

Article

A Green Way for the Synthesis of Ester Oil by an Ionic Liquid as Both a Catalyst and Lubricant Additive

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ABSTRACT: A series of ionic liquids 1-alkyl-3-methylimidazole bis(2-ethylhexyl) phosphate, were prepared, and the catalytic performance of ionic liquids was evaluated through the esterification reaction of pentaerythritol and hexanoic acid at a stoichiometric ratio as a model reaction. The results showed that the [BMIM][DEHP] and [HMIM][DEHP] exhibited good catalytic activity. The [HMIM][DEHP] was chosen as a lubricant additive to further investigate the tribological properties after the reaction, and the results for both COF and WSD and wear volume indicate that the introduction of [HMIM][DEHP] has improved the friction reducing and anti-wear properties of pentaerythritol tetra-hexanoate.

Keywords: Ionic liquid; Catalytic; Lubricant; Pentaerythritol; Additive



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1. Introduction

Excessive friction and wear contribute substantially to energy losses and environmental contamination. With the developing global need for energy and the growing environmental concerns. A new generation of lubricants, characterized by biodegradability, high energy efficiency, and environmental compatibility, is on the horizon. As a type of biodegradable lubricant, long-chain fatty acid esters have been widely used in industry due to their characteristics such as high viscosity index, thermal stability, and biodegradability [1–4]. The traditional method of synthesizing pentaerythritol fatty acid esters is to esterify pentaerythritol with fatty acids. The esterification reaction can proceed without a catalyst, but the reaction rate is slow. The catalyst is essential for driving the esterification reaction: The sulfuric acid, solid acid catalyst, brønsted acid ionic liquid have been studied since the 1990s [5–7]. However, these catalysts always need to be separated from the products, which brings great inconvenience to industrial production for ester oils. Therefore, it is urgent to develop a new type of material that does not require separation after esterification and then acts as a lubricant additive, which is one of the effective ways to solve the problem of separating the catalyst from ester oil products.

Ionic liquids have attracted considerable interest in recent years due to their unique physicochemical properties, such as non-volatile, non-flammable and explosive, relatively high chemical and thermodynamic stability, *etc.* In addition, ionic liquids also have a wide range of characteristics such as a broad liquid temperature range, good solubility for organic and inorganic compounds, a wide electrochemical window, designable structure, and tunable properties [8–10]. Ionic liquids have shown good catalytic performance in the field of catalysis: esterification [11–13], transesterification [14,15], esterification of phosphinic acids, phosphonic acids and phosphoric acid monoesters [16,17] included. In recent years, ionic liquids have emerged as promising alternatives, serving as a catalyst favored by the majority of scientific researchers due to their performance of environmentally friendly. Multiple brønsted acidic ionic liquids are catalysts for esterification reactions, with high catalytic activity and easy separation [18–20]. Actually, the

lubricating performance of ionic liquids has also attracted much attention: ionic liquids, as a lubricant, have a wide temperature range and extremely low vapor pressure, endowing them with excellent comprehensive lubrication performance unmatched by other lubricating materials. For example, ionic liquids can solve problems such as easy solidification and volatilization of lubricants under harsh conditions [21–26].

The introduction of two or more functional groups into an ionic liquid can regulate the multifunctionalization of the ionic liquid, to construct a functional ionic liquid with a novel structure and more prominent advantages. A series of functionalized ionic liquids were prepared as green reaction media and catalysts [27–29], however, up to now, there have been no reports on the research and application of bi-functionalized ionic liquids as catalysts for the synthesis of ester oils, and can also play the role of lubricant additives in the synthesized ester oil. In this paper, the bi-functionalized ionic liquids were prepared, and the chain length of the substituent of the ionic liquid can be reasonably controlled to realize the bi-functionalized ionic liquid coordination and optimization of catalytic performance and lubrication performance. Meanwhile, the problem of separating the catalyst from ester oil products was solved.

2. Materials and Methods

All chemicals were obtained commercially without further purification. The purity and manufacturer are listed in the Supplementary Materials Table S1.

