Tribology International 81 (2015) 38–42

Contents lists available at ScienceDirect

Tribology International

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

Ionic liquid modified multi-walled carbon nanotubes as lubricant additive

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ARTICLE INFO

Article history:
Received 29 May 2014
Received in revised form
15 July 2014
Accepted 22 July 2014
Available online 1 August 2014

Keywords:
Ionic liquid
Additive
Anti-wear
Lubrication mechanism

ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were modified by imidazolium-based ionic liquid (IL), 1-hydroxyethyl-3-hexyl imidazolium tetrafluoroborate and used as an additive in base stock IL 1-methyl-3-butylimidazolium tetrafluoroborate as the base lubricant. The effectiveness of using the IL- modified MWCNTs as lubricant additive was evaluated using a ball-on-plate configuration on an Optimol SRV oscillating friction and wear tester. The worn surfaces were examined using scanning electron microscope and the chemical composition on wear tracks was analyzed on an X-ray photoelectron spectrometer. Results suggest excellent anti-wear properties for the IL-modified MWCNTs as lubricant additive.

1. Introduction

The fundamental research on carbon nanotubes (CNTs) have been well conducted in past two decades [1–6]. Due to their intrinsic structures, good mechanical and electron transport properties, CNTs have many potential applications, such as nanoelectronic devices [7–9], probe tips for scanning probe microscopy [10], batteries [11], sensors [12], and field emitters [13].

To facilitate wider usage, several methods have been employed to modify CNTs surface noncovalently or covalently [4,5] to improve the compatibility of CNTs with other materials. Composites derived from CNTs have demonstrated interesting mechanical and tribological properties that are not found in the individual components [14–16].

Ionic liquids are molten salts which have low melting point. Ionic liquids have drawn increasing attention due to their remarkable properties which include chemical and thermal stability, negligible volatility, electrochemical stability and high ionic conductivity [17]. Ionic liquids have been employed as green solvents in many fields such as synthesis, electrochemistry, catalysis and extraction [17–22].

ILs has good solubility in many organic and inorganic solvents and shows good lubricant property as base stock and lubricant additive [23–27]. They can be used to adjust CNT's interfacial properties [28–31]. So far, limited literature has studied mechanical and tribological properties for IL modified CNTs [32–36]. The IL modified CNTs might be suitable as additives for various lubricating systems via tailoring the molecular structure. Our previous work has reported tribological property under slight loads at room temperature [33]. As a follow-on study, this paper presents the performances of IL-modified CNTs as lubricant additives under higher applied loads and a range of temperatures.

2. Experimental section

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) were provided by Shenzhen Nanoport Company, China. The diameter of raw MWCNTs is around 60 nm. IL 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ($HMImBF_4$) was synthesized using the method described in Ref [37] to modify MWCNTs. 1-methyl-3-butylimidazolium tetrafluoroborate (L-B104) was synthesized to be used as the base lubricant.

2.2. Sample preparation and characterization

MWCNTs were purified and then modifed by grafting $HMImBF_4$ to their surface [30]. Fig. 1 illustrates the chemical modification procedure.

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http://dx.doi.org/10.1016/j.triboint.2014.07.019
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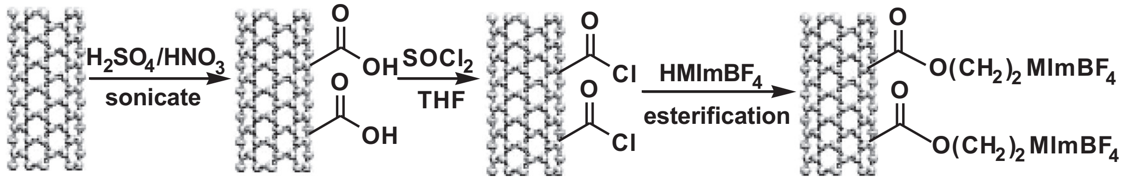

Fig. 1. Schematic depiction of the process for IL modified MWCNTs.

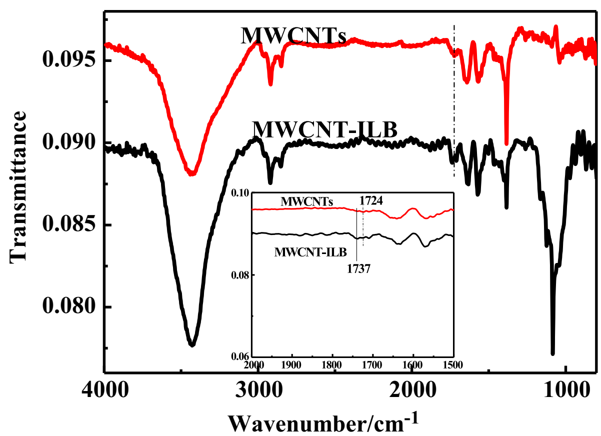

Fig. 2. FTIR spectra of MWCNTs and MWCNT-ILB.

