

Chapter 2

Current Developments of Biodegradable Grease

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Introduction

The modern definition of lubricating grease, according to the American Society for Testing and Materials (ASTM), is a solid or semi-solid product obtained by the dispersion of a thickening agent in a liquid lubricant. This system may also include other ingredients that impart special properties (see the American Society for Testing and Materials, Standard Definition of Terms Relating to Petroleum Products, 2000). This definition was further extended by the National Lubricating Grease Institute (NLGI): “The material we disperse in a liquid lubricant is usually a solid. The dispersion . . . will not settle out when left standing. In order to develop thickening, the solid and the lubricating liquid had best have some affinity for each other. This affinity also helps keep the dispersion stable” (1).

Lubricating greases are semi-solid colloidal dispersions of a thickening agent in a liquid lubricant matrix. They owe their consistency to a gel-forming network where the thickening agent is dispersed in the lubricating base fluid. The fluid lubricant that performs the actual lubrication can be petroleum (mineral) oil, synthetic oil, or vegetable oil. The thickener gives grease its characteristic consistency (hardness) that is sometimes thought of as a “three-dimensional fibrous network” or “sponge” that holds the oil in place. Therefore, the base fluid imparts lubricating properties to the grease while the thickener, essentially the gelling agent, holds the matrix together. This is a two-stage process. First, the absorption and adhesion of base oil in the soap structure results, and secondly, there is a swelling of the soap structure when the remaining oil is added to the reaction mixture.

A typical grease composition contains 60–95% base fluid (mineral, synthetic, or vegetable oil), 5–25% thickener (common thickeners are fatty acid soaps and organic or inorganic non-soap thickeners), and 0–10% additives (antioxidants, corrosion inhibitors, anti-wear/extreme pressure, antifoam, tackiness agents, etc.) (2) (Fig. 2.1). Additives enhance performance and protect the grease and lubricated surfaces (3).

Grease has been described as a temperature-regulated feeding device: when the lubricant film between wearing surfaces thins, the resulting heat softens the adjacent grease, which expands and releases oil to restore film thickness. The

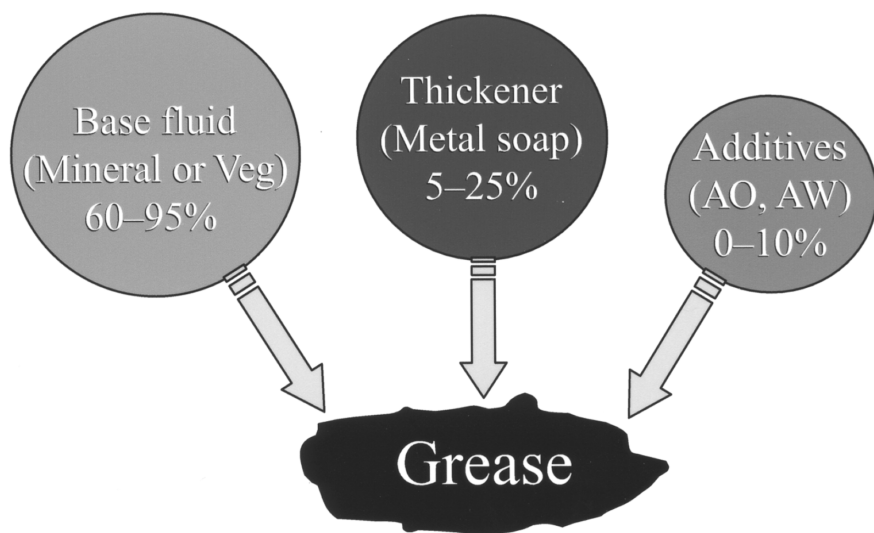


Fig. 2.1. Grease composition.

semi-solid nature of lubricating grease has several advantages over lubricating oils. Oxidative stability and consistency of the grease matrix controls a wide variety of performance properties in grease lubrication. Some of these properties are the ability to flow under force and subsequently lubricate hard-to-reach points; lower friction coefficient through adhesion on surface (4); wide temperature range effectiveness; water stability; the ability to seal out contaminants as a physical barrier; decreased dripping, spattering, and frequency of relubrication (act as sink for lubricating oils). It is important to note at this point that grease structure and composition undergoes significant modification while working by shearing and oxidation. The usefulness of grease in a particular application is controlled to a large extent by the ability of the grease to sustain change in temperature, pressure, operating environment, and shearing force.

Liquid lubricants possess certain shortcomings and are not able to cope with an exponential rise in performance requirements in automotive and industrial sectors. Technology is constantly being challenged to develop multifunctional lubricants to operate at higher temperatures, higher pressures, and with a variety of contact surfaces to minimize friction and increase system efficiency. This has triggered a steady rise in the development and application of greases in elastohydrodynamic regimes. Thickness and stability of lubricant film is largely dependent on the unique chemistry and composition delivered by greases. The function of grease is to remain in contact with and lubricate moving surfaces without leaking out under gravity or centrifugal action, or be squeezed out under applied pressure.

