Growth of ultra-dense MoS₂ nanosheets on carbon fibers to improve the mechanical and tribological properties of polyimide composites

Jin YANG, Qingfeng XIAO, Zhe LIN, Yong LI, Xiaohua JIA*, Haojie SONG*

School of Materials Science & Engineering, Shaanxi Key Laboratory of Green Preparation and Functionalization for Inorganic Materials, Shaanxi University of Science & Technology, Xi'an 710021, China

Received: 29 February 2020 / Revised: 20 April 2020 / Accepted: 03 June 2020

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Abstract: To enhance the interface bonding of polyimide (PI)/carbon fiber (CF) composites, CFs were functionalized by introducing a polydopamine (PDA) transition layer, whose active groups provide absorption sites for the growth of molybdenum disulfide (MoS₂) nanosheets and improve the bonding strength with PI. Uniform and dense MoS₂ nanosheets with thicknesses of 30–40 nm on the surface of the PDA@CF were obtained via a subsequent hydrothermal method. As a result, the interface between the CF and the PI matrix becomes more compact with the help of the PDA transition layer and MoS₂ nanosheets. This is beneficial in forming PI/CF–MoS₂ composites with better thermal stability, higher tensile strength, and enhanced tribological properties. The lubricating and reinforcing effects of the hybrid CF–MoS₂ in the PI composite are discussed in detail. The tensile strength of the PI/CF–MoS₂ composite increases by 43%, and the friction coefficient and the wear rate reduce by 57% and 77%, respectively, compared to those of the pure PI. These values are higher than those of the PI/CF composites without MoS₂ nanosheets. These results indicate that the CF–MoS₂ hybrid material can be used as an additive to improve the mechanical and tribological properties of polymers.

Keywords: carbon fibers (CFs); polydopamine; MoS₂ nanosheets; interface; tribology

1 Introduction

Polyimide (PI) exhibits both good stability and excellent mechanical properties. It is one of the most important high-performance polymers and has been widely used in the aerospace and microelectronics fields [1–3]. Nevertheless, the high friction coefficient and poor wear resistance of pure PI limit its application in tribology [4]. It is well known that the addition of fillers constitutes an effective method for improving the tribological properties of polymers [5, 6]. Carbon fibers (CFs) are commonly used to improve the tribological properties of several materials owing to their excellent mechanical, friction-reducing,

and anti-wear characteristics as well as their uniform dispersion in a polymer matrix [7–13]. However, the interface between a CF and PI is poor because of the chemical inertness and low surface energy of the former component. Moreover, the CF can be easily detached from the matrix during friction, resulting in a lower than expected material performance [14–16]. Currently, the binding force between the CF and matrix is improved by growing nanoparticles, nanorods, and nanosheets onto the CF. This strategy increases the roughness of the CF and improves its binding force with the matrix via mechanical interlocking. Yadav et al. [17] reported that by coating the surface of a CF with nickel

* Corresponding authors: Xiaohua JIA, E-mail: jiaxiaohua@sust.edu.cn; Haojie SONG, E-mail: songhaojie@sust.edu.cn

particles, its binding force with the polymer was improved by mechanical interlocking among the nickel particles and the epoxy resin matrix. Fei et al. [18] prepared TiO_2 nanorods on woven CFs via a hydrothermal method to reinforce resin composites. Their results show that the bond strength between the woven CFs and the resin can be improved by growing TiO_2 nanorods. Chen et al. [19] prepared a new hybrid material by growing molybdenum disulfide (MoS_2) onto the surface of a CF to improve the tribological properties of the epoxy. These studies prove that such nanostructures can effectively improve the bonding strength between CFs and polymers. However, because of the inertness of the CF surface, the micro/nanostructures growing onto the CF are not dense enough. For this reason, the binding force improvement between the CF and the polymers is limited, resulting in CF shedding during friction.

