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FABRICATION OF MoS_2ULTRATHIN NANOSHEETS AND ITS TRIBOLOGICAL PROPERTIES AS LUBRICATING ADDITIVE OF POLYIMIDE

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In this paper, MoS_2 ultrathin nanosheets with high purity were successfully synthesized via a facile hydrothermal method. The microstructure and morphology of as-prepared MoS_2 were characterized by High solution transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD), and Raman spectrum (RS). When evaluated as a lubricating additive for polyimide composites, the results of friction and wear test showed that PI-MoS_2 composites exhibited outstanding friction-reducing and anti-wear properties. In particular,when the MoS_2 content was 7wt.%., the friction coefficient and wear rate of corresponding composite decreased 29% and 88%, respectively. More importantly, the PI-7wt.%MoS_2 composite still possessed low friction coefficient and wear rate under high load or sliding rate. This implied that MoS_2 ultrathin nanosheets owned excellent self-lubricating property, and was a promising lubricating additive to enhance the tribological properties of polymer.

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1. Introduction

As well known, laminar materials are generally characterized by excellent friction and wear properties and thus widely applied in tribology field. And the outstanding lubricating properties of the laminar materials are ascribed to the easy shearing between their molecular layers [1, 2].For example, graphite can decrease the friction coefficient and improve the wear resistance of materials due to its multilaminate microstructure easily being sheared off and forming transfer films [3, 4].

Transition metal dichalcogenides MS_2 (M: Mo, W) have been receiving great attention because of their unique structure and superior properties [5-7]. Molybdenum disulfide (MoS_2), a typical transition metal dichalcogenide, has a layered structure with weak van der Waals interactions between individual sandwiched S-Mo-S layers [8]. So MoS_2 shows a low friction coefficient and gives rise its excellent tribological properties with numerous potential applications, such as lubricating fluid additives [9], anti-wear coatings [10], and solid lubricants [11]. Kalin et al. have studied the tribological behavior of MoS_2 as an additive in lubricating oils. And results show that MoS_2 significantly decreases the friction and wear compared to the base lubricant. The friction is more than 2 times lower and the wear as much as 5-9 times lower [12]. Xu et al. have found that MoS_2/TiO_2 improves the tribological properties of rapeseed oil due the formation of lubricating film composed of MoO_3, Fe_2O_3, $Fe_2(SO_4)_3$ etc. [13]. Wang et al. have investigated the influence of MoS_2 filler on the tribological properties of carbon fiber reinforced nylon 1010 composites, and

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found that MoS_2 particles can help the formation of thin, uniform and continuous transfer film to increase the wear resistance of nylon composites [14]. Therefore, MoS_2 has enjoyed the reputation of "the king of lubrication" for a long time.

Nanomaterials have gained renewed interests due to its unique properties, i.e., large specific surface area, small size effect, high surface activity etc.. And recent investigations show that smaller size of MoS_2 shows much better tribological properties than bulk MoS_2 [15, 16].And MoS_2 nanomaterial with different microstructure, including nano-plates [17], nanotubes [18], nanowires [19], nanoflowers[20]etc. Xu et al. have prepared solid sphere-like MoS_2 nanoparticles via a modified chemical method, and found that the as-prepared nano-MoS_2 particles can improve the tribological properties of dioctylsebacate more compared with a commercial micro-MoS_2. And the main reason is that when the nano-MoS_2 is applied, a solid complex adsorption film beside the tribofilm is formed on thefriction surface to reduce the friction and wear [21]. Tang et al have fabricated flower-like MoS_2, and it has superior anti-wear and friction-reducing properties as lubrication additive compared to pure base oil [8]. Liu have prepared double-hollow-sphere MoS_2 nanoparticles on sericite mica, and found that they are used as additive in polyalpaolefinoil, friction and wear are decreased by 22.4% and 63.5% respectively [22].

Recently, MoS_2 nanosheets have attracted many interests thanks to crystallographic structure consisting of S-Mo-S tri-layers in analogy to graphene [23, 24]. Many several methods are used to prepare MoS_2nanosheets, i.e., high temperature sulfurization, chemical vapor deposition, mechanochemical treatment method etc. Herein, we report a facile method of MoS_2 ultrathin nanosheets via one-step hydrothermal method. And the microstructure and phase composition of as-prepared MoS_2 are characterizedby High-solution Transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD), and Raman spectrum (RS). In addition, the effects of MoS_2nanosheets on the density, hardness, and thermal properties of polyimide (PI) are investigated. More importantly, the tribological properties of MoS_2 nanosheets as the lubricating additive of PI are investigated in detail. Hopefully, this work can provide some insight into the design of nanostructure for enhancing the friction and wear properties of polymer composites.

2. Experimental

2.1. Preparation of MoS_2 ultrathin nanosheets

$(NH_4)_6Mo_7O_{24}$●$4H_2O$ and CSN_2H_4 were provided by Sinopharm Chemical Reagent Co. Ltd. And they were analytical grade and used without further purification.And the preparation procedure was as follows: 1.24g of $(NH_4)_6Mo_7O_{24}$●$4H_2O$ and 2.28g of CSN_2H_4 were dissolved in appropriