Modification of Epoxidized Soybean Oil for Lubricant Formulations with Improved Oxidative Stability and Low Pour Point

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ABSTRACT: To produce soybean oil-based lubricants with good oxidative stability and low pour point, epoxidized soybean oil (SBO) was chemically modified. Epoxidized SBO was reacted with various alcohols in the presence of sulfuric acid as a catalyst to give a ring-opened intermediate product. In this step, the epoxy group was transformed to the functional group of $-CH(OR^1)CH(OH)-$ (where the R^1 = methyl, 1-butyl, 2-butyl, 1-hexyl, cyclohexyl, 2,2-dimethyl-1-propyl, or 1-decyl). The ^1H nuclear magnetic resonance spectra of the products indicated that transesterification was accompanied by the ring-opening reaction except when the bulky 2,2-dimethyl-1-propanol was used. Acid anhydride was used to esterify the hydroxy groups in the ring-opened product. This resulted in a fluid that is a lubricant candidate with the functional group of $-CH(OR^1)CH(OCOR^2)-$. Pour point studies of the resulting products showed that the pour points varied with the substituents, R^1 and R^2. Products with $R^1 = CH_3(CH_2)_5-$ and $R^2 = CH_3(CH_2)_2-$, $(CH_3)_2CH-$, or $CH_3(CH_2)_4-$ showed the lowest pour points (–39, –39, and –45°C, respectively) when 1% of pour point depressant was added. For the oxidative stability test, two products, in which R^1, $R^2 = CH_3(CH_2)_5-$, $(CH_3)_2CH-$ and R^1, $R^2 = CH_3(CH_2)_5-$, $CH_3(CH_2)_4-$, were chosen for a modified Penn State micro-oxidation test. In the oxidative stability test, the products gave 69–71% of oxidative evaporation and 10–17% of tetrahydrofuran-insoluble deposits in 3 h at 175°C. The amounts of deposits were much lower than those of soybean oil (96%) and epoxidized SBO (83%) and even less than those of most petroleum-based lubricant basestocks (3–93%).

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KEY WORDS: Epoxidized soybean oil, lubricant, oxidative stability, Penn State micro-oxidation, pour point, ring-opening reaction.

For utilization of vegetable oils as lubricants, the major problems of inadequate oxidative stability and poor low-temperature properties need to be resolved (1–3). The poor oxidative stability of a vegetable oil is typically attributed to the rapid reactions occurring at the double-bond functional groups in the molecule. Free radical oxidation and ionic reaction of the double bond, including hydrogen abstraction, addition reaction, fragmentation, rearrangement, disproportion reaction, and polymerization, cause the problem (4,5). Many research groups have focused on adding commercially available antioxidants to the oil, preparing new antioxidants, or genetically modifying

plants from which vegetable oils are derived in an attempt to solve the problem (6). Poor low-temperature properties include cloudiness, precipitation, poor flowability, and solidification at relatively high temperatures (7). Efforts have been made to improve the low-temperature properties by blending the vegetable oils with diluents such as poly α olefin, diisodecyl adipate, and oleates (8). The other possible way to control these obstacles is structural modification of the oils by chemical reaction (3). It has been reported that triacylglycerols with more diverse chemical structures have lower solidification temperatures (9,10). Chemical modification of the vegetable oils to give more complex structures should improve the low-temperature properties.

Epoxidized soybean oil (ESO) is a promising intermediate for this purpose, since the epoxy group is readily functionalized. Although many valuable polymeric materials derived from ESO have been reported (11–13), preparation of lubricants from the ESO was not found. Gast *et al.* (14) prepared products with pour points ranging from –32 to –51°C by a ring-opening reaction of epoxidized fatty acid esters followed by esterification of the resulting hydroxy groups. Herein, we report the preparation of lubricant candidates from ESO and their pour points and oxidative stabilities. The fluids were prepared from ESO by an acid-catalyzed ring-opening reaction using an alcohol followed by esterification with an acid anhydride. Correlation between pour points and structural variation in the molecules has been studied.

Oxidative stability of the oils can be evaluated using many techniques. In this study the micro-oxidation developed at Pennsylvania State University (15,16) was used. The Penn State micro-oxidation is a thin-film oxidation test used widely in the lubricant industry and considered to be more suitable in testing antioxidant-free basestocks than other techniques.

EXPERIMENTAL PROCEDURES

Materials. The ESO (100% epoxidized) was purchased from Elf Atochem Inc. (Philadelphia, PA) and used as received. Unless otherwise specified, all other chemicals including alcohols and acid anhydrides (99% purities) were purchased from Aldrich Chemical Co. (Milwaukee, WI), and used without further purification. Polystyrene standards with molecular weights of 1,700, 2,450, 5,050, 7,000, 9,200, 11,600, 66,000, and 435,500 were obtained from Polymer Laboratories, Ltd. (Amherst, MA) for GPC calibration.

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Analysis. [1]H nuclear magnetic resonance (NMR) was performed with a Bruker (Rheinstetten, Germany) ARX 400 spectrometer. Fourier transform-infrared (FTIR) spectra were obtained with a PerkinElmer (Bucks, England) Spectrum RX FT-IR System as film on NaCl plates.

Pour point measurement. The pour point apparatus and procedure used followed ASTM D 97 (17). The cloud and pour point test apparatus manufactured by Petrolab Corporation (Latham, NY) was used. Test jars, thermometers, corks, and rubber rings fully met ASTM D 97 specifications. All runs were carried out at least in duplicate. Sample temperature was measured in 3°C increments at the top of the sample until it stopped pouring. The temperature of cooling media was kept constant at –18, –33, –51, and –69°C as the sample temperature reached the specified ranges of +9 to –6, –6 to –24, –24 to –42, and –42 to –45°C, respectively.

Micro-oxidation test. Micro-oxidation experiments were carried out using the Penn State Micro-oxidation Kit (16). A modified Penn State method was used in this research. A small amount of oil (20 μL) was placed on an activated high-carbon steel catalyst to make a thin film. The catalyst with the oil was placed on a hot plate, which maintained temperature at 175 ± 1°C. An air flow (20 cm^3/min) was maintained over the sample. After a specified time length, the sample of catalyst with oxidized oil was removed from the oxidation chamber and weighed to determine the sample loss by oxidative volatility. After cooling to room temperature, the catalyst was soaked in tetrahydrofuran (THF, 20 mL) for 30 min to dissolve out the soluble portion of oxidized oil. The catalyst containing the insoluble deposit was placed in a desiccator to dry and then weighed to determine the insoluble deposit formation. A sample of the THF-soluble oxidized oil was subjected to gel permeation chromatography (GPC). The analysis was carried out on an instrument of Thermo Separation Inc. (San Jose, CA), fitted with P400 pump and AS 3000 autosampler injection port. Of the sample solution 100 μL was injected, and flow rate for the mobile phase (THF) was maintained at 3 mL/min. A series of four GPC columns of PL gel 5 μm (300 × 7.3 mm) with pore sizes of 50, 100, 500, and 10^3 Å and adequate guard column from Polymer Lab Ltd. (Shropshire,

United Kingdom) were used. The columns were maintained in an air bath at 40 ± 1°C. Data from ultraviolet and refractive index detectors were simultaneously recorded.

Ring-opening reaction. To a mixture of ESO (100% epoxidized, 120 g, 0.57 mol of epoxy groups) and an alcohol (1.33 mol) were added 50 drops of sulfuric acid at 70–80°C, and the mixture was stirred under the reaction conditions shown in Table 1. The reaction mixture was cooled by adding ice, and then saturated aqueous sodium bicarbonate (100 mL) was added. The mixture was extracted with ethyl acetate (100 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated, and any remaining solvent and the excess alcohol were removed by heating at 80°C under high vacuum (0.5–1 torr) to give the ring-opened product (yield: 95–99%). The yield was calculated by comparison of the amount of the isolated product with the theoretical amount after the workup procedure: % yield = 100% × product (g)/ [ESO (g) + alcohol (g) – recovered alcohol (g) by distillation – theoretical loss of glycerol (g)].