2.1. Ionic Liquid Preparation

120 mL dichloromethane and 5 mL deionized water were added to a 250 mL round bottom flask. A certain amount of 1-alkyl-3-methylimidazolium bromide and bis(2-ethylhexyl) hydrogen phosphate was introduced and stirred at room temperature. A 30% wt sodium hydroxide solution was dropped into the bottom flask and stirred for 2 h at 25 °C. The products were washed with deionized water 6 times and then evaporated to remove water and dichloromethane. After that, a bi-functionalized ionic liquid 1-alkyl-3-methylimidazolium bis(2-ethylhexyl)hydrogen phosphate was obtained by vacuum drying at 70 °C. 1-butyl-3-methylimidazolium bis(2-ethylhexyl) phosphate was labeled as [BMIM][DEHP]; 1-hexyl-3-methylimidazolium bis(2-ethylhexyl) phosphate was labeled as [HMIM][DEHP]; 1-octyl-3-methylimidazolium bis(2-ethylhexyl) phosphate was labeled as [OMIM][DEHP]; 1-decyl-3-methylimidazolium bis(2-ethylhexyl) phosphate was labeled as [DMIM][DEHP].

2.2. Catalytic Performance Test of Ionic Liquids

Using the esterification reaction of pentaerythritol and hexanoic acid in a stoichiometric ratio as a model reaction, magnetic stirring was performed in a 100 mL three-necked round bottom flask. 0.013 mol of pentaerythritol, 0.052 mol of hexanoic acid, and 0.16 mmol of catalyst were added, along with 2 mL of toluene as a water scavenger. The reaction was carried out at 165 °C for a specified time. The product was purified by rotary evaporation. The acid value of the product was determined according to ISO 6618: 1997(E) [30], and the degree of esterification of the product was analyzed based on the acid value. The following formula can calculate the esterification rate:

$$\text{Er/\%} = [(1 - \text{AN}_a/\text{AN}_b) \times R/4] \times 100\%$$

In the formula, Er represents the esterification reaction of pentaerythritol and hexanoic acid, AN_a is the acid value of the product after the reaction, AN_b is the acid value of the substrate before the reaction. R denotes the molar ratio of hexanoic acid to pentaerythritol.

2.3. Tribological Performance Test of [HMIM][DEHP]

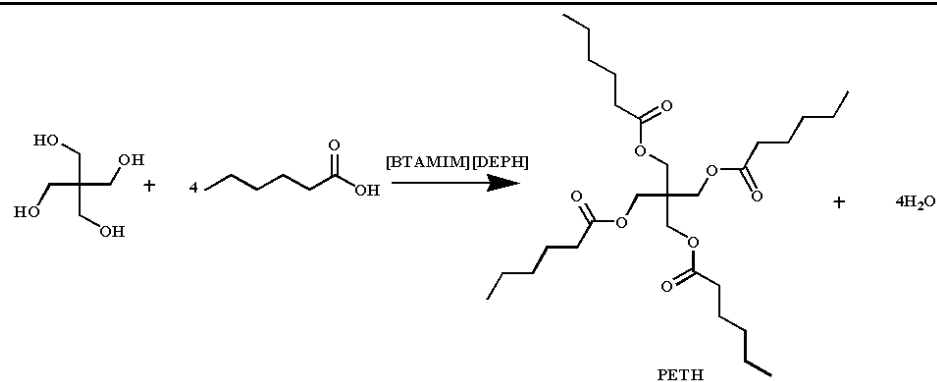
The tribological properties were tested by an optimmol SRV tester under the condition of load 50 N, frequency 50 Hz, temperature 50 °C, stroke 1 mm, time 30 min. The upper ball was AISI52100 steel, with a diameter of 10 mm and a rock-well hardness of 58–62 HRC. The lower disc was AISI52100 steel with a rock-well hardness of 60–64 HRC, and the diameter of the disc is 24 mm. The COF was recorded automatically.

3. Results and Discussion

3.1. Catalytic Properties

The esterification reaction of pentaerythritol with hexanoic acid was selected as the model reaction for the study of ionic liquid catalytic performance. The influence of the carbon chain length of 1-alkyl-3-methylimidazolium bis(2-ethylhexyl) phosphates and the reaction time was investigated, and the results are shown in Table 1. Comparing the esterification of the pentaerythritol with hexanoic acid by 1-alkyl-3-methylimidazolium bis(2-ethylhexyl) phosphates with different length of carbon chain in imidazoline cation, the 1-alkyl-3-methylimidazolium bis(2-ethylhexyl) phosphate with 4 carbons in imidazoline cation exhibited the best catalytic activity. Meanwhile, the ionic liquid with 6 carbons in the imidazoline cation also showed a good catalytic activity. Since the acidity of 1-alkyl-3-methylimidazolium bis(2-ethylhexyl) phosphate decreases with the carbon chain length in imidazoline cation, we select [HMIM][DEHP] to further examine the effect of reaction time on the activity of pentaerythritol esterification with hexanoic acid catalyst. It can be seen that the esterification was up to 99% when the reaction time was 7 h. Therefore, all 1-alkyl-3-methylimidazolium bis(2-ethylhexyl) phosphates had catalytic properties, and the [HMIM][DEHP] was the optimum one.

