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Inorganic nanoparticle-based ionic liquid lubricants

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ABSTRACT

This work deals with the tribological properties of recently described mixtures of nanoparticles (NPs) and ionic liquids (ILs), specifically mixtures of SiO_2 (silica) nanoparticles and 1-butyl-3-methylimidazolium (trifluoromethysulfony)imide. Friction force profiles, kinetic friction coefficients, friction traces, rheological properties, and wear behavior of these mixtures were compared with that of the pristine ionic liquids at various concentrations of nanoparticles for a tribo-pair of stainless steel ball and a steel surface. It was shown that NP concentration significantly influences the tribological properties of the NP-IL mixtures: the friction coefficient for the optimum NP concentration (0.05 wt%) was ~35% less than that for high NP concentrations (> 3 wt%) and 25% less than that for low NP concentrations (< 0.01 wt%). At the optimum NP concentration, while the friction force was slightly lower for NP-IL mixture at low loads, the friction force was about 28% lower for NP-IL mixture at high loads, compared to the pristine ionic liquid. In addition, the wear volume was found to decrease by 24% upon the addition of the optimum amount of nanoparticles into ionic liquid. Overall, this study concludes that promising tribological properties of ionic liquids can be further enhanced by incorporating nanoparticles into ionic liquids.

1. Introduction

Ionic Liquids (ILs) are a relatively new class of materials that consist entirely of ionic species with a melting point lower than 375.15 K. Owing to their relatively low vapor pressure, they have been of considerable interest to chemists and green chemistry since they cannot emit volatile organic compounds [1]. Other interesting properties of ILs include non-flammability, high-thermal and chemical stability, low melting point, and wide ranges of viscosity to name a few [2,3]. These properties have enabled them to be potential candidates in various applications such as solvents for synthesis, catalysis, analytical chemistry, space and electronics applications [4–6]. In addition, the aforementioned properties of ILs are highly desired in the field of tribology [7]. While the very first attempt to use ionic liquid as lubricant was described in 1961 [8], it was not until almost forty years later that ILs were broadly recognized as potential lubricants [9]. Since then, tens of articles have been published in various journals on the evaluation of the tribological properties of ionic liquids [9–21].

Past decades have witnessed an explosive growth in studies focusing on the tribology of inorganic nanoparticles that are dispersed in base oils such as paraffin oil and polyalphaolefins [22–36]. These studies have shown that they deposit on the rubbing surface and improve the tribological properties of the base oil, displaying superior friction and wear reduction characteristics. Considering the promising results of nanoparticles in improving lubrication properties of base oil, we hypothesize that the dispersion of inorganic nanoparticles in ionic liquids can improve their tribological properties. To test this hypothesis, we investigate the tribological properties of spherical SiO_2 (silica) nanoparticles dispersed in the ionic liquid 1-butyl-3-methylimidazolium (trifluoromethysulfony)imide (BMIM TFSI) in comparison to the pristine ionic liquid for steel/steel contact under ambient conditions.

2. Experimental details

2.1. Materials

All materials were used as received. The ionic liquid 1-butyl-3-methylimidazolium (trifluoromethysulfony) imide (BASF quality, ≥98%) was purchased from Sigma Aldrich. Silicon dioxide nanopowder (10–20 nm in size) was also purchased from Sigma Aldrich. Stainless steel sheets with a mirror polish were purchased from Metals Depot (Winchester, KY).

2.2. Surface preparation

The steel sheets were cut in the shape of a 2 cm × 2 cm square to form the substrate. Prior to testing, the substrate was cleaned with acetone and blown dry with nitrogen. After testing and shearing the surfaces, the lubricant was removed by rinsing the substrate

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with acetone, and the substrate was stored for post-shearing characterization.

2.3. Friction measurements

Friction response was undertaken by a nano-tribometer (CSM Instruments, Switzerland) at a constant sliding speed of 0.0005 m/s and a total distance of 0.05 m. Tests were conducted using a very smooth stainless steel sphere (diameter ~2 mm) with *rms* roughness of 2.14 ± 0.45 nm along with a medium-load cantilever with normal and tangential stiffnesses of 150 N/m and 128 N/m, respectively. All tests were conducted with normal loads of 2.5, 5.0, 10.0, 15.0, 20.0, and 40.0 mN, and each load was applied at least three different times at various locations on the sample until the coefficient of variation was less than 0.1. In this study, two different types of lubrication conditions were investigated: simple lubrication (steel surfaces across IL), and composite lubrication (steel surfaces across silica nanoparticles dispersed in IL). For the composite lubrication case, various concentrations of silica nanoparticles were used in an effort to understand the effect of concentration on the lubricating behavior. Throughout this study, the humidity was maintained between 45–50%.

