

Lignin composite ionic liquid lubricants with excellent anti-corrosion, anti-oxidation, and tribological properties

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Abstract: A new type of lubricating material (BTA-P₄₄₄₄-Lig) was synthesized by combining lignin with tetrabutylphosphorus and benzotriazole. The tribological properties, corrosion resistance, and anti-oxidation properties of BTA-P₄₄₄₄-Lig as a lubricant were investigated. The lubricating material exhibits excellent friction reduction and wear resistance, as well as good thermal stability and excellent oxidation resistance. Mechanistic analysis reveals that the active elements N and P in the lubricating material react with the metal substrate, and the reaction film effectively blocks direct contact between the friction pairs, affording excellent friction reduction and wear resistance. At the same time, the phenolic hydroxyl group in lignin reacts with oxygen free radicals to form a resonance-stable semi-quinone free radical, which interrupts the chain reaction and affords good anti-oxidant activity.

Keywords: lignin; lubrication; ionic liquid; anti-oxidant

1 Introduction

Since environmental pollution is difficult to control, the demand for green lubrication is increasing, which requires lubricants to have the characteristics of environmental protection and environment-friendliness. Therefore, lubricants are required to be non-polluting, non-corrosive, and non-toxic, and have excellent friction reduction and anti-wear properties. It has been proved that biomacromolecules can be used as lubricating additives. However, biomacromolecules often have molecular weights of tens of thousands to millions, along with complex molecular structures, making their practical applications difficult. Lignin is a renewable resource and is also the second-largest source of natural biopolymer [1–3]. Oxidative

degradation of lignins affords aromatic aldehydes, such as vanillin and p-hydroxybenzaldehyde, which can be widely used in perfumes, medicine, and other fields [3–6]. However, lignin has a complex and diverse molecular structure, and it is difficult to dissolve lignin in a variety of organic solvents. In the field of production and processing, lignin is often treated as waste and is converted into energy by combustion or other means, resulting in low energy conversion efficiency and air pollution [7, 8]. Improving the utilization efficiency of lignin remains an urgent challenge.

Ionic liquids, which are composed of cations and anions, have unique and excellent physico-chemical properties, such as low vapor pressure, nonvolatility, incombustibility, excellent thermal stability, and good

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solubility [9–12]. At the same time, ionic liquids act as aprotic polar solvents, which have strong selective solubility for organic matter. To improve the utilization of lignin, the dissolution of lignin biomacromolecules can be realized by controlling the molecular structure design of ionic liquids [13, 14]. Cao et al. [15] reported that lignin as a lubricating additive significantly improved the lubricating performance of polyethylene glycol (PEG), and the wear volume (WV) decreased by 93.8%. Mu et al. [16] reported for the first time that a lignin dissolved in an ionic liquid and used it as a lubricant. It was found that the addition of lignin to the ionic liquid improved the thermal stability of the ionic liquid, as well as the anti-wear and anti-corrosion performances of the system [16]. Abbott et al. [17] dissolved corncob and rice straw in an ionic liquid and found that the lignin content was maximized when the pretreatment temperature reached 120 °C, at which lignin was effectively dissolved. Some studies have shown that lignin is a feasible lubricating additive. Meanwhile, through molecular design of ionic liquid, such as imidazolyl ionic liquid, the solubility of lignin in ionic liquid is improved by enhancing hydrogen bonding and π - π interactions, and the tribological properties of ionic liquid are improved by lignin addition. Benzotriazole is a green organic substance with excellent anti-corrosion performance [18]. Its imidazole functional groups can effectively improve the dissolution of lignin [19]. At the same time, this work is based on green chemistry, and considering the characteristics of low toxicity and good biocompatibility of the designed composites, benzotriazole ionic liquid was selected as lubricant. In this experiment, a BTA-type ionic liquid (hereinafter referred to as BTA)

was prepared by the acid–base neutralization reaction between benzotriazole and tetrabutylphosphorus hydroxide. The green lignin–ionic liquid composite lubricant (BTA-P₄₄₄₄-Lig) was prepared by dissolving lignin in the ionic liquid. The effects of different lignin contents on the tribological and anti-oxidant properties of BTA-P₄₄₄₄-Lig were investigated based on mechanistic analysis, and the lubrication mechanism of the compound lubricant was elucidated. Taking green chemistry as the starting point, this work designs a multifunctional composite lubricant with lubrication, anti-corrosion, and anti-oxidation by dissolving lignin with ionic liquid, so as to improve the utilization rate of lignin. Compared with traditional lubricants, the lubricant has less environmental pollution, which can be used as a reference for the future development of green lubricants.

2 Materials and methods

2.1 Experimental materials

Benzotriazole (purity 98%), tetrabutylphosphorus hydroxide (40% soluble in water), and alkali lignin (98%) used in the experiment were purchased from Shanghai Sanen Chemical Technology Co., Ltd., (China).

2.2 Synthesis and preparation of BTA-P₄₄₄₄-Lig composite lubricant

BTA-P₄₄₄₄-Lig synthesis process is shown in Fig. 1. Benzotriazole and tetrabutylphosphorus hydroxide were mixed at room temperature at a molar ratio of 1:1 and stirred for 8 h. After the reaction, chloroform

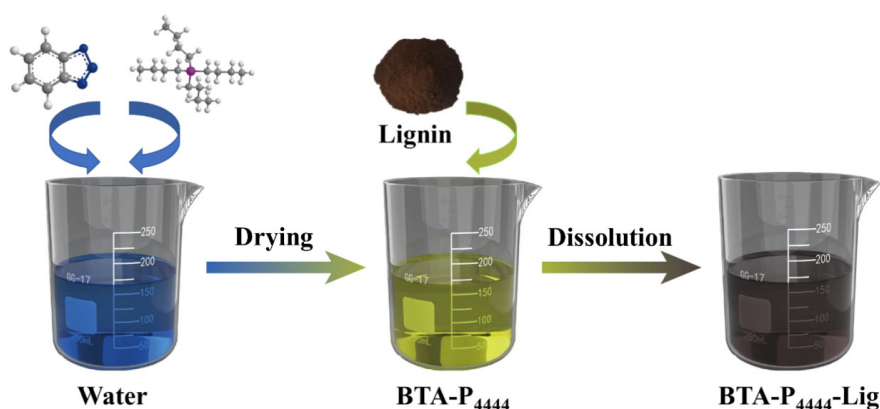


Fig. 1 Synthesis process and molecular mechanism of BTA-P₄₄₄₄-Lig.



was added to extract the aqueous phase, the solvent was removed by vacuum distillation, anhydrous magnesium sulfate was added to dry the organic phase overnight, and the solid phase was filtered out to obtain BTA-P₄₄₄₄ ionic liquid. The BTA-P₄₄₄₄ ionic liquid was heated at 90 °C and mixed with different quantities of lignin to obtain the composite lubricants of 0% BTA-P₄₄₄₄-Lig, 1% BTA-P₄₄₄₄-Lig, 3% BTA-P₄₄₄₄-Lig, and 5% BTA-P₄₄₄₄-Lig.

2.3 Physical and chemical properties of BTA-P₄₄₄₄-Lig composite lubricant

According to the GB/T 265 Standard, the kinematic viscosities of BTA-P₄₄₄₄-Lig composite lubricating materials with different lignin contents were measured at 40 and 100 °C using a kinematic viscosity tester (SYP 1003-III) (temperature control accuracy ± 0.1 °C), and the viscosity index of the BTA-P₄₄₄₄-Lig composite lubricating material was calculated.

