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Research Article

Friction and wear behaviors of MoS₂-multi-walled-carbon-nanotube hybrid reinforced polyurethane composite coating

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Abstract: MoS₂-multi-walled-carbon-nanotube (MWCNT) hybrids containing two-dimensional MoS₂ and one-dimensional MWCNTs were synthesized through a one-step hydrothermal reaction. X-ray-diffraction and transmission-electron-microscopy results demonstrated that MoS₂ nanosheets were successfully synthesized, and uniformly anchored on the MWCNTs’ surfaces. Furthermore, the effects of the MoS₂-MWCNT hybrids on the tribological performances of polyurethane composite coatings were investigated using a UMT-2MT tribo-tester. Friction and wear test results revealed that the friction coefficient and wear rate of a 3 wt% MoS₂-MWCNT-1 filled polyurethane composite coating were reduced by 25.6% and 65.5%, respectively. The outstanding tribological performance of the MoS₂-MWCNT-1 reinforced polyurethane composite coating was attributed to the excellent load-carrying capacity of the MWCNTs and good lubricant ability of MoS₂. The surface morphologies of the worn surfaces and counterpart ball surfaces were investigated to reveal the wear mechanisms.

Keywords: adhesion; coating; friction; wear; polyurethane

1 Introduction

In recent years, polymer matrix composites have emerged as attractive materials in the industrial community. Nowadays, they are used as alternatives to metallic matrix composites, in various applications including the aircraft industry, defense industry materials, automotive industry, and medical devices owing to their excellent mechanical properties, small weight, corrosion resistance and design flexibility [1–4]. Among them, thermoplastic polyurethane composites have attracted a significant attention owing to their unique lamellar structure and superior lubricant properties [5–7]. Although polyurethane exhibits these properties, there are challenges associated to friction and wear performance [8]. By adding inorganic (MWCNTs, MoS₂, SiO₂ etc.) or organic (PTFE, PFW, etc.) fillers into polymer matrix composites, the mechanical and tribological performance can significantly improve [9–15].

Two-dimensional (2D) nano-materials have attracted a significant attention owing to their unique lamellar structure and superior lubricant properties [16–23]. MoS₂, with a unique lamellar structure and layers bonded by weak van der Waals forces, can reduce the friction coefficient by sliding among two nanosheets. Rabaso et al. [20] fabricated fullerene-like MoS₂ nanoparticles and investigated the effect of the particle size on friction coefficient by sliding among two nanosheets. Tang et al. [21] demonstrated that the friction coefficient and wear rate were reduced using flower-like MoS₂ as a lubrication additive. Hu et al. [22] have synthesized
ball-like amorphous MoS$_2$ nanoparticles and investigated the tribological properties of a polyoxymethylene (POM) composite with MoS$_2$ nanoparticles. The results showed that the MoS$_2$ nanoparticle reinforced POM composite exhibited a better tribological performance than that with MoS$_2$ microparticles. Zalaznik et al. [23] have compared the effects of MoS$_2$ and WS$_2$ shapes and sizes on mechanical and tribological behaviors of PEEK composites. Compared to pure PEEK, the friction coefficient was decreased by up to 30%.

MWCNTs discovered in 1991 have been widely used as fillers to enhance the mechanical and tribological properties of polymer matrix composites [24, 25]. Owing to their unique structure, the Young’s modulus and tensile strength were up to 100 GPa and 15 GPa, respectively. Wang et al. [26] have synthesized MWCNT reinforced polyimide composites by an in-situ polymerization approach. The thermal stability, tensile strength, and electrical conductivity were significantly improved by incorporating 0.5–0.75 wt% MWCNTs owing to the good dispersion and high compatibility of MWCNTs in the polyimide matrix. Li et al. [27] studied the mechanical properties of plasma functionalized MWCNT reinforced cyanate ester/epoxy composites. The results indicated that the impact strength and tensile strength were enhanced at room temperature and 77 K. Guignier et al. [28] have reported that MWCNTs grafted on carbon fibers can improve the fibre/matrix interface bonding strength and tribological properties of carbon fabric composites attributed to the transfer film formed on the counterpart surfaces. Kim et al. [29] have prepared fluorinated polyimide/PMMA-grafted-MWCNT composite coatings and investigated their tribological properties using a ball-on-disk wear tester. The composite coating with 3 wt% PMMA-grafted-MWCNTs exhibited the lowest friction coefficient among the samples.