2.4. Rheological Measurements

Rheological measurements were performed with an Anton Paar Rheometer Physica MCR 301(Ashland, VA). Viscosity data were collected for a range of shear rates extending from 0.01 s^{-1} to 1000 s^{-1}. Each data point corresponds to an average of three different readings. The experiments were conducted using Neat IL, and 3 different nanoparticle concentrations (0.05 wt%, 1 wt%, and 5 wt%) dispersed in IL at 22 °C. Each of these conditions was repeated three times for statistical analysis.

2.5. X-ray photoelectron spectroscopy (XPS)

Tribochemical changes were characterized using KRATOS Axis Ultra Imaging Instrument (Kratos Analytical, Manchester, UK). Photoelectrons were excited using an incident monochromated X-Ray beam emanating from the Al target (1486.71 eV, 8 mA). The beam was focused on a 300 μm × 700 μm area of the sample surface with high resolution scans (40 eV pass energy) for all surface elements. The spectra were reported as an average of three measurements for each condition. XPS characterization was performed on different samples, specifically the contact and non-contact areas of steel surfaces that were sheared with IL and IL+SiO_2 NPs.

3. Results and discussion

3.1. Effect of nanoparticles on friction

Fig. 1. displays a friction force versus normal load plot for the ionic liquid with and without NPs. It was found that at normal loads less than 15 mN, the frictional forces for the composite lubrication condition are slightly lower than those of the simple lubrication condition. However, the effect of incorporating 0.05 wt% silica nanoparticles into the ionic liquid on the frictional forces becomes more pronounced at loads above 15 mN. Furthermore, it was observed that, for the simple lubrication case, the friction force was a linear function of the normal load, which is in accordance with the well-known Amontons' law [37]. On the other hand, for the composite lubrication case, a deviation from linearity is observed at high loads.

One possible explanation for these behaviors is related to the formation of particulate network by the silica nanoparticles. It is known that bare nanoparticles dispersed in ILs adhere to each other and form aggregates leading to the formation of particulate network and subsequently the gelation of the ionic liquid [38,39]. This network, which confers a higher viscosity to the ionic liquid, presumably leads to an enhancement of the mechanical properties (i.e. load carrying capacity) of the composite lubricant [38]. At low loads, the particulate network may be maintained for the duration of the shearing test due to insufficient loading force (i.e. low normal load). During this period the nanoparticulate network may not fully penetrate the interface or fill the valleys (due to the large network size). Therefore, the slight reduction in frictional forces at low loads may be attributed to the increased load carrying capacity of the lubricant. However, at high loads there is a high possibility that the particulate network is disrupted more rapidly as shown in Fig. 2., leading to high fluidity under shear [38] and allowing the nanoparticles to smooth out the valleys, thereby providing better lubrication. This explanation agrees well with previous studies on non-adhering nanoparticles that act as effective lubricants when they are not squeezed out of contact regions of mating surfaces i.e. when they prevent two surfaces from forming cold-welds [27,34,40,41].

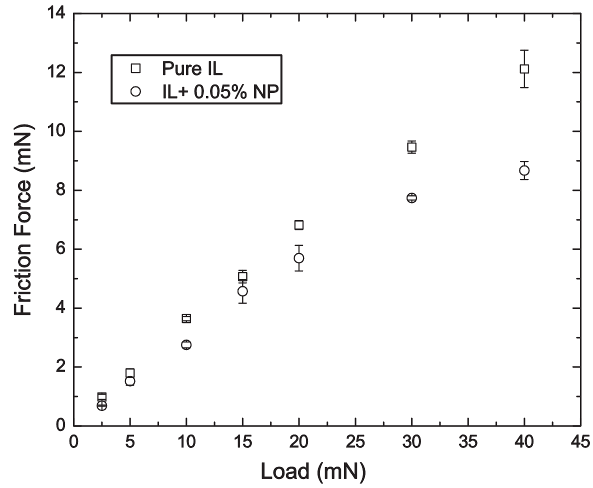

Fig. 1. The friction force as a function of load for simply and compositely lubricated conditions.

3.2. Effect of nanoparticle concentration

Eight different concentrations ranging from 0.01 wt% to 5 wt% were used in this study in order to cover three different concentration regimes: dilute, intermediate and concentrated solutions. As can be seen in Fig. 3., the friction coefficient decreases with increasing nanoparticle concentration and then increases gradually as the nanoparticle concentration rises above 0.05 wt%. Therefore, 0.05 wt% is considered to be the optimal concentration of silica nanoparticles in the ionic liquid.

These results can be explained as follows: at very low concentrations, the nanoparticle coverage is low and therefore there are not enough nanoparticles to form a protective film or to prevent contact between asperities, causing the friction coefficient to be relatively high. On the other hand, at high concentrations the nanoparticles tend to form large aggregates and cannot properly fill the valleys between the asperities [42,43]. Instead, they may behave similar to the debris particles that are known to scratch and wear shearing surfaces under loading and sliding. All of these factors combined suggest that high nanoparticle concentration can have a detrimental effect on the lubrication of shearing surfaces, illustrated by an increase in the friction coefficient [44]. Therefore, it can be concluded that the optimal concentration of 0.05 wt%