A Study of the Oxidation and Wear Properties of Vegetable Oils: Soybean Oil Without Additives

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ABSTRACT: The use of biodegradable lubricants in diverse applications continues to increase. Vegetable oils (e.g., soybean oil) are the main biodegradable lubricant base stocks used worldwide. However, there are concerns about their oxidative stability and low-temperature performance. Improvements in oxidative stability can be made through chemical or genetic modifications. This work compared the effects of oils with different chemical compositions. Soybean oil, high-oleic soybean oil, and epoxidized soybean oil were compared in laboratory bench tests. The tests conducted include the Penn State sequential four-ball wear test and the Penn State micro-oxidation test. Oxidation products from the micro-oxidation test were analyzed by FTIR and gel permeation chromatography. In this paper, all oils were evaluated neat, without additives.

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It is only natural that lubricant technology has advanced as a result of concerns for protecting and preserving the environment in all aspects of our lives. Research and development in lubricant technology to find better ways to protect the environment—or at least to reduce environmental pollutants—is driven by public demand, industry concerns, and governmental agency policies. The negative impact of the spillage or leakage of lubricants has led to the development of oils and greases that are less detrimental to the environment if inadvertently spilled or leaked.

As a result of these growing environmental concerns, vegetable oils and their derivatives are finding their way into lubricants used in industrial and transportation applications. Vegetable oils can offer significant environmental advantages with respect to biodegradability and renewability, as well as satisfactory performance in a variety of applications. However, vegetable oils differ from traditional mineral or synthetic oils in that they are composed of TAG, which have different amounts and types of FA attached to the glycerol portion of the vegetable oil structure. The FA vary in the length of their hydrocarbon chains and degree of unsaturation (1). A direct consequence of this unique composition is that such oils oxidize much more rapidly than other lubricant base fluids because of the presence of double bonds. As a result, improving the oxidative stability of vegetable oils is a major objective. One approach used to improve their performance is to modify the FA structure either chemically or genetically (2).

In this study, the oxidative and wear performance of oils were compared to better understand how the chemical composition of the base stock affects these properties. The oxidative stability of the base oils can be evaluated by different techniques. In this study, the Penn State micro-oxidation test (PSMO), a thin-film test used extensively to study the oxidative stability of mineral and synthetic oils, was selected. This relatively simple thin-film test requires a much smaller sample size than most oxidation tests; it is not oxygen-diffusion limited and requires relatively short test durations (3,4). The wear performance of the test fluids was evaluated using a sequential four-ball wear test (SFBT). In a previous study, the differences in the chemical composition of base fluids were found to affect their wear and friction properties (5).

EXPERIMENTAL PROCEDURES

Test fluids. The vegetable oils used were refined soybean oil (SBO) and two modified vegetable oils, high-oleic soybean oil (HOSO) and epoxidized soybean oil (ESO). The SBO was obtained from Custom Shortening & Oils (Charlotte, NC); the HOSO was from Optimum Quality Grains, LLC (Des Moines, IA); and the ESO was from ATOFINA Chemicals, Inc. (Philadelphia, PA). The oils were used as received without any further purification. The FA compositions of the SBO and HOSO provided by each supplier were as follows (in %): SBO: palmitic, 10.5; stearic, 4.1; oleic, 23.4; linoleic, 52.6; linolenic, 7.2; HOSO: palmitic, 7; stearic, 4; oleic, 83; linoleic, 3; linolenic, 2. Some physical properties of the vegetable base stocks evaluated are listed in Table 1.

In this study, all fluids were tested without additives.

Test method. (i) Oxidation. Oxidation tests were performed using the PSMO. The method has been described in detail in the literature (6,7).

