Macromolecular Nanotechnology

Synthesis of water-soluble carbon nanotubes via surface initiated redox polymerization and their tribological properties as water-based lubricant additive

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ABSTRACT

Polyacrylamide (PAM)-grafted multi-walled carbon nanotubes (MWCNTs-g-PAM) which are dispersable in water were prepared by the surface initiated redox polymerization of acrylamide using ceric ammonium nitrate (CAN) as initiator. They are soluble in polar solvents such as water, tetrahydrofuran and acetone. The chemical structure of the resulting product and the quantities of grafted polymer were determined by FT-IR, TGA. TEM, and FE-SEM observations indicated that the nanotubes were coated with a PAM layer, exhibiting core-shell nanostructures, with the PAM chains as a brush-like or hairy shell, and the MWCNTs as a hard backbone. Furthermore, the tribological properties of the prepared MWCNTs-g-PAM composites as an additive in water were evaluated with a four-ball machine. The results confirmed that the composites exhibit good anti-wear and friction reduction properties as well as load-carrying capacity. This was attributed to the possibility of the composites acting as nanometer sized tiny bearings during lubrication.

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1. Introduction

Owing to their unique structures and properties in the fields of nanoscience, nanotechnology, and bioengineering, carbon nanotubes (CNTs), including both single- and multi-walled, have attracted worldwide attention [1,2]. In terms of mechanical properties, CNTs are quite stiff, and exceptionally strong. Therefore, CNTs are believed to be the ideal material for composites with high performance, e.g. excellent tribological properties [3–8]. The tubelike structures of CNTs lead to high load-carrying capacities. However, there is no good solvent that can dissolve them, and this dramatically limits the research and exploitation of CNTs as lubricant additives. An appropriate energy input

by sonication treatment is a way to separate the disentangled tubes, whereas surface functionalization is a possible strategy to disperse the material in solution permanently.

Among the functionalization of CNTs, covalently attaching polymer chains onto the surfaces of CNTs has recently attracted considerable attention because it endows the surface with novel structures and properties. Using this strategy various linear polymers, copolymers, dendritic, and hyperbranched polymers were successfully grafted onto the sidewall of CNTs [9] through a series of reaction strategies such as atom transfer radical polymerization (ATRP), ring-opening polymerization (ROP), reversible addition and fragmentation chain transfer polymerization (RAFT) [10–19]. However, the preparation of water-soluble CNTs via redox polymerization has seldom been studied. Tasis et al. [20] reported the preparation of water-soluble CNTs by grafting polyacrylamide chains from the graphitic surface via ceric ion-induced redox radical polymerization. They firstly covalent attach organic radicals which generated from organic peroxides to the sidewall of CNTs. Then

the polyacrylamide-coated CNTs were prepared by applying a ceric ion-induced redox process. As a versatile method for the growth of polymer chains, the redox radical polymerization can provide a powerful strategy for modifying the surface of CNTs with polymer chains. The main advantage of this grafting method is that it proceeds in aqueous media and at room temperature.

Recently, water-based lubricants are widely used for numerous areas such as hydraulic fluid, cutting fluid, metal-forming operations, and oil extraction industry. Compared with conventional oil and grease lubricants, water-based lubricants consisting of less than 5% additives may offer many merits, such as being eco-friendly, high thermal conductivity, saving oil resources, low working temperature, etc. Therefore, it is a new, necessary and promising domain to develop a high-performance lubricating additive in water.

Up to this date, the tribological properties of water-soluble CNTs and their derivatives have seldom been studied. Considering the above mentioned factors, we describe a new process to graft water-soluble polymer chains from the surface of MWCNTs. This process was followed by the surface initiated radical graft polymerization of acrylamide using a redox system consisting of ceric ion and reducing groups (amino) on the surface of MWCNTs as initiator. The radical formed by the redox reaction of ceric ions with amino groups on MWCNTs-NH_2 initiate the polymerization. This surface initiated polymerization offers a promising and versatile method of preparing water-soluble CNTs-based composites which can be used as water-based lubricant additives. Furthermore, the potential tribological property of this composite as water-based lubricant additive was also investigated. A schematic description of the above processes is given in Fig. 1.

