

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 shown to be a suitable additive to expand the range of operating conditions under which fluid film lubrication is sustained, mainly at high temperature. However significant solubility problems were detected 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 an available viscosity range at 40 °C between 62-493 cSt, and viscosity indexes fitted into group III ($VI \geq 120$) 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 in 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.

Keywords: Biolubricant, ethyl cellulose, solubility, castor oil, high oleic sunflower oil, additive

1. Introduction

Lubricants are made by combining a base oil with suitable additives that enhance the oil's inherent characteristics 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 Asadauskas, 2000). For this reason, vegetable oil-based lubricants represents 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 Asadauskas, 2000; Adhvaryu and Erhan, 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, E., 2004.; Arumugam, G. Sriram , 2013), coconut (Jayada et al, 2007), palm (Cheenkachorn and Fungtamasan, 2010; Syahrullail, S., et al., 2011), jatropha (Golshokouh et al; 2013) and karanja (Tirth et al, 2015) oils.

Among all of these vegetable oils, there are two that are potentially especially applicable as base oils, castor oil and high-oleic sunflower oil. Castor oil is interesting due to its being 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, the 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. temperatures (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 a previous studies (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, significant 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 formulation for use in many 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. 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: 3.891·10⁴, 6.896·10⁴, 7.653·10⁴, and 8.217·10⁴ (g/mol) (Table 2). Ethyl cellulose is an infirmly 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.

Methods

2.2.1. 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 repeats 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).

2.2.2. 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 5–10 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.

2.2.3. 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 were determined according to the standard ASTM D97 test method.

2.2.4. Tribological properties

An ultrathin film interferometry were used to determine the film-forming properties of the lubricant samples under normal forces of 20 N (0.54 GPa), within a temperature range of 40–100°C and a range of entrainment speeds between 0.005 and 3.0 m/s. For this purpose, an EHL optical interferometry rig (PCS Instruments, UK) was used as previously described by Quinchia et al. (2014).

Stribeck friction curves were determined in rolling-sliding lubricated contact (slide-to-roll ratio (SRR) of 0.5) using a minitraction machine (MTM) under normal forces of 30 N (0.93 GPa), within a temperature range of 40–100 °C and varying the entrainment speed within 0.005–2.5 m/s, as previously described by Quinchia et al. (2014).

Statistical analysis

At least, two repeats of each test were done on fresh samples and data shown have statistically significant values, i.e. they did not exceed a significance level of 0.05 in Student's t-test and had a 95% confidence interval.

3. Results and discussion

3.1. The suitable ethyl cellulose molecular weight

To study the influence of the ethyl cellulose molecular weight, 0.5 wt.% solutions of each EC in CO were studied. Castor oil was selected because of its good solubility in this polymer, consequence of the presence of the –OH group in the ricinoleic fatty acid molecule (Ogunniyi 2006; Quinchia et al., 2014). Table 2 show kinematic viscosities, at 40 and 100 °C, and the respective increases in viscosity were analysed in order to select the most suitable viscosity improver. Thus, a significant increase in kinematic viscosity within the temperature range studied is noticed for all the ethyl cellulose compounds used. Nevertheless, the values of kinematic viscosity are quite similar for lubricants containing ethyl cellulose molecular weights close to or higher than $7 \cdot 10^4$ g/mol. On the other hand, it is worth pointing out that an increase in ethyl cellulose molecular weight reduces the shear stability of the blends and therefore may shorten the shelf-life

of the lubricants (Mang and Dresel, 2001). In consequence, a molecular weight of $6.90 \cdot 10^4$ g/mol (EC_45 cP) was selected in this study as a promising viscosity improver for vegetable-oil based lubricants.

3.1.1. Influence of ethyl cellulose concentration on the viscous flow behaviour of the biolubricant

Addition of viscosity improvers to a biolubricant may yield a non-Newtonian flow behaviour (Lansdown, 2004; Quinchia et al., 2009). To investigate this, different vegetable oil/EC blends were prepared to study the effect of ethyl cellulose concentration on the viscous flow behaviour of vegetable oil-based base stocks. Figure 1 shows the viscous flow curves, in a shear rate range of $5\text{-}500\text{ s}^{-1}$ and at $25\text{ }^{\circ}\text{C}$, as a function of EC concentration (0.5-2.0 wt.%) in CO and in HOSO. As can be observed, an increase in ethyl cellulose concentration yields a significant increase in the viscosity of the blend. However, the viscous behaviour of the blends depends on the nature of the vegetable base oil. Thus, blends with CO showed a non-Newtonian behaviour with a clear tendency to reach a zero-shear-rate-limiting viscosity. On the other hand, blends with HOSO also show a non-Newtonian behaviour, but with a clear tendency to reach a high-shear-rate-limiting viscosity. This soft gel-like behaviour observed is mainly consequence of both Van der Waals or hydrogen bridge forces with -OH groups in the ethyl cellulose molecule (Sánchez et al., 2011). These characteristic interaction forces associated to the hydroxyl group are more dependent on temperature (Smith et al., 2005). This weak forces are very dependent on temperature. In this last case, it is worth pointing out that although a

homogeneous single phase was obtained, the blends became cloudy after some hours.

According to the viscous flow behaviours shown in Figure 1, two different rheological models, Williamson's (equation 1) and Sisko's models (equation 2), were selected to fit the viscous flow behaviour of CO/EC and HOSO/EC blends, respectively.

$$\eta = \frac{\eta_0}{1 + (K \dot{\gamma})^m} \quad (1)$$

$$\eta = K_s \dot{\gamma}^{n-1} + \eta_\infty \quad (2)$$

where, η is the non-Newtonian viscosity, η_0 is the zero-shear-rate-limiting viscosity, η_∞ is the high-shear-rate-limiting viscosity, $\dot{\gamma}$ is the shear rate, m and n are parameters related to the slope of the shear-thinning region, K is a constant whose reciprocal coincides with the shear rate at which $\eta = \eta_0/2$, and K_s is the consistency index.