In this study, a small amount of vegetable oil (20 μL) was spread as a thin film on a tared low-carbon steel coupon and weighed. The metal coupons were then placed into glass reactors which were inserted in a heating block that was equilibrated at the desired temperature. Oxidation tests were carried out at 175 and 200°C for various lengths of time (30, 60, 90, and 120 min). The PSMO unit maintained the test temperature

TABLE 1
Physical Properties of Vegetable Base Stocks[a]

	Results			
Properties	SBO	HOSO	ESO	Method
Color	0.6	2.4	—	Lovinbond red
Color	—	—	150 max	APHA
FFA (%)	0.03	0.03	—	—
Iodine value	129.47	81.9	—	—
PV (meq/kg)	0	0.01	—	—
Active oxygen method (h)	>10	95	—	—
Acid value	—	—	0.5 max	ASTM D 974
Viscosity @ 25°C (cSt)	—	—	4.2	AOCS Tq 1a-64
Specific gravity @ 25°C (g/mL)	—	—	0.993	ASTM D 1298
Saponification value	—	—	—	AOCS Cd 3-25
M.W.	—	—	1000	—

[a]Data obtained by suppliers. SBO, soybean oil; HOSO, high-oleic soybean oil; ESO, epoxidized soybean oil.

to within one degree. An air flow of 20 cc/min was maintained over the samples. After a specified length of time, the coupons with the oxidized oil were removed from the glass reactor and rapidly cooled to room temperature to prevent further reaction. The coupons were then stored in a desiccator overnight.

To measure evaporation loss of the sample, the oxidized test samples were weighed. The differences between weights before and after oxidation yielded the evaporation loss. The test coupons with the oxidized oil were then washed twice by soaking them in 5 mL of THF for 15 min at room temperature. This removed the soluble constituents from the oxidized oil. The coupons containing any insoluble deposits were placed in a desiccator overnight to dry and then weighed to determine the formation of insoluble deposits. The percentage of deposit formation of the sample was then calculated from the original sample weight and the difference between the final weight and the tared weight of the test coupon before oxidation. In this study, the average of four test runs was obtained for every test condition.

The soluble oxidation products were analyzed by gel permeation chromatography (GPC) and FTIR to study the oxypolymerization products formed during the oxidation process. The GPC analysis was carried out on a Waters–Millipore HPLC/GPC instrument with a Waters 600 pump controller. The THF flow rate was 1 cc/min. Two columns connected in series, a Styragel HR1® and a Styragel HR4® (Waters, Milford, MA), which covered a M.W. range between 100 and 100,000 amu, were maintained in the air bath at 30 ± 1°C. Refractive index detector data, obtained from a Waters 410 differential refractometer, were used to measure the corresponding peak areas of the chromatogram of the oxidized samples and were normalized by using Millennium Software® (8). The results were interpreted as weight percentages of the material depleted or generated in the test.

A Nicolet Avatar 360 IR spectrometer was used to determine the functional groups of the oxidative products using FTIR analysis. All the spectra were recorded and processed using OMNIC ESP 5.0® processing software (9).

Friction and wear tests. The SFBT was used to determine the relative wear properties of the fluids under sliding metal surface boundary conditions. In this study, friction and wear were obtained using the Penn State SFBT. The method is described in detail in the literature (5). This test involves conducting three sequential 30-min tests using the same set of 0.5-in.-diameter AISE 52100 balls. The Falex wear test machine was used in all tests in this study. The tests were conducted at 75°C (167°F) and 600 rpm, and a 40-kg load (492N) was applied.

In the sequential test, the first segment was a 30-min "run-in" (RI) using the test fluid. At the end of 30 min, the ball pot was removed from the wear tester and cleaned without disturbing the position of the balls. The wear scars were measured, new test fluid was added, and the ball pot was repositioned in the wear tester. The second 30-min segment was a "steady state" (SS) run. At the end of the second segment, the ball pot was again removed, rinsed, and the scar measured. The third segment of the test was run using a white oil without additives as the test fluid and was an "additive evaluation" (AE) run. Friction readings were obtained and recorded during all three segments, and the average friction coefficient for each test segment was determined. Duplicate tests were run with each oil sample.