Development of vegetable oil-based greases has been an area of active research for several decades (5,6). Technical progress taking place in industry and

agriculture has caused an intensive exploitation of natural resources like mineral oil. The search for environmentally friendly materials to replace mineral oil is currently being considered a top priority research in the fuel and energy sector. This emphasis is largely due to the rapid depletion of world fossil fuel reserves and increasing concern for environmental pollution from excessive mineral oil use and disposal. Renewable resources like seed oils and their derivatives are being considered as potential replacements for mineral oil base stocks in certain lubricant applications, where immediate contact with the environment is anticipated. The nontoxic and readily biodegradable characteristics of vegetable oil based lubricants pose less danger to soil, water, flora and fauna in case of accidental spillage or during disposal (7).

Environmentally friendly lubricants and greases are already in market (8). These products are highly desired in total loss lubricants like railroads, as their accidental spillage doesn't invoke alarm and cause any harm to environment. Dwivedi *et al.* described the preparation of total vegetable oil-based grease using castor oil (9). Florea *et al.* have studied the effect of different base fluids on the properties of biodegradable greases (10). A suitable composition of grease is desired with good performance properties capable of use in multifunctional products. Despite the overwhelming importance of biodegradable greases, very little is known about the relationship between their composition and performance properties.

Biodegradable Grease

Base Oils

Base fluids make up to 75 to 95% of the total composition of grease. Generally, the base oils can be divided into two main categories: (i) water miscible, and (ii) non-water miscible. Glycols are exclusively water soluble; the most frequently used are monopropylene glycol or polyethylene glycol with an average molecular weight of 200–1500. The advantages of these compounds lies in their resistance to aging and hydrolysis, while the major disadvantages are solubility in water and incompatibility with mineral base oils. Non-water soluble base oils can be subdivided into two groups: (i) vegetable oils, and (ii) synthetic esters (11,12). This class of compounds basically has the same structure, and therefore, similar physical and chemical properties.

The search for bio-based material as industrial and automotive lubricants has accelerated in recent years. This trend is primarily due to the nontoxic and biodegradable characteristics of seed oils and esters (13) that can substitute mineral oil as base fluid in grease making. The performance properties of grease are primarily dependent on their ability to provide lubrication to mechanically operating moving parts by supplying base oil as a thin film separating the metallic surfaces, and also removing heat and wear debris from the friction zone. Today, greases are expected to work under extreme operating conditions, including shock load, wide temperature range, varying pressure, surface material and environment. As

mechanical systems become more complex in operation, eco-friendly base oils are used that can deliver performance properties similar to mineral base fluids and yet are nontoxic to the environment.

Synthetic esters are generally obtained from branched alcohols and long-chain fatty acids (e.g., oleic acids) for better properties. Long-chain esters with several branching sites exhibit good low-temperature properties and resistance to hydrolytic degradation (14). Among the esters used for grease making are trimethylolpropane, pentaerythritol, and neopentylpolyol. Compared to vegetable oils, these fluids deliver good thermal stability, solvency, low temperature fluidity, sub-ambient storage stability, lubricity, compatibility with mineral oil, biodegradability, and longer service life. Diesters of a number of fatty acids like oleic and stearic acid or dibasic acids like adipic, azelaic, phthalic and sebacic acids are widely used for grease making.

A real need exists for research and development of new technologies for production of lubricants according to the most advanced, “ecological” trends. The best approach seems to focus on alternative, renewable, widely available, natural resources, such as vegetable oils. They are naturally occurring triacylglycerols that are formed by the reaction of one mole of glycerol with three moles of fatty acids or a mixture of fatty acids (Fig. 2.2). Preferably the fatty acids are oleic acid, linoleic acid and linolenic acid or mixtures thereof. Vegetable oils are a potential source of environmentally friendly base oils that have the additional advantage of not disturbing the global carbon dioxide equilibrium. They exhibit excellent lubrication properties due to unbalanced electrical charges which make them attach to metal surfaces. Vegetable oils that are extensively used for biodegradable grease preparations are soybean, rapeseed, sunflower, and castor oil. Other vegetable oils used are olive, peanut, palm, corn, cottonseed, safflower, lesquerella, coconut and linseed. Genetically modified vegetable oils typically contain higher than normal oleic acid content. For example, normal sunflower oil has an oleic acid content of 20–30% which can be up to 60–90% in genetically modified high oleic sunflower