2. Experimental

2.1. Materials and instrumentation

The MWCNTs used in this study were purchased from Shenzhen Nanotech Port Co. Ltd., the purity is higher than 95%. Ceric ammonium nitrate (CAN), thionyl chloride ($SOCl_2$), ethylenediamine, and nitric acid (AR, 1st Chemical Reagent Factory, Shanghai, China) were used without further purification. Acrylamide (AR, 1st Chemical Reagent Factory, Shanghai, China) was purified by recrystallisation

from methanol (two times) and dried in vacuum oven at 45 °C overnight. Tetrahydrofuran (THF) was refluxed over sodium and distilled twice before use. All other regents were used without further purification.

Fourier transformation IR (FTIR) spectra were recorded on an IFS 66v/S FTIR spectrometer (Bruker, Germany) using the KBr disk method. Thermal gravimetric analysis (TGA) were made with a Perkin–Elmer TGA-7 instrument under air atmosphere at a heating rate of 283 K/min. The field emission scanning electron microscopy (FE-SEM) images were obtained on a JEOL JSM-6701 F field emission scanning electron microscope. Because the conductivity of the samples were not sufficient for SEM. Therefore, the samples were loaded on the surface of copper substrate previously sputter-coated with a homogeneous gold layer for charge dissipation during the SEM imaging. Transmission electron microscopy (TEM) analyses were conducted on a Hitachi Model H-600 electron microscope at 100 kV. Scanning electron microscopy (SEM) images were examined using a JEM-1200EX (JEOL, Japan) microscope. The test of friction and wear properties were conducted on a four-ball friction, and wear tester (made in Jinan Testing Machine Factory of China). All wear experiments were conducted at room temperature at a rotating rate of 1450 rpm. The maximum nonseized load (PB Value) was obtained by GB3142–82 (Chinese Standard); wear scar diameter (WSD) was measured under a load of 392 N and a test duration of 30 min; friction coefficient was measured under a load of 392 N and a test duration of 10 s. The balls (diameter 12.7 mm, HRc 59–61) were made of GCr15 bearing steel (AISI-51200). The wear scar diameters were measured using an optical microscope to an accuracy of ±0.01 mm and the base stock was an aqueous solution of 2 wt% triethanolamine and 1 wt% S-(carboxylpropyl)-N-diethyl dithiocarbamic acid (CDDA, which we prepared).

2.2. Acid treatment of MWCNTs

A 100 mL flask charged with 2.0 g of pristine MWCNTs and 30 mL of 60% HNO_3 aqueous solution was sonicated in a bath (40 kHz) for 30 min and stirred for 20 h at reflux. After cooling to room temperature, the mixture was vacuum-filtered through a 0.22 μm polycarbonate membrane and washed with distilled water until the pH of the filtrate was 7.0. The filtered solid was dried under vacuum for 24 h at 60 °C to give about 1.3 g of carboxylic acid-functionalized MWCNTs (MWCNTs-COOH).
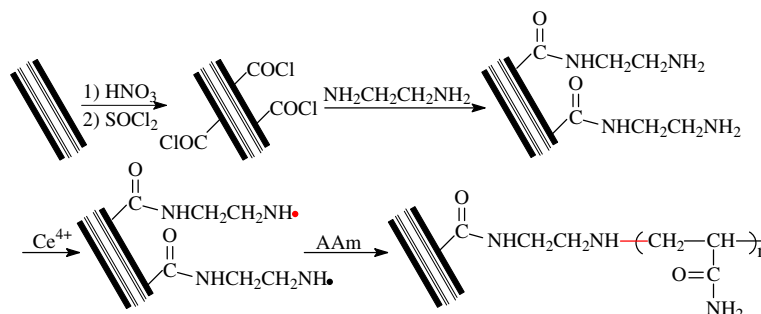

Fig. 1. Outlines of the surface initiated redox polymerization of acrylamide from MWCNTs.

