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RESEARCH ARTICLE

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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

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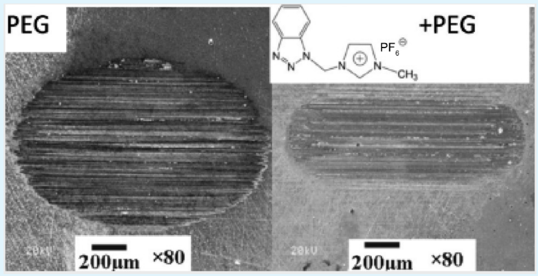
ABSTRACT: The imidazolium ionic liquids (ILs) bearing benzotriazole group were synthesized and evaluated as antiwear (AW) and anticorrosion additive in poly(ethylene glycol) (PEG) and polyurea grease for steel/steel contacts at room temperature and 150 °C. The physical properties of the synthetic ILs and PEG with the additive were measured. The anticorrosion property of the synthetic ILs was assessed via the accelerated corrosion test and copper strip corrosion test, which reveals the excellent anticorrosion properties in comparison with pure PEG and the selected conventional ILs having no benzotriazole group. Tribological results indicated that these ILs as the additives could effectively reduce friction and wear of sliding pairs in PEG and also in polyurea grease. The tribological properties were generally better than the normally used zincdialkyldithiophosphate-based additive package (T204) in polyurea grease. The wear mechanisms are tentatively discussed according to the morphology observation of worn surfaces of steel discs by scanning electron microscope (SEM) and the surface composition analysis by X-ray photoelectron spectroscopy (XPS).



KEYWORDS: ionic liquids, benzotriazole, anticorrosion, antiwear additives

1. INTRODUCTION

In long-term lubricated sliding components, mechanical thermal stress, and storage process, oils may experience both thermal degradation and oxidation degradation, in particular,at high temperature and in the presence of oxygen, moisture, etc., under which conditions the acidic compounds and sludges might be produced. Most of these acidic substances and sludges will cause erosion and so the increased mechanical wear and the lubricity thus become poor and fuel efficiency is dramatically reduced.[1] Therefore, the use of powerful antioxidant, anticorrosion additive in mineral oils, synthetic oils, greases, and other lubricants is necessary.

It is well-known that ionic liquids(ILs) have attracted considerable attention as the effective lubricants with remarkable lubrication and antiwear capability.[2,3] This may be attributed to the dipolar structure of ILs and excellent physical properties such as extremely low volatility, nonflammability, high thermal stability and low melting points.[4,5] ILs can be used as high-performance lubricants,[6−21] as friction reduction and AW additives[22−31] and as thin films.[31−34] ILs, such as 1-ethyl-3-hexylimidazolium tetrafluoroborate (LB206) IL[2] and asymmetrical tetraalkylphosphonium[9,11] have shown generally better friction reduction and antiwear properties than the synthetic partially fluorinated hexaphenoxy cyclotriphosphazene (X-1P) and perfluoropolyether(PFPE) oils for steel/aluminum and steel/steel contacts. The alkylimidazolium hexafluorophosphate ILs as lubricants for steel/steel contacts showed superior friction-reducing abilities and load-carrying capacities than 2 wt % zinc dialkyldithiophosphate (ZDDP) additivated liquid paraffin.[7] The performance of imidazolium ILs having bis(trifluoromethylsulfonyl)-imide (NTf_2) is generally the best among other counterpart anions, e.g., BF_4, PF_6, etc.[8] High thermal stability allows ILs to perform very well up to 300 °C.[18,19] The ammonium-based $[C_8H_{17}]_3NH.Tf_2N$, imidazolium-based C_{10}mim. Tf_2N and ILs with boron based anions[32] could generally provide better lubrication for aluminum compared to the fully formulated 15W40 engine oil.[17] ILs as additives in paraffinic−nafthenic mineral base oil and synthetic esters could significantly reduce both friction and wear with respect to the base oil.[23,27] Qu et al. have shown that 10 vol % protic alkylammonium ILs had lower wear than either the base oil or neat ILs alone.[24] The ammonium ILs and imidazolium ILs as a neat lubricant and 15W40 engine oil additives have better friction reduction and AW compared to the fully formulated 15W40 diesel engine oil in lubricating a Cr-plated engine piston ring against a cast iron flat. The results suggested the great potential of ILs for use as base lubricants or lubricant additives for diesel engine applications.[25] Several imidazolium ILs as AW additives in poly(ethylene glycol) were evaluated,[28] but most ILs have limited miscibility with low polarity hydrocarbon oils. ILs showed strong potential as lubricants for micro/nanoelectromechanical

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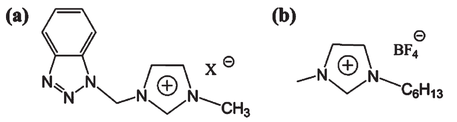


Figure 1. Molecular structures of ILs: (a) X = BF_4, [BTAMIM][BF_4]; X = $N(CF_3SO_2)_2$, [BTAMIM][NTf_2]; X = PF_6, [BTAMIM][PF_6]; (b) LB106.

systems(MEMS/NEMS), not only because of their low friction, wear resistance, but also the favorable charge dissipation properties in comparison with the well-known lubricant, Z-TETRAOL (a hydroxyl functionalized PFPE).[33] Bai et al. investigated the effect of the anions[34] and cations[35] on the tribological properties of ILs nanofilms on surface-modified silicon wafers. Among, different anions BF_4^-, PF_6^-, and adipate counterpart with 1-alkyl-3-methyl imidazolium, the hexafluorerophosphate IL showed the best tribological properties. The imidazolium salt was generally better that tetraalkylphosphonium and N-butyl-pyridinium when the anion was tetrafluoroborate.[35]

Recently, there has been a tendency to synthesize functionalized ILs to tackle the existing problems, such as thermo-oxidation and corrosion.[3] Substitution of H at 2-position of imidazolium ring can reduce its oxidation and so improve the tribological properties.[28] Sterically hindered phenol group was incorporated into ILs to improve its antioxidation capability.[30] Corrosion of ILs generally comes from the impurity of halogen during the synthesis or from the fluorine containing anions that are prone to hydrolysis. Substitution of fluorine with fluoroalkyl chains from PF_6 to $(C_2F_5)_3PF_3^-$ can improve ILs friction reduction and AW properties and alleviate the corrosion.[12] Another way is to completely avoid use of fluorine containing anions, for example, dialkylphosphate anion can be used and may have synergistic effect with the imidazolium ring besides the corrosion resistance.[14] N-substituted benzotriazole compounds, such as N-t-alkylated benzotriazoles, toluotriazole, and n-butyl vinyl ether addition product, are used as metal deactivators, anticorrosion and antioxidants in mineral oils, synthetic lubricants, and grease and have excellent anticorrosion and antioxidation properties.[36−38] Benzotriazole has been added into ILs as an effective anticorrosive additive.[16] However, free benzotriazole molecules have limited sublimation temperature and cannot function at high temperatures. The solution to the problem is to incorporate benzotriazole group into ILs by molecule design, which is the focus of the present work. The combination may or may not further improve the lubrication properties of ILs, but hopefully it will improve the tribological and anticorrosive/antioxidative properties of base oils. If so, it will also be helpful reference to extend the use of ILs in other areas, such as in prevention of corrosion/oxidation when being used as solid electrolytes and as the reaction media in catalysis. The present paper reports tribological properties of imidazolium ILs bearing benzotriazole group as the AW and anticorrosion additives in PEG and polyurea grease for steel/steel contacts.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The chemical structures of novel imidazolium bearing benzotriazole group ILs and LB106 are given in Figure 1. 3-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)-1-methyl-1H -imidazolium tetrafluoroborate ([BTAMIM][BF_4]), (Trifluoromethylsulfonyl)-imide ([BTAMIM][NTf_2]), hexafluorophosphates ([BTAMIM][PF_6]) and 3-hexyl-1-methyl- imidazolium tetrafluoroborates (LB106) ILs were synthesized according to previously reported methods.[39,40] 1-(chloromethyl)-1H-benzo[d][1,2,3]triazole was synthesized according to literature.[41] The formaldehyde solution (37%-40%) and benzotriazole was obtained from a Tianjin Chemical Reagent No. 1 Plant and Sinopharm Chemical Reagent Co. Ltd., respectively. Sodium tetrafluoroborate and ammonium hexafluorophosphate were purchased from a Shanghai Tongshi Reagent Company and Shanghai Daocheng Reagent Company, respectively. 1-Methylimidazole was obtained from a Shanghai Weite Reagent Company and redistilled before use. Lithium bis(trifluoromethylsulfonyl)imide (99%) was purchased from Fluka. All other chemicals utilized in this work were of AR grade.