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze MWCNTs sample before and after chemical modification. As compared in Fig. 2, the C=O vibration shifts from 1724 cm^{-1} to 1737 cm^{-1} after the surface modification. This is attributed to the transition from –COOH to –COO–. The characteristic band of 1084 cm^{-1} was assigned to the B–F stretching vibration in MWCNT-ILB. The FTIR data confirmed that $HMImBF_4$ was covalently attached onto the MWCNTs surface.

IL-modified MWCNTs are prone to be dispersed in traditional ionic liquids and many solvents [23,24]. L-B104 was used as a base lubricant in this study and MWCNT-ILB was added as additive with good dispersibility.

Lubricants with various concentrations of MWCNT-ILB in L-B104 were prepared. The tribological performance was evaluated on an Optimol SRV (SRV is the abridged name for German Schwinggung, Reibung, Verchleiss) reciprocating sliding tribo-tester. The upper ball (10 mm in diameter, SAE_52100 steel) rubs against the stationary lower steel flat (SAE_52100 steel). All tests were conducted with a stroke of 1 mm under a frequency of 30 Hz for 20 min sliding. Five drops of lubricant were applied to the ball-disc contact area before each test. The friction coefficient was recorded in-situ. The wear volume was measured using a non-contact 3D surface interferometer (Micro MAX, ADE phase shift) after the test. The worn surface morphologies were examined using a JSM-5600LV scanning electron microscope (SEM). The chemical composition on the wear tracks was determined by a PHI-5702 multifunctional X-ray photoelectron spectrometer (XPS) using Al Kα radiation as the exciting source. The binding energies of target elements were determined at the pass energy of 29.35 eV, with a resolution of about ± 0.3 eV, using the binding energy of contaminated carbon (C1s: 284.8 eV).

3. Results and discussion

Fig. 3 shows the friction and wear results when L-B104 with various concentrations of MWCNT-ILB as additive at 20 °C under various applied loads.

From Fig. 3a, it can be seen that friction coefficient decreases when additive concentrations are lower than 0.05% under all applied loads. The best friction-reduction results were observed at the concentration of 0.01%. The higher concentration of MWCNT-ILB would be disadvantage to form the oil film. So the oil film between the two sliding surfaces is not intact in the friction process. It will result in the higher friction coefficients. Fig. 3b and c presents the wear volumes of upper steel balls and lower steel discs respectively. It is seen that the additive demonstrates good anti-wear performance especially under higher loads. The lubricant containing 0.01% MWCNT-ILB provided the smallest wear volumes on the steel discs. The lubricant containing lower concentrations of additive yielded excellent anti-wear properties whereas those containing higher concentrations generate moderate anti-wear performance. Above results indicate that MWCNT-ILB could enhance friction-reduction and wear-resistant properties when it dispersed in L-B104 with lower concentrations.

Fig. 4 shows the variation of friction coefficients and wear volumes with different concentrations of additive under various tested temperatures for a load of 600 N. Fig. 4a shows that friction coefficient increases with the test temperature. The friction-reduction ability seems to deteriorate when the temperature increases up to 150 °C. Typically, the lower viscosity of ionic liquids at higher temperature can decrease the friction coefficient. The base stocks with lower viscosity at 50 °C and 100 °C might result in lower friction coefficients. The additive can play its reducing friction role in the lubricating system. At 150 °C, L-B104 cannot keep its excellent friction-reduction ability due to thermal decomposition [38,39]. The decomposed base stock will influence the friction coefficient because of worse physical property. Here, it is hypothesized that there are more metal particles and MWCNT-ILB to interrupt the oil film between the two sliding surfaces because of higher temperature. Then the friction coefficients increased. From Fig. 4b and c, it can be stated that MWCNT-ILB plays an excellent role at lower concentrations under various tested temperatures. Under various evaluated temperatures, the wear volumes of 0.02% MWCNT-ILB/L-B 104 are smaller than those of lubricants with other concentrations additives. It can be attributed to the base stocks have lower visicosity at higher temperatures.

Fig. 5 presents SEM images of the worn surfaces of the steel balls lubricated by neat L-B104 and L-B104 with 0.01% MWCNT-ILB at 600 N under room temperature respectively. As observed in Fig. 5, under lubricated by L-B104 with 0.01% additive, the diameter of wear scar was smaller. The slighter scuffing extent on worn surfaces can attribute to MWCNT-ILB as additive.

Fig. 6 displays SEM images of the wear scars on the steel discs when neat L-B104 and L-B104 with 0.01% MWCNT-ILB are used as lubricants under room temperature at 600 N. The grooves seen on the worn surfaces are believed to be the result of galling. The amplitude and the frequency of reciprocating motion during the tests are similar to those seen in contacts subjected to fretting. As shown in Fig. 6a, severe damage was observed on steel disc surface lubricated by neat L-B104, while Fig. 6b suggests lubricant additive MWCNT-ILB reduces the damage. As known, both adhesion and abrasion occur in a contact subjected to fretting motion. When tangential reciprocating motion is imposed on the surfaces against