Applied Physics A (2018) 124:777
https://doi.org/10.1007/s00339-018-2207-z

Applied Physics A
Materials Science & Processing

Colloidal suspension of graphene oxide in ionic liquid as lubricant

Tingxia He[1] · Qingwen Dai[1] · Wei Huang[1] · Xiaolei Wang[1]

Received: 22 July 2018 / Accepted: 19 October 2018

Abstract

In this paper, we successfully prepared stable colloidal suspensions of chemically modified graphene oxide (MGO) in hydrophobic ionic liquid (IL) as a lubricant. The graphene oxide (GO) sheets were synthesized from natural graphite by modified Hummers method. To achieve stable dispersion, a surfactant containing ionic liquid unit with carboxylic acid group was synthesized and covalently grafted on GO sheets surfaces. The stability of the MGO/IL colloid was attributed to the high affinity of the surfactant, which might provide sufficient steric and electrostatic repulsions. Tribological results showed that the lubrication property of MGO/IL nanofluids has been improved significantly compared with neat IL. In addition, the lubricating effect is connected with the concentration of the MGO in IL. At the low concentration, the lubricity is ineffective. While at high concentration, the MGO sheets aggregate and the characteristic of interlayer sliding of MGO is no more active. The nanofluids with moderate MGO concentration exhibit good performance both in friction and wear resistance.

1 Introduction

Ionic liquids (ILs) are organic salts with melting points below 100 °C [1]. Owing to the excellent low vapor pressure, high thermal stability, and nonflammability [2], they have been explored as promising novel lubricants since 2001 [3]. The most notable feature that distinguishes ILs from other traditional oils is their high polarity. The high polarity of ILs makes them easily adsorbing on the sliding surfaces to form strong effective boundary film and ready tribochemical reaction, which contributes to their prominent anti-wear capacity [4].

Besides polarity, the anti-wear properties of ILs can also be improved by means of additive technology. Simple compounds such as carboxylic acids [5] and benzotriazole [6] are considered as potential additives for ILs. Research shows that 1 wt% of tricresyl phosphate in [IMM][BF_4] helps to establish a tribofilm very rapidly at high temperature [7]. The addition of aspartic acid derivatives to [BMIM][TFSA] significantly reduces friction and wear by 20% and 40%, respectively [8]. All these additives mentioned above are organic matters.

On the other hand, nanoparticles as additives in base oils have been investigated extensively. In general, when adding nanoparticles, the extreme pressure property and load carrying capacity are improved and friction coefficient reduces. Recently, graphene as additive has been used in ILs to enhance their lubrication performance. The result shows that graphene/ILs nanohybrid materials can be serves as effective lubricants [9]. Similar to graphene with the layer structure, graphene oxide (GO) is also expected as a potential solid lubricant. Nowadays, GO as additive used in water [10, 11] and oil [12–16] has attracted great attention in tribological area. Experimental results showed that due to the layer structure, GO with its excellent lubricity and nontoxicity can act as a good water/oil additive. Taking account of the excellent lubricity of GO, how about dispersing GO into ILs and can anti-wear property be further achieved? What is about the optimized GO concentration in ILs for effective lubrication? To date, there is little knowledge about this. Before that, the priority issue is to achieve long-term stable GO/IL colloidal suspension that is much important for consequent application.

This paper aims at investigating the tribological performance of GO as friction modifiers in ILs. To achieve stable colloidal suspension, GO was decorated with a surfactant containing ionic liquid unit with carboxylic acid group. Then the coated GO sheets were dispersed into hydrophobic IL of 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([EMIM][TF_2N], Purity: 99%) and the stability

---

✉ Wei Huang
huangwei@nuaa.edu.cn

[1] College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, Yudao Street 29#, Nanjing 210016, China

of the colloid system was qualitatively evaluated. Finally, the lubrication performance of the MGO/IL nanofluids was investigated using a ball on disc tribometer. To the best of our knowledge, it is for the first time on the use of stable GO based IL nanofluids as lubricants.

