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Surface-modified carbon nanotubes and the effect of their addition on the tribological behavior of a polyurethane coating

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Abstract

The toluene-2,4-diisocyanate (TDI) treatment was used to bind isocyanate functional groups (O=C=N–) on the surface of multi-walled carbon nanotubes (MWCNTs), after which the TDI modified MWCNTs and unmodified MWCNTs were added to the polyurethane (PU) to produce composite coatings with improved wear properties. When the modified MWCNTs were added to the PU binder, the grafting TDI can take part in the curing of the PU binder so that chemical bonding was established between the MWCNTs and the matrix. Friction and wear tests indicated that modified MWCNT reinforced PU composite coating has the highest coefficient of friction and the highest wear resistance of the examined composite coating. Furthermore, the effects of sliding speed and applied load on the friction and wear behavior of the PU coating filled with MWCNTs or MWCNTs-TDI were also studied. The results showed that the coefficient of friction decreased with increasing sliding speed and applied load, and the anti-wear behavior of the PU coating filled with MWCNTs-TDI was the best under 320 N at a speed of 3.0 m s^{-1}.

Keywords: Carbon nanotubes; Tribological behaviors; Polyurethane coating; Transfer film

1. Introduction

Organic coatings are widely applied for decoration and protection of metals. With the development of nanotechnology, nanoparticles have been increasingly applied to organic coatings [1–5].

The one-dimensional structure, mechanical strength and electrical properties of carbon nanotubes make them ideal fillers for incorporation into composite systems for the development of advanced multifunctional materials [6]. But several issues, including dispersion of carbon nanotubes within the matrix and their incompatibility with organic resin, exfoliation of carbon nanotube bundles and interaction of carbon nanotube with the host polymer, have to be addressed in order to realize the true potential of these composites. Especially

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for applications as structural reinforcements, the interface strength between the carbon nanotubes and polymers has to be enhanced to maximize load transfer. The best way of ensuring favorable interactions between matrix and carbon nanotubes is chemical functionalization of the carbon nanotube surface with suitable groups. A lot of methods, such as surface-active agent, coupling agent, fatty acid and alcohol, can be used to modify carbon nanotubes [7–9].

Due to the effects of the reinforcement, CNTs can be used to fabricate the nanocomposites with excellent tribological properties. The tribological behaviors of the UHMWPE-CNTs [10], carbon-CNTs [11], Ni–P-CNTs composite coatings [12,13], polyimide-CNTs [14], polytetrafluoroethylene-CNTs [15] and PMMA-CNTs [16] nanocomposites have been investigated. It was found that CNTs-based nanocomposites exhibited excellent anti-wear life compared with the pure substrates matrix, which results in the improvements on wear resistance.

With the aim of improving the dispersion of carbon nanotubes and the interfacial adhesion between carbon nanotubes and the polyurethane matrix, we design a scheme in which MWCNTs first react with toluene-2,4-diisocyanate (TDI). TDI is selected because the active hydrogen atoms of amide of the polyurethane (PU) matrix might react with isocyanate functional groups (O=C=N–) during curing and form three-dimensional networks throughout the composite coating, so that the MWCNTs could be connected with the PU matrix covalently and take effect desirably. Significant improvements in the tribological behaviors of the PU composite coating filled with MWCNTs-TDI (when compared to both the unfilled PU coating and the one filled with MWCNTs) were observed even at low loading (1.0 wt.%).

2. Experiments

2.1. Materials

Single-component polyurethane (PU) was provided by Xinhua Resin Company of Shanghai, and the ash content and the isocyanate (O=C=N–) content were 50 and 5–8 wt.%, respectively. Commercial polyfluo150 wax powder (Mircopowder company, USA) with an average particle size ranging from 3 μm to 4 μm was selected as starting precursor materials. Multi-walled carbon nanotubes (MWCNTs) (purity > 95 wt.%, diameter < 8 nm, 50 μm length) were purchased from Shenzhen Nanotech Port Co., Ltd. Toluene-2,4-diisocyanate (TDI) was provided by China Medicine Shanghai Chemical Reagent Corporation. Dibutyltin dilaurate was supplied by Tianjin No. 1 Chemical Reagent Factory, China. The mixture of acetone/xylene/cyclohexanone in a volume fraction of 4:2:1 was employed in the present work as a solvent.

In our work, steel 45 (12.7 mm × 12.7 mm × 19 mm) was used as substrate of the coating. An AISI-C-52100 ring of 49.2 mm in diameter and 12 mm in thickness (Hardness Hv850) was made of bearing steel. The chemical compositions of steel 45 and AISI-C-52100 bearing steel are shown in Table 1.

2.2. Surface treatment of MWCNTs

2.2.1. Oxidation of MWCNTs

MWCNTs were treated with a mixture of H_2SO_4 and HNO_3 with a weight ratio of H_2SO_4 to HNO_3 of 3:1 and a weight ratio of the mixed acid to the MWCNTs of 400:1 by stirring at 80 °C for 2 h to obtain acid-modified MWCNTs. Then, the mixture was vacuum-filtered through 0.2-μm Millipote PTFE 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, obtaining oxidized MWCNTs.

2.2.2. Reduction of MWCNTs

The reduction of the oxidized MWCNTs was realized using lithium aluminum hydride ($LiAlH_4$) with the method similar to that of Ma et al. [9]. Typically, 1.0 g of oxidized MWCNTs were dispersed in toluene by ultrasonication (in a water bath) for 30 min, and then 250 mg of $LiAlH_4$ was added gently. The solution was stirred for 1 h at room temperature, followed by adding 200 ml of 2.0 M hydrochloric acid into the solution to remove the lithium and aluminum. The reduced MWCNTs were obtained by filtration of the solution and washed with toluene, absolute ethanol and acetone, and then dried in a vacuum oven at 80 °C overnight.