2.4 Solubility test

A series of BTA-P₄₄₄₄-Lig composite lubricating materials with different lignin contents was prepared in Fig. 2. With increasing lignin contents, the composite materials exhibit good solubility in the BTA-P₄₄₄₄ ionic liquid. When the lignin content reached 5%, the viscosity index decreased to 33, but the composite remained in a liquid state (Fig. 2(b)) (weight percentage is taken as the standard).

2.5 Thermal stability and oxidation resistance

The thermal stability of the BTA-P₄₄₄₄-Lig composite was analyzed using a thermogravimetric analysis–

differential scanning calorimetry (TGA–DSC) synchronous thermal analyzer (STA 449 F3, NETZSCH, Germany). The experimental conditions were as follows: nitrogen atmosphere; heating rate = 10 °C/min; and temperature ranged from room temperature to 800 °C. The oxidation resistance of the BTA-P₄₄₄₄-Lig composite lubricant was evaluated using a differential scanning calorimeter (DSC 204 HP, NETZSCH, Germany). According to ASTM D6186-08 (2013), about 3.0 mg of the sample was placed on an open aluminum plate and oxidized under a static oxygen pressure of 3.5 ± 0.2 MPa by increasing the temperature from room temperature to 350 °C at a heating rate of 10 °C/min. The initial oxidation temperature (TP) was measured and calculated using a rotating oxygen bomb instrument (15200-5, Stanhope-Seta, UK). According to ASTM D 2272-09, 50 ± 0.5 g of sample was added to the sample bottle, and 5 mL of deionized water and catalytic copper coil were added successively. The container was ventilated after filled with oxygen, and this was repeated three times until the air inside the bomb was completely replaced. The oxygen bomb was then fixed in an oil bath at 150 °C, and the time taken to record the pressure drop at 175 kPa was determined as the oxidation induction period.

2.6 Rheological properties

The rheological properties of BTA-P₄₄₄₄-Lig composite lubricants with different lignin contents were studied using a rheometer (RS 6000, Haake, Germany). The rheometer test conditions were as follows: the plate P35TiL diameter was 35 mm, the parallel plate spacing was 1 mm, and the shear stress was in the range from 0.01 to 700 Pa.

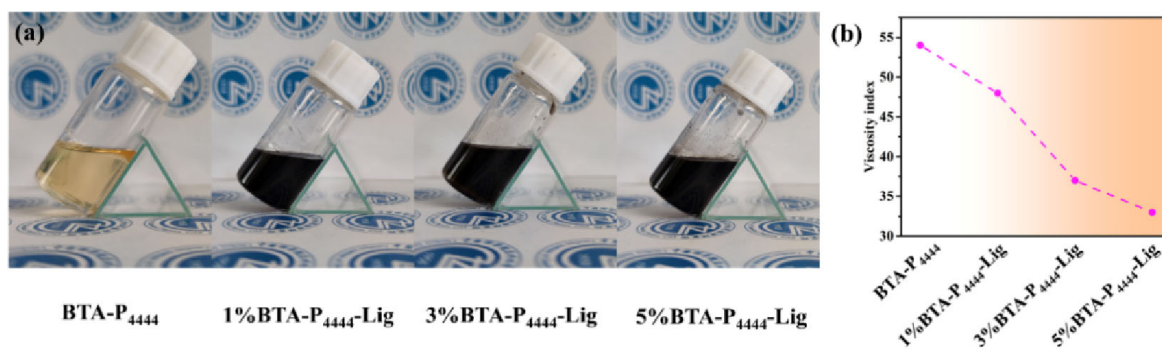


Fig. 2 (a) Optical photos of BTA-P₄₄₄₄, 1% BTA-P₄₄₄₄-Lig, 3% BTA-P₄₄₄₄-Lig, and 5% BTA-P₄₄₄₄-Lig; (b) determination of viscosity index.

2.7 Tribology experiment

The tribological properties of BTA-P₄₄₄₄-Lig composite lubricants with different lignin contents were evaluated using a micro-vibration friction and wear tester (SRV-V, Optimol Oil, Germany). Among them, the contact mode of the friction pair of the SRV-V micro-vibration friction and wear tester was ball-disk point contact, and the test sample was $\varnothing 10$ mm, while the hardness of the steel ball was 59–61 HRC AISI 52100; on the other hand, the lower sample was $\varnothing 24$ mm, while the hardness of the AISI 52100 steel block with a thickness of 7.9 mm was 59–61 HRC. A scanning electron microscope (SEM; FEG-250, FEI, USA) was used to observe the wear scar after the SRV friction and wear tests. A non-contact three-dimensional profilometer (NPFLEX, Bruker, Germany) was used to measure the WV of the wear scar. The chemical elements on the surface of the wear scar were determined using an X-ray photoelectron spectroscope (XPS; PHI-5702).

2.8 Corrosion test

The anti-corrosion performance of the BTA-P₄₄₄₄-Lig composite lubricant was determined by a foam corrosion test. Two identical iron blocks were placed in air and immersed in a BTA-P₄₄₄₄-Lig composite lubricant with a lignin content of 1 wt% for 2 months. Corrosion was observed, and simultaneously, the elemental contents on the surface of the iron block were determined by the energy dispersive X-ray spectrometry (EDS).

2.9 Quartz crystal microbalance (QCM) test

A QCM with dissipation (QCM-D) microbalance

(QCM-D, Biolin Scientific, Sweden) was employed for the QCM tests. Gold-coated quartz crystal sensors (QSX-301, Q-sense AB, Sweden) were applied. The adsorption behavior of ionic liquids was detected by flow injection at 25 ± 0.02 °C. Dissolve the 1% BTA-P₄₄₄₄-Lig in ethanol at 1 wt%, and pass the diluted liquid through a Teflon tube (inner diameter = 0.75 mm) with a flow rate of 100 $\mu\text{L/s}$. Frequency shifts and dissipation factors were recorded at the 3rd (15 MHz), 5th (25 MHz), 7th (35 MHz), 9th (45 MHz), and 11th (55 MHz) overtones using the Q-soft 401 software.

3 Results and discussion

3.1 Rheology experiment

The rheological properties of the BTA-P₄₄₄₄-Lig composite lubricant were investigated. By changing the shear stress, the curves of the storage modulus (G') and loss modulus (G'') with the shear stress were obtained, as shown in Figs. 3(a) and 3(b). It is generally believed that G' and G'' affect the viscoelasticity of materials, i.e., the greater the G' , the greater the elasticity will be; and the greater the G'' , the greater the viscosity will be. Figure 3(a) shows that the G' values of ionic liquids with different lignin contents are similar, and the G' values increase with increasing the shear stress. As shown in Fig. 3(b), with the increase in lignin content, the G'' value increased, which is consistent with the variation in viscosity. With increasing the shear stress, the G'' value of ionic liquids with the same concentration decreases, and shear thinning occurs. We speculate that the stabilities of the cation and anion of the ionic liquid depend on electrostatic interactions. With increasing the shear stress, the

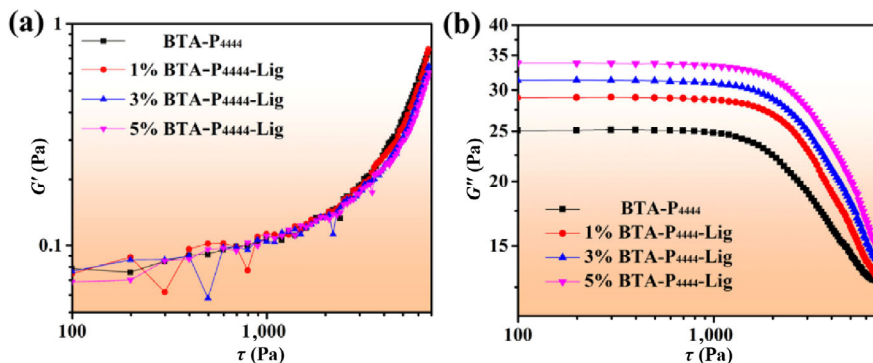


Fig. 3 Curves of storage modulus (G') and loss modulus (G'') of lubricating materials with shear stress.



electrostatic interaction is not sufficient to maintain the combination of cations and anions, leading to shear thinning. The low viscosity brought by shear thinning reduces the friction resistance and friction energy consumption in the friction process of the machine, which is conducive to improving the economic benefits.