2 Experimental details

2.1 Material preparations

2.1.1 Preparation of GO sheets

The GO sheets were synthesized from natural graphite by modified Hummers method [17]. In brief, graphite powder (2.0 g) was dispersed in H_2SO_4 (1M, 100 mL) in ice water bath under stirring for 1 h. Subsequently $KMnO_4$ (10.0 g) was added in the mixture with constant stirring. 2 h later, deionized water (100 mL) was slowly added in the reaction mixture followed by heating at 90 °C for 2 h. Then, H_2O_2 (30%, 40 mL) was put in the mixture for further 2 h of stirring. After that, the precipitated was filtered and washed with HCl (30%, 50 mL) and deionized water (100 mL). The resulting mixture was obtained by centrifugation (8000 rpm, 10 min). Finally, the brown sample was dried under vacuum at 65 °C to obtain GO nanosheets.

2.1.2 Preparation of surfactant

The most challenge hindering the dispersion of GO in ILs is the achievement of long-term colloidal stability. To solve the settling and dispersing problems, surface modification is an efficient way. Taking account of the compatibility with the ILs and increasing the steric repulsion between the GO sufficiently, a surfactant containing ionic liquid unit with carboxylic acid group was prepared via substitution. The detailed synthesis procedure was reported in ref [18]. Simply, the mixture of 1-butylimidazole and 10-bromodecanoic acid in the ratio of 1:1 was heated in oil-bath at 120 °C for 9 h to obtain the required surfactant, 1-butyl-3-(9-carboxydecyl)-1*H*-imidazol-3-ium bromide (ILC_9-COOH), shown in Fig. 1.

2.1.3 Preparation of MGO/IL nanofluids

The hydrophobic IL [EMIM][TF_2N] was chosen as carrier liquid to prepare GO based IL nanofluids. During the preparation process (see in Fig. 1), the GO sheets and surfactant ILC_9-COOH with a mass ratio of 1:1 were firstly dissolved in alcohol using the ultrasound method and stirred for 12 h at room temperature under nitrogen protection to ensure full reaction. Then the mixed solution was washed with ethyl acetate to remove excess surfactant and the ILC_9-COOH modified graphene oxide (MGO) were dried at 80 °C for 24 h. Importing a surfactant, which partially resembles the chemical structure of the chosen IL, may lead to a high miscibility between GO sheets and hydrophobic IL due to the surfactant is supposedly interacting with both the particles and the IL. Finally, to obtain the MGO/IL nanofluids, the MGO was dispersed into IL by ultrasound for 2 h at room temperature with different mass ratios of 0.2, 0.4, 0.8 and 1.0 wt%, respectively.

2.2 Material characterizations

The structures of graphite and GO were detected via X-ray diffraction using an X'Pert Pro diffractometer (Panalytical) at a scan rate of 2°/min. The morphology of the GO sample was determined using a scanning electron microscopy (SEM, Hitachi S3400) and a transmission electron microscope (TEM, JEOL JEM-200CX). Fourier transform infrared (FT-IR) spectra of the bare GO and MGO samples dispersed in KBr pellets was recorded on an infrared spectroscopy (NEXUS870, NICOLET).

The suspension stability of the MGO/IL nanofluids was checked by qualitative observations of the particle sedimentation. Before each test, all the fluid samples were redispersed by ultrasound to ensure the same initial conditions.

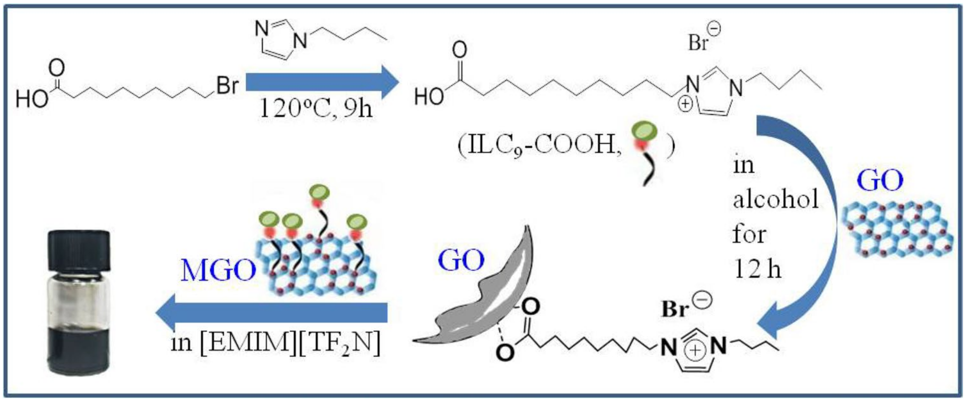

Fig. 1 Scheme of the synthesis of the surfactants ILC_9-COOH and functionalization of GO sheets with the surfactant, followed by redispersion of the functionalized GO in ILs of the [EMIM][TF_2N]