2.2.3. TDI grafting of MWCNTs

The complete scheme for the MWCNTs modified with toluene-2,4-diisocyanate (TDI) can be illustrated in Fig. 1. The typical grafting of MWCNTs proceeded as follows. A 150 ml round-bottomed flask was charged with 0.5 g of the reduction

Table 1
The chemical compositions of the AISI-C-52100 bearing steel and steel 45 (in wt.%)

	C	Si	Mn	P	S	Cr	Ni	Cu	Fe
Steel 45	0.42–0.5	0.17–0.37	0.50–0.80	0.035	0.035	0.25	0.25	0.25	Balance
Bear steel	0.98–1.1	0.15–0.35	0.25–0.45			1.3–1.6			Balance

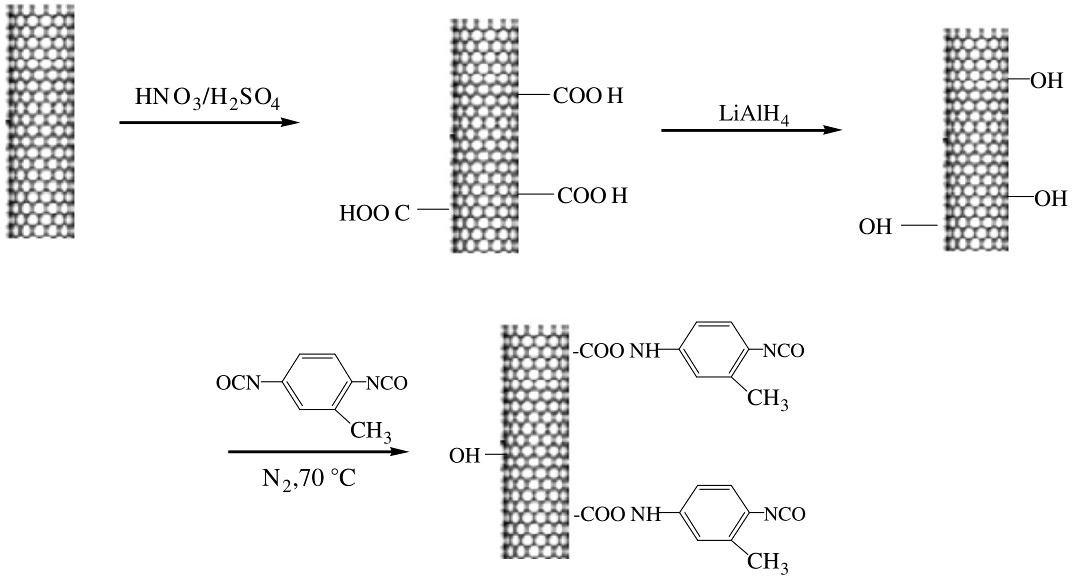

Fig. 1. Fabrication procedure of MWCNTs-TDI.

MWCNTs, 50 ml benzene, 20 ml TDI and 2–3 drops dibutyltin dilaurate. The mixture was stirred at 80 °C for 10 h under a slow stream of N_2. The solid was separated by filtration through a 0.2-μm Millipore PVDF membrane, thoroughly washed with benzene and dried at 60 °C for 24 h under vacuum to obtain MWCNTs modified with TDI (MWCNTs-TDI).

2.3. Coating preparation

The manufacture process of the composite coating was as follows: To obtain a slurry of MWCNTs and Polyfluo150 wax powder (PFW), PFW and MWCNTs with desired proportion were dispersed in the mixed solvent with ultrasonic stirring for 15 min. Then, both the PU binder and the suspension was carefully mixed by mechanical stirring and ultrasonication. The quantity of the solid lubricant of PFW used was 30% of the mass of PU binder. The coatings on blocks were prepared by spraying the prepared slurry with 0.2 MPa nitrogen gas using spray gun. The surface of steel 45 substrates was rinsed with acetone and roughened by spraying corundum. All the samples were cured in a container with relative humidity of 50–60% and temperature of 25 °C. After solvent evaporation, a thin film was obtained on the substrate. The thickness of the cured coatings was 50–60μm.

2.4. Evaluation of the tribological behavior of the PU coatings

An MHK-500 ring-on-block wear tester (made by the Jinan Testing Machine Factory, China) with a similar configuration to a Timken tester was used to evaluate the friction and wear behaviors of the PU composite coatings. The contact schematic of the frictional couple is shown in Fig. 2. A steel ring was rotated against the PU coating filled with MWCNTs or MWCNTs-TDI at speeds of 1.28–3.84 m s^{-1} and load of 320–620 N. The sliding time of 60 min was used in all friction tests. Before each test, the steel ring was abraded with 900 grade water proof abrasive paper. Then the steel ring was cleaned with acetone followed by drying. The

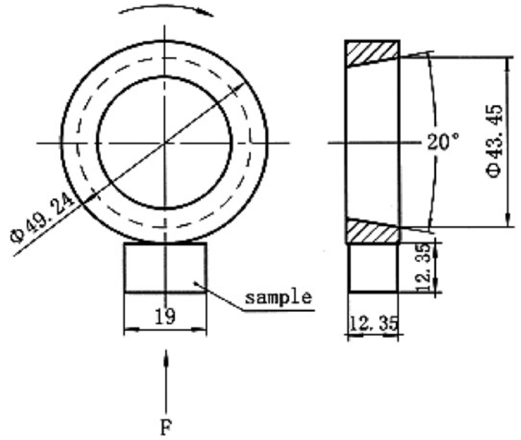

Fig. 2. Contact schematic for the frictional couple.

sliding distance was calculated from the product of the sliding speed and the sliding time. The wear life of the coatings was calculated after dividing the sliding distance by the corresponding coating thickness in micrometers. All the friction and wear tests were carried out at 20–25 °C and a relative humidity of 40–60%. After the wear test, SEM (JSM-5600LV) was used to observe the worn surfaces of the PU coatings filled with MWCNTs. Prior to SEM observation, specimens were Au coated.

3. Results and discussion

3.1. Morphology of MWCNTs

Fig. 3a and b show TEM images of the pristine MWCNTs and oxidized MWCNTs, respectively. Compared with that of pristine MWCNTs, the final product after 2 h of mixed acid treatment was observed clean tubes with no apparent catalyst particles.