Inspired by the adhesion ability of the mussel adhesion protein on various substrates, dopamine oxidative self-polymerization to synthesize a poly-dopamine (PDA) coating is considered as a suitable method for surface modification [20, 21]. The active groups introduced by the resulting PDA coating can serve as auxiliary functions to satisfy the requirements of various applications [22, 23]. Yuan et al. [24] used PDA as a transition layer to covalently graft an aminofunctional silane layer onto the surface of a mixed Nomex/polytetrafluoroethylene (PTFE) fabric. In the previous studies of our research group, PDA was polymerized onto a graphene surface to form a transition layer with the reactive functional groups: This provides a series of anchor points that can be grown via simple reduction to produce uniform copper nanoparticles [25]. Therefore, introducing more reactive functional groups via PDA surface modification is an advantageous method to grow such micro/nanostructures onto the CF surface.

Herein, a CF was functionalized by forming a PDA transition layer, which contains many reactive functional groups onto the CF surface, such as catechol, amines, and imines. The active functional group provided the absorption site. Moreover, the ability of CF to adsorb metal ions was enhanced to generate a uniform

and dense growth of MoS_2 nanosheets. The MoS_2 nanosheets were uniformly anchored onto the surface of the functionalized CF via a hydrothermal method to synthesize the CF- MoS_2 , which were added to the PI matrix to prepare the PI/CF- MoS_2 composite. Compared to the pure PI, the tensile strength of the PI/CF- MoS_2 composite increases by 43%, and the friction coefficient and the wear rate reduce by 57% and 77%, respectively. These values are higher than those for the PI/CF composite without MoS_2 nanosheets. The results show that PDA-modified CF can effectively promote a uniform and dense growth of MoS_2 onto the CF and improve the binding between the CF and the PI matrix, thus increasing the wear resistance and mechanical properties of PI. The lubricating and reinforcing effects of hybrid CF- MoS_2 in the PI composite are discussed in detail.

2 Experimental

2.1 Materials

The CF investigated in this study was provided by Nanjing Weida Composite Material Co., Ltd., China. Dopamine hydrochloride ($\text{C}_8\text{H}_{11}\text{NO}_2\cdot\text{HCl}$) was purchased from Shanghai Macklin Biochemical Co., Ltd., China. Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), 4,4'-diaminodiphenyl ether (ODA), pyromellitic dianhydride (PMDA), and sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$) were obtained from Sinopharm Group Chemical Reagent Co., Ltd. Thiourea ($\text{CH}_4\text{N}_2\text{S}$) and cetyltrimethylammonium bromide (CTAB) were produced by Tianjin Damao Chemical Reagent Factory.

2.2 Synthesis of the polyimide acid (PAA)

Initially, ODA was added to dimethylacetamide and the solution was vigorously stirred in an ice bath until ODA was completely dissolved. Successively, PMDA was added into the solution in batches and continuously stirred for 2 h. When synthesizing the PAA, the molar mass ratio of ODA and PMDA was strictly maintained to 1:1. The resulting PAA colloid (5 wt%) was kept at a low temperature and

in a dry environment.

2.3 Preparation of CF-MoS₂

The preparation of CF-MoS₂ can be divided into two steps: 1) 0.65 g of C₈H₁₁NO₂·HCl was dissolved into 50 mL of Tris buffer and magnetically stirred for 30 min, and then 2 g of CF was added at 30 °C in a water bath and stirred for 24 h. Subsequently, the excess PDA was removed with a distilled water centrifugal detergent, and the PDA@CF sample was dried in a vacuum oven for 24 h. 2) 0.88 g of Na₂MoO₄·2H₂O, 0.725 g of NH₂OH·HCl, 1.4 g of CH₄N₂S, and 0.18 g of CTAB were added into 50 mL of deionized water and the solution was stirred for 1 h. The PDA@CF was added and the solution was adjusted to pH ≈ 6 using HCl. The mixed solution was transferred into a Teflon-lined stainless steel autoclave at 180 °C for 24 h. The obtained CF-MoS₂ was collected and washed with deionized water and ethanol and dried at 60 °C for 24 h.