The lubrication properties of the stable MGO/IL nanofluids were carried out using a reciprocating sliding tribometer (Sinto Scientific, JAP). A 304 stainless steel ball of 10 mm in diameter was fixed in a stationary holder sustained by a beam and a 304 stainless steel plate was then mounted on a reciprocating table. The surface of the plate was sanded and polished with a roughness, Ra, ranging from10 to 20 nm. The friction tests were conducted at a stroke of 10 mm (average speed of 10 mm/s) under a normal load of 0.5 N, corresponding to the Hertzian contact pressure of 350 MPa. The volume of the lubricants used each time was fixed at 5 μL. The morphologies of wear surface on the lower plates were analyzed by 3D surface mapping microscope profilometer.

3 Results and discussion

3.1 XRD, SEM and TEM analysis

Figure 2a shows the XRD patterns of graphite and GO. From the pattern of graphite, very intense and narrow peak at 2θ of 26.44° corresponds to the (002) planes of graphene layers [19]. During the course of a strong oxidation, the structure of graphite expands as oxygen-containing groups are incorporated between the carbon sheets. The XRD pattern of GO depicts a strong diffraction peak at approximately 2θ of 9.62°. According to Bragg Eq. ($2d \sin\theta = n\lambda$), the calculated interlayer spacing is about 0.5 nm.

Figure 2b, c presents the SEM and TEM images of GO. In SEM, the lamellar structures with wrinkled film morphology are observed. The GO sheets aggregation may be attributed to their high specific area. Different degrees of transparency of GO can be seen in Fig. 2c (TEM) and some dark lines with large contrast can also be found, which clearly illustrates that GO sheets are wrinkled or folded. The electron diffraction pattern reveals that the GO sheets are hexagonal close-packed crystal structure with several layers. The HRTEM image clearly indicates interlayer distances of 0.45 nm, which is supported by the XRD data.

3.2 FT-IR analysis

Figure 3 shows the FT-IR spectrums of graphite, GO and MGO. From the spectra of graphite, a smooth curve can be found, indicating weak absorption peak of graphite functional groups. While from the data of GO and MGO, the absorption peak at 3400/cm assigned to the O–H stretching vibrations. Peaks at 1729/cm and 1051/cm indicated the C=O and –OH, respectively. The presence of oxygen-containing functional groups illustrates that the graphite has been oxidized.

Compared with the GO curve, double peaks of MGO at 2927/cm and 2845/cm, assigned to C–H stretching vibrations, which came from the surfactant of ILC$_9$-COOH. In addition, we observed the peak at 1150/cm, which is the characterization peak of C–O–C [20]. It seems that the chemical reaction between the oxygen-containing functional