2.2. Characterization. PEG was purchased from Shanghai Chemical Reagent Company. The average molecular weight was between 190 and 210 g/mol. It has kinematic viscosity of 22.30 mm^2/s at 40 °C and 4.13 mm^2/s at 100 °C. Base oil and additives were mixed thoroughly before testing. The miscibility or solubility values are shown in Table 1. The IL [BTAMIM][NTf_2] had a solubility over 35 wt % in PEG. The other two ILs also have good solubility in PEG. The density, viscosity, and viscosity-temperature index of the PEG with ILs were measured by a SVM3000 Stabinger viscometer. Polyurea grease was obtained from Lanzhou Petrochemical Grease Factory. The basic parameters of the polyurea grease were listed in previous work.[31]

Zinc dialkyldithiophosphate package (T204) was purchased from LuBoRun Lanzhou LanLian Additive Co., Ltd. The base grease and additives were mixed thoroughly prior to the tests. Briefly, the grease was combined with 2 wt % of additives. For full dissolution, 98 wt % of the polyurea grease was then added to the additivated grease by agitation with a mechanical stirrer at room temperature.

The thermal properties of ILs were measured on an STA 449 C Jupiter simultaneous TG-DSC instrument from ambient temperatures to approximately 800 °C at a heating rate of 10 °C/min in air. The morphology and chemical composition of the worn surfaces were analyzed by JSM-5600LV SEM and PHI-5702 multifunctional XPS using Al KR radiation as the excitation source. The binding energies of the target elements were determined at a pass energy of 29.35 eV with a resolution of approximately ±0.3 eV using the binding energy of the contaminated carbon (C1s: 284.6 eV) as reference.[42]

2.3. Corrosion Test. *2.3.1. Accelerated Corrosion Test.* To make the test solution, the IL was dissolved in 25 mL of methanol and then added to 25 mL of saturated calcium hydroxide [$Ca(OH)_2$]. The copper piece and tinplate piece specimens were incubated in IL solutions saturated with $Ca(OH)_2$ for a certain time[43] for 15 days and for 4 months, respectively.

2.3.2. Copper Strip Corrosion Test. The test was performed according to GB-T5096-1985(91) procedure and the equivalent ASTM D130 83 method. A piece of bright finish copper was immersed in 20 mL of ILs additivated PEG and heated for 15 h at 150 °C. At the end of the test cycle, the copper strip was washed and compared with the copper strip corrosion standards.

2.4. Tribological Tests. The tribological behavior of the ILs as additives in PEG and polyurea grease for steel/steel contacts was evaluated on an Optimol SRV-IV oscillating reciprocating friction and wear tester. Friction and wear tests were performed at room temperature and at 150 °C, respectively, in a ball-on-block configuration. The contact between the frictional pairs was achieved by pressing the upper running ball (10 mm in diameter, AISI 52100 steel, hardness of approximately 59−61 HRC) against the lower stationary disk (ø 24 mm ×7.9 mm, AISI 52100 steel, hardness of approximately 65−67 HRC) in the reciprocating mode under a normal load of 100−500 N [corresponding to the maximum Hertzian pressure in the range of 2.14−3.66 GPa] at a frequency of 25 Hz, a sliding amplitude of 1 mm, a relative humidity of 15−20%, and for a duration of 30 min. The wear volume of the lower disk was measured using a MicroXAM 3D noncontact surface mapping profiler. Three repetitive measurements were performed for each type

Table 1. Solubility of [BTAMIM][BF_4], [BTAMIM][PF_6] and [BTAMIM][NTf_2] in PEG Base Oil at Room Temperature

	[BTAMIM][BF_4] (%)	[BTAMIM][PF_6] (%)	[BTAMIM][NTf_2] (%)
miscibility or solubility (weight fraction)	14−15	17−18	>35

Table 2. Physical Properties of PEG and PEG with Different Additives

	kinematic viscosity (mm^2/s)			
lubricant	40 °C	100 °C	viscosity index	density(kg/m^3) at 25 °C
PEG	22.30	4.13	74.2	1128.0
0.05% [BTAMIM][PF_6]	22.71	4.20	77.5	1128.1
0.5% [BTAMIM][PF_6]	23.09	4.24	77.7	1129.7
1% [BTAMIM][PF_6]	23.55	4.27	75.4	1131.1
2% [BTAMIM][PF_6]	23.89	4.31	75.0	1135.7
3% [BTAMIM][PF_6]	25.24	4.44	75.2	1138.6
1% [BTAMIM][BF_4]	24.04	4.36	79.8	1132.1
1% [BTAMIM][NTf_2]	23.18	4.26	77.6	1131.3

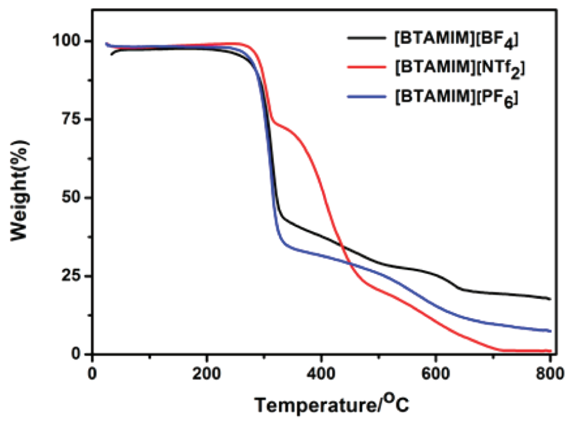


Figure 2. TGA curves of [BTAMIM][BF_4], [BTAMIM][NTf_2], and [BTAMIM][PF_6] in air atmosphere.

of disk, and the averaged values of wear rates are reported. The wear rates of the worn surface were calculated using the equation $K = V/SF$, where V is the wear volume (in mm^3), S is the total sliding distance (in m), and F is the normal load (in N).[28]

3. RESULTS AND DISCUSSION

3.1. Physical Properties of the Synthesized ILs. Polyether lubricating oil has been widely used in industry. In present work, we have used PEG with molecular weight of 190−210 g/mol as the model base oil for study. The density, viscosity and viscosity−temperature index of PEG and PEG with ILs are shown in Table 2. The data have shown that the addition of ILs to PEG only slightly increases its viscosity both at room temperature and at 100 °C. With [BTAMIM][PF_6] as an example, the viscosity also increases as the concentration increases. Obviously, the viscosity change is not that much and would have trivial impact on the lubricating properties, highlighting the effect of ILs themselves as lubrication additives as will be shown in the following. One key aspect of oil additives is the thermal stability. Figure 2 presents the TGA curves of the synthesized ILs. It is seen that the newly synthesized ILs does not exhibit any weight loss below 280 °C and their decomposition temperatures are all about 300 °C. Furthermore, the temperature for total decomposition is approximately 700 °C, indicating the high thermal stability. The character is not like the neat benzotriazole that has very low sublimation temperature of about 100 °C. The thermal stability of benzotriazole type of additive is significantly improved by incorporating into ILs compounds that are normally very stable. It is expected the novel compounds can combine both the antifriction and AW properties of ILs and anticorrosion properties of benzotriazole compounds.

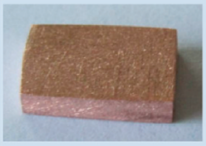
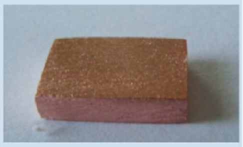
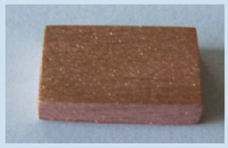
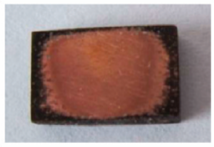
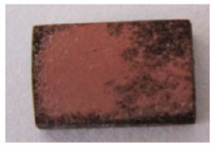
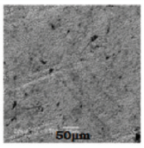
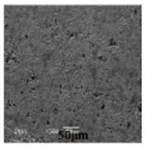
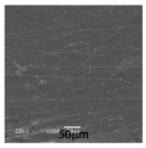
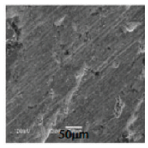
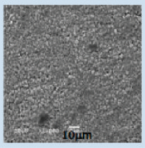
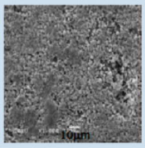
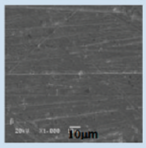
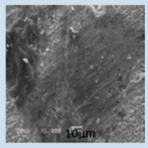
Table 3. Results of Copper Corrosion Strip Tests