2.4 Preparation of the PI/CF-MoS₂ composite

CF-MoS₂ with a mass fraction of 0.1 wt%–0.4 wt% was added to the PAA colloid (5 wt%), and the resulting mixture was stirred for 30 min. The mixture was then sonicated for 1 h to remove the bubbles and evenly distribute CF-MoS₂. It was then cast into a film, baked in a vacuum drying box at 70 °C for 3 h, and then heated up to 100, 130, 160, 190, 220, and 250 °C for 30 min at each temperature stage to promote the imidization transformation. The films were naturally cooled down to room temperature and PI/CF-MoS₂ composites were obtained. The content of CF-MoS₂ in the obtained composite was 2 wt%–8 wt%. Additionally, the CF and CF/MoS₂ mixture with the same content was used to prepare PI composites as comparative samples.

2.5 Characterization

The morphology and microstructure of the samples were characterized via scanning electron microscopy (SEM, FEI Verios 460, USA) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN, USA). The microscopic crystal sample structures were obtained via X-ray diffraction (XRD, D/MAX2500PC, Japan) measurements in the 2θ range

of 5°–80°. The functional groups and the surface structures contained in the samples were detected by using a Thermo Fisher Scientific's Fourier transform infrared spectrometer (FT-IR, Nicolet iS10) and a Raman spectrometer (DXR, Thermofisher, UK), respectively. X-ray photoelectron spectrometry (XPS, Kratos Axis Supra, Japan) was used to characterize the surface elemental composition of the specimens.

2.6 Tribological properties of the PI/CF-MoS₂ composite

The tribological properties of the composites were analyzed by using a ball-on-disk tribometer (MS-T3000). Friction tests were carried out at different loads (0.5, 1, 2, and 3 N), rotating speeds (100, 200, 300, and 400 rpm), and by varying the additive content from 2 wt% to 8 wt%. The samples were fixed on grade 45 steel surfaces (20 mm × 3 mm). The steel ball used had a diameter of 4 mm and was made of a GCr15 bearing steel with a hardness of 62 HRC. The wear width was measured via optical microscopy (OM, Zeiss Observer Z1m).

3 Results and discussion

3.1 Microstructure of the CF-MoS₂

The preparation of the PI/CF-MoS₂ composite is shown in Fig. 1. When CFs were added into a weak alkaline dopamine solution, the catechol groups of dopamine were oxidized to form a quinone structure and generate an intermediate by nucleophilic reaction and rearrangement. Subsequent intermolecular cross-linking resulted in the formation of PDA on the surface of CFs [23]. The PDA molecules provided much more abundant active anchoring sites such as catechol and imino, which could catch and strongly bind MoO₄²⁺ through electrostatic attraction [25, 26]. In the following hydrothermal reaction, the adsorbed MoO₄²⁺ ions were transformed to MoS₂ nanosheets on the PDA@CF [27]. The reaction equations to generate MoS₂ are as follows:

Fig. 1 Schematic of the synthesis of the PI/CF-MoS₂ composite.

When the prepared CF-MoS₂ was mixed with a PAA solution, a brown PI/CF-MoS₂ composite was obtained after high-temperature curing. Moreover, the reaction between PDA and PAA was easily carried out under a solution state because they are alkaline and acid, respectively [28]. During the PAA imidization process, the imino groups of PDA could react with the carboxyl groups of PAA to enhance the interface binding of the PI/CF-MoS₂ composite.

