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Lithium-based ionic liquids functionalized by sym-triazine and cyclotriphosphazene as high temperature lubricants

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ABSTRACT

Two kinds of lithium-based and sym-triazine- or cyclotriphosphazene-functionalized ionic liquids (ILs, L-C3N3 and L-P3N3) were synthesized by simply blending an appropriate molar ratio of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) with tri(methoxyethoxyethoxyethoxy)triazine ($C_3N_3(OR)_3$) or hexa(methoxyethoxyethoxyethoxy) cyclotriphosphazene ($P_3N_3(OR)_6$). The ILs were evaluated as high temperature lubricants for Si_3N_4/steel contact and found to have significantly improved friction–reducing and anti-wear proprieties compared with conventional alkylimidazolium ILs, 1-ethyl-3-methylimidazolium bis(trifluoro methylsulfonyl)imide (L-F102) and 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (L-F104), at some condition. The morphologies of the worn surfaces were analyzed by scanning electron microscope (SEM). The wear mechanisms were discussed according to the surface composition analysis by X-ray photoelectron spectroscopy (XPS).

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1. Introduction

Since the first report in tribological field of Ye et al. [1], lubrication with ionic liquids (ILs) has received a lot of attention. There are numerous research articles [2–9] and review articles [10–14] on similar applications published in international tribology journals. Most of these studies refer to steel/steel contacts and other less commonly studied materials [15–18], such as titanium alloys and ceramic coatings, are also reported. This is because they have some unique properties such as negligible volatility, low flammability, high thermal stability [19,20], a low melting point and a wide liquid range [21]. However, these IL lubricants have significant cost drawbacks associated with the preparation. Besides, their endurances of friction–reducing and anti-wear proprieties at high temperature need to be improved. We presented a new class of lithium-based ILs as lubricant additives in a recent report, where the ILs are formed in-situ (only by blending) [22,23]. It was described that glymes are relatively strong Lewis-bases due to the lone electron pairs of oxygen atoms in their structures, which result in a high ability to coordinate with alkali metal cation Li^+ to form weak Lewis-acid cations $[Li(glyme)]^+$. Then $[Li(glyme)]^+$ can form ILs ([Li(glyme)]TFSI) with weakly Lewis-basic anion $TFSI^-$ [24]. These ILs as lubricant additives exhibit excellent friction–reducing and anti-wear properties for lubrication of steel/steel contact. It opens a novel research direction of IL lubricants obtained only by blending. Our present work expands the idea by designing novel ILs with heterocyclic structure, i.e. triazine and cyclophosphazene, aiming at enhancing their high temperature tribological properties when used as lubricants. Two kinds of lithium-based and sym-triazine- or cyclotriphosphazene-functionalized novel ILs (L-C3N3 and L-P3N3) were synthesized and proved to be qualified high temperature (200 °C) lubricants for Si_3N_4/steel contact. As a comparison, the tribological properties of 1-ethyl-3-methylimidazolium bis(trifluoro methylsulfonyl)imide (L-F102) and 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (L-F104) were evaluated under the same conditions.

2. Experimental

2.1. Synthesis of the ILs

The following reagents and materials were used as received: chlorotriazine ($C_3N_3Cl_3$) (Alfa Aesar), hexachlorocyclotriphosphazene ($P_3N_3Cl_6$) (Alfa Aesar), triglycol monomethyl ether (J&K) and LiTFSI (J&K). Two kinds of sym-triazine and cyclotriphosphazene functionalized polyether, $C_3N_3(OR)_3$ and $P_3N_3(OR)_6$, were synthesized according to the literature [25]. L-F102 and L-F104 were synthesized according to previously reported methods [26]. Lubricants, L-C3N3 and L-P3N3, were prepared by simply mixing $C_3N_3(OR)_3$ or $P_3N_3(OR)_6$ with LiTFSI. And then they needed moderate stir with heat at 80 °C until forming homogeneous