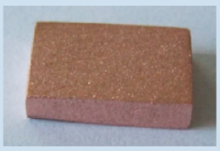
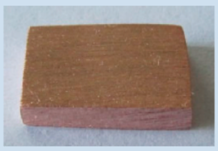
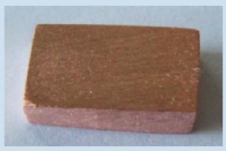
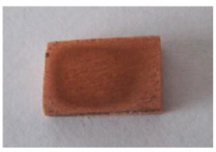
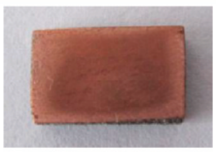
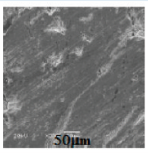
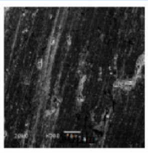
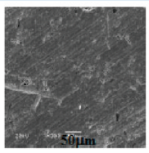
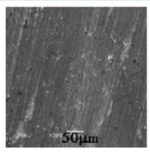
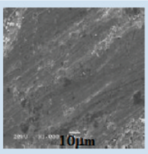
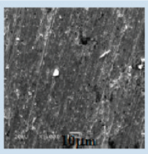
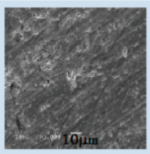
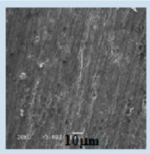
lubricants	corrosion grade
PEG	3b
PEG+1% [BTAMIM][PF_6]	1b
PEG+1% [BTAMIM][BF_4]	1b
PEG+1% [BTAMIM][NTf_2]	1a

3.2. Corrosion Test. *3.2.1. Copper Strip Corrosion Tests.* Table 3 shows the results of the copper strip corrosion tests. The corrosion grades are assigned according to the ASTM D130 83 and also the equivalent GB-T5096−1985(91). In 1 wt % [BTAMIM][NTf_2] additivated PEG, there is not any color change compared with the fresh copper, so the corrosion grade is 1a. The color of the copper strip in 1 wt % [BTAMIM][PF_6] and 1 wt % [BTAMIM][BF_4] exhibited only a mild discoloration after the test, and no serious corrosion to copper strip occurred. The copper corrosion control standard shade guide was used to determine the corrosion level as 1b, i.e. slight tarnish with color turning from light orange to deep orange. However, the copper strip color of PEG exhibited malachite green, dark tarnish and the corrosion level is defined as 3b. The copper strip test results indicate that ILs is qualified as the anticorrosion additives in PEG. It worth noting that the PEG additivated with conventional ILs LB106 shows no apparent anticorrosion difference from that with [BTAMIM][NTf_2] (1b vs 1a), which makes us to carry out speeded-up experiment under more harsh conditions in order to verify the function of the incorporated benzotriazole group.

3.2.2. Accelerated Corrosion Test. The accelerated corrosion test was carried out in a specially selected solution. The copper

Table 4. Copper Corrosion Tests of ILs

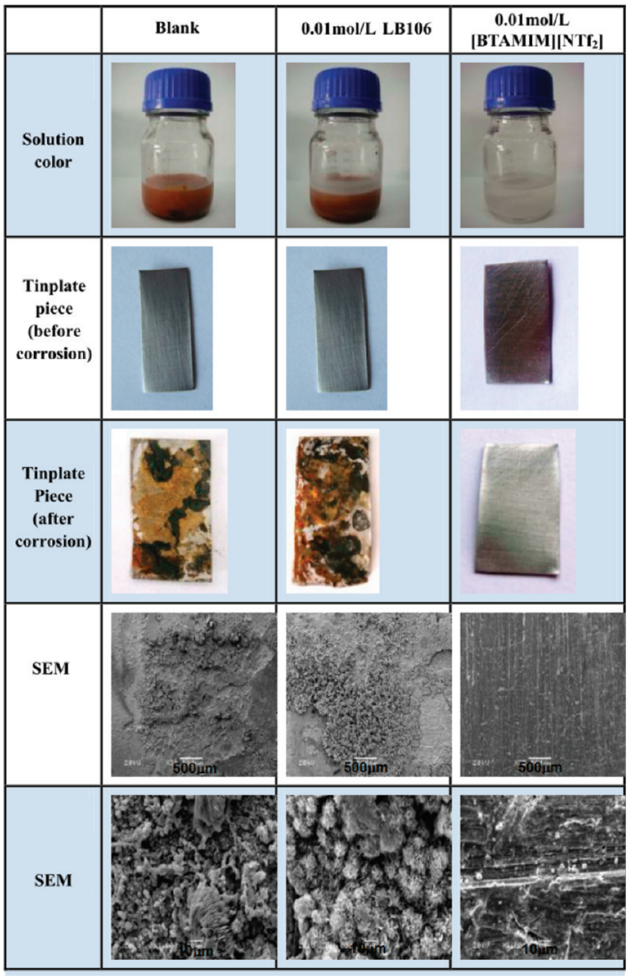
	Blank	0.01mol/L LB106	0.01mol/L [BTAMIM][PF_6]	0.01 mol/L LB106 + 0.01 mol/L [BTAMIM][PF_6]
Copper (before corrosion)				
Copper (after corrosion)				
SEM				
SEM				

	0.01mol/L [BTAMIM][BF_4]	0.01mol/L LB106+0.01mol/L [BTAMIM][BF_4]	0.01mol/L [BTAMIM][NTf2]	0.01 mol/L LB106 + 0.01 mol/L [BTAMIM][NTf2]
Copper (before corrosion)				
Copper (after corrosion)				
SEM				
SEM				

pieces were incubated in ILs solutions saturated with $Ca(OH)_2$ for 15 days, and made comparison with blank solution and the normal LB106 IL. The anticorrosion behavior of the synthesized ILs is listed in Table 4 and Table 5. Table 4 shows the copper piece corrosion tests of ILs. It is seen that severe corrosion occurred on copper piece soaked in blank solution and that containing LB106. The copper pieces in both solutions were seriously corroded and the color turned to black. The SEM morphologies of copper pieces show that the copper top surface layer had been eroded away. However, under the same condition, the copper sheets in the solution containing [BTAMIM][PF_6] or [BTAMIM][PF_6] + LB106 only have been slightly corroded. The copper color in solutions containing [BTAMIM][BF_4], [BTAMIM][BF_4] + LB106, and [BTAMIM][NTf_2] + LB106 show a little change and the copper surfaces have only a little corrosion. The copper piece colors in solutions containing [BTAMIM][NTf_2] do not show any change at all, and the texture structure on steel surfaces due to mechanical polishing before is still clearly seen, indicating no obvious damage of the initial morphology. So the synthesized ILs have significant anticorrosion capability for copper. Among them, [BTAMIM][NTf_2] clearly shows the best anticorrosion behavior.

The tinplate as a form of anticorrosive engineering iron has been widely applied in industry. Its anticorrosive capability is generally low than the steel, i.e., it is more active than steel and so is used for accelerated corrosion test, whereas the following tribological studies were carried out with steel. Corrosion tests of steel plates under the same conditions did not show too much difference. More long-term test should be done. The tinplate piece corrosion tests of ILs will provide useful clue to corrosion to steel since basically both are mainly composed of iron. The results are shown in Table 5. The tinplates were incubated in ILs solutions saturated with $Ca(OH)_2$ for four months and the anticorrosion behavior to tinplate pieces were made comparison with blank solution and normal ILs LB106. It is seen that in blank solution and that containing LB106 severe corrosion occurred, and solution color turned into deep brown and the tinplate surfaces were seriously corroded. The SEM morphologies of tinplate piece verify generation of a very rough oxidative layer. However, under the same condition, the solution color containing [BTAMIM][NTf_2] and the color of tinplate surface have not changed at all. The above experimental data show that [BTAMIM][NTf_2] has excellent corrosion behavior for tinplate. This also proves that [BTAMIM][NTf_2] ILs has significant anticorrosion capability for different materials, such as copper and tinplate.