2.3. Synthesis of MWCNTs-NH$_2$

Dried MWCNTs-COOH (1.0 g) was reacted with excess neat SOCl$_2$ (25 mL) at 70 °C for 24 h. The residual SOCl$_2$ was removed by distill under reduced pressure at 30 °C. The remaining solid (MWCNTs-COCl) was washed three times with anhydrous THF and was dried under vacuum at room temperature for 5 h. Then the solid (MWCNTs-COCl) (0.8 g) were reacted with 50 mL ethylenediamine at 100 °C for 2 days. After cooling to room temperature, the MWCNTs were washed with ethanol for five times to remove excess ethylenediamine. Finally, the black solid was dried at room temperature overnight under vacuum.

2.4. Surface initiated graft polymerization of acrylamide

For the surface initiated graft polymerization, 50 mg of MWCNTs-NH$_2$ were dispersed in 10 ml of deionized water under sonication for 30 min. Then 10 mL of 1 M aqueous solution of acrylamide were added. After deaeration of the system by bubbling nitrogen, 0.5 mL of 0.2 M solution of CAN in 1 M nitric acid was slowly added to initiate graft copolymerization. Graczyk and Hornof [21] reported that stirring speed is an important variable in determining percent conversion of monomer to polymer during graft polymerization. Therefore, the reaction mixture was stirred at a constant rate to avoid the effect of stirring on the rate of graft copolymerization. The polymerization was conducted at 30 °C under dry nitrogen for some times. After the reaction, the MWCNTs-g-PAM was separated by membrane filtrations and washed with distilled water. After repeated washing and filtration, the resulting solid was dried overnight in a vacuum.

2.4. Parallel experiment

In order to prove the covalent linkage of PAM onto MWCNTs and investigate the grafting mechanism, a parallel experiment was conducted. Typically, 50 mg of crude MWCNTs were dispersed in 10 ml of deionized water under sonication for 30 min. Then 10 mL of 1 M aqueous solution of acrylamide were added. After deaeration of the system by bubbling nitrogen, 0.5 mL of 0.2 M solution of CAN in 1 M nitric acid was slowly added to initiate graft copolymerization. The reaction mixture was stirred at a constant rate and the polymerization was conducted at 30 °C under dry nitrogen for some times. After the reaction, the solid was separated by membrane filtrations and washed with distilled water. After repeated washing and filtration, the resulting solid was dried overnight in a vacuum (the sample was called as CPAM in this paper).

3. Results and Discussion

3.1. Synthesis of MWCNTs-g-PAM via surface initiated redox polymerization

It has been reported that vinyl polymerizations are initiated by ceric ions in combination with organic reducing agents such as alcohols and amines [22–24]. In this paper, the polymerization of acrylamide was carried out using a redox system consisting of ceric ion and reducing groups (amino) on the surface of MWCNTs as initiator. In order to prove the covalent linkage of PAM onto MWCNTs and investigate the grafting mechanism, a parallel experiment was conducted. We dispersed crude MWCNTs in aqueous acrylamide solution in the presence of ceric ions. The reaction mixture was stirred at a constant rate and the polymerization was conducted at 30 °C under dry nitrogen for some times. After the reaction, the solid was separated by repeated washing and filtration, the resulting solid was dried overnight in a vacuum. FT-IR analysis indicates that the FT-IR spectra of CPAM is very similar to that of crude MWCNTs and no obvious characteristic absorption peaks of PAM can be found in this spectra. Furthermore, CPAM is insoluble in distilled water, this data further indicates that no PAM was grafted or mixed in the sample of CPAM. According to the above analysis we can conclude that the system consisting of ceric ions and crude MWCNTs has no ability to initiate the polymerization. On the contrary, the polymerization of acrylamide was found to proceed in the coexistence of ceric ions and MWCNTs-NH$_2$. Furthermore, PAM-grafted MWCNTs can be dispersed in water as a black suspension for at least one month before noticeable flocculates are observed. These results indicate that the radical formed by the redox reaction of ceric ions with amino groups on MWCNTs-NH$_2$ initiate the polymerization.