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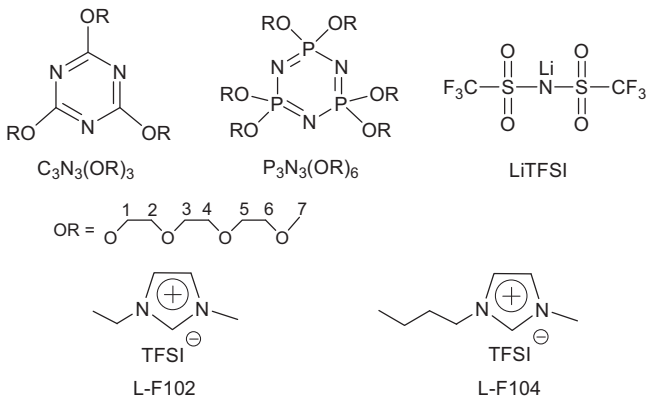

Fig. 1. Molecular structures of $C_3N_3(OR)_3$, $P_3N_3(OR)_6$, LiTFSI, L-F102 and L-F104.

liquids. The molar ratios of $C_3N_3(OR)_3$/LiTFSI and $P_3N_3(OR)_6$/LiTFSI are 1.0:3.0 and 1.0:6.0, respectively [24]. The molecular structures of $C_3N_3(OR)_3$, $P_3N_3(OR)_6$, LiTFSI, L-F102 and L-F104 are presented in Fig. 1. $C_3N_3(OR)_3$ and $P_3N_3(OR)_6$ were confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS. The data are as follows:

$C_3N_3(OR)_3$: ^{1}H NMR (DMSO-d_6, 400 MHz, δ/ppm): 4.43–4.41 (m, 6H; H1), 3.72–3.70 (m, 6H; H2), 3.56–3.54 (m, 6H; H3), 3.52–3.49 (m, 12H; H4 and H5), 3.41–3.39 (m, 6H; H6), 3.22 (s, 9H; H7). ^{13}C NMR (DMSO-d_6, 100 MHz, δ/ppm): 172.5 (C in the heterocyclic), 71.3 (C6), 69.8 (2C, C3 and C4), 69.6 (C2), 68.2 (C5), 67.1 (C1), 58.0 (C7). HRMS (ESI) calcd for $C_{24}H_{45}N_3O_{12}$ $(M+Na)^+$ 590.2895, found 590.2894.

$P_3N_3(OR)_6$: 1H NMR (DMSO-d_6, 400 MHz, δ/ppm): 3.94–3.90 (br, 12H; H1), 3.58 (t, J=4.8 Hz, 12H; H2), 3.54–3.49 (m, 36H; H3, H4 and H5), 3.43–3.40 (m, 12H; H6), 3.22 (s, 18H; H7). ^{13}C NMR (DMSO-d_6, 100 MHz, δ/ppm): 71.3 (C6), 69.8 (2C, C3 and C4), 69.6 (C2), 69.3 (C5), 64.6 (C1), 58.0 (C7). ^{31}P NMR (DMSO-d6, 162 MHz, δ/ppm): 19.125. HRMS (ESI) calcd for $C_{42}H_{90}N_3O_{24}P_3$ $(M+Na)^+$ 1136.5019, found 1136.5030.

2.2. Spectroscopic characterization

The structures of $C_3N_3(OR)_3$ and $P_3N_3(OR)_6$ were characterized by proton nuclear magnetic resonance (^{1}H NMR, 400 MHz), carbon nuclear magnetic resonance (^{13}C NMR, 100 MHz), phosphorus nuclear magnetic resonance (^{31}P NMR, 162 MHz) and high resolution mass spectrometer (HRMS). The HRMS spectra were obtained on a Bruker Daltonics microTOF–QIImass spectrometer. As to L-C3N3 and L-P3N3, the coordination between Li^+ and CH_2–O groups was confirmed by a Fourier transform infrared spectrometer (FTIR). The FTIR spectra were recorded on a Nicolet iS10 FTIR spectrometer between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 1 cm^{-1}. A droplet of the liquid sample was spread on a dry KBr pellet for the infrared (IR) spectroscopic measurement.

2.3. Thermal analysis

The thermal behaviors were studied on an STA 449C Jupiter®-simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC). The sample was heated from room temperature (RT) to 700 °C at a rate of 10 °C/min in air. The phase transition temperatures of the ILs were measured by a DSC 200F3 differential scanning calorimeter (DSC, NETZSCH) with liquid nitrogen at a rate of 10 °C/min.