The CF surfaces before and after modification were observed via SEM (Fig. 2). Initially, the neat

CF surface exhibits several grooves and colloidal substances (Fig. 2(a)). Figure 2(b) shows the surface morphology of the CF modified with PDA, which evenly covers the CF. The microstructure of the CF-MoS₂ specimen is illustrated in Figs. 2(c) and 2(d). The CF is completely covered by uniform and dense MoS₂ nanosheets with lengths of 100–200 nm. Furthermore, as displayed in Figs. 2(d) and 2(e), the MoS₂ nanosheets have multi-layer structures with a thickness of 30–40 nm. Figure 2(f) shows that the MoS₂ layer spacing measures 0.86 nm. This indicates

Fig. 2 SEM images of (a) CF, (b) PDA@CF, and (c, d) CF-MoS₂. (e, f) TEM images of CF-MoS₂. EDS images of the (g) C, (h) Mo, and (i) S elements.

that CTAB entered the MoS₂ crystal plane and increased the crystal plane spacing of MoS₂. The EDS analysis reveals that the Mo and S elements are uniformly distributed onto the CF surface. C is almost invisible probably because of the dense growth of the MoS₂ nanosheets, which completely cover the CF (Figs. 2(g)–2(i)). However, without PDA as a transition layer, MoS₂ is difficult to grow on the surface of CF owing to its chemical inertness. As depicted in Fig. S1 (Electronic Supplementary Material (ESM)), only some spherical particles accumulate on the surface of CF, which is not suitable for the interface modification of the PI composite.

The crystallographic structures of the CF, MoS₂, and CF–MoS₂ samples were examined by XRD (Fig. 3(a)). A wide diffraction peak corresponding to the (002) plane of the CF appears at 25.1°. The diffraction peaks located at 8.8°, 17.2°, 32.6°, 43.3°, and 57.8° correspond to the (002), (100), (103), (006), and (110) planes of MoS₂ [29]. According to the Bragg equation, the interplanar spacing of MoS₂ increases from 0.64 to 0.86 nm.

The analysis of the hybrid CF–MoS₂ sample via Raman spectroscopy is illustrated in Fig. 3(b). The characteristic peaks of the hexagonal MoS₂ structure appear at 378 cm^{−1} and 401.2 cm^{−1} and correspond to the E_{2g} mode of the internal vibration of the sulfur atom with respect to the molybdenum layer and the A_{1g} mode generated by the vibration of the

sulfur atom along the C axis, respectively [30–33]. The number of layers of MoS₂ can be inferred from the red and blue shifts of the characteristic peaks of MoS₂ [34, 35]. The difference between the Raman peaks of the CF–MoS₂ hybrid sample measures 23.2 cm^{−1}, confirming that this material has few layers [36].

The FT-IR spectra of the samples are presented in Fig. 3(c). For the original CF, the FT-IR spectrum shows that almost no active agent groups can be found on the CF surface because of the surface inertia. Compared to the pure CF sample, the characteristic peaks of PDA@CF at 3,440 and 3,140 cm^{−1} can be attributed to the stretching vibrations of the –OH and N–H groups [37], respectively. In addition, new peaks at 1,630, 1,400, and 1,110 cm^{−1}, corresponding to the stretching vibrations of C=C, C–N, and C–O, respectively, appear [38]. These results show that PDA was successfully recombined with CF, which is consistent with the SEM image of the PDA@CF sample (Fig. 2(b)). The FT-IR results show that the CF–MoS₂ still contains –OH, whereas the C–N and N–H bonds indicate that the reactive functional groups introduced by the PDA are still present (Fig. 3(c)). This allows the CF–MoS₂ to chemically cross-link during the PAA imidization process to facilitate the generation of the bond between CF–MoS₂ and PI.

The CF–MoS₂ was examined using XPS and the

Fig. 3 (a) XRD patterns of CF, MoS₂, and CF–MoS₂. (b) Raman spectrum of CF–MoS₂. (c) FT-IR spectra of CF, PDA@CF, and CF–MoS₂. XPS spectra of CF–MoS₂: (d) C 1s XPS spectrum, (e) Mo 3d XPS spectrum, and (f) S 2p XPS spectrum.