Recently, various studies investigated the tribological properties of hybrid filler reinforced polymer composites [30–39]. However, studies on the friction and wear properties of a polyurethane composite coating reinforced by MoS$_2$-MWCNT hybrid composites have been rarely reported. In this study, MoS$_2$-MWCNT hybrid nano-materials were successfully fabricated by a one-step hydrothermal reaction. The MoS$_2$-MWCNT hybrids were used as lubricant fillers to improve the tribological performance of polyurethane composite coatings. In the MoS$_2$-MWCNT composite, MoS$_2$ nanosheets are uniformly anchored on MWCNTs surfaces. This hybrid structure can effectively reduce the friction coefficient and wear rate owing to the synergistic effects of MoS$_2$ and MWCNTs. Polyurethane composite coatings with MoS$_2$-MWCNTs were fabricated and their tribological performances were systematically investigated. In addition, the morphologies of the wear track and counterpart ball were investigated in detail to understand the synergistic lubricating effects of MoS$_2$ and MWCNTs.

### 2 Materials and methods

#### 2.1 Materials

In this study, a steel 45 block (12.7 mm × 12.7 mm × 19 mm) was used as the substrate of the polyurethane composite coatings. (NH$_4$)$_2$MoS$_4$ (analytical reagent 99.95%) was purchased from Alfa-Aesar. Graphitized MWCNTs (diameter 50 nm, length 10–20 μm) were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Science. Polyurethane was provided by Xinhua Resin Company Shanghai (China), the ash and isocyanate (NCO) contents were 50% and 5−8 wt%, respectively. Polyfluoro-150 (PFW) with an average particle size of 3−4 μm was purchased from Micro-powder USA. Concentrated sulfuric and nitric acids were purchased from Xilong Chemicals Co. Ltd. N,N,N-dimethylformamide (DMF), ethanol, acetone, and ethyl acetate were used as received (analytical grade). The chemical composition of the steel 45 is shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>MnP</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
</tr>
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<tbody>
<tr>
<td>Steel 45</td>
<td>0.42−0.5</td>
<td>0.17−0.37</td>
<td>0.50−0.80</td>
<td>0.035</td>
<td>0.035</td>
<td>0.25</td>
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### 2.2 Synthesis procedure of MoS$_2$-MWCNTs

In order to improve the surface performance of the MWCNTs, 2 g MWCNTs were added into a mixture solvent of concentrated sulfuric and nitric acids (volume
ratio 3:1) and ultrasonically treated for 30 min. The mixture was heated to 80°C within 15 min and then refluxed at 80°C for 3 h. After the reaction, the mixture was filtered and washed several times with water. The deionized water was removed by freeze drying.

In a typical procedure to synthesize the MoS$_2$-MWCNT hybrids, MWCNTs (60 mg) and (NH$_4$)$_2$MoS$_4$ were dispersed ultrasonically into the mixture solvent (60 ml) (DMF and H$_2$O at a volume ratio of 2:1). After sonication for 30 min, the above solution was transferred into a 100 ml Teflon-lined autoclave and sealed, which was heated to 200°C and maintained for 12 h. The resultant MoS$_2$-MWCNT hybrid was collected by filtration and rinsed with distilled water and ethanol. In order to improve the dispersion, the deionized water was removed by freeze drying. The MoS$_2$-MWCNT hybrids were denoted as MoS$_2$-MWCNT-1 (weight ratio of precursor 1:1), and MoS$_2$-MWCNT-2 (weight ratio of precursor 0.5:1).

### 2.3 Preparation of polyurethane composite coatings

Further, we present the preparation procedure of the polyurethane composite coatings. First, PFW and fillers (MWCNTs, MoS$_2$, MoS$_2$-MWCNT-1, or MoS$_2$-MWCNT-2) were ultrasonically dispersed in the mixed solvent (acetone: ethanol: ethyl acetate in a volume fraction of 1:1:1) for 15 min. Polyurethane adhesive was added into the above suspension by mechanical stirring and ultrasonic treatment. The polyurethane composite coatings were prepared by spraying the mixture solution with a 0.2 MPa nitrogen gas (nozzle size: 0.8 mm). The polyurethane composite coatings were cured at 60°C, 120°C, and 150°C for 2 h. The PFW and filler weight fractions were 20 wt% and 3 wt%, respectively. The hardness values of the polyurethane composite coatings reinforced with different types of fillers are shown in Table 2.