3.2 Friction and wear test

The tribological properties of the BTA-P₄₄₄₄-Lig composite lubricant were investigated. The coefficients of friction (COFs) and WVs of BTA-P₄₄₄₄-Lig composite lubricants with different lignin contents were measured by the SRV under optimal conditions (Fig. 4). The results showed that when the lignin content was 0%, there were many instances of bites, and the COF and WV were larger. With increasing the lignin content, the COF and WV are decreased, the number of bites is reduced, the occurrence time of bite is delayed, and the degree of bite is reduced, resulting in better tribological properties. When the lignin content was increased to 5 wt%, compared with BTA-P₄₄₄₄, the COF decreased by 12%, and the WV decreased by 43%, which indicated that lignin addition effectively improved the anti-friction performance of ionic liquids and greatly enhanced the anti-wear performance of ionic liquids. It is speculated that the polar elements N and P in ionic liquids are released during friction, and the metal substrate is subjected to a friction chemical reaction, forming a boundary lubrication protective film [20]. At the same time, the phenolic hydroxyl group of lignin interacts with the metal on the friction pair surface, breaks down the molecular fragments during the friction process, and fills the

friction and wear area [21, 22]. Excellent friction and wear resistance performance were obtained by the synergistic lubrication of the ionic liquid and lignin.

The surface wear of wear spots can be observed directly from the three-dimensional pictures and SEM images of steel block wear marks obtained using a three-dimensional profilometer and a field-emission scanning electron microscope, respectively, under the lubrication condition of BTA-P₄₄₄₄-Lig compound lubricants with different lignin contents (Fig. 5). When the lignin content was 0%, the wear spots were wide and deep. Parallel furrows were observed under the SEM, along with severe metal spalling, abrasive wear, and adhesive wear [23, 24]. With increasing lignin contents, the size and quantity of metal spalling decreased. When the lignin content reached 5%, no metal spalling was observed, and the main reason was abrasive wear, which indicated that the addition of lignin limited the damage depth of the friction pair and improved the ability of the metal to resist adhesive wear. Combined with the above-mentioned experiments, lignin adsorbed on the metal surface during the friction process increased the thickness of the surface film, and broke into small molecular fragments when rubbing, filling on the surface of the abrasive spot, which hindered the direct contact between the friction pairs, resulting in good reduce-friction and anti-wear properties [25, 26].

The tribological properties of the BTA-P₄₄₄₄-Lig composite lubricant at high temperatures were investigated. Figure 6 shows the COFs and WVs of the BTA-P₄₄₄₄-Lig composite lubricants with different lignin contents at 150 °C. We found that BTA-P₄₄₄₄ and 1% BTA-P₄₄₄₄-Lig had a long running period,

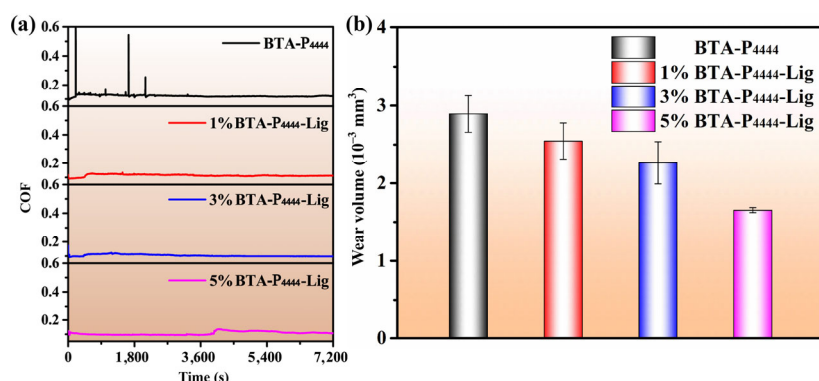


Fig. 4 COF evolution and WVs of BTA-P₄₄₄₄-Lig as a lubricant for steel/steel friction pairs (test conditions: 300 N, 50 Hz, 1 mm, 50 °C, and 120 min).

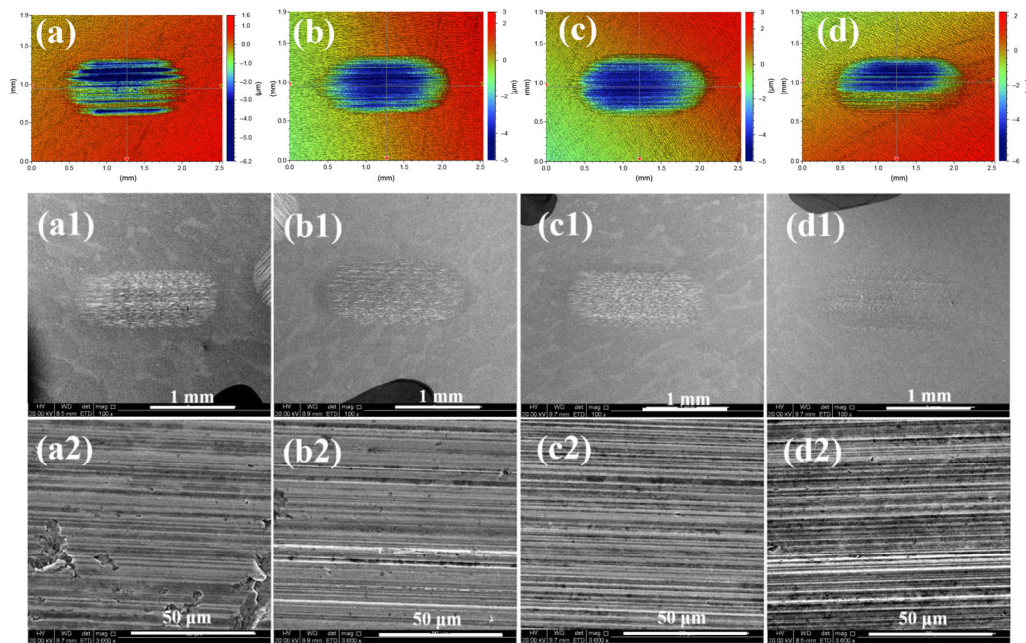


Fig. 5 Three-dimensional contours of the lubricating materials: (a) BTA-P₄₄₄₄, (b) 1% BTA-P₄₄₄₄-Lig, (c) 3% BTA-P₄₄₄₄-Lig, and (d) 5% BTA-P₄₄₄₄-Lig lubricating materials; (a1–d1) full views of the wear spots under the SEM at 100-time magnification; and (a2–d2) surface morphologies of the wear spots observed under the SEM at 3,000-time magnification.

