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Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers

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ABSTRACT

The amphiphilic properties that result from the fatty acid composition of vegetable oils contribute to a better lubricity and effectiveness as anti-wear compounds than mineral or synthetic lubricant oils. Despite these advantages, vegetable oils show only a limited range of viscosities and this constrains their use as suitable biolubricants in many industrial applications. For the reason, ethylene–vinyl acetate copolymer (EVA) and ethyl cellulose (EC) have been added to the vegetable oil-based lubricants studied. To address this issue, the frictional and lubricant film-forming properties of improved vegetable oil-based lubricants (high oleic sunflower (HOSO), soybean (SYO) and castor (CO) oils), blended with 4% (w/w) of EVA and 1% (w/w) of EC, have been studied. It has been found that castor oil shows the best lubricant properties, when compared to high oleic sunflower and soybean oil, with very good film-forming properties and excellent friction and wear behaviour. This can be attributed to its hydroxyl functional group that increases both the viscosity and polarity of this vegetable oil. Regarding the effect of the viscosity modifiers studied, ethylene–vinyl acetate copolymer exerts a slight effect on lubricant film-forming properties and, thus, helps to reduce friction and wear mainly in the mixed lubrication region. Ethyl cellulose, on the other hand, was much more effective, mainly with castor oil, in improving both mixed and boundary lubrication.

1. Introduction

Lubricants have an important role in world industrial and economic development, mainly by reducing friction and wear in mechanical contacts [1,2]. Thus, about 38 million metric tonnes per year of lubricants have been used globally in last decade, with the majority of these being petroleum-based [3,4].

In the last 25 years, there has been an increasing interest in the use of biodegradable products. This has been driven by environmental problems that have heightened the need to limit pollution from lubricants and hydraulic fluids based on mineral oils. Vegetable oils are potential substitutes for petroleum-based oils; not only they are environmentally friendly, renewable and less toxic, but also they have excellent lubricating properties such as high viscosity index, high lubricity and low volatility [5,6]. For these reasons, vegetable oil-based lubricants are being actively demanded for many green industrial activities [7,8].

Vegetable oils can act as anti-wear additives and friction modifiers, due to strong interactions with the lubricated surfaces. Their amphiphilic nature gives them a good film/force relationship, due to long fatty acid chains and the presence of polar groups in the vegetable oil structure [9,10]. For this reason, vegetable oil-based lubricants have the peculiarity of being effective as both boundary and hydrodynamic lubricants [2,9,11]. However, to understand fully the tribological properties of vegetable oils, it is important to know the effects of the variability in fatty acid composition on their lubricating properties, film thickness formed, friction and wear [12].

Despite their safety, efficacy and advantages as mentioned above, vegetable oils suffer from several major drawbacks in terms of thermal and oxidative stability, which preclude their use above 120 °C, crystallisation at relatively high temperatures, and the limited range of viscosities available [13–15]. The last of these is critical since a range of lubricant viscosities are required depending on the industrial application. For instance, kinematic viscosity, at 40 °C, ranges typically from 30 mm^2/s in the automotive industry, to 120 mm^2/s for lubricants used on bearings, while viscosities higher than 240 mm^2/s are demanded in lubricants for four-stroke engines and some gear assemblies [5,16]. In previous

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works, the authors have investigated the use of environmentally friendly additives to improve some of these shortcomings [14,15,17,18]. More specifically, ethylene–vinyl acetate copolymer (EVA) and ethyl cellulose were tested to increase the viscosity range of different vegetable oils and improve their thermal susceptibilities [14,15,18]. However, the introduction of these additives could alter the properties required in lubricant applications; therefore, it is necessary to determine the tribological behaviour of these vegetable oil-based lubricants.

The contribution of viscosity modifiers to the viscous flow behaviour of lubricants has been extensively studied and is well understood. However, their influence on the friction and wear is less clear [19,20]. This is because these additives may behave in different and complex ways in lubricated contacts, each of which might contribute to a greater or lesser extent to film formation and, thus, friction and wear [19]. Previous studies with mineral oils have shown that some viscosity modifiers are able to adsorb on to metal surfaces, improving the boundary film formation under low speed and high temperature, producing a significant reduction in friction and wear [19,21,22]. In this sense, the main objective of the research described in this paper was to determine the tribological behaviour of three potential vegetable oil-based lubricants blended with polymers and, in this way, identify links between lubricant composition, friction and wear performance to find the suitable biolubricants features for use in industrial applications.