Table 1. Catalytic performance of 1-alkyl-3-methylimidazolium bis(2-ethylhexyl) phosphates for the esterification ^a.



Entry	Catalyst	Time/h	AN/(mg KOH/g)	Er/%
1	none	1	306	29
2	[BMIM][DEHP]	1	131	70
3	[HMIM][DEHP]	1	139	68
4	[OMIM][DEHP]	1	165	62
5	[DMIM][DEHP]	1	187	56
6	[HMIM][DEHP]	3	49	89
7	[HMIM][DEHP]	5	32	93
8 ^b	[HMIM][DEHP]	7	2	99

^a Reaction conditions: 0.13 mmol catalyst, 0.013 mol pentaerythritol, 0.052 mol hexanoic acid, 2 mL toluene, reaction temperature: 165 °C; ¹H NMR and ¹³C NMR characterization of [HMIM][DEHP] were prepared in Figure S1 and Figure S2. ^b Using triphenylmethane as an internal standard, the yield of PETH was quantitatively determined by ¹H NMR. The ¹H NMR spectrum is provided in Figure S3 (*m*_{triphenylmethane}: 5.08 mg, *m*_{weighing}: 11.01 mg).

3.2. Tribological Properties

Figure 1 shows the variation of the friction coefficients of pentaerythritol tetra-hexanoate and the pentaerythritol tetra-hexanoate plus [HMIM][DEHP]. The friction coefficient of the pentaerythritol tetra-hexanoate with [HMIM][DEHP] as catalyst and additive decreased, which shows that pentaerythritol tetra-hexanoate with [HMIM][DEHP] as catalyst and additive had better friction-reducing properties than the pentaerythritol tetra-hexanoate. The result confirms that the [HMIM][DEHP] could improve the tribological properties of pentaerythritol tetra-hexanoate.

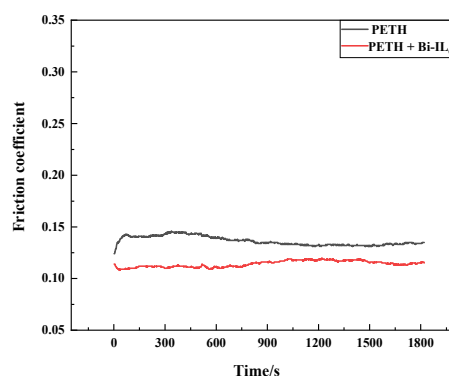


Figure 1. Variation of friction coefficient with time for PETH and PETH + [HMIM][DEHP].

The wear scar diameter of the upper running ball was tested by an optical microscope (OLYMPUS BX41, Olympus Corporation, Tokyo, Japan), and the images are shown in Figure 2, and the Table 2 lists the specific data. The wear scar diameter of the upper running ball lubricated with pentaerythritol tetra-hexanoate is higher than that lubricated with pentaerythritol tetra-hexanoate with [HMIM][DEHP] as catalyst and lubricant additive, and the result indicates that the introduction of [HMIM][DEHP] could improve the anti-wear performance of pentaerythritol tetra-hexanoate. This is consistent with the result of SRV friction test.

Table 2. The specific value of wear scar diameter of the upper running ball lubricated by PETH and PETH+[HMIM][DEHP] ^a.

Lubricant	PETH	PETH + [HMIM][DEHP]
WSD (wear scar diameter)/mm	0.59	0.47

^a SRV load: 50 N, frequency: 50 Hz, temperature: 50 °C, stroke: 1 mm.