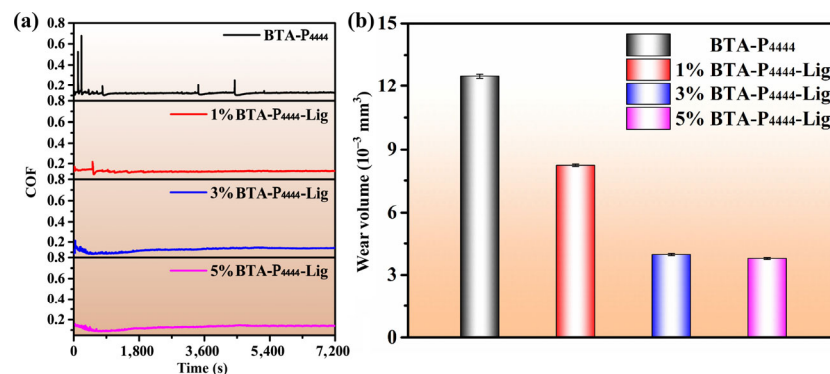


Fig. 6 COF evolution and WVs of BTA-P₄₄₄₄-Lig as a lubricant for steel/steel friction pairs (test conditions: 300 N, 50 Hz, 1 mm, 150 °C, and 120 min).

there were many instances of bites during the test, and the WV was too large. With increasing the lignin content, the phenomenon of clasp disappears, the COF curve is stable, and the WV decreases. Compared with the experimental data at 50 °C, when the lignin content was 0%, the WV increased by an order of magnitude, and the thermal stability was poor. With increasing the lignin content, the difference between the WVs at 150 and 50 °C decreases gradually. When the lignin content reached 5 wt%, the WV only increased by $2.13 \times 10^{-3} \text{ mm}^3$. It still has excellent friction and wear resistance at high temperatures, which indicates that the addition of lignin improves

the thermal stability of the ionic liquid.

Figure 7 shows the three-dimensional profiles and SEM images of BTA-P₄₄₄₄-Lig compound lubricants with different lignin contents at high temperature. When the lignin content is 0%, the wear spot is wide and deep, and there is serious metal spalling on the surface. With increasing lignin contents, the wear spot and the metal spalling phenomenon decrease gradually, though the decrease is not obvious. Compared with 50 °C, the wear spot of ionic liquid without lignin is larger, and the wear is more serious. When the lignin content was increased by 5%, the change in the wear spot size was not obvious, which

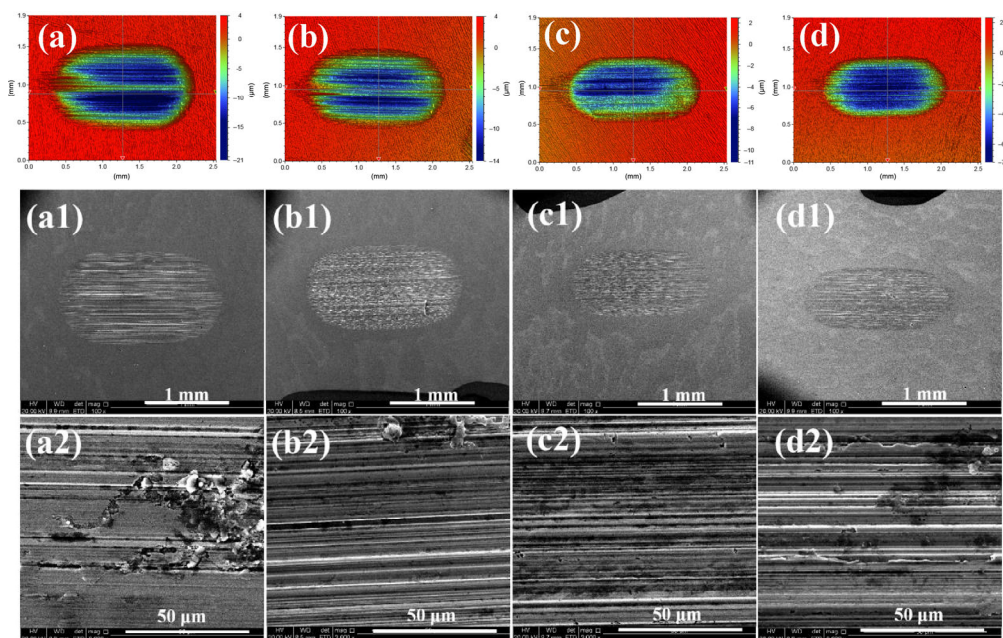


Fig. 7 Three-dimensional profiles of (a) BTA-P₄₄₄₄, (b) 1% BTA-P₄₄₄₄-Lig, (c) 3% BTA-P₄₄₄₄-Lig, and (d) 5% BTA-P₄₄₄₄-Lig lubricating materials at high temperatures; (a1–d1) overall appearances of wear spots photographed by the SEM at 100-time magnification; and (a2–d2) surface morphologies of wear spots photographed by the SEM at 3,000-time magnification.

implied good thermal stability. Combined with the experimental results in Fig. 5, we speculate that when the lignin content is 0%, the polar elements N and P in the BTA-P₄₄₄₄ are released during the friction process and react with the metal substrate to form a chemical reaction protective film, which effectively blocks the direct contact between the friction pairs, so it has certain anti-wear performance. When lignin exists in BTA-P₄₄₄₄-Lig, in addition to the role of ionic liquid in the friction process, the benzene ring of benzotriazole and the benzene ring of lignin interact with each other by π bond, and the synergistic lubrication effect improves the anti-friction and anti-wear performance of the lubricant. At the same time, lignin breaks into molecular fragments during the friction process and fills the friction and wear area, which effectively improves the wear resistance of the composites.

The performance changes after adding lignin were further evaluated by variable-temperature and frequency conversion friction experiments. Figure 8(a) shows the results of a variable-temperature experiment. The temperature increased with a gradient of 50 °C from 27 to 277 °C, and the test time was 2 min at each temperature. It also shows that the COF of the ionic liquid with 5% lignin is smaller, and the number of

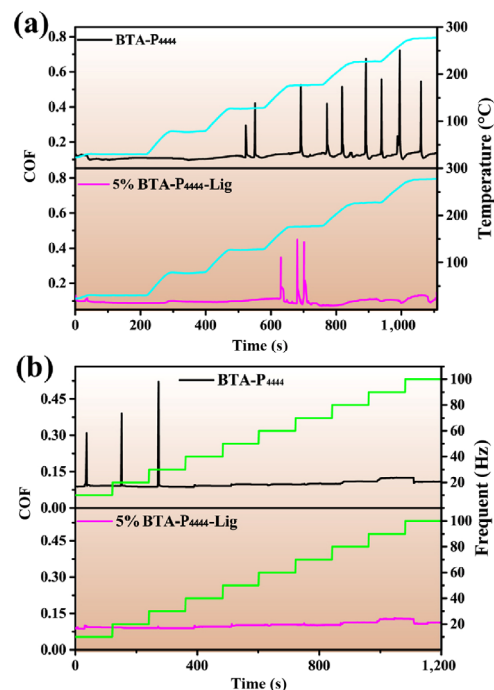


Fig. 8 (a) Effect of changing temperature on the COFs of BTA-P₄₄₄₄ and 5% BTA-P₄₄₄₄-Lig lubricating materials and (b) influence of changing frequency on the COFs of BTA-P₄₄₄₄ and 5% BTA-P₄₄₄₄-Lig lubricating materials.

bites is lower. The occurrence time of the bite is delayed, indicating that lignin addition improves the thermal stability of the ionic liquid. Figure 8(b)

shows the results of a frequency-varying experiment, with frequencies ranging from 10 to 100 Hz, increasing with a gradient of 10 Hz, and the test time of each frequency was 2 min. Figure 8(b) shows that biting appeared in the BTA-P₄₄₄₄ at the early stage of the experiment. With increasing frequency, this phenomenon disappeared, and no biting appeared in 5 wt% BTA-P₄₄₄₄-Lig, implying the good anti-frequency performance.

