A low-viscosity ionic liquid demonstrating superior lubricating performance from mixed to boundary lubrication

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ARTICLE INFO

ABSTRACT

This study reports on an ionic liquid (IL) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as a promising engine lubricant candidate . This IL has a relatively low viscosity of 4.7 cSt (similar to 0W-10 racing engine oil), a low viscosity–pressure (V–P) coefficient of 6.5 GPa^{-1} at 100 °C, a high viscosity index of 159, and a high onset decomposition temperature of 472 °C. The ionic liquid delivers substantially lower friction in mixed lubrication (ML) and provides better scuffing protection in boundary lubrication (BL) than those of hydrocarbon lubricants with similar viscosities. The low ML friction is possibly attributed to its low V–P coefficient and a hypothetical multi-layer boundary film at the interface. In BL, the tribochemical reactions between the IL and the contact surfaces to form a protective tribo-film are believed to be responsible for the IL's superior anti-scuffing behavior. Microstructural examination and chemical composition analysis were conducted on the wear scars from both the top surface and the cross section to study the wear mode and characterize the tribo-film and near-surface structure.

1. Introduction

Engine and power train parts like piston rings and cylinder bores, valve guides, cams and tappets, fuel injector pumps and plungers, transmission gearing, and face seals are all affected to some degree by friction [1]. The magnitude of such friction-induced losses depends on engine design, materials of construction, operating conditions, and most importantly lubrication. Lubrication regimes [2] can be divided into four general categories: boundary (BL), mixed (ML), elastohydrodynamic (EHL), and hydrodynamic lubrication (HL), among which BL has the highest friction and wear.

Modern engines have been designed to minimize the contribution of BL, and the frictional energy loss is caused primarily by the traction resulting from shearing of the lubricant film in EHL. For example, at the interface of a piston ring against a cylinder liner, most of the stroke is under EHL. Since the friction force in EHL is due to resistance to shearing of the pressurized lubricant film at the sliding interface, a lubricant with lower viscosity at Hertzian pressure would, other rheology being equal, reduce the EHL friction and thus increase the engine mechanical efficiency. Over the last decade, the viscosity grade of standard internal combustion engine oils has been continuously reduced in an attempt to improve fuel economy, from SAE 10W-30 to 5W-30, 5W-20, and now 0W-20. On the other hand, the bearing interfaces under BL, such as the top ring reversal region inside the cylinder, set a floor for engine lubricant viscosity to prevent excessive wear. One approach to allowing the use of low-viscosity lubricants is advances in anti-wear additives [3–5]. Alternatively, developing new low-viscosity base lubricants to reduce hydrodynamic drag and meanwhile minimize the wear penalty is of great interest.

Ionic liquids (ILs) have been explored as a new category of lubricants since 2001 [6–8]. Much research focused on the lubricating behavior of ILs under BL and their tribo-chemical interactions with metallic surfaces [4–6,9–21]. Few studies, however, have investigated the friction behavior of ILs under ML or EHL [10,22,23] or the viscosity–pressure (V–P) coefficient [24–26]. This study reports on a low-viscosity IL that has demonstrated promisingly low friction in ML and superior anti-scuffing characteristics in BL. The low ML friction may be attributed to its low V–P coefficient and helped by a hypothetical layered-structure boundary film physically adsorbed on the

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contact surfaces, and the high scuffing resistance is enabled by the tribochemical reactions with the contact surfaces to form an anti-wear tribo-film.

2. Experimental

Fig. 1 shows the molecular structure of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf$_2$]). It was purchased from Sigma-Aldrich with $\geq$ 98% purity and $\leq$ 0.5% water.

Two hydrocarbon lubricating oils, Mobil 1™ poly-alpha-olefin (PAO) 4 cSt base oil (generously provided by ExxonMobil) and Royal Purple™ 0W-10 racing engine oil, were selected to compare with [BMIM][NTf$_2$] because they all have similar kinematic viscosities at 100 °C (see Table 1). Viscosities of the IL and reference oils were measured in the temperature range of 0–100 °C using a Petrolab MINIVIS II viscometer base with the falling-ball technique. Each measurement used 0.5 mL of fluid and involved at least four repeated ball drops to ensure a $< 2\%$ statistical deviation.