3.2. TGA and FTIR of MWCNTs and modified MWCNTs

Fig. 4 shows the FTIR results of the MWCNTs obtained at different processing steps. The FTIR spectrum (Fig. 4a) of the oxidized MWCNTs shows the two bands appeared at 1730 and 1160 cm^{-1}, which are attributed to the C=O and C–O stretching vibrations of the carboxylic groups (–COOH), respectively. The FTIR spectrum of the reduced MWCNTs (Fig. 4b) shows the reduction of the –COOH groups to –OH groups, as verified by the disappearance of the band at 1730 cm^{-1} and the appearance of a band at 1384 cm^{-1}. Because the –OH groups were introduced on the surface of MWCNTs, it is very beneficial for these functional groups to anchor TDI molecule on the surface of MWCNTs through the covalent bond between the –OH groups of MWCNTs and –N=C=O groups of TDI.

After modification with TDI, the characteristic peaks of the TDI are observed at about 3373 cm^{-1}, 2924 cm^{-1}, 2886 cm^{-1}, 2278 cm^{-1}, 1562 cm^{-1}, 1480 cm^{-1}, respectively. The two new peaks at 3373 cm^{-1} and 2278 cm^{-1} are attributed to –NH$_2$ and –N=C=O stretching mode. In addition, the new peaks observed at 1562 cm^{-1} and 1480 cm^{-1} should be attributed to benzenoid unit of TDI. According to the FTIR results, it was concluded that the surfaces of MWCNTs were coated with TDI through covalent bond and physical attraction.

In order to estimate the effect of surface modification on the thermal stability of the MWCNTs, thermal scans of MWCNTs and MWCNTs-TDI were carried out from 25 °C to 700 °C by the TGA in nitrogen atmosphere in Fig. 5. It can be

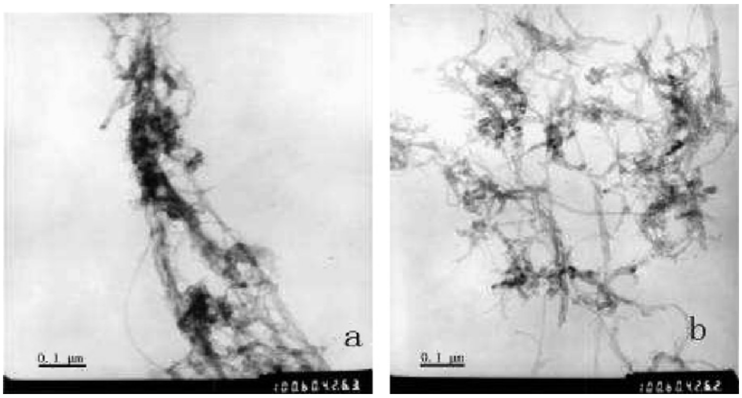

Fig. 3. The TEM images of pristine MWCNTs and oxidized MWCNTs.

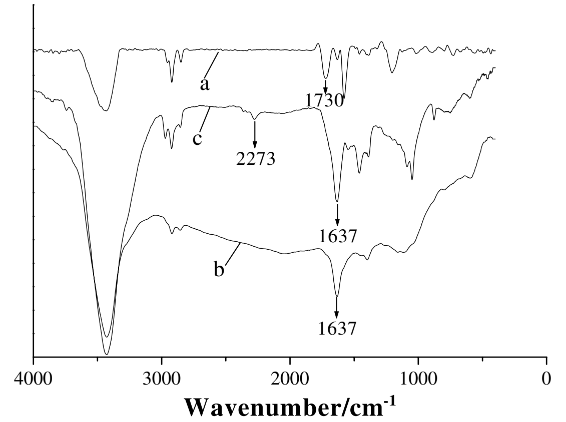

Fig. 4. The FTIR results of the MWCNT obtained at different processing steps: (a) the oxidized MWCNTs; (b) the reduced MWCNTs and (c) the TDI modified MWCNTs.

seen that the weight loss of pristine MWCNTs at 500 °C is negligible. The MWCNTs-TDI show mass loss around 250 °C, which corresponds to the degradation of the TDI. The broad degradations observed at higher temperatures (>500 °C) are related to the thermal decomposition of the MWCNTs. Mass loss values from the thermograms indicate the TDI contents ranging from 20% to 25% by weight of pristine MWCNTs added.

3.3. Friction and wear behaviors

The sliding wear behavior of the PU coating are compared in Fig. 6 as a function of untreated and treated MWCNT content. It can be seen that the coefficient of friction obviously increases when contents of MWCNTs and MWCNTs-TDI are below 3.0 wt.%. The data show that of the samples studied the coefficient of friction has its highest value when 3.0 wt.% of MWCNTs or MWCNTs-TDI are present. The coefficient of friction of the material filled with MWCNTs sharply decreases from 3.0 wt.% to 5.0 wt.%, then increases but at a slower rate with further increase of the content of MWCNTs and is higher in comparison with that of the unfilled one. This reason is that MWCNTs comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk, which endows it without self-lubricating characteristics. When the contents of MWCNTs-TDI exceed 5.0 wt.%, the coefficient of friction linearly decreases with increasing content of MWCNTs-TDI. The wear life of the PU coating filled with 1.0 wt.% of MWCNTs is increased by nearly 70% as compared with that of the unfilled one. As the contents of MWCNTs are increased up to 1.0 wt.%, the wear life increases gradually. The wear resistance of the PU composite coating filled with 3.0 wt.% of MWCNTs-TDI is improved by about 150% as compared with that of the unfilled one. With further increasing content of MWCNTs-TDI, the wear life of the PU coating linearly decreases. As a result, additions of MWCNTs or MWCNTs-TDI are able to enhance the coefficient of friction of and the wear life of the PU coating, especially, the wear life is the best when the content of MWCNTs-TDI is at 3.0 wt.%. At the first stage of sliding wear, the PU matrix on a sample's surface was removed in a brittle mode. The MWCNTs were then exposed to the sliding interface. Because the MWCNTs have a high strength, they reduce the wear rate significantly. Nevertheless, the MWCNTs underwent severe deformation leading to the removal of their caps and distortion of their walls which causes the increase of the coefficient of friction of the PU coating. Therefore, it can be concluded that MWCNTs can significantly improve the tribological performance of the PU composite coatings. The favorable effects of MWCNTs on the tribological properties are attributed to improved mechanical properties and unique topological structure of the hollow nanotubes [17].