As can be expected, CO/EC blends show the highest values of viscosities, due to the presence of a hydroxyl group in the ricinoleic acid chain, which interacts with the hydroxyl group in the ethyl cellulose molecule (Ogunniyi, 2006). As compared to the viscosity of neat CO, a maximum increase to 283% of this value at 40 °C was obtained by adding 2 wt.% of EC, and 329% at 100 °C, which may correspond to an ISO VG 460 grade, used for gear applications (Stachowiak and Batchelor, 2013). In the case of HOSO, the viscosity of HOSO/EC blends only increased 155% at 40°C, and 190% at 100 °C, for blends containing 2 wt.% of EC, which may correspond to an ISO VG 46, used as crankcase oil (Stachowiak and Batchelor, 2013).

3.1.2. Influence of ethyl cellulose concentration on the viscosity-temperature dependence of the biolubricant

In addition to its role as viscosity improver, ethyl cellulose may also influence the viscosity index of vegetable oil-based lubricants. Figure 2 displays the effect of temperature on the viscous flow behaviour of CO/EC blends with ethyl cellulose concentrations ranging between 0.5-2.0 wt.%. The influence of temperature on the viscous flow behaviour of vegetable oil/EC blends is discussed based on the results obtained for CO/EC blends, since the solubility of EC_45 cP in CO is much higher than in HOSO. As can be observed in this figure, the viscous flow behaviour of these blends is largely influenced by an increase in temperature, showing an apparent non-Newtonian behaviour at temperatures lower than 70 °C and almost a Newtonian behaviour at higher temperature. As consequence, the viscosity of CO/EC blends showed an asymptotic tendency with EC weight content for temperatures lower than 70°C, but a linear tendency within the temperature region in which Newtonian behaviour was observed (Table 3).

Due to the non-Newtonian behaviour observed, the viscosity-temperature dependence of these blends was characterized at a specific shear rate. Thus, as previously justified by Quinchia et al. (2009), a shear rate of 500 s^{-1} was selected for these non-Newtonian blends. The kinematic viscosities, at 500 s^{-1} , for CO and HOSO and the whole set of blends with ethyl cellulose studied over a temperature range of 25-120 °C are shown in Table 3. This temperature range was selected to include the traditional temperature range used to characterize lubricating oils (40 and 100°C).

In relation to the temperature-dependence viscous flow behaviour over room temperature, viscosity index (VI) shown in Table 3 demonstrate that CO/EC blends show the largest thermal susceptibility of viscosity, which could be a consequence of the higher temperature dependence of the characteristic interactions associated to the hydroxyl group (Smith et al., 2005). A significant increase in VI values was obtained for CO/EC blends by raising EC concentration up to 2 wt.% (from 116 up to 176), which places this blend into group III of API classification of base fluids. On the other hand, the most significant increment in VI values was obtained for HOSO/EC blends, increasing from 257 to 342 for the blend containing 2 wt.% EC. All HOSO/EC blends can be assigned to group III API classification, which indicates their availability for multi-range applications (Lansdown, 2004).

In relation to the low-temperature viscous flow behaviour, Figure 3 shows the viscosities at 10 s^{-1} for HOSO, CO, and their 1 wt.% of EC blends, over the temperature range between 25 and -40°C . As was previously pointed out by Quinchia et al. (2012), a sharp increase in viscosity is observed for HOSO at low temperature, as a consequence of the beginning of a fast crystal growth process. The addition of EC at 1 wt.% slows down the wax crystallization process of HOSO, thus acting as pour point depressant (PPD), and yielding comparable results to those obtained with standard PPDs normally used for mineral oils, such as, for example, those containing a polymethacrylate backbone. On the other hand, the ethyl cellulose does not negatively affect the low-temperature viscous flow behaviour of CO, since neat castor oil does not show the above-mentioned sharp increase in viscosity within the temperature

range studied, although a steady increase in viscosity is also noted (see Figure 3).

These results were compared with the pour point values obtained from ASTM D 97-09 test. Addition of 1 wt.% EC delayed the wax crystallization of HOSO from -18 to -21 °C, and improved CO pour point temperature from -21 to -33 °C. Therefore, the effect of EC as PPD is significantly better than that of other additives, such as ethylene-vinyl acetate copolymer or even additives containing a polymethacrylate backbone, which suggest the possibility of using EC as pour point depressant alongside its role as viscosity and VI improver, or boundary lubricity additive.

3.2. *The ternary HOSO/CO/EC blend*

From the experimental results previously shown, it is worth highlighting both the high viscosities obtained for blends of CO and EC and the promising viscosity index values and stability against oxidation obtained for the blends of the later with high-oleic sunflower oil. This might suggest that HOSO/CO/EC blends could combine all these improvements, allowing us to formulate vegetable oil-based base stocks for a wide range of applications, such as hydraulic, metal working, gearboxes, differentials, bearings, etc. **Nevertheless, wear tests should be done in order to investigate the possibility of chemical reactions at high temperatures between ethyl cellulose and fatty acid and its consequence on the lubrication process at extreme boundary lubrication conditions.**

In relation with the solubility of ethyl cellulose on both HOSO and CO, ethyl cellulose showed a high solubility in castor oil but not in high-oleic sunflower oil. However, a mixture of HOSO and CO might overcome this constraint. On this

basis, time-viscosity dependence of HOSO/CO/EC blends was monitored for 460 days in order to study the stability of their ternary blends. Figure 4 shows the viscous flow behaviour and the viscosity values at high shear rate (500 s^{-1}) of HOSO/CO (1:1) with 1 wt.% EC, at 40°C , as a function of ageing. As can be observed in Figure 4a, a shear-thinning behaviour (defined by Sisko's model) is noticed. In addition, the consistency index continuously increases with ageing time, which is a consequence of a gelification process due to interactions between ethyl cellulose and high-oleic sunflower oil, more important (much lower values of the flow index) after 150 days ageing. However, the viscosity values at 500 s^{-1} do not increase with ageing because of higher shear-thinning characteristics (lower values of the flow index, due to the progress of the gelification process) resulting from a dramatic network breakdown at high shear rates.