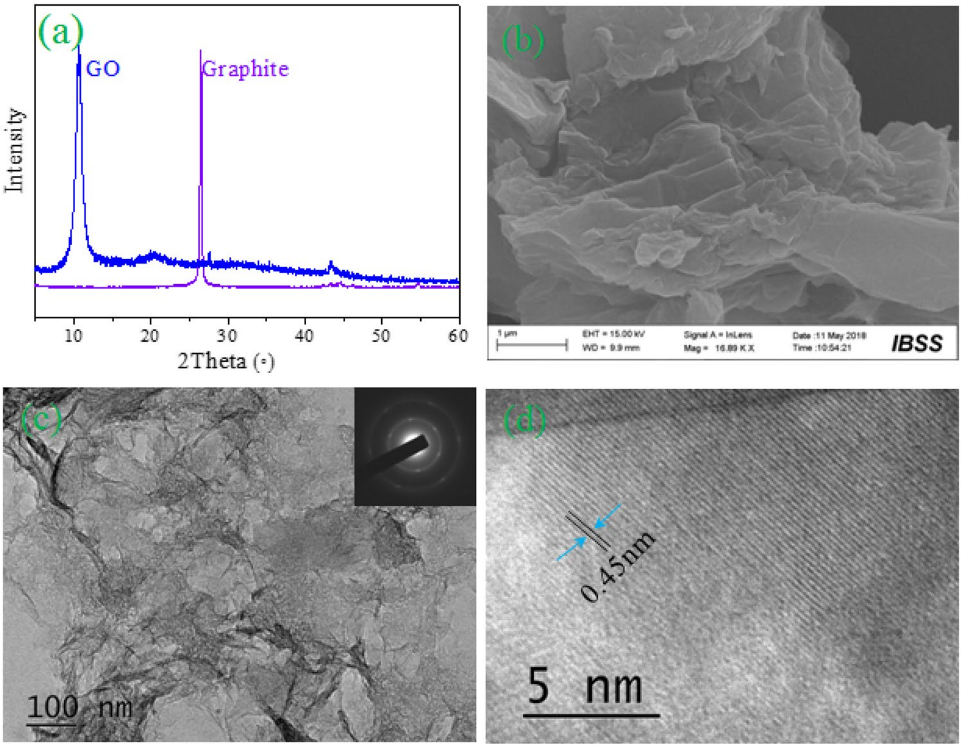

Fig. 2 **a** XRD patterns of graphite and GO, **b** SEM image of GO, **c** TEM image of GO, **d** HRTEM of GO

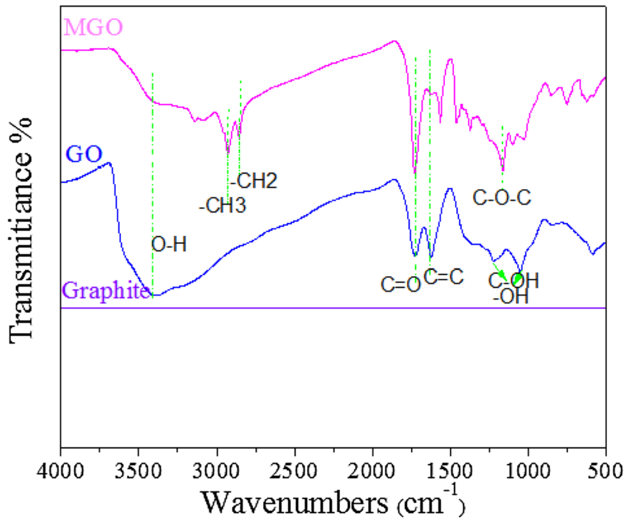

Fig. 3 FI-IR spectra of the graphite, GO and MGO

groups of GO and ILC$_9$-COOH happened due to the Van der Waals interaction and hydrogen bonding, and the surfactant is chemisorbed onto the GO surfaces as a carboxylate.

3.3 Stability analysis

Surface modification is closely related to the dispersibility of GO sheets in IL. Figure 4 shows different stability of GO and MGO in the IL ([EMIM][TF$_2$N]). Although the concentration is low (0.2 wt%), obvious solid–liquid separation was observed for the bare GO sheets. However, the surfactant-modified MGO dispersed in IL exhibited excellent stability over a period of 120 h, even at higher concentration of 1.0 wt%.

Maintaining a good dispersion requires introducing an energy barrier to aggregation. The long-term dispersion stability of MGO in IL may be attributed to the following reasons: (1) Since the MGO sheets are coated with a surfactant containing ionic liquid unit, a high affinity will ready be generated between the surfactant and IL based on the theory of similarity-intermiscibility. The polar coating layer may make the MGO compatible with the IL as a carrier liquid, resulting in a stable dispersion [21]. (2) The long cationic alkyl chain of the surfactant (ILC$_9$-COOH) on the surfaces of MGO might provide sufficient repulsive solvation force [22, 23] and steric repulsion [24] via covalent functionalization to keep them in suspension for a considerable period of time. (3) As mentioned in ref.[25], electrostatic repulsion of the carboxylate groups may also maintain the stability of MGO dispersion. Therefore, it is believed that the stabilization by ILC$_9$-COOH can potentially enhance the colloidal suspension of MGO in IL.

