**Table 2**
Viscosity–pressure coefficients of [BMIM][$NTf_2$] and PAO 4 cSt oil.

| Lubricant | 22 °C | 40 °C | 70 °C | 100 °C | 140 °C | 150 °C | 180 °C |
|---|---|---|---|---|---|---|---|
| [BMIM][$NTf_2$] | 11.1 | | | 6.5 | | 5.5 | |
| PAO 4 base oil | | 15.0 [29] | 12.4 [28] | 10.9 [29], 10.6 [28] | 9.4 [28] | | 8.4 [28] |

**Table 3**
Central lubricant film thickness ($h$) and lambda ratio ($\lambda$) in rolling–sliding tests at 100 °C.

| $U_e$ (m/s) | 0.1 | | 0.5 | | 1.0 | | 3.2 | |
|---|---|---|---|---|---|---|---|---|
| Lubricant | $h$ (μm) | $\lambda$ | $h$ (μm) | $\lambda$ | $h$ (μm) | $\lambda$ | $h$ (μm) | $\lambda$ |
| [BMIM][$NTf_2$] | 0.008 | 0.3 | 0.024 | 0.9 | 0.039 | 1.4 | 0.085 | 3.0 |
| PAO 4 base oil | 0.007 | 0.2 | 0.020 | 0.7 | 0.031 | 1.1 | 0.068 | 2.4 |

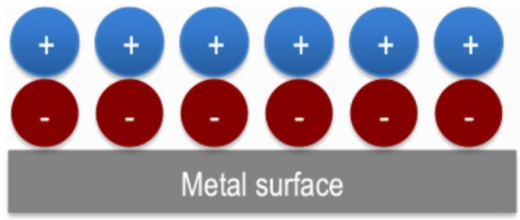


**Fig. 5.** Schematic of a layer-structured IL film on a metal surface.

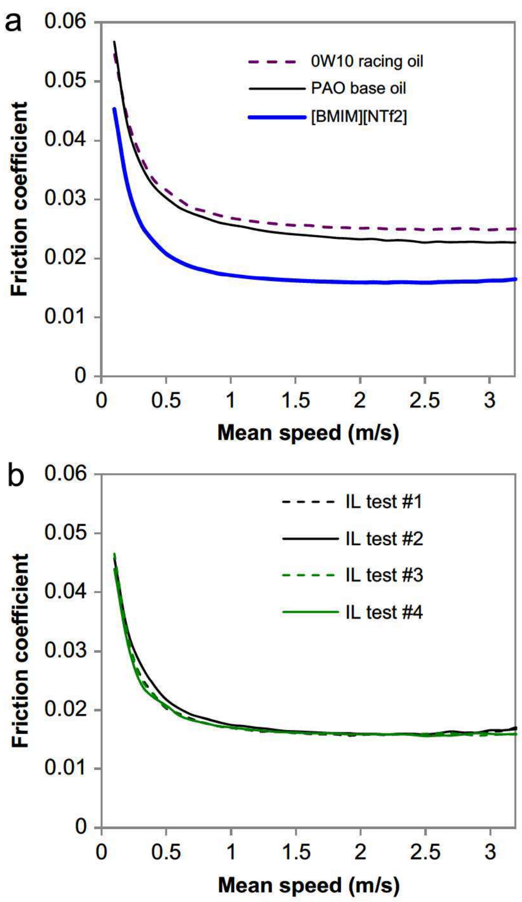


**Fig. 4.** Stribeck curves at 100 °C showing (a) lower ML friction for [BMIM][$NTf_2$] than those of baseline oils and (b) high repeatability from test to test for [BMIM][$NTf_2$].

Although [BMIM][$NTf_2$] has a higher dynamic viscosity (6.5 cP) than those of PAO 4 (3.0 cP) or 0W-10 (4.2 cP), it exhibited significant lower friction coefficient by ~30% in ML, as shown in Fig. 4a. ML can be considered as regions of EHL separated by scattered asperity contacts. The much lower $V$–$P$ coefficient of the IL compared to that of the PAO oil may help reduce the shear resistance in the EHL regions, as a result of a less-increased viscosity than those of the oils at the rolling–sliding contact. The viscosity response to shear is unknown for the IL but could play a role as well. For the asperity collisions, the friction is largely affected by the mechanical properties of the contact surfaces. When a metal surface is lubricated by an IL, a layer-structured IL film may hypothetically form on it by physical adsorption [10], as illustrated in Fig. 5. First, anions tend to be attracted by and adsorbed onto the naturally positively charged metal surface to form a mono-layer by Coulombic forces. Cations then form a second layer due to Coulombic forces and, sometimes, weak hydrogen bonds. An ordered multi-layer film may build up that possesses low traction (slip) at the interface under sliding, which may help reduce the ML friction.

