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Effect of multi-walled carbon nanotubes on tribological properties of lubricant①

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Abstract: After purified by mixture of sulfuric acid and nitric acid, the multi-walled carbon nanotubes(MWNTs) were modified with stearic acid(SA). The modified carbon nanotubes as lubricant additive were utilized to prepare lubricant, and the effects of carbon nanotubes on the tribological properties were investigated by using a pin-on-plate wear tester. The surface structure of MWNTs was examined by transmission electron microscopy, Raman spectroscopy and infrared spectroscopy. The results show that the surfaces of MWNTs are coated with a modified layer of SA. Furthermore, the modified MWNTs as lubricant additive can effectively improve the friction-reduction and anti-wear ability of lubricant. The friction coefficient of base lubricant decreases by about 10% and the wear loss of base lubricant decreases by 30%-40% when the concentration of modified MWNTs in lubricant is 0.45%. In addition, the mass ratio of SA to MWNTs influences the friction-reduction and anti-wear ability of the modified MWNTs as lubricant additive. The optimum mass ratio of MWNTs to stearic acid is about 3∶8-1∶2.

Key words: carbon nanotube; modification; lubricant additive; tribological property
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1 INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991[1], the CNTs have attracted a great deal of attention because of their unique structural, electronical, and mechanical properties. Many potential applications of CNTs, such as nanodevices, quantum wires, ultrahigh-strength engineering fibers, sensors, and catalyst supports[2-6], have been found. CNTs as reinforcing elements can improve the properties of metal base composite significantly[7-10], but it is well known that the CNTs are chemically inert, and the use of CNTs as reinforcing elements will suffer from poor dispersion capability and weak interfacial interactions. Therefore, activating and modifying CNTs are an essential prerequisite for improving the activity of CNTs and expanding their application areas. Currently, chemical modification of CNTs is an efficient means for modifying the chemical properties, physical properties and the wettability of CNTs. For example, surfactants and polymers have improved the dispersions of CNTs in solution[11-13]. Organic molecules like dyes, proteins or nucleic acids may be coupled with functionalized CNTs for sensor application[14]. Certain proteins and DNA have been demonstrated to modify the multi-walled carbon nanotubes(MWNTs)[15].

In addition, chemical modified CNTs provide an attractive method to improve the properties of CNTs composites. Hernadi et al[16] reported that the wettability of CNTs in composite material was improved by a proper inorganic coating. Gojng et al[17] used multi-functional amines to modify MWNTs, and then the functionalized nanotubes were embedded in the epoxy resin. Their results indicate that the functionalization leads to a reduced agglomeration and an improved interfacial interaction between the CNTs and the epoxy resin. In spite of various attempts of researchers, using CNTs as reinforcing additives, there are three major obstacles to overcome, such as, the poor solubility of CNTs in solvent, the wettability of CNTs surface and the load transfer from the matrix to CNTs. Hence, further development in the modification of CNTs is still required.

The stearic acid(SA), which is one of the most important lubricant and dispersant, was proposed as good candidate for practical applications. In this paper, a simple approach to modify MWNTs with SA through esterification was reported and the tribological properties of modified MWNTs as lubricant additive were investigated. Moreover, the variations of friction coefficient and

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wear loss with the mass ratio of SA to MWNTs were investigated.