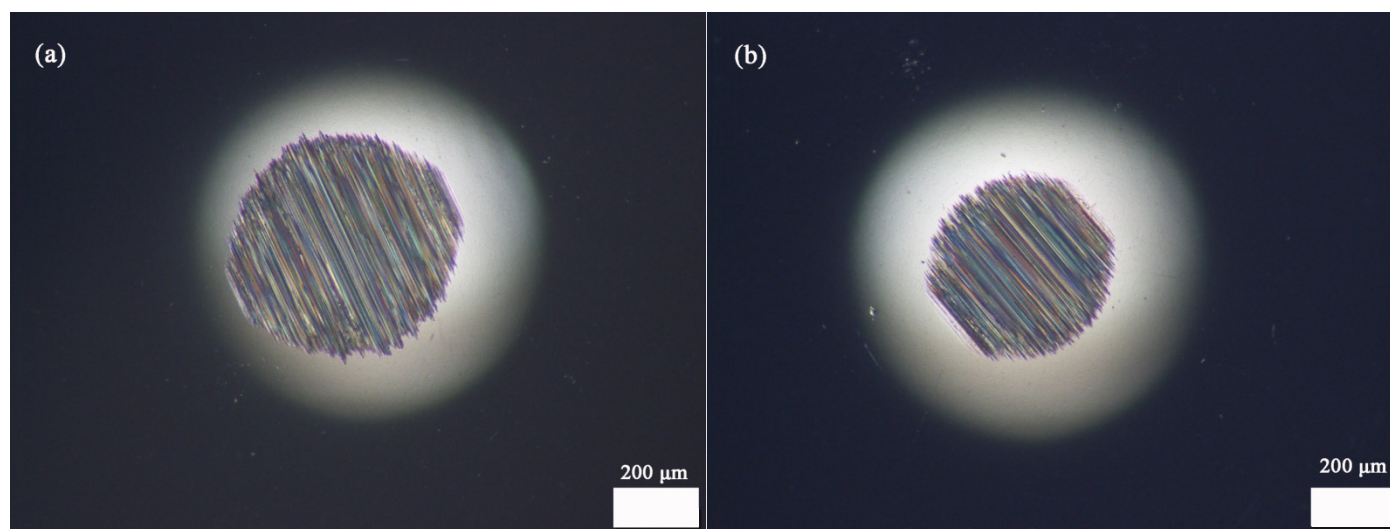


Figure 2. Lubricated ball wear scar diameter (a) PETH, (b) PETH + [HMIM][DEHP].

3.3. Characterization of Materials

3.3.1. The Stability of [HMIM][DEHP]

The TG/DTG analysis of [HMIM][DEHP] was conducted, with the results shown in Figure 3. The decomposition of [HMIM][DEHP] commenced at approximately 261.1 °C and was completed at 429.9 °C. Simultaneously, the esterification reaction was carried out at 165 °C, which is significantly lower than the initial decomposition temperature of [HMIM][DEHP]. Thus, [HMIM][DEHP] exhibited excellent stability during the reaction process.

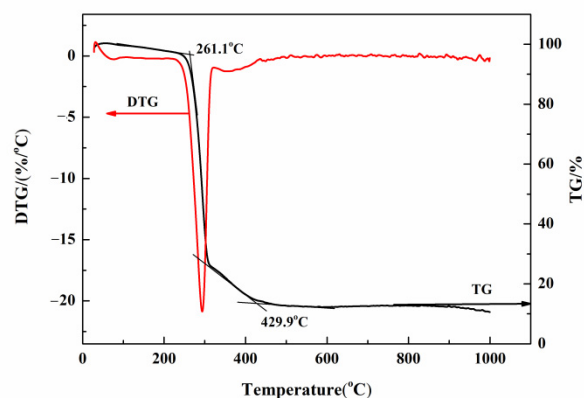


Figure 3. The TG/DTG characterizations of [HMIM][DEHP].

The XPS spectra of N1s and P2p for [HMIM][DEHP] and [HMIM][DEHP] + PETH (the product without catalyst separation) are shown in Figure 4. It can be observed that the binding energies of N1s and P2p for [HMIM][DEHP] are consistent with those for [HMIM][DEHP] + PETH. The results indicate that [HMIM][DEHP] remains stable during the esterification process, as confirmed by TG/DTG analysis.

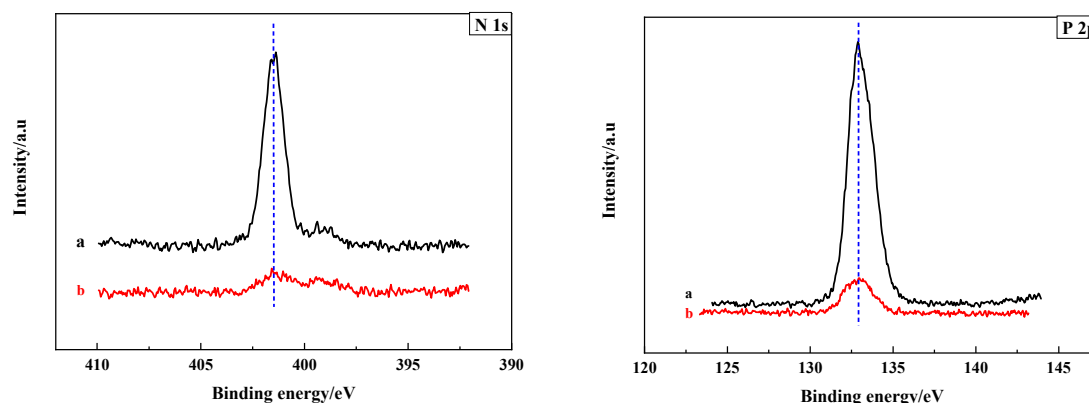


Figure 4. The XPS spectra of N1s and P2p in (a) [HMIM][DEHP], (b) PETH + [HMIM][DEHP].