3.4 Lubrication analysis

Figure 5 shows the relationship between the lubrication properties and the concentration of the MGO/IL nanofluids. It can be found that the friction coefficient of the neat IL lubrication is about 0.22, which is much higher than that of the nanofluids. The value decreases up to 23% using 0.2 wt% concentration of MGO in the IL. As the concentration increased to 0.4 wt%, the value of friction coefficient

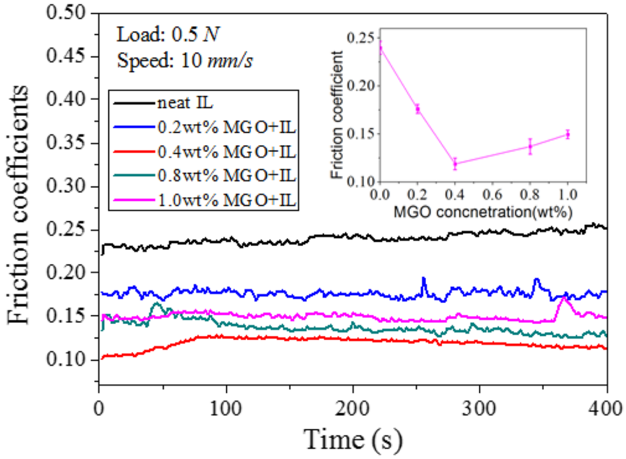

Fig. 5 Friction curves lubricated with ILs and MGO/ILs nanofluids (The inset shows the friction coefficients as a function of MGO concentration)

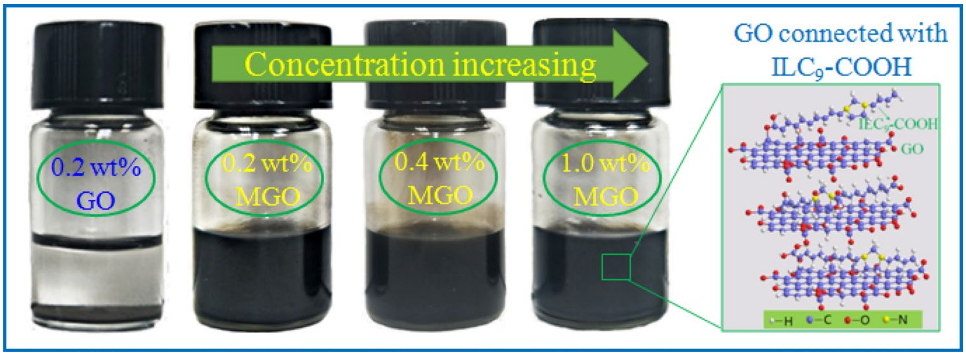

Fig. 4 Suspension stability of GO and MGO sheets with different concentrations in IL (the pictures were taken after 120 h standing)

reduces to 0.11, which is lower than the graphene/ionic liquid (0.22) [9] and GO/PAG-46 oil hybrids (0.14) [16].

The width of the wear track is indicative of the degree of wear. According to the 3D profile images (see Fig. 6), the width of wear scar reduces to almost 50% for the nanofluid with 0.4 wt% MGO concentration as compared to neat IL (Fig. 6a, c). Meanwhile, the depth of the wear scar is the shallowest among the four samples. Based on the morphology of the wear track, evidence of adhesive wear mechanism is apparent on the wear track for pure IL lubrication specimen. For the nanofluids lubricated specimens, the wear track morphology is relatively smooth with evidence of grooves along the sliding direction. However, with the increasing of the concentration, the friction coefficients increase at the MGO concentrations of 0.8 wt% and 1.0 wt%. Wear depth (see Fig. 6d) also increases in the same trend as friction coefficient. It should be pointed that optimized concentration of MGO in the nanofluids is not a universal value. But the experimental results also mean that the lubrication property of the GO/IL nanofluids could be adjusted to some extent by controlling the concentration of MGO in IL.

The above results show that, compared with neat IL, the lubricity of MGO/IL nanofluids has been improved significantly. It is proposed that MGO sheets can easily enter the interfaces of frictional pairs due to the intrinsic lamellar structure [26]. The formed MGO film with low shear-strength may not only decrease the friction force, but also improve the load carrying capacity of the nanofluids, which result in micro-polish and self-mend to the wear scar [27]. Thus, the friction reduction and anti-wear ability of the nanofluids appear.