Esterification of the resulting hydroxy groups in the ring-opened product. A mixture of the ring-opened product (50 g), pyridine (16 mL, 0.19 mol), and acid anhydride (0.19 mol) was stirred at 80°C for 3 h. Water (30 mL) and pyridine (10 mL) were then added and stirred at 60°C for 2 h to destroy the excess acid anhydride. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (100 mL), washed successively with water (100 mL), 10% NaOH (2 × 100 mL), 10% HCl (100 mL), and 5% aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, and evaporated to give the product (yield: 97–99%; the yield was obtained by comparison of the amount of the isolated product with the theoretical amount). Completion of the esterification reaction has been confirmed by checking disappearance of the hydroxy group at 3450–3480 cm^{-1} in the infrared spectrum.

RESULTS AND DISCUSSION

Reaction of ESO with an alcohol in the presence of a catalytic amount of sulfuric acid gave the ring-opened products as well as many other types of products, as shown in Scheme 1. For investigation of the alkyl group effect on the low-temperature

TABLE 1
Reaction Conditions, Product Proportions, Pour Points With and Without 1% (vol/vol) of PPD[a] for Ring-Opening Reaction Products Obtained from Epoxidized Soybean Oil and Alcohols

Entry	Alcohol	Reaction conditions	Ring-opening (%)	Transesterification (%)	Pour point (°C)	Pour point with 1% (vol/vol) of PDD[a] (°C)
1	Methanol	Reflux[b], 5 h	100	70	0	–3 (0)[c]
2	1-Butanol	100°C, 3 h	100	73	–3	–6 (–6)[c]
3	2-Butanol	100°C, 7 h	100	74	0	0
4	1-Hexanol	100°C, 5 h	100	85	0	–9
5	Cyclohexanol	110°C, 5 h	100	44	9	6
6	2,2-Dimethyl-1-propanol	110°C, 5 h	100	0	3	3
7	1-Decanol	100°C, 5 h	100	84	0	3 (6)[c]
8	Epoxidized soybean oil				0	0

[a]Pour point depressant; Lubrizol[TM] 7670 made of sunflower oil and mineral oil from Lubrizol Corporation (Wickliffe, OH).
[b]The reaction flask equipped with a reflux condenser was placed in an oil bath at 80°C.
[c]Numbers in the parentheses indicate pour points with 0.5% (vol/vol) of PPD.
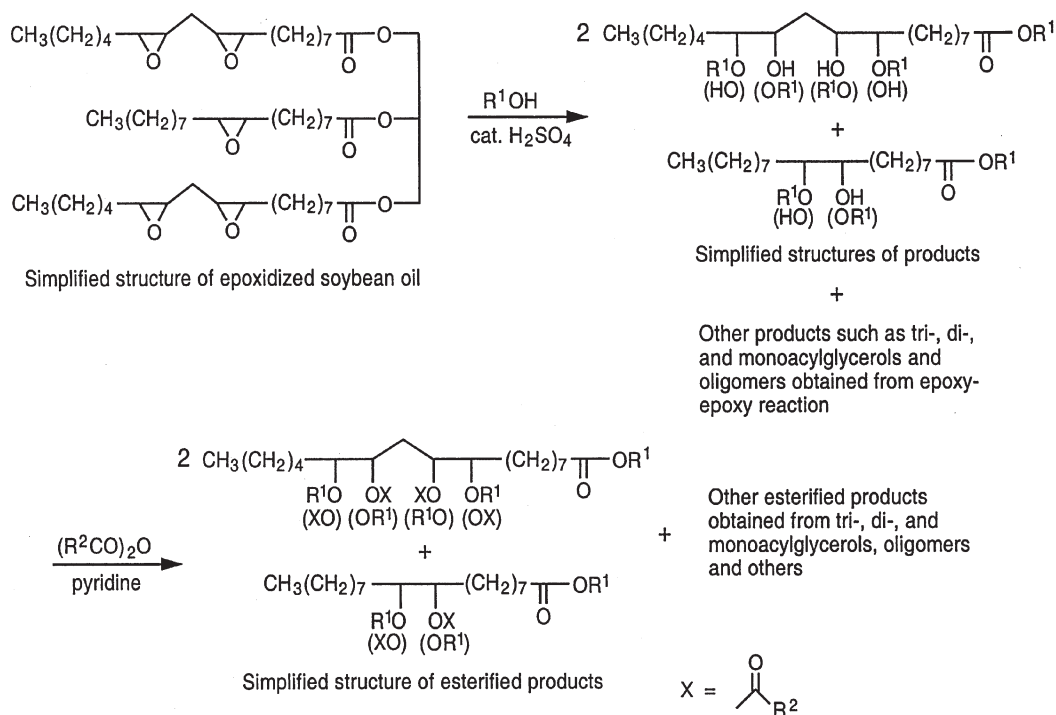
SCHEME 1

