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A green method for the synthesis of lubricating ester oil using a bi-functional ionic liquid†

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A bi-functional ionic liquid 1-(benzotriazole-1-methylene)-3-methylimidazole bis(2-ethylhexyl) phosphate ([BTAMIM][DEHP]) was prepared. It exhibited high activity and selectivity for the esterification of pentaerythritol with caproic acid to pentaerythritol tetra-hexanoate (PETH). Meanwhile, the friction reduction and anti-wear performance of pentaerythritol tetra-hexanoate were improved significantly by [BTAMIM][DEHP].

Synthetic ester oil is a lubricant that has emerged with the development of aero-engine technology and the demand for high-performance lubricating materials. It has been playing an indispensable role as a key component of aviation lubricating oil in the aviation field owing to its excellent high and low-temperature properties, tribological properties and other good comprehensive properties.^{1–3} One of the advantages of synthetic ester as a lubricating material is the adjustability of its molecular structure, and its various properties, including thermal stability, oxidation stability, hydrolysis stability, viscosity grade and viscosimetric temperature performance, lubrication, solubility, and biodegradability, show great differences with changes in its molecular composition and structure. At the same time, because of its renewable raw material source and environmental friendliness, it has significant potential applications in automobile, metallurgy, cement and other industries. A lot of research work has been carried out worldwide on the structure–activity relationship, preparation process, properties and applications of synthetic ester, but the depth and systematization of the research still need to be further deepened and enhanced.^{4–7} Therefore, the development of high-performance synthetic ester lubricating base oil is the key factor for solving the abovementioned problems.

Generally, the synthetic ester oil is synthesized through esterification using an acid catalyst.^{8–13} However, the residue of the catalyst always has an adverse effect on many properties of the synthetic ester: The corrosion resistance of the synthetic ester is greatly reduced by the residual liquid acid, and the friction reduction and anti-wear properties of the synthetic ester are adversely affected in the presence of solid catalyst particles. Therefore, the development of a new type of catalyst that not only acts as a catalyst for synthesizing the ester oil but also serves as a lubricant additive after the esterification without separation is an effective way to solve the problem arising from the harmful residue of the reaction catalyst.

Ionic liquids exhibit unique physical and chemical properties compared to traditional solids and liquids due to their special structure and composition, exhibiting characteristics such as vapor pressure approximately equal to zero, non-volatility, non-flammability, non-explosiveness, and high chemical and thermodynamic stability. In addition, ionic liquids have a wide liquid temperature range, good solubility for organic and inorganic compounds, wide electrochemical window, designable structure and adjustable performance and many other characteristics.^{14–19} Ionic liquids have shown not only good catalytic performance in the field of organic synthesis and catalysis^{20–22} but also excellent tribological properties as a lubricant.^{23–26} However, to date, there is no report on the application of ionic liquids, which can be used as both a catalyst and a lubricant additive in the process of synthesis of ester lubricants. Herein, we document the first demonstration of an efficient bi-functional ionic liquid that can be used as a catalyst for the ester oil synthesis and then as a lubricant additive for the ester oil after the reaction without separation from the reaction system.

In the current study, an efficient and novel bi-functional ionic liquid 1-(benzotriazole-1-methylene)-3-methylimidazole bis(2-ethylhexyl) phosphate ([BTAMIM][DEHP]) was prepared (ESI†) and the ¹H NMR and ¹³C NMR of [BTAMIM][DEHP] are provided in the ESI† (Fig S2 and S3). Pentaerythritol esters of the straight-chain saturated aliphatic acids have good lubricity and thermal stability.²⁷ By applying the esterification of pentaerythritol with caproic acid as a model reaction, the catalytic

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Table 1 The catalytic activity of [BTAMIM][DEHP]^a

Entry	Catalyst	AN ^b /(mg KOH per g)	Er ^c /%
1	None	80.61	78
2	[BTAMIM][DEHP]	9.17	98

^a Reaction conditions (the reaction device was shown in Fig. S1, ESI): 0.00013 mol (0.0681 g) [BTAMIM][DEHP], 0.013 mol (1.770 g) pentaerythritol, 0.052 mol (6.040 g) caproic acid, 2 mL toluene, temperature: 160 °C, Time: 7 h. ^b AN: acid number (quantity of base, expressed in milligrams of potassium hydroxide (KOH) per gram of sample that is required to titrate the acid constituents present in 1 g of sample when titrated under prescribed conditions). ^c Er: Esterification.