results are shown in Figs. 3(e) and 3(f). Figure 3(d) illustrates the spectral analysis of C 1s: The three peaks correspond to the C atom of the functional groups C–C (284.3 eV), C–O (286.0 eV), and C=O (288.1 eV) [39]. Four sub-peaks appear at the binding energies of 225.2, 229.1, 232.4, and 235.8 eV (Fig. 3(e)), which may correspond to Mo 3d. The peaks at 229.1 and 232.4 eV correspond to Mo 3d_{5/2} and Mo 3d_{3/2} of Mo⁴⁺ in the MoS₂ nanosheets. The peak located at 235.8 eV corresponds to Mo⁶⁺ 3d_{3/2}, indicating that a Mo–O–C bond is formed between the CF and the MoS₂ nanosheets [29]. In addition, the peak located at 225.2 eV corresponds to S 2s. The two peaks, which appear at 162 and 163.3 eV, corresponding to S 2p_{3/2} and 2p_{1/2} of the divalent sulfide ion (S²⁻) [40], respectively (Fig. 3(f)). The results reveal that the MoS₂ nanosheets were successfully grown onto the CF surface.

3.2 Thermal stability of the PI/CF–MoS₂ composite

The effects of CF and CF–MoS₂ on the thermal stability of PI are depicted in Fig. 4 and Table 1. The temperatures of the PI, PI/CF, and PI/CF–MoS₂ composites for a 5% (*T* (5 wt%)) mass loss are 570.0, 575.1, and 593.2 °C, respectively. In particular, the temperature of the PI/CF–MoS₂ composite is 23.2 °C higher than that of the pure PI sample and 18.1 °C higher than that of the PI/CF composites. This is because the physical barrier formed by adding CF–MoS₂ to the PI matrix can reduce the migration rate of thermal decomposition products in the matrix. The thermogravimetric analysis curve shows that the thermal decomposition temperature of the PI/CF–MoS₂ composite at various stages is the highest. At 850 °C, the remaining mass fractions of the PI, PI/CF, and PI/CF–MoS₂ composites measure 62.48%, 64.46%, and 68.62%, respectively. Generally, the frictional heat generated during rubbing causes a softening in the polymer material, which can easily peel off when subjected to a shearing force. In this case, the wear rate increases. Therefore, improving the thermal stability of material is beneficial for improving its tribological properties.

3.3 Tribological and mechanical properties of the PI/CF–MoS₂ composite

The mechanical properties of PI and its composites

Fig. 4 Thermogravimetric analysis of the PI, PI/CF, and PI/CF–MoS₂ composites.

Table 1 Thermal properties of PI and its composites.

Materials	<i>T</i> (5 wt%, °C)	Residual weight fraction (wt%, 850 °C)
PI	570.0	62.48
PI/CF	575.1	64.46
PI/CF–MoS ₂	593.2	68.62

were tested by performing a series of tensile tests. The stress–strain curve (Fig. 5(a)) shows that the tensile strengths of the PI/CF and PI/CF–MoS₂ composites are larger than those of pure PI films. In particular, the PI/CF–MoS₂ composite exhibits the best mechanical properties, and its tensile strength is 43% and 18% higher than those of the pure PI and PI/CF composites, respectively. This is due to the mechanical cross-linking produced by the CF and PI matrix after the addition of the CF. In general, CFs have a high creep resistance, hardness, and compressive strength. For this reason, they can be used as ideal reinforcement materials. During stretching, the tensile stress can be transferred from the substrate to the CF, thereby improving the tensile strength of the PI. However, owing to the inertia of the untreated CFs and their weak adhesion to the PI matrix, the improvement in the mechanical properties of this material is limited. The growth of a MoS₂ layer onto the surface of a CF can improve the binding between PI and the CF and improve the tensile strength of PI/CF–MoS₂. This is consistent with the experimental results, which show that PI/CF–MoS₂ has the highest tensile strength among the investigated materials.

