Analysis and Comparison of Tribological Performance of Fatty Acid-based Lubricant Additives with Phosphorus and Sulfur

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A B S T R A C T

Two environmentally friendly, water-based lubricant additives (phosphorus-containing ricinoleic acid (PRA) and sulfur-containing ricinoleic acid (SRA)) were prepared. The lubrication performance of the additives in a water-based lubricant was tested using a four-ball tribotester. The stainless steel surface was analyzed by using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The additives reduced the coefficient of friction (COF) value, wear scar diameter (WSD) and improved the extreme pressure (PB) value. Water-based fluids containing the PRA exhibited lower COF, WSD, and PB values than the SRA. The good tribological performances of the PRA and SRA were attributed to the synergistic action of long aliphatic chains and highly active phosphorus and sulfur elements.

1. Introduction

Mineral oil-based lubricants are commonly used in industrial applications to reduce mechanical friction and extend machine life. However, water-based lubricants are preferred due to the disadvantages like flammability, environmental damage, non-renewability. Water-based lubricants also offer good fire-resistance, storage stability, and cooling properties (Wang et al., 2019; Wu et al., 2019b).

Compared with mineral or synthetic-based oils, the low surface tension and viscosity, making water difficult to be used as lubricating base oil. To solve these problems, a number of water-based lubricant additives (friction modifier, extreme pressure additives, and so on) have been developed. The extreme pressure additive offers a degree of solubility in water (or other water-based liquids) which can significantly improve the anti-wear or extreme pressure properties of water-based lubricants. Sulfur and phosphorus offer good extreme pressure and anti-wear performance and are commonly used as extreme pressure lubricating additives (Wan and Xue, 1995; Evans et al., 2007; Kinoshita et al., 2014; Shahnazar et al., 2016; Wang et al., 2018). Lei et al. (2002) synthesized a novel fullerene-styrene sulfonic acid copolymer and used as the water-based lubricant additive, and the lubricants concentration was more than 2.0 wt%, the wear resistance, load-carrying capacity and anti-friction of base stock were improved. Yang et al. (2016) studied the tribological performance of nonylphenol polyoxyethylene ether phosphate ester (PPE) solution in water based lubricant. While the PPE solutions decreased the friction coefficient to 0.15 and reduced the wear volume up to 50%. When the lubricants concentration was more than 0.5 wt%, the PPE solution can meet the requirements of lubricating and antiwear properties.

Traditional water-based lubricating fluids use mineral oil-based extreme pressure lubricant additives with poor biodegradability and great harm for human environment. Vegetable oil-based, extreme pressure lubricant additives have attracted

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attention recently. Vegetable oil is a clean and abundant resource with great potential for development. According to the US Department of Agriculture, global production of vegetable oil was 176 million tons in 2015 (Cheng et al., 2019). Ricinoleic acid is the hydrolysate product of renewable castor oils which has good lubricity and biodegradability due to the long organic fatty chains, carbonyls, and unsaturated double bonds (Deivajothi et al., 2019). However, the extreme pressure properties of ricinoleic acid-based additives for water-based lubricants are poor. These properties can be enhanced by introducing phosphorus and sulfur elements into the fatty acid molecular structure. Zheng et al. (2018) synthesized ionic liquids (ILs) with fatty acid and phosphite. The friction performance of the ILs was better than that of the commercial lubricant additive T308B, and the ILs exhibited good tribological and extreme pressure performance in vegetable oil. He et al. (2004) studied the tribological performance of S-P-N type friendly lubricating oil additives in rapeseed oil. These additives improved the load-carrying capacity and the anti-wear and anti-friction properties of the lubricant.

In view of the advantages of ricinoleic acid and water-based lubricant additives, we synthesized two environmentally friendly, water-based, lubricant additives using sulfur-containing ricinoleic acid (SRA) and phosphorus-containing ricinoleic acid (PRA) for use in water-based lubricants. The extreme pressure (PB) values, anti-wear, and anti-friction properties of the PRA and SRA in water were analyzed and compared. The friction mechanisms of the synthesized additives were analyzed based on wear scars as determined using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

2. Materials and Methods

2.1. Materials

Ricinoleic acid (RA), p-Toluenesulfonyl isocyanate, ethylene glycol, benzyl triethylammonium chloride, methyl alcohol, triethylamine, triethanolamine, ethyl acetate, and tetrahydrofuran (THF) were obtained from the Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Phenyl dichlorophosphate (PDCP) was obtained from the Xuchang Huizhong Fine Chemical Co., Ltd. (Xuchang, China).