2 EXPERIMENTAL

2.1 Preparation and purification of multi-walled carbon nanotube

The MWNTs used in this study were prepared by the chemical catalytic vapor deposition process (CCVD). The details of the MWNTs preparation have been discussed in Ref. [18]. MWNTs growth was obtained on the catalyst at 725 ℃ with a flow rate of acetylene 50 mL/min and nitrogen 300 mL/min for 30 min. As-prepared products were purified by immersing in a mixture of concentrated HNO_3 and HCl($V(HNO_3)$: $V(HCl)$ = 1 : 5) and refluxed for 2 h. After filtered and washed with de-ionized water, the products were dried at 120 ℃. The purified MWNTs were mechanically milled for 20 h with a planetary ball mill under nitrogen protection at a rotating speed of 257 r/min. The mass ratio of steel ball to purified MWNTs is 50 : 1. In order to remove the impurity in MWNTs and generate oxygenated functional groups, the ball-milled MWNTs were suspended in a mixture of concentrated H_2SO_4 and HNO_3 ($V(H_2SO_4)$: $V(HNO_3)$ = 3 : 1) and refluxed for 0.5 h, then filtered and washed with de-ionized water again, finally dried at 120 ℃. The MWNTs samples were characterized by transmission electron microscopy (H800, TEM), Raman spectroscopy (Jobin Yvon, Labran-010, maded in France) and infrared spectroscopy (300E Jasco spectrometer).

2.2 Modification of MWNTs

The preparation of modified MWNTs with stearic acid is as follows: firstly, the purified MWNTs were added into distilled water, and the mixture of MWNTs was ultrasoniced to disperse the MWNTs; secondly, the SA was added into the suspension of the MWNTs; thirdly, 10 mL sulfuric acid (2 mol/L) was dropped into the suspension of MWNTs, stirred and refluxed under 100 ℃ for 2 h, the reaction mixture was cooled to ambient temperature and extracted with chloroform, then precipitated into hexane; finally, this suspension was filtered using a membrane with 0.1 μm pore size and dried at 60 ℃. The resultant MWNTs was examined by TEM, Raman spectroscopy and infrared spectroscopy.

2.3 Preparation of composite lubricant

For the preparation of various lubricant, the modified MWNTs were dispersed in lubricant through sonication and stirring of magnetic force for 1 h under 80 ℃ (rotate speed is 500 r/min). For comparison, the lubricants of graphite were prepared under the same condition. The mass fraction of graphite is 0.15% in lubricant.

2.4 Measurement of tribological properties

The friction and wear tests were conducted on a MPX-2000 model ring-on-plate wear-testing machine (made in Xinhua Hebei Tester Factory of China). A bearing steel plates used in the test were bearing steel of 34 mm in diameter and 10 mm in height with a hardness of HRC60, coupling with a bearing steel ring which inner diameter is 20 mm, outer diameter is 32 mm and hardness is HRC60. The steel plates were fixed in lubricant bath and the bearing steel ring rotated over the plate. All wear experiments were conducted at room temperature and rotating rate of 384 r/min. The test duration was 100 min. The wear tests were evaluated according to the mass loss of the bearing steel plate after wear testing by an analytical electron balance (precision 10^{-6} kg). Before measuring, all plates were cleaned with alcohol in an ultrasonic bath for 10 min, and then dried at room temperature in air. The friction coefficients were measured simultaneously during the process of wear test.

3 RESULTS AND DISCUSSION

3.1 Morphology of carbon nanotubes

Fig. 1 shows the morphology of CNTs. A low magnification TEM image (Fig. 1(a)) shows that the raw materials contain CNTs and non-nanotubes materials. After purified by acid, the metal particles, the oxide particles and nano-nanotubes carbon materials have been eliminated completely, and the high purity MWNTs have been obtained without damage. The MWNTs made by CVD have central hollow tubes; the outer diameter of most of the MWNTs ranges from 20 nm to 40 nm, as shown in Fig. 1(b). In addition, it can also be seen form Fig. 1(b) that the MWNTs are not only curved after purification, but also entangled into large mass. So, in order to obtain short and straight MWNTs, ball milling should be performed. TEM image of the ball-milled MWNTs for 20 h is shown in Fig. 1(c). It can be seen that the average length of the MWNTs after ball milling is reduced obviously. Moreover, all the MWNTs are distributed in the form of isolated tube. Fig. 1(d) shows the TEM microstructure of MWNTs after modified. From this figure it can be seen that the SA appears as aggregates on the surfaces of the MWNTs. The result indicates that the MWNTs are coated by stearic acid.