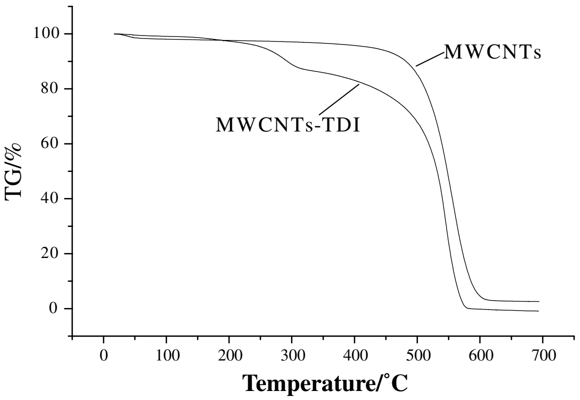

Fig. 5. The TGA curves of MWCNTs and MWCNTs-TDI.

The coefficient of friction and the wear life of the unfilled and the PU coating filled with 1.0 wt.% of MWCNTs or 1.0 wt.% of MWCNTs-TDI under different applied loads at a speed of 2.56 m s^{-1} are shown in Fig. 7. It can be seen that the coefficient of friction of these coatings tends to decrease with the increase of applied load. Compared with the unfilled and the PU coating filled with MWCNTs, the one filled with MWCNTs-TDI exhibits a the

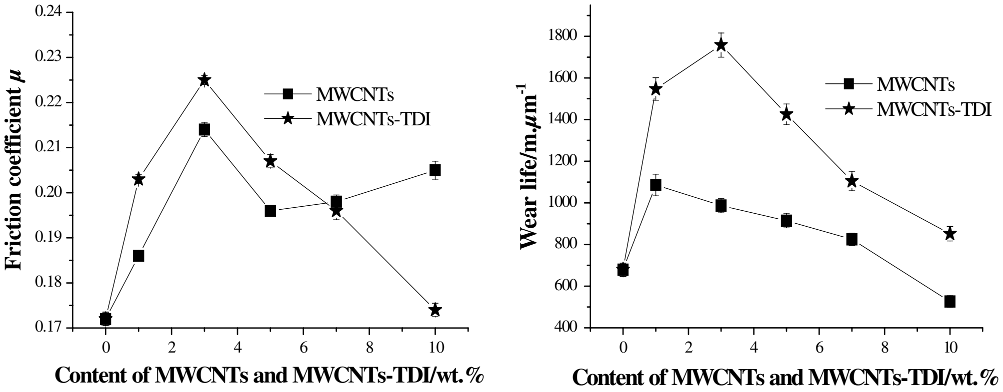

Fig. 6. Coefficient of friction and wear life of the PU coating filled with MWCNTs or MWCNTs-TDI as a function of filler content (320 N, 2.56 m s^{-1}, 60 min).

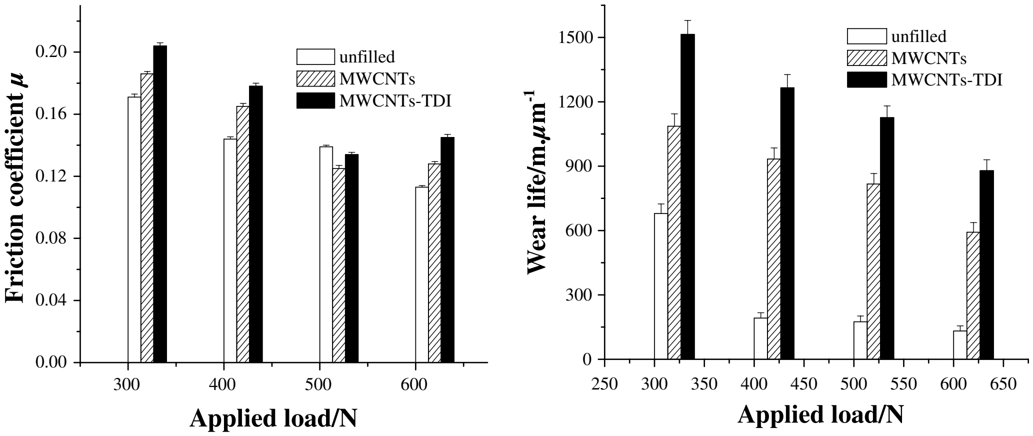

Fig. 7. Effect of applied load on the coefficient of friction and the wear life of the unfilled and the PU coating filled with 1.0 wt.% of MWCNTs or 1.0 wt.% of MWCNTs-TDI under 2.56 m s^{-1}.

highest coefficient of friction throughout applied loads. At the same time, all PU composite coatings have excellent anti-wear abilities under lower applied load. But under higher applied load, they fail in many cases since higher applied load will lead to severe plastic deformation of the PU composite coating owing to the mechanical incompatibility between the PU coating and the substrate [18]. Compared with the unfilled PU coating, the one filled with MWCNTs or MWCNTs-TDI appears to have better anti-wear behaviors under different applied loads. The results indicate that addition of MWCNTs or MWCNTs-TDI could improve the ability of carried load of the PU coating. Due to an increased active group resulting from the grafting TDI, it is believed that this is beneficial for MWCNT/matrix miscibility and hence enhances MWCNT/matrix adhesion by chain entanglement and/or chemical bonding between the grafting TDI and the matrix PU binder.