3.2.1. Influence of HOSO/CO ratio on the viscous flow behaviour and viscosity/temperature dependence of the ternary HOSO/CO/EC blend.

The HOSO/CO/EC blends showed different viscous flow behaviours depending on HOSO/CO ratio. At 25°C , all of them displayed a shear-thinning behaviour at 25°C (Table 4). However, the viscous flow behaviour of ternary blends with low HOSO/CO ratios (lower than 50%) was described by Williamson's model (equation 1), while for higher HOSO/CO ratio, the viscous flow behaviour was described by Sisko's model (equation 2). On the other hand, a Newtonian behaviour was noticed for temperatures above 40°C . Finally, it is worth remarking that a decrease in HOSO/CO ratio led to higher viscosities and increased viscosity-temperature dependence, as expected (Figure 5).

Table 5 shows both viscosity and viscosity index values for HOSO/CO/EC blends with 1 wt.% EC. As can be seen, a wide range of vegetable oil-based base stocks could be formulated by using these ternary blends, with kinematic viscosities at 40 °C ranging from 62 to 493 cSt. This suggests they can provide a suitable viscosity range for a wide number of lubricant applications, such as hydraulic, metal working, gearboxes, differentials, bearings, etc. The blends studied belong to group III ($VI \geq 120$), according to the API Base Oil classification, or to groups ranging from VG68 to VG 460, according to ISO viscosity grade classification (ASTM D2422).

Concerning these results, the empirical mixing rule previously proposed by Quinchia et al. (2010) was used in this work to predict the viscosity of HOSO/CO/EC blends with 1 wt.% EC,

$$\log \nu_{mix} = \sum_i x_i \log \nu_i + \Delta \nu_{mix} \quad (3)$$

where ν_{mix} is the kinematic viscosity of HOSO/CO/EC blends, ν_i is the kinematic viscosity of binary blends, x_i is the weight fraction of the binary vegetable oil/EC mixtures, and $\Delta \nu_{mix}$ is the mixing contribution, which takes into account possible interactions. The mixing contribution is, in all cases, less than 4% and, in most cases, lower than 2%, independently on HOSO/CO ratio and temperature. Consequently this proposed mixing rule predicts the viscosities of the above mentioned ternary blends fairly well.

Apart from their good stability during ageing, the promising viscosity index values and the wide range of kinematic viscosities available for this set of HOSO/CO/EC blends, these blends also show enhanced low-temperature viscous flow behaviour. Figure 6 demonstrates that the crystallization event is

shifted to a lower temperature when HOSO is blended with EC and CO. Thus the temperature for the onset of this event drops 1.3 °C when 1 wt.% EC is added to HOSO and almost 5 °C for the ternary HOSO/CO/EC blend. In this sense, the ternary blend shows an onset crystallization temperature of around -40 °C, with the feature that the crystallization enthalpy tends to decrease as CO concentration increases in the ternary system.

3.2.2. Lubrication performance of the ternary HOSO/CO/EC blend.

As it is well known, an optimal control of the lubrication process would require constant viscosity values over the standard shear rate range for a particular application. Thus, HOSO/CO/EC blends with a Sisko-like flow behaviour would be more convenient than a Williamson-like behaviour. On the other hand, lower HOSO/CO ratio should be preferred, due to both the high viscosity and excellent lubrication properties of castor oil. As consequence, HOSO/CO (1:1) ratio was selected to study the lubrication performance of the ternary HOSO/CO/EC blend (Figure 7).

As highlighted in previous work (Quinchia et al, 2014), ethyl cellulose on HOSO formed a very thick boundary film of around 70 nm at low speed and 40 °C, while the effect of EC on castor oil film thickness was marginal at 40 °C over the whole entrainment speed range studied. However, at 100 °C, the CO/EC blend showed a slightly thicker film across the whole entrainment speed range studied. HOSO/CO/EC blends combine these behaviours and dampen the effect of temperature on film thickness. Thus, HOSO/CO/EC blends do not form a gel and the EHD-film generated is stable in the whole temperature range studied. At 40 °C, a boundary film of around 40 nm was measured at 0.01 m/s

(Figure 7a), whilst, at 100 °C, the thickness of the boundary film of this ternary blend was 20 nm (Figure 7b). Thus, the HOSO/CO/EC blend showed, at 100 °C, the thickest boundary film at low entrainment speed, which suggests better boundary properties in comparison with the HOSO/EC or/and CO/EC binary blends.

The boundary lubricity capacity of this ternary system is displayed in the friction coefficient versus entrainment speed curves Figure 8, which can be considered equivalent to the Stribeck curve, since both normal force and viscosity at high shear rate are constant in all tests. Quinchia et al. (2014) pointed out that CO and HOSO showed very different lubricating behaviour. In consequence, HOSO/CO blend try to combine the advantages of both vegetable oils. Thus, the mixed boundary-EHD region is shorter and the friction coefficient for this region is lower than those for HOSO, showing a decrease in the friction coefficient at 0.01 m/s from 0.037 (for HOSO) to 0.028 (for HOSO/CO blend). By contrast HOSO/CO EHD friction coefficient is higher than that of HOSO (increasing from 0.020 up to 0.026), probably due to the existence of intermolecular bonding between the hydroxyl groups present in CO molecules. Therefore, the variation of friction coefficient over the whole entrainment speed range studied is much lower than for HOSO. Moreover, the sudden drop in castor oil friction coefficient at large sliding speed is minimized when it is blended with HOSO. In addition, almost identical results were obtained for the ternary HOSO/CO/EC blend.