3.2. Characterization of MWCNTs-gPAM

Fig. 2 shows the FTIR spectra of pristine MWCNTs, MWCNTs-NH$_2$, MWCNTs-g-PAM and pure PAM. Compared with pristine MWCNTs (Fig. 2a), the FTIR spectra of MWCNTs-NH$_2$ (Fig. 2b) clearly shows the peaks at 1652 and 1575 cm^{-1} are due to the amide groups (amide band I and II, respectively), and the peaks at 3420 and 2925 cm^{-1} are due to N–H and C–H stretching, respectively. The FTIR spectra of MWCNTs-g-PAM is shown in Fig. 2c. After polymerization, the characteristic absorption peaks of PAM, such as N–H at 3420 cm^{-1}, C=O at 1653 cm^{-1}, –CH-CO– at 1450 cm^{-1}, and C–H at 2925 cm^{-1} can be found in Fig. 2c. These results indicate that PAM chains had successfully grafted from the surface of MWCNTs via surface initiated redox polymerization.
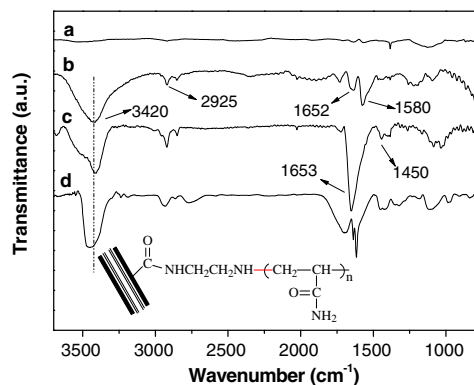

Fig. 2. FTIR spectra of (a) pristine MWCNTs; (b) MWCNTs-NH$_2$; (c) MWCNTs-g-PAM; (d) pure PAM.

Further evidence for PAM chains grafted from the surface of MWCNTs via surface initiated redox polymerization has been provided by TGA analysis. Fig. 3 displays the TGA weight loss curves of pristine MWCNTs, MWCNTs-NH$_2$, MWCNTs-g-PAM and pure PAM. The sample of pristine MWCNTs is stable without evident weight loss below 600 °C. On the contrary, there is a weight loss stage between 100 and 500 °C for MWCNTs-NH$_2$ (10.3%). This weight loss results from the losing of functional groups on the surface of MWCNTs. Compared with pristine MWCNTs, the TGA curve of MWCNTs-g-PAM showed a major decomposition at a temperature range from 230 to 500 °C corresponding to PAM layer on the surface of MWCNTs. The amount of polymer shell calculated from TGA data varies from 22.5% to 53.9% when polymerization time increased from 12 to 36 h. The onset of the decomposition temperature (T_d) of the PAM moieties in MWCNTs-g-PAM approached 230 °C, 50 °C higher than that (ca.180 °C) of pure PAM. Therefore, the thermal stability of the PAM chains can be dramatically improved by linkage with MWCNTs.

Dispersion of pristine MWCNTs into aqueous solution or organic solvent was very difficult even after it was sonicated. However, dispersion of MWCNTs-g-PAM into polar solvents such as water, tetrahydrofuran and acetone was very easy. So the solubility or dispersibility of the functionalized MWCNTs strongly depends on the structure and amounts of the grafted moieties. Fig. 4 gives the digital photos of pristine MWCNTs in distilled water and MWCNTs-g-PAM in distilled water. It is clear that the dispersibility of pristine MWCNTs in distilled water is very poor, and there was much sedimentation at the bottom of vial (Fig. 4A). However, MWCNTs-g-PAM is dispersable in distilled water, forming a homogeneous dispersion, and there was no sedimentation observed even after one month as shown in Fig. 4B. For comparison, we attempted to disperse the mixture of pristine MWCNTs (20%) and homo-PAM (80%) into distilled water, but it is shown that homo-PAM is a poor dispersant for MWCNTs in distilled water. All of the evidence indicates that PAM chains have grafted onto the surface of MWCNTs.

