Fabrication and Investigation the Microtribological Behaviors of Ionic Liquid-Graphene Composite Films

Wenjie Zhao a b, Zhixiang Zeng a, Shusen Peng a, Xuedong Wu a, Qunji Xue a & Jianmin Chen a

a Ningbo Key Laboratory of Marine Protection Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, China
b State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

Accepted author version posted online: 10 Jan 2013. Published online: 29 Mar 2013.

To cite this article: Wenjie Zhao, Zhixiang Zeng, Shusen Peng, Xuedong Wu, Qunji Xue & Jianmin Chen (2013) Fabrication and Investigation the Microtribological Behaviors of Ionic Liquid-Graphene Composite Films, Tribology Transactions, 56:3, 480-487, DOI: 10.1080/10402004.2012.754071

To link to this article: http://dx.doi.org/10.1080/10402004.2012.754071

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions
A novel thin composite film, which contained both ionic liquids (ILs) and graphene, was fabricated successfully on silicon substrate using a dip-coating method. The formation and surface properties of the films were analyzed using scanning electron microscopy (SEM) and multifunctional X-ray photoelectron spectroscopy. A ball-on-plate tribometer was used to evaluate the influence of graphene content on the microtribological performance of the thin composite films. The results showed that compared to the single IL film deposited directly on the silicon surface, the as-prepared IL–graphene (IL-G) film showed improved friction reduction properties, which was attributed to the synergistic effect of IL and graphene. The composite IL-G film also exhibited decreasing wear resistance compared to the single IL film. We postulate that this is due to the fact that IL films become more discontinuous with the incorporation of graphene powder. This was verified by SEM imaging, which showed that the film was not continuous enough to prevent direct contact between the steel ball counterpart and Si surface.

KEY WORDS
IL; Graphene; Composite Film; Microtribological Properties; Synergistic Effect

INTRODUCTION

In the field of tribology, the use of ionic liquids (ILs) as lubricants was first reported in 2001 (Ye, et al. (1)). Since then, there has been an explosive growth of research on ILs as “green” lubricants due to their favorable features, such as high thermooxidative stability, a broad liquid range, nonvolatility, nonflammability, high ionic conductivity, and controlled miscibility with organic compounds, all of which meet the demands of high-performance lubricants (Ye, et al. (1); Blanco, et al. (2); Zhou, et al. (3); Palacio and Bhushan (4); Street, et al. (5)).