The viscosity–pressure coefficient of [BMIM][NTf$_2$] at various temperatures was determined following the procedure described in [27,28] using a high-pressure (up to 400 MPa), and high-temperature (up to 150 °C) viscometer at the Center for High-Pressure Rheology, Georgia Institute of Technology, to measure the limiting-low-shear viscosity. The V–P coefficient α^* here is defined by the reciprocal asymptotic isoviscous pressure coefficient as shown in Eq. (1) [2], which is the coefficient employed in the Hamrock and Dowson formulas [2] for lubricant film thickness calculations:

$$\alpha^* = \frac{1}{P_{iv,as}} = \left[\eta_0 \int_0^\infty \frac{d\eta}{\eta(P)} \right]^{-1} \quad (1)$$

where $P_{iv,as}$ is the asymptotic isoviscous pressure [2], $\eta(P)$ is the lubricant low-shear viscosity under pressure (p), and η_0 is the lubricant atmospheric low-shear viscosity.

Thermogravimetric analysis (TGA) was used to determine the decomposition temperature of the ionic liquid and oil lubricants. Tests were carried out on a TA Instruments TGA-2950 at a 10°C/min heating rate in a nitrogen atmosphere.

The corrosivity of the IL was evaluated using a procedure similar to that described in the ASTM standard D 6594-08,

Fig. 1. Molecular structure of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

"Standard Test Method for Evaluation of Corrosiveness of Diesel Engine Oil at 135 °C." Gray cast iron and aluminum sticks were dipped into the IL at a constant temperature of 135 °C for 7 days. By the end of the test, the aluminum and iron surfaces appeared intact without evidence of corrosion.

Tribological evaluations were conducted in lubrication regimes from hydrodynamic to boundary. Stribeck curves were generated using ball-on-disc rolling–sliding tests on a PCS Instrument Mini Traction Machine (MTM2) tribotester. Both the ball and disc were made of AISI 52100 steel. The grade-10 bearing ball had a nominal diameter of 19.05 mm, surface hardness of 64 Rc, and maximum arithmetic average roughness (R_a) of 0.025 μm. The disc was 46 mm in diameter (wear track diameter: 42 mm) with a measured hardness of 62.5 Rc and R_a of 0.010 μm. The contact area was submerged in a tank of 40 mL lubricant. Tests were conducted under a constant load of 75 N at 100 °C. The slide-to-roll ratio (SRR), as defined in Eq. (2), was maintained at a constant 50%, and the mean velocity (U_e) was started at 3.2 m/s in each test and gradually decreased to 0.1 m/s by the end of the test. The dwell time at each speed was 6 s.

$$SRR = \Delta U / U_e \quad (2)$$

where $\Delta U = U_1 - U_2$ is the sliding velocity and $U_e = (U_1 + U_2)/2$ is the mean velocity.

The boundary lubrication behavior was evaluated using a pin-on-disc unidirectional sliding test under starved BL at 150 °C on a CSM Instrument High-Temperature Tribometer. The material pair was again self-mated AISI 52100 steel. The pin was a grade-25 bearing ball with a 10 mm nominal diameter with maximum R_a of 0.051 μm. The disc was 30 mm in diameter with R_a of 0.020 μm. Only two drops of lubricant were applied prior to each test and no lubricant was added during the test. Tests were conducted under a constant load of 4 N and a sliding speed of 0.5 m/s for 10,803 m of sliding if no scuffing failure; otherwise they were stopped at the onset of scuffing (captured by a sudden rise of the friction coefficient to > 0.5). For both the tribological tests, at least two repeat tests were conducted under each test condition. The friction force was acquired in situ during the test and normalized by the normal load to calculate the friction coefficient.