3.3 Lubrication mechanism analysis

3.3.1 XPS analysis

The XPS was used to analyze the chemical changes that occur during the friction process, which helps understand the chemical reactions during the friction process. Combining the O 1s peak with the Fe 2p peak, we speculate that FeO, FeO₂, Fe₂O₃, FeOH, Fe₂OH, and Fe₃O₄ may be generated during the friction process [26], and combining the O 1s peak with the N 1s and P 2p peaks, we speculate that CN, CNO, NO₃, and PO₃ may be generated (Fig. 9) [27]. These results indicate that a complex tribochemical reaction occurs during the friction process. The active elements N and P in the ionic liquid were released during the friction process and participated in the tribochemical reaction. They reacted with the metal iron on the surface of the friction pair. The metal inorganic salts formed blocked the direct contact between the friction pairs and showed good tribological properties [28].

3.3.2 TOF-SIMS analysis

The results of the XPS analysis were supplemented by those of the time-of-flight secondary ion mass spectrometry (TOF-SIMS). Figures 10(a) and 10(b) show the TOF-SIMS mass spectra of positive and negative ions, respectively, and Figs. 10(a1) and 10(b1) show the two-dimensional TOF-SIMS images of the corresponding ions.

From the mass spectra of positive and negative ions for tribofilm, different mass-charge ratios imply different ion fragments. Most hydrocarbon ion fragments ($C_xH_y^+$) can be found in the cation spectrum, indicating that lignin and cation parts can be decomposed into short chains with different chain lengths during friction, which is a response to tribochemical reactions. For the anion part, many characteristic peaks containing nitrogen, oxygen, and phosphorus were detected, e.g., CN^- , C_3N^- , CNO^- , NO_2^- , PO_2^- , and PO_3^- plasma fragments, indicating that the ionic liquid participated in the tribochemical reaction on the metal surface. The combination of typical iron ions (Fe^+ , Fe_2OH^+ , and FeO_2^+) measured on the friction surface with phosphorus (PO_2^-) and nitrogen (CN^- , C_3N^- , CNO^- , and NO_2^-) is closely related to the friction stress and the protection provided by the boundary layer, which proves that there is a tribochemical reaction between ionic liquid and steel oxide. The active elements N and P form a complex friction film on the metal substrate during

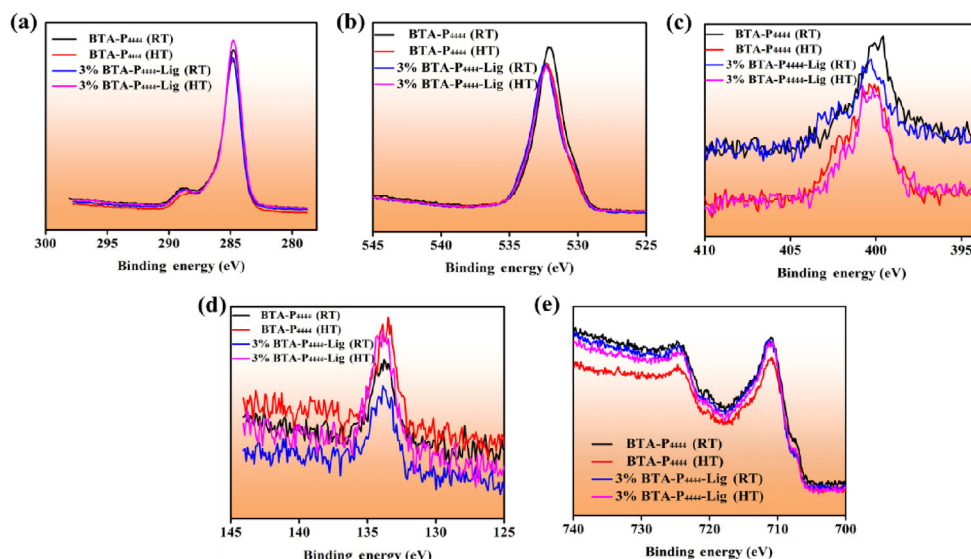


Fig. 9 XPS analysis: (a) C 1s; (b) O 1s; (c) N 1s; (d) P 2p; and (e) Fe 2p (RT and HT represent 50 and 150 °C, respectively).



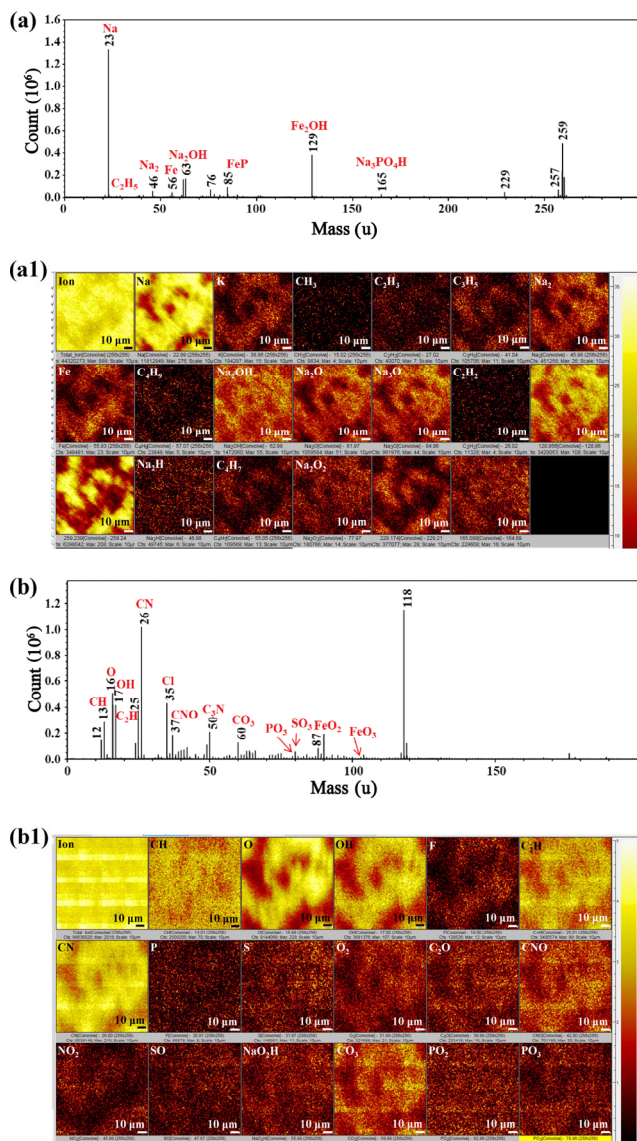


Fig. 10 (a and b) TOF-SIMS mass spectrometry and (a1 and b1) two-dimensional TOF-SIMS imaging of positive and negative ions generated by friction films on steel wear surfaces under water lubrication containing 1 wt% BTA-P₄₄₄₄-Lig at 50 °C

the friction process, thereby blocking direct contact between the friction pairs, which is consistent with the XPS analysis results [29–31].