2.2. Preparation of sulfur-containing ricinoleic acid

The following were introduced into a four-neck flask with a mechanical stirrer and a thermometer: 2.98 g RA, 1.97 g p-Toluenesulfonyl isocyanate, 0.025 g (0.5 wt% of RA and p-Toluenesulfonyl isocyanate) dibutyltin dilaurate, and 20 mL ethyl acetate. The mixture was heated to 70–75 °C and reacted for 4 h to obtain the SRA (Fig. 1).
2.3. Preparation of phosphorus-containing ricinoleic acid

In this preparation, 2.11 g PDCP and 40 mL THF were added into a three-necked flask, then stirred and maintained at 5 °C. Under an N\textsubscript{2} atmosphere, 2.02 g triethylamine was dropped into the PDCP solution for 30 min. A solution of 0.30 g methyl alcohol and 10 mL THF was then slowly dropped into the flask for 30 min. The solution was stirred at 25 °C for 8 h. Finally, 2.98 g RA and 20 mL of dried THF were slowly dropped into the flask and stirred at 25 °C for 12 h. The mixture was then filtered and rotary evaporated to obtain the PRA (Fig. 2).

![Synthesis route and structure of phosphorus-containing ricinoleic acid (PRA)](image)

2.4. Structure characterization

The chemical structures of the SRA and PRA were characterized by using Fourier transform infrared (FT-IR) spectrometer (IS10, Thermo Fisher Nicolet, USA) and an AVANCE 400 Bruker spectrometer (\textsuperscript{1}H NMR) with chloroform-d (CDCl\textsubscript{3}) as the solvent.

2.5. Measurement of tribology properties

The SRA and PRA were dispersed in distilled water at the mass concentration of 0.5%, 1.0%, 1.5% and 2.0%. The friction, anti-wear, and PB values were examinated using a four-ball tribometer (MRS-10A type, Xiamen Tianji Automation Co., Ltd., China), according to the ASTM D-2783 Standard. The PB values were measured at 1450 r/min for 10 s. The coefficient of friction (COF) and wear scar diameter (WSD) test conditions were 1450 r/min (spindle speed), 200 N (loads), and 30 min (testing time). The balls (diameter 12.7 mm, HRC 61–64) were made of High-carbon chromium bearing steel (GCr 15) standard steel balls (SAE-52100). The wear scar diameters of the three low balls were examinated by using an optical microscope at an accuracy of 0.01 mm.

2.6. The SEM and XPS analyses of worn surface

The worn surface morphologies and chemical composition of the wear scars on steel surfaces lubricated with different SRA and PRA concentrations were examined by using SEM (FEI Quanta 200, Holland) and XPS (PHI 5000 Versa Probe, Japan).
3. Results and Discussion

3.1. Characterization of SRA and PRA

Figure 3 shows the FT-IR analyses of the RA, SRA, and PRA. The peak at 1705 cm\(^{-1}\) corresponded to the carbonyl stretching vibration in the RA. The new absorption peaks at 3237, 1602, and 1740 cm\(^{-1}\) are assigned to the characteristic absorptions of the –NH and carbonyl in the amide group, and the peak for –OH was not observed. The characteristic absorption peaks of S=O and C-S were observed at 1342, 1158, and 763 cm\(^{-1}\). When the RA reacted with methyl alcohol and PDCP, new absorption peaks at 1213 cm\(^{-1}\) and 1014–930 cm\(^{-1}\) were assigned to the characteristic absorption peaks of the P=O and P–O–C. A peak for –OH was not observed.