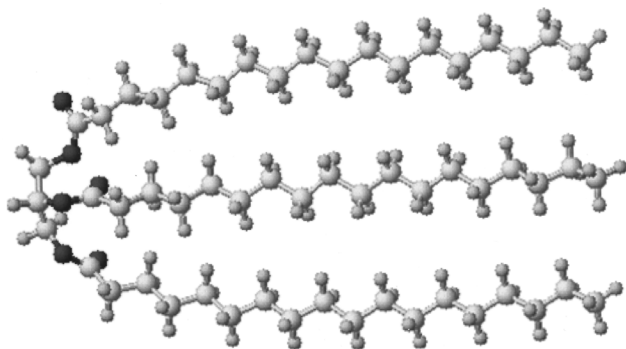


Fig. 2.2. Typical vegetable oil structure.

oil. It may be noted that genetically modified vegetable oils have a high oleic acid content at the expense of the di- and tri-unsaturated acids.

The presence of a polar group with a long hydrocarbon chain makes vegetable oil amphiphilic in nature, allowing it to be used as a boundary lubricant. The molecules have strong affinity for and interact strongly with metal surfaces. The long hydrocarbon chain is oriented away from the metal surface to form a monomolecular layer with excellent boundary lubrication properties. When the molecule is adsorbed on the metal surface, two types of interactions occur. The adhesive interaction between the ester group and metal is very sensitive to the type and number of functional groups. The lateral interaction caused by dipole-dipole and dispersive interaction between the hydrocarbon chains is sensitive to structural properties including chain length, unsaturation, and stereochemistry (15).

Castor Oil. Castor oil consists of triacylglycerols with the major fatty acid component being ricinoleic acid (~89 wt%) (16). It is a nondrying oil with high viscosity and is quite suitable for various lubricant applications. It can be mixed with other vegetable oils to obtain various viscosity grades (17) and offer excellent viscosity-temperature characteristics. Phoronic acid (having shorter chain length as compared to 12-hydroxystearic acid) derived from castor oil is superior in making greases since it has a higher metal content, delivering long grease life at higher temperatures. The shorter chain of phoronic acid is less subject to shear degradation when used in a grease matrix (18). Castor oil has also been used to prepare total vegetable oil based grease with sodium and lithium gallants. Vegetable oil, alcohol, and alkali are taken in such a ratio as to give a predetermined ratio of soap and ester in the product. The alkali is selected based on the type of grease to be formed (Li, Na or Ca) and alcohol selection controls the viscosity of the lubricant. Higher carbon number and molecular weight of the alcohol produces lubricants with higher viscosity (19). The residual hydroxyl group in the ricinoleic acid chain offers an active site for adherence to metal surfaces. It is therefore expected that greases prepared from castor oil will have better extreme pressure characteristics.

Rapeseed Oil. Rapeseed oil has a high viscosity and is often used as a lubricant base oil mixed with other seed and mineral oils. Lithium greases prepared with soap made from rapeseed oil and lithium hydroxide had better mechanical stability if some calcium hydroxide was used in the mixture (20).

Soybean Oil. Soybean is the second highest value cash crop in the United States. The farm value of soybean production in the crop year 2000 was \$13 billion. The 3.1 billion gallons of soybean oil produced in the United States is half of the 6.2 billion gallons produced worldwide. Soy oil (typically 18% of the weight of the soybean) can be used in its raw or refined form in a variety of industrial products (fuels, inks, paints, industrial fluids, etc.). This oil is a good source if a high unsaturation in the triacylglycerol is desired for grease formulation. Current develop-

ments on bioengineered (high oleic and/or low linoleic) soybean oil may provide highly desirable improvements for fuels and other industrial products. Unlike petroleum-based grease that takes 12 to 18 months to decompose, soy-based products are less toxic than traditional products and are less likely to catch fire. The use of oils from genetically modified seeds has opened up several possibilities in the field of nonfood uses of vegetable oils. DuPont has developed a genetically modified soybean that would produce soy oil with enhanced stability for a variety of industrial uses including application in grease making (21).

Soap Thickeners

Vegetable oil-based greases are semi-solid colloidal dispersions of a thickening agent (a metal soap), in a liquid lubricant matrix (vegetable oil). The thickener is a reaction product of a metal (alkali or alkaline earth metal) based material (oxide, hydroxide, carbonate or bicarbonate) and carboxylic acid or its ester. Acids can be derived from animal fat such as beef tallow, lard, butter, fish oil, or from vegetable fat such as olive, castor, soybean, or peanut oils. The most common alkalies used are the hydroxides from earth metals such as aluminum, calcium, lithium, sodium, and titanium. Soap is created when a long-carbon-chain fatty acid reacts with the metal hydroxide. This reaction often produces some amount of water. For certain types of grease, the water assists in forming the soap structure. The metal is incorporated into the carbon chain and the resultant compound develops a polarity. The polar molecules form a fibrous network that holds a certain amount of base fluid by interaction forces. The soap structure is very important to the performance of the grease and will vary in thickness, length and oil solubility, depending on the type of metal hydroxide used. These variations are ultimately displayed in the final properties of the grease. Listed in [Table 2.1](#) are some of the important physical properties of grease affected by the structure of fatty acids.