The Fourier Transform Infrared Spectroscopy (FT-IR) spectra are shown in Figure 5. As can be known from Figure 5, the peak at 1150 cm^{-1} belongs to the P-O-C stretching vibration, and the peak at 1360 cm^{-1} belongs to the P=O stretching vibration [31]. The positions of the two adsorption peaks of [HMIM][DEHP] have not changed after the reaction, illustrating that the structure of [HMIM][DEHP] is stable. This result verifies the conclusions of TG and XPS.

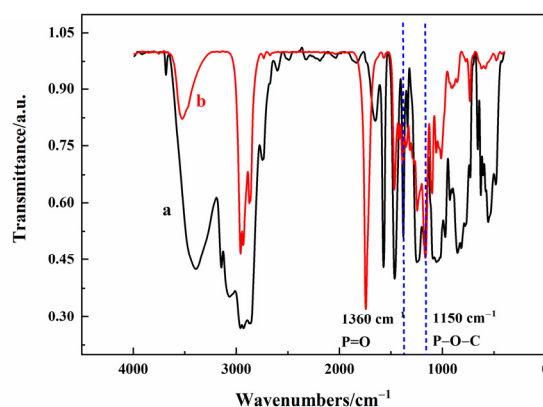


Figure 5. The FT-IR spectra of (a) [HMIM][DEHP] and (b) PETH + [HMIM][DEHP].

3.3.2. The Worn Surface Analysis

The worn surface morphology of the lower steel disc lubricated with PETH and PETH + [HMIM][DEHP] was characterized using scanning electron microscopy (SEM, model JSM-6701F, Japan Electron Optics Laboratory, Tokyo, Japan). The results are presented in Figure 6. It was observed that the wear scar on the disc lubricated with PETH alone was significantly wider and deeper than that on the disc lubricated with PETH + [HMIM][DEHP]. In contrast, the wear scar on the disc lubricated with the PETH + [HMIM][DEHP] combination was relatively narrow and exhibited a smoother surface morphology. These findings are consistent with the optical microscopy observations of the wear on the upper running ball, further supporting the improved lubricating performance of PETH in the presence [HMIM][DEHP].

