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Tribological study of nitrogen plasma polymerized soybean oil with nitrogen heterocyclic structures

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ABSTRACT

Two types of polymerized oils with high viscosities were synthesized by nitrogen plasma polymerization of soybean oil. The results of elemental analysis indicated that the N atoms were incorporated into the molecule of polymerized oil, which was pyrolyzed by pyrolysis gas chromatography with a mass selective detector to clarify the structure with nitrogen atoms. It was confirmed that in the molecule of polymerized oil, there were three nitrogen heterocyclic compounds, which played a key role in improving the tribological characteristics of the polymerized oils. The lubricating properties of polymerized oils were performed on the four ball friction and wear testers. The load-carrying capacities of polymerized oils reached 940.8 N and 1049 N, respectively, higher than that of soybean oil (646.8 N). Meanwhile, they showed better anti-wear properties under all tested loads and possessed preferable friction-reducing performances when the applied load surpassed 250 N. The friction surfaces lubricated by soybean oil and polymerized oil were observed by a scanning electron microscope (SEM), and the chemical states and compositions of the tribofilms generated during the rubbing process were analyzed by X-ray photoelectron spectroscopy (XPS). It was found that the nitrogen heterocyclic structure containing six N atoms possessed higher coordination capacity than the ester groups of soybean oil, and could form a durable organic nitrogen complex film on the metal surface. Simultaneously, the blended oils with different viscosity grades, which were prepared by diluting the polymerized oil with dioctyl sebacate, showed excellent receptivity on the anti-wear/extreme pressure additives of zinc dialkyl dithiophosphates and sulfurized isobutylene.

1. Introduction

The base stocks of most liquid lubricants come from mineral oils, which are non-degradable and toxic to the environment. Industry experts estimate that 70–80% of hydraulic fluids leave systems and enter the environment through leaks, spills, line breakage and fitting failure (Johnson and Miller, 2010), so it is significant to protect the ecological environment by developing environmental friendly lubricants to substitute for lubricants based on petroleum.

Vegetable oils, which are renewable and are biodegradable and less toxic, display good viscosity temperature performance (Luna et al., 2011; Ting and Chen, 2011), and can be used as environmentally friendly lubricants to substitute for mineral oils. Oil soluble surfactants with polarities such as carboxylic acids and esters, which have been used as friction-reducing additives in lubricating oils, are commonly called “oiliness additives”. The long fatty acid chain and polar ester groups of vegetable oil can make it suitable for oiliness additives in low polarity base oils such as mineral oils and polyalphaolefin (Fernández Rico et al., 2002; Ratoi et al., 2000). Moreover, vegetable oil has higher dissolving capacity for anti-wear and extreme pressure additives than mineral oil (Cao et al., 2000; Jayadas and Prabhakaran Nair, 2007; Zeng et al., 2007). However, the viscosity ranges of most vegetable oils except castor oil are very narrow (ISO VG32-46) (Noureddini et al., 1992; Scholz and da Silva, 2008), and many applications, such as gear oils and hydraulic oils, need higher viscosity.

Erhan (Adhvaryu et al., 2004; Erhan et al., 2008; Sharma et al., 2008) synthesized the chemically modified soybean oil derivatives and tested the friction-wear properties using four-ball and ball-on-disk configurations. Cermak (Cermak et al., 2006, 2013; Cermak and Isbell, 2002, 2003) synthesized estolides with better low-temperature properties from various fatty acids. Guner (Guner, 1997) investigated the thermal polymerization kinetics of anchovy oil with anthraquinone as a catalyst. Refvik (Refvik et al., 1999) developed a process for the acyclic diene metathesis of unsaturated vegetable oils to obtain oligomers with higher molecular weight. Biswas (Biswas et al., 2007) evaluated the lubricities of the microwave-irradiated soybean oil with higher viscosity.

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Table 1
Fatty acid content of soybean oil.

No.	Fatty acid	Content (%)	No.	Fatty acid	Content (%)
1	$C_{14:0}$[a]	0.100	9	$C_{18:3}$	2.69
2	$C_{16:0}$	15.0	10	$C_{20:0}$	0.610
3	$C_{16:1}$	0.150	11	$C_{20:1}$	0.520
4	$C_{17:0}$	0.150	12	$C_{21:0}$	0.0500
5	$C_{17:1}$	0.140	13	$C_{22:0}$	0.660
6	$C_{18:0}$	6.78	14	$C_{23:0}$	0.0600
7	$C_{18:1}$	26.6	15	$C_{24:0}$	0.190
8	$C_{18:2}$	46.3			

[a] $C_{14:0}$ means there are 14 carbon atoms in the fatty acid chain and there is no double bond in the chain.