activity of [BTAMIM][DEHP] was tested, and the results are shown in Table 1. By comparing the acid number of products catalyzed with and without the catalyst, the acid number of the reaction product catalyzed by [BTAMIM][DEHP] is much lower than that of the reaction product catalyzed without the catalyst, and as such the esterification of pentaerythritol is much higher (98%) than that in the reaction proceeded without the catalyst. Meanwhile, the yield of pentaerythritol tetra-hexanoate was up to 91% under mild reaction conditions, and the ¹H NMR was prepared as per the procedure in the ESI† (Fig. S4). The results demonstrated that the bi-functional ionic liquid [BTAMIM][DEHP] has good catalytic properties for the ester oil synthesis. The thermogravimetric (TG) of [BTAMIM][DEHP] was tested, and the result is shown in Fig. 1. The decomposition of [BTAMIM][DEHP] started around 229.1 °C and was completed at 290.5 °C. Meanwhile, the esterification was tested at 160 °C, which was much lower than the start of the decomposition temperature of [BTAMIM][DEHP], as such the bi-functional

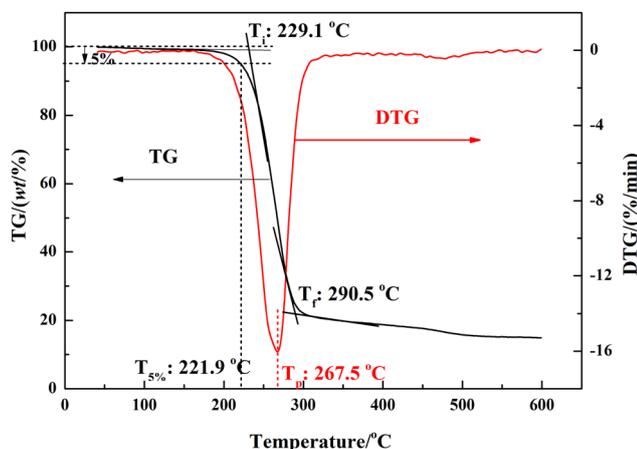


Fig. 1 The thermogravimetric characterization of [BTAMIM][DEHP].

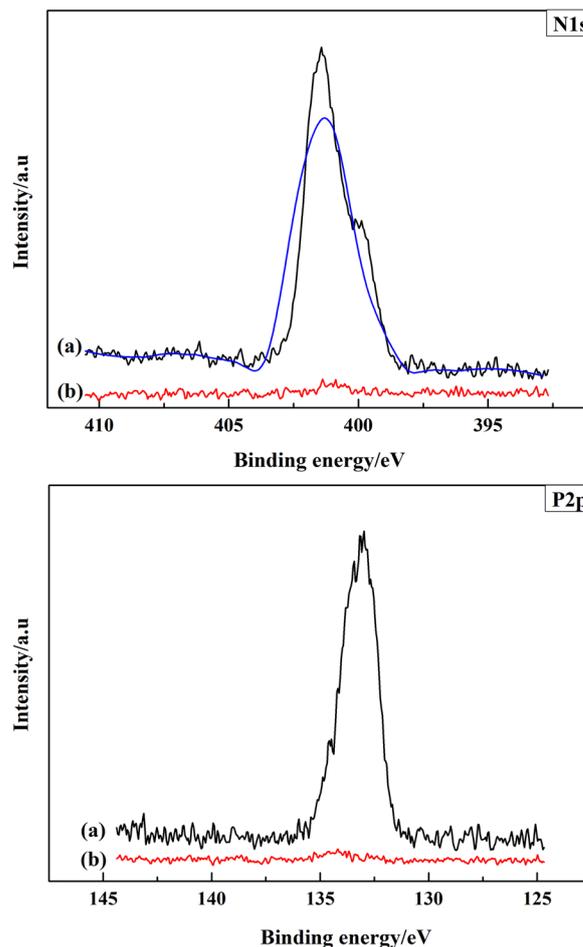


Fig. 2 XPS spectra of N 1s in (a) [BTAMIM][DEHP] and (b) PETH + [BTAMIM][DEHP].

ionic liquid [BTAMIM][DEHP] could exhibit good stability during the reaction. X-ray photoelectron spectroscopy (XPS) analysis was measured using a K-alpha-surface analysis instrument with Al K α radiation (1486.8 eV) to further investigate the thermal stability of [BTAMIM][DEHP]. The spectra of N 1s and P 2p of [BTAMIM][DEHP] and PETH + [BTAMIM][DEHP] (the product after the esterification without catalyst separation) are shown in Fig. 2. It could be found that the binding energies of N 1s and P 2p of [BTAMIM][DEHP] are consistent with those of PETH + [BTAMIM][DEHP]. It illustrates that the [BTAMIM][DEHP] is stable during the esterification, and the result is verified by TG. According to the Fourier transform infrared spectroscopy (FT-IR) spectra (Fig. 3) we can see that the peak at 1150 cm⁻¹ is attributed to the P–O–C stretching vibration, and the peak at 1360 cm⁻¹ is assigned to P=O stretching vibration.²⁸ The position of the two adsorption peaks of [BTAMIM][DEHP] did not change after the reaction, which reveals that the structure of [BTAMIM][DEHP] is stable. This result verified the conclusion of TG and XPS.