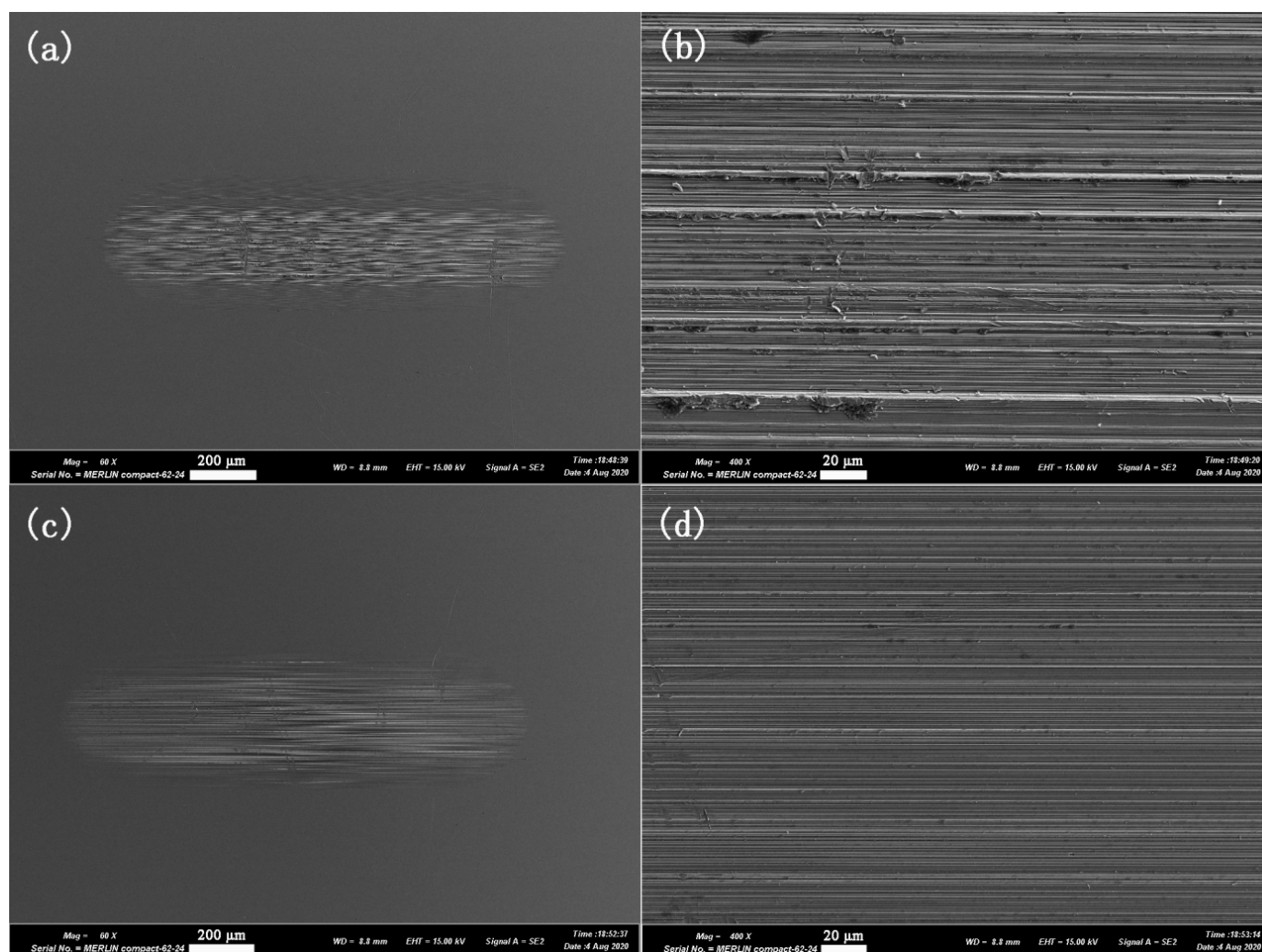


Figure 6. The SEM images of the worn surfaces lubricated with (a,b) PETH, (c,d) PETH + [HMIM][DEHP].

Wear volume and Surface profiles of wear surfaces after the friction test were characterized by a KLA-TENCOR MicroXAM-800 white light interferometry three-dimensional profiler, and the images were presented in Figures 7 and 8. As presented in Figure 7, compared with the base oil PETH, introducing [HMIM][DEHP] reduces the wear volume of the lubricants, which means an improvement in the anti-wear performance of the lubricants. The reduction in wear volume can reach up to 46.8% when the ionic liquid [HMIM][DEHP] content is only 1% (molar ratio). As shown in Figure 8, the wear tracks for PETH + [HMIM][DEHP] are notably narrower and shallower than those for the base oil PETH, which is consistent with the wear volume data and further supports the friction-reducing properties indicated by the friction coefficient.

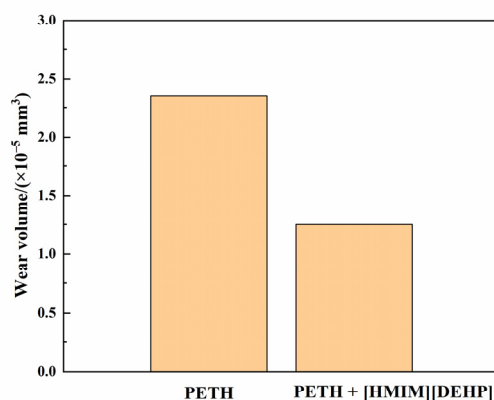


Figure 7. The wear volume of wear surfaces after the friction test.