RESULTS AND DISCUSSION

Oxidation studies. Figure 1 shows the evaporation losses of vegetable oils evaluated at 175 and 200°C. The data show temperature effects on the oxidative stabilities of the vegetable oils. One can see that an increase in temperature significantly promoted the oxidation process and resulted in a higher evaporation loss owing to the formation of volatile products from the breakdown of the FA chain. The volatile products formed during the oxidation process included peroxides, alcohols, aldehydes, ketones, and other compounds of low M.W. (10). Evaporation loss increased at higher temperatures because of the increased oxidation rate, which led to higher fragmentation and decomposition.

HOSO showed a higher evaporation loss than ESO or SBO at the temperatures evaluated. This can be attributed to their
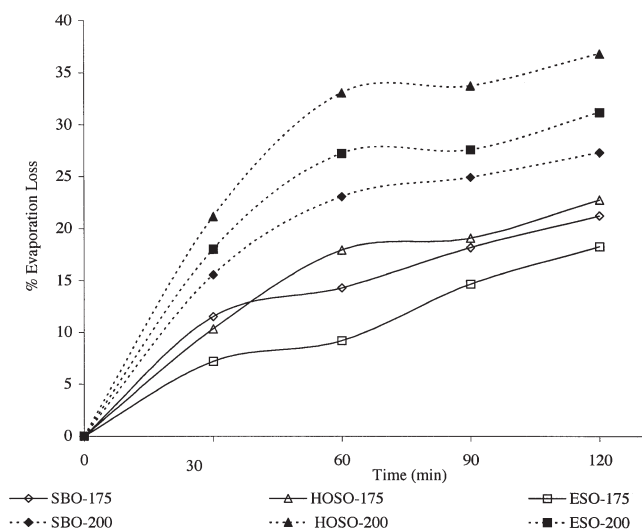
FIG. 1. Evaporation loss of vegetable oils at 175 and 200°C. SBO, soybean oil; HOSO, high-oleic soybean oil; ESO, epoxidized soybean oil.

FIG. 2. Percentage deposit formation of vegetable oils at 175 and 200°C. For abbreviations see Figure 1.

oleic acid content (~83%). Once oleate hydroperoxides were produced, the formation of volatile products occurred *via* scission alpha to the hydroperoxide group with a loss of water and a low-M.W. hydrocarbon fragment. The scission of the oleate hydroperoxide produced volatile compounds with higher M.W. than did linoleate and linolineate hydroperoxides (11,12).

The deposit formation of the vegetable oils studied is shown in Figure 2. In general, as the oxidation time and temperature increased, the deposit formation was higher. At 175°C, we observed that SBO and HOSO had a deposit induction time of about 30 min before the deposit formation rate started to increase significantly with time, whereas ESO had an induction time of about 60 min. As the temperature was increased to 200°C, there was essentially no rapid increase in induction time or deposit formation.

The higher rate of deposit formation of the SBO at different times, compared with ESO and HOSO, was mainly due to the higher content of PUFA, which made SBO more susceptible to oxidation. These results are in agreement with the literature, which has reported that the relative rate of auto-oxidation of oleate/linoleate/linolenate is 1:40–50:100 on the basis of oxygen uptake and 1:12:25 on the basis of peroxide formation (13).

