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Tribological behavior of biolubricant base stocks and additives

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ABSTRACT

Biolubricants are gaining popularity and acceptance globally due to their sustainable and environmentally friendly properties; being derived from feedstocks from vegetable oils. Indeed, the potential for biolubricants to eventually replace conventional lubricants is currently viewed in the literature as a real possibility. This study will provide valuable information pertaining to the formulation of biolubricants, by assessing and evidencing the tribological performances of various types of biolubricant base stocks and their related additives. This study begins with a presentation of the basic tribological parameters in lubrication. Following that, the criteria for the molecular structure of biolubricant base stocks for high tribological performance are discussed, based both on the tabulation of the friction coefficient and on the measurement of wear scar from experimental studies. The biolubricant base stocks under review in this study include vegetable oils (VO), epoxidized VO, ring-opened products from epoxidized VO, estolides, and polyol esters. This review also discusses recent advances in eco-friendly tribological additives such as plant-derived compounds and polymers, particulate and layered materials, and ionic liquids. The performance and various applications of these additives are also reviewed.

1. Introduction

Biolubricants, or bio-based lubricants, are generally perceived as environmentally friendly, biodegradable and non-toxic lubricants which are derived from renewable resources such as plant oils and animal fats. Most biolubricant products currently on the market are made up either entirely or partially from bio-based oils, providing these oils fulfill the requirements of international standards in terms of renewability, biodegradability, toxicity and technical performance. According to European standards [1,2], a certified biolubricant must have a bio-based carbon content of at least 25% and biodegradability of at least 60%. The biolubricant must also be non-toxic to the environment and fit for the purpose of an application. The market demand for biolubricants is driven by various factors, which include: consumer environmental awareness, government directives and the global demand for lubricants. A long-running and increasingly urgent issue is the environmental cost of hazardous and non-degradable lubricants entering the ecosystem through total loss applications, spillages and so on [3]. It is, in fact, well-attested that about half of the total production of lubricants in the world accumulates in the environment every year [3,4]. Continuing efforts have been made to fight this crisis through various government directives and environmental legislation. For instance, the European Union (EU) Renewable Energy Directives 2009/28/EC were mandated to promote the use of energy from renewable sources in various sectors including fuels and lubricants [5]. At a consumer level, environmental awareness is being raised by the awarding of environmental labels such as Blue Angel, Nordic Swan and European Eco-label for lubricant products [3], with the aim of highlighting the consequences of consumer purchasing and hiring decisions for the planet. In addition to the above initiatives, the market growth of biolubricants is further substantiated by the increase in global lubricant demand due to the specific development of end-user industries in China, India, South Africa, Brazil and Iran [6,7]. In the current scenario, the global market for lubricants is growing at approximately 2% annually; amounting to approximately 144.45 billion USD in 2015 [7]. Indeed, the global biolubricant market has always been rising steadily at 10% annually, in spite of it constituting only about 1% of the total market in lubricants [8,9]. From this perspective, the shift towards bio-based lubricants represents a global trend in the global lubricant market; as part of the global effort to mitigate the environmental impact of hazardous and non-degradable conventional lubricants.

The successful formulation of any lubricant product is built upon a multi-objective optimization of the types and concentrations of base stocks and additives, to meet specific application specifications and requirements [10]. On average, a typical lubricating oil consists of 93% base stock and 7% additives, though the additive content may vary

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from 1%, as in simple compressor oils, or up to 30%, as in gear oil and metal-working fluids [11,12]. In any lubricant formulation, base stock is viewed as the essential part of the lubricating oil, as base stock possesses the vital lubricant physical properties such as viscosity, thermal stability, lubricity and so forth. Among all base stocks, vegetable oil (VO) is the simplest choice for a biolubricant [13–19]. It has in fact always been the alternative to mineral oil due to its superior lubricity, viscosity index, and wear resistance; not to mention its biodegradability and the sustainability of its feedstock [13,20–22]. Unfortunately, VO is known to have poor thermal and oxidative stability [23–25], but by means of chemical modifications, VO may be converted into better-performing products such as epoxidized VO [26–28], ring-opened products from epoxidized VO [23,29–31], estolides [32–35], and polyol esters [36–42]. These base stocks have been seen as promising for use in biolubricant formulations. Further improvement to VO-based lubricant performance is possible through additivation. Additives are able to enhance the physical properties of the lubricant by providing additional features, including anti-corrosion, metal scavenging, and anti-wear to the base stock [12]. The most important group of additives are tribological additives, as far as lubrication is concerned, since the ability to reduce wear and damage to machines is ultimately the goal. Indeed, the aim of any new formulation is to achieve better performance, higher energy efficiency, and a longer life cycle for the machinery, as well as longer intervals for the replacement of the lubricating oil [43]. It should be mentioned here, of course, that not all conventionally-used additives are compatible with biolubricant base stock [12], but tribological additives for biolubricants have so far been advanced in the field with favorable regard to their lubricity, wear protection and load-carrying capacity. The additives from this group which are currently enjoying most research focus are those containing sulfur and phosphorus [44–47], environmental-friendly polymers [15,48–50], plant-derived compounds [35,51], particulates [52–56], two-dimensional (2D) layered materials [57–60], and ionic liquids [61–64].