3.2 Spectroscopy of MWNTS

The spectrum analyses of MWNTs are shown in Fig. 2. The FTIR spectrum of the acid-treated

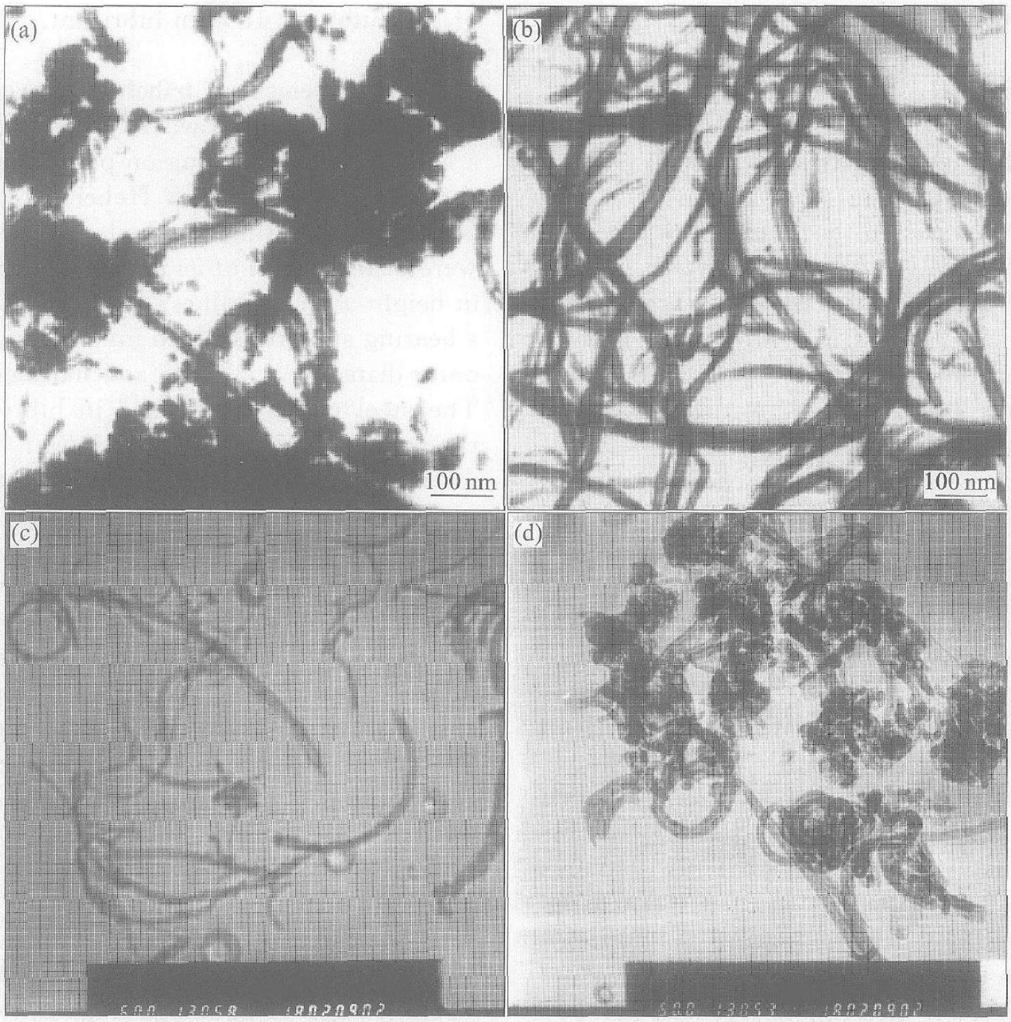

Fig. 1 Microsturctures of CNTs
(a) —As-produced crude materials; (b) —Before ball-milling; (c) —After ball-milling; (d) —After steric acid modification