Variations of the coefficient of friction and the wear life of the unfilled and the one filled with 1.0 wt.% of MWCNTs or 1.0 wt.% of MWCNTs-TDI with sliding speed under 320 N are shown in Fig. 8. It can be seen that the coefficient of friction of the coatings records a slight decrease with increasing sliding speed, but then increases at a slower rate with further increasing sliding speed. Moreover, it is also found that the wear life of the coatings is adversely affected by increasing sliding speed. The wear life of the coatings obviously increases when sliding speed is below 3.0 m s^{-1} and then slightly decreases as the sliding speed rises from 3.0 m s^{-1} to 3.84 m s^{-1}. Accordingly, it should

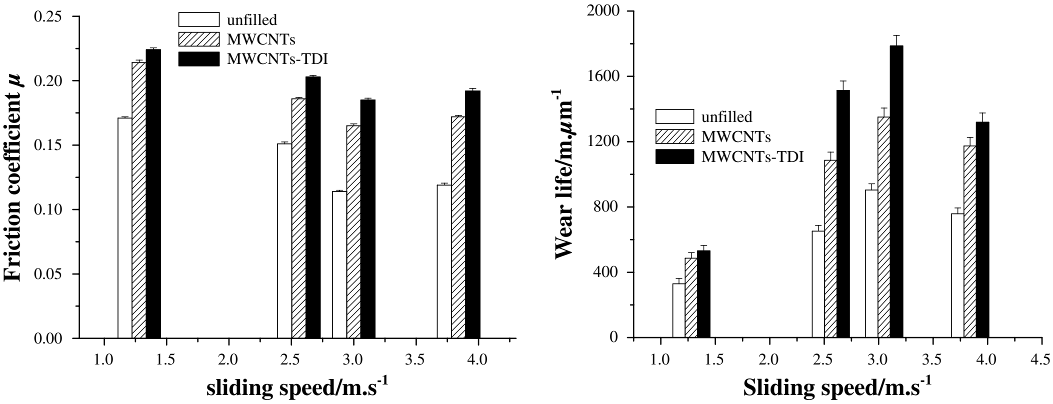

Fig. 8. Effect of sliding speed on the coefficient of friction and the wear life of the unfilled PU coating and the one filled with 1.0 wt.% of MWCNTs or 1.0 wt.% of MWCNTs-TDI under 320 N.

be pointed out that the PU coating filled with MWCNTs-TDI has the best anti-wear behaviors at a speed of 3.0 m s^{-1}. The MWCNTs in the composite coating will slowly release onto the metal surface during the wear and friction test. The MWCNTs on the surface serve as spacers, preventing rough contact between counterparts, thereby slowing the wear rate considerably. It is supposed that the variations in the coefficient of friction and the wear life with sliding speed are closely related to the friction-induced heat. Namely, since the friction-induced heat plays a larger role in the frictional interface at a higher sliding speed than at a lower one, the degradation and decomposition of the PU matrix and PFW fillers would be accelerated and hence the wear of the composite coating becomes more severe at high sliding speed above 3.0 m s^{-1}.

3.4. FTIR analysis

To investigate the surface structure changes of the worn surface at different sliding speeds, FTIR spectra were obtained for the worn surface of the PU coating filled with 1.0 wt.% of MWCNTs-TDI in Fig. 9. It can be seen that the strong absorption bands of -OH, –NH_2, –CH, –N═C═O and –C═O appear on the original coating (Fig. 9a), but these bands fade or disappear with increasing sliding speed. Especially, –N═C═O peak at 2272 cm^{-1} is consumed slightly when sliding speed was at 1.28 m s^{-1} (Fig. 9b), but greatly at 3.84 m s^{-1} (Fig. 9c).

The chemical reactions during the curing process of the PU coatings could be described as follows:

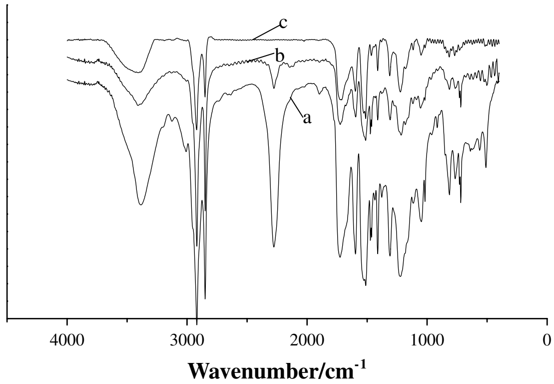

Fig. 9. FTIR spectra of the worn surface of the PU coating filled with 1.0 wt.% of MWCNTs-TDI at different sliding speeds (320 N, 60 min): (a) the unworn surface; (b) at 1.28 m s^{-1} and (c) at 3.84 m s^{-1}.

$$\mathrm{R{-}NCO + H_2O \rightarrow [R{-}NH{-}COOH]} \tag{1}$$

$$\mathrm{[RNH{-}COOH] \rightarrow R{-}NH_2 + CO_2} \tag{2}$$

$$\mathrm{R{-}NCO + R'{-}NH_2 \rightarrow R{-}NH{-}CO{-}NH{-}R'} \tag{3}$$

Because the curing of the PU binder was strongly dependent on the reactions between the –N═C═O radical in the binder and the –OH and –NH_2 radicals originated from PU matrix, a certain curing temperature was essential for the curing chemical reactions [19].

According to the results of FTIR analysis of the worn surface at different sliding speeds, it can be concluded that the structural change of the PU coating filled with MWCNTs-TDI during the friction process was due to the friction heat, which caused disordering and partial decomposition of the PU binder.

3.5. TG analysis

The effect of the MWCNTs on the thermal stability of the PU coating was estimated using TGA analysis. The TGA curves were obtained by heating the sample up to 800 °C at a rate of 20 °C/min with N_2 gas purging. As shown in Fig. 10, the unfilled PU coating began to degrade at approximately 200 °C and was completely decomposed at 500 °C, and approximately 1.0 wt.% of the MWCNTs in the PU composite coating began to degrade at approximately 300 °C and was completely decomposed at 650 °C. Furthermore, Fig. 10 indicates that the MWCNTs filled PU composite coating decompose at higher temperature, which suggests that the incorporation of MWCNTs increases the thermal stability of the PU composite coating. It is well-known that the enhanced thermal conductivity of a polymer composite can facilitate heat transport and increase its thermal stability through the incorporation of high thermal conducting MWCNTs [20].