In practice, the varying performance of different lubrications in terms of friction and wear is usually assessed based on the coefficient of friction (COF) and wear scar diameter (WSD), or volume (WSV), respectively [13,35,65,66]. COF denotes the ratio of friction force between two bodies and the normal force pressing the bodies together [67], whereas WSD and WSV are respectively the diameter and volume of wear after sliding activity. These measurements are often used in sub-scale machine or laboratory tests to investigate the tribological behavior of lubricant products in the workings of real machinery. When evaluating and comparing the tribological behavior of different lubrications, it is important to specify the type of lubricant, the tribosystem, and the lubrication conditions to minimize the discrepancy between the laboratory test and the field performance [65,67]. In the context of biolubricants, most of the literature simply discusses overviews, developments, synthesis and applications of biolubricants in a very general context [24,28,68–76], or in specific applications [77–87], while other studies focus only on the development and performance of a specific type of additive [88–95]. In fact, a thorough search of the relevant research yielded no reviews which provided any adequate detail about aspects of tribological behaviors. This review, therefore, seeks to address this gap in the literature by providing comprehensive evidence and valuable discussion pertaining to the tribological performances of recent biolubricant base stocks, and related additives. This study focuses on their influencing parameters, molecular structure criteria, synergisms, and mechanisms; concerning lubricity, wear protection, and load-carrying capacity. In addition, a detailed tabulation of friction and wear responses of various biolubricants is presented for comparison purposes. The aim is for interested parties to be able to utilize the tribological information presented in this review as a guide to selecting and formulating biolubricants for their own applications.

2. Basic tribological parameters

The most important consideration for selecting a suitable lubricant is that it fulfills the lubrication requirements of the particular application, especially in its tribological aspects. Tribological performance in lubrication concerns lubricity, friction and wear. Generally speaking, lubricity is associated with the formation of the lubrication layer, or tribofilm, on sliding surfaces. High lubricity reduces the direct contacts of the surface asperities and thereby lowers friction and energy loss [11,96]. High lubricity is not always accompanied by better wear protection, since the mechanism of forming a protective layer on the sliding surfaces occurs through the adsorption of the surface active materials of the lubricant, which can be certain types of base stock or additives [97]. Whenever there is surface asperity contact during the sliding activity, there is the possibility that three types of mechanical wear are produced: abrasion, adhesion, and fatigue [46,97]. Abrasive wear (e.g. grooves) is produced via the removal of a certain volume of surface material by hard asperities on the sliding surface [98]; adhesive wear (e.g. attachment of wear debris) is the result of plastic deformation and strong bonding of the interface materials [98]; fatigue wear (e.g. crack, fracture) is due to the weakening of surface materials after repeatedly contact with high local stress for a large number of times [98]. The obvious solution to the wear problem is to employ thicker tribofilm, though this is not always efficient and desirable in some applications, such as metalworking. Prior to any discussion of tribological performance, it is essential to understand what are known as the three basic tribological parameters: the mechanical properties of a tribosystem; the lubrication regime and its conditions; and also the physical properties and tribochemistry of the lubricant as illustrated in Fig. 1. The details of each parameter are elucidated as follows.

2.1. Mechanical properties of a tribosystem

The mechanical characteristics of a tribosystem can essentially be described as the material hardness, the surface roughness, the contact geometry, and the sliding mechanism of the interacting part and its counterpart, as presented in Fig. 1(A). Limiting the discussion to the laboratory tribometer, most sliding materials have a 30–64 Rockwell C Hardness (HRC) and a 0.01–1.0 μm surface roughness, depending on the following: the type of material (e.g. steel, magnesium, copper), the hardening process (e.g. nitriding, carburizing), and the coating (e.g. carbon-based coating, ultra-high molecular weight polyethylene) [15–17,26,37,66,99]. Basically, a higher hardness value provides a lower wear rate, while a lower roughness value provides better lubricity [100]. Comparing tribological results across different types of tribometers is not possible due to varying sliding geometries (e.g. four-ball, pin-on-disk, ball-on-disk) and the particular sliding mechanism (e.g. unidirectional or reciprocating, sliding to rolling ratio) [65,67]. For a valid comparison, the measurements should be conducted using a similar type of machine and method (e.g. ASTM D5183, ASTM D4172, and ASTM D6079). Even if all of these conditions are closely matched, researchers are required to reproduce the measurements in their instruments to ensure accuracy.

2.2. Lubrication regimes and conditions

The operating conditions of any tribosystem play a significant role in characterizing tribofilm and, subsequently, tribological behavior. According to the famous Stribeck curve [67,101] there are three lubrication regimes, namely: boundary; mixed and elastohydrodynamic (EHL); and hydrodynamic lubrication regimes, as illustrated in Fig. 1(B). Boundary lubrication usually occurs at high contact load or low sliding speed lubrication, whereby thin or unstable tribofilm is formed, causing the contacting surfaces to rub against each other and generate high friction and wear [102]. As the film thickness in this regime is less than the surface roughness [102], the presence of surface