Vegetable oil-based grease thickened with polyurea is environmentally friendly and biodegradable in nature (22). Polyurea is the most important organic nonsoap thickener and has excellent oxidation resistance due to the absence of metal soaps (which tend to initiate oxidation). It effectively lubricates over a wide temperature range (-20 to 177°C) and has a long service life that makes it suitable in sealed-for-life bearing applications. Polyurea complex grease is produced when a complexing agent, most commonly calcium acetate or calcium phosphate, is incorporated into the polymer chain. Such greases showed good shear stability when subjected to the roll stability test.

Organic clay, though readily biodegradable, is a naturally occurring nontoxic material, so its carbon content is not counted in the determination of ready biodegradability (23). Thickeners based on organic clay pose the least manufacturing challenges for biodegradable greases. When vegetable oil is used, the required concentration of organo-clay is typically 14%, which may be higher for NLGI No. 2 consistency. Organo-clay thickeners have amorphous gel-like structure rather than

TABLE 2.1

Fatty Acid Structures and Grease Properties

Fatty acid structure	Grease property
Distribution of chain length	Variations in grease hardness
Amount of unsaturation	Variations in dropping point
Degree of branching	Non-uniform crystalline structure
Polar groups in the fatty acid structure	Positive effects on intermolecular interactions

the fibrous, crystalline structures of soap thickeners. This grease has excellent heat-resistance since clay does not melt and can effectively lubricate up to 260°C.

The high temperature application of modern machinery has lead to the development of “complex” soap greases. A complex soap is formed by the reaction of a fatty acid and alkali (soap), and the simultaneous reaction of the alkali with a short-chain organic or inorganic acid to form a metallic salt (the complexing agent). Basically, complex grease is made when a complex soap is formed in the presence of base oil. Common organic acids are acetic or lactic, and common inorganic acids are carbonates or chlorides. The dropping point of complex grease is at least 38°C (100°F) higher than its normal soap-thickened counterpart, and its maximum usable temperature is around 177°C (350°F). Generally, complex greases have good all-around properties and can be used in multipurpose applications. Grives has discussed commercial methods of biodegradable grease preparation using different thickener systems (24).

Although it is known that the general structure of the soap phase in grease consists of crystallites, which take the form of fibers, this does not clearly explain why a small amount of a solid (soap) could immobilize a large volume of the base oil in grease. These fiber structures form a complex network that traps the base oil molecules in two ways: (i) by direct sorption of the oil by polar ends of soap molecule, and (ii) penetration of base oil in the interlacing structure of soap fiber. The oil-retaining property of grease may be due to the attractive influence of soap fibers extending through many layers of the base oil molecule and not to the swelling of the fibers (25). Therefore, the physical and chemical behavior of grease is largely controlled by the consistency or hardness, which is dependent upon the microstructure of soap fibers. Thus, a somewhat rigid gel-like material “grease” is developed. Base oil and composition of the thickening agent plays an important role in grease consistency. For low and high temperature applications, regulating the base oil quantity and fatty acid composition can be used to control grease hardness. Therefore, preparation of lubricating grease is a complicated trial-and-error process in which the optimization of the reactants and the reaction protocol are critical to achieve the desired grease consistency.

The chemistry of the fatty acid soap structure is responsible for certain performance characteristics of grease including rust/corrosion inhibition, friction, and wear resistance (26). Polar components in grease are surface active and therefore

have a strong affinity for metal surfaces while the hydrocarbon tail is directed away resulting in the prevention of oxygen and water (rust and corrosion agents), and dust particles from coming in direct contact with metal surfaces. Also, the tightly adsorbed grease layer on metal is highly effective in lowering metal-to-metal friction (27). Therefore, the application of bio-based grease is particularly useful in open lubrication systems where the lubricant is in direct contact with environment.

Grease is the preferred form of lubrication in hard-to-reach places in a mechanically rubbing or dynamic system. Much of the functional properties of grease are dependent on their ability to flow under force, have shear stability, resist viscosity changes with temperature and pressure, maintain water stability, seal out contaminants, and decrease dripping and spattering. The dependability of lubricating grease relies on physical properties that are structurally related, which are obtained by the proper selection of ingredients and processing. Thus, it is pertinent to understand the grease microstructure as it contributes significantly to various functional properties of grease. Grease consistency [or National Lubricating Grease Institute (NLGI) hardness] (28) is largely dependent upon the thickener fiber structure and its distribution in the grease medium.