Table 5. Tinplate Corrosion Tests



3.3. Tribological Properties of Ionic Liquids As Additives in PEG. *3.3.1. Room Temperature Tests.* Figure 3 shows the evolution of friction coefficient with the time at a constant load of 100 N and the frequency of 25 Hz for PEG plus [BTAMIM][PF_6] additive at different concentrations and the wear rates of the discs after the tests. Figure 3a shows the single friction curves under different lubrication conditions (Note: the friction curves overlapped very well in different tests), whereas Figure 3b shows the averaged wear rates from 3 different tests. When the concentration of [BTAMIM][PF_6] is 0.5 wt %, in the initial friction stage, the [BTAMIM][PF_6] additive may form boundary lubricating film and the curve shape was stable for the initial 150 s. Then the boundary film might be worn away and could not complement rapidly probably because of low absorption strength and low concentration, the friction coefficient suddenly increased to 0.160, lasted for 300−400s, and afterward stabilized at the value equal to that of pure PEG. So at late stage, lubrication was basically provided purely by base oil. When the concentration of [BTAMIM][PF_6] reaches 1 wt %, the mixture not only has very low and stable friction coefficient (Figure 3a), but also the lowest wear rate (Figure 3b). Further increasing the concentration of [BTAMIM][PF_6] above 1 wt %, AW property

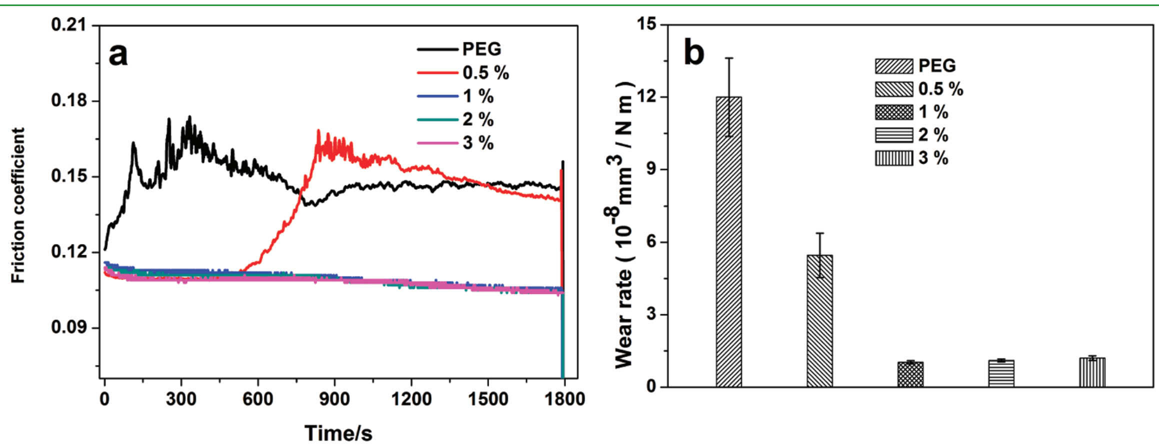


Figure 3. (a) Evolution of friction coefficient with time at 100 N for PEG plus [BTAMIM][PF_6] additive at different concentrations; (b) wear rate of the steel discs lubricated by PEG with [BTAMIM][PF_6] additive at different concentrations after the constant load tests. (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 20 °C).

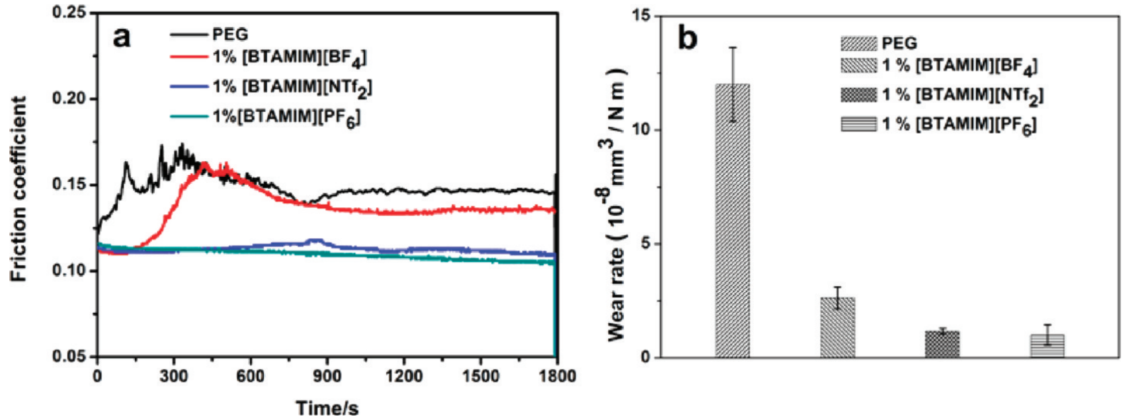


Figure 4. (a) Friction coefficient and (b) wear rates of steel discs lubricated by PEG plus 1 wt % each of [BTAMIM][BF_4], [BTAMIM][NTf_2], and [BTAMIM][PF_6] at room temperature (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz).

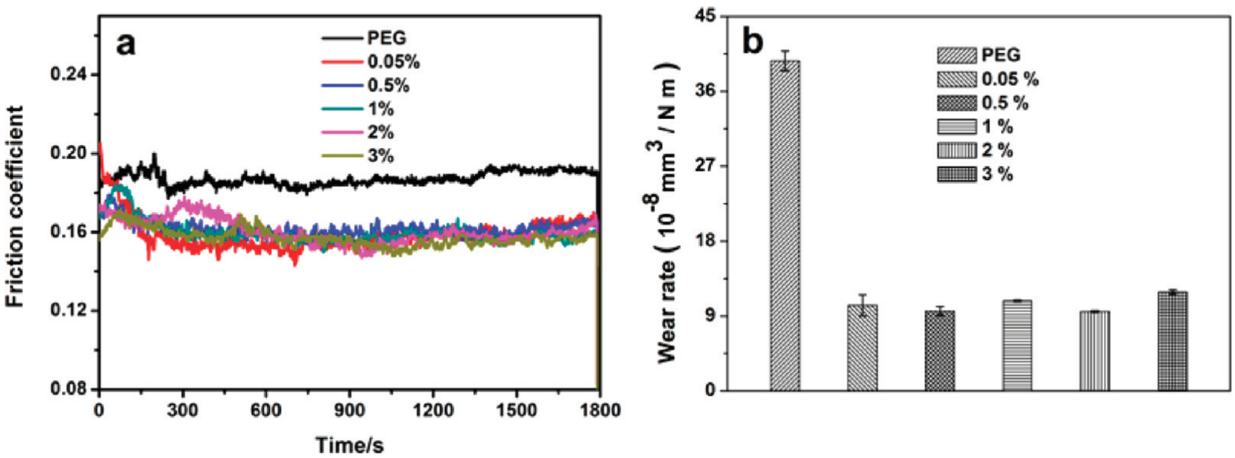


Figure 5. (a) Friction coefficient and (b) wear rate of steel discs lubricated by PEG plus [BTAMIM][PF_6] additive at different concentrations at 150 °C. (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min).

could not be improved any more. It is seen that 1 wt % [BTAMIM][PF_6] can improve the AW properties of the base oil by 3 times and 10 times as compared with 0.5 wt % [BTAMIM][PF_6] and pure PEG respectively. So 1 wt % [BTAMIM][PF_6] is the optimum concentration to provide significant friction and wear reduction. The concentration dependence is very similar according to the supplementary tests, i.e., 1% is the optimum concentration for all three compounds although the actual value will be different. This is probably because of very similar action mechanism of the three imidazolium salts. The minor anticorrosion difference of the three compounds cannot be detected from tribological tests in short time.

To illustrate the effect of anions on tribological properties, the friction and wear of 1 wt % three compounds in PEG at a constant load of 100 N and the frequency of 25 Hz were measured and the results are shown in Figure 4. Figure 4 displays the friction coefficients of the four lubricants increasing in the following sequence: [BTAMIM][PF_6] | [BTAMIM][NTf_2] < [BTAMIM][BF_4] < PEG, the wear rates of the discs increase in the following sequence: [BTAMIM][PF_6] | [BTAMIM][NTf_2] < [BTAMIM][BF_4] < PEG. The tribological properties are significantly affected by anions. Despite the high molecular number of [BTAMIM][BF_4] per unit PEG (because of small molecular weight), 1 wt % [BTAMIM][BF_4] additivated PEG exhibits friction behavior that is comparable to the PEG base oil: both have the relatively long running-in period with larger friction coefficients. [BTAMIM][BF_4] additivated PEG displays dramatically better AW property than PEG despite the comparable friction coefficient, which is ascribed to the enhanced AW property of additive due to the tribochemical reaction between heteroatoms in [BTAMIM][BF_4], such as N, B, F, and iron. When the additives are [BTAMIM][NTf_2] and [BTAMIM]-[PF_6], the friction coefficients keep relatively stable at low level, indicating they are more liable to form boundary film on steel surface. The addition of 1 wt % [BTAMIM][PF_6] and 1 wt % [BTAMIM][NTf_2] can reduce the wear rates by 12 times with respect to the pure base oil. Both have excellent friction reduction and AW property.

3.3.2. High-Temperature Tests. Figure 5 shows the effect of the concentration on the tribological behavior of 0.05−3 wt % [BTAMIM][PF_6] in PEG. This is under the same test conditions (at a constant load of 100 N and the frequency was 25 Hz) as that in Figure 3 except at a temperature of 150 °C. When the concentration of [BTAMIM][PF_6] is merely 0.05 wt %, the mixture exhibits considerably better friction reduction and AW property than the base oil. As the concentration of [BTAMIM][PF_6] increased, the friction coefficients and wear

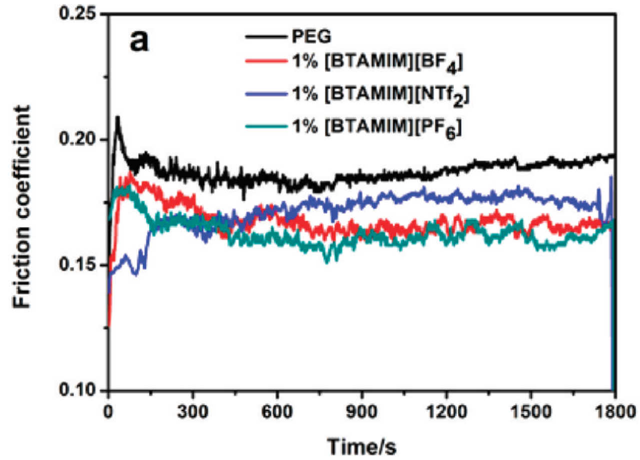


Figure 6. (a) Friction coefficient and (b) wear rate of steel discs lubricated by PEG plus 1 wt % each of [BTAMIM][BF_4], [BTAMIM][NTf_2], and [BTAMIM][PF_6] at 150 °C. (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz).

