



Oxidation and low temperature stability of polymerized soybean oil-based lubricants[☆]



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ABSTRACT

Oxidation and low temperature stability of polymerized soybean oil (PSO)-based lubricants have been investigated by the pressurized differential scanning calorimetry (PDSC) method. It was found that PSO samples have lower oxidative stability than their precursor, soybean oil. The main reason for the decreased stability is the generation of tertiary carbons during polymerization. By using antioxidant additives, the PSO samples responded very well and increased their onset temperature (OT) by 70–80 °C. Thermogravimetric analyses have been performed on the PSO samples and it was observed that they are thermally stable at temperatures up to 250 °C. Cold flow property data shows that the PSO samples are good for use in formulating high temperature lubricants. Two model compounds which have terminal double bonds, triacyl-10-undecenoate and allyl 10-undecenoate, have been polymerized. The oxidation stability of these two compounds was investigated by the PDSC method and compared to that of the PSO samples. This study will help us understand the relationships between oxidation stability and molecular structure of PSO-based lubricants. In addition, oxidation stability data of polyethylene (PE) and polypropylene (PP) were used in helping to explain the oxidation stability results of the PSO samples.

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1. Introduction

Environmental concerns and petroleum shortages have encouraged extensive research on biolubricants. Because of their biodegradability, low ecotoxicity, and excellent tribological properties, vegetable oil-based lubricants, such as soybean oil (SBO), find application in many areas, from greases to hydraulic fluids, which offer lower coefficient of friction, excellent wear characteristics, higher viscosity index, lower volatility, and lower flash points than mineral-based oils. Over the past 15 years, the demand for fossil oil has increased oil prices approximately

10-fold. The global lubricant demand was 38.7 metric million tons (MMT) in 2012 and is forecast to reach 42.1 MMT in 2017, growing about 2% per year [1]. The lubricant growth rates are expected to be stagnant for Europe (0.6% per year) and North America (0.4% annual growth), while there will be a decent demand in other regions, such as Asia-Pacific (2.7%), South America (2.4%), Africa, and the Middle East (1.4%). The global lubricant market was worth \$44 billion US Dollars (USD) and the value of global lubricants will grow even faster than the volume, rising at a compound annual growth rate (CAGR) of 5.5% from 2012 to 2018, and is expected to reach \$65.2 billion USD in 2018. This is caused by the estimated increase in the price of lubricants from \$960 USD per ton in 2005 to \$1,330 USD by 2015.

However, one of the drawbacks of vegetable oils is their poor oxidative stability [2–4], primarily due to the presence of bis-allylic protons. These protons are highly susceptible to radical attack and, subsequently, undergo oxidative degradation to form polar oxy compounds, which ultimately results in an insoluble deposit formation and an increase in oil acidity, viscosity, corrosion, and

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volatility when used as lubricant base oils. Some studies utilizing additives [5–7] and chemical modification [8–11] have been performed in order to overcome these drawbacks.

Gear oils are essential for automotive and industrial lubrication, where they are commonly used in transmissions, differentials, power take-offs, and non-drive applications. They are required to minimize friction and wear, reduce noise, remove wear particles, inhibit corrosion, transfer heat, and improve efficiency [12]. In order to provide this protection in both the hydrodynamic and elastohydrodynamic regions, specific viscosity characteristics are required. In their natural state, vegetable oils do not have sufficient viscosity for these applications. This problem can be overcome by using thermal polymerization of the oil. Recently, Arca et al. [13] reported the use of thermally polymerized soybean oil (PSO) mixed with additives and diluents for the formulation of the bio-based gear oil that was compared with the commercially available gear oils on lubricity, viscosity index, and oxidation stability. The properties in these categories are comparable to the commercially available gear oils. In our previous study, we have reported the polymerization of soybean oil (PSO) in supercritical carbon dioxide [14]. Viscosities of these SBO-based materials range from 100 to 2000 mPa and their molecular weights (M_w) range between 1350 and 25,000 Da, which contain oligomers and lower molecular weight polymers. They are suitable to formulate with additives to make fluids of various viscosities for gear oil applications. The present study will utilize PDSC to investigate oxidation of the SBO-based lubricants. In the PDSC method, the sample is heated and pressurized with oxygen and the onset of the exothermic oxidation reaction is determined. The oxidation stability of SBO-based lubricants was also studied using the oxidation induction time (OIT) obtained in PDSC isothermal experiments at 180 °C under a constant pressure of 200 psi with an air flow rate of 34 ± 3 ml/min. Due to the double bonds of unsaturated fatty acids located in the middle of the chains, the tertiary carbons were generated during polymerization of SBO. Therefore, two model compounds which have terminal double bonds, triacyl-10-undecenoate and allyl 10-undecenoate, have been synthesized. They are shown in Fig. 1 and have also been polymerized in order to compare their oxidation stabilities with SBO-based lubricants. In addition, we have compared the oxidation stability of polyethylene (PE) with polypropylene (PP) as a model to study the effect of molecular structure on oxidation stability and to better understand the relationship between structure and properties of vegetable oil-based lubricants.