### 2.4 Characterization

The phase compositions of the MoS$_2$-MWCNT hybrids were investigated using a Philips Corp X-ray diffractometer (XRD) with Cu-K radiation. The morphology and microstructure of the MoS$_2$-MWCNTs were characterized using a FEI Tecnai F30 transmission electron microscope (TEM). Fourier transform infrared (FTIR) spectra were acquired using a Nexus 870 spectrometer. Scanning electron microscopy (SEM) images of worn surfaces and counterpart pin surfaces were obtained using a scanning electron microscope (JSM-5600LV) equipped with an energy dispersive X-ray analyzer.

The tribological properties of the polyurethane composite coatings were investigated using a UMT-2MT tribo-tester (UMT-2MT, CETR Corporation Ltd, USA) with a linear reciprocating ball-on-flat configuration. The counterpart ball was made of AISI 52100 steel with a diameter of 6 mm; it was cleaned ultrasonically in acetone for 20 min. Friction and wear tests were performed under dry friction, duration of 30 min, sliding speeds of 5 Hz and 8 Hz, and normal loads of 3 N and 5 N. Each tribological test was repeated three times to obtain the average friction coefficient and wear rate. A contact three-dimensional (3D) surface interferometer was used to measure wear depth and width. The wear volume and wear rate were calculated as:

\[
V = \frac{b}{2R} \arcsin \left( \frac{b}{2R} \right) - \frac{b}{2} \sqrt{\frac{b^2}{4} + \frac{R^2}{4}}
\]

where \(V\) is the wear volume (m$^3$), \(B\) is the wear track (0.005 m), \(R\) is the radius of the steel ball (0.006 m), \(b\) is the width of the wear track (m), \(\omega\) is the wear rate (m$^3$·N$^{-1}$·m$^{-1}$), \(L\) is the sliding distance (m) and \(P\) is the applied load.

### 3 Results and discussion

#### 3.1 Microstructures and morphologies of the MoS$_2$-MWCNT hybrids

Untreated and mixed acid treated MWCNTs were
investigated using FTIR spectroscopy. As shown in Fig. 1, the pristine MWCNT sample exhibits weak peaks at 3,444 cm$^{-1}$, 2,962 cm$^{-1}$, 2,869 cm$^{-1}$, and 1,731 cm$^{-1}$, attributed to the absorptions of $\text{--OH}$, $\text{--CH}_2$, and $\text{--C=O}$, respectively. After the treatment in the acid mixture, the adsorption intensities at 3,444 cm$^{-1}$ and 1,079 cm$^{-1}$ increased. This result confirmed that modification with acid can induce active groups on the MWCNTs’ surfaces.

Figure 2 shows XRD patterns of MoS$_2$, MWCNT, and MoS$_2$-MWCNT hybrids. The results show typical patterns of MoS$_2$ at 13.08°, 33.51°, 38.63°, and 56.7°, corresponding to the (002), (100), (103), and (110) reflection planes, respectively (see Fig. 2(a)). For the MWCNTs, the high intensity peak at 26.56° was assigned to the (002) plane of the hexagonal graphite structure (see Fig. 2(a)). It is worth noting that, diffraction peaks of MoS$_2$ and MWCNTs can be simultaneously observed in the MoS$_2$-MWCNTs (see Fig. 2(b)); no impurity phase was observed, indicating that MoS$_2$-MWCNTs with a high purity were synthesized successfully by a one-step hydrothermal process.

TEM images of the MoS$_2$, MWCNT, and MoS$_2$-MWCNT hybrids are shown in Fig. 3. Figure 3(a) reveals that the synthesized MoS$_2$ nano-sheets which exhibited a typical laminated structure were very thin and transparent. Numerous wrinkles can be observed on the margins. A TEM image of the MWCNTs is shown in Fig. 3(b). The surfaces of the MWCNTs were smooth and clear, the MWCNTs exhibited a uniform tubular structure. Figures 3(c) and 3(d) reveal that the MoS$_2$ nanosheets are evenly anchored on the surfaces of the MWCNTs.