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) were
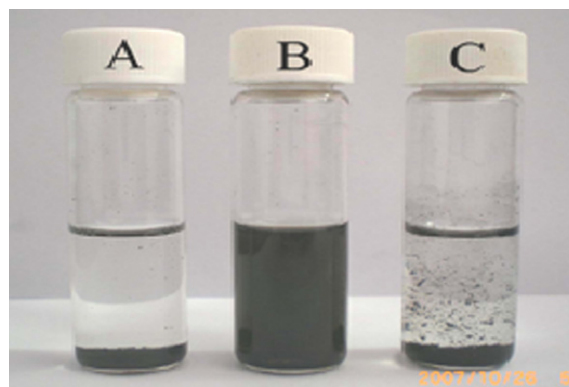

Fig. 4. (A) Photograph of pristine MWCNTs in distilled water; (B) MWCNTs-g-PAM in distilled water; (C) pristine MWCNTs (20%) and homo-PAM (80%) in distilled water.

employed to detect the structure and morphology of the resulting samples (Fig. 5). In the image of pristine MWCNTs (Fig. 5A), it is clear that many pristine MWCNTs were piled up and the average diameter of pristine MWCNTs is in the range of 20–40 nm. The surface of pristine MWCNTs is featureless, and there are little or no traces of amorphous carbon. Furthermore, FE-SEM image of pristine MWCNTs is also shown (Fig. 5a), exhibiting clearly distinctive tubelike morphology. The convex surfaces of pristine MWCNTs seem to be smooth with nothing adhering to them. In contrast, it can be found that after surface initiated redox polymerization, the surfaces of MWCNTs are coated with a PAM layer (Fig. 5B). Obviously, a core-shell structure with MWCNTs at the center can be clearly observed for the nanohybrids. The PAM grafted MWCNTs are individually dispersed, this can be attributed to the increased solubility of functionalized MWCNTs after surface modification. Furthermore, compared with pristine MWCNTs, the external diameters of the functionalized MWCNTs was about 60–80 nm which was remarkably increased. As a consequence, we believe such ideal wrapping would be the result of covalent grafting. In FE-SEM image of MWCNTs-g-PAM (Fig. 5b), a rod-like morphology or a compact mass is observed when the MWCNTs were grafted with PAM. These results indicate that a core–shell PAM brushes-anchored MWCNTs were prepared via surface initiated redox polymerization.

3.3. Tribological properties of MWCNTs-g-PAM as water-based lubricant additive

Since pure water has poor lubricity and bad corrosion-inhibiting property, a 2 wt% of triethanolamine and 1 wt% CDDA aqueous solution was chosen as base stock. As the additive, functionalized MWCNTs-g-PAM was well dispersed in the base stock and the tribological properties of base stock and base stock containing MWCNTs-g-PAM with various concentrations were evaluated using a four-ball friction and wear tester.

The relationship between the concentration of the functionalized MWCNTs (polymerized for 24 h) as additives to the base stock and the maximum nonseized load
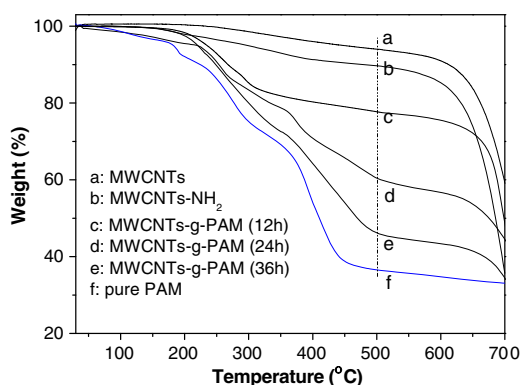

