Tribology International 123 (2018) 316–324

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Fatty acid based phosphite ionic liquids as multifunctional lubricant additives in mineral oil and refined vegetable oil

Ganlin Zheng[a], Tongmei Ding[a], Yixu Huang[a], Lei Zheng[b], Tianhui Ren[a,*]

[a] School of Chemistry and Chemical Engineering, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Shanghai Jiao Tong University, Shanghai, 200240, PR China

[b] Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100039, PR China

ARTICLE INFO

Keywords:
Oil-dispersible ILs
Phosphite
Fatty acid
Surface analysis

ABSTRACT

Ionic liquids (ILs) are highly attractive lubricant additives for their nonflammability, low vapor pressures, structural diversity and reasonable tribological properties. A convenient synthesis route to oil-dispersible ILs has been presented in this paper. Phosphite binds to aliphatic acid as anion and triethylbenzylammonium serve as a cation, which could be applied as lubricant additives in mineral oil (5CST) and refined vegetable oil (RSO). Results demonstrated that these ILs could effectively enhance the antiwear, friction-reducing and extreme pressure properties of 5CST and RSO. The chain length and unsaturation of fatty acid is significant in improving the tribological properties of base oil. TEY and FY mode K-edge XANES analysis of the formed tribofilms showed that the improvement of anti-wear and friction-reducing properties was closely related to the content of phosphate species on the near surface.

1. Introduction

As one of the most widely used base oil in lubricant industry, mineral oil has many advantages of high chemical stability, reasonable thermal and oxidative stability and economical price [1]. Due to the depleting mineral oil reserve and stringent environment regulation, it is necessary to develop new and environmentally benign lubricants directly from renewable natural raw materials [2]. Vegetable oil is considered to be potential substitutes for mineral oil. It possesses superior natural properties including biodegradability, reproducibility and lubrication properties [3]. It has been used as lubricating additive or base oil to substitute conventional combinations [4,5]. But they are about twice as expensive as mineral oil based lubricating oil [6]. Although the use of mineral oil as base oil is gradually reduced [7], it is difficult to be completely replaced in short term. Therefore, developing additive for vegetable oil and mineral oil is very significant to alleviate the current problems.

Ionic liquids (ILs) are promising lubricant due to their unique properties of high thermal stability, negligible volatility, nonflammability, and low melting point [8–11]. Many groups have carried out relevant exploration derived from cations such as pyridinium, imidazolium, ammonium and anions such as bis(trifluoromethylsulfonyl) imide (TFSI) and BF_4 [12–16]. However, ILs suffer from some drawbacks, such as strong corrosion to the interacting surface, tedious preparing procedure, high production cost, hydrolytic instability and low solubility in base oil [17–19]. Recently, fully organic protic ILs, oil-miscible and non-corrosive ILs, environmentally friendly ILs, multifunctional ILs and water-soluble ILs are developed [20–27]. To the best of our knowledge, few researchers use existing low cost and high performance raw material to construct ILs.

Tribochemistry studies the relationship between the worn surface chemical composition and the lubrication effectiveness [28], which could help us to understand the effectiveness of lubrication and the development of new additive. The current cognition focuses on the tribochemical reaction of P, S, N, B, and Mo on the worn surface [29–31], especially the study of P containing additives. The improvement of tribological properties could be ascribed to the formation of phosphate and polyphosphate on the worn surface [32]. However, it is a great challenge to utilize the existing principles of tribochemistry for molecular design because of the changes in molecular structure, leading to great difference in the tribochemical processes during frictional process.

Dialkyl phosphite is widely used as extreme pressure, friction-reducing and antiwear additives in mineral or vegetable oil [33]. Alkyl group could improve the adsorption and dispersion property of additive molecule in base oil and phosphite acts as a functional group to form phosphate or polyphosphate on the worn surface during frictional process. Vegetable oil has long been used as a lubricant, and its acid has

* Corresponding author.
E-mail address: thren@sjtu.edu.cn (T. Ren).

https://doi.org/10.1016/j.triboint.2018.03.028
Received 4 January 2018; Received in revised form 26 March 2018; Accepted 26 March 2018
Available online 27 March 2018

been reported as a lubricant additive recently [34]. Fatty acid can produce metal soap and avoid the direct contact of asperities, but its tribological properties could not meet the requirement of severe lubrication conditions. Quaternary ammonium base has good phase transfer, adsorption and dispersion characteristics over a wide range of base liquids [35].