2. Materials and methods

2.1. Vegetable oils and additives

The environmentally friendly base-stocks (vegetable oils) used in this work were soybean oil (SYO), castor oil (CO), and high-oleic sunflower oil with 85% (w/w) oleic acid (HOSO). SYO was supplied by Fresenius Kabi (Germany), CO was received from Guinama (Spain) and HOSO was kindly supplied by the "Instituto de la Grasa", CSIC (Spain). All of them were commercial grade oils without any further purification. The fatty acid compositions and physical properties of the vegetable oils are shown in Tables 1 and 2, respectively.

Ethylene–vinyl acetate copolymer (EVA) with 33% vinyl acetate content (density, at 23 °C, 0.956 g cm^{-3}; molecular weight, 60250 g mol^{-1}; melting temperature, 59 °C), was kindly supplied, in the form of pellets, by Repsol YPF, S.A. (Spain). EVA copolymer is considered inert, nontoxic, and stable material. It is not expected to be biodegradable but is not hazardous, according to the Commission Directive 93/21/EEC [23]. The other viscosity modifier, and biodegradable material, used was ethyl cellulose (EC) (density, at 25 °C, 1.14 g cm^{-3}; molecular weight, 68960 g mol^{-1}; melting temperature, 155 °C). This viscosity modifier is commercially available and was obtained from Sigma Aldrich.

2.2. Preparation of environmentally friendly lubricating formulations

EVA and EC were blended with the different vegetable oils used in this study, at a concentration of 4% (w/w) and 1% (w/w), respectively. Blends were prepared by stirring in an open vessel (800 g), at constant velocity (150 rpm) and using an anchor impeller geometry, to disperse the polymer in the oil. EVA and EC blends were heated up to 120 °C and 155 °C, respectively, for approximately 1 h. After that, when the polymers were completely dissolved, the mixtures were returned to room temperature by natural convective cooling. A homogeneous single phase was obtained in all cases, except the blend HOSO/EC that, after some hours, became cloudy.

2.3. Viscosity and density measurements

Dynamic viscosities were measured with a rotational controlled-strain rheometer (ARES, TA Instruments, USA), over a temperature range of 25–100 °C. Viscous flow tests were carried out, in a shear rate range of 5–500 s^{-1}, using coaxial cylinders geometry (inner radius 16 mm, outer radius 17 mm, cylinder length 33.35 mm). Kinematic viscosity values, ν, were obtained as the ratio of the dynamic viscosity to the density, at each temperature. The viscosity indexes (VI) were obtained according to ASTM D-2270.

A capillary densimeter, model DMA-5000 (Anton Paar, Austria), was used to measure sample densities in a temperature range of 15–100 °C.

2.4. Film thickness measurement

The film forming properties of the lubricant samples were determined using ultrathin film interferometry. For this purpose, an EHL optical interferometry rig (PCS Instruments, UK) was used. A high-pressure contact is formed between the flat surface of a glass disk and a reflective steel ball. The glass disk is coated with chromium and silica layers (5 nm and 500 nm, respectively). The principle of this technique is fully described by Johnston et al. [24]. Film thickness measurements were made using a 19.5 mm diameter steel ball in nominally pure rolling contact with a coated glass disk of 100 mm diameter. Both ball and disk were ultrasonically cleaned in toluene, followed by acetone, prior to a test, and a new ball was used for each test. The load applied was 20 N, corresponding to a maximum Hertz contact pressure of 0.54 GPa. Film thickness measurements were carried out over a temperature range of 40–100 °C, and a range of entrainment speeds between 0.005 and 3.0 m/s.

The refractive index of the lubricant film must be known to determine the actual film thickness. In the current work, this was measured using an Abbe 60 refractometer from Bellingham and Stanley Ltd. (UK). The measurements were made over a temperature range of 40–100 °C for each vegetable oil and its blends with the viscosity modifier.

2.5. Friction measurements

The minitraction machine (MTM) technique allows determination of the "Stribeck curve", which plays an important role in the identification of the different lubrication regimes: hydrodynamic (HL), elastohydrodynamic (EHL), mixed lubrication (ML) and boundary lubrication (BL) [25]. In this method, a rolling-sliding lubricated contact is formed between a steel ball and the flat

Table 1
Fatty acid composition of the vegetable oils studied.

Vegetable oils	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Ricinoleic (18:1:OH)	Unsaturated/saturated ratio
HOSO	3.84	4.42	83.66	8.08	–	–	11.10
CO	2.63	1.51	4.74	8.36	–	82.8	23.20
SYO	11.28	2.70	24.39	56.28	5.34	–	6.15