### 3.3. *Lubricating behavior–BL*

The IL has demonstrated a lower friction coefficient in the ML regime; however, its low $V$–$P$ coefficient increases the wear challenge in BL. To investigate the lubricating behavior in BL, scuffing tests were conducted at 150 °C using a pin-on-disc unidirectional sliding configuration under starved lubrication. The composite roughness was estimated to be 0.066 μm. The viscosity and $V$–$P$ coefficient of [BMIM][$NTf_2$] at 150 °C were measured at 3.1 cP and 5.5 $GPa^{-1}$, respectively. The PAO's viscosity and $V$–$P$ coefficient at 150 °C were not readily available and so were interpolated from their data at 100, 140, and 180 °C [28]. For both the IL and the PAO oil, the lubricant film thickness was calculated at below 0.01 μm and the lambda ratios were about 0.1 ($<1$)– confirming the BL regime.

In the scuffing tests, the friction coefficient for all lubricants started at around 0.1, the typical value in BL, and showed a rapid transition to above 0.5 when scuffing occurred, as shown in Fig. 6. In both repeat tests, [BMIM][$NTf_2$] resisted the scuffing much longer than did the oils (it was unexpected that the 0W-10 racing engine oil had the worst performance, with scuffing occurring in a very early stage of testing). It is known that anti-scuffing/anti-wear performance largely depends on the lubricant's ability to form a protective tribo-film on the contact surfaces. For steady-state BL, direct evidence of tribo-film formation has been revealed in the literature for oil lubricants containing zinc dithiophosphate (ZDDP) [31,32] and ILs as either neat lubricants [21] or oil additives [4].

To study the wear mode and tribo-film, the worn surface morphology was first examined. Fig. 7 compares the SEM top views (300× and 1000×) of the wear tracks on the discs tested in the IL and the oils. The arrow on each image indicates the sliding direction. The scuffing damage on all three wear tracks appears to be dominated by discrete material spallation upon lubricant failure, suggesting adhesive wear in a "stick–slip" mode. The scuffed zone produced in the IL lubricant (Fig. 7a) is narrower and the surface damage seems less severe compared with the scuffed areas produced in the two hydrocarbon oils (Fig. 7b and c).

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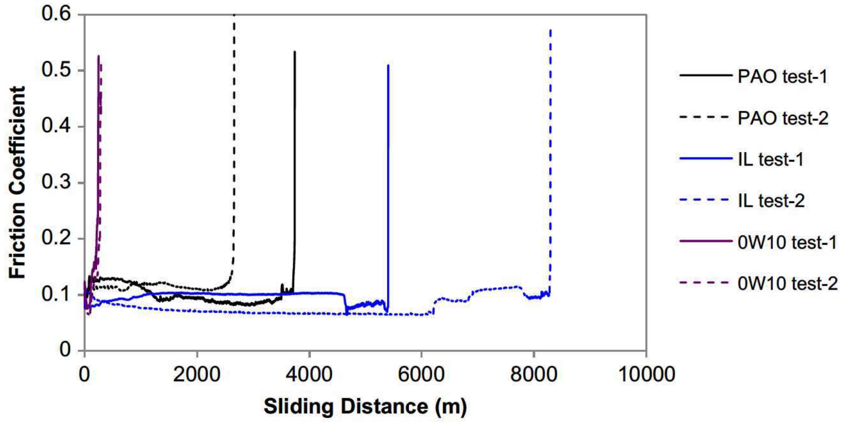


**Fig. 6.** Friction traces of BL scuffing tests showing higher scuffing resistance of [BMIM][$NTf_2$] than those of baseline oils.