At 100°C (Figure 8.b), all base stocks showed qualitatively similar Stribeck curves. Nevertheless, it is apparent that the friction coefficient of the HOSO/CO blend is lower than those for CO or HOSO at most of the entrainment speeds

studied. At high temperature, the boundary lubricity capacity of ethyl cellulose is more relevant. Thus, the ternary HOSO/CO/EC blend shows an important reduction in friction coefficient at low entrainment speed, which is related to the thicker film formation observed at low speed when 1 wt.% EC is added to a HOSO/CO blend.

4. Conclusions

Blends of castor and high oleic sunflower oils not only combine the high viscosity of CO and the superior stability against oxidation of HOSO, but also serve to enhance the solubility of polar lubricant additives in an otherwise nonpolar vegetable oil-based base oil. This enables ethyl cellulose to be used as an eco-friendly multifunctional additive in HOSO/CO blends.

A wide set of vegetable oil-based base fluids may be formulated based on the above mentioned ternary blends. Thus, taking into account the CO/HOSO blend (1:1) taken as reference, addition of 1 wt.% EC to this HOSO/CO blend yields viscosities of 174 cSt at 40 °C and 26 cSt at 100 °C. These viscosities fit into group from VG150, according to ISO viscosity grade classification (ASTM D2422). For other CO/HOSO blends, increments up to 795% at 40 °C and 229% at 100 °C can be reached increasing the content of castor oil, which fit into groups ranging from VG68 to VG 460, according to ISO viscosity grade classification (ASTM D2422). Overall, all CO/HOSO blends have viscosity indices fit into group III ($VI \geq 120$) of API classification of base fluids.

The addition of ethyl cellulose hinders the wax crystallization process of HOSO, acting as a more effective pour point depressant than additives such as ethylene-vinyl acetate copolymer or even additives containing a polymethacrylate backbone, which are normally used for mineral oils. Thus 1

wt.% EC delayed wax crystallization of HOSO from -18 to -21 °C (ASTM D 97-09) and from -21 to -33 °C (ASTM D 97-09) for CO. In addition to this, the HOSO/CO crystallization event, measured by DSC, dropped around 5 °C after addition of 1 wt.% EC.

In relation to lubrication, ethyl cellulose may enlarge the range of operating conditions under which a lubricant film is sustained, especially at high temperature. HOSO/CO (1:1) blends with up to 2 wt.% EC did not gel and generated stable EHD-film at all temperatures studied. At 100 °C, the ternary blend showed the thickest boundary film (around 20 nm) at low entrainment speed, which suggests better boundary properties than HOSO/EC or CO/EC blends. At 40 °C, HOSO/CO/EC blend showed a boundary film of around 40 nm at 0.01 m/s. This boundary lubricity capability of ethyl cellulose can also be seen in Stribeck friction curves, especially at 100°C. Thus, the friction coefficient at low entrainment speed (0.01 m/s) is lower than that obtained for EC-free HOSO/CO blends, in this instance 36% lower. At 40°C, the mixed boundary-EHD region of the ternary blend was narrower and the variation of the friction coefficient at low entrainment speed was much lower than for HOSO and CO.

It can be concluded that blends of castor and high oleic sunflower oils with ethyl cellulose allow us to formulate a set of eco-friendly base stocks with a wide kinematic viscosity range, better low-temperature viscous flow behaviour and better viscosity-temperature dependence than many mineral or synthetic oils lubricants, and excellent boundary lubrication properties. This makes them suitable for a number of lubricating applications (i.e. hydraulic, metal working, gearboxes, differentials, bearings, etc.).

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Figure Captions

Figure 1. Viscous flow curves and model parameters for CO/EC (a) and HOSO/EC (b) blends, as a function of EC concentration, at 25 °C (solid lines represent the fitting of the rheological model).

Figure 2. Viscous flow curves of CO/EC blends, as a function of EC concentration, and at different temperatures, (solid lines show the fitting of the rheological models).

Figure 3. Apparent viscosities, at 10 s^{-1} , for HOSO, CO and their binary blends with 1 wt.% EC, in a temperature range between +25 and -40 °C.

Figure 4. Influence of ageing on viscous flow curves, at 40°C (a) and viscosities at 500 s^{-1} (b), for HOSO/CO/EC blends (EC concentration: 1 wt.%).

Figure 5. Evolution of dynamic viscosity with temperature for selected HOSO/CO/EC blends (different HOSO/CO ratios, EC concentration: 1 wt.%). Arrhenius' equation fitting parameters (A and E_a) are shown at the legend.

Figure 6. Downward DSC temperature sweep heat flow curves (10 °C/min) for HOSO, CO and HOSO/CO blends with and without EC (1 wt.%).

Figure 7. Film thickness formation, as a function of entrainment speed, for HOSO, CO and their blends with 1 wt.% EC at (a) 40 °C and (b) 100 °C.

Figure 8. Friction coefficient versus entrainment speed curves for HOSO, CO and their blends with 1 wt.% EC at (a) 40 °C and (b) 100 °C.