2.4. Friction and wear test

The tribological properties of the ILs were evaluated by an optimol SRV-IV oscillating reciprocating friction and wear tester at 200 °C. The tests were conducted at an amplitude of 1 mm, a frequency of 25 Hz, a test duration of 30 min (or 3 h for long-time test) and a relative humidity of 20–50%. The contact between the frictional pairs was achieved by pressing the upper running ball against the lower stationary disc. The initial contact pressures for all friction and wear tests were 50 N with duration of 30 s, then rose up to objective values. The upper ball with a diameter of 10 mm was made of Si_3N_4; the stationary disc (ø24 mm × 7.9 mm) was made of W18Cr4V tool steel. Prior to the test, a moderate amount of lubricant was put onto the ball-disc contact area. The corresponding friction curves were recorded automatically by the SRV test rig. The wear volume losses from lower discs were measured using a MicroXAM-3D non-contact surface mapping microscope profilometer. All the tests were repeated at least 3 times.

The morphologies of the worn surfaces were obtained using a JSM-5600LV scanning electron microscope (SEM). The XPS analyses were performed to examine the chemical composition of the wear scar and the possible tribochemical changes involved in the friction process. The XPS measurements were carried out on K-Alpha X-ray photoelectron spectrometer, with Al-Kα radiation as the excitation source and a spot size of 650 μm. The binding energies of the target elements were determined at pass energy of 50.0 eV.

3. Results and discussion

3.1. Spectroscopic characterization

The ^{1}H NMR data of 4.43–4.41, 3.72–3.70, 3.56–3.54, 3.52–3.49, 3.41–3.39, and 3.22 are correspond to H1, H2, H3, H4/H5, H6 and H7 in the oligoether groups of $C_3N_3(OR)_3$. And the ^{13}C NMR data of 172.5, 71.3, 69.8, 69.6, 68.2, 67.1, 58.0 are correspond to C in the heterocyclic, C6, C3/C4, C2, C5, C1 and C7. As to $P_3N_3(OR)_6$, the ^{1}H NMR peaks of H1, H2, H3 (and H4, H5), H6 and H7 appear at 3.94–3.90, 3.58, 3.54–3.49, 3.43–3.40 and 3.22, respectively. The ^{13}C NMR peaks of C6, C3/C4, C2, C5, C1 and C7 appear at 71.3, 69.8, 69.6, 69.3, 64.6 and 58.0, respectively.

Fig. 2 shows the IR spectra of the C–H stretching mode of the coordinated ILs. The corresponding stretching modes in $C_3N_3(OR)_3$ and $P_3N_3(OR)_6$ were adopted as comparisons. From Fig. 2, It is clearly seen that the strong bands at 2883 cm^{-1} in the IR spectra of $C_3N_3(OR)_3$ and $P_3N_3(OR)_6$ are attributed to the C–H symmetric and antisymmetric stretching modes. When lithium salts were introduced into $C_3N_3(OR)_3$ and $P_3N_3(OR)_6$, however, the corresponding bands in L-C3N3 and

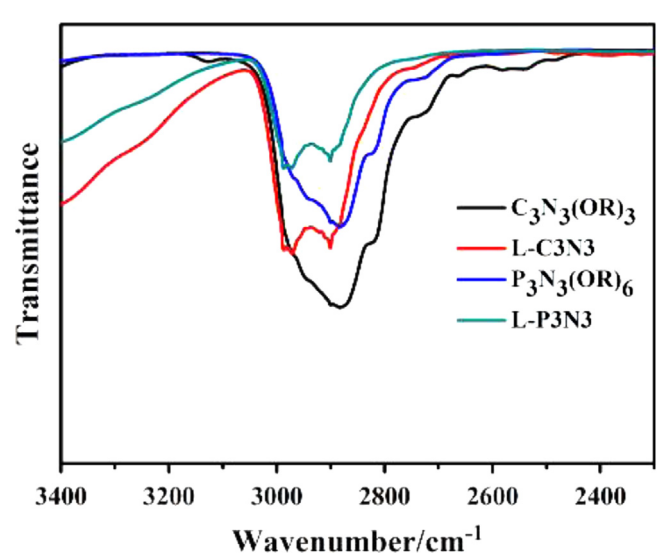

Fig. 2. FTIR spectra of the C–H stretching mode of the ILs.

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