Combined with the benefits of ILs, fatty acid and phosphite, we report the synthesis, characterization, tribo-evaluation and lubrication mechanism of phosphite-based halogen-free ILs additives for vegetable oil and mineral oil. We focus on the influence of ILs concentration on tribological properties of the base oil. The tribological performance of ILs as lubricant additive was evaluated using a four-ball tester. A KEYENCE vk-x200 laser scanning microscope (CLSM) was used to examine the morphology and wear volume of steel ball surface. XANES analysis was carried out to examine the chemical composition on the wear scar and the possible tribochemical changes involved in the frictional process.

2. Materials and experimental details

2.1. Materials

Oleic acid, linoleic acid, stearic acid, and palmitic acid were purchased from KLK OLEO and used to synthesize four ILs without further treatment. RSO (trade name Arawana 1:1:1) was commercially available from Xi'an Jiali Oil and Grease Factory of China. A commercial mineral oil (referred to 5CST), was provided by Petro China Lanzhou Lubricating Oil R&D Institute in Lanzhou, China. T308B were obtained from Zibo Hui Hua Chemical Corporation and used without further purification. Other chemicals utilized in this article were all analytical grade and procured commercially. The steel balls used in experiments were obtained from Shanghai Ningxing steel ball Co., Ltd. and had the following specifications:φ12.7 mm; HRC59-61; GCr15 (chemical composition: 0.95–1.05 wt % C; 0.15–0.35 wt % Si; 0.20–0.40 wt % Mn; 0.027 wt % P; 0.020 wt % S; 1.30–1.65 wt % Cr; 0.30 wt % Ni; 0.25 wt % Cu).

2.2. Preparation of additives

Four ILs with quaternary ammonium group, OAPN, LAPN, SAPN and PAPN, were synthesized in three steps (Fig. 1). The desired mixture 1 was obtained from a slight excess of epoxy propane and aliphatic acid with triethylamine as the catalyst, and toluene as the solvent at 60 °C after 8 h. The mixture 2 was prepared by mixing l and dimethyl phosphite stirring at about 120 °C until no CH_3OH formed. In the third sequence of reactions, mixture 3 was obtained by neutralization with quaternary ammonium base at 70 °C for 4 h. Finally it was obtained by filtration and reduced pressure distillation. Additionally, a commercial additive was also provided for compare and its chemical structure was shown in Fig. 1.

2.3. Characterization

The structure of ILs was characterized by ^{1}H, ^{13}C NMR spectroscopy, Fourier transform infrared (FT-IR) spectroscopy (see Fig. 2 and Table 1) and Elemental Analysis (EA) (see Table 2). In order to estimate the decomposition behavior of synthesized ILs under thermal conditions (oxygen free), T_{onset} (thermal decomposition temperature) was determined on a Perkin Elmer TGA 7 thermo-gravimetric analysis device.

OAPN: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85–0.93 (t, 6H), 1.22–1.28 (m, 44H), 1.29–1.35 (t, 9H), 1.46–1.51 (t, 6H), 1.56–1.66 (m, 4H), 2.25–2.35 (m, 4H), 3.35–3.41 (t, 6H), 3.67–3.69 (s, 4H),4.65–4.70 (s, 2H), 4.85–5.1 (s,2H), 7.44–7.53 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.25, 14.04, 22.66, 24.91, 29.50, 31.93, 34.13, 35.08, 51.45, 52.86, 61.15, 127.16, 129.27, 130.6, 130.83,132.39, 174.40, 177.87.