2. Experimental

2.1. Materials studied

SBOs were polymerized under supercritical carbon dioxide using boron trifluoride diethyl etherate, $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, as catalyst. Details of this synthesis, reaction optimization, and product characterization using NMR and FTIR were described elsewhere [14]. All PSO samples in this study include PSO samples prepared by using different amounts of catalyst and at different temperatures. Antioxidant additives used were zinc diamyl dithiocarbamate (ZDDC) and butylated hydroxy toluene (BHT), as well as the pour-point depressant (PPD), poly alpha olefin.

2.2. PDSC method-temperature ramping

The PDSC experiments use a computerized DSC 2910 thermal analyzer from TA Instruments (New Castle, DE, USA). Typically a 2 μl sample is placed in a hermetically sealed aluminum pan containing a pinhole lid for interaction of the sample and the reactant gas (dry air). The 2 μl sample results in a film thickness of less than 1 mm. This ensures proper oil–air interaction and eliminates gas diffusion limitations. The module is temperature calibrated using indium metal (m.p. 156.6 °C) and a 10 °C/min heating rate. Dry air (Gateway Airgas, St. Louis, MO, USA) is used to pressurize the module at a constant pressure of 1379 kPa (200 psi). A scanning rate of 10 °C/min was used in the temperature ramping experiments. The onset temperature (OT) of oxidation is calculated from the exotherm in each case.

2.3. PDSC-isothermal method

The oxidation stability of PSO samples as lubricants was also studied in the PDSC method using the OIT obtained in isothermal experiments at 180 °C in a constant pressure mode at 200 psi with an air flow rate of 34 ± 3 ml/min. In isothermal OIT tests, the materials are first heated under a protective gas, nitrogen gas used here, then held at a constant temperature for several minutes to establish equilibrium and subsequently exposed to an atmosphere of oxygen or air. The time span from the first contact with oxygen until the beginning of oxidation is called the Oxidation Inductive Time.

2.4. Low temperature performance

Pour points and cloud points were measured by following the ASTM D-5949 and ASTM D-5773 methods, respectively, using a

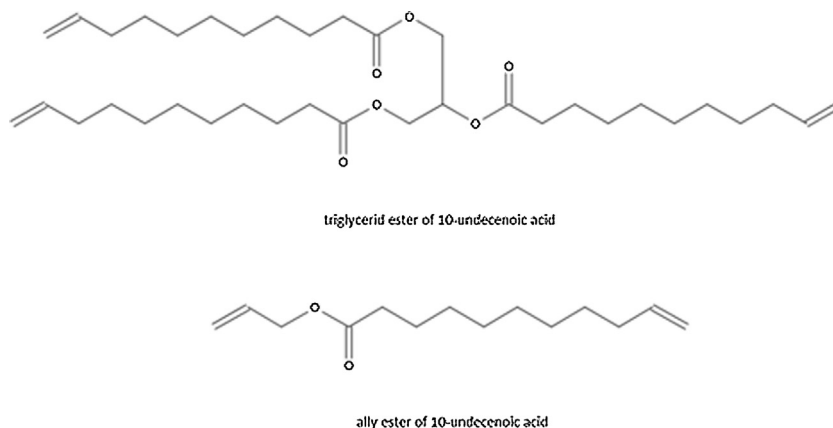


Fig. 1. Structures of triacyl-10-undecenoate and allyl 10-undecenoate.

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