Grease hardness depends primarily on a metal soap thickener microstructure and experimental data show that the fatty acid chain length and C-C unsaturation influences soap fiber structure/networking mechanisms. An understanding of fiber growth and their network structure in a grease matrix is required to relate base oil holding capacity and oil release by shear degradation of soap thickener during operation to additive compatibility, bleed resistance, viscosity, thermal stability, texture, and appearance. Critical physiochemical properties are, therefore, dependent on the consistency of grease and their behavior in the mechanical system. Controlling the growth and distribution of soap fiber during grease manufacturing processes can result in products with the desired physical, chemical, and performance properties.

The soap fibers derived from short-chain fatty acids are not well developed and sufficiently elaborate to create a strong interaction with the base oil. Increasing the fatty acid chain length (C_n ; n = number of carbon atoms) in soap resulted in stronger bonding interaction and a harder grease matrix. Beginning with a C_{13} fatty acid chain length, there is a significant increase in grease hardness up to C_{15} , with an optimum at C_{17} resulting in NLGI grade 2 grease (using a 1:1 equivalent ratio of metal to fatty acid and 75 wt% of soy oil in the grease mixture) (Fig. 2.3).

In a study using transmission electron microscopy (TEM), formation of disperiod structure with compact network with an increase in the chain length of the fatty acid in lithium soap was observed. With more interlocking resulting from the long-chain fiber structure, increased interactions with base oil in the matrix can be achieved. Grease developed under such conditions shows high consistency resulting in higher hardness. The TEM of palmitic [$CH_3(CH_2)_{14}COOH$] and stearic [$CH_3(CH_2)_{16}COOH$] acids used in the lithium soap to develop soybean oil-based grease are shown in Figures 2.4a and 2.4b, respectively.

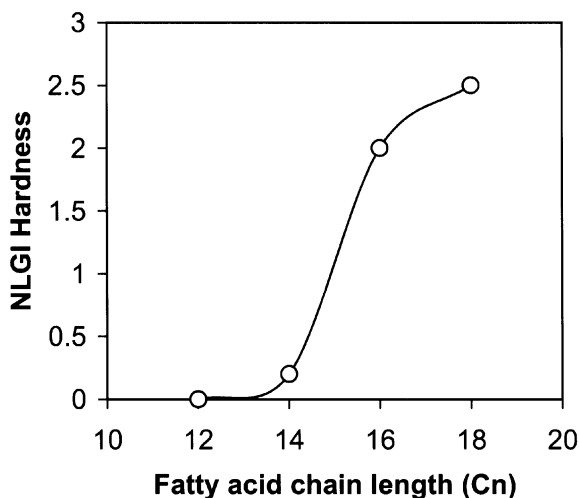


Fig. 2.3. Lithium soap fatty acid chain length effect on soy-grease NLGI hardness.

It appears that such compact mesh structure can hold relatively larger amounts of base oil in the soap matrix due to the excellent interaction. This increases the ability of the grease to resist deformation with increasing fiber length, because a long fiber can make more contacts with neighboring fibers than a short fiber with the same diameter. It may be noted at this stage that during extreme shear stress, when a fiber breaks into smaller fragments, the consistency will decrease, whereas when they split into thinner fragments, the consistency will increase. Therefore, the hardness of grease as a result of soap structure can affect oxidation stability, water washout, oil bleeding at higher temperature, and lubricity (29,30).

Unsaturation in the fatty acid structure of soap molecules has significant impact on the grease fiber structure. Linoleic acid ($C_{18:2}$) (Fig. 2.5b) with two sites of C-C unsaturation in the chain shows a much thinner and compact fiber network

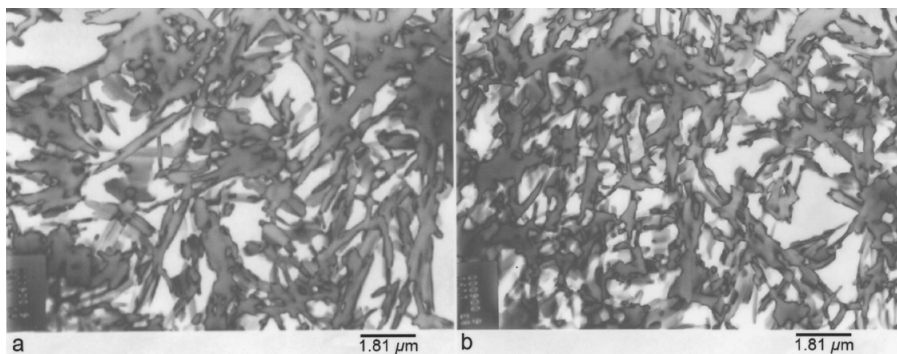


Fig. 2.4. TEM of (a) palmitic and (b) stearic acid used to develop soybean oil-based grease.