In order to further demonstrate that MWCNTs were successfully enwrapped by MoS$_2$ nanosheets, high-resolution (HR) TEM and selected area electron diffraction characterizations were performed and the obtained images are shown in Fig. 4. As shown in Fig. 4(b), the synthesized MoS$_2$ exhibited a lamellar
structure. This result is consistent with that in a previous study [40]. The selected area electron diffraction pattern confirmed that the synthesized MoS2 possessed a polycrystalline structure. Elemental mapping images are shown in Figs. 4(d)–4(h). S and Mo were uniformly dispersed on the MWCNTs’ surfaces, which further confirms that MoS2 nanosheets were evenly anchored on the MWCNTs’ surfaces.

3.2 Cross sections of the polyurethane composite coatings

SEM images of the cross sections of the pristine and 3 wt% MoS2-MWCNT-1 filled polyurethane composite coatings are presented in Fig. 5. Compared with the pure polyurethane composite coating (see Fig. 5(a)), the MoS2-MWCNT-1 reinforced composite coating was well bonded with the metal matrix (see Fig. 5(b)). Furthermore, energy-dispersive-X-ray-spectroscopy-(EDS) results demonstrated that Mo and S were uniformly dispersed on the surface of the polyurethane composite coating, which also confirmed that the MoS2-MWCNT-1 hybrid was evenly dispersed in the composite coating (see Fig. 5(b)).

3.3 Friction and wear properties

Figure 6(a) shows the effects of the fillers on the average friction coefficients of the polyurethane composite coatings. The friction coefficients of the polyurethane composite coatings decreased upon the incorporation of the fillers. Compared with the pristine polyurethane composite coating, the MoS2-MWCNT-1 filled polyurethane composite coating exhibited a
lower friction coefficient. The friction coefficient of the 3 wt% MoS2-MWCNT-1 reinforced polyurethane composite coating was reduced by 25.6%. However, when 3 wt% MoS2-MWCNT-2 was incorporated into the polyurethane composite coating, the friction coefficient slightly increased. The dependences of the friction coefficients on the time for the different filler reinforced polyurethane composite coatings are shown in Fig. 6(b). For the pristine polyurethane composite coating, the friction coefficient initially decreased, followed by a rapid increase. It significantly fluctuated during the sliding process. Nevertheless, the polyurethane composite coatings reinforced by the fillers exhibited very stable friction coefficients during the whole sliding process. The above results are mainly attributed to the synergistic lubricating effects of MWCNTs and MoS2. MWCNTs possess excellent mechanical properties which can support a large applied load and reduce the wear rate by confining the polyurethane composite coating deformation and crack propagation [41]. In addition, the MWCNTs slid and roll easily during the slide process owing to their unique seamless cylinders structure [42]. Furthermore, MoS2 layers were linked only by weak van der Waals bonding, which contributed to the reduction of the friction coefficient. Therefore, the MoS2-MWCNT-1 filled polyurethane composite coating exhibited the lowest friction coefficient.

Figure 7 shows the influences of the various fillers on the wear rates of the polyurethane composite coatings. The wear rate decreased when the fillers were incorporated into the polyurethane composite coatings. Compared with the pristine polyurethane composite coating, the polyurethane composite coating reinforced by MoS2-MWCNT-1 exhibited a lower wear rate decreased by 65.5%. The excellent friction and wear properties of the MoS2-MWCNT-1 filled polyurethane composite coating could be attributed to the excellent lubricant ability of MoS2 and outstanding load-carrying capacity of the MWCNTs [22, 25].