LAPN: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86–0.91 (t, 6H), 1.20–1.40 (m, 32H), 1.46–1.50 (t, 4H), 1.55–1.67 (m, 2H), 2.24–2.37 (m, 2H), 3.38–3.43 (t, 3H), 3.67–3.69 (s, 4H), 4.70–4.75 (s, 2H), 4.85–5.1 (s,2H), 7.42–7.56 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.27, 14.12, 22.63, 24.91, 29.36, 31.97, 34.12, 51.48, 127.17, 129.50, 130.77, 132.43, 174.37, 177.22.

PAPN: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88–0.92 (t, 6H), 1.26–1.39 (t, 40H), 1.60–1.68 (m, 4H), 1.95–2.10 (m, 8H), 2.32–2.38 (m, 4H), 2.60–2.85 (m, 6H), 3.61–3.65 (m, 4H), 3.66–3.69 (t, 6H), 3.70–3.73 (t, 6H), 3.73–3.80 (m, 4H), 4.22–4.28 (m, 4H), 7.41–7.49 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.08, 22.42, 24.59, 24.90, 27.22, 29.12, 31.53, 34.20, 61.65, 63.35, 69.27, 70.53, 72.55, 127.78, 130.22, 174.10.

SAPN: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88–0.93 (t, 6H), 1.26–1.39 (t, 60H), 1.47–1.51 (t, 4H), 1.58–1.68 (m,4H), 1.96–2.12 (m, 4H), 2.28–2.37 (m, 4H), 2.72–2.84 (m, 2H), 3.37–3.42 (m, 2H), 3.67–3.90 (s, 2H), 4.03–4.20 (m, 2H), 7.46–7.54 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.21, 14.13, 22.56, 24.95, 25.64, 27.23, 29.16, 31.54, 31.85, 34.07, 51.46, 52.78, 127.90, 128.04, 129.52, 174.44.

The measured values of C, H, P, N elements are close to their calculated values. The NMR, EA and FT-IR results confirmed that the designed molecules were successfully synthesized.

2.4. Lubricant preparation and oil solubility of ILs

The additives were mixed with RSO or 5CST at a fixed concentration, and the solution was stirred at fixed temperature (60 °C) for 10 min. And the solubility data of the synthesized ILs for both blends was measured at highest concentration (3 wt %)

2.5. Tribological evaluation

The tribological properties of ILs as additives in RSO and 5CST were evaluated using a MS-10J four-ball tester manufactured by Xia men tenkey automation Co. Ltd, China. Four-ball tester consists of a mobile ball bearing that is rotated in contact with three fixed ball bearings which are immersed in the test lubricant, as shown in Fig. 3. The antiwear and friction-reducing test were conducted on four-ball tester at a speed of 1450 rpm, load 40 Kg and room temperature (25 °C) for 30 min. The wear scar diameters (WSDs) were collected by an optical microscope with accuracy of ± 0.01 mm. The friction coefficient (COF) was automatically calculated from measured torque and load data. The extreme pressure (EP) performance was conducted following GB12583-98 test procedure: speed, 1760 rpm; temperature, ambient; load, variable; test duration, 10 s, which was similar to ASTMD-2783 method. EP tests were conducted with increasing loads until welding of steel balls is occurred. The load before which welding occurs is called the maximum nonseized load (P_B value), and the load is an EP property of the test lubricant. For each sample, three identical tests were performed so as to minimize data scattering. After the tribological evaluation, the steel balls were gently rinsed in acetone and dried with tissue paper.

2.6. Analysis of the worn surface morphology and chemical composition

The morphology of the worn surface was obtained using a KEYENCE vk-x200 laser scanning microscope (CLSM). Chemical composition measurement on the worn surface was carried out on an X-ray absorption near edge structure spectroscopy (XANES) which was located at the Institute of High-Energy Physics (IHEP), Chinese Academy of Science [36]. Sample spectra were collected in partial fluorescence yield (FY) mode for bulk information or total electron yield (TEY) mode for near surface information. All spectras were recorded from 2140 to 2165eV with a step size of 1.0eV on the region of 2140–2145 eV, 0.50 eV in pre-edge region of 2145–2150 eV, and 0.20 eV in near edge region of 2150–2165 eV.