Tribology International 125 (2018) 39–45

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Understanding the synergistic lubrication effect of 2-mercaptobenzothiazolate based ionic liquids and Mo nanoparticles as hybrid additives

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ARTICLE INFO

Keywords:
Ionic liquids
Nanoparticle additives
Hybrid lubricant additives
Synergistic effect

ABSTRACT

Ionic liquids (ILs) are increasingly expected to be used as lubricants or additives in industry as they feature many attractive properties. The interaction effects between ILs and traditional additives become significant for future application. This paper investigates the synergistic effects of 2-Mercaptobenzothiazolate based ILs and Mo nanoparticles in polyethylene glycol (PEG) base oil. The hybrid additives outperform neat PEG oil and PEG with single additives. Surface analyses (SEM-EDS, Raman, XPS, cross-sectional TEM-EDS) demonstrate that MoS_2 formed in the tribofilm, which is a critical factor to the observed excellent tribological properties. The outcomes of this work can not only provide fundamental insights into the formation of the tribofilm, but also promote the industrial application of ILs as lubricating additives.

1. Introduction

Tribological effects, such as friction and wear, are generally unfavorable in modern machinery because they reduce energy efficiency and working life. Lubricants play a critical role in minimizing friction and wear by acting as a barrier between moving surfaces [1]. There is a constant requirement to develop new lubricants as very small tribological performance improvements bring enormous economic benefits [2].

Commercial lubricants contain a common base oil and a variety of functional additives [3]. Polyethylene glycol (PEG) is one of commonly used base oils among various synthetic lubricants due to its ecofriendly and degradable property [4]. There have been a great amount of research focusing on lubrication performances of various additives in PEG base oil [5–7]. However, the interaction mechanisms between these functional additives, which play an essential role in controlling the friction and wear performances, is currently poorly known.

Ionic liquids (ILs) are salts with melting points below 100 °C. ILs are excellent candidates for lubricant base oils and additives due to their designable nature and excellent properties, such as low vapor pressure, high thermal and chemical stability, and good thermal conductivity [8–10]. Since 2001, numerous studies have been conducted to investigate the lubrication of ILs for various engineering contacts [11–15]. To date, most of studies focus on the lubrication mechanisms of ILs as neat lubricants or additives alone [10,16,17]. Few studies have mixed ILs with other functional additives, e.g. zinc dialkyldithiophosphate (ZDDP) in lubricant base oils [18,19], thus the synergistic effects or antagonistic effects between ILs and other functional additives are unknown, which restrict the application of ILs as additives in commercial functionalized lubricant compounds.

In the past few decades, nanoparticles have been widely investigated as lubricant additives [20–23]. The excellent anti-wear and friction-reduction performances of these nanoparticle additives have been attributed to the formation of the protective tribofilm or rolling as nano-bearings between the moving surfaces [20,24]. The application of nanoparticles and ILs as hybrid functional additives for lubricating oils may lead to new and high performing functionalized lubricants. However, very limited research has been conducted on the synergistic effects of nanoparticles and ILs as hybrid additives for lubricating oils. Furthermore, the exact synergistic lubrication mechanism is not yet known.

We have developed a new series of 2-mercaptobenzothiazole (MBT) based ILs, N, N, N-trimethyl-N-dodecylammonium 2-mercaptobenzothiazolate (N12) and 1-ethyl-3-methylimidazolium 2-

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https://doi.org/10.1016/j.triboint.2018.04.019
Received 14 March 2018; Received in revised form 16 April 2018; Accepted 18 April 2018
Available online 19 April 2018

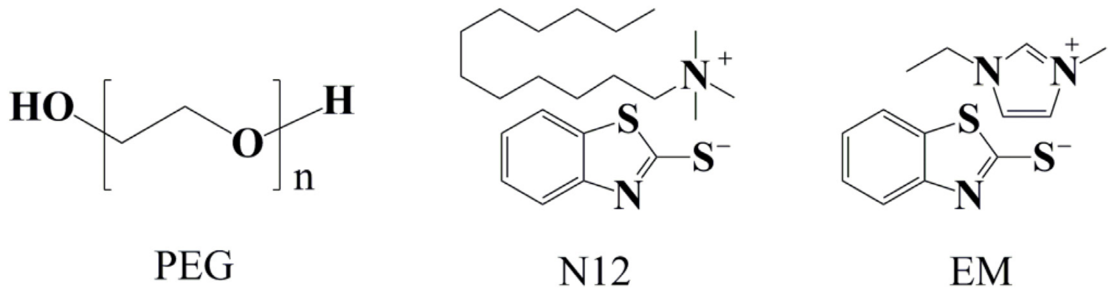

Fig. 1. Chemical structures of PEG base oil and MBT based ILs used in this study: polyethylene glycol 200 (PEG); N, N, N-trimethyl-N-dodecylammonium 2-mercaptobenzothiazolate (N12); 1-ethyl-3-methylimidazolium 2-mercaptobenzothiazolate (EM).

mercaptobenzothiazolate (EM), cf. Fig. 1, which exhibit low corrosion and excellent lubricity for steel/bronze system [10]. In this paper, we investigate MBT based ILs and Mo nanoparticles as hybrid additives for steel/steel contact. The synergistic effects between these two additives on lubrication performances are assessed systematically. The outcomes help to reveal the interaction mechanisms between ILs and metal nanoparticles when using as hybrid lubricant additives and facilitate the development of new and effective lubricants.