than oleic acid ($C_{18:1}$) (Fig. 2.5a) in the soap composition. Excessive thinning of the fiber strand may result in softer grease due to a weak mesh structure that is unable to hold the base oil in the grease matrix. Furthermore, the presence or absence of C-C unsaturation with the same chain length acids (Fig. 2.4b and 2.5b) in the soap structure results in a distinct difference in the shape and distribution of the fibers. With process parameters and composition remaining the same, and with a decrease in the soap fiber length, there is a tendency to form softer grease (31). Because the growth of soap fibers in the grease matrix is a result of fusion and solidification of adjoining short fibers, this phenomenon is also controlled to a large extent by the procedure used to manufacture grease (32). Soap molecules with oleic acid show a comparatively larger fiber structure than linoleic acid.

It has been observed that decreasing the soap concentration or lowering the cooling rate could produce long-fiber grease. Moreover, fiber length of grease increases with an increase in the heat-retention time. Especially the addition of soap powder to grease in the heat retention process resulted in gigantic fibers. In contrast, short-fiber grease could be produced by increasing the soap concentration or raising the cooling rate. A very high cooling rate results in lowering the ratio of fiber length L to width D , L/D , resulting in a softer grease. The soap fibers in grease are considered to grow when the grease is maintained near the melting point of soap (33). The fluctuation in temperature leads to the fusion and solidification of the soap fiber, leading to the disappearance of short fibers and the growth of long fibers (34).

Additive Effects

Additives are usually introduced during the cooling phase of grease making and remain dispersed in the matrix. These additives are found to enhance some of the functional properties of the base oil in the grease such as oxidation, load-bearing, anti-wear, anti-corrosion and anti-rust (7,35–37). Due to the presence of additives, the soap thickener structure can be influenced to a large extent by either changing the solubility of the soap in the base oil or influencing its crystallization. Similarly,

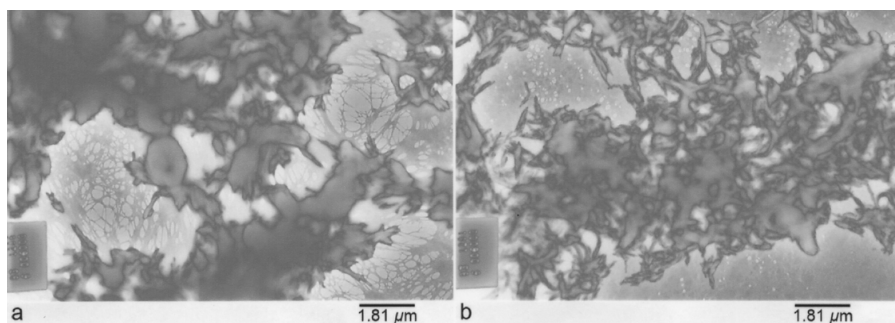


Fig. 2.5. TEM of (a) oleic acid and (b) linoleic acid.

the optimum condition for fiber growth through crystallization may vary with different additives. It is believed that the additive molecules are first bound to the soap fibers and the chains attached to additives hold the oil. The TEM (Figs. 2.6a and 2.6b) show the effect of antimony dithiocarbamate additive on Li-stearate soap structure. Under magnification ($1.81\ \mu\text{m}$), the additive-doped grease has a looser network structure with larger fibers than the nonadditive-doped grease with a similar metal, fatty acid, and base oil composition. It may be noted, however, that due to the presence of additive molecules, grease hardness is not altered significantly as a result of changes in the soap fiber length and their distribution in the matrix.

There are various reports in the literature where researchers have investigated additive effects on grease performance. Kato *et al.* (38) have reported the effectiveness of antioxidants in obtaining long lubricant life of grease with a rapeseed oil base. It was observed that the main causes of a reduced grease life are chemical deterioration due to oxidation and polymerization of the base oil. The antioxidants can delay such processes, but as soon as they are consumed, the degradation starts rapidly.

The performance properties of grease are primarily dependent on their ability to provide lubrication to mechanically moving parts by supplying base oil as a thin film to separate the metallic surfaces, and also by removing heat and wear debris from the friction zone. Similarly, the nature of the fatty acid in the soap structure of grease has a significant influence on the physical and chemical properties. Soaps can lubricate and are considered to be more important than the lubricating oil because they can improve the lubricating ability of the oil. Elliott (39) found that the chain length of the fatty acid was an important factor in determining grease characteristics. The starting and running torques are less for the grease than for the oil itself. Using the Four-Ball Tester, Jiang (40) showed that a lithium grease could prevent seizure at a load of 35 Kgs., whereas the oil film broke and failed. Physical and chemical degradation of grease during use (41,42) and failure of various