In addition, the concentration of MGO dispersing in IL shows obvious effect on the tribological performance of the nanofluids and the reason may be ascribed to MGO particle agglomeration. Possible lubrication mechanisms related to concentration of the nanofluids are shown in Fig. 7. At low concentration, it is highly suggested that the MGO sheets in IL attach to the worn surface to form a discrete film, thus protecting the rubbing surfaces from severe wear and reducing the friction (see in Figs. 5, 6b). As the concentration increases to a moderate range, the tribological performance reaches to its optimal state, corresponding to the lowest coefficients and wear (see in Figs. 5, 6c). At high concentration,

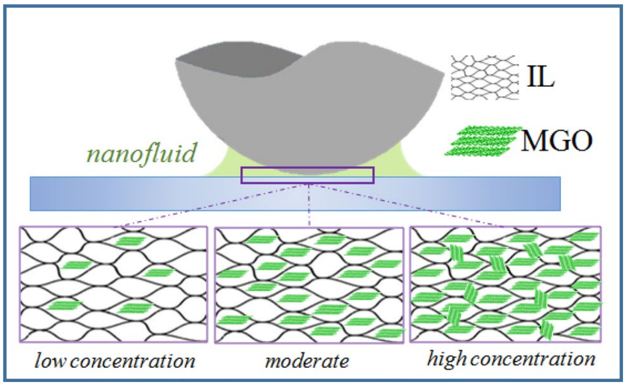

Fig. 7 Lubrication mechanism of MGO/ILs nanofluids

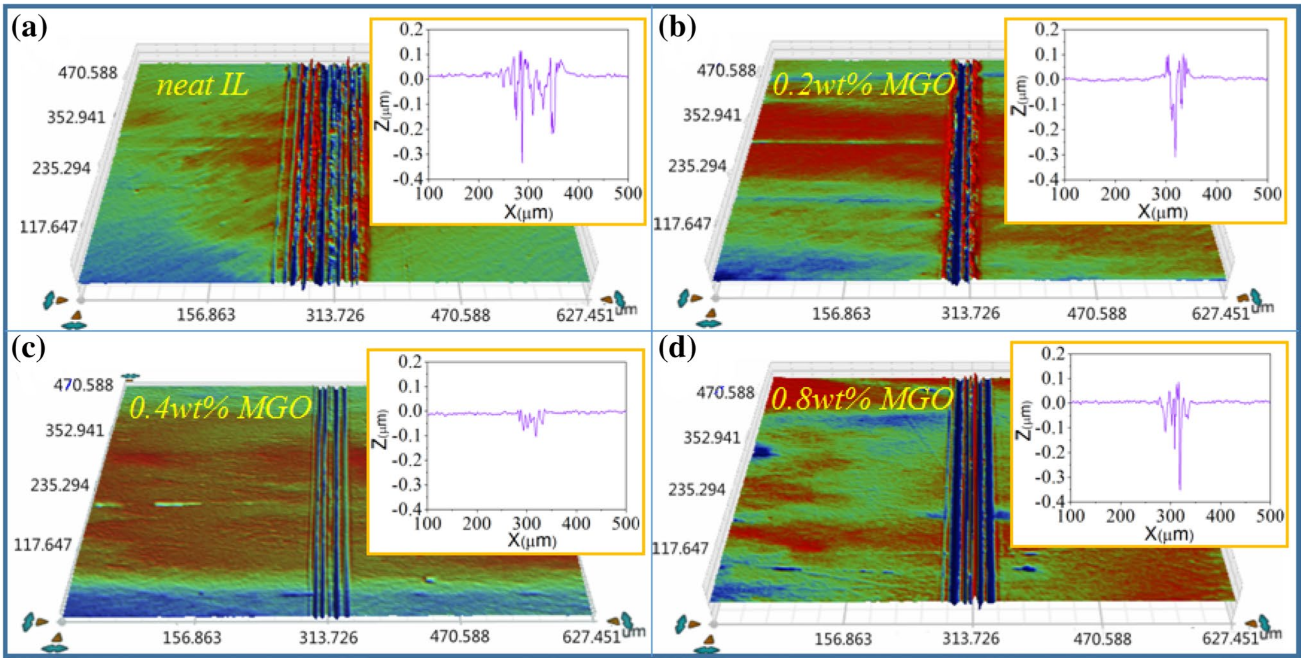

Fig. 6 3D images of the wear tracks when lubricated with IL and MGO/IL nanofluids (The inset was the surface profile of the corresponding wear scar)

particle agglomeration can hardly be avoided and randomly oriented MGO instinctively form the obstacles between the sliding surfaces while intercepting the interfacial sliding. Therefore, the lubricity is ineffective, increasing the friction and wear (see in Figs. 5, 6d).