The research on plasma polymerization has attracted more and more attentions for the past few years. Dilsiz (Dilsiz and Akovali, 1996) investigated the effects of plasma power, different gases and monomers on the structures of the plasma polymers. Girard-Lauriault (Girard-Lauriault et al., 2008) synthesized novel families of N-rich plasma polymers, using methane, ethylene and acetylene in a dielectric barrier discharge apparatus filled with nitrogen gas. Morales (Morales et al., 2009) adopted hexane to produce thin films of polyethylene by plasma polymerization without catalysts or other chemical compounds. Polyacrylic acid films for biomedical applications were deposited in an atmospheric pressure nitrogen plasma jet (Carton et al., 2012). In this paper, the plasma polymerized soybean oils were produced by an original plasma reactor filled with nitrogen gas. The element composition and structure of polymerized oil were analyzed by elemental analyzer and pyrolysis gas chromatography, respectively. The tribological properties of polymerized oils as lubricant base stocks were evaluated and compared with soybean oil and mineral oil (150BS) on four ball friction and wear testers. The tribological mechanism of polymerized oil was discussed through the XPS analysis of the worn surface. Meanwhile, the receptivity of blended oils on the anti-wear/extreme pressure additives was also evaluated.

2. Experimental method and materials

2.1. Materials

The commercial soybean oil, employed for nitrogen plasma polymerization, was provided by Shanghai Liangyou Haishi Oils & Fats Industry Company. The fatty acid composition of soybean oil was shown in Table 1. The fatty acid distribution showed high degree of unsaturation for soybean oil molecule. The physical and chemical properties of soybean oil and an industrial mineral oil (150BS) were listed in Table 2. Dioctyl sebacate, employed to dilute polymerized soybean oil according to ISO 3448 (ISO, 1992), was supplied by Aladdin Industrial Corporation. The anti-wear/extreme pressure additives, such as zinc dialkyl dithiophosphates and sulfurized isobutylene, were both commercial products.

2.2. The synthesis of polymerized soybean oil by nitrogen plasma

A plasma reactor was used to prepare polymerized soybean oils for this work. The major component of the equipment was a non-pressurized vessel containing two parallel graphite electrodes (150 mm × 25 mm × 200 mm), between which two quartz glass plates (6 mm separation) were used as the insulating medium. Power for generating glow discharge was supplied by a CTP-2000 K plasma power source (Nanjing Suman Electronics Co., Ltd.), which operated at output frequency 7.30 kHz. The rated output power was about 500 W.

About 300 mL soybean oil with a constant temperature in a storage tank was pumped in the reactor filled with nitrogen gas, and flowed circularly at a certain flow velocity. In the polymerization process kept the plasma power at 120 W. And adjusted the frequency to obtain glow discharges. The polymerized soybean oil samples (referred to as PSO1 and PSO2, respectively) were withdrawn at predetermined time. The characteristics of PSO1 and PSO2 were listed in Table 2.

2.3. Physicochemical properties test

Viscosities (40.0 and 100.0 °C) and viscosity index were measured and calculated according to ASTM D445 (ASTM, 2012a) and ASTM D2270 (ASTM, 2010), respectively. Pour points were measured by ASTM D97 (ASTM, 2012b). Iodine values were determined by International Standard ISO 3961 (ISO, 2013).

2.4. The pyrolysis experiment of nitrogen plasma polymerized oil

The oil sample of PN2 was pyrolyzed using a PY-2020iD double-shot pyrolyzer (Frontier Lab of Japan) coupled to a GC7089A gas chromatograph. Detection was carried out with a MS5975C mass selective detector. In the experiment, the pyrolysis temperature was 500 °C and the temperature was kept constant for 20 s. The GC oven temperature was 2 min at 40 °C, an increase of 10 °C/min to 310 °C, and finally 40 min at 310 °C. Helium was used as the carrier gas and as an inert atmosphere in the pyrolysis interface.

2.5. Friction and wear test

The tribological properties were conducted at ambient temperature on a MS-800 four-ball friction and wear tester produced by Xiamen Tenkey Automation Company Limited of China.

The test material was GCr15 bearing steel ball with 12.7 mm diameter supplied by Shanghai Steel Ball Plant of China. The chemical composition and hardness of this steel ball were listed in Table 3.

The maximum non-seizure loads (referred to as P_B value) were measured according to ASTM D-2783 (ASTM, 2009). The test conditions of P_B value were a rotating speed of 1450 rpm for duration of 10 s at room temperature. The anti-wear tests were carried out at a rotating speed of 1450 rpm and loads of 98 N, 196 N, 294 N and

Table 2
Characteristics of soybean oil, nitrogen plasma polymerized oils and mineral oil.

Sample	Viscosity (cSt)		Viscosity index	Iodine value (g I_2/100 g)	P_B[a] (N)	Elemental composition (%, w/w)			
	40 °C	100 °C				C	H	N	O
Soybean oil	33.8	7.84	215	130	646.8	76.71	10.64	–	12.65
PSO1[b]	285	45.4	220	108	940.8	76.02	10.84	0.18	12.96
PSO2[c]	576	108	283	96.3	1049	75.38	10.99	0.30	13.34
150BS[d]	601	31.4	77	-	646.8	–	–	–	–

[a] Test conditions for the maximum non-seizure load: 10 s and 1450 rpm.
[b] Polymerized soybean oil with certain viscosity.
[c] Polymerized soybean oil with certain viscosity.
[d] One kind of industrial mineral oil called as bright stock.