3.6. SEM analysis

In order to understand the effect of the MWCNTs and MWCNTs-TDI on the friction and wear behavior of the PU composite coating, the worn surface morphologies of the composite coating as well as wear debris were studied by SEM.

Fig. 11 shows the SEM morphologies of the worn surfaces of the unfilled and filled PU coatings under 320 N and 2.56 m s^{-1}, respectively. It can be seen that evident plucked marks appear on the wear scars of the unfilled PU coating (Fig. 11a), while a close view (Fig. 11b) shows that micrometer size blocks of the PU coating materials have left the surface of the materials. This is indicative for fatigue-delamination generated under repeated loading during sliding. Fatigue wear has been regarded as a main mechanism responsible for the sliding of the unfilled PU coating against a hard counterpart [21]. The model is based on the sub-surface crack nucleation and coalescence due to shear deformation of the softer surface induced by the traction of the harder asperities [22]. For the PU coating filled with 1.0 wt.% of MWCNTs, the worn surfaces are characterized by slight scuffing (Fig. 11c). Close examination of the pictures at higher magnification (Fig. 11d) shows that severe wear associated with the detachment of bulk materials for the unfilled PU coating is replaced by adhesion for the PU coating filled with 1.0 wt.% of MWCNTs. Furthermore, the worn surfaces of the PU coating filled with 1.0 wt.% of MWCNTs-TDI only show the traces of mild wear (Fig. 11e). With a magnified view, as seen in Fig. 11f, the image of the filled PU coating identifies the presence of some individual MWCNTs embedded within the PU matrix, which imply that the MWCNTs were well separated in PU matrix and protected from aggregating with one another by functionalization. These phenomena must be correlated with the role of the grafted TDI. Actually, MWCNTs are very difficult to be uniformly dispersed in PU binder because of the strong attraction between the MWCNTs and the limited shear force during compounding. Consequently, the PU coating filled with MWCNTs usually contains a number of loosened clusters of MWCNTs, which may lead to extensive material loss as a result of disintegration and crumbling of the agglomerate of the MWCNTs under tribological conditions.

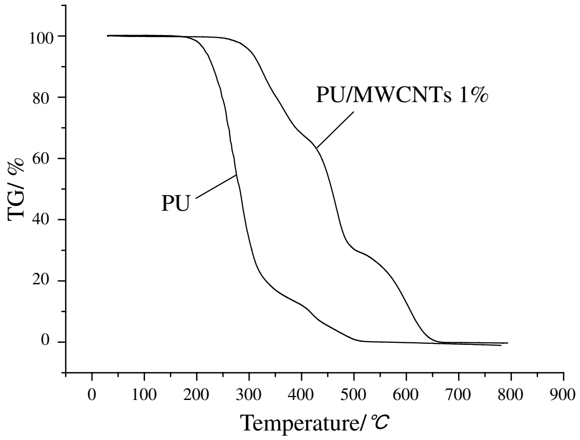

Fig. 10. TGA curves of the unfilled and MWCNT 1 wt.% filled PU composite coating.

OM analysis of transfer films formed on the counterpart ring surface for the unfilled and filled PU coating is shown in Fig. 12. Fig. 12a reveals that the thick, discontinuous transfer films formed on the surface of the counterpart ring, and were easy to be scaled off during friction process, so the protection from transfer films was non-existent anymore. However, the transfer films of the PU coating filled with 1.0 wt.% of MWCNTs or 1.0 wt.% of MWCNTs-TDI sliding against the counterpart ring are comparatively thin, uniform and continuous (Fig. 12b and c), which agreed well

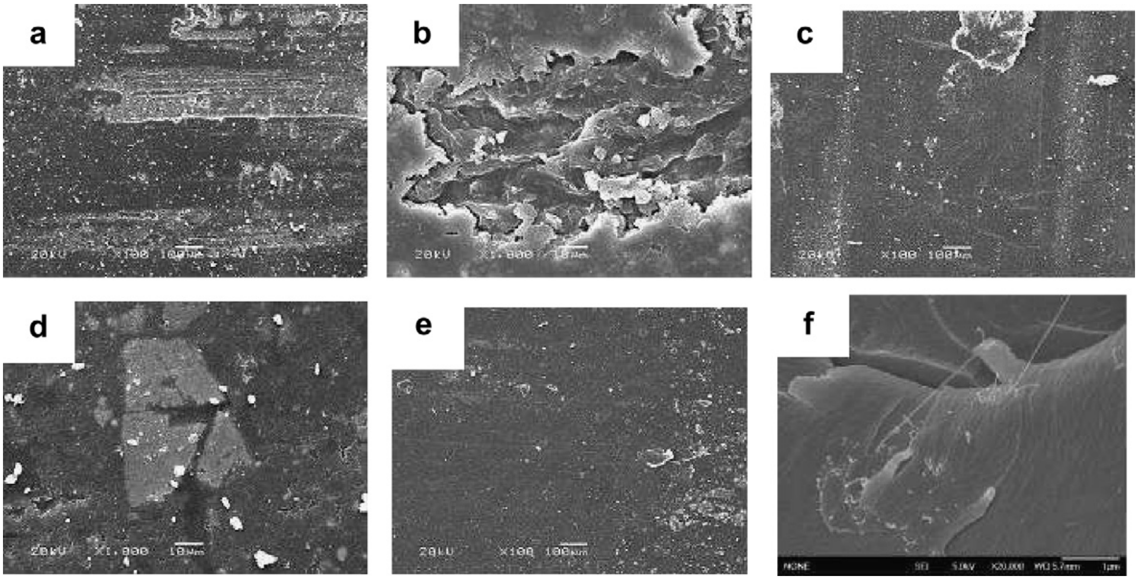

Fig. 11. SEM micrographs of the worn surfaces of the unfilled PU coating and the one filled with MWCNTs or MWCNTs-TDI (320 N, 2.56 m s^{-1}, 60 min). (a) the unfilled; (b) the higher magnification of (a); (c) with 1.0 wt.% of MWCNTs; (d) the higher magnification of (c); (e) with 1.0 wt.% of MWCNTs-TDI; (f) the higher magnification of (e).