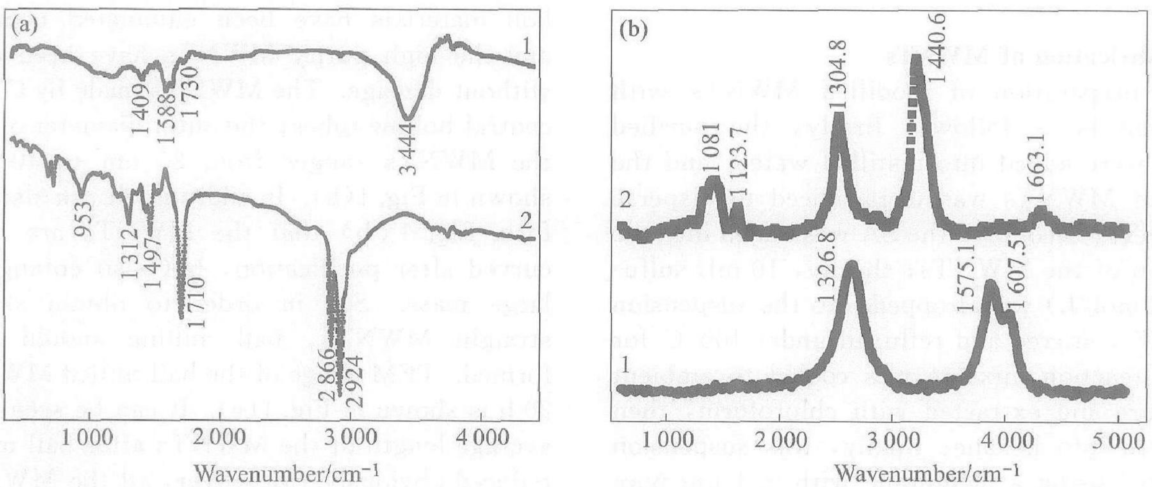

Fig. 2 Infrared spectrums (a) and Raman spectrums (b) of CNTS
(1 —Before modification; 2 —After modification)

MWNTs shows the presence of many groups on the surface of the acid-treated MWNTs, such as carbonyl groups reveal at about 1 730 cm^{-1}, oxygen-hydrogen bonds and C —C bonds at about 3 444 cm^{-1} and 1 588 cm^{-1}, respectively (as shown in the curve 1 of Fig. 2(a)). After modified with SA, the characteristic peaks of the SA are observed on the MWNTs at about 2 924 cm^{-1}, 2 866 cm^{-1}, 1 312 cm^{-1} and 953 cm^{-1}, respectively (see Fig. 2(a)). The two new peaks at 2 924 cm^{-1} and 2 866 cm^{-1} are attributed to CH_3 and CH_2 stretching mode, respectively. In addition, the new peak observed at about 1 497 cm^{-1} should be attributed to —COO^-, which is considered a shift from —COOH to —

COO^-. This confirms the effect of linkage between —OH on MWNTs and —COOH on SA by eaterification.

From curve 1 of Fig. 2(b), it can be seen that the D and G modes of MWNTs are observed at about 1 326.8 cm^{-1} and 1 575.1 cm^{-1}, respectively. Moreover, a very strong peak is observed at 1 607.5 cm^{-1}, designated as the D′ modes of MWNTs. The experimental measurements are very close to the earlier experimental result of Tan et al[19]. After MWNTs are modified, the G mode and D′ disappear, and two new peaks at 1 440.6 cm^{-1} and 1 081 cm^{-1} corresponding to CH_3 and CH_2 modes are observed (see Fig. 2(b)). It is further confirmed that the MWNTs are coated by SA.

3.4 Tribological properties of MWNTs as lubricant additive

3.4.1 Effect of stearic acid content

Fig. 3 depicts the variation of the friction coefficient and wear loss with content of SA for lubricant containing 0.2% MWNTs under 1 000 N. The results indicate that under a load of 1 000 N, the friction coefficient decreases with the increasing content of SA when the content of SA is below 0.4%. However, as the content of SA increases beyond 0.4%, the friction coefficient increases with the increasing content of SA (Fig. 3(a)). Also, when the stearic acid content in the lubricant surpasses 0.4%, the wear loss increases with the increasing content of SA, as shown in Fig. 3(b).