Fig. 3. TGA curves of (a) pristine MWCNTs; (b) MWCNTs-NH$_2$; (c) MWCNTs-g-PAM (polymerized for 12 h); (d) MWCNTs-g-PAM (polymerized for 24 h); (e) MWCNTs-g-PAM (polymerized for 36 h); (f) pure PAM.
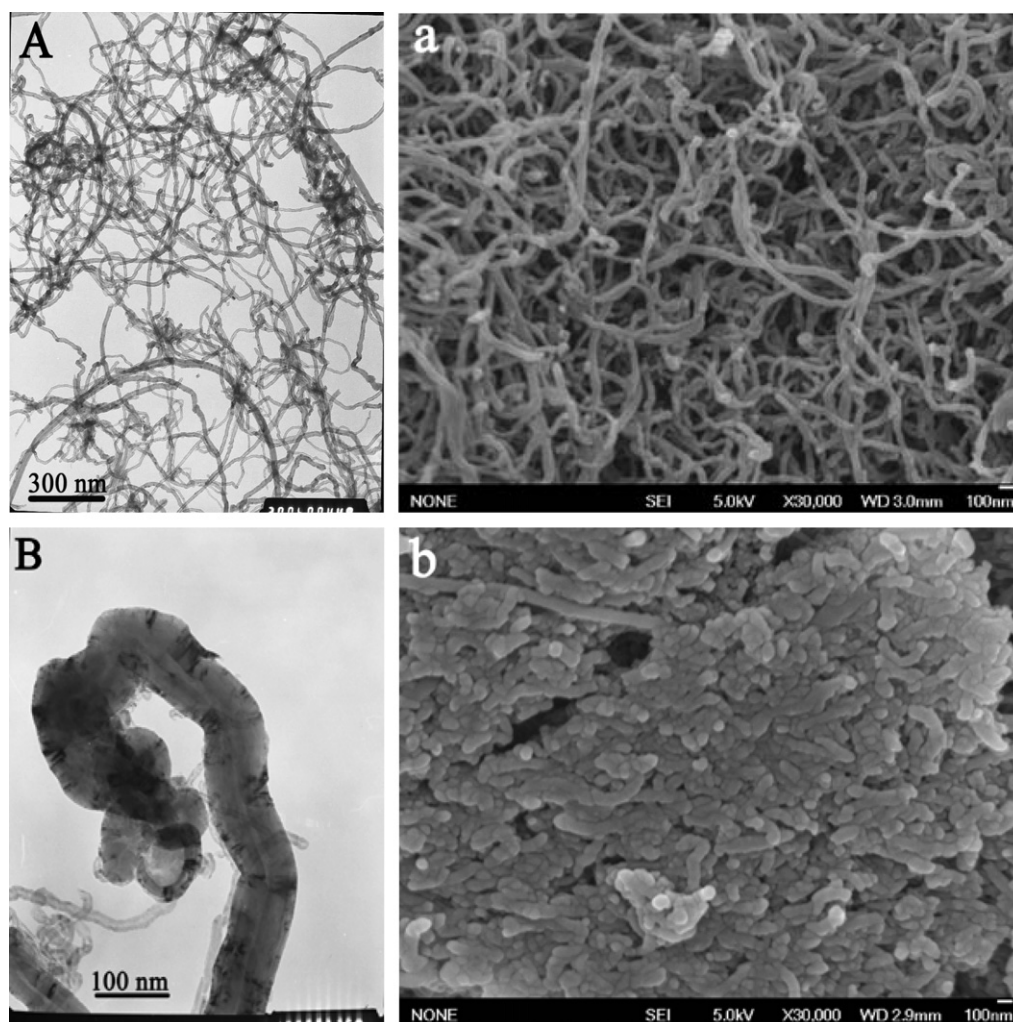
Fig. 5. TEM images of pristine MWCNTs (A), MWCNTs-g-PAM (B); and FE-SEM images of pristine MWCNTs (a), MWCNTs-g-PAM (b).

(PB values) is given in Fig. 6. Generally, the PB value represents the load-carrying capacity of a lubricant. Functionalized MWCNTs significantly improved the extreme pressure of the stock. The PB value of the base stock was 510 N, but the base stock with MWCNTs-g-PAM composites showed much higher PB value. When the concentration of functionalized MWCNTs reached 0.2 wt%, the PB value reached
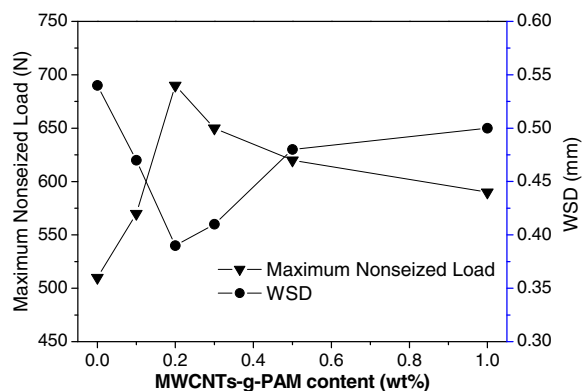