ILs are salts formed by a weakly associated anion and an organic cation. The physical and chemical properties of ILs are determined by the cation and anion. It is possible to consider an artist’s palette of anions and cations being combined to create numerous kinds of ILs that exhibit various physical and chemical performances (Bermúdez, et al. (6)). ILs, as neat lubricants or lubricant additives, have shown better lubrication and anti-wear properties than commonly used synthetic, mineral, or engine oils for a large number of sliding pairs (Liu, et al. (7); Yao, et al. (8); Xia, et al. (9); Xie, et al. (10); Jiménez and Bermúdez (11); Minami, et al. (12)). ILs are attractive as lubricants for micro- and nanoelectromechanical systems (MEMS/NEMS) due to their superior thermal stability and electrical conductivity, which can minimize contact resistance between sliding surfaces compared to conventional lubricants, such as currently used perfluoropolyethers (PFPEs), which is required for various electrical applications (Zhou, et al. (3)). The large surface area-to-volume ratio of surface microstructures makes MEMS/NEMS devices particularly vulnerable to adhesion to the underlying substrates or to adjacent microstructures (Wang, et al. (13); Zou, et al. (14)). Ultrainf IL films have also been proven to be effective and beneficial for anti-adhesion, friction reduction, and antiwear on several surfaces and have demonstrated potential as lubricant films for MEMS/NEMS. Several kinds of IL films have been exploited by a number of researchers aiming to understand the micro/nanotribological behaviors in molecular detail (Bermúdez, et al. (6); Zhu, et al. (15); Bhushan, et al. (16); Mo, et al. (17); Zhao, et al. (18)–(20); Zhu, et al. (21); Pu, et al. (22), (23)). It was observed that three key factors, including the molecular structures (including the anion, cation, and the functional group), bonding fraction (bonding, partially bonding, and unbonding), and working environment (relative humidity and temperature), significantly influence the adhesion and micro/nanotribological behaviors of ultrathin IL films (Bermúdez, et al. (6); Zhu, et al.
the two-dimensional material graphene” (“Andre Geim, Konstantin Novoselov win 2010 Nobel Prize in Physics”, English People’s Daily Online, accessed 9/11/2011, http://english.peopledaily.com.cn/90001/90781/90879/7157883.html). Graphene, a two-dimensional atomically thick crystal with carbon atoms arranged in a honeycomb crystal lattice, has stirred much interest from both theoretical and experimental scientists in the field of material science (Wei and Liu 24)). Because of its structural homogeneity and physical stability, graphene combines excellent mechanical properties and outstanding electrical properties with atomic thickness and has been regarded as one of the most promising candidates for the basic building block of future MEMS/NEMS (Park, et al. (25); Lee, et al. (26)). Graphene is one of the most promising resources for developing new thin-film materials and composites for multifunctional applications. Despite its low thickness, graphene has superb frictional properties and relatively high wear resistance, which makes it an attractive material for various applications in nanotechnology (Lin, et al. (27); Lee, et al. (28)). For graphene-based composite materials, it is important to control the thickness of graphene sheets, which should be as thin as possible, and to disperse and incorporate them as homogeneously as possible in the matrix (Rani, et al. (29)). Park, et al. (25) have fabricated graphene thin films successfully via layer-by-layer assembly of charged graphene nanosheets based on electrostatic interactions. Ou, et al. (30) prepared reduced graphene oxide (RGO) sheets on silicon wafers via a multistep route based on the chemical adsorption and thermal reduction of graphene oxide and investigated its tribological behavior. The results showed that the assembled RGO possessed good friction reduction and wear resistance due to its intrinsic structure; that is, the covalent bonding to the substrate and self-lubricating property of RGO. Pu, et al. (31) prepared various functionalized graphene–IL nanocomposite ultrathin lubrication films on Si substrates by an electrostatic adsorption method. It was found that appropriate amounts of functionalized graphene nanosheets greatly enhanced the load-carrying capacity of the ultrathin lubrication films, and these kind of nanocomposite films may have potential application in the lubrication of MEMS/NEMS.

With the aim of further enhancing the microtribological performances of the IL-based thin films, the exploitation of IL–graphene (IL-G) composite films is necessary. In this work, we present a facile means of preparing IL-G thin composite films via a simple dip-coating method. The morphology, composition, and microtribological behaviors of the IL-G composite films with different graphene contents were investigated in detail. Combined with graphene, 1-octyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide ([OMIm] NTf₂), which exhibits good thermal stability and hydrophobic properties, was chosen to fabricate IL-G composite thin films.

**EXPERIMENTAL DETAILS**

**Materials**

The chemical structure of the IL used in this work is shown in Fig. 1. 1-Octyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide ([OMIm] NTf₂) with ≥99% purity was purchased from Lanzhou Greenchem (ILS, LICP, CAS, China). Graphene powder, for which detailed information is provided in Table 1, was purchased from Sinocarbon Materials Technology Co., Ltd. (Taiyuan, China). P-type polished single-crystal Si (100) wafers (obtained from GRINM Semiconductor Materials Co., Beijing, China) were used as substrates. All other reagents of analytical grade were used as received.