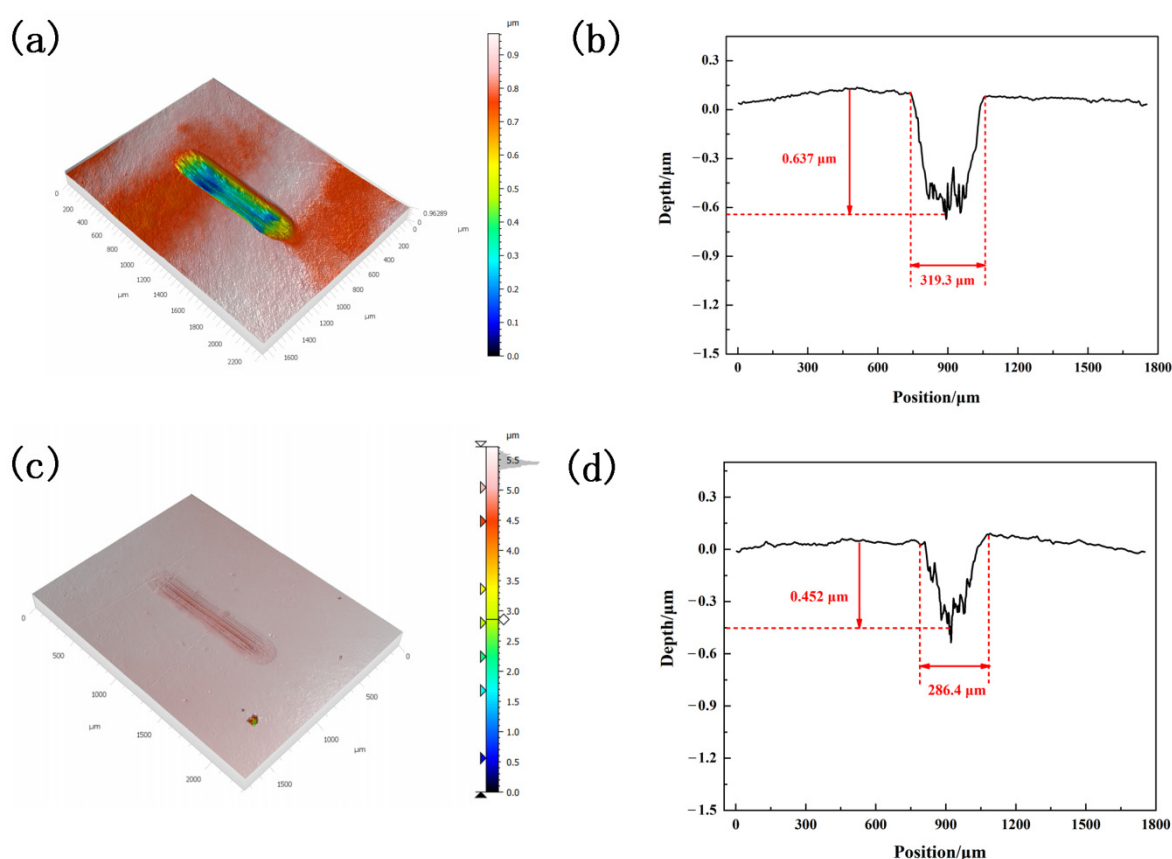


Figure 8. Surface profiles of wear surfaces after friction test (a,b) Base oil PETH, (c,d) PETH + [HMIM][DEHP].

To further investigate the lubrication mechanism of [HMIM][DEHP], XPS analysis was performed to examine the chemical states of Fe2p, N1s, P2p, and O1s on the worn surface lubricated with PETH + [HMIM][DEHP]. The corresponding spectra are presented in Figure 9. Significant changes were observed in the N1s, P2p, and O1s spectra from the worn surface compared to those of pure [HMIM][DEHP] and pure PETH, indicating that complex tribochemical reactions occurred during the friction process. The Fe2p spectra exhibited peaks at approximately 707.1 eV, 710.3 eV, 719.2 eV, and 724.3 eV, which can be attributed to FeP, Fe₂P, FeO, Fe₃O₄, and Fe₂O₃ [32–34]. The P2p signal at 133.70 eV is assigned to FePO₄, while the O1s peaks around 531.9 eV and 530.1 eV correspond to FeO, Fe₂O₃, and Fe₃O₄ [32,35,36]. Additionally, the N1s peak at 402.6 eV may be associated with oxynitride or nitrogen-nitrogen double bonds. The combined effects of high pressure, heat, catalytic activity, and mechanical energy during friction induced these tribochemical reactions, forming compounds such as FeP, Fe₂P, FeO, Fe₃O₄, Fe₂O₃, and FePO₄. These

products suggest the development of a boundary lubrication film in the contact zone during the SRV test. As a result, the friction-reducing and anti-wear properties were significantly improved.