Figures 5(b) and 5(c) display the tensile cross-

Fig. 5 (a) Stress–strain curves of PI and its composites. SEM of PI and its composite material section: (b) PI/CF and (c) PI/CF–MoS₂. EDS images of (d) C, (e) Mo, and (f) S of the PI/CF–MoS₂ composite.

sections of the PI/CF and PI/CF–MoS₂ composites. Owing to the surface inertness of the CF and its poor combination with the PI matrix, a large gap can be observed between the CF and the PI matrix, and even some CFs are pulled out (Fig. 5(b)). For the PI/CF–MoS₂ composite, the interface between the CF and the PI substrate does not exhibit either shedding or separation from the CF. The MoS₂ nanosheets are completely covered by the PI matrix (Fig. 5(c)), causing a large amount of C element to appear on the surface of the CF–MoS₂ (Fig. 5(d)). Additionally, the elements of Mo and S are still enriched on the surface of the CF–MoS₂ (Figs. 5(e) and 5(f)), indicating a strong combination between MoS₂ nanosheets and CF under the action of PDA. The EDS results of other elements are provided in Fig. S2 (ESM).

The tribological properties of PI and its composites were compared under dry friction. The addition of the CF–MoS₂ hybrid material to the PI matrix sign-

ificantly improves the tribological properties of PI. As depicted in Figs. 6(a) and 6(b), the tribological properties of the PI/CF–MoS₂ composites are optimal when the CF–MoS₂ content is 4 wt%. The friction coefficient and the wear rate of PI/CF–MoS₂ composite are reduced by 53% and 77%, respectively, compared with those of PI. With an increase in the CF–MoS₂ content, the tribological properties of the PI/CF–MoS₂ composites show a negative trend. This is because the CF–MoS₂ content is extremely high, which adversely affects the imidization process of the PI matrix. Moreover, it causes a reaction that deteriorates the performance of the matrix itself. Additionally, for the PI/CF and PI/CF/MoS₂ composites, although their friction coefficients are lower compared with that of PI, the wear rates are still much greater than that of the PI/CF–MoS₂ composite. The poor interface bonding between the CF and the PI matrix results in severe wear on the surface of the composite. After modification by growing MoS₂ on

Fig. 6 (a) Variation of the friction coefficients of PI, PI/CF, PI/CF/MoS₂, and PI/CF–MoS₂ composites with time. (b) Friction coefficients and wear rates of the PI, PI/CF, PI/CF/MoS₂, and PI/CF–MoS₂ composites (2 N, 200 r/min).

the surface of CF, the strong interface bonding can prevent CF from coming out of the PI matrix. Since the PI on the surface of the PI/CF–MoS₂ composite is stripped during friction, the CF–MoS₂ is exposed between the friction pairs. The CF bears the load to prevent the PI from peeling off, whereas MoS₂ forms a protective film between the friction pairs owing to its excellent self-lubricating performance, reducing the friction. Under this synergistic effect generated by CF and MoS₂, the tribological properties of PI can be significantly improved.

In general, the effect of different loads on the tribological properties of the materials is very evident. Figure 7(a) presents the tribological properties of the PI/CF–MoS₂ composite at different loads. A comparison of the results shows that the PI/CF–MoS₂ composite exhibits better tribological properties at low loads. With the increase in load, the friction coefficient decreases first and then increases. During friction, the PI matrix is softened owing to frictional heat, which makes the PI easy to peel off; thus, it has a lower coefficient of friction. Heavy loads always lead to high frictional heat and soften polymer materials, which increase the actual contact area between counterparts and enhance adhesion of the polymer to the counterpart, consequently increasing the friction coefficient and wear rate. When the load reaches 3 N, the friction coefficient of PI/CF–MoS₂ increases to 0.32, and the wear rate is almost twice that at 0.5 N. In addition, at high loads, CF–MoS₂ can easily be stripped out, which can cause material failure. When CF is broken, the anti-wear effect is weakened, which leads to an increase in the friction coefficient and wear rate. The tribological properties at different sliding speeds are displayed

in Fig. 7(b). A low friction coefficient for high-speed sliding can be noticed despite the increase in wear rate. The pronounced shear action of the high-speed sliding composite increases the possibility of slipping, resulting in a decrease in the friction coefficient and an increase in the wear rate.