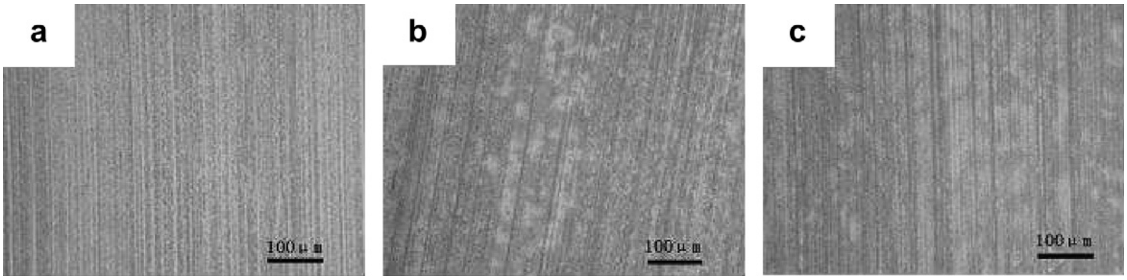

Fig. 12. Optical micrographs (OM) of the transfer films formed on the counterpart ring surface for the unfilled and filled PU coating (320 N, 2.56 m s^{-1}, 60 min): (a) the unfilled; (b) with 1.0 wt.% of MWCTs and (c) with 1.0 wt.% of MWCNTs-TDI.

with its relatively excellent wear-resistance properties as compared with the unfilled coatings. As is well-known, the tribological behaviors of polymers and their composites sliding against a ring under dry friction conditions are strongly influenced by their ability to form a transfer film on the counterface. Once transfer films are formed, subsequent interaction occurs between the polymer and a layer of similar material [23].

Therefore, it can be inferred that 1.0 wt.% of MWCNTs or 1.0 wt.% of MWCNTs-TDI can strengthen interactive force between the transfer films and the counterpart surface and facilitate formation of transfer films on the surface of steel ring, which results in much lower wear for the PU composite coating.

The PU coating filled with 1.0 wt.% of MWCNTs-TDI was selected as an example to investigate effects of the sliding speeds on the worn surface, as is shown in Fig. 13. It can be seen that the worn surfaces of the filled PU coating are smooth at 2.0 m s^{-1} under 320 N, and the adhesion and plough marks on the worn surfaces are nearly invisible (see Fig. 13a). With the increase of sliding speed, the plastic transfiguration of the coating material was enhanced. It can be seen that the sample surface was intenerated and viscous flow occurred at 3.0 m s^{-1} and 3.84 m s^{-1} (see Fig. 13b and c). Moreover, we find that there are some holes on the surface of the coating when sliding speed is at 3.84 m s^{-1}. According to the above FTIR analysis, the curing reaction of the PU binder would be too

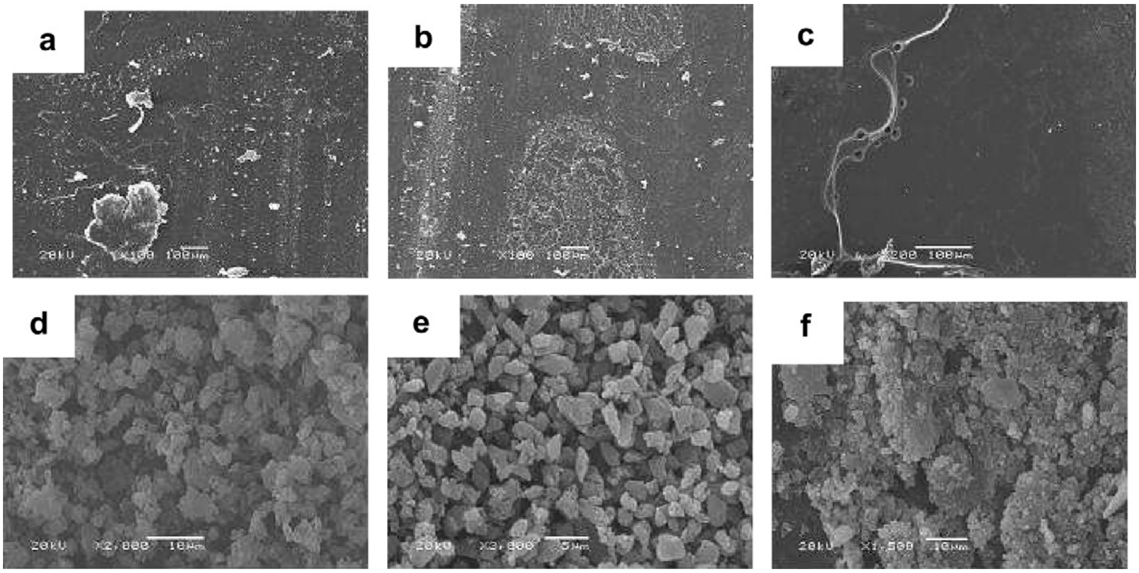

Fig. 13. SEM pictures of the worn surfaces and wear debris of the PU coating reinforced with 1.0 wt.% of MWCNTs-TDI under different sliding speeds (320 N, 60 min); (a) 2.0 m s^{-1}; (b) 3.0 m s^{-1}; (c) 3.86 m s^{-1}; (d) debris of (a); (e) wear debris of (b); (f) wear debris of (c).

quick and accelerate the evaporation of the solvent or CO_2 from the coating when the sliding speed was too high, which leads to many holes on the surface of the coating and makes the anti-wear and mechanical properties of the coating deteriorate.