3.4 Corrosion resistance

The optical and SEM images of the iron sheet placed in air and immersed in the BTA-P₄₄₄₄-Lig compound lubricant for 2 months (Fig. 11) shows that the change in the iron sheet immersed in the BTA-P₄₄₄₄-Lig composite lubricant was not obvious compared with the foam sheet, and a large number of N and P elements were observed on the surface of the EDS. It is speculated that the π electrons of the benzene ring of ionic liquids and the off-domain electrons on the imidazole base are complexed with the space d orbital of iron, and a stable chemical adsorption protective film is formed on the surface of the sheet metal, which hinders the further corrosion of the sheet metal and shows good corrosion resistance [32–34].

3.5 QCM test

Through the EDS analysis, we preliminarily speculate that ionic liquids form a stable chemical adsorption protective film on the metal surface and show good corrosion resistance. In order to further explore the adsorption capacity of additive molecules on metal surface, the QCM test is carried out by changes in frequency of a quartz chip (Fig. 12). The frequency value change (Δf) recorded by the experimental instrument is positively correlated with the quality (Δm) of the adsorption film on the gold-coated quartz wafer [13]. The larger the Δf , the stronger the adsorption on the gold-plated quartz wafer is, which is more conducive to the formation of a stable adsorption

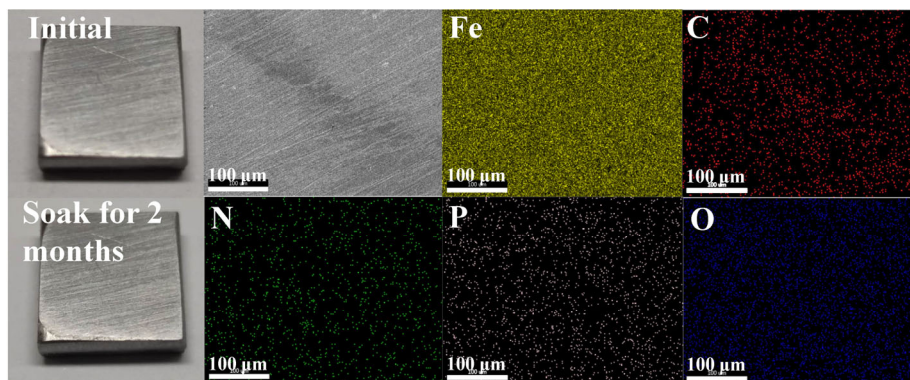


Fig. 11 Optical photos before and after the corrosion test and EDS analysis of the iron surface after two months of immersion.

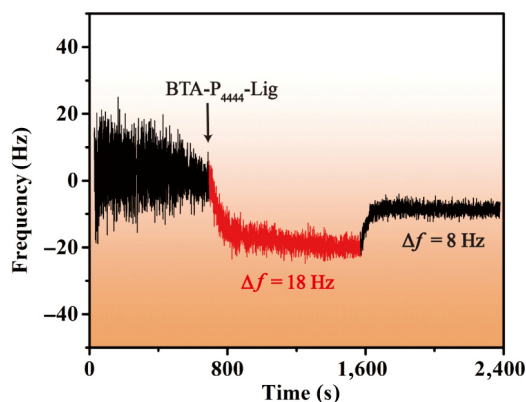


Fig. 12 Changes in frequency and corresponding dissipation of QCM chip gold (the solvent of ethanol is the baseline).

film to ensure corrosion resistance. As shown in Fig. 12, with the addition of BTA-P₄₄₄₄-Lig, the frequency value changed rapidly and reached 18 Hz. This indicates the existence of adsorption behavior between the BTA-P₄₄₄₄-Lig and the metal substrate. Meanwhile, with the addition of ethanol, the frequency value finally stayed at 8 Hz, indicating the existence of reversible physisorption and strong chemisorption throughout the adsorption process. The combined effect of physical adsorption and chemical adsorption improves the corrosion resistance of BTA-P₄₄₄₄-Lig. Combined with the friction experiment, this strong adsorption helps the BTA-P₄₄₄₄-Lig to form a stable and effective tribofilm during the friction process and improves the lubricating performance of the BTA-P₄₄₄₄-Lig.

3.6 Thermal stability and oxidation resistance test

The high-temperature tribological experiments show that the addition of lignin can effectively improve the thermal stability of ionic liquids. In response to this situation, TGA, pressure differential scanning

calorimetry (PDSC), and rotating pressure vessel oxidation test (RPVOT) were used to evaluate the oxidation resistance and thermal stability of BTA-P₄₄₄₄-Lig composite lubricants. The experimental results are presented in Fig. 13. The initial oxidation temperature refers to the temperature at the intersection of the two tangents on the heat flow vs. temperature curve (Fig. 13(a)). The higher the initial oxidation temperature, the stronger the oxidation resistance of the ionic liquid is. When the lignin was not added, the initial oxidation temperature of the ionic liquid was 219.8 °C. With the addition of lignin, the initial oxidation temperature shifted to the right. When the lignin content increased to 5%, the initial oxidation temperature reached 257.4 °C. This shows that the addition of lignin effectively improved the oxidation resistance of the composite lubricant. In Fig. 13(b), the oxidation induction period refers to the time required for the pressure to drop to the specified pressure. The longer the oxidation induction period, the better the oxidation resistance of the ionic liquid is. From the figure, we find that the oxidation induction period of the ionic liquid without lignin is shorter, only 15.1 min. With increasing lignin contents, the oxidation induction period gradually increased. When the lignin content increased to 5%, the oxidation induction period reached 75.1 min, which was four times longer than that of the ionic liquid without lignin. TGA revealed that with increasing lignin contents, the thermal stability improved. When the lignin content increased to 5%, the thermal decomposition temperature reached 353.33 °C, showing good thermal stability. These experimental results show that the addition of lignin effectively improves the thermal stability of the ionic liquid and greatly improves the oxidation resistance of the composite

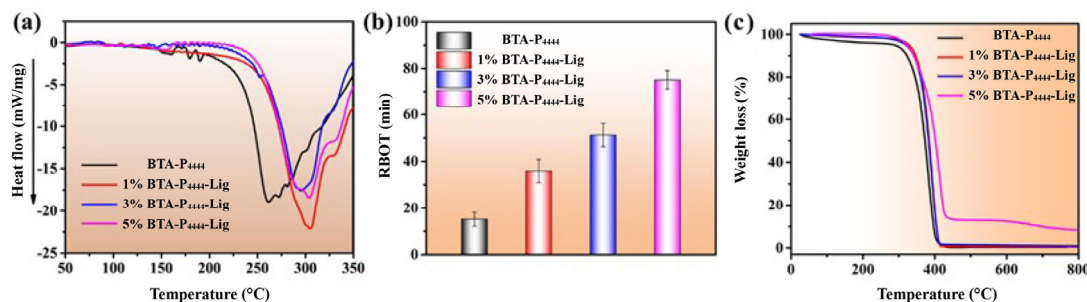


Fig. 13 Evaluation of oxidation resistance of Lig lubricating materials. Results of (a) TGA, (b) PDSC, and (c) rotating oxygen bomb method for BTA-P₄₄₄₄, 1% BTA-P₄₄₄₄-Lig, 3% BTA-P₄₄₄₄-Lig, and 5% BTA-P₄₄₄₄-Lig.



lubricant. We speculate that intramolecular hydrogen bonds are easily formed between the phenolic hydroxyl groups in lignin, which is conducive to the stability of phenolic oxygen radicals. At the same time, the phenolic hydroxyl group reacts with oxygen free radicals to form a resonance-stable semiquinone free radical to interrupt the chain reaction, thus having excellent anti-oxidant properties [35, 36].

