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Synthesis of novel alkoxylated triacylglycerols and their lubricant base oil properties☆

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Abstract

Development and application of bio-based fluids in industrial and automotive sectors are rapidly increasing due to their non-toxic and biodegradable character unlike mineral oil-based products. Synthetic lubricant base fluid with improved high and low-temperature stability was prepared by chemical modification of epoxidized soybean oil (ESBO). The reaction was carried out in two-steps: (i) synthesis of dihydroxylated soybean oil from ESBO with $HClO_4$, (ii) reaction of acetic, butyric and hexanoic anhydride with the dihydroxylated product. The composition of the reaction products were confirmed by NMR and FTIR analysis. Chain length variation of the anhydrides used in the synthesis resulted in base fluids with different physical and chemical properties. Low-temperature stability was excellent for hexanoic anhydride derivative. When compared with SBO, thermal and oxidative stabilities were improved. Viscosity, volatility and other lubricant base oil properties were evaluated qualitatively. Bio-fluids based on this chemical modification offer great potential for the development of industrial fluids and products based on such fluids.

Keywords: Vegetable oils; Epoxidized soybean oil; Dihydroxylation; Alkoxylated triacylglycerol; Oxidation; Pour point

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1. Introduction

During the last decade due to strict government and environmental regulations, there has been a constant demand for environmentally friendly lubricants (Rhee, 1996). Most of the lubricants originate from petroleum stock, which is toxic to environment and difficult to dispose. Vegetable oils with high oleic content are considered to be potential candidates to substitute conventional mineral oil-based lubricating oils and synthetic esters (Randles and Wright, 1992; Asadauskas et al., 1996). Vegetable oils are preferred over synthetic fluids because they are renewable resources and cheaper.

Vegetable oils as lubricants are preferred because they are biodegradable and non-toxic, unlike conventional mineral-based oils (Randles and Wright, 1992; Battersby et al., 1998). They have very low volatility due to the high molecular weight of the triacylglycerol

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☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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molecule and have a narrow range of viscosity changes with temperature. Polar ester groups are able to adhere to metal surfaces, and therefore, possess good boundary lubrication properties. In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules.

On the other hand, vegetable oils have poor oxidative stability (Gapinski et al., 1994; Becker and Knorr, 1996) primarily due to the presence of bis allylic protons and are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy compounds. This phenomena result in insoluble deposits and increases in oil acidity and viscosity. Vegetable oils also show poor corrosion protection (Ohkawa et al., 1995). The presence of ester functionality renders these oils susceptible to hydrolytic breakdown (Rhodes et al., 1995). Therefore, contamination with water in the form of emulsion must be prevented at every stage. Low-temperature study has also shown that most vegetable oils undergo cloudiness, precipitation, poor flow, and solidification at $-10\,^{\circ}\mathrm{C}$ upon long-term exposure to cold temperature (Rhee et al., 1995; Kassfeldt and Goran, 1997) in sharp contrast to mineral oil-based fluids.

In this study, we present a novel synthetic approach for chemical modification of vegetable oils to improve their thermo-oxidative and low-temperature stability. The structural modification is carried out in two stages, (i) synthesis of di-hydroxylated soybean oil from epoxidized soybean oil and (ii) reaction of anhydride with the di-hydroxylated product.

2. Experimental procedure

2.1. Synthesis of di-hydroxylated soybean oil from epoxidized soybean oil

Epoxidized soybean oil (ESBO) was obtained from Elf Atochem (Philadelphia, PA) and used without any further purification. Perchloric acid ($HClO_4$, 70%) was obtained from Aldrich Chemical Company (Milwaukee, WI). The reaction was carried out in a three-neck, 5000 ml round bottom flask (Ace Glass Inc., Vineland, NJ). A 2450 ml aqueous solution of 127.4 g epoxidized soybean oil was refluxed for 48 h at 100 °C in the presence of $HClO_4$ (26.05 g) added dropwise into the reaction vessel. A mechanical stirrer (Stir-pak^R, Cole Parmer Instrument, Vernon Hills, IL) was used for continuous stirring of the reaction mixture. After the reaction was complete, the mixture was cooled to room temperature, and the organic phase extracted with chloroform ($CHCl_3$, Fisher Scientific, Springfield, NJ) and washed three times with water to remove any traces of residual acid in the system. The solvent was removed under reduced pressure and the product stored overnight under dry vacuum.

2.2. Synthesis of di-hexanoyl-soybean oil from di-hydroxylated soybean oil

To 40 g of di-hydroxylated product (di-OH-SBO) prepared previously, 40 g of hexanoic anhydride (99%, Aldrich Chemical Company) was added in a 1:1 ratio, and to this mixture 19.97 g of pyridine (Aldrich Chemical Company) was added in equimolar ratio. The mixture was mechanically stirred in a 500 ml glass round bottom flask for 48 h at room temperature. The product mixture was then quenched with ice water and stirred for an additional 12 h, and later extracted several times with diethyl ether (Fisher Scientific, Springfield, NJ). The organic phase was washed with 100 ml 3% HCl and 5% $NaHCO_3$ (each three times) and finally dried over anhydrous $MgSO_4$ (Fisher Scientific, Springfield, NJ) for 24 h. Diethyl ether was removed under reduced pressure and the product stored under vacuum.

2.3. NMR analysis

All the ^1H and ^{13}C NMR spectra were recorded quantitatively using a Bruker ARX-400 spectrometer (Bruker, Rheinstetten, Germany) at a frequency of 400 and 100 MHz, respectively, using a 5 mm dual probe. For the ^1H and ^{13}C experiments, sample solutions were prepared in deuterated chloroform ($CDCl_3$, 99.8% D, Aldrich Chemical Company) in 15 and 30% (v/v) concentrations, respectively. Proton NMR spectra were obtained from 16 co-added FIDs with a delay time of 1 s. For the distorsionless enhancement by polarization transfer (DEPT 135) measurements, similar sample concentration as in ^{13}C experiment was used ($NS = 5000$, $AQ = 0.62$ s, $DW = 19\,\mu s$, $D1 = 0.1$ s). This technique was useful to identify and compute the relative distribution of $–CH_n–$ ($n = 0–3$) carbons in the products.