Fig. 6. Effect of the MWCNTs-g-PAM (polymerized for 24 h) content on maximum nonseized load (P_B value) and WSD.
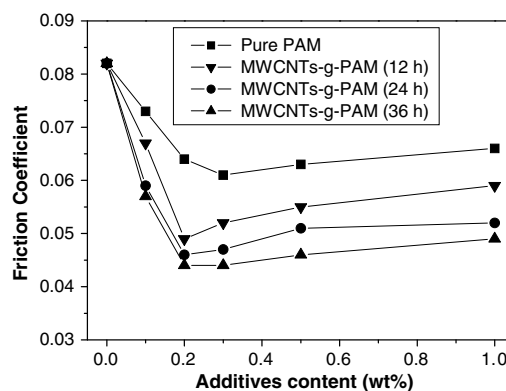

Fig. 7. Variations of the friction coefficient with the content of various additives.
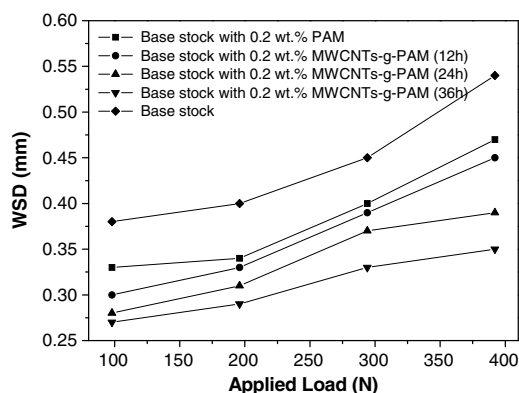
Fig. 8. Variations of the WSD with applied load for various lubricating system.

a maximum of 690 N. This is attributed to that the added MWCNTs-g-PAM composites could act as mechanical reinforcing agents during friction, and therefore significantly strengthen the load-carrying capacity of the base stock. When the concentration of CNTs/PAM was increased above 0.2 wt%, the PB value decreased slowly. Then excessive composite additives resulted in a decrease in load-carrying capacity of the base stock. This result indicates that MWCNTs-g-PAM composites strengthened PB value of the stock. The relationship between concentrations of MWCNTs-g-PAM composites as additives to the base stock and wear scar diameter (WSD) under 392 N for 30 min are also shown in Fig. 6. The addition of MWCNTs-g-PAM composites decreased WSD of the base stock at low weight per-

centages of additive. When the concentration of MWCNTs-g-PAM composites reached 0.2 wt%, the WSD is minimum, which is much smaller than that from the base stock. But excessive MWCNTs-g-PAM additives exhibit an increasing WSD. In other words, the excessive MWCNTs-g-PAM additives resulted in the formation of lumps in the friction interfaces which can decrease the lubricating efficacy. Therefore, we can conclude that the lubricating capability of base stock could be greatly improved when the MWCNTs-g-PAM composites were added in the proper r ratio.

Fig. 7 shows the variations of the friction coefficient with the content of various additive. It is obviously that with the increasing of the concentration of various additive, the friction coefficient reduces rapidly. But the friction coefficient just slightly decreased when pure PAM used as additive. Compared with CNTs, the relative poorer lubricating ability of pure PAM would due to the innate shortage in mechanic properties. When the concentration of additives reached 0.2 wt%, the friction coefficient was at a minimum. Furthermore, we can observe that with the increasing of the grafted PAM, the friction coefficient reduce too. This attributed to the functionalized MWCNTs dispersed well in base lubricant with the increasing of the grafted PAM. The reduction in friction coefficient implies that the MWCNTs-g-PAM composites can serve as spacers, preventing rough contact between counterparts, thereby improving the tribological property of base lubricant considerably.