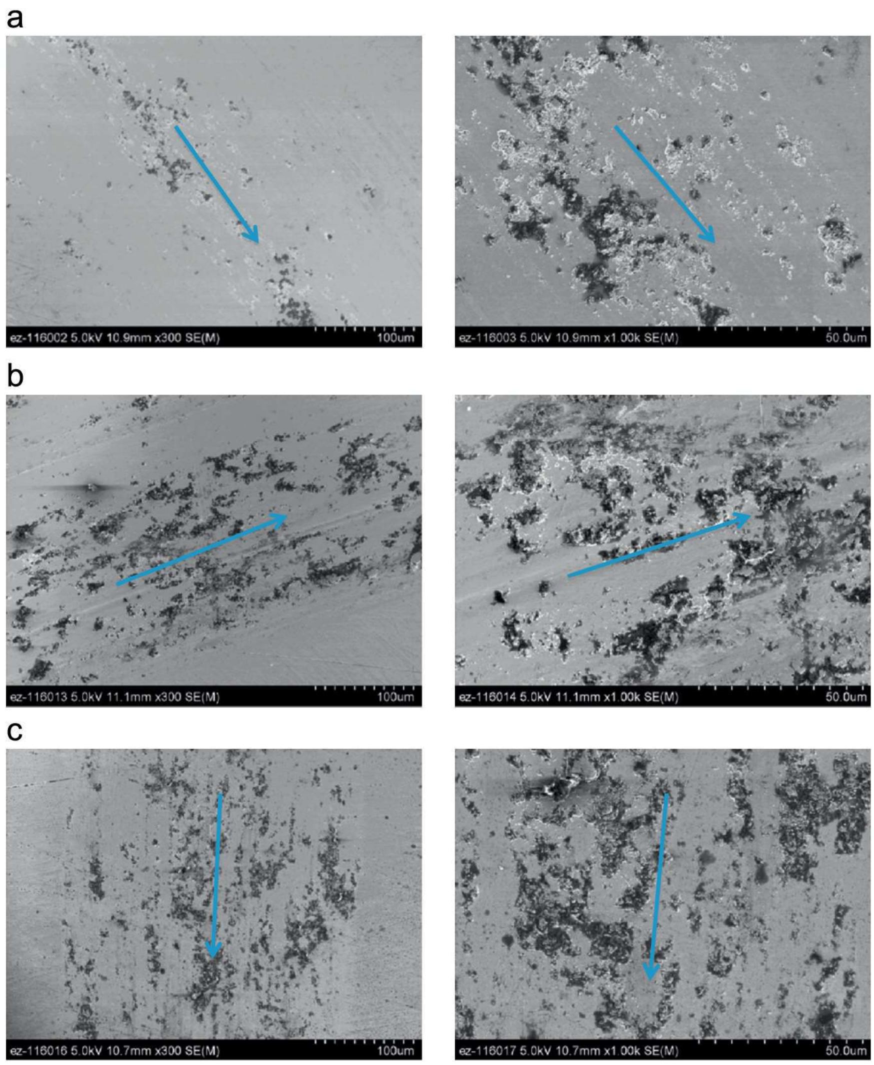


**Fig. 7.** SEM top views (300 × and 1000 × ) of the disc wear tracks tested in (a) [BMIM][$NTf_2$], (b) PAO 4 cSt base oil and (c) 0W-10 racing engine oil. The arrow on each image indicates the sliding direction.

TEM and EDS were used for further examination from the cross section, as shown in Fig. 8. Aided by FIB, thin sections were lifted from the wear tracks along the sliding direction, as illustrated in Fig. 2. All samples were extracted from relatively smooth, less-scuffed regions. Fig. 8a shows a TEM image and an EDS element map from the cross section for the disc worn surface tested in [BMIM][$NTf_2$]. A thin tribo-film was observed on the surface under TEM and the sulfur concentration as detected by EDS suggests that it is a result of the tribochemical reactions between the steel surface and the IL. The tribo-films formed in bis(trifluoromethylsulfonyl)imide ILs usually contain fluorine compounds [18,19,21], but fluorine was not resolved in the EDS elemental mapping because the x-ray energy peaks of fluorine and iron largely overlap. The ~20 nm tribo-film presented here is, however, significantly thinner than the 60–100 nm