2. Experimental details

The two MBT based ILs (N12 and EM) investigated in this paper were synthesized following the methods described in previous studies [10]. The chemical structures of N12 and EM IL are presented in Fig. 1. The structure analysis of EM ILs is described in our previous study [10]. The structure analysis data for N12 ILs is presented in Appendix.

Mo nanoparticles were purchased from Shanghai ChaoWei Nanotechnology Co., Ltd. The size of nanoparticles was measured using the JEM-1200EX/S TEM; results were presented in Fig. 2. The size of Mo nanoparticles distributes from 20 nm to 100 nm. The base oil was polyethylene glycol 200 (PEG) (Guangdong Xilong Chemical Regent Company). PEG oil samples containing 1.0 wt% nanoparticles or 1.0 wt % ILs were prepared by stirring for 5 min and then ultrasonically dispersing for 3 min. PEG oil samples containing hybrid additives (0.5 wt% ILs + 0.5 wt% Mo nanoparticles) were prepared using the same method above.

The tribological properties of neat PEG oil and PEG with different additives were tested using an optimal SRV-IV oscillating reciprocating friction and wear tester. The upper running ball is AISI 52100 steel with a diameter of 10 mm. The lower stationary disk is AISI 52100 steel with a diameter of 24 mm and thickness of 7.9 mm. Before the test, the disk was abraded and polished to gain a smooth surface with a roughness (Ra) of 0.025 μm. After that, the specimens were rinsed in acetone ultrasonically, and dried in N_2 flow. The contact force between the frictional pairs was achieved by pressing upper steel ball on the lower steel disk. The lubrication properties were tested at 20 °C and 100 °C, respectively. All the tests were carried out under certain conditions (frequency: 25 Hz, amplitude: 1.0 mm, load: 100 N, relative humidity: 10–30%). The wear volumes of lower disks were calculated by MicroXAM-800 3D surface mapping microscope profilometer.

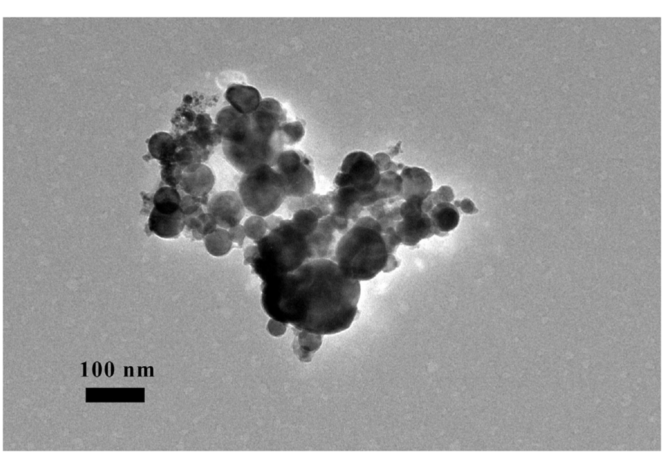

Fig. 2. The TEM micrographs of Mo nanoparticles.

A JSM-5600LV Scanning Electron Microscope (SEM) equipped with a Kevex energy-dispersive X-ray spectrometer (EDS) attachment was used to detect the morphologies and chemical composition of worn surfaces. The X-ray photoelectron spectrometer (XPS) aided by Ar-ion sputtering was utilized to test the chemical changes of elements on the worn surfaces. The exciting source of XPS was Al Kα radiation. Ar ion sputtering was under 2 KeV ion beam energy. The spectra were recorded after 30 s of Ar ion sputtering on the surface, which was used to remove the contaminants on the worn surfaces. The reference binding energy 284.8 eV for C1s was used to calibrate binding energies of elements. Raman spectroscopy (LabRAM HR Evolution, 532 nm laser excitation) was employed to characterize the structural features of worn surface. The cross-sectional TEM samples were prepared using FEI Helios Nanolab G3 CX Dual Beam-Focused Ion Beam (FIB) System with a Pt source as protecting layer. TEM images and EDS elemental mapping were acquired using Titan G2 80-200 TEM/STEM equipped with Super-X 4-SDD, windowless EDS system. Before these tests, specimens were cleaned in acetone ultrasonically for 5 min at least.

3. Results and discussion

3.1. Lubrication performances of MBT based ILs and Mo nanoparticles

Two MBT based ILs (N12 and EM) and Mo nanoparticles as hybrid lubricant additives in PEG base oil were investigated for steel/steel contact at 100 °C and 20 °C, respectively. Fig. 3a shows the evolution of friction coefficients with time at 100 °C. The friction coefficient of PEG base oil fluctuates significantly in the first 300 s, and then becomes smoother but presents an ascending tendency till the end. This result indicates that PEG base oil lubricates the steel surface poorly at 100 °C. The addition of Mo nanoparticles in PEG oil reduces the friction coefficient by ~10% in the initial period. After that the friction coefficient curve increases gradually and overlaps with PEG base oil, which means that the addition of Mo nanoparticles in PEG oil has limited effect on the friction-reduction properties. For the addition of N12 IL, after a *run-in* period of 300 s, the friction coefficient curve becomes smooth and steady. N12 IL as additive in PEG oil exhibits better friction-reduction effect than Mo nanoparticles when the sliding process is longer than 1800 s. When combining the N12 IL and Mo nanoparticles together and using them as hybrid additives in PEG oil, the friction coefficient curve is similar with neat PEG base oil in the first 600 s. Afterwards, the hybrid additive system shows the lowest friction coefficient, which is ~40% lower than that of neat PEG oil.

Fig. 3b shows the evolution of friction coefficient curves with time at 20 °C. For neat PEG oil, after the initial fluctuant *run-in* period of