3.7 Possible lubrication mechanism

According to the results of tribological experiment, corrosion experiment, and oxidation resistance experiment, we speculate the possible lubrication mechanism in the friction process (Fig. 14). Firstly, ionic liquids combine with metal substrates through chemical adsorption, which makes tribochemical reactions take place effectively in the process of friction. The polar elements N and P in the ionic liquid are released during the friction process, and tribochemical reaction occurs with the metal substrate to form a chemical reaction protective film, which effectively blocks the direct contact between the friction pairs. On the one hand, lignin and long-chain cations break during friction and fill in the wear area, which improves the tribological properties of the composites. On the other hand, the benzene ring of benzotriazole and the benzene ring of lignin interact with each other by π bond, and the synergistic lubrication effect improves the anti-friction and wear resistance of the lubricant. In terms of anti-corrosion, ionic liquids can effectively improve the anti-corrosion

performance of metals through firm chemical adsorption. At the same time, lignin is coordinated and adsorbed with metal substrate through phenolic hydroxyl functional group, and phenolic hydroxyl reacts with oxygen radical to form resonance stable semiquinone radical, which interrupts the chain reaction and shows excellent anti-corrosion performance.

4 Conclusions

In this study, a functional anti-corrosive ionic liquid lubricant was synthesized, and lignin was dissolved to prepare a BTA-P₄₄₄₄-Lig composite lubricating material. Consistent with the expected results, the synthesized BTA-P₄₄₄₄-Lig composite lubricating additive exhibited better anti-friction and anti-wear performance with increasing amount of lignin. When the lignin content was increased to 5%, the coefficient of friction decreased by 12%, and the wear volume decreased by 43%. It exhibits good anti-friction and anti-wear performance at high temperatures. The corrosion test showed that the ionic liquid has good anti-corrosion properties. We speculate that the π electrons of the benzene ring and the electrons delocalized on the imidazole group in the ionic liquid are coordinated with the empty d orbital of iron to form an adsorption protective film on the surface of the iron sheet. The stable adsorption protective film prevents further corrosion of the iron sheet. The experimental results of TGA, PDSC, and RPVOT show that intramolecular hydrogen bonds are easily

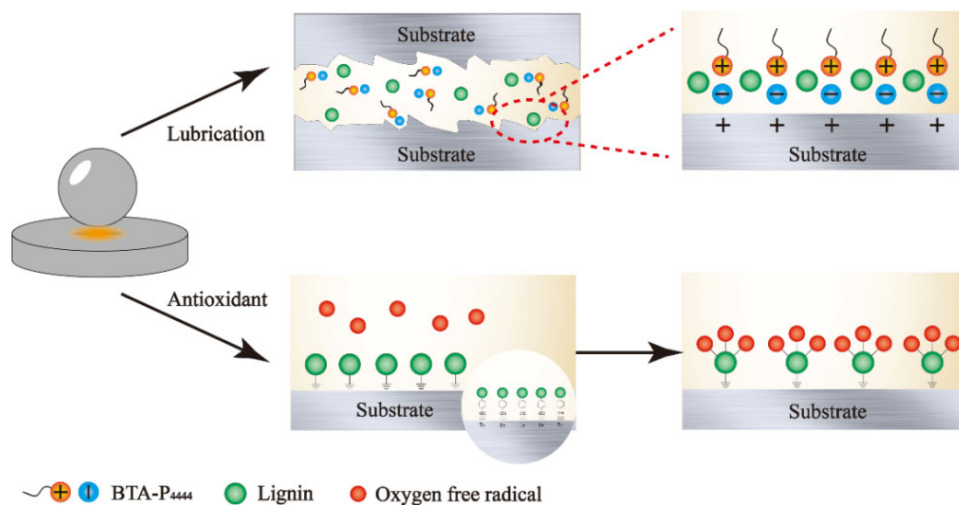


Fig. 14 Lubrication mechanism.

formed between the phenolic hydroxyl groups in lignin, which is beneficial to the stability of phenolic oxygen radicals. At the same time, the phenolic hydroxyl group also reacts with oxygen free radicals to form a resonance-stable semiquinone free radical that interrupts the chain reaction, thus affording excellent anti-oxidant properties. The results of the XPS and TOF-SIMS analyses show that the ionic liquid undergoes a tribochemical reaction during the friction process and the formed chemical reaction film blocks direct contact between the friction pairs, leading to good lubrication performance. The above experiments show that BTA-P₄₄₄₄-Lig has the potential to become a lubricating material. At the same time, it improves the utilization rate of lignin, which has considerable significance in terms of green chemistry and the development of new materials.

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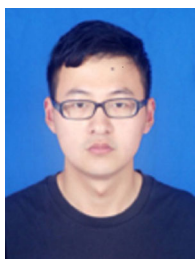
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References

- [1] Zhou F, Liang Y M, Liu W M. Ionic liquid lubricants: Designed chemistry for engineering applications. *Chem Soc Rev* **38**(9): 2590–2599 (2009)
- [2] Li D M, Cai M R, Feng D P, Zhou F, Liu W M. Excellent lubrication performance and superior corrosion resistance of vinyl functionalized ionic liquid lubricants at elevated temperature. *Tribol Int* **44**(10): 1111–1117 (2011)
- [3] Dong R, Wen P, Zhang S, Zhang C Y, Sun W J, Fan M J, Yang D S, Zhou F, Liu W M. The synthesis and tribological properties of dicarboxylic acid ionic liquids. *Tribol Int* **114**: 132–140 (2017)
- [4] Fan M J, Yang D S, Wang X L, Liu W M, Fu H Z. DOSS-based QAILs: As both neat lubricants and lubricant additives with excellent tribological properties and good detergency. *Ind Eng Chem Res* **53**(46): 17952–17960 (2014)
- [5] Gusain R, Gupta P, Saran S, Khatri O P. Halogen-free bis(imidazolium)/bis(ammonium)-di[bis(salicylato)borate] ionic liquids as energy-efficient and environmentally friendly lubricant additives. *ACS Appl Mater Interfaces* **6**(17): 15318–15328 (2014)
- [6] Yu Q L, Zhang C Y, Dong R, Shi Y J, Wang Y R, Bai Y Y, Zhang J Y, Cai M R, Zhou F. Novel N-, P-containing oil-soluble ionic liquids with excellent tribological and anti-corrosion performance. *Tribol Int* **132**: 118–129 (2019)
- [7] Yu Q L, Ma Z F, Cai M R, Zhou F, Liu W M. Tribological behavior of laser textured steel impregnated with supramolecular gel lubricant. *Proc Inst Mech Eng Part J J Eng Tribol* **231**(9): 1151–1159 (2017)
- [8] Cai M R, Liang Y M, Zhou F, Liu W M. Tribological properties of novel imidazolium ionic liquids bearing benzotriazole group as the antiwear/anticorrosion additive in poly(ethylene glycol) and polyurea grease for steel/steel contacts. *ACS Appl Mater Interfaces* **3**(12): 4580–4592 (2011)
- [9] Qu J, Luo H M, Chi M F, Ma C, Blau P J, Dai S, Viola M B. Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive. *Tribol Int* **71**: 88–97 (2014)
- [10] Yu Q L, Wang Y R, Huang G W, Ma Z F, Shi Y J, Cai M R, Zhou F, Liu W M. Task-specific oil-miscible ionic liquids lubricate steel/light metal alloy: A tribochemistry study. *Adv Mater Interfaces* **5**(19): 1800791 (2018)
- [11] Wang Y R, Yu Q L, Ma Z F, Huang G W, Cai M R, Zhou F, Liu W M. Significant enhancement of anti-friction capability of cationic surfactant by phosphonate functionality as additive in water. *Tribol Int* **112**: 86–93 (2017)
- [12] Cai M R, Yu Q L, Liu W M, Zhou F. Ionic liquid lubricants: When chemistry meets tribology. *Chem Soc Rev* **49**(21): 7753–7818 (2020)