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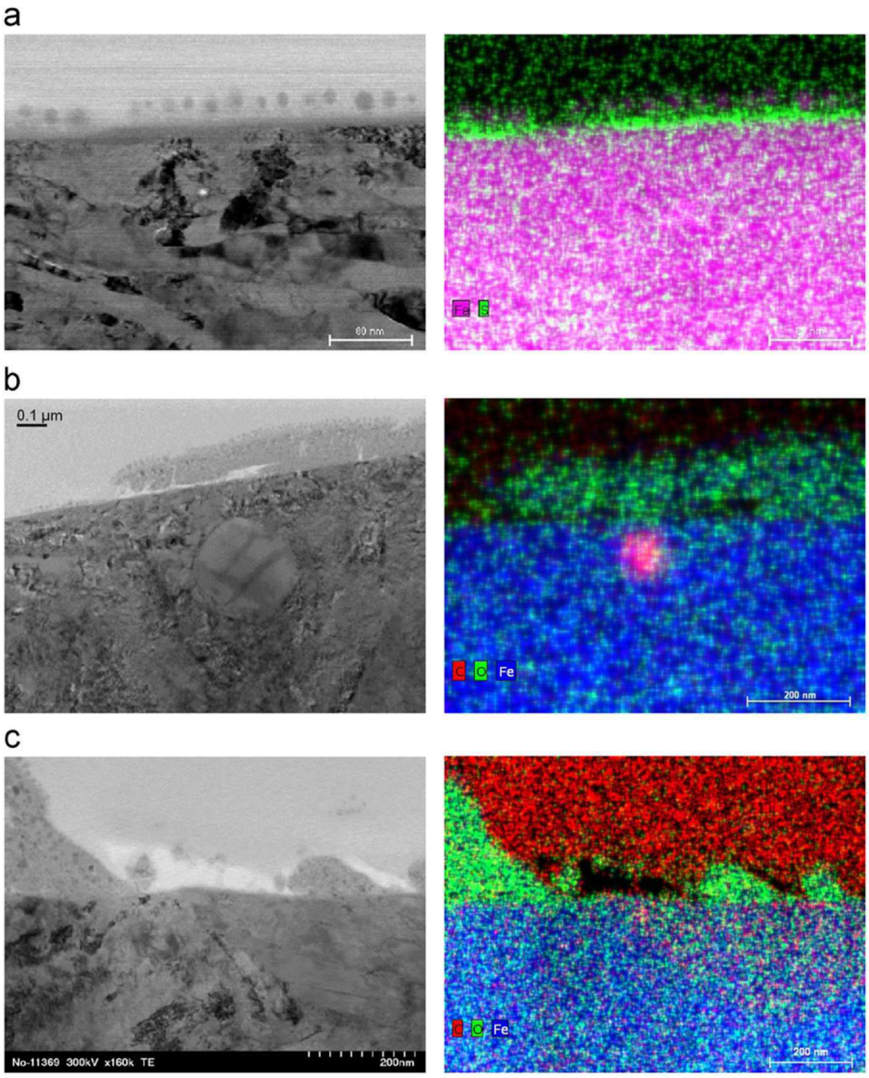


**Fig. 8.** TEM images and EDS element maps of the cross sections of the disc wear tracks tested in (a) [BMIM][$NTf_2$], (b) PAO 4 cSt base oil and (c) 0W-10 racing engine oil.

tribo-film reported [21] for a steel surface (non-scuffed) under steady-state lubrication by an IL with a longer alkyl on the cation but otherwise identical in molecular structure to [BMIM][$NTf_2$]. Although we cannot entirely rule out the effect of the IL molecular structure on the tribo-film thickness, we attribute the thinner tribo-film primarily to the scuffing damage. The tribo-film formation and removal (due to wear) are two competing processes and eventually reach equilibrium in steady-state BL. When scuffing occurs, the wear rate increases by orders of magnitude, breaking the equilibrium and quickly destroying the tribo-film. As a result, no tribo-film was found on the wear tracks tested in the two oils, as shown in Fig. 8b and c. EDS results suggest that the loose material on the oil-lubricated surface is composed of oxides and no active lubricant agent such as phosphorous or sulfur was detected. The sustained tribo-film in IL lubrication (though relatively thin) suggests stronger tribo-film forming activity, which may be responsible for the IL's higher resistance to scuffing and surface damage propagation compared to the hydrocarbon oils.

## 4. Conclusion

A IL [BMIM][$NTf_2$] was evaluated as a candidate lubricant. Its viscosity at 100 °C is 4.7 cSt, similar to that of PAO 4 cSt base oil and 0W-10 racing engine oil, but it has a higher viscosity index than those of the oils. This IL is more thermally stable than hydrocarbon oils: it can sustain up to 472 °C whereas most oils decompose at around 250 °C. The lubricating performance of [BMIM][$NTf_2$] was benchmarked against that of PAO and 0W-10 oils under both ML and BL. The ML friction coefficient of the IL was consistently lower than that of the oils by ~30%. This is possibly due to the IL's lower *V–P* coefficient and a hypothetical layered-structure boundary film. Although a low *V–P* coefficient usually is a challenge to BL, the IL exhibited higher scuffing resistance and less surface damage than oils did in the scuffing tests. This is attributed to the formation of a protective tribo-film in IL lubrication, which was revealed by FIB-aided cross-sectional TEM microstructural examination and EDS analysis.

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