The GPC results (Fig. 3) show the rate of formation of the high-M.W. (HMW) products and same-M.W. (SMW) products found in the soluble fraction of the vegetables oils evaluated at 175°C. The HMW fraction contained deposit precursors and built up as the oxidation proceeded. At 30 min, HMW products were formed at a higher rate for SBO and HOSO than for ESO, correlating well with the deposit formation results. The smaller amount of HMW products formed in the case of ESO was an indication of the improved oxidative stability. The amount of SMW products reacting to form deposits was also lower than for the other base stocks. As the test time increased, a decrease was seen in the amount of HMW products. This is normally
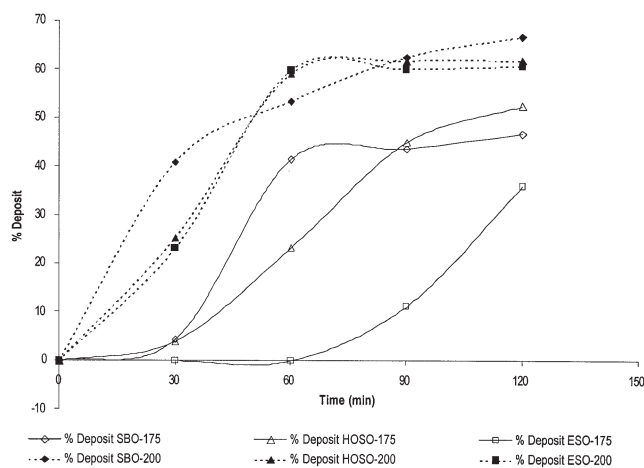
seen when the rate of formation of oil-insoluble sludge and varnish exceeds the rate of formation of HMW precursors. Evaporation losses also contributed to this decrease.

The quantity of SMW products decreased rapidly with time due to evaporation and oxidation. The SMW products of ESO decreased slower than those of SBO and HOSO primarily because of improved oxidative stability. This improvement in oxidative stability resulted in better deposit-forming tendencies.

At 200°C (Fig. 4), one can see that the HMW products increased rapidly during the first 30 min for all samples and decreased suddenly at 60 min. This suggests that during the early stage of oxidation, the rate of formation of HMW products was higher than the rate of deposit formation. As the time increased, a decrease was seen in the amount of oil-soluble HMW products. All these facts correlated well with the deposit formation trend obtained. The results for the SMW products of the vegetable oils
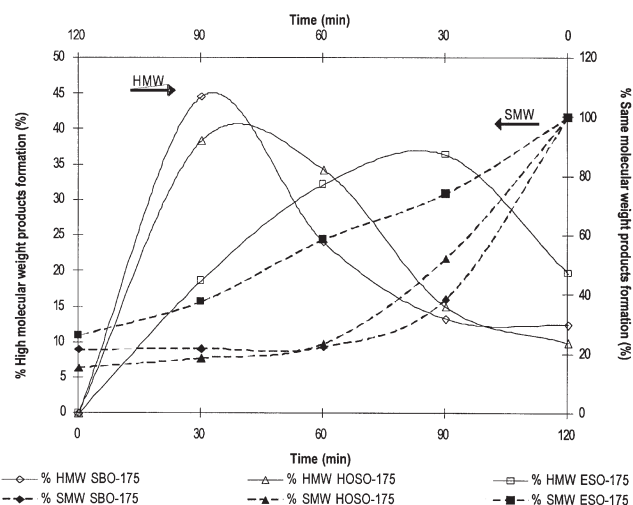

FIG. 3. Percentage high-M.W. (HMW) products and small-M.W. (SMW) products of vegetable oils evaluated in Penn State micro-oxidation test (PSMO) at 175°C. For other abbreviations see Figure 1.
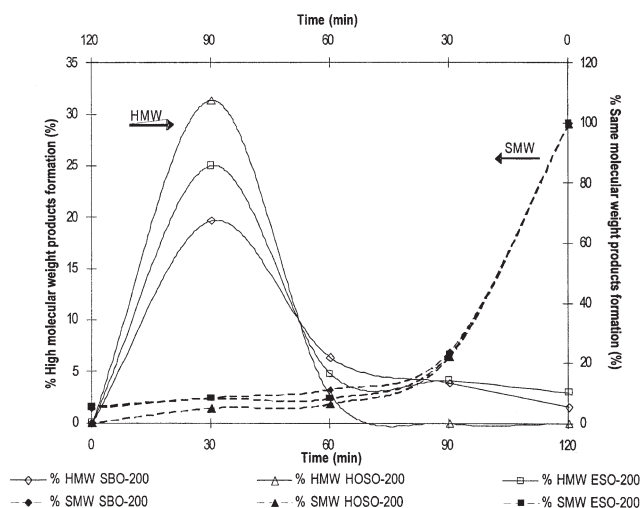
FIG. 4. Percentage of HMW products and SMW products of vegetable oils evaluated in the PSMO at 200°C. For abbreviations see Figures 1 and 3.

studied at 200°C were quite different from those obtained at 175°C. All three base oils oxidized rapidly and depleted at 200°C.