- [13] Yang Z Q, Sun C F, Zhang C Y, Zhao S J, Cai M R, Liu Z L, Yu Q L. Amino acid ionic liquids as anticorrosive and lubricating additives for water and their environmental impact. *Tribol Int* **153**: 106663 (2021)
- [14] Qiao D, Wang H Z, Feng D P. Benzimidazolyl phosphates as anti-wear additives in poly(ethylene glycol) for steel/steel contacts. *Lubr Sci* **26**(1): 1–11 (2014)
- [15] Cao Z F, Xia Y Q, Chen C. Fabrication of novel ionic liquids-doped polyaniline as lubricant additive for anti-corrosion and tribological properties. *Tribol Int* **120**: 446–454 (2018)
- [16] Mu L W, Ma X F, Guo X J, Chen M J, Ji T, Hua J, Zhu J H, Shi Y J. Structural strategies to design bio-ionic liquid: Tuning molecular interaction with lignin for enhanced lubrication. *J Mol Liq* **280**: 49–57 (2019)
- [17] Abbott A P, Ahmed E I, Harris R C, Ryder K S. Evaluating water miscible deep eutectic solvents (DESs) and ionic liquids as potential lubricants. *Green Chem* **16**(9): 4156–4161 (2014)
- [18] Zhang S, Ma L, Dong R, Zhang C Y, Sun W J, Fan M J, Yang D S, Zhou F, Liu W M. Study on the synthesis and tribological properties of anti-corrosion benzotriazole ionic liquid. *RSC Adv* **7**(18): 11030–11040 (2017)
- [19] Li W Y, Sun N, Stoner B, Jiang X Y, Lu X M, Rogers R D. Rapid dissolution of lignocellulosic biomass in ionic liquids using temperatures above the glass transition of lignin. *Green Chem* **13**(8): 2038–2047 (2011)
- [20] Yu Q L, Wang J B, Fan F Q, Qu M H, Zhang C Y, Yang Z Q, Zhou X G, Tang Z P, Cai M R, Zhou F. The relationship between the chain length and tribological properties of N/P halogen-free ionic liquid lubricants. *Tribology* **40**(5): 673–679 (2020) (in Chinese)
- [21] Yao M H, Fan M J, Liang Y M, Zhou F, Xia Y Q. Imidazolium hexafluorophosphate ionic liquids as high temperature lubricants for steel–steel contacts. *Wear* **268**(1–2): 67–71 (2010)
- [22] Ye C F, Liu W M, Chen Y X, Yu L G. Room-temperature ionic liquids: A novel versatile lubricant. *Chem Commun* (21): 2244–2245 (2001)
- [23] Mu L W, Shi Y J, Wang H Y, Zhu J H. Lignin in ethylene glycol and poly(ethylene glycol): Fortified lubricants with internal hydrogen bonding. *ACS Sustainable Chem Eng* **4**(3): 1840–1849 (2016)
- [24] Mu L W, Wu J, Matsakas L, Chen M J, Vahidi A, Grahn M, Rova U, Christakopoulos P, Zhu J H, Shi Y J. Lignin from hardwood and softwood biomass as a lubricating additive to ethylene glycol. *Molecules* **23**(3): 537 (2018)
- [25] Jiang C, Li W M, Nian J Y, Lou W J, Wang X B. Tribological evaluation of environmentally friendly ionic liquids derived from renewable biomaterials. *Friction* **6**(2): 208–218 (2018)
- [26] Huang G W, Yu Q L, Ma Z F, Cai M R, Zhou F, Liu W M. Oil-soluble ionic liquids as antiwear and extreme pressure additives in poly- α -olefin for steel/steel contacts. *Friction* **7**(1): 18–31 (2019)
- [27] Pei X, Pu W, Zhang Y, Huang L. Surface topography and friction coefficient evolution during sliding wear in a mixed lubricated rolling–sliding contact. *Tribol Int* **137**: 303–312 (2019)
- [28] Wang J, Li Z P, Xu Y, Hu W J, Zheng G L, Zheng L, Ren T H. Synthesis and tribological behavior of bridged bicyclic polymers as lubricants. *Ind Eng Chem Res* **59**(47): 20730–20739 (2020)
- [29] Zhang C Y, Lu Z L, Li F Z, Jia L, Yang Z Q, Chen G Q, Yu Q L, Dong R, Cai M R. Corrosion and lubrication properties of a halogen-free Gemini room-temperature ionic liquid for titanium alloys. *Tribol Int* **156**: 106850 (2021)
- [30] Dong R, Bao L Y, Yu Q L, Wu Y, Ma Z F, Zhang J Y, Cai M R, Zhou F, Liu W M. Effect of electric potential and chain length on tribological performances of ionic liquids as additives for aqueous systems and molecular dynamics simulations. *ACS Appl Mater Interfaces* **12**(35): 39910–39919 (2020)
- [31] Yu Q L, Zhang C Y, Dong R, Shi Y J, Wang Y R, Bai Y Y, Zhang J Y, Cai M R, Zhou F, Liu W M. Physicochemical and tribological properties of gemini-type halogen-free dicationic ionic liquids. *Friction* **9**(2): 344–355 (2021)
- [32] González R, Ramos D, Blanco D, Fernández-González A, Viesca J L, Hadfield M, Hernández Battez A. Tribological performance of tributylmethylammonium bis(trifluoromethylsulfonyl)amide as neat lubricant and as an additive in a polar oil. *Friction* **7**(3): 282–288 (2019)
- [33] Velusamy S, Sakthivel S, Neelakantan L, Sangwai J S. Imidazolium-based ionic liquids as an anticorrosive agent for completion fluid design. *J Earth Sci* **28**(5): 949–961 (2017)
- [34] Pagano F, Gabler C, Zare P, Mahrova M, Dörr N, Bayon R, Fernandez X, Binder W H, Hernaiz M, Tojo E, et al. Dicationic ionic liquids as lubricants. *Proc Inst Mech Eng Part J J Eng Tribol* **226**(11): 952–964 (2012)
- [35] Sadeghifar H, Argyropoulos D S. Correlations of the antioxidant properties of softwood kraft lignin fractions with the thermal stability of its blends with polyethylene. *ACS Sustain Chem Eng* **3**(2): 349–356 (2015)
- [36] Zhang X, Yang M K, Yuan Q P, Cheng G. Controlled preparation of corncob lignin nanoparticles and their size-dependent antioxidant properties: Toward high value utilization of lignin. *ACS Sustainable Chem Eng* **7**(20): 17166–17174 (2019)



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