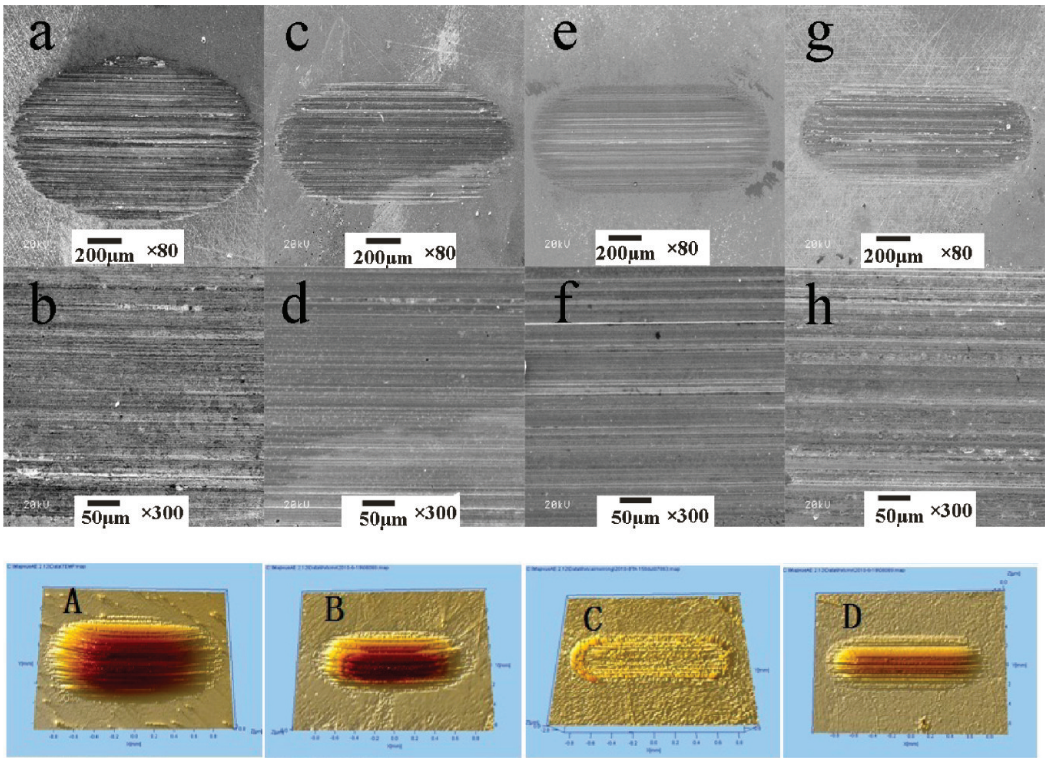


Figure 7. SEM morphologies of worn surfaces lubricated by PEG and different IL additives: (a, b) PEG, (c, d) 1 wt % [BTAMIM][BF_4], (e, f) 1 wt % [BTAMIM][NTf_2], and (g, h) 1 wt % [BTAMIM][PF_6]. The 3D optical microscropic images of wear tracks corresponding to a, c, e, g. (magnification: top images, 80×; and bottom images, 300×; load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 150 °C).

rate of [BTAMIM][PF_6] changed little. It is clearly seen that the effect of additive concentration on tribological properties of base oil is very different under the high temperature and low temperature. Under high temperature, the friction is more sensitive to the additives at low concentration and significant friction reduction and antiwear performance occur. This is in contrast to that at room temperature where the optimum concentration is 1 wt %. The possible reason might be relevant to the freedom of additives in bulk oil. At high temperature, the freedom of additive molecules in bulk oil is fairly large and they can form boundary film at interface more rapidly once boundary film is swept away, whereas at low temperature, the additive molecules at interface cannot be supplied timely due to the relative high viscosity of bulky oil and restricted motion of additive molecules. Besides, AW compounds via tribochemical reaction film are more easily generated at high temperature.

We also investigated that the effect of anion on the tribological behavior of the three additive+PEG mixtures at a constant load of 100 N and 150 °C. Figure 6 shows that the friction coefficients of three kinds of additive+PEG mixtures increase in the following sequence: 1 wt % [BTAMIM][NTf_2] | 1 wt % [BTAMIM][PF_6] < 1 wt % [BTAMIM][BF_4] < PEG. The wear rates of the lubricants

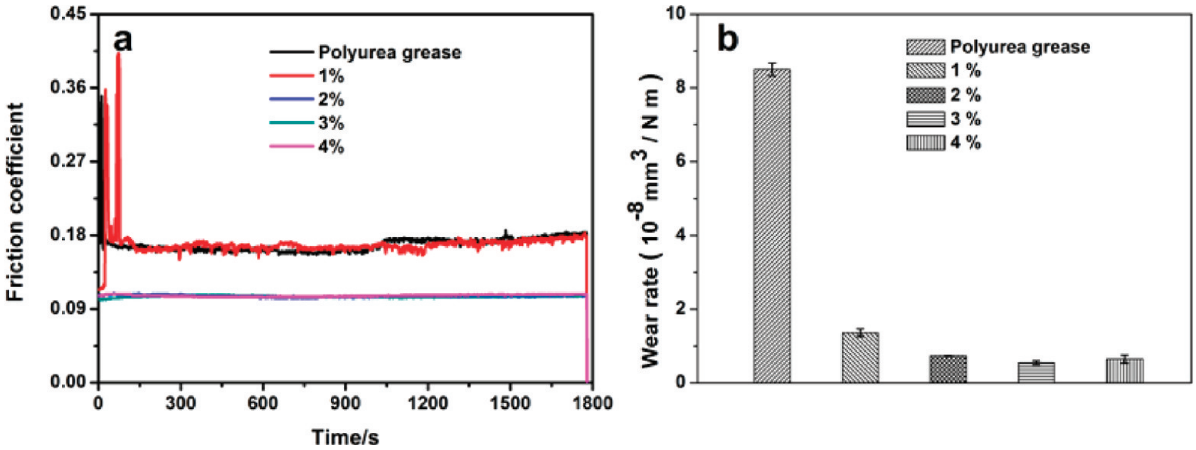


Figure 8. (a) Friction coefficient and (b) wear rate of steel discs lubricated by polyurea grease plus [BTAMIM][PF_6] additive at different concentrations at 150 °C. (SRV load, 300 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min).

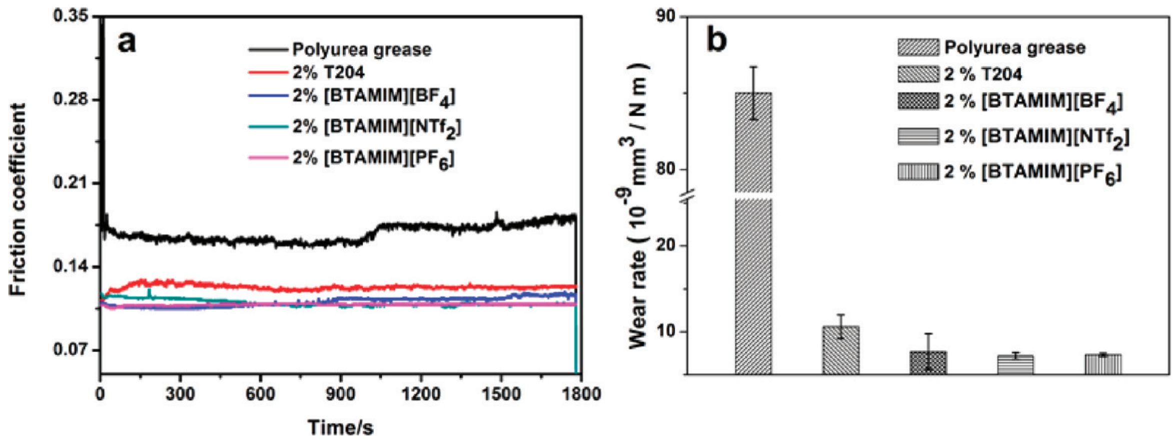


Figure 9. (a) Friction coefficient. (b) wear rate of steel discs lubricated by polyurea grease plus 2 wt % each of [BTAMIM][BF_4], [BTAMIM][NTf_2] and [BTAMIM][PF_6] at 150 °C. (SRV load, 300 N; stroke, 1 mm; frequency, 25 Hz).

increase in the following sequence: 1 wt % [BTAMIM][PF_6] < 1 wt % [BTAMIM][NTf_2] < 1 wt %[BTAMIM][BF_4] < PEG. Both friction and wear trend have the similar sequence to that at RT. However, by looking closely, they show a completely different scenario. The friction coefficients are all relatively large than that at RT, one plausible reason being that at high temperature all the additives cannot form stable boundary films that exists in a thermodynamic equilibrium state. However, the AW properties are prominent. It is seen that the addition of 1 wt % [BTAMIM][BF_4], 1 wt % [BTAMIM][NTf_2], and 1 wt % [BTAMIM][PF_6] can improve the AW properties of PEG by 2.5, 4.5, and 5.5 times, respectively. It is assumed that at high temperature, the tribochemical reaction products play a key role in preventing substrates from wear. In a word, the results indicate that ILs as additives for PEG exhibit friction reduction and outstanding antiwear properties at high temperature.