4 Conclusions

In this paper, we successfully prepared stable dispersions of GO in hydrophobic IL ([EMIM][TF_2N]) as a kind of lubricant. The surface of the GO sheets was coated with an ionic liquid type surfactant (ILC_9-COOH). As confirmed by FT-IR spectroscopy, the modified GO contain positively charged butylimidazole moieties on their surfaces. After surface modification, stable colloidal suspensions of the MGO in the IL were obtained at different concentrations. The stability of the nanofluids was attributed to the high affinity of the surfactant, which might provide sufficient steric and electrostatic repulsions. The lubrication properties of the nanofluids were assessed by referencing them against neat IL. It shows that, the lubrication performances of MGO/IL nanofluids have been promoted significantly compared with neat IL. Besides, the concentration of the MGO dispersing IL dominates the lubrication effect. When the concentration is low, the lubricity is ineffective. In contrast, at high concentration, the MGO sheets aggregate and the characteristic of weak interlayer sliding of MGO is no more active. However, at moderate concentration, both friction coefficient and wear reduced observably.

Friction tests first manifest that stable colloidal suspension of GO/IL nanofluids possess better lubricity than carrier liquid (neat IL). Furthermore, the MGO concentration affects the lubrication properties and the nanofluids with proper MGO concentration exhibit optimal performances both in friction and wear resistance. This study has proved the great potential of GO as an additive for IL-based lubricants.

Acknowledgements The authors are grateful for the support provided by the National Natural Science Foundation of China (No. 51475241) and the Fundamental Research Funds for the Central Universities (No. NE2017104).