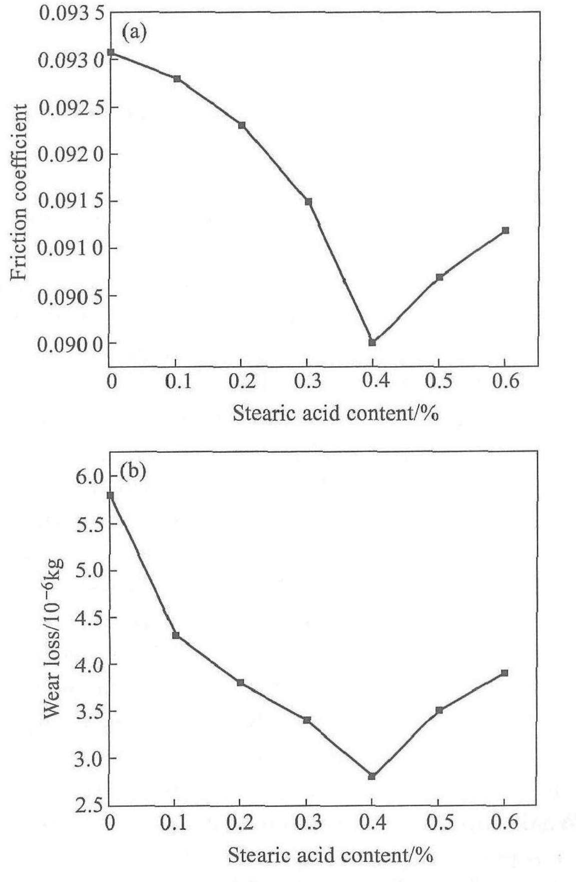

Fig. 3 Variations of friction coefficient (a) and wear loss (b) with content of SA for lubricant containing 0.2% MWNTs under 1 000 N

3.4.2 Effect of MWNTs content

Fig. 4 shows variation of friction coefficient and wear loss with MWNTs content for lubricant containing 0.4% stearic acid under a load of 1 000 N. When the content of MWNTs in lubricant is below 0.15%, the friction coefficient and the wear loss show a steadily decreasing trend with the increasing content of MWNTs. However, with the increasing content of MWNTs higher than 0.15%, the friction coefficient and wear loss increase. The increasing friction coefficient and wear loss is likely to be attributing to that the MWNTs are easily conglomerated with the increasing concentration of MWNTs in lubricant. As discussed above, the presence of MWNTs can improve the friction-reduction and anti-wear ability of pure lubricant significantly. Furthermore, these results indicate that there is an optimum ratio between MWNTs and SA in improving the friction-reduction and anti-wear ability of lubricant, and the optimum ratio