**Film Preparation**

Three solutions of IL–graphene powder were prepared as follows: The IL and graphene powder were dissolved in ethanol solution and ultrasonicated. The IL concentration was 3 mg/mL and different concentrations of graphene were used: 0, 0.2, and 0.4 mg/mL. Si wafers with dimensions of 20 × 15 × 0.5 mm were ultrasonically cleaned in acetone followed by ethanol for 10 min and hydroxylated in freshly prepared piranha solution (a mixture of 7:3 (v/v) 98% H₂SO₄ and 30% H₂O₂) at 90 °C for 40 min. The piranha-treated Si wafers were rinsed thoroughly with deionized water and dried in a stream of N₂. Then the silicon wafers were dipped in the as-prepared ethanol dispersions with various graphene concentrations at a uniform velocity of 60 mm/min and immersed in the solution for up to 30 s in order to obtain a uniform coating (PCTL 0.01 Dip Coater, Shenyang Kejing Auto-Instrument Co. Ltd., Ningbo, China). The Si wafers were allowed to dry in air in a clean room prior to the following measurements, including the systematic investigation of surface morphology, surface chemistry, and microtribological properties of as-prepared ionic liquid-graphene composite films. The obtained thin composite films were defined as IL, IL/(0.2)f-G, and IL/(0.4)f-G, respectively.

**IL and Graphene Characterization**

Thermogravimetric analysis was carried out on a PYRIS Diamond thermogravimetric analyzer (Perkin-Elmer, USA) at a
heating rate of 10°C/min in both air and an N2 atmosphere over a temperature range from ambient to about 800°C.

Microstructural characterization of the graphene powder was performed using a high-resolution transmission electron microscope (HR-TEM; Tecna F20 TEM, FEI, USA) operated at 200 kV. The graphene powder was diluted in an abundant volume of ethanol and the mixture was used for TEM observations after ultrasonic treatment for 20 min.

**Film Characterization**

A field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan) was used to characterize the surface morphology of the obtained IL-G composite films.

X-ray photoelectron spectroscopy (XPS; Axis Ultra DLD, Japan) with Al (mono) Ka irradiation with a pass energy of 160 eV was used to characterize the chemical compositions and structures of the IL-G composite films under a chamber pressure of about $3 \times 10^{-8}$ Torr. The binding energy of adventitious carbon of C1s at 284.8 eV was used as the reference.

**Microtribological Properties**

The microtribological properties of these IL-G films were evaluated on a UMT-2MT tribometer (CETR, USA) in reciprocating-sliding mode. Commercially available AISI-52100 steel balls with a diameter of 3.18 mm were selected as the stationary upper counterparts, and the lower specimens were mounted onto a reciprocating table with a traveling distance of 5 mm. The number of reciprocating travel per second was defined as frequency. The friction coefficient was recorded in a computer and the sliding time was recorded as the antiwear life of the thin films when the friction coefficient sharply increased to 0.6, at which point lubrication failure of the thin films occurred. The measurements were performed three times for each test condition.

The wear scar morphologies of the thin films were analyzed using a MicroXAM 3D noncontact interferometric microscope in phase mode (ADE, USA). All tests were conducted at 20°C and relative humidity of 30%.

**RESULTS AND DISCUSSION**

**Thermal Stability**

The long-term thermal stability of ILs is of utmost importance for their industrial application. Thermogravimetric analysis was conducted in air as well as under a nitrogen atmosphere using a PYRIS Diamond thermogravimetric analyzer at a heating rate of 10°C/min to study the thermal stability of ILs; multiply-alkylated cyclopentanes (MACs) and PFPEs were also evaluated as a reference. MACs and PFPEs have good chemical and thermal stability and are regarded as high-performance lubricants widely applied in many industrial applications to reduce the friction and wear of an interface (Liu and Bhushan (32); Wang, et al. (33)). As shown in Fig. 2, compared to Zdol and MACs, IL has the highest decomposition temperature and very low vapor loss, as well as nominal weight loss below 420°C in N2. According to previous reports, the decomposition temperature strongly depends on the type of anion as well as cation of ILs (Zhao, et al. (18), (19)). ILs with poorly proton-abstracting anions, such as the bis(trifluoromethylsulfonyl)imide anion, are most stable to high-temperature decomposition, whereas ILs with nucleophilic and highly proton-abstracting anions, such as halides, decompose at much lower temperatures (Ngo, et al. (34); Awad, et al. (35)). Imidazolium-based ILs appear to have a better thermal stability than pyridinium-based and tetraalkylammonium-based ILs (Ngo, et al. (34); Tokuda, et al. (36)). Our experimental results support this conclusion. Among the three lubricants, Zdol exhibited the poorest thermal stability in both air and N2 and started to decompose at 280°C. Further, it was found that the atmosphere has an impact on the thermal stability of ILs; ILs decomposed at lower temperatures in an air atmosphere compared to a nitrogen atmosphere. It was assumed that ILs are more easily oxidized and degraded in air than in N2 (Ngo, et al. (34)). The decomposition temperature for MACs and Zdol is not sensitive to the presence of oxygen, because similar thermal decomposition behaviors were observed in both air and N2 environments.