The wear situation of sliding pairs were further checked with SEM. Figure 7 displays the SEM micrographs of the worn surfaces of steel discs lubricated by PEG and three additives at 100 N and 150 °C, and all the SEM images were obtained under the same conditions. As can be seen from images a and b in Figure 7, the worn surface of the steel lubricated by PEG shows considerably wider and deeper wear scar, with a number of deep and narrow grooves, indicating severe scuffing occurred in this case. The addition of 1 wt % [BTAMIM][BF_4] can make the worn surface of the steel becomes relatively narrow and shallow, showing that [BTAMIM][BF_4] has some certain AW property. When 1 wt % [BTAMIM][NTf_2] and 1 wt % [BTAMIM][PF_6] are added into PEG, not only does the width of wear scars become smaller in size, but the abrasions are also fewer and smoother (Figure 7e−h). This is consistent with previously measured wear rates, which also proves that [BTAMIM][NTf_2] and [BTAMIM][PF_6] as the additive in PEG can remarkably reduce the wear of sliding pairs. Figure 7A−D shows the three-dimensional morphology of wear scars, which clearly shows the wear scenario under different lubrication conditions. Wear scar lubricated with PEG is very wide and deep, indicating serious wear occurred. Wear scar lubricated with [BTAMIM][NTf_2] additivated PEG shows very smooth trace and very little wear.

3.4. Tribological Properties of Ionic Liquids As Polyurea Grease Additives. Polyurea grease is mainly used for lubricating various equipments at high temperature with good oxidation stability, mechanical stability and wider use temperature range.[44−46] It is important that additives with high thermal stability ensure that the grease is not affected in the course of the performance. Fox et al. studied ILs as additives in grease, showing surprisingly large increases in the welding load during the four-ball extreme pressure test.[29] The

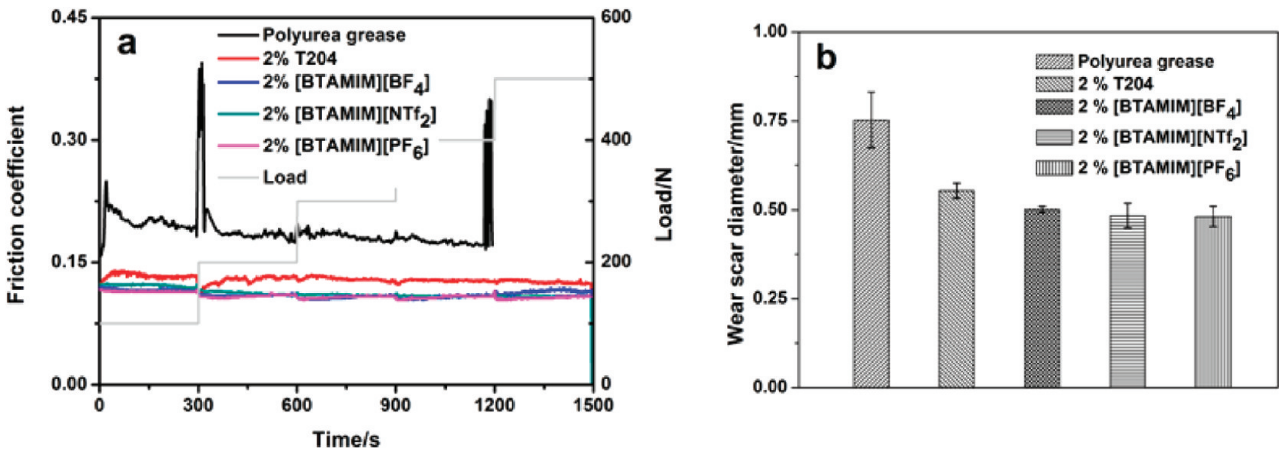


Figure 10. (a) Evolution of friction coefficient with time during a load ramp test from 100 to 500 N for polyurea grease with different additives at 150 °C. (b) Wear scar diameter of steel balls lubricated by polyurea grease with different additives at 150 °C. (load,100−500 N; stroke,1 mm; frequency, 25 Hz).

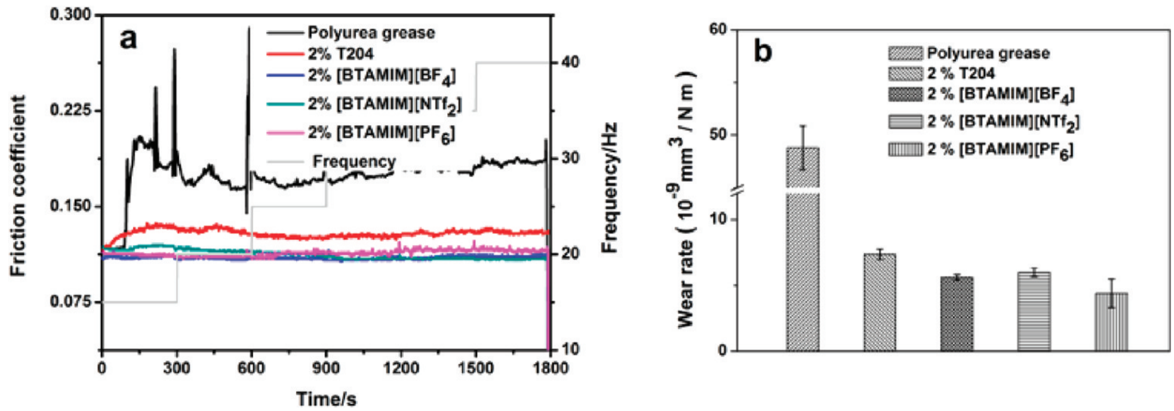


Figure 11. (a) Evolution of friction coefficient with time during a frequency ramp test from 15 to 40 Hz for polyurea grease with different additives at 150 °C. (b) wear rate of steel discs lubricated by polyurea grease plus 2 wt % each of T204, [BTAMIM][BF_4], [BTAMIM][NTf_2] and [BTAMIM][PF_6] at 150 °C. (load, 200 N; stroke, 1 mm; frequency, 15−40 Hz).

1 wt % alkyl imidazolium ILs in polyurea grease can significantly improve the friction reduction and antiwear properties of polyurea grease compared to base grease containing 1 wt % zinc dialkyldithiophosphate (T204), a very popular sulfur containing additive.[31] However, in addition to the above research, ILs as lubrication grease additives have rarely been studied.

The present benzotriazole-bearing imidazolium salt can be potential additives in polyurea grease. They might be a potential alternative in place of currently used sulfur containing additive, such as T204, a zinc dialkyldithiophosphates (that is normally used below a concentration of 2 wt %). We investigated the tribological behavior of ILs as additives in polyurea grease for steel/steel contacts. Figure 8 demonstrates the evolution of the friction coefficient with time for [BTAMIM][PF_6]+polyurea grease with different additive concentrations at 300 N and the measured wear rates of the steel discs after testing. The mixture exhibited a friction behavior that was comparable to the base oil when the concentration of [BTAMIM][PF_6] was 1 wt %, and both had long running-in time with larger friction coefficients. When the concentration of [BTAMIM][PF_6] reached 2 wt %, almost no running-in time was found, indicating they could form stable and successive boundary lubricating film instantly from the very beginning. They displayed very stable and low friction coefficient. Again, the timely supply of additive to the interface during friction could be effectively provided when the concentration of additive was above 2 wt %, whereas below critical concentration, additive deficiency at the interface occurred. We suppose that at low additive concentration, both the quality of boundary film and the formation speed is not that enough to provide friction reduction. As can be seen from Figure 8 that no further improvement in friction reduction and AW property can be observed after increasing the concentration of [BTAMIM][PF_6] above 2 wt %. It shows the best friction reduction and AW capability when the additive concentration of [BTAMIM][PF_6] reach 2 wt % under the testing conditions.