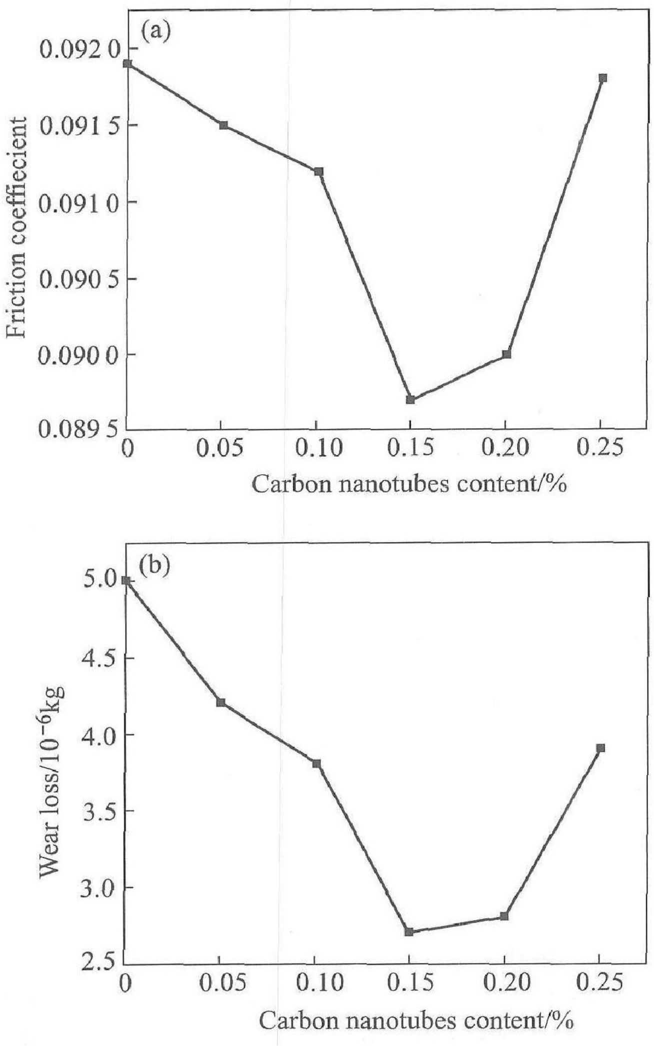

Fig. 4 Variations of friction coefficient (a) and wear loss (b) with MWNTs content for lubricant containing 0.4% stearic acid under 1 000 N

between MWNTs and stearic acid is about 3∶8−1∶2.

3.4.3 Effect of different additives

The variations of friction coefficient (a) and wear loss (b) with load are depicted in Fig. 5. The concentration of MWNTs additive in lubricant is 0.45%. From Fig. 5, it is very evident that the modified MWNTs as lubricant additive have lower friction coefficient and wear loss than pure lubricant. In addition, the friction coefficient and wear loss of different additives under load of 700 N are listed in Table 1. It can be seen that the modified MWNTs as lubricant additive have lower friction coefficient and wear loss than pure lubricant, the ball-milled MWNTs and modified graphite with stearic acid. The results imply that the modified MWNTs with SA can improve the friction-reduction and anti-wear ability of pure lubricant. Furthermore, it can be seen from Table 1 that the friction coefficient of ball-milled MWNTs is higher than that of the modified graphite, but the wear loss is lower than that of the modified graphite. The higher frictional coefficient is likely to be attributing to that the ball-milled MWNTs are easily conglomerated. However, the MWNTs have outstanding mechanical properties, resulting in decreasing the wear loss.

Table 1 Friction coefficient and wear loss of different additive under 700 N

Lubricant	Friction coefficient	Wear loss/10^{-6}kg
Based lubricant	0.096 7	4.2
Ball-milled MWNTs	0.095 6	3.0
Modified graphite	0.093 4	3.4
Modified MWNTs	0.090 3	2.8

3.4.4 Discussion

Because the friction-reduction and anti-wear ability of nano-particle as lubricant additive depend on both the property of nano-particle and the dispersion of nano-particle in lubricant, the friction-reduction and anti-wear ability of the modified MWNTs with SA as lubricant additive can be explained by well dispersion in lubricant and superior property of MWNTs. Due to the enormous aspect ratio and the very small diameter of MWNTs, there are a very strong van der Waals attraction forces between MWNTs, resulting in forming the large MWNTs bundles. So, the ball-milled MWNTs without modification as lubricant additive possess higher frictional coefficient. However, the MWNTs have more superior mechanical property and better self-lubricant property than the graphite, leading to the decreasing wear loss.