The influence of different environmental conditions on the tribological properties of materials cannot be ignored in tribology. Therefore, the tribological properties of the PI/CF–MoS₂ composite were investigated in various media (Fig. 8). In the liquid environment, fluid lubrication can avoid direct contact of friction pairs. Water and oil effectively reduce the frictional heat and prevent the PI matrix from softening. As a result, the friction coefficients of the PI/CF–MoS₂ composite in water and oil measure 0.131 and 0.083, and the corresponding wear rates are 0.28×10^{-6} and $0.0031 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$. However, severe oxidation of MoS₂ will occur in a humid environment. MoO₃ (an oxidation product of this reaction) can restrict the slippage between MoS₂ molecular layers, which will increase the friction coefficient and wear rate on the PI/CF–MoS₂ composite surface [41]. Especially in the seawater environment, the oxidation of MoS₂ can be intensified, increasing the friction coefficient and wear rate to 0.215×10^{-6} and $0.95 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$, respectively. These results indicate that the PI/CF–MoS₂ composite is more suitable for oil lubrication.

To investigate the mechanism of the CF–MoS₂ addition in improving the tribological properties of the PI substrates, the worn surface was analyzed by performing a series of tribological tests on the PI, PI/CF, and PI/CF–MoS₂ composites using OM, EDS, and SEM. The wear scar widths of PI, PI/CF,

Fig. 7 (a) Friction coefficients and wear rates of the PI/CF–MoS₂ composite under different loads at 200 r/min sliding speed. (b) Friction coefficients and wear rates of the PI/CF–MoS₂ composite under different sliding speeds at 2 N load.

Fig. 8 Friction coefficients and wear rates at different media (2 N, 200 r/min).

and PI/CF–MoS₂ measure 634.84, 554.65, and 283.45 μm , respectively (Figs. 9(a)–9(c)). As indicated in Fig. 9(d), the PI worn surface exhibits wide grooves and debris. However, the wear performance of PI has been significantly improved after the addition of CF, and its surface exhibits only a little wear debris (Fig. 9(e)). Owing to the progression of friction, the CFs fall off from the substrate under the effect of shear stress, leaving defects on the

worn surface. In addition, the worn surface of the PI/CF–MoS₂ composite has almost no wear marks and the presence of CF is visible on the worn surface (Fig. 9(f)). Owing to the growth of MoS₂ nanosheets onto the CF, the bond between the CF and the PI matrix is firm and does not fail during friction. Additionally, the EDS analysis shows that C, Mo, and S are distributed on the worn surface (Figs. 9(d)–9(f)). During the friction process, the exposed MoS₂ nanosheets on the CF can be peeled off, forming a transfer film at the contact interface. It can be observed from Figs. 9(e) and 9(f) that the Mo and S elements are transferred from the CF to the entire worn surface, leading to an obvious decrease on the top surface of the CF. Moreover, the Mo and S elements can be detected on the frictional ball (Fig. S3 (ESM)). Because of the weak van der Waals force among the layers of the MoS₂ lamellar structure, the sliding of the layers reduces the friction coefficient. Overall, the MoS₂ avoided the direct contact between the matrix and the friction pair, thus enhancing the tribological properties of the PI/CF–MoS₂ composite.

Fig. 9 OM of the worn surface of (a) PI, (b) PI/CF, and (c) PI/CF–MoS₂ sliding against stainless steel under dry friction. SEM of the worn surface of (d) PI, (e) PI/CF, and (f) PI/CF–MoS₂ sliding against a stainless steel ball under dry friction. EDS images of (g) C, (h) Mo, and (i) S in the PI/CF–MoS₂ composite.

Fig. 10 Schematic of the friction and wear processes of the PI/CF-MoS₂ composite.