Figure 9 shows the variation in the friction coefficients and wear rate of the sliding discs under lubrication of polyurea grease plus 2 wt % T204, 2 wt % [BTAMIM][BF_4], 2 wt % [BTAMIM][NTf_2], and 2 wt % [BTAMIM][PF_6] at a constant load of 300 N and 150 °C. We can see that the friction coefficient and wear rate of ILs additives in polyurea grease lubricants are almost similar. The friction coefficients of polyurea grease and additives increase in the following sequence: 2 wt % ILs < 2 wt % T204 < polyurea grease. At this temperature, all the additives can form effective boundary lubricating films. This can be further strengthened by dramatically increased wear rate when lubricated by pure grease,

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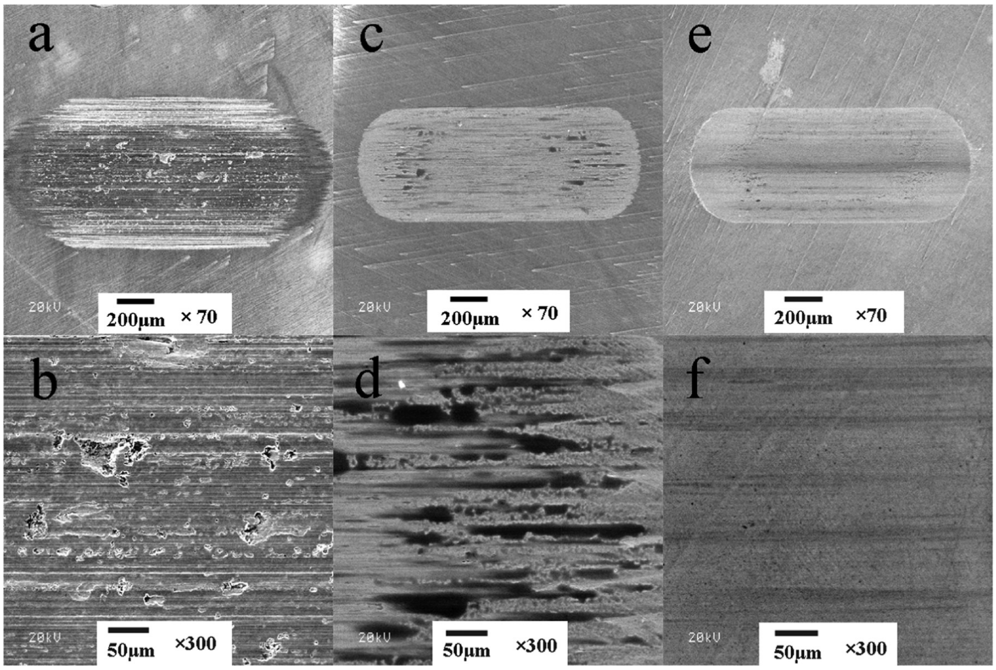

Figure 12. SEM morphologies of worn surfaces lubricated by polyurea grease and different IL additives: (a, b) polyurea grease, (c, d) 2 wt % T204, and (e, f) 2 wt % [BTAMIM][PF_6], (magnification on the above is 70×, and on the below is 300×; load, 300 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 150 °C).

whereas wear rates under lubrication of the additivated grease remained low level. The wear rate of the discs increased in the following orders: 2 wt % ILs < 2 wt % T204 < polyurea grease. It is clearly seen that 2 wt % ILs and 2 wt % T204 can improve the AW properties of polyurea grease by about 12 times for all three ILs and 8 times, respectively. So ILs as the additive in polyurea grease have better friction reduction and AW properties than T204. The prospect of the novel additive can be further valued by nonsulfur nature.

The boundary lubricating capability of an additive was further tested by varying applied loads and sliding speeds by changing the reciprocating frequencies. Good lubricants will not change friction coefficient very much when varying loads and sliding speeds. Figure 10a displays a load ramp test from 100 up to 500 N stepped by 100 N at 150 °C for five kinds of lubricants. The test duration for each load was 5 min. We can see that all the additivated grease register with a load-carrying capacity that is greater than 500 N at 150 °C. However, the maximum load-carrying capacity of pure polyurea grease was only 400 N. Both polyurea grease and that with 2 wt % T204 have a running-in period. The friction coefficient fluctuated all the time when lubricated with pure grease. It is seen that three kinds of ILs behaved similarly, and they had very stable friction and a much lower friction coefficient with the increase of load up to 500 N and even beyond as anticipated. Figure 10b displays that the wear scar (WSD) diameter of the steel balls increased in the order of: 2 wt % ILs < 2 wt % T204 < polyurea grease. The enhancement of the AW property is not that prominent, but the ability to stabilize friction is. All IL additives behaved quite similarly to each other.

Figure 11a shows a frequency ramp test from 15 up to 40 Hz by 5 Hz at a load of 200 N for different additives and polyurea grease at 150 °C. The test duration for each frequency was 5 min, and the corresponding wear rate after this experiment is given in Figure 11b. It is seen that polyurea grease and 2 wt % T204 also experienced a running-in time with larger friction coefficients. The addition of 2 wt % [BTAMIM][BF_4], 2 wt % [BTAMIM][NTf_2], and 2 wt % [BTAMIM][PF_6] could reduce friction and rendered a stable and smaller friction coefficient. Figure 11b demonstrates that the wear rate increased in the following sequence: 2 wt % ILs < 2 wt % T204 < polyurea grease. This is consistent with the results shown in Figures 9 and 10. Both the friction reduction and AW wear capability were very prominent during the test. The anticorrosive ILs had even lower friction coefficient and wear volumes than that lubricated by T204 under the same conditions. These results verify that ILs as additives in polyurea grease both in the constant load, variable load, and variable frequency tests have better tribological performance for steel/steel contacts at 150 °C. This may be attributed to high thermal stability, and the capability to form effective boundary films.[26,47]

The SEM morphologies of the worn surfaces of the steels lubricated with polyurea grease, 2 wt % T204 and 2 wt % [BTAMIM][PF_6] under the load of 300 N at 150 °C are shown in Figure 12, and all the wear scars were obtained under the same conditions. As shown in images a and b in Figure 12, the worn steel surface under lubrication of pure polyurea grease displays severe scuffing, with a much wide and deep wear scar as was measured with profilometer. The wear volume is very large. Images c and d in Figure 12 show the worn surfaces under the lubrication of 2 wt % T204. Despite of stable and low friction coefficient, the wear scar is very rough, but the diameter is considerably reduced. There are a lot of small furrows and scratches on the friction surface, indicating adhesive wear occurred. However, the worn surface under 2 wt % [BTAMIM][PF_6] lubrication (Figure 12e, f) is quite smooth and shows only slight grooves. This demonstrates the distinguishable AW properties of the synthetic ionic liquids and the result is also consistent with the measured wear rates in Figures 10 and 11.

3.5. Surface Analysis. To further explore the friction reduction and AW mechanism of the IL additives, we obtained the XPS spectra of neat [BTAMIM][PF_6] and the corresponding worn