properties, different alcohols including methanol, 1-butanol, 2-butanol, 1-hexanol, cyclohexanol, 2,2-dimethyl-1-propanol, and 1-decanol were used in the reaction. The reaction was monitored by following the disappearance of the epoxy group at 1158, 845, and 822 cm^{-1} in the IR spectrum and stopped when the ring-opening reaction was completed. The reaction's completion was further confirmed by checking disappearance of peaks at 2.8–3.0 ppm in the ^{1}H NMR spectrum corresponding to hydrogens in the epoxy ring. As summarized in Table 1 (column 3), different alcohols required different conditions to complete the reaction. Longer or bulkier alcohols required longer reaction times and/or higher temperatures to complete the ring-opening reaction. For example, while 3 h at 100°C was required to complete the reaction with 1-butanol, a longer reaction time (5 h) was required for the higher molecular weight alcohols such as 1-hexanol and 1-decanol. Reaction with a secondary alcohol, 2-butanol, required an even longer reaction time (7 h) than the reaction with 1-butanol (3 h). Reactions with bulkier alcohols, such as cyclohexanol and 2,2-dimethyl-1-propanol, required higher temperature (110°C) and longer reaction time (5 h) relative to 1-butanol.

Considerable amounts of transesterification products were produced during the ring-opening reaction with the exception of the reaction with 2,2-dimethyl-1-propanol. The relative transesterification taking place during the desired ring-opening reaction was determined by ^{1}H NMR and is summarized in Table 1 (column 5). To determine the percentage of transesterification, the area for the hydrogen signals inherent to the transesterified products, namely, the alkyl hydrogens alpha to the ester oxygen atom derived from the alcohol portion of the newly formed esters, is compared to the hydrogen signals of

the glycerol molecule inherent to tri- di-, and monoacylglycerol products. Table 2 summarizes the chemical shifts observed for the hydrogen signals of the various esters produced by transesterification and the hydrogen signals of the glycerol

TABLE 2
Chemical Shifts and Splitting Patterns of Hydrogens Used in Calculation of Percentage Transesterification

Hydrogens	Chemical shift (ppm)	Splitting pattern
Hydrogens in transesterified products		
—COCH$_3$	3.63	Singlet
—COCH$_2$(CH$_2$)$_2$CH$_3$	4.05	Triplet
—COCH(CH$_3$)CH$_2$CH$_3$	4.81	Multiplet
—COCH$_2$(CH$_2$)$_4$CH$_3$	4.03	Triplet
—COCH⟨⟩	4.73	Multiplet
—COCH$_2$(CH$_2$)$_8$CH$_3$	4.03	Triplet
Hydrogens in triacylglycerol backbone		
H$_2$C—CH—CH$_2$	4.10–4.30	Multiplet