**HR-TEM Images**

In order to obtain the structural information, the as-prepared graphene powder was characterized by HR-TEM, and Fig. 3 depicts the TEM bright-field images and the selected-area electron diffraction (SAED) pattern of the graphene material. The as-prepared graphene showed a crinkled morphology and had a thickness of a few nanometers. Generally, the graphene layers can be distinguished through the folded edge (Li, et al. (37)). According to HR-TEM observations, the graphene was predominantly a few-layer structure with four to six layers. The corresponding SAED pattern of the few-layer graphene presented in Fig. 3b displays an obvious sixfold pattern, revealing the crystalline nature of the graphene.

**Morphologies of IL-G Composite Films**

To obtain microstructural information on the thin IL-G composite films, SEM was used for observation of the surface morphology, and a silicon surface was characterized as a comparison. Figures 4a–4d show the SEM micrographs of the silicon surface, IL film, IL/(0.2)f-G film, and IL/(0.4)f-G film, respectively. It can be seen that the silicon surface was very smooth and homogenous. However, Fig. 4b reveals that when the IL was deposited on the silicon surface, IL molecules did not completely coat the whole silicon surface to form a uniform and continuous film; rather, only...
A nanoscale island-like liquid droplet was formed. This is possibly because the IL was not completely compatible with the hydroxylated silicon surface. The IL film became discontinuous after incorporation of graphene and became more discontinuous with an increase in the graphene fraction, which may be due to the aggregation of graphene.

**Chemical Composition of IL-G Composite Films**

XPS analysis was conducted to clarify the chemical states of several typical elements on the IL-G boundary film formed on the silicon surface, and a silicon surface also was evaluated as a reference. Figure 5 presents the XPS spectra of the IL-G composite films including both full-scan survey spectra and fine survey spectra of fluorine (F1s; Fig. 5b), nitrogen (N1s; Fig. 5c), and Carbon (C1s) (Fig. 5d) spectra. In Figs. 5a–5d (top to bottom), the black, red, blue, and green curves represent the chemical composition of the silicon surface, IL film, IL/(0.2)f-G film, and IL/(0.4)f-G film, respectively. As shown in Fig. 5a, the appearance of F1s and N1s in the full-scan survey spectra for all of the IL-G films indicates that IL-G films were prepared successfully on the silicon surface. It was also observed in Figs. 5b and 5c that there were no signals of F1s and N1s on the silicon surface. Furthermore, from the IL film, to the IL/(0.2)f-G film, to the IL/(0.4)f-G film, the peak height of F1s and N1s decreased but C1s increased due to the increase in graphene content.

**Microtribological Behaviors of IL-G Composite Films**

The friction reduction ability and wear resistance of thin films are important for their potential use as a surface protective layer. The microtribological behaviors of the films mentioned above were tested on a ball-on-plate microtribometer under different conditions. Figure 6 shows a plot of the friction coefficient with
Fig. 5—XPS spectra of IL-G composite films: (a) full-scan survey spectra and (b) fine survey spectra of F1s, (c) N1s and (d) C1s spectra (color figure available online).