Worn surface morphology was examined using scanning electron microscopy (SEM). Transmission electron microscopy (TEM) and energy-dispersive x-ray spectroscopy (EDS) were used to study the nanostructure and chemical composition of the tribo-film and near-surface zone from the cross section. TEM samples were prepared using a Hitachi NB-5000 dual-beam focused ion beam (FIB) system with a gallium source to extract thin cross-sections of the disc wear tracks generated by the scuffing tests. A thin layer of carbon and then a second layer of tungsten were deposited onto the surface prior to the FIB process to protect the surface structure. The FIB lift-out and sample thinning process are illustrated in Fig. 2. The SEM system was a Hitachi S-4800 field-emission SEM and the TEM system was a Hitachi HF-3300 TEM/STEM at 300 kV (1.3 Å resolution) equipped with a Bruker solid-state EDS detector with a 30 mm^2 active area. All surfaces were
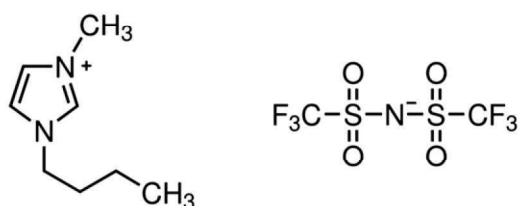
Table 1
Physical properties of [BMIM][NTf$_2$] and baseline oils.

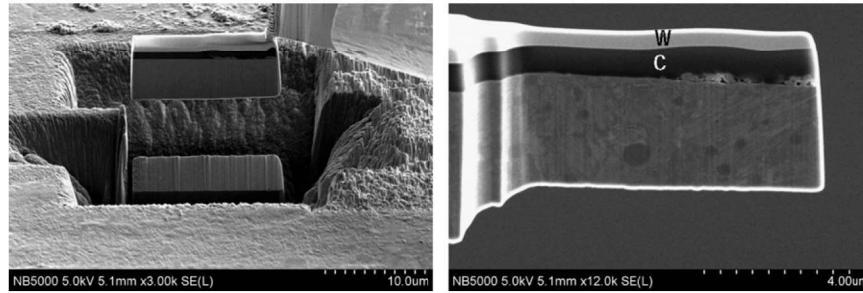| Lubricant	Density (g/ml, @23 °C)	Dynamic viscosity (cP)				Kinematic viscosity (cSt)	Viscosity index	Decomposition temperature (°C)
		0 °C	23 °C	40 °C	100 °C	100 °C		
[BMIM][NTf$_2$]	1.44	207.6	56.8	28.4	6.5	4.6	159	472
PAO 4 base oil	0.80	95.2	27.6	14.0	3.0	3.9	111	250
0W-10 engine oil	0.87	158.7	44.0	21.4	4.2	5.0	128	236

Fig. 2. TEM sample preparation using FIB: (a) a thin cross-section lifted out from the worn surface lubricated by 0W-10 engine oil and (b) sample thinning.
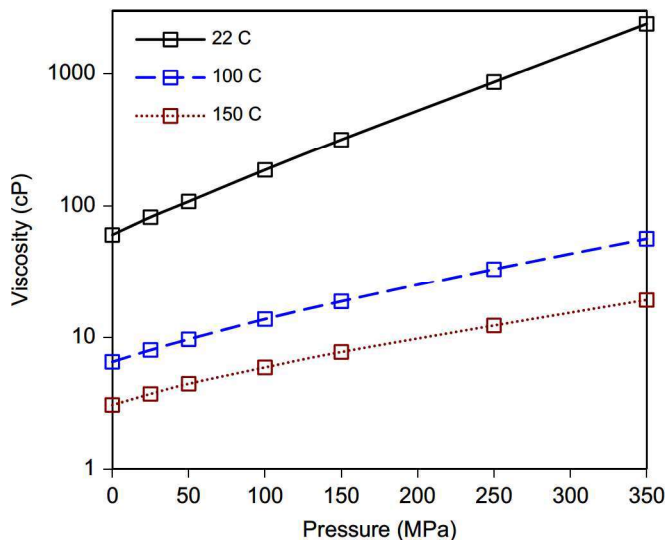

Fig. 3. Viscosity–pressure curves of [BMIM][NTf$_2$] at various temperatures.

carefully cleaned using acetone followed by isopropanol and dried prior to microscopic examinations.

