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Suitability of ethyl cellulose as multifunctional additive for blends of vegetable oil-based lubricants

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ABSTRACT

In a previous study, ethyl cellulose was successfully blended with castor oil and the results demonstrated its suitability to be used as additive to expand the range of operating conditions under which fluid film lubrication is sustained, mainly at high temperature. However, apparent solubility problems were detected when mixed with other vegetable oils with lower polarity than castor oil. In this work, a suitable combination of ethyl cellulose (EC) with both high oleic sunflower (HOSO) and castor (CO) oils was found able to reach stable and non gel-like blends with viscosities at 40 °C ranging between 62 and 493 cSt, and viscosity indexes fitting into group III (VI ≥ 120) of API classification of base fluids. The ternary HOSO/CO/EC blend showed an important reduction in friction coefficient at low entrainment speed, and generated a stable EHD-film at 100 °C of around 20 nm, which suggests better boundary properties than HOSO/EC or CO/EC blends. On the other hand, ethyl cellulose hindered wax crystallization process of these vegetable oil-based lubricants at 5 °C, yielding comparable results to those obtained with standard polymethacrylate backbone additives. Therefore, the suitable combination of both castor and HOSO with EC as multifunctional additive allow a set of eco-friendly base fluids to be formulated with a wide kinematic viscosity range, better viscosity-temperature dependence than many mineral or synthetic oils lubricants and excellent boundary lubrication properties, making them suitable for many lubricant applications.

1. Introduction

Lubricants are made by combining a base oil with suitable additives that enhance inherent characteristics of the oil or impart new performance properties to the blend. The base oil is the main constituent and has traditionally been of mineral or synthetic nature (Erhan and Adhvaryu, 2002). However, most base stocks have a negative impact on the environment since they are not readily biodegradable (Lawate, 2006).

It has been estimated that around 1 million tonnes of loss lubricants (20% of the total market) are released into the environment every year. Consequently, worldwide environmental concerns have started to become aware of pollution from lubricating oils via spills or leakage (Bartz, 1998; Garcés et al., 2011). Governmental directives are now in place regarding the preservation of the environment and product ecolabelling has been introduced, i.e. the EU ecolabel defined in the Commission Decision 05/360/EC. This has reinforced the relevance of base oil biodegradability, which is now one of the most important design criteria for both selection of the base oil and overall formulation of the finished lubricant (Erhan and Asadaukas, 2000). For this reason, vegetable oil-based lubricants represent an important alternative to mineral oils in environmentally-sensitive applications, for instance, chain saw-bar oils, two-stroke engine oils, marine oils and outboard engine lubricants (Lawate, 2006).

Besides biodegradability and low toxicity, vegetable oils-based lubricants show other advantages against traditional lubricating oils, such as low volatility, good lubricity and high viscosity index (Miles, 1998; Erhan and Asadaukas, 2000; Adhvaryu and Erhan,

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2002). Consequently, significant scientific efforts have been applied to the exploration of lubricant applications of vegetable oils such as jojoba (Sivasankaran et al., 1988; Bisht et al., 1993), sunflower, high-oleic sunflower (Asadaukas et al., 1996; Quinchia et al., 2009), soybean (Honary, 1996; Castro et al., 2006), castor (Ogunniyi, 2006; Mutlu and Meier, 2010; Quinchia et al., 2012), rapeseed (Durak, 2004; Arumugam and Sriram, 2013), coconut (Jayadas et al., 2007), palm (Cheenkachorn and Fungtammasan, 2010; Syahrullail et al., 2011), jatropha (Golshokouh et al., 2013) and karanja (Panchal et al., 2015) oils.

Among all of these vegetable oils, there are two that are potentially applicable as lubricant base oils, castor oil and high-oleic sunflower oil. Castor oil is a non-edible crop, showing good performance at low temperatures, high kinematic viscosity and excellent lubrication properties (Ogunniyi, 2006; Mutlu and Meier, 2010; Quinchia et al., 2012). The high viscosity of this vegetal oil is unusual and a result of the hydrogen bonding of the hydroxyl group in the predominant ricinoleic fatty acid (Ogunniyi, 2006). On the other hand, high-oleic sunflower oil is considered a potential base stock because of its high content in oleic acid and low level of polyunsaturated fatty acids, resulting in a suitable thermal resistance at high temperatures in comparison with other vegetable oils, such as soybean, sunflower, rapeseed, etc. (Quinchia et al., 2009).

In spite of these benefits, vegetable oil-based lubricants have important disadvantages such as low thermo-oxidative stabilities, narrow viscosity range and higher pour points than petroleum-based lubricants (Miles, 1998; Erhan and Asadaukas, 2000; Adhvaryu and Erhan, 2002). Efforts have been made to overcome these performance limitations and to make vegetable oil-based lubricants a feasible alternative to petroleum-based lubricants. Most are focused on chemical modification of vegetable oils (Adhvaryu and Erhan, 2004; Erhan et al., 2006; Sharma et al., 2006; Campanella et al., 2010; McNutt and He, 2016), the synthesis of estolides from fatty acid as viscosity improvers (Cermak and Isbell, 2001; García-Zapateiro et al., 2013) or their blends with antioxidants, viscosity modifiers, wear reducers, pour point depressant additives, among others (Maleque et al., 2003; Quinchia et al., 2009, 2010; González et al., 2016).