Fig. 8 shows the relationship between applied load and anti-wear properties for various lubricating system. Under testing loads, the WSD of base stock containing 0.2 wt%
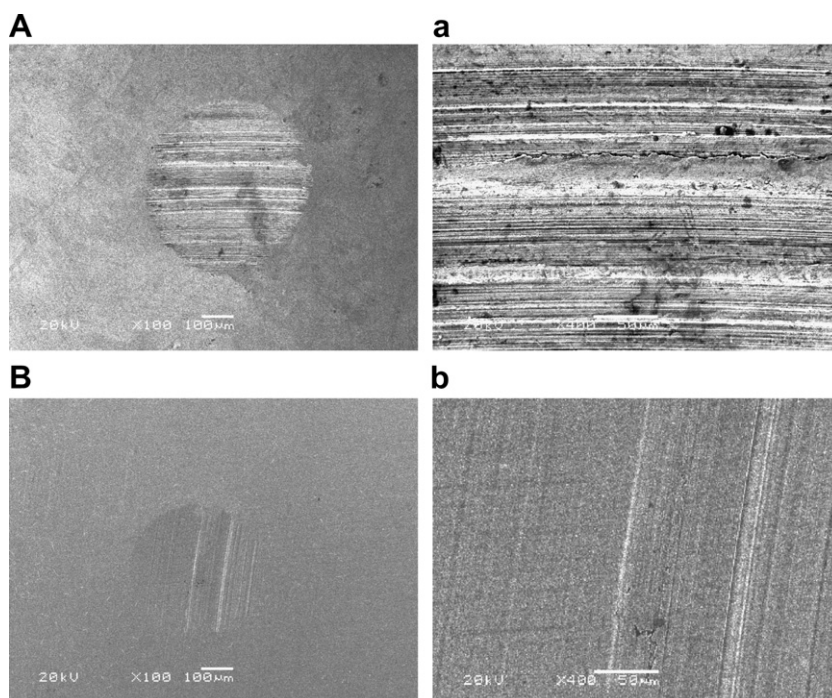

Fig. 9. Morphology of the wear scar lubricated by: (A) base stock; (B) base stock with 0.2 wt% functionalized MWCNTs (polymerized for 24 h); (a, b) magnification of (A, B), respectively.

MWCNTs-g-PAM composites are smaller than containing 0.2 wt% polyacrylamide and pure base stock. It means that, the presence of functionalized MWCNTs can effectively strengthen the wear resistance of base stock and the functionalized MWCNTs exhibit good anti-wear property in a relatively wide range of applied load. Furthermore, under testing loads, we can observe that with the increasing of the grafted PAM, the WSD of base stock containing 0.2 wt% functionalized MWVNTs reduce too. This indicates that the elastic PAM outer shell has favorable anti-wear properties.

The worn surfaces in four-ball machine testing, which were obtained under a load of 392 N and a testing time of 30 min, were observed by SEM. Fig. 9 shows the morphology of the worn surfaces lubricated by base stock, and base stock with 0.2 wt% functionalized MWCNTs (polymerized for 24 h). It can be observed that the wear scar lubricated base stock with 0.2 wt% functionalized MWCNTs is obviously smaller and exhibit mild scratches, however, large wear scar, sharp tracks and obvious scuffing are characterized for the wear scar lubricated by base stock. In other words, the functionalized MWCNTs can improve wear condition.

Based on the above tribological test and worn surface analyses, it can be concluded that the functionalized MWCNT as lubricant additive can effectively improve the lubrication properties.

4. Conclusions

MWCNTs dispersable in water were prepared by the surface initiated redox polymerization of acrylamide using ceric ammonium nitrate (CAN) as initiator were investigated. TEM and FE-SEM observations showed that the nanotubes were coated with polymer layer, exhibiting core-shell nanostructures, with the PAM chains as a brush-like or hairy shell, and the MWCNTs as a hard backbone. When the prepared water-soluble MWCNTs were used as a water-based lubricant additive, the anti-wear performance and load-carrying capacity of the base stock were significantly raised and the friction coefficient decreased. This was attributed to the possibility of this water-soluble MWCNTs acting as nanometer tiny bearings during lubrication. Therefore, our work provided a potential applied foreground to the research of high-performance water-based additive. The related applications and expanding tribological mechanism work are in progress.

Acknowledgment

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