References

1. M.-D. Bermúdez, A.-E. Jiménez, J. Sanes, F.-J. Carrión, Ionic liquids as advanced lubricant fluids. Molecules **14**, 2888–2908 (2009)
2. Y. Kondo, S. Yagi, T. Koyama, R. Tsuboi, S. Sasaki, Lubricity and corrosiveness of ionic liquids for steel-on-steel sliding contacts. Proc. Inst. Mech. Eng. Part J J. Eng. Tribol. **226**, 991–1006 (2012)
3. C. Ye, W. Liu, Y. Chen, L. Yu, Room-temperature ionic liquids: a novel versatile lubricant. Chem. Commun. **21**, 2244–2245 (2001)
4. F. Zhou, Y. Liang, W. Liu, Ionic liquid lubricants: designed chemistry for engineering applications. Chem. Soc. Rev. **38**, 2590–2599 (2009)
5. H. Kamimura, T. Kubo, I. Minami, S. Mori, Effect and mechanism of additives for ionic liquids as new lubricants. Tribol. Int. **40**, 620–625 (2007)
6. B. Yu, F. Zhou, C. Pang, B. Wang, Y. Liang, W. Liu, Tribological evaluation of α, -diimidazoliumalkylene hexafluorophosphate ionic liquid and benzotriazole as additive. Tribol. Int. **41**, 797–801 (2008)
7. M.F. Fox, M. Priest, Tribological properties of ionic liquids as lubricants and additives. Part 1: synergistic tribofilm formation between ionic liquids and tricresyl phosphate. Proc. Inst. Mech. Eng. Part J J. Eng. Tribol. **222**, 291–303 (2008)
8. I. Minami, N. Watanabe, H. Nanao, S. Mori, K. Fukumoto, H. Ohno, Improvement in the tribological properties of imidazolium-derived ionic liquids by additive technology. J. Synth. Lubr. **25**, 45–55 (2008)
9. V. Khare, M.-Q. Pham, N. Kumari, H.-S. Yoon, C.-S. Kim, J.-I.L. Park et al., Graphene–ionic liquid based hybrid nanomaterials as novel lubricant for low friction and wear. ACS Appl. Mater. Interfaces **5**, 4063–4075 (2013)
10. H. Kinoshita, Y. Nishina, A.A. Alias, M. Fujii, Tribological properties of monolayer graphene oxide sheets as water-based lubricant additives. Carbon **66**, 720–723 (2014)
11. O. Elomaa, V.K. Singh, A. Iyer, T.J. Hakala, J. Koskinen, Graphene oxide in water lubrication on diamond-like carbon vs. stainless steel high-load contacts. Diam. Relat. Mater. **52**, 43–48 (2015)
12. B. Gupta, N. Kumar, K. Panda, S. Dash, A.K. Tyagi, Energy efficient reduced graphene oxide additives: mechanism of effective lubrication and antiwear properties. Sci. Rep. **6**, 18372 (2016)
13. X. Fan, L. Wang, High-performance lubricant additives based on modified graphene oxide by ionic liquids. J. Colloid Interface Sci. **452**, 98–108 (2015)
14. S. Samanta, S. Singh, R.R. Sahoo, Simultaneous chemical reduction and surface functionalization of graphene oxide for efficient lubrication of steel–steel contact. Rsc Adv. **5**, 61888–61899 (2015)
15. W. Zhang, M. Zhou, H. Zhu, Y. Tian, K. Wang, J. Wei et al., Tribological properties of oleic acid-modified graphene as lubricant oil additives. J. Phys. D Appl. Phys. **44**, 205303 (2011)
16. V. D'Agostino, M. Pisaturo, C. Cirillo, M. Sarno, A. Senatore, Tribological effectiveness of graphene oxide and ionic liquids in PAG oil. Could absorbed water play beneficial role? Hidraulica **2**, 13–25 (2016)
17. J. Chen, B. Yao, C. Li, G. Shi, An improved Hummers method for eco-friendly synthesis of graphene oxide. Carbon **64**, 225–229 (2013)
18. R. Abu-Reziq, D. Wang, M. Post, H. Alper, Platinum nanoparticles supported on ionic liquid-modified magnetic nanoparticles: selective hydrogenation catalysts. Adv. Synth. Catal. **349**, 2145–2150 (2007)
19. O.C. Compton, D.A. Dikin, K.W. Putz, L.C. Brinson, S.T. Nguyen, Electrically conductive "alkylated" graphene paper via chemical reduction of amine-functionalized graphene oxide paper. Adv. Mater. **22**, 892–896 (2010)
20. J.F. Villena, E. Domínguez, D. Stewart, A. Heredia, Characterization and biosynthesis of non-degradable polymers in plant cuticles. Planta **208**, 181–187 (1999)
21. L. Rodríguez-Arco, M.T. López-López, F. González-Caballero, J.D.G. Durán, Steric repulsion as a way to achieve the required stability for the preparation of ionic liquid-based ferrofluids. J. Colloid Interface Sci. **357**, 252–254 (2011)

22. K. Ueno, M. Watanabe, From colloidal stability in ionic liquids to advanced soft materials using unique media. Langmuir **27**, 9105–9115 (2011)
23. X. Shi, W. Huang, X. Wang, Ionic liquids-based magnetic nanofluids as lubricants. Lubr. Sci. **30**, 73–82 (2018)
24. B.J. Hong, O.C. Compton, Z. An, I. Eryazici, S.T. Nguyen, Successful stabilization of graphene oxide in electrolyte solutions: enhancement of biofunctionalization and cellular uptake. ACS Nano **6**, 63–73 (2012)
25. D.W. Johnson, B.P. Dobson, K.S. Coleman, A manufacturing perspective on graphene dispersions. Curr. Opin. Colloid Interface Sci. **20**, 367–382 (2015)
26. L. Zhang, Y. He, S. Feng, L. Zhang, L. Zhang, Z. Jiao et al., Preparation and tribological properties of novel boehmite/graphene oxide nano-hybrid. Ceram. Int. **42**, 6178–6186 (2016)
27. H. Song, Z. Wang, J. Yang, Tribological properties of graphene oxide and carbon spheres as lubricating additives. Appl. Phys. A **122**, 933 (2016)