backbone that were used for percentage of transesterification calculations. Therefore, the percentage of transesterification denotes the molar percentage of the transesterification products: % transesterification = 100% mol of alkyl (R^1) ester/[mol of alkyl (R^1) ester + moles of molecules with triacylglycerol backbone]. Many other possible reactions such as inter- and intramolecular epoxy–epoxy reaction would give a variety of products including oligomers. Total analysis of products, however, will not be addressed in this report but will be the subject of a separate study. A preliminary GPC analysis has shown that some oligomers are obtained by intermolecular epoxy–epoxy reaction, but the major products are the alkyl (R^1) esters of fatty acids containing –CH(OR^1)CH(OH)– in place of the epoxy groups as shown in Scheme 1. The rate of transesterification was affected by bulkiness of the alcohol used in the reaction. The bulky 2,2-dimethyl-1-propanol gave no transesterification product, while other alcohols gave 44–85% of transesterification products under the reaction conditions required for completion of the ring-opening reaction.

The pour points of the ring-opened products were measured by using a standard method (ASTM D 97) with and without 1% pour point depressant (PPD) (Lubrizol™ 7670 made of sunflower oil and mineral oil from Lubrizol Corporation, Wickliffe, OH), and the results are shown in Table 1 (columns 6 and 7). Except for the ring-opened product from 1-butanol, whose pour point was –3°C, all other products showed pour points similar to or higher than the pour point (0°C) of the parent ESO. When 1% of PPD was added, only the products of methanol, 1-butanol, and 1-hexanol showed slightly lower pour points (–3, –6, and –9°C, respectively) than ESO with 1% PPD (0°C).

The relatively high pour point of the ring-opening reaction products may be attributed to hydrogen bonding of the many hydroxy groups present in the products produced after the ring-opening reaction. For transformation of the hydroxy groups to ester groups, the products were reacted with an acid anhydride at 80°C for 3 h (Scheme 1). To destroy excess anhydride, water and pyridine were added, and the mixture was stirred for an additional 2 h at 60°C. After basic and acidic workup procedures, the esterified products were obtained. To investigate the structural effects of the ester groups, acetic, butyric, 2-methylpropionic, and hexanoic anhydrides were used as esterification reagents.

The pour points of the esterified products were determined and are summarized in Table 3. The esterification reaction products themselves did not show very low pour points, but when 1% PPD was added to the products, pour points were markedly lowered for many of the esterified products. Pour points of products with 0.5% PPD were generally slightly higher than those with 1% PPD. Referring to the products found in Table 3, the lowest pour points were observed for **4** [R^1 = 1-butyl, R^2 = $CH_3(CH_2)_4$–], **8** [R^1 = 1-hexyl, R^2 = $CH_3(CH_2)_2$–], **9** (R^1 = 1-hexyl, R^2 = $(CH_3)_2CH$–], and **10** [R^1 = 1-hexyl, R^2 = $CH_3(CH_2)_4$–], whose pour points were –33, –39, –39, and –45°C, respectively when 1% PPD was added. Cloud points of the products **4** and **8–10** were measured at –9°C.