The \(^1\)H NMR analysis results for the RA, SRA, and PRA are shown in Fig. 4. The \(^1\)H NMR (400 MHz, CDCl\(_3\)), for RA, \(\delta\) (×10\(^{-6}\)) = 1.98 (–OH), \(\delta\) (×10\(^{-6}\)) = 3.60 (–CH–OH), \(\delta\) (×10\(^{-4}\)) = 5.23–5.55 (–CH=CH–). For the SPA, \(\delta\) (×10\(^{-6}\)) = 4.74 (–NH), \(\delta\) (×10\(^{-6}\)) = 7.25–8.00 (benzene-H), \(\delta\) (×10\(^{-6}\)) = 4.13 (–CH\(_2\)–O–). For the PRA, \(\delta\) (×10\(^{-6}\)) = 0.85 (–CH\(_3\)), \(\delta\) (×10\(^{-6}\)) = 1.06–1.66 (–CH\(_2\)–CH\(_2\)–), \(\delta\) (×10\(^{-6}\)) = 2.78 (–CH\(_2\)–COOH), \(\delta\) (×10\(^{-6}\)) = 5.36 (–CH=CH–), \(\delta\) (×10\(^{-6}\)) = 3.43–4.25 (–CH\(_2\)CH(OH)CH\(_2\)OH), \(\delta\) (×10\(^{-6}\)) = 2.01 (–OH), \(\delta\) (×10\(^{-6}\)) = 7.00–7.30 (benzene-H), \(\delta\) (×10\(^{-6}\)) = 3.30–3.70 (–CH\(_2\)–O–).

3.2. Anti-wear and friction-reducing performance

Figure 5 shows the COF and WSD of water at different SRA and PRA concentrations under a load of 200 N for 30 min. It can be observed that the addition of SRA and PRA improved the anti-wear and anti-friction properties of pure water at all concentrations. The COF of the SRA/water solutions increased with SRA concentration (from 0.5 wt% to 2.0 wt%). As for the PRA in water, the COF gradually decreased with increased concentration. The PRA produced significantly lower COF values as compared with the SRA. The trend of the WSD is similar to that of the COF, indicating that the SRA and PRA improved the anti-friction and...
anti-wear performance of pure water. This be ascribed to the long alkyl chains and active sulfur and phosphorus form a boundary lubrication film that serves as a physical lubrication film and tribochemical reaction film on the stainless steel surface. In addition, The COF of the SRA/water solutions increased with the SRA concentration. This be ascribed to the metal sulfide film is relatively brittle and the sulfur element is more corrosive than the phosphorus element under high temperature and pressure (Ding et al., 2018; He et al., 2018; Wu et al., 2019c).

3.3. Extreme pressure property

The adsorption and reaction activities of the additive molecules and extreme pressure elements are closely related to the extreme pressure properties. Figure 6 shows the relationship between the SRA and PRA concentration (in water) and PB values. The PB value of water is 95 N, indicating that water has difficulty with physical adsorption to the film on the stainless steel surface, and thus has difficulty lubricating the surface. The addition of the SRA and PRA improved the PB values. The PB values increased with increased SRA and PRA concentrations. At 2.0 wt% SRA and PRA, the PB values for the SRA were 842 N and 8.7 times that of pure water, while the values for the PRA were 725 N and 7.6 times that of pure water. The results contribute to the synergistic effect of long fatty chains, active sulfur and phosphorus elements in the SRA and PRA, which indicates that the SRA and PRA can produce physical adsorption and chemical reactions film on the stainless steel surface. However, at the same concentration, the PB value of the SRA is much higher than that of the PRA. This can be ascribed to greater reactivity of sulfur and adsorption with friction metal surfaces under high loads. In addition, metal sulfide films have good heat resistance (Bai et al., 2018; Bhaumik et al., 2018; Yu et al., 2019).