Figure 8(a) shows the average friction coefficients for the polyurethane composite coatings tested at different applied loads and sliding speeds. With the increase of the applied load, the friction coefficient slightly decreased. However, the sliding speed had a small influence on the friction coefficient. Compared with the pristine polyurethane composite coating, the MoS2-MWCNT-1 filled polyurethane composite coating exhibited a significantly lower friction coefficient under different test conditions. The variations of the friction coefficients of the pristine and MoS2-MWCNT-1
reinforced polyurethane composite coatings as a function of the sliding time are presented in Fig. 8(b). The MoS2-MWCNT-1 reinforced polyurethane composite coating exhibited a lower and more stable friction coefficient than that of the pristine polyurethane composite coating during the sliding process. These results indicate that the MoS2-MWCNT-1 hybrid as a lubricant filler has a significant influence on the tribological performance of the polyurethane composite coating. The influences of the applied load and sliding speed on the wear rates of the pristine and MoS2-MWCNT-1 filled polyurethane composite coatings are presented in Fig. 9. As shown in Fig. 9, the wear rates of the two types of polyurethane composite coating decreased with the increase of the applied load and sliding speed. The MoS2-MWCNT-1 reinforced polyurethane composite coating exhibited a lower wear rate under all test conditions.

3.4 SEM observations of the worn surfaces and transfer films

SEM images of the pristine and different filler reinforced polyurethane composite coatings are shown in Fig. 10. For the pristine polyurethane composite coating, large amounts of ploughed furrows and wear debris were detected indicating abrasive and fatigue wear, which supported their severely wear behavior and high wear rate (see Fig. 10(a)). When the MWCNTs were incorporated into the polyurethane composite coating, the amount of ploughed features considerably decreased. However, a large amount of smaller wear debris was observed on the worn surface (see Fig. 10(b)). As shown in Fig. 10(c), many adhered polymer flakes were detected on the worn surface of the MoS2 reinforced polyurethane composite coating. In contrast, the worn surfaces of the MoS2-MWCNT hybrid filled polyurethane composite coatings were very smooth and only small amounts of wear debris were observed on them (see Figs. 10(d) and 10(e)). The SEM results further demonstrated that the MoS2-MWCNT hybrids can significantly improve the tribological properties of the polyurethane composite coatings.

Figure 11 shows the counterpart surfaces of the pristine and MoS2-MWCNT-1 reinforced polyurethane composite coatings under conditions of 5 N and 3 Hz. As shown in Fig. 11(a), the counterpart surface of the pristine polyurethane composite coating was quite rough, with large amounts of wear debris and furrows. These results indicated that a non-continuous rough transfer film formed on the counterpart surface. However, as seen from Fig. 11(b), a smooth transfer
film was formed on the counterpart surface of the MoS₂-MWCNT-1 reinforced polyurethane composite coating. In order to further confirm the components of the transfer film, an EDS characterization was performed (Figs. 11(c) and 11(d)), which demonstrated that the MoS₂-MWCNT-1 hybrid contributed to the formation of a uniform continuous transfer film on the counterpart ball surface.

4 Conclusions

MoS₂-MWCNT hybrid composites were synthesized using a one-step hydrothermal reaction. Subsequently, the MoS₂-MWCNT hybrids as lubricant fillers were incorporated into a polyurethane matrix to prepare polyurethane composite coatings. The XRD and TEM characterization results demonstrated that MoS₂ nanosheets were successfully fabricated and uniformly decorated the MWCNTs’ surfaces. Furthermore, the friction and wear properties of the polyurethane composite coatings were investigated using a UMT-2 tribo-tester. When the MoS₂-MWCNT hybrid content was 3 wt%, the polyurethane composite coatings exhibited an outstanding tribological performance. Furthermore, compared with pristine polyurethane composite coating, the friction coefficient and wear rate of the MoS₂-MWCNT-1-reinforced polyurethane composite coating decreased by values as high as

Fig. 10  SEM images of the worn surfaces of the (a) pristine, (b) MWCNT filled, (c) MoS₂ reinforced, (d) MoS₂-MWCNT-1 reinforced and (e) MoS₂-MWCNT-2 reinforced polyurethane composite coatings.

Fig. 11  EDS analysis of the transfer films formed on the counterpart ball surfaces of the: pristine coating (a) and MoS₂-MWCNT-1 reinforced polyurethane composite coatings (b)–(d).
25.6% and 65.5%, respectively, respectively. This result indicated that the MoS2-MWCNT-1 can significantly improve the tribological properties, which was mainly attributed to the synergistic effect of the excellent lubricant ability of MoS2 and outstanding load-carrying capacity of the MWCNTs.

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References


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