TABLE 3
Pour Points of Esterified Products With and Without PPD

Products	$^aR^1$	$^aR^2$	Pour point (°C)	Pour point with 1% (vol/vol) of PPD (°C)
1	–CH$_3$	–CH$_3$	0	–6 (–3)^b
2	–CH$_3$	–(CH$_2$)$_4$CH$_3$	–9	–27 (–24)^b
3	1-Butyl	–CH$_3$	–3	–9
4	1-Butyl	–(CH$_2$)$_4$CH$_3$	–6	–33 (–30)^b
5	2-Butyl	–CH (CH$_3$)$_2$	0	–3
6	2-Butyl	–(CH$_2$)$_4$CH$_3$	–3	–12
7	1-Hexyl	–CH$_3$	–3	–28
8	1-Hexyl	–(CH$_2$)$_2$CH$_3$	–6	–39 (–36)^b
9	1-Hexyl	–CH (CH$_3$)$_2$	–3	–39
10	1-Hexyl	–(CH$_2$)$_4$CH$_3$	–6	–45
11	Cyclohexyl	–CH$_3$	0	–3
12	Cyclohexyl	–(CH$_2$)$_2$CH$_3$	–3	–9
13	Cyclohexyl	–CH (CH$_3$)$_2$	–3	–9 (–6)^b
14	Cyclohexyl	–(CH$_2$)$_4$CH$_3$	–6	–24 (–21)^b
15	2,2-Dimethyl-1-propyl	–(CH$_2$)$_2$CH$_3$	–6	–12
16	2,2-Dimethyl-1-propyl	–CH (CH$_3$)$_2$	–6	–12
17	2,2-Dimethyl-1-propyl	–(CH$_2$)$_4$CH$_3$	–6	–15
18	1-Decyl	–CH$_3$	6	0 (6)^b
19	1-Decyl	–(CH$_2$)$_2$CH$_3$	6	0 (6)^b
20	1-Decyl	–(CH$_2$)$_4$CH$_3$	3	–3 (3)^b

^{a}Alkyl groups designated as R^1 and R^2 in Scheme 1.
^{b}Numbers in the parentheses indicate pour point with 0.5% (vol/vol) of PPD. See Table 1 for abbreviation.

The effect of the alkyl group length of R^1 is illustrated in Figure 1. With the same R^2 such as methyl (Fig. 1A) or pentyl (Fig. 1B), by changing the R^1 from methyl to longer alkyl chains up to the hexyl group, pour points were depressed further. Based only on these results, an assumption that the longer alkyl chain gives a lower pour point could be made. However, when the decyl group was incorporated in the product at R^1 position, the pour points increased remarkably in both cases when R^2 = –CH$_3$ and R^2 = –(CH$_2$)$_4$CH$_3$.
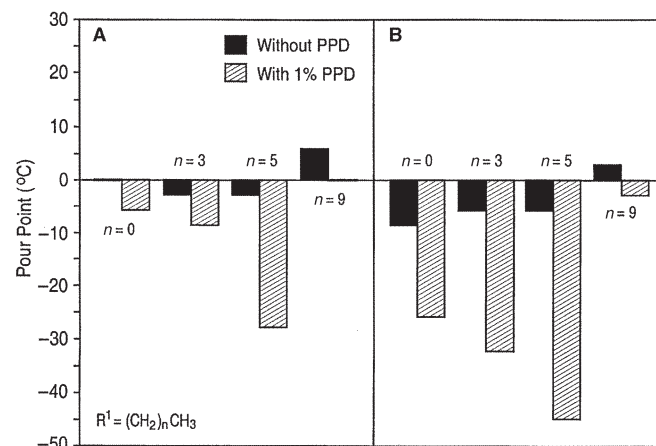

FIG. 1. Correlation between pour points and chain length of R^1 when (A) R^2 = –CH$_3$ and (B) R^2 = –(CH$_2$)$_4$CH$_3$. PPD, pour point depressant.

In general, branched alkyl groups depress the pour point of a lubricant oil, but a noticeable negative effect of a branched R^1 on pour points was found in comparison between **4** and **6**, where the R^1 = 1-butyl and 2-butyl, especially, for pour points with 1% of PPD. Likewise, other branched R^1 such as cyclohexyl and 2,2-dimethyl-1-propyl groups did not depress pour points as much as straight chain groups such as butyl and hexyl.

Comparison between products **1** and **2** (Table 3) showed that when the products have the same R^1, a longer R^2 gives a lower pour point. This general trend was found in many other products shown in Table 3. The effect of alkyl groups longer than $CH_3(CH_2)_4-$ for R^2 was not examined in this study because development of such lubricants is currently restricted by the generally high prices of commercially available anhydrides with alkyl chains longer than $CH_3(CH_2)_4-$.