In previous studies, different authors (Quinchia et al., 2014; Davidovich-Pinhas et al., 2015) tested the possible use of ethyl cellulose as an additive in a variety of vegetable oils. Ethyl cellulose was found to improve both the viscometric and tribological behaviour of the vegetable oils, in particular by increasing viscosity index and reducing pour point. However, remarkable solubility problems were found with vegetable oils of lower polarity than castor oil, for instance, with high oleic sunflower and soybean oils. The current work extends this previous research by addressing the solubility problems of ethyl cellulose in vegetable oil-based lubricants. The goal is, by investigating the influence of EC molecular weight and concentration on blend properties, to show that this environmental friendly polymer can be a successful additive for vegetable oil-based lubricant formulations for use in lubricant applications.

2. Materials and methods

2.1. Materials

Two vegetable oils were used as base stocks: castor oil and high-oleic sunflower (85 wt.% oleic acid) oil. CO was received from Guinama (Spain) and HOSO was kindly supplied by “Instituto de la Grasa-CSIC” (Spain). The oils were used as received without any further purification. The vegetable oils fatty acid compositions are shown in Table 1.

Ethyl celluloses (48% ethoxy content) (EC) were supplied by Sigma Aldrich (Spain). Their density, at 25 °C (ASTM D-792), was 1.140 g cm^{-3} and melting temperature 150 °C. Four ethyl cellulose derivatives, with different molecular weights, were studied: $3.891 \cdot 10^4$, $6.896 \cdot 10^4$, $7.653 \cdot 10^4$, and $8.217 \cdot 10^4$ (g/mol) (Table 2). Ethyl cellulose is a polar and water-insoluble polymer. The main chain of EC is given by anhydroglucose units linked by 1,4-β-glucosidic bonds (Shi et al., 2008). It is a natural polymer, biodegradable and not hazardous according to the Commission Directive 93/21/EEC.

2.2. Preparation of biolubricant formulations

Ethyl cellulose was added to HOSO, CO and their blends (HOSO/CO) at a concentration range of 0.5–2 wt.%. Sánchez et al. (2009) previously stated this upper limit. Various proportions of the two vegetable base oils were studied, corresponding to 10 wt.%, 30 wt.%, 50 wt.%, 70 wt%. and 90 wt.% CO in HOSO. Blends were prepared according to method proposed by Quinchia et al. (2010). Afterwards samples were cooled down to room temperature.

2.3. Methods

2.3.1. Viscosity and density measurements

A controlled-strain rotational rheometer, model ARES (Rheometric Scientific, UK) was used to measure the dynamic viscosities, over a temperature range between −40 and 120 °C. Viscous flow curves were obtained using a Couette geometry (inner radius: 16 mm, outer radius: 17 mm, cylinder length: 33.35 mm), in a shear rate range of 5–500 s^{-1}. In addition to this, cooling ramps at 10 s^{-1} and 1 °C/min were performed in a temperature range between 25 and −40 °C. At least two replicates of each test were performed on fresh samples.

Kinematic viscosity values were obtained as the ratio of the dynamic viscosity to density. The viscosity index (VI) was calculated according to ASTM D 2270.

Densities were measured within a temperature range of 25–120 °C using a capillary densimeter, model DMA-5000 (Anton Paar, Austria).

2.3.2. Thermal analysis by DSC

Cooling curves of both vegetable oils studied and their blends were obtained using a differential scanning calorimetry (DSC) Q-100 (TA instrument Waters, USA). Between 5 and 10 mg samples were sealed in hermetic aluminium pans at 25 °C and cooled immediately to −80 °C, with a cooling rate of 5 °C/min. Samples were purged with nitrogen, at a flow rate of 50 mL/min. The cooling curve for each sample was analysed to determine wax appearance and onset temperature of freezing.

2.3.3. Pour point temperature measurement

The pour point is defined as the lowest temperature at which the oil flows when it is cooled (Quinchia et al., 2012). The pour point of neat vegetable oils and their blends was determined according to

Table 1
Fatty acid composition of the different vegetable oils studied (Quinchia et al., 2010).

Fatty-acids	Vegetable oils	
	HOSO	CO
Palmitic (C16:0)	3.84	1.70
Stearic (C18:0)	4.42	1.96
Oleic (C18:1)	83.66	5.34
Ricinoleic (C18:1:OH)	TRACE	82.48
Linoleic (C18:2)	8.08	7.01
Linolenic (C18:3)	TRACE	1.51