3.4. The SEM analysis

To investigate the lubricating mechanisms of the SRA and PRA, we analyzed worn steel surfaces using SEM and XPS. The SEM morphologies for stainless steel surfaces lubricated by various concentrations of the SRA and PRA are shown in Fig. 7 and Fig. 8. As the SRA concentration increased, wear scars became widen and deepen, and it showed adhesive wear and abrasive wear. It indicated that the lubricating mechanisms of the SRA was mainly adhesive and abrasive wear. However, as the PRA concentration increased, wear scars became shallower and smoother, and the adhesive and abrasive wear weaken. This meant that pure water with the PRA could form the boundary film on the stainless steel surface to reduce the friction. Meanwhile, at the same concentrations, abrasive scars smaller with the PRA additive than with the SRA, indicating better anti-friction and anti-wear performance with the PRA (Xia et al., 2018; Kerni et al., 2019; Wu et al., 2019a).
3.5. The XPS analysis

Figures 9 shows the XPS survey spectra of the PRA and SRA samples in which the characteristic C, O, P, S, and Fe elements are detected. Data for the analysis are shown in Table 1. The binding energy of C1s at 284.8 and 288.8 eV are assigned to C–H, C–C, C=O, and C–O. It indicates that the PRA and SRA samples formed a physical adsorption film composed of carbon, esters, and so on. The XPS peaks of O1s appear at the binding energies of 529.4 eV, which might be ascribed to FeO and Fe₂O₃. The peaks at 530.3 and 532.6 eV are ascribed to Fe(OH)₃ and Fe₂(PO₄)₃. The binding energy of P2p at 133.2 eV might be ascribed to PO₄³⁻. The S2p peaks at 161.7 and 168.9 eV were attributed to ferrous sulfide and ferrous sulfate. The Fe2p peaks at approximately 710.0 and 723.4 eV combined with the O1s peaks at 529.4, 530.3 and 532.6 eV, indicating the existence of iron oxide and iron phosphate (Fe₂O₃, FeO, FeSO₄, and Fe₂(PO₄)₃) on the stainless steel surface (Gao et al., 2017; Wu et al., 2017; Zhang et al., 2019).

Fig. 9 The XPS spectra of worn surfaces lubricated with 2.0 wt% PRA and SRA (200 N for 30 min)
Given the SEM and XPS results, we found that the PRA and SRA formed effective lubricant films of iron sulfide, iron oxide, and iron phosphate compounds and thus, improved the lubrication properties of water solutions.

3.6. Possible lubrication mechanism

Based on the above analysis, the PRA and SRA solutions primarily offered boundary lubrication. The possible lubrication mechanisms of the PRA and SRA were summarized as follows and in Fig. 10 and Fig. 11. As for the PRA, fatty chain had good adsorption, and its lubrication mechanism was that the long carbon chain molecules of fatty acid could be more effectively adsorbed on the metal surface to form a physically adsorbed lubricating film, and exerted a certain anti-friction and anti-wear effect. As the pressure increased, the physical adsorption film ruptured, and the friction chemical reaction lubrication film appeared, which was the coverage of the organic phosphorus and inorganic nitrogen film formed on the surface of the friction pair, and the long-chain fatty acid chain acted to reduce the direct contact between the steel ball and the oxygen in the water, thereby preventing the frictional wear and oxidation of the steel ball.

The possible lubrication mechanisms of the SRA was similar to that of the PRA. First, the polar groups of the SRA were physically adsorbed onto the stainless steel surface to form a physical and chemical adsorption layer, and this adsorption was due to the synergistic action of the long aliphatic chain and the highly active sulfur. Second, the highly active sulfur elements reacted with the friction pair to rapidly form a more stable chemical reaction film (iron sulfide, iron oxide etc.) and reduced direct contact with the friction pair surfaces.

Thus we found how the PRA and SRA improved the extreme pressure and friction properties of water solutions.

4. Conclusions

Two environmentally friendly, water-based lubricant additives (PRA and SRA) were successfully prepared by using ricinoleic acid. The PRA and SRA solutions were found to improve the anti-friction, anti-wear, and extreme pressure properties of water solutions. We found that the PRA yielded lower COF and WSD values than the SRA. Furthermore, the extreme pressure properties of the SRA were superior to those of the PRA. The results suggested that the phosphorus element primarily acted as an anti-wear agent under medium load conditions, while the sulfur element acted as a polar pressure agent under high temperature and load conditions. The lubricating mechanisms of the PRA and SRA were due to the formation of a stable lubricating film of ferrous sulfide, ferrous sulfate, FeO, Fe₂O₃, and Fe₂(PO₄)₃ on steel surfaces to greatly reduce friction and wear.

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References