Fig. 6—Variation in the friction coefficient with time for various IL-G composite films at different applied loads: (a) IL film, (b) IL/(0.2)f-G film, and (c) IL/(0.4)f-G film (color figure available online).
sliding time for IL-G composite films with different graphene contents. For the pure IL film, as shown in Fig. 6a, the average friction coefficient was about 0.11 at a normal load of 100 mN. When the normal load was increased to 300 mN, the average friction coefficient decreased to about 0.1 and remained stable even after sliding for 1,800 s. When the normal load increased to 400 mN, the average friction coefficient decreased to about 0.1 and increased to 0.6 after sliding for 1,650 s, which indicated film failure. When the normal load increased to 500 mN, the friction coefficient increased sharply to 0.6 just after sliding for 530 s.

As depicted in Fig. 6b, the friction reduction ability of the IL film was enhanced after incorporation of graphene. An average friction coefficient of 0.10 was recorded for IL/(0.2)f-G film and decreased to 0.09 with an increase in normal load. The friction coefficient remained almost constant with increasing sliding time at a load of 200 mN. This implies that IL/(0.2)f-G film can remain as an effective lubricant layer for more than 1,800 s at a load of 300 mN and the average friction coefficient decreased to 0.09, which was still almost stable for all sliding times. However, when a load of 400 mN was applied, the film was worn out after 340 s, as witnessed by the sudden increase in the friction coefficient.

As depicted in Fig. 6b, the friction reduction ability of the IL film was enhanced after incorporation of graphene. An average friction coefficient of 0.10 was recorded for IL/(0.2)f-G film and decreased to 0.09 with an increase in normal load. The friction coefficient remained almost constant with increasing sliding time at a load of 200 mN. This implies that IL/(0.2)f-G film can remain as an effective lubricant layer for more than 1,800 s at a load of 300 mN and the average friction coefficient decreased to 0.09, which was still almost stable for all sliding times. However, when a load of 400 mN was applied, the film was worn out after 340 s, as witnessed by the sudden increase in the friction coefficient.

From these results, one may conclude that both the friction coefficient and the wear resistance of IL films deceased with an increase in graphene content. The former results was expected but the latter result was surprising. The greatly enhanced lubricating property might be attributed to the synergic effect of IL-G composite films. The decrease in the friction coefficient with increasing graphene content can be attributed to the intrinsic properties of graphene. There is weak bonding between the basal planes, so graphene can be easily peeled off from the building block, which leads to the excellent friction reduction properties of graphite (Lin, et al. (27)).

A possible reason for decreasing antiwear ability with increased graphene content is that the IL film become more discontinuous with the incorporation of graphene powder. This was verified by the SEM images. The films were not continuous enough to prevent direct contact between the steel ball counterpart and Si surfaces. Graphene agglomeration resulted in decreased wear resistance of the IL-G composite films.

**CONCLUSIONS**

In this work, a novel IL-G composite film was successfully prepared on a silicon substrate using a dip-coating method. The
appearance of FIs and NIs in the full-scan survey spectra for all of the IL-G films indicated that IL-G films were formed successfully on the silicon surface. SEM images indicated that the IL film became more discontinuous with an increase in the fraction of graphene, which may be due to the aggregation of graphene. The microtribological results demonstrated that both the friction coefficient and wear resistance of the IL film decreased with an increase in graphene content. The enhanced friction reduction property might be attributed to the synergetic effect of IL-G composite film. The reason for their decreasing antiwear ability was that IL film become more discontinuous with the incorporation of graphene powder, and then the film was not continuous enough to prevent direct contact between the steel ball counterpart and Si surfaces. The present work provides a strategy to fabricate IL–graphene composite films with excellent friction reduction properties via chemical composition design. Obtaining uniform and continuous IL-G composite films with excellent wear resistance is an important area of research.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the National Nature Science Foundation (51202263), the China Postdoctoral Science Foundation (20110491832), the Municipal Nature Science Foundation (2011A610098), the Outstanding Talent Recruiting Program from the Ningbo municipal government (2009A31004), and the Open Fund of the State Key Laboratory of Solid Lubrication, Chinese Academy of Sciences (1004).

REFERENCES