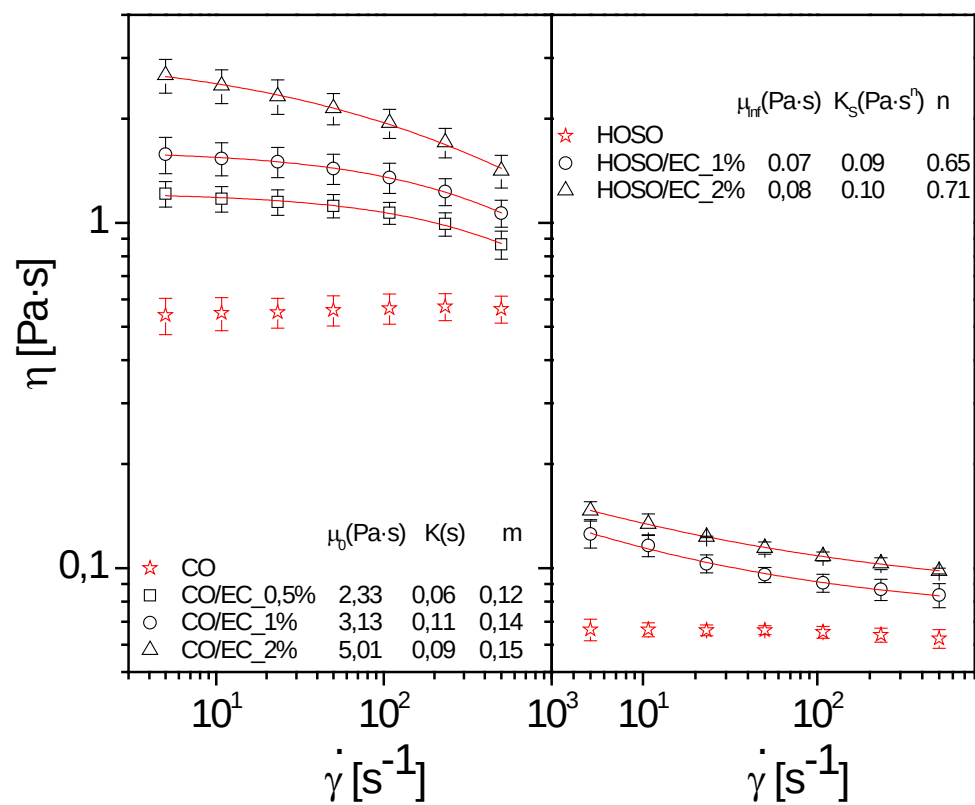


Figure 1

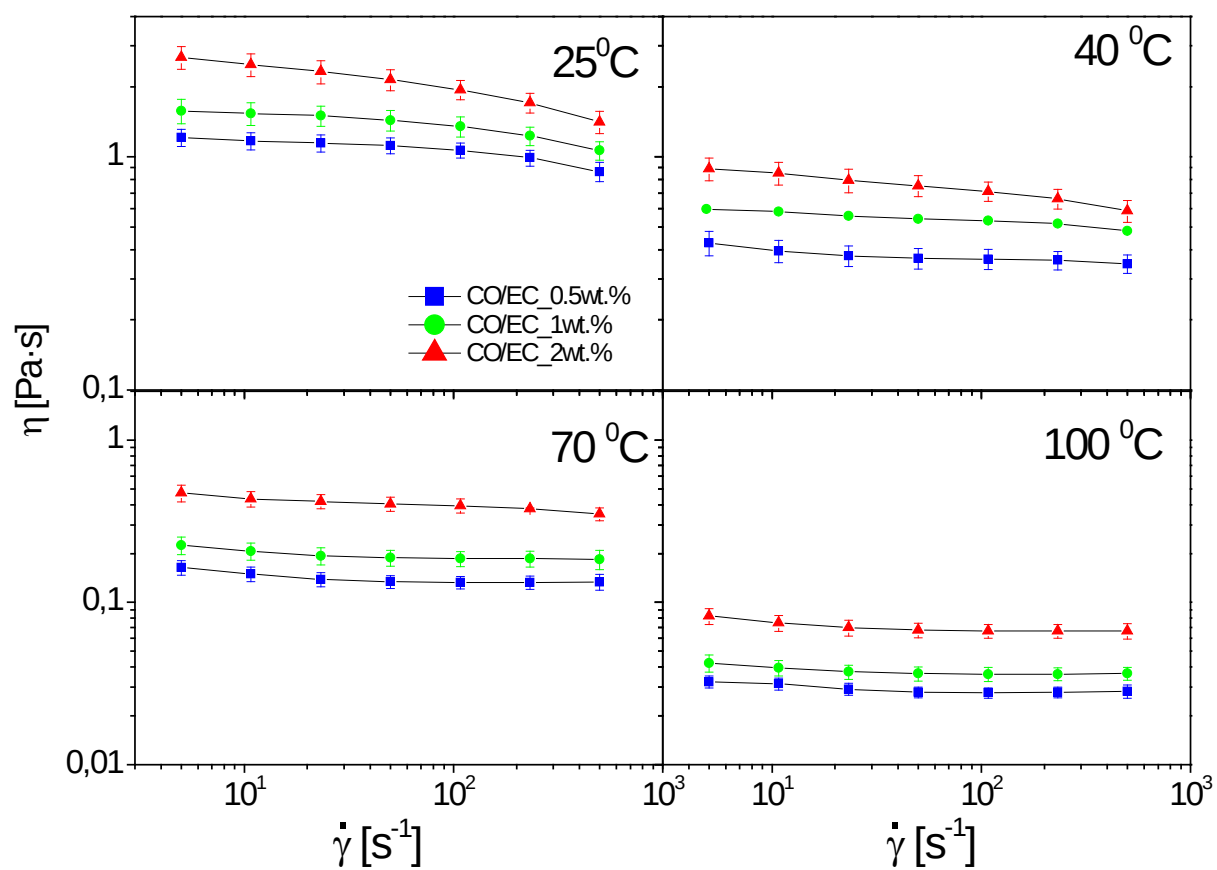


Figure 2

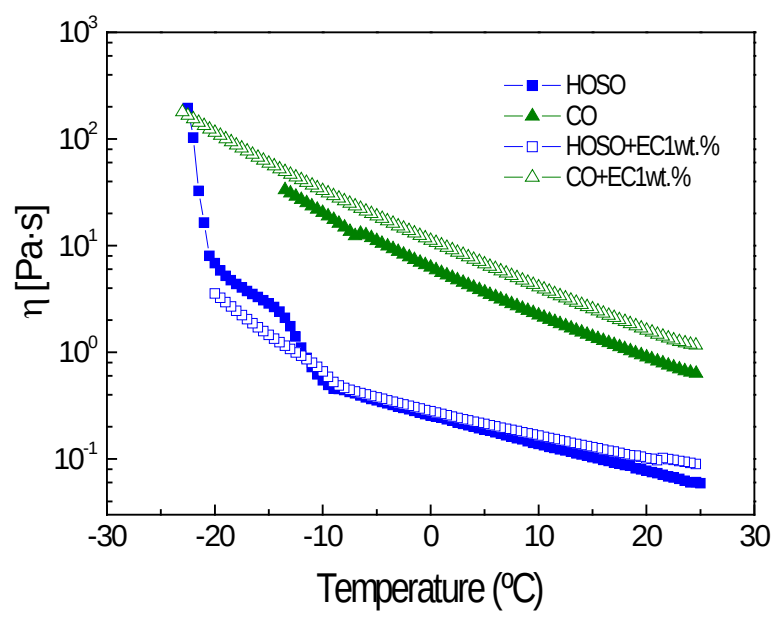


Figure 3

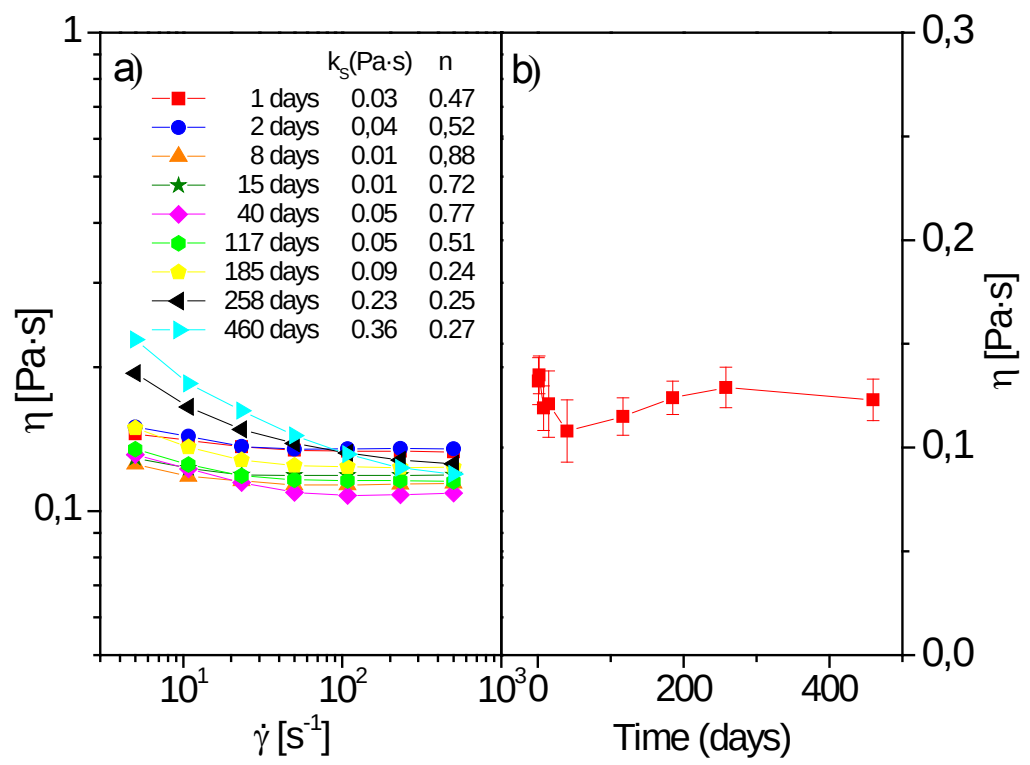


Figure 4

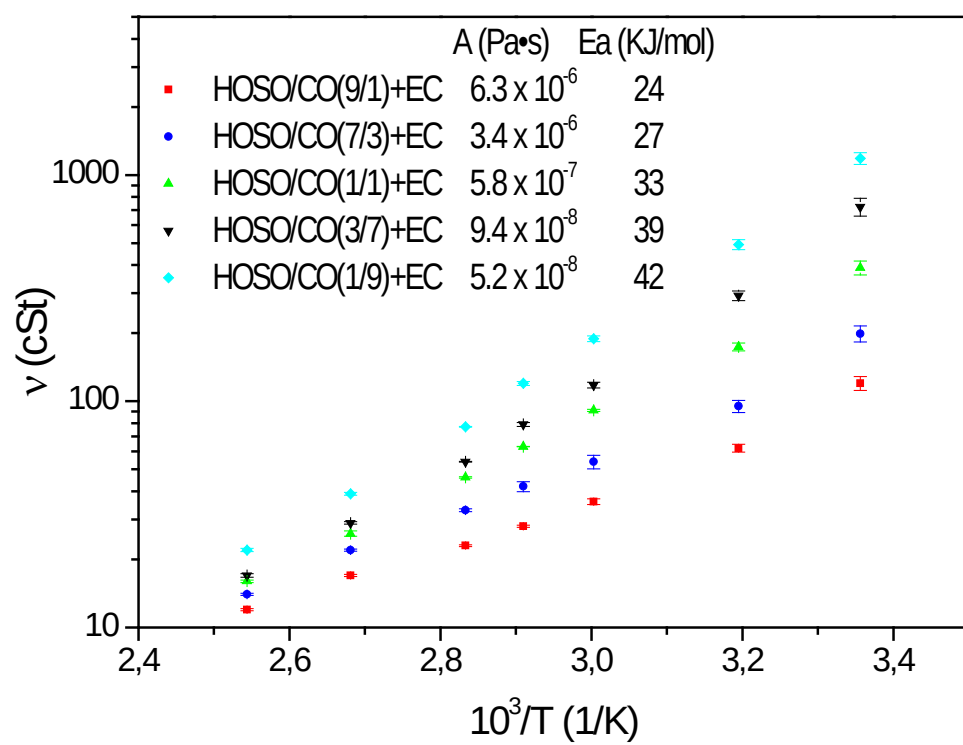


Figure 5

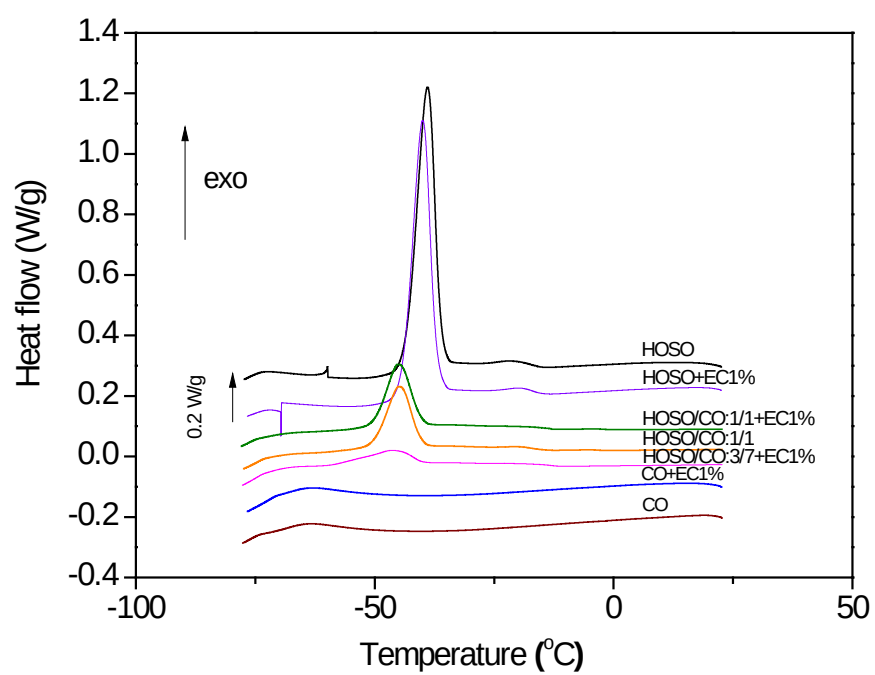


Figure 6

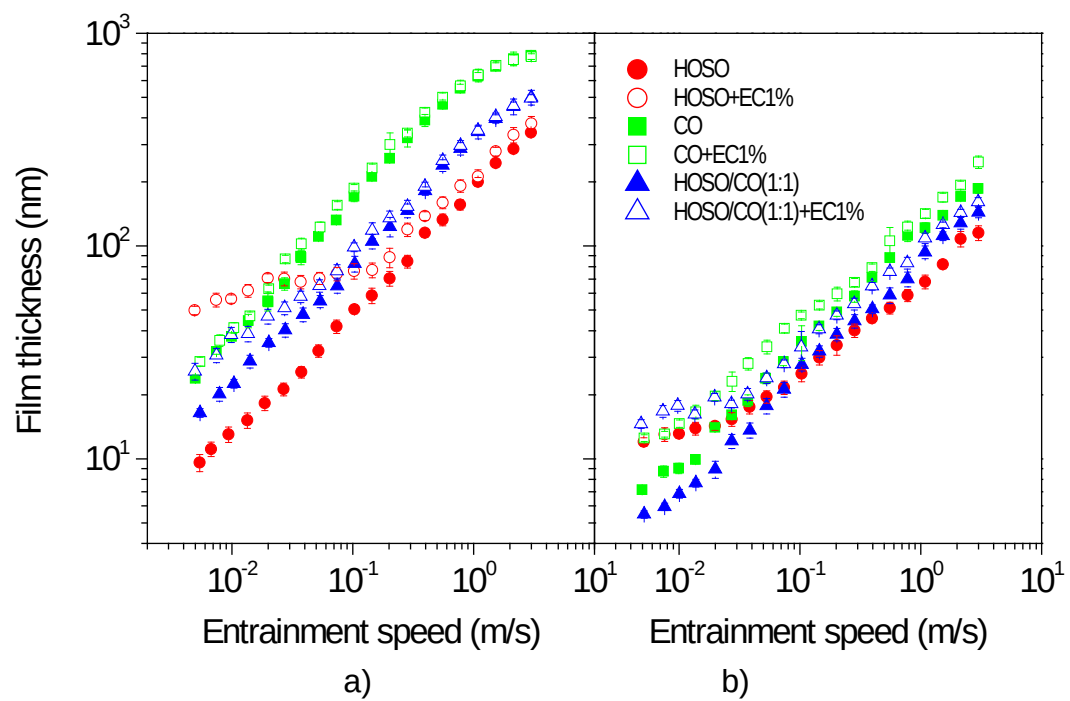


Figure 7

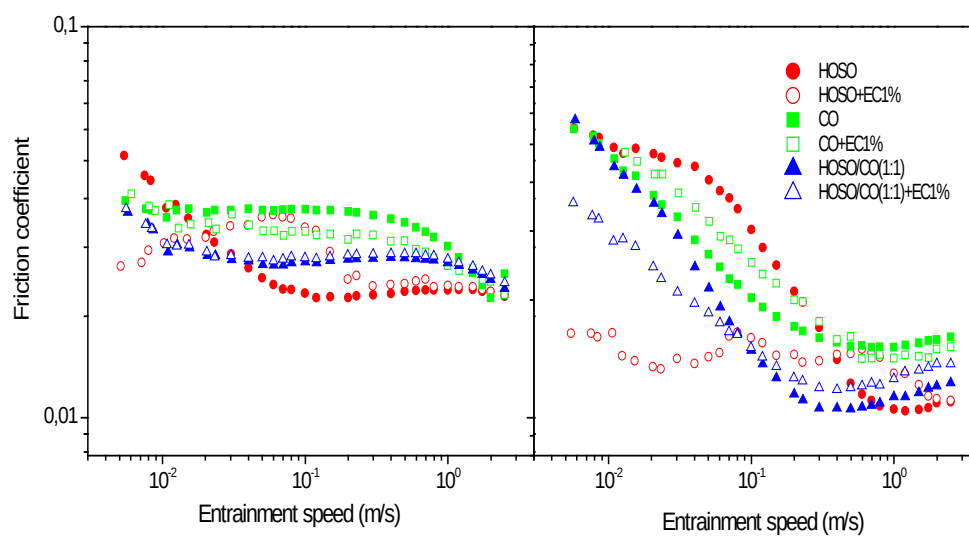


Figure 8

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

Table 2. Kinematic viscosities and viscosity indexes of castor oil and its blends with different ethyl cellulose derivatives (0.5% wt.%)

Sample	M _w (g/mol) of ethyl cellulose	Kinematic viscosity (cSt)		Viscosity Index
