties;improvements in additive chemistry; and improvements in formulation expertise have allowed thedevelopment of biodegradable products with performance similar to or better than conventional petroleum– based additives.In spite of the improvements in the performance of bio–lubricants, the market for these products has been slow to develop, mainly due to high cost and limited availability of biolubricant feedstock. Bio–lubricant products are generally more expensive thantheir mineral oil counterparts, with some notable exceptions and the reasons include feedstock prices, plant's capacity, feedstock quality, processing technology and cost for purification and storage. Again, despite some efforts to recycle bio–based lubricants, it is currentlynot profitable. However, the environmental advantageof bio–based lubricants lies in the biodegradability of theexhaust and leakage which always account for utilization of bio–based lubricants more in place of lubricants derived from non–renewable sources. But it is also a fact that without regulatorypressures it is difficult to convince a user to change from what they know to be acceptableperformance from traditional mineral oil– based products.

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