The FTIR spectra of the vegetable oils oxidized for 60 min at 200°C are shown in Figure 5. Besides a C–H stretching band, three major peaks were present at around 3350, 1740, and 1720 cm^{-1}. The 1740 cm^{-1} band arose mainly from peroxy acids and ester compounds, whereas the 1720 cm^{-1} band was from ketonic species. Absorbance at 3350 cm^{-1} is characteristic of hydroxyl groups and can indicate the presence of a hydroperoxide group, corroborating the peaks at 925–1060 cm^{-1}. These assignments revealed the formation of oxygenated structures such as peroxy acids, esters, and ketones during the oxidation of vegetable oils. The formation of such compounds has also been reported in other previous studies (4,14). The trend observed in the FTIR spectra of vegetable oils oxidized at 200°C showed that as oxidation progressed, the absorption of the O–H and C=O peaks decreased, suggesting that polymerization of the carbonyl compounds had taken place. This produced polymers that were precursors for the deposits. All these facts were consistent with the HMW product and deposit formations obtained for these vegetable oils.

Wear and friction studies. Figure 6 presents the average results obtained in the SFBT test of the vegetable oils without additives. The results showed differences in the wear characteristics of these fluids. HOSO showed the best antiwear performance, with a total delta wear value (RI + SS) of 0.236
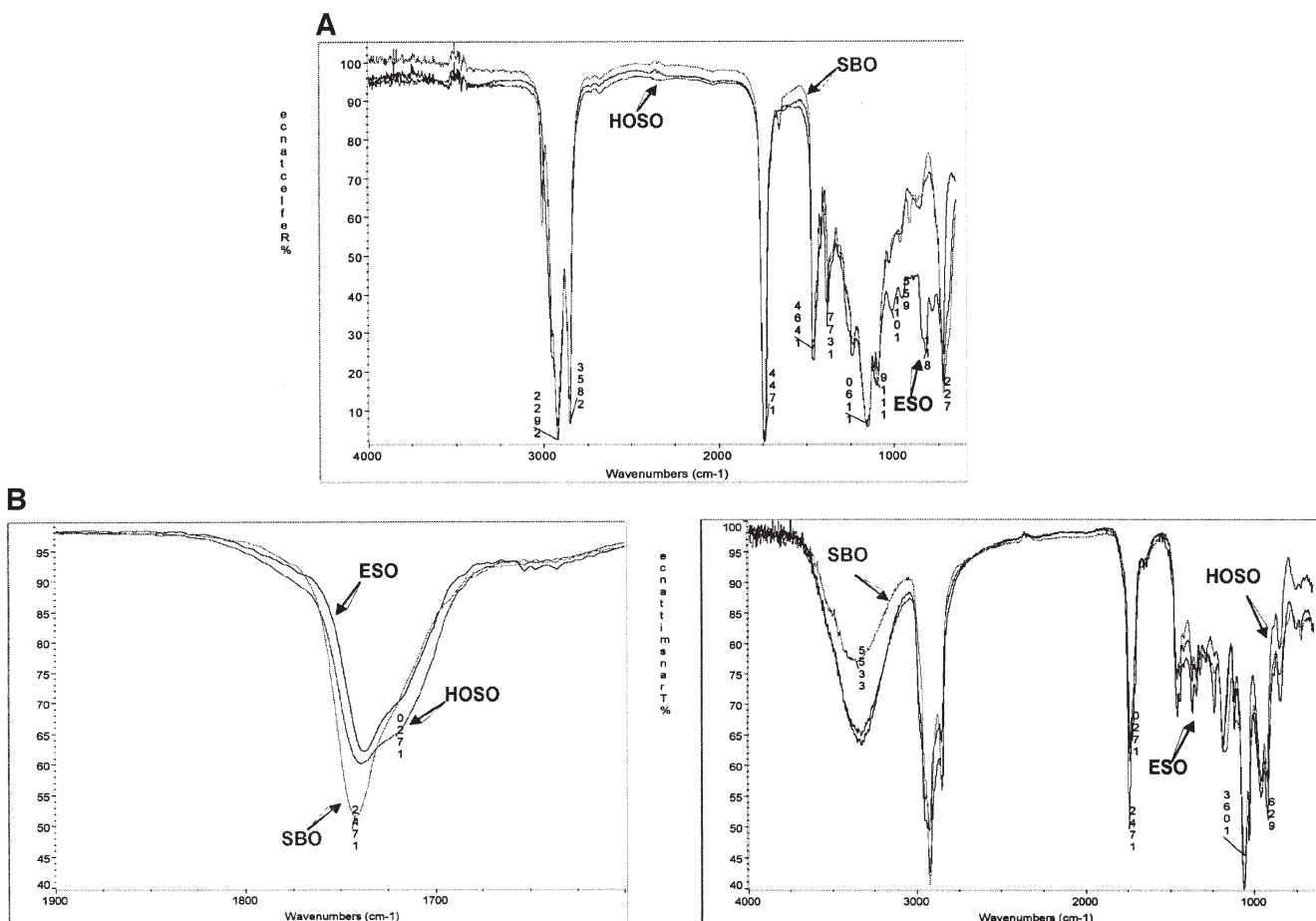