To examine the effect of branched R^2 on pour point depression, 2-methylpropionic anhydride was used as an esterification reaction to give products **9**, **13**, and **16** (Table 3). The comparison of pour points with their corresponding products bearing straight R^2 (**8**, **12**, and **16**, respectively) shows no noticeable improvement in pour point depression when branched alkyl chains are incorporated at R^2.

The oxidative stabilities of these products were examined by a modified Penn State micro-oxidation method at 175°C. Products **9** and **10** were chosen for this test because they had the lowest pour points. Samples were analyzed after 60, 90, 120, 150, and 180 min of oil film oxidation on high-carbon steel catalysts. The oxidative evaporation was measured by differences in weights of the samples before and after the oxidation experiment (Fig. 2). The oxidative evaporation of a sample is caused not only by simple evaporation but also by other chemical reactions such as thermal decomposition and *cis*-elimination of ester groups (18). The percentage evaporations of **9** and **10** are relatively high compared to soybean oil and ESO. Four different refined mineral oil basestocks (mineral-1, -2, -3, and -4) with 93–97% saturation were compared with **9** and **10**. The evaporative losses of products **9** and **10** were higher than less volatile petroleum-based lubricant basestocks (mineral-1 and -4) and lower than more volatile basestocks (mineral-2 and -3).
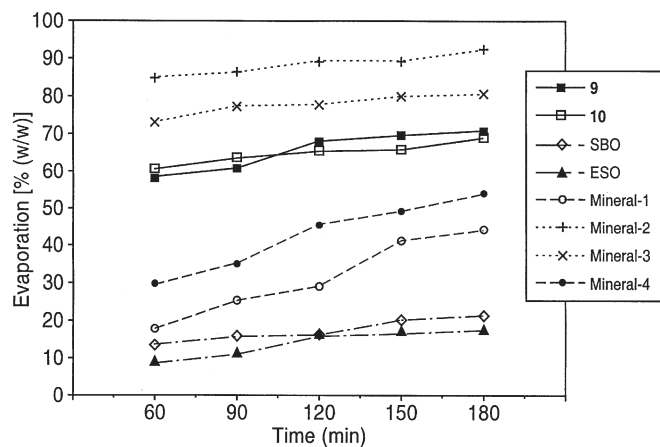
Figure 3 shows the amounts of insoluble deposits after oxidation, which were determined by measuring the amounts of the oxidized materials that were THF-insoluble. The samples were prepared by soaking the metal catalyst containing the deposit in THF for 30 min and then drying in a desiccator. Due to the absence of the double bonds or epoxy groups, the amounts of the insoluble deposits of the products **9** and **10** were much lower than those from the soybean oil or ESO and even lower than those of most of the petroleum-based lubricant basestocks except mineral-1.

GPC was performed on the soluble portion of the deposit to study the molecular weight change in the oxidized oil; chromatograms are shown in Figure 4. Polystyrenes were used as GPC calibration standards. Errors that could be made by differences in polarities between the standards and the samples in this study were ignored. Mineral-1 had a very small amount of deposit and showed an interesting polymerization pattern. The molecular weight of the soluble deposit increased gradually through the reaction times of 60, 90, 120, and 150 min. At 180 min, the amount of high molecular weight polymers slightly decreased, presumably owing to decomposition of high molecular weight components (Fig. 4A).

Unlike mineral-1, molecular weight of THF-soluble deposit of mineral-2, whose insoluble deposits were relatively largely increased with reaction time, increased until 90 min and then decreased over extended time periods (Fig. 4B). The result shows that fast polymerization occurs to give higher molecular weight polymers during the 90-min oxidation period. Beyond 90 min, the amount of the higher molecular weight polymers decreases by further polymerization to give insoluble deposits, as shown in Figure 3. Decomposition of high molecular weight polymers would be another reason, as Figure 2 shows, that slight oxidative evaporation still occurs beyond 90 min. The same trend was observed for mineral oil-3 and -4, which gave relatively large amounts of insoluble deposits.