The results of kinematic viscosity, viscosity index and copper strip test of PETH and PETH + [BTAMIM][DEHP] are shown in Table 2. It can be seen that the viscosity at 40 °C and 100 °C of



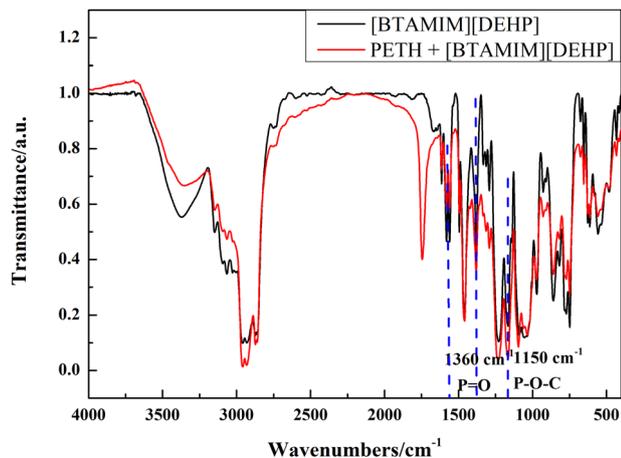


Fig. 3 FT-IR spectra of [BTAMIM][DEHP] and PETH + [BTAMIM][DEHP].

PETH + [BTAMIM][DEHP] only slightly increases. There is not any color change of PETH and PETH + [BTAMIM][DEHP] compared with the fresh copper during the copper strip tests. This indicates that the bifunctional ionic liquid [BTAMIM][DEHP] qualifies as an additive in PETH.

Subsequently, the tribological properties of the PETH plus [BTAMIM][DEHP] were investigated. It is well known that a good lubricant usually has a low friction coefficient and small wear scar diameter. A lubricant with a low friction coefficient means that it can reduce the friction force during the mechanical operation, at the same time, a small wear scar diameter indicates that the lubricant can effectively reduce wear. The mean friction coefficient with time at a constant load of 50 N, temperature of 100 °C and frequency of 25 Hz for PETH and PETH + [BTAMIM][DEHP] is shown in Fig. 4 and the wear scar diameter of the upper running ball lubricated by PETH and PETH + [BTAMIM][DEHP] measured using an optical microscope (OLYMPUS DSX1000) is shown in Fig. 5, and the detail data are shown in Table 3. It can be seen that PETH + [BTAMIM][DEHP] shows a stable and much lower friction coefficient compared with the base oil PETH and the wear scar diameter of the upper running ball lubricated by PETH is 1.5 times more than that of lubricated by PETH + [BTAMIM][DEHP]. The friction coefficient of the base oil is reduced and meanwhile, the wear scar diameter is decreased after the addition of the bi-functional ionic liquid [BTAMIM][DEHP]. These results demonstrated that the introduction of the

Table 2 Physical and chemical properties of PETH and PETH + [BTAMIM][DEHP]

Lubricant		PETH	PETH + [BTAMIM][DEHP]
Kinematic	40 °C	18.13	19.12
Viscosity/(mm ² s ⁻¹)	100 °C	4.150	4.270
Viscosity index ^a		132	130
Copper strip test/corrosion grade ^b		1a	1a

^a The viscosity index was determined by ASTM D 2270-10. ^b The copper strip test was performed according to the ASTM D procedure 130-10 (temperature: 100 °C, time: 3 h).

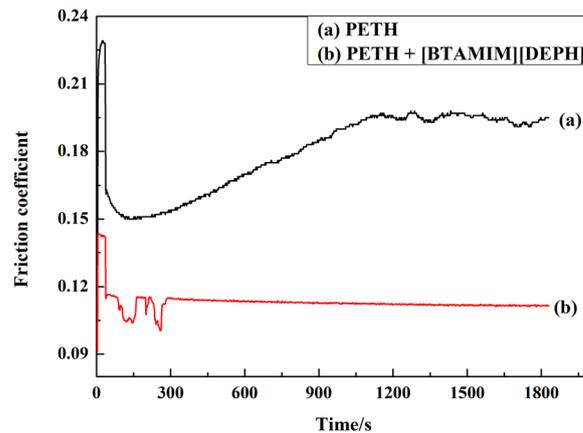


Fig. 4 Evolution of the friction coefficient with time of PETH and PETH + [BTAMIM][DEHP]. (SRV load: 50 N, frequency: 25 Hz, temperature: 100 °C, stroke: 1 mm).