FIG. 5. FTIR of vegetable oils evaluated (A) unoxidized and (B) oxidized in PSMO at 200°C, 60 min. For abbreviations see Figures 1 and 3.
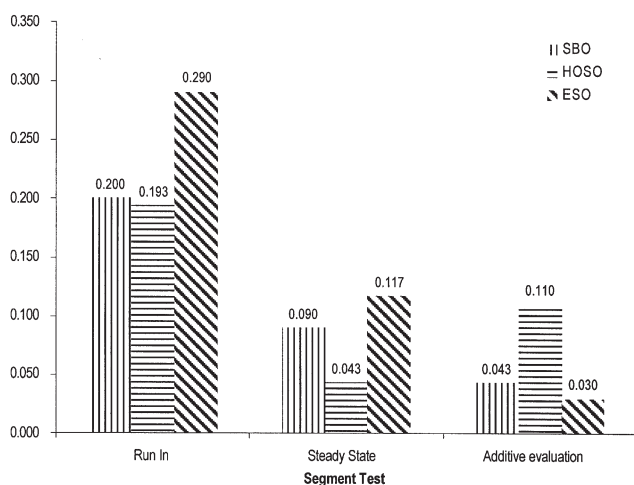
FIG. 6. Wear test results: sequential four-ball test (SFBT) of vegetable oils without antiwear additives. Conditions: 75°C, 40 kgf, 600 rpm. For other abbreviations see Figure 1.

mm, whereas ESO gave the highest total delta wear value, 0.407 mm. ESO, which had the best oxidative stability, showed the poorest wear characteristics of the three base stocks studied.

Molecular structure played a role in the rate of wear obtained for the fluids evaluated. The surface phenomena that determine the behavior of boundary lubricants can be described in the following terms: physically absorbed layers of lubricants, chemically absorbed layers, and films formed by chemical reaction (15). SBO has a high PUFA content (~60%), which is more sus-

ceptible to oxidation and the formation of HMW products, and this may give some wear protection. Hence, SBO showed less wear than ESO. In some cases, the acidic products can increase wear. Cheenkachorn (16) showed that some vegetable oils with a high PUFA content exhibited excessive wear in the steady-state segment of a sequential wear test. This appeared to be due to the chemical reaction that occurs during the process, which destroys the protective film on the surface, resulting in a definitive increase in wear. Unlike SBO, HOSO has a lower PUFA content (5%), which results in better antiwear performance due to the formation of a more stable polymeric film.