		40°C	100°C	
Castor oil	-	242±21.9	21±2.0	116
CO/EC_4 cP	3.891·10 ⁴	281±17.5	24±2.1	106
CO/EC_45 cP	6.896·10 ⁴	420±37.8	31±2.3	114
CO/EC_100 cP	7.653·10 ⁴	379±24.3	31±0.9	115
CO/EC_300 cP	8.217·10 ⁴	390±30.9	33±1.5	123

* Intrinsic viscosity (in cP) is based on standard TAPPI 230

Table 3. Kinematic viscosities (cSt) at 500 s⁻¹ in a temperature range of 25–120°C and viscosity indexes (VI) for the different CO/EC and HOSO/EC blends studied

Temperature (°C)	Castor oil				High oleic sunflower oil		
	EC 0%	EC 0.5%	EC 1%	EC 2%	EC 0%	EC 1%	EC 2%
25	574±54.0	1141±96.3	1408±115.0	1741±168.5	74±4.7	95±8.4	111±6.5
40	242±21.9	420±37.8	547±21.6	686±43.9	39±0.8	51±5.6	59±0.9
60	81±10.9	147±25.4	202±9.2	378±25.8	24±0.1	30±0.8	37±1.2
70	53±6.0	92±10.4	125±3.1	239±7.5	18±2.4	24±2.2	29±0.8
80	37±3.5	60±3.1	81±1.7	155±5.2	15±0.1	20±0.2	24±0.3
100	21±2.0	31±2.9	40±0.1	69±0.5	10±0.9	15±1.6	19±1.5
120	13±0.0	18±0.1	22±0.0	37±0.2	7.0±0.1	11±0.1	16±0.2
VI (ASTM D 2270)	116	104	117	176	257	314	342

Table 4. Williamson's and Sisko's model parameters for HOSO/CO + EC (1 wt.%) blends, at 25 °C

Ternary blends	Sisko's model			Williamson's model		
	η_{∞} (Pa·s)	K_s (Pa·s ⁿ)	n	η_0 (Pa·s)	K (s)	m
HOSO/CO(9/1)+EC	0.095	0.26	0.48	-	-	-
HOSO/CO(7/3)+EC	0.14	0.49	0.57	-	-	-
HOSO/CO(1/1)+EC	0.10	0.46	0.87	-	-	-
HOSO/CO(3/7)+EC	-	-	-	1.33	0.11	0.06
HOSO/CO(1/9)+EC	-	-	-	2.44	0.14	0.10

Table 5. Kinematic viscosities (cSt), in a temperature range of 25–120°C, and viscosity indexes (VI) for the different ternary HOSO/CO + EC (1wt.%) blends studied

Temperature (°C)	HOSO/CO(9/1)	HOSO/CO(7/3)	HOSO/CO(1/1)	HOSO/CO(3/7)	HOSO/CO(1/9)
25	120±8.4	199±15.9	389±28	724±65.2	1186±71.2
40	62±2.5	95±5.7	174±6.7	293±14.7	493±24.7
60	36±1.1	54±3.8	91±1.0	118±3.5	189±5.7
70	28±0.3	42±2.1	62±0.1	79±1.6	120±2.4
80	23±0.2	33±0.4	46±0.3	54±0.2	77±0.3
100	17±0.2	22±0.2	26±0.7	29±0.4	39±0.6
120	12±0.1	14±0.2	16±0.2	17±0.3	22±0.4
VI (ASTM D 2270)	284	264	185	134	122
ISO Grade	ISO VG68	ISO VG100	ISO VG150	ISO VG320	ISO VG460

Toc graphic