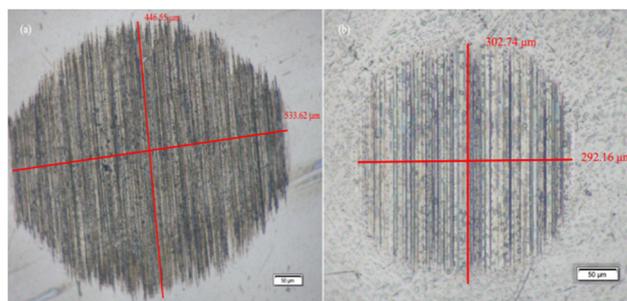


Fig. 5 The wear scar diameter of the upper running ball lubricated by (a) PETH, (b) PETH + [BTAMIM][DEHP]. (SRV load: 50 N, frequency: 25 Hz, temperature: 100 °C, stroke: 1 mm).

Table 3 The friction coefficient (COF) of PETH and PETH + [BTAMIM][DEHP], and the wear scar diameter (WSD) of the upper running ball lubricated by PETH and PETH + [BTAMIM][DEHP]^a

Lubricant	COF mean	WSD/mm
PETH	0.180	0.49
PETH + [BTAMIM][DEHP]	0.113	0.30

^a SRV conditions: load: 50 N, frequency: 25 Hz, temperature: 100 °C, stroke: 1 mm.

bi-functional ionic liquid [BTAMIM][DEHP] significantly improved the friction reduction and anti-wear performance of PETH.

The morphologies of the worn surfaces of the lower steel disc lubricated by PETH and PETH + [BTAMIM][DEHP] were characterized by SEM (JSM-6701F), and the results are shown in Fig. 6. It was found that the worn surface of the steel disc lubricated by PETH was much wider and deeper than the surface lubricated by PETH + [BTAMIM][DEHP]. The wear scar of the lower steel disc lubricated by PETH + [BTAMIM][DEHP] was relatively narrow and the abrasion became smoother. This



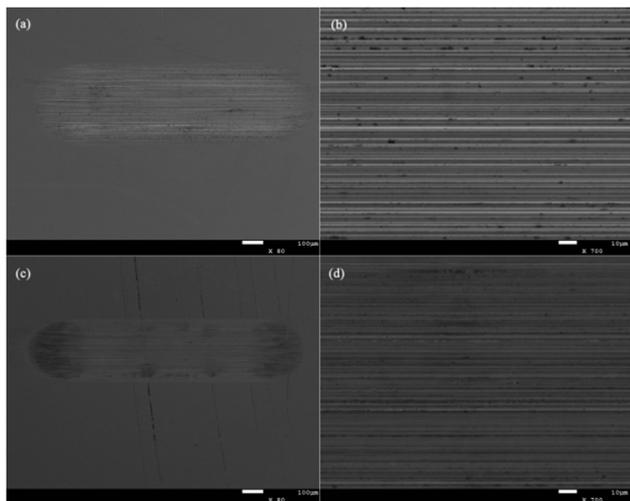


Fig. 6 SEM morphologies of worn surfaces lubricated by (a) and (b) PETH, (c) and (d) PETH + [BTAMIM][DEHP]. (SRV load: 50 N, frequency: 25 Hz, temperature: 100 °C, stroke: 1 mm).

result is consistent with the characterization of the test of the upper running ball with the optical microscope.

Conclusions

In summary, we prepared a bi-functional ionic liquid [BTAMIM][DEHP] which plays dual roles in the synthetic ester oil: synthetic catalyst and friction reduction and anti-wear additive. [BTAMIM][DEHP] exhibited good catalytic activity in the esterification reaction, and the conversion of caproic acid was up to 98% under the substrate ratio at stoichiometric conditions. Meanwhile, [BTAMIM][DEHP] plays a friction reduction and anti-wear additive role without the separation after the reaction and can significantly improve the tribological properties of the base oil pentaerythritol tetra-hexanoate, which shortened the preparation procedure of synthetic ester oil, which is beneficial to industrial production.

Author contributions

Yanan Wang: experimental designing, data collection and analysis, writing the manuscript. Qilong Zhao: Investigation. Jun Yin: formal analysis. Huaigang Su: supervision. Hongyuan Yu: conceptualization. Wenjing Lou: editing. All authors have read and approved the final manuscript.

Data availability

The data supporting this article have been included as part of the ESI.† Raw data for each experiment are available by contacting the corresponding author.

Conflicts of interest

There are no conflicts to declare.

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