The high delta wear scar of ESO can be attributed to its particular chemical structure and oxidative stability. In comparison with HOSO, it does not have a long, straight nonpolar chain that will orient itself perpendicularly to the surface and thus create a thick film. The presence of oxyrane rings in the structure of ESO could reduce the binding to the surface in rigidifying the molecule (17), which could hinder the film-forming ability of this molecule at the metal surface. Although HOSO had good wear characteristics, it did not appear to form a permanent film that was as stable as SBO and ESO. Stable films reduced wear in the third segment of the sequential test. For some lubrication applications, it is necessary to incorporate antiwear additives to improve performance.

Contrary to the results obtained in the wear behavior of the other vegetable oils evaluated, ESO showed a lower friction coefficient compared with HOSO and SBO, respectively (Fig. 7). This fact can be due to the formation of a tribochemical reaction on the surface. The three-membered ring of oxyrane in ESO could form polyester or polyether materials caused by
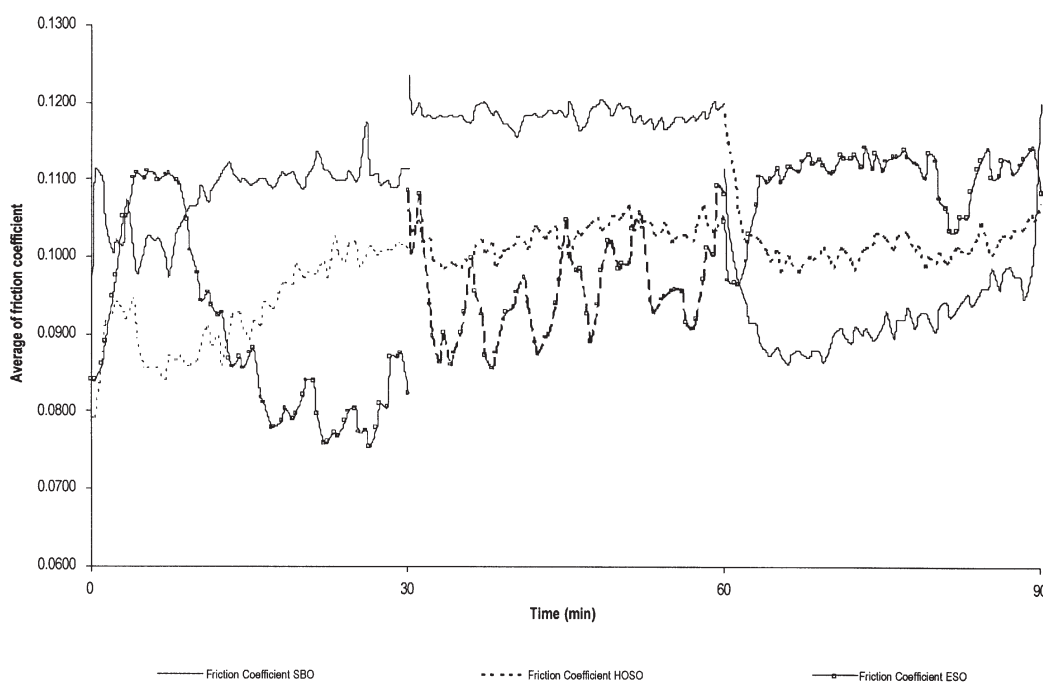

FIG. 7. Average of friction coefficients of the vegetable oils studied without antiwear additives. Conditions: 75°C, 40 kgf, 600 rpm. For abbreviations see Figure 1.

tribopolymerization reactions during the process. These films are tribologically effective in reducing friction (18).

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