Molecular weights of THF-soluble deposits produced by oxidation of soybean oil and ESO, which give large amounts of deposits, decreased dramatically over time. The result implies that the double bonds in soybean oil and epoxy groups
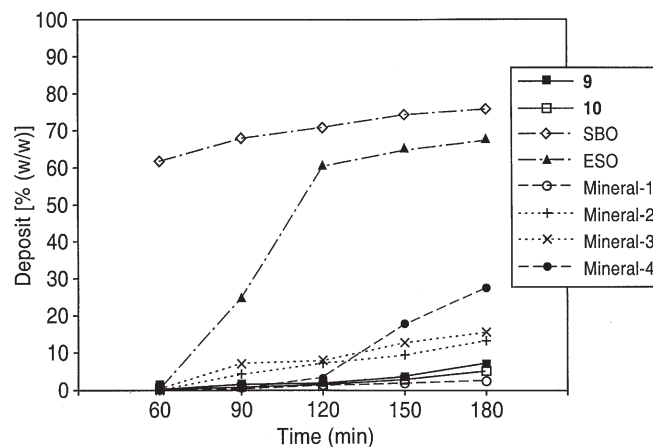

FIG. 2. Sample evaporation during the Penn State micro-oxidation test. ESO, epoxidized soybean oil; SBO, soybean oil.

FIG. 3. Insoluble deposits obtained during the Penn State micro-oxidation test. See Figure 2 for abbreviations.
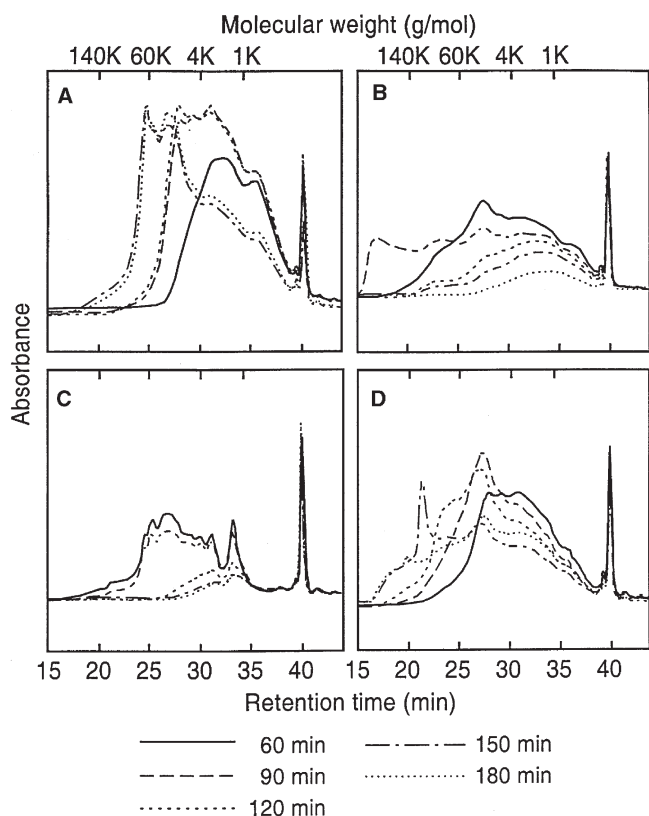
FIG. 4. Gel permeation chromatography chromatograms of soluble deposits obtained from the Penn State micro-oxidation tests of (A) mineral-1, (B) mineral-2, (C) epoxidized soybean oil), and (D) product **9**.

in ESO produce insoluble cross-linked polymers very quickly when heat and air are supplied; an example of this can be seen in the GPC chromatogram of ESO (Fig. 4C).

The products **9** and **10** behaved more similarly to the stable mineral-1. The GPC chromatogram of **9**, shown in Figure 4D, suggests that the molecular distribution of higher molecular weight soluble polymers increases over time up to 150 min, and beyond that point slightly decreases. When this result is compared to the result in Figure 3, in which the amount of the deposit increases between 150 and 180 min, it can be concluded that 150 min is the onset time for cross-linking polymerization to produce deposits.

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