Based on the results reported in this section, the role of CF-MoS₂ in enhancing the tribological properties of the PI substrates is depicted in Fig. 10. Because of the poor tribological properties of PI, the PI matrix is quickly worn away under the effect of shear stress at the beginning of the friction process. However, upon wearing of the PI matrix, the CF-MoS₂ hybrid material becomes exposed between the friction pairs. At this point, the stress on the substrate is transferred to the CF. Owing to the excellent strength and robustness of the CF, the wear rate of the PI substrate can be effectively reduced. More importantly, MoS₂ forms a protective film between the friction pairs. Since the MoS₂ sheet is obtained by exploiting the weak van der Waals forces and it easily slides when subjected to tangential forces, it has an excellent lubrication property and it can effectively reduce the friction of PI. Simultaneously, a mechanical lock forms between the MoS₂ nanosheet and the PI substrate to protect the CF from falling off. This indicates that CF decoration with MoS₂ nanosheets improves the friction and wear performance of PI.

4 Conclusions

Uniform and dense MoS₂ nanosheets were grown onto a CF via a simple PDA modification. The thickness of the MoS₂ nanosheets measured 30–40 nm, and the interlayer spacing was 0.86 nm. The prepared CF-MoS₂ composite can be well dispersed in the PI matrix and was used as lubricating and reinforcing materials. The PI/CF-MoS₂ composite exhibited optimal tribological and mechanical properties when 0.2 wt% of CF-MoS₂ was added to the PI matrix. The tensile strength of PI/CF-MoS₂ increased by 43%,

the friction coefficient and the wear rate reduced by 57% and 77%, respectively, and the thermal stability of the sample was improved. The tribology and tensile properties of PI/CF-MoS₂ were not only generated by the synergy between the CF and MoS₂, but also by the presence of the uniform and dense MoS₂ nanosheets onto the CF surface. This greatly improved the interface bonding between the PI and the CF. In this way, the CF did not fall from the PI matrix during the stretching or friction processes, which supported the main load and improved the friction and mechanical properties of PI. The results demonstrate that the CF-MoS₂ hybrid composites are promising materials, which can be used as lubricant additives to improve the tribological properties of polymers.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (51875330 and 51975342) and the National Science Foundation of Shaanxi Province (2018JZ5003 and 2019JZ-24).

Electronic Supplementary Material: Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40544-020-0413-0>.

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Jin YANG. He is currently an associate professor at Shaanxi University of Science and Technology. He received his B.S. degree from Liaocheng University in 2007 and

a Ph.D. degree from Lanzhou Institute of Chemical Physics in 2012. His current research interests include the development of carbon-based materials for lubrication and designing materials with special surface wettability.

Qingfeng XIAO. He is currently a master degree candidate at Shaanxi University of Science & Technology. He received his B.S. degree in 2018 from Xi'an Aeronautical University,

Xi'an, China. His current research interests are focused on improving the tribological properties of polymer composites with CFs and studying the corresponding mechanisms.

Zhe LIN. He received his B.S. degree in 2018 from Xi'an Aeronautical University, Xi'an, China. He is a master student in the Institute of Material Friction and Green

Protection, Shaanxi University of Science & Technology. His research interests include CF reinforced polymer composite and their tribological performances.

Yong LI. He received his B.S. degree in chemical engineering and technology from Henan University of Science and Technology in 2013 and Ph.D. degree in 2018 in materials science from Lanzhou

Institute of Chemical Physics, University of Chinese Academy of Sciences. Now he is a lecturer in Shaanxi University of Science & Technology and his current research is focused on self-repairing materials with wear resistance and lubricity and multifunctional surfaces with special wettability.

Xiaohua JIA. She is currently a professor at Shaanxi University of Science & Technology. She received her M.S. degree from Henan Normal

University in 2006 and Ph.D. degree from Northwestern Polytechnical University in 2011. Her current research is focused on the carbon-based functional materials and chemical sensors.

Haojie SONG. He is currently a professor at Shaanxi University of Science & Technology. He received his B.S. degree from Henan Normal University in 2003 and Ph.D. degree

from Lanzhou Institute of Chemical Physics in 2008. Now, he is interested in the development of the tribological properties of carbon matrix composites.