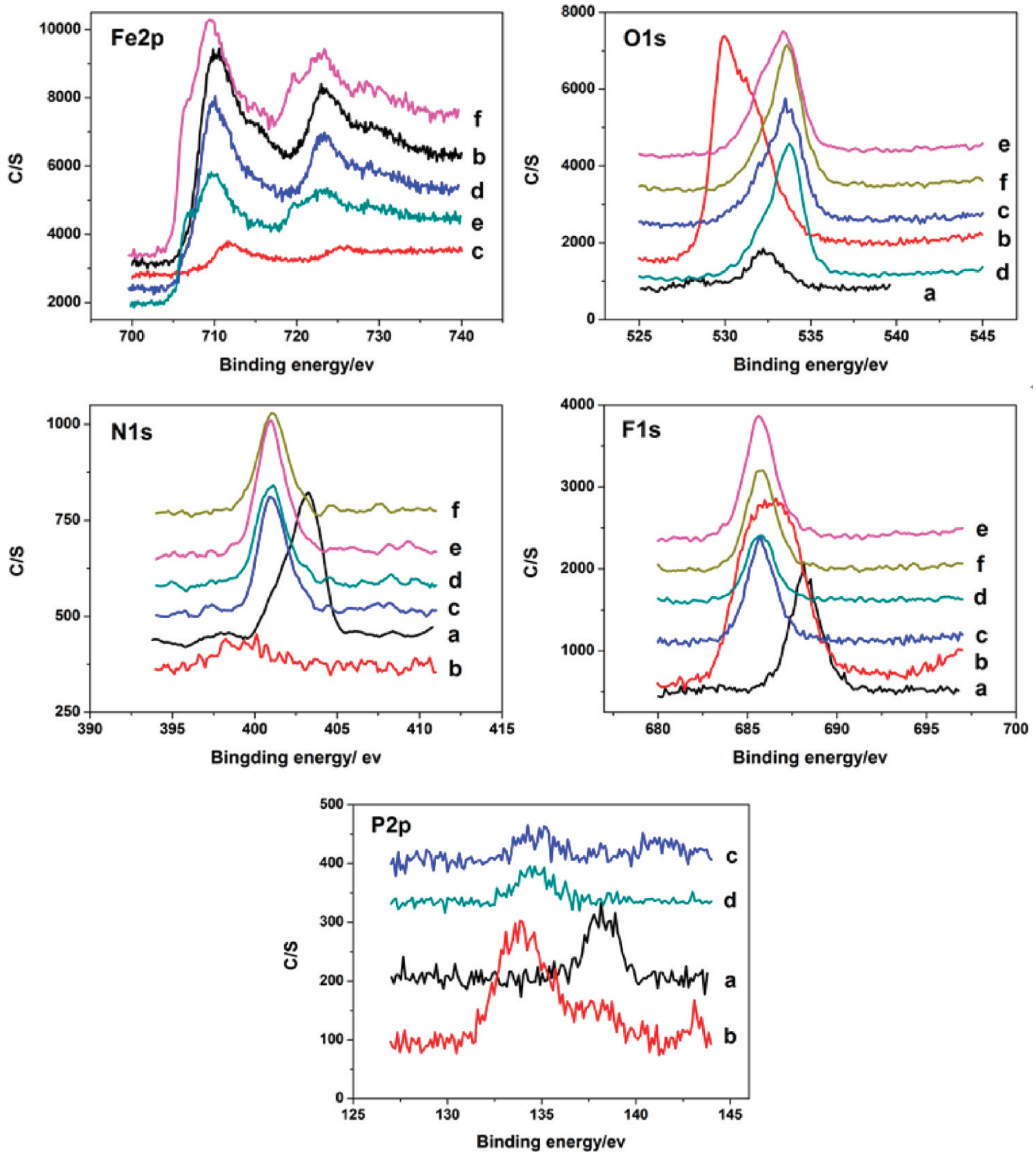

Figure 13. XPS spectra of Fe2p, O1s, N1s, F1s, and P2p of (a) neat ILs [BTAMIM][PF_6] and worn surfaces lubricated by (b) polyurea grease + 2 wt % [BTAMIM][PF_6] at 150 °C, (c) PEG + 1 wt % [BTAMIM][PF_6] at 20 °C, (d) PEG + 1 wt % [BTAMIM][PF_6] at 150 °C, (e) PEG + 1 wt % [BTAMIM][BF_4] at 150 °C, and (f) PEG + 1 wt % [BTAMIM][NTf_2] at 150 °C.

surface to verify the tribochemical products on friction surface for hypothesizing any possible tribochemical reactions (Figure.13). Figure 13a shows the XPS spectra of neat [BTAMIM][PF_6]. Figure 13c (at 20 °C) and Figure 13b, d−f (at 150 °C) display the XPS spectra of worn steel discs surfaces, and the binding energies of all samples are presented in Table 6. Table 6 shows that the binding energies of N, O, F, and P of the worn surfaces lubricated by [BTAMIM][PF_6] at 20 °C and those of [BTAMIM][PF_6] at 150 °C all differ from the binding energies of neat [BTAMIM][PF_6]. It is assumed that they were all involved in specific tribochemical reactions during the friction process and formed new compounds. It is interesting that the binding energies of Fe, O, F and N of the worn surfaces lubricated by 1 wt % [BTAMIM][PF_6], 1 wt % [BTAMIM][BF_4] and 1 wt % [BTAMIM][NTf_2] at 150 °C are similar to each other. This result shows that three kinds of additives on the worn surface had similar tribochemical reactions. However, we can also see that the binding energy of O, F, N, and P of worn surfaces lubricated by polyurea grease + 2 wt %[BTAMIM][PF_6] are different from those of PEG + 1 wt % [BTAMIM][PF_6], which shows that the base oils have influence on the tribochemical reactions of additives. Figure 13 shows the peaks of F1s at about 685.6 and 686.4 eV, which indicates the presence of fluorine anions, possibly due to the formation of ionic compounds on the worn steel surface, such as FeF_2.[48,49] In order to determine the actual types of reaction, the XPS of Fe2p was studied. As shown in Figure 13b−f, Fe2p appears at

Table 6. Binding Energies of Typical Elements from the XPS Measurements

		binding energy (eV)				
	additive	Fe	O	N	F	P
a	neat [BTAMIM][PF_6]		532.2	403.2	688.2	138.2
b	2% [BTAMIM][PF_6]	710.3, 723.2	530.0	399.2− 400.1	685.6− 686.9	133.7
c	1% [BTAMIM][PF_6]	711.5, 725.6	533.6	401.0	685.6	134.5
d	1% [BTAMIM][PF_6]	710.0, 723.1	533.7	401.0	685.6	134.5
e	1% [BTAMIM][BF_4]	710.0, 723.3	533.5	401.0	685.7	
f	1% [BTAMIM][NTf_2]	710.0, 723.1	533.7	401.0	685.6	

approximately 710.3, 711.4, 723.5, and 725.1 eV, which may correspond to FeF_2, Fe(OH)O, Fe_2O_3, and Fe_3O_4.[30,49] Additionally, the binding energies of Fe2p (Figure 13e, f) appear at 707 eV, which might attribute to metallic iron. This suggests that the films formed in 1 wt % [BTAMIM][BF_4] and 1 wt % [BTAMIM][NTf_2] were thinner than 1 wt % [BTAMIM][PF_6] under the same conditions, and not enough to form a protective boundary film, which is consistent with the tribological results: 1 wt % [BTAMIM][PF_6] had better friction reduction and AW properties than the other ILs. Figure 13b displays the N1s spectra of the worn surface at 399.2 eV, possibly corresponding to carbonitride and/or nitrogen oxide.[30] XPS peak of N 1s (Figure 13c−f) appears at the binding energies of 401 eV, which may correspond to nitrogen oxide or nitrogen double bond compounds.[30] This may indicate that ILs additives have physical adsorption on the worn surfaces. Figure.13b reveals that the O1s peak appears at 530.0 eV indicating the generation of complex oxide species. It has a difference from the binding energies of blank polyurea grease (O1s appearing 531.3 eV) indicating that under lubrication of polyurea grease the surface iron have experienced a completely different tribochemical reaction.[31,49] Almost no difference is observed in XPS peaks of O1s (Figure 13c-f) on the worn surfaces. The peaks of O1s appear at 533.4−533.7 eV, which may include P−O bonding, C−O bonding, and nitrogen transformation to nitrogen oxide.[48] Figure 13b reveals that the XPS spectra of P2p appear at 133.7 eV, which corresponds to $FePO_4$.[7,28,48] The peaks of P2p on the worn surface (Figure 13c,d) at 134.5 eV can be assigned to P−O bonding and phosphate with reference to the standard spectra of the elements.[49] The phosphorus compounds are only coming from the anions that under rigorous condition decompose and react with surface to form novel AW agents.

XPS analysis reveals that under a collective impact of high pressure, exoelectron emission, and frictional heat on the specimen surface, complicated tribochemical reactions occurred on the surfaces. Active elements F and P of the ILs additives in polyurea grease reacted with the fresh metal surface, forming Fe_2O_3, Fe_3O_4, FeF_2, and $FePO_4$ and compounds containing the P−O, which together with carbonitride significantly contributes to the friction reduction and antiwear properties.[48] However, not only could ILs as additive in PEG complicate tribochemical reactions occur, leading to a surface protective film composed of Fe_2O_3, Fe_3O_4, Fe(OH)O, FeF_2, phosphate, and compound containing the P−O bonding on the lubricated metal surface, but physical adsorption films containing nitrogen double-bond compounds also formed. Both benefit friction reduction and AW.

4. CONCLUSIONS

A series of imidazolium ILs bearing benzotriazole group, [BTAMIM][BF_4], [BTAMIM][NTf_2], and [BTAMIM][PF_6], were synthesized. They possess good miscibility with PEG and polyurea grease. Accelerated corrosion test and copper strip corrosion test revealed that the synthesized ILs had significant anticorrosion capacity due to the presence of benzotriazole groups. The addition of 1 wt % [BTAMIM][NTf_2] and [BTAMIM][PF_6] in PEG dramatically reduced the friction coefficient and wear volume. For polyurea grease, the addition of 2 wt % ILs additives had excellent friction reduction and antiwear performance. XPS analysis revealed that complicated tribochemical reactions occurred during the friction process. These reactions generated new compounds with substrate irons to prevent serious wear and improve the load carrying capacity. The incorporation of functional groups into ILs provides a synthetic route for solving problematic issues of ILs when they are used either as lubricants or for other uses.

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