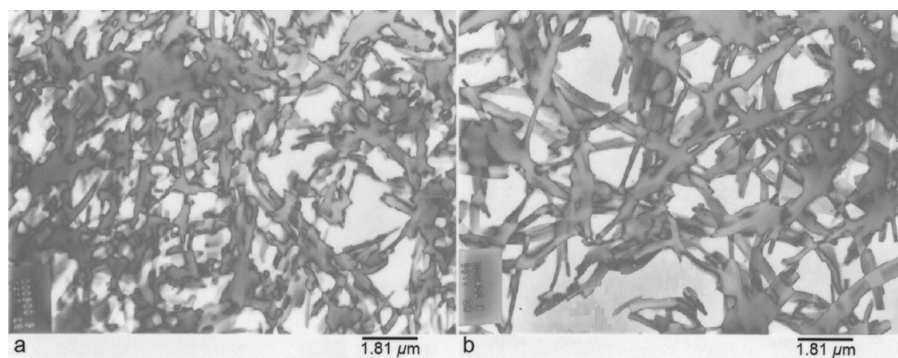


Fig. 2.6. TEM showing the effect of antimony dithiocarbamate additive on Li-stearate soap structure.

mechanical parts due to inadequate lubrication (43) have been reported. Several mechanisms have been proposed on timed lubricant release and replenishment of starved lubricant sites during operation. Laboratory simulations range from simple thermal stability tests to more complex lubrication measurements (44–46).

Functional Properties

Grease is used when it is not practical or convenient to use oil in a dynamic system. The use of grease is largely dictated by the design of the machinery and operating conditions that are suitable for a desired lubricant characteristic. Grease functions as a sealant (based on consistency) to minimize leakage, keep out contaminants and prevent entrance of corrosive foreign materials into the system. Grease, unlike oils, by virtue of its rigidity, is easily confined with simplified, less costly retention devices. The major practical requirement of grease is to retain its functional properties under shear at all temperatures it is subjected to during use. They have the ability to hold finely ground solid lubricants and additives in a stable dispersed condition and are able to deliver them at the point of metal contact for better lubrication. Grease maintains thicker films in clearances enlarged by wear and can extend the life of worn parts that were previously oil lubricated. Thicker grease films also provide noise insulation. Therefore, grease is mainly applied in equipment that is seldom used or is in storage for an extended period of time. High quality greases are also used in areas that are inaccessible to frequent relubrication and sealed-for-life type devices (e.g., motors and gear boxes). They also find use in applications involving extreme temperature, pressure, shear stress, shock loads, etc. Under these circumstances, grease provides thicker film cushions to protect and deliver adequate lubrication, where oil films can fail due to thinning.

Grease Characteristics

Consistency. This is an important parameter of grease that controls most of its physicochemical characteristics. Hard grease will not lubricate properly while very fluid grease may leak out of the system. Grease consistency depends on the type and amount of thickener used and the viscosity of its base oil. Grease's consistency is its resistance to deformation by an applied force and is generally measured by ASTM D 217 and D 1403 methods (47).

Corrosion and Rust Resistance. This denotes the ability of grease to protect metal parts from chemical attack. The thickener type provides most of the natural resistance of grease; however corrosion and rust inhibitors are often used in actual formulations.

Oxidation Stability. Oxidation is the most important chemical property of grease that results in insoluble gum, sludge, deposits and therefore leads to sluggish operation, reduced metal wetability, decreased wear protection and increased corrosion,

among others. Oxidation is also associated with evaporation which causes grease to harden due to increased thickener concentration. Excessive temperatures result in accelerated oxidation or even carbonization where grease hardens or forms a crust. Therefore, higher evaporation rates require more frequent relubrication. A number of studies have been reported on various aspects of thermo-oxidative stability (42,48,49) and oxidative degradation using chromatographic and spectroscopic techniques (41).

Bleeding. This is a condition where long storage periods and high temperatures induce a liquid lubricant to separate from the grease thickener. When the oil separates from the grease, thickener concentration increases resulting in grease plugging. Under certain circumstances, when two greases are in contact, the oil may migrate from one grease to the other, changing the structure of either grease. Grease, when subjected to high temperature for an extended length of time, loses its consistency and becomes fluid enough to drip. The dropping point indicates the upper temperature limit at which the grease retains its structure. However, a few greases have the ability to regain their original fiber structure after cooling down from the dropping point.

Low Temperature Stability. Grease hardens at low temperatures, leading to poor pumpability and rheological properties. Typically the base oil's pour point is considered the low-temperature limit of grease.

Biodegradability

In 2002, around 57 million tons of lubricant was used worldwide, and it is estimated that as much as 35% finds its way back into the environment unchanged. Some of this will degrade but there are potential dangers to the environment such as bioaccumulation and biocidal effects.