Fig. 13d, e and f show SEM micrographs of the wear debris of the PU coating filled with 1.0 wt.% of MWCNTs-TDI under different sliding speeds. It is seen that the size of the wear debris varies from each other under different sliding speeds. The size of the wear debris under 3.0 m s^{-1} is much smaller than that under 2.56 m s^{-1} or 3.84 m s^{-1}. As a result, the fine debris and/or MWCNTs pulled out from the composite coating would provide lubricating effect at the interface between the surface of coating material and the steel ring.

4. Conclusion

Modification of MWCNTs through grafting active TDI monomers which increased the interfacial interaction between the MWCNTs and the PU matrix through chemical bonding represents an attractive route to give full play to MWCNTs in improving the tribological performance of the PU coating. The addition of untreated MWCNTs into the polyurethane coating can enhance the wear life of it at lower filler loading, but a more significant improvement of the tribological properties can be obtained by incorporating the MWCNTs modified with TDI. The key effects of the modified MWCNTs lie in the strengthening interactive force between the transfer film and the counterpart surface and facilitating formation of transfer film on the steel ring surface besides the increase of the interfacial adhesion between the MWCNTs and the PU matrix.

The applied load and sliding speed have great effect on the PU composite coating. With the increase of applied load, the wear life of the PU composite coating decreased. The reason was that under high-applied load, the PU composite coating fails in many cases since high-applied load will lead to severe plastic deformation of the PU coating owing to the mechanical incompatibility between the PU coating and the substrate. The differences in friction and wear behaviors of the PU composite coating under different sliding speeds appeared to be mainly ascribed to the influence of the contact temperature of the two relative sliding parts.

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References

[1] Wang Y, Lim S, Luo JL, Xu ZH. Tribological and corrosion behaviors of Al_2O_3/polymer nanocomposite coatings. Wear 2006;260:976–83.

[2] Soloukhin VA, Posthumus W, Brokken-Zijp JCM, Loos J, With G. Mechanical properties of silica-(meth)acrylate hybrid coatings on polycarbonate substrate. Polymer 2002; 43:6169–81.

[3] Chen WX, Tu JP, Wang LY, Gan HY. Tribological application of carbon nanotubes in a metal-based composite coating and composites. Carbon 2003;41:215–22.

[4] Chen Y, Zhang TH, Gan CH, Yu G. Wear studies of hydroxyapatite composite coating reinforced by carbon nanotubes. Carbon 2007;45:998–1004.

[5] Gan DJ, Lu SQ, Song CS, Wang ZJ. Mechanical properties and frictional behavior of a mica-filled poly (aryl ether ketone) composite. Eur Polym J 2001;37(7):1359–65.

[6] Valentini L, Kenny JM. Novel approaches to developing carbon nanotube based polymer composites: fundamental studies and nanotech applications. Polymer 2005;46:6715–8.

[7] Yi B, Rajagopalan R, Foley HC, Kim UJ, Liu XM, Eklund PC. Catalytic polymerization and facile grafting of poly(furfuryl alcohol) to single-wall carbon nanotube: preparation of nanocomposite carbon. J Am Chem Soc 2006;128(34): 11307–13.

[8] Wang M, Pramoda KP, Goh SH. Enhancement of the mechanical properties of poly(styrene-co-acrylonitrile) with poly(methyl methacrylate)-grafted multiwalled carbon nanotubes. Polymer 2005;46:11510–6.

[9] Ma PC, Kim JK, Tang BZ. Functionalization of carbon nanotubes using a silane coupling agent. Carbon 2006; 44:3232–8.

[10] Xue Y, Wei W, Jacobs O, Schädel B. Tribological behaviour of UHMWPE/HDPE blends reinforced with multi-wall carbon nanotubes. Polym Test 2006;25:221–9.

[11] Lim DS, An JW, Lee HJ. Effect of carbon nanotube addition on the tribological behavior of carbon/carbon composites. Wear 2002;252:512–7.

[12] Yang Z, Xu H, Li MK, Shi YL, Huang Y, Li HL. Preparation and properties of Ni/P/single-walled carbon nanotubes composite coatings by means of electroless plating. Thin Solid Films 2004;466:86.

[13] Chen WX, Tu JP, Wang LY, Gan HY, Xu ZD, Zhang XB. Tribological application of carbon nanotubes in a metal-based composite coating and composites. Carbon 2003;41:215.

[14] Cai H, Yuan FY, Xue QJ. Investigation of tribological properties of polyimide/carbon nanotube nanocomposites. Mater Sci Eng A 2004;364:94.

[15] Chen WX, Li F, Han G, Xia JB, Wang LY, Tu JP, et al. Tribol Lett 2003;15:275.

[16] Yang Z, Dong B, Huang Y, Liu L, Yan FY, Li HL. A study on carbon nanotubes reinforced poly(methyl methacrylate) nanocomposites. Mater Lett 2005;59:2128–32.

[17] Calvert P. Nanotube composites: a recipe for strength. Nature 1999;399:210–1.

[18] Bassani R, Levita G, Meozzi M, Palla G. Friction and wear of epoxy resin on inox steel: remarks on the influence of velocity, load and induced thermal state. Wear 2001;247:125–32.

[19] Tian J, Huang YL. Antiwear and lubrication properties of polyurethane/polytetrafluoroethylene-bonded coating. J Appl Polym Sci 2002;86:3454–9.

[20] Gao J, Itkis ME, Yu A, Bekyarova E, Zhao B, Haddon RC. J Am Chem Soc 2005;127(11):3847–54.

[21] Bonfield W, Edwards BC, Markham AJ, White JR. Wear transfer films formed by carbon fibre reinforced epoxy resin sliding on stainless steel. Wear 1976;37:113–21.

[22] Suh NP. The delamination theory of wear. Wear 1973; 25:111–24.

[23] Bahadur S, Sunkara C. Effect of transfer film structure, composition and bonding on the tribological behavior of polyphenylene sulfide filled with nano particles of TiO_2, ZnO, CuO and SiC. Wear 2005;258:1411–21.