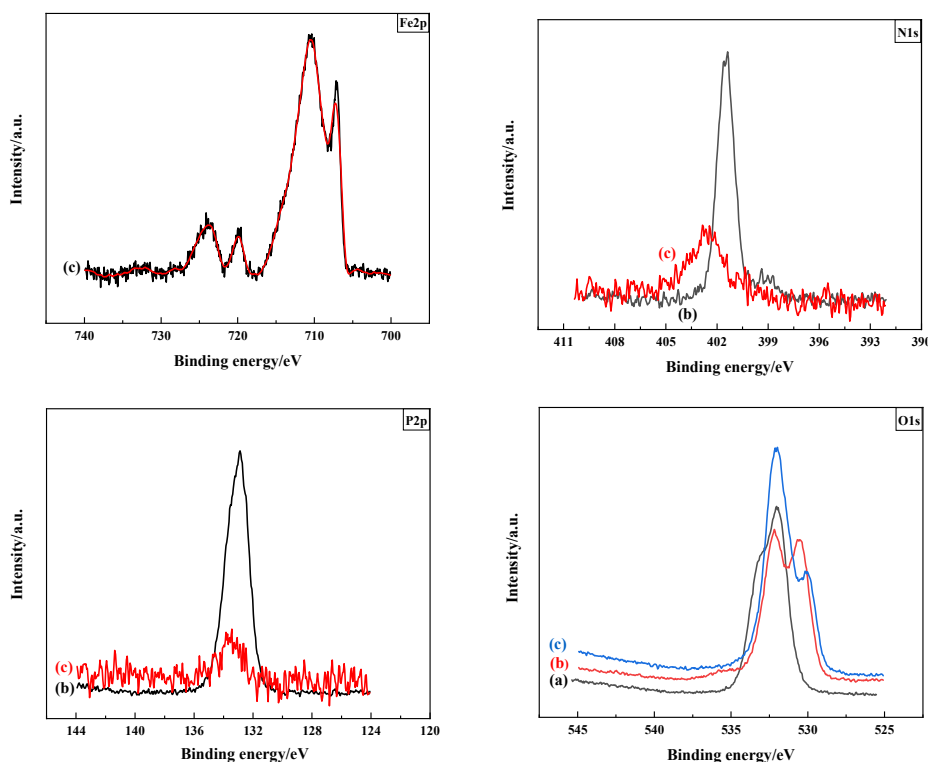


Figure 9. The XPS spectra of (a) pure PETH, (b) pure [HMIM][DEHP] and (c) worn surface lubricated with PETH + [HMIM][DEHP].

4. Conclusions

A series of bi-functional ionic liquids 1-alkyl-3-methylimidazolium bis(2-ethylhexyl) phosphate were prepared: 1-butyl-3-methylimidazole bis(2-ethylhexyl) phosphate, 1-hexyl-3-methylimidazole bis(2-ethylhexyl) phosphate, 1-octyl-3-methylimidazole bis(2-ethylhexyl) phosphate, 1-decyl-3-methylimidazole bis(2-ethylhexyl) phosphate, and the 1-hexyl-3-methylimidazole bis(2-ethylhexyl) phosphate ([HMIM][DEHP]) was chosen to investigate the catalytic and tribological properties. The conclusions were as follows:

The catalytic properties of 1-hexyl-3-methylimidazole bis(2-ethylhexyl) phosphate were examined by the esterification of pentaerythritol with hexanoic acid at a stoichiometric ratio. The conversion of hexanoic acid is up to 99% under mild conditions, and the ionic liquid catalyst does not need to be separated after the reaction, which can solve the scientific and technical problems of the widespread negative impact of residual catalyst on synthetic ester oil. The preparation procedure of the synthetic ester is shortened, which is conducive to industrial production and promotes its wide application.

The coefficient of friction and the wear scar of the up running ball lubricated by pentaerythritol tetra-hexanoate an pentaerythritol tetra-hexanoate plus [HMIM][DEHP] indicated that the [HMIM][DEHP] had good friction-reducing and anti-wear properties. The ionic liquid catalyst does not need to be separated after the reaction and plays the role of a lubricant additive in the ester oil. It not only helps to improve the performance of ester lubricating oil significantly, but also gives full play to the synergistic lubrication effect of synthetic ester lubricating oil and ionic liquid.

Supplementary Materials

The following supporting information can be found at: <https://www.sciepublish.com/article/pii/663>. Figure S1: The ^1H NMR spectra of [HMIM][DEHP]; Figure S2: The ^{13}C NMR spectra of [HMIM][DEHP]; Figure S3: The ^1H NMR spectra of PETH + [HMIM][DEHP]. Table S1: The vendors and quality or grade of chemicals.

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Author Contributions

Experimental designing, data collection and analysis, writing manuscript, Y.W.; supervision, H.S. and C.J.; formal analysis, Q.Z. (Qin Zhao); investigation, Q.Z. (Qilong Zhao); editing, W.L.; conceptualization, Q.J. All authors have read and agreed to the published version of the manuscript.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Data will be made available on request.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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