During biodegradation, the material is gradually broken down through the metabolic action of such living organisms as bacteria, fungi, yeast and algae. Naturally, this process is not entirely predictable and can be influenced by the mix of living organisms present, the ambient temperature, and the humidity. Sometimes a material that may easily degrade under one set of circumstances may not readily degrade under others. The minimum basic requirements are sufficient bacteria population, correct oxygen levels and a suitable temperature range. The rate of biodegradation is also affected by parameters such as fluid viscosity, pH levels, sunlight, mineral salt content, nitrogen availability, solubility and the ability of the bacteria to adapt to the source of oil nutrient. Ideally, in due course of time, the lubricant should be reduced to its simplest natural form while leaving no harmful by-products that could have a detrimental and long-term effect on the local environment.

Biodegradability and renewability are becoming increasingly important to formulators as new federal environmental regulations go into effect. Environmentally

sensitive application areas typically involve exposure to the elements, where there is a definite potential for the grease to contaminate the ecosystem through washout or accidental leak. Further, it is almost impossible to prevent accidental breaking of one of the small grease lines, the consequence of which is that grease can find its way into the water or at the very least into landfills. Currently, many greases are used in loss-lubrication systems, where a certain amount of grease ends up in the environment. Such applications include but are not limited to: forestry (chainsaw/grapples); agriculture (tractors, harvesters); lubricants (marine, boat trailer bearings); railway (curve/axle greases); mining (conveyor greases); manufacturing (hot and cold rolling mills); construction (waterways, bridges, locks, dams). Accordingly, biodegradability has become vital.

It is well known that mineral oils are not readily degradable under normal environmental conditions. Therefore, they have a high potential to accumulate in the environment. Mineral oils are also known to taint water and fish, making them unsuitable for consumption. Vegetable oils are not toxic to aquatic organisms and biodegrade relatively fast and completely. Soybean grease, for instance, decomposes within weeks; petroleum-based grease, however, takes from a year to 18 months to decompose. Metal soaps used in greases are commonly based on stearates, the main component of a natural soap, and are biodegradable to a large extent with the only exception of the type of metal present. Inorganic thickeners such as clay-like materials, that are found abundant in nature, however, are not entirely biodegradable, but are also not toxic to aquatic organisms. The additives constitute a very diverse range of chemicals and are often present in small quantities, possessing a wide range of biodegradability and aquatic toxicity. Some additives present in smaller quantity in the grease, and sparingly soluble in water, may increase several-fold due to the presence of other solubility-enhancing materials. Therefore, its effect is much higher than could be expected based on the small amount present in the grease. Therefore, it is difficult to make any generalized statement on additive biodegradation and aquatic toxicity (50).

One of the most important methods used to determine biodegradability is also the only one available for testing products immiscible with water: CEC-L-33-A-93 (formerly CEC-L-33-T-82). All of the test methods were initially designed mainly for use with single chemical species that have demonstrated water solubility. In a biodegradation test the microbe feeds on the substrate (compound to be tested) and degrades it. In general, this process is monitored by measuring oxygen consumption, carbon dioxide production, and the drop in dissolved organic carbon. According to CEC test methods, the biodegradability of a lubricant (i.e., grease) is plotted over a period of 21 days in comparison with white oil (20–30% biodegradability) and di-iso-tridecyladipate (100% biodegradability). The results are evaluated by measuring the fluctuations in the $\text{CH}_3\text{--CH}_2$ bands at the 2930 cm^{-1} using an infrared spectrometer. According to CEC-L-33-T-82, if the product is more than 80% biodegradable the German “Blue Angle” criteria makes it readily biodegradable (51,52). Biodegradability of used lubricants can be altered by contamination and can be as much as 15%. A lubricant that is 90% degradable when fresh may only be 75% degradable when used.

Conclusions

Lubricants based on renewable materials have been around for a long time and have only recently been extensively researched for nonfood industrial applications to be more competitive with petroleum-based products. Pollution from petroleum products has been a big concern for the environment. Of the 2.5 billion gallons of lubricant sold in the U.S. market, 30 to 40% escape into the environment through accidental spillage, leaks and evaporation. Since these lubricants are directly released on the ground or into the water, it is important they are biodegradable and will not persist in the environment for too long. Lubricants based on fossil fuels are persistent, and therefore not suitable in these applications. Vegetable oil-based lubricants in the form of greases are biodegradable and can be formulated to meet or exceed industry specifications. This will increase the use of agricultural products such as vegetable oils in industrial (nonfood) applications and therefore increase the agricultural land use and work. Further, the environment is protected by the introduction of an environmentally friendly lubricant in an industrial application, and finally, the dependence on import-oriented mineral oil is largely averted.

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