3. Results and discussion

3.1. Physical properties

Table 1 compares the density, viscosity, viscosity index, and decomposition temperature of the IL and the two hydrocarbon oils. The density of [BMIM][NTf$_2$] is higher (1.44 g/ml) than that of the oils. The IL has excellent thermal stability and does not decompose until above 472 °C. This onset-of-decomposition temperature is much higher than that of the two baseline oils, PAO 4 cSt base oil and 0W-10 racing engine oil (250 and 236 °C, respectively). The dynamic viscosity of the IL at 100 °C is higher than that of the oils but the kinematic viscosity falls in between those of the two oils. The viscosity index (VI=159) of the IL is substantially higher than that of the PAO base oil (VI=111) or the formulated 0W-10 racing engine oil (VI=128).

The measured viscosity–pressure curves of [BMIM][NTf$_2$] at three temperatures are shown in Fig. 3. Based on the measurements, the V–P coefficient α^* was calculated (using Eq. (1)) as 11.1, 6.5, and 5.5 GPa^{-1} at 22, 100, and 150 °C, respectively. These values are substantially lower than the V–P coefficients of common hydrocarbon lubricating oils (including mineral oils and PAOs), which are reported in the range of 15–25 GPa^{-1} at room temperature and 10–15 GPa^{-1} at 100 °C [28–30]. Specifically, the V–P coefficient α^* of the PAO 4 cSt base oil was reported to be 15.0 and 10.9 GPa^{-1} at 40 and 100 °C in [29] and 12.4, 10.6,

9.4, and 8.4 GPa^{-1} at 70, 100, 140, and 180 °C in [28], respectively. The V–P coefficients of the ionic liquid and PAO 4 cSt oil are compared in Table 2 for readers' convenience. A low V–P coefficient is usually considered as a two-edged sword. The less-increased viscosity under the contact pressure may lead to a lower friction coefficient under EHL and ML, if the trend persists to the contact pressure (1.3 GPa for the rolling–sliding tests in this study). On the other hand, a low V–P coefficient is also expected to decrease the lubricant film thickness, challenging the wear protection.

3.2. Lubricating behavior–ML

In theoretical modeling, the minimum lubricant film thickness is designated for lambda ratio calculation to determine the lubrication regime. In practical situations, the central film thickness is more often used because the lubricant film between the surfaces in relative motion has an almost constant thickness and the central value can well represent much of the Hertzian contact zone [2]. For the rolling–sliding tests in this study, the central lubricant film thickness (h) was estimated using the Hamrock and Dowson formulas [2] for the IL and the PAO oil at the mean speeds of 0.1, 0.5, 1.0, and 3.2 m/s, as shown in Table 3 (note that the 0W-10 engine oil is multigrade in viscosity and so the classical film thickness formulas do not apply). Since the bearing balls in grades 10 and 5 have R_a tolerances of 0.025 and 0.013 μm, respectively, we assume the R_a of the grade 10 test ball at the median point to be 0.019 μm. In general, R_q is 20–40% higher than R_a and here we assume $R_q \approx 1.3 R_a$. Thus, the composite roughness σ of the contact surfaces, as defined in Eq. (3), was estimated to be 0.028 μm. The lambda ratio ($\lambda = h/\sigma$) was computed accordingly and is shown in Table 3. The lambda ratios suggest that the rolling–sliding tests started at ML with relatively high lambda ratios (near EHL) at 3.2 m/s and transited to BL between 1.0 and 0.5 m/s.

$$\sigma = \sqrt{R_{q,1}^2 + R_{q,2}^2} \qquad (3)$$

where the $R_{q,1}$ and $R_{q,2}$ are the *root-mean-square* average roughness of the contact surfaces.

The measured Stribeck curves of [BMIM][NTf$_2$] and baseline oils from the rolling–sliding tests are compared in Fig. 4a, where each curve represents an average of 2–4 repeat tests. High repeatability was observed as demonstrated by the four curves for [BMIM][NTf$_2$] in Fig. 4b. For all lubricants at the mean speed of 1.0 m/s or above, the friction coefficient was relatively stable and below 0.03, a typical level for ML with a relatively high lambda ratio (near EHL). The rapid change of friction coefficient from 0.02–0.03 to ~0.05 suggests a transition from ML to BL. The experimental observations in Fig. 4 are in line with the predicted lubrication regimes in Table 3.