Furthermore, as one of the good dispersant, SA could be efficient in preventing MWNTs from

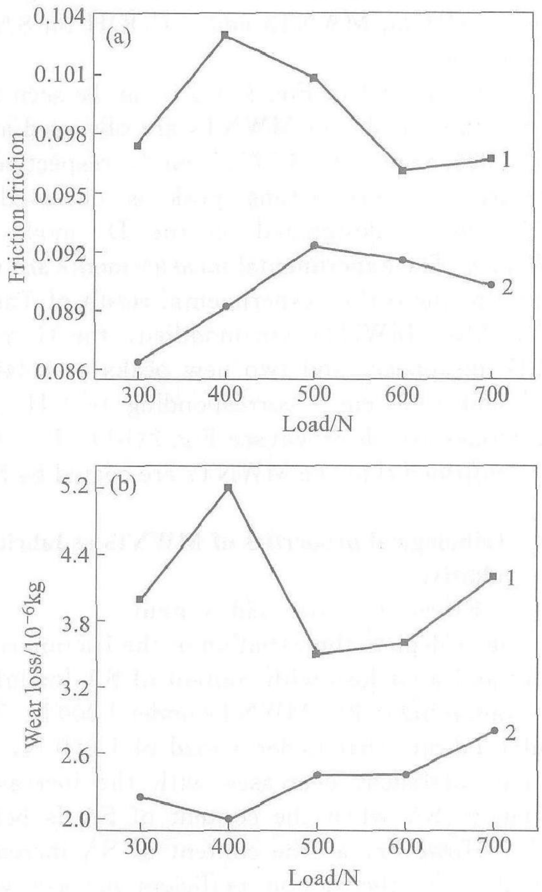

Fig. 5 Variations of friction coefficient (a) and wear loss (b) with load
1 —Pure lubricant;
2 —Modified MWNTs with stearic acid
(Lubricant contains 0.45% modified MWNTs which mass ratio of MWNTs to SA is 1∶2)

flocculating in base lubricant. It is well known that the SA molecules are long hydrocarbon chain molecules, which are a hydrocarbon segment (alkyl chain) and hydrophilic segment (carboxylic groups). Moreover, it can be seen from the infrared spectrum (Fig. 2(a)) that there were many hydroxy groups and carboxylic groups on the surface of MWNTs after oxidized by mixture acid. So, after the ball-milled MWNTs are modified with SA, many SA molecules are adsorbed on surface of MWNTs by the esterification reaction or physical attraction, i.e. the hydrophilic segment of SA molecules are anchored on the surface of MWNTs. When the modified MWNTs are dispersed in base lubricant, the long hydrocarbon segment (alkyl chain) stretched into base lubricant very easily, resulting in the formation of steric hindrance force. The steric hindrance force can conquer the van der Waals interaction between MWNTs, thereby help to separate them from each other. At the same time, the steric hindrance force can conquer the gravity and prevent the MWNTs from coagulating[20−22].

Because the modified MWNTs with SA can

stability disperse in lubricant, two mating wear surfaces are easily filled with the dispersed MWNTs during the wear process, and then the MWNTs on wear surface can serve as spacers, preventing rough contact between the two mating wear surfaces, thereby improving the friction-reduction and anti-wear ability of pure lubricant considerably. Moreover, owing to MWNTs being shortened, the short and tube shape of the MWNTs will provide very easy shear and more easy slide or roll between the two mating wear surfaces, leading to decreasing the friction coefficient and wear loss.

In addition, it is well known that the SA is both good dispersant and good lubricant. With the addition of SA, the dispersion of MWNTs in lubricant is improved. Moreover, the SA on the surface of the MWNTs can form a layer of SA molecule in lubricant, resulting in forming the effective membrane of lubricant during the wear process, therefore the friction-reduction and anti-wear ability of lubricant are improved significantly. However, when the concentration of SA further increases in lubricant, the SA is easily decomposed and oxidized during the wear process due to instability of SA at high temperature, resulting in the friction coefficient and wear loss increase.

4 CONCLUSIONS

The SA direct-modified MWNTs can be produced by esterification reaction. The modified MWNTs with SA can effectively improve the friction-reduction and anti-wear ability of pure lubricant. When the concentration of modified MWNTs in lubricant is 0.45%, the friction coefficient of base lubricant decreases by about 10% and the wear loss decreases by 30%－40%. Moreover, the optimum ratio of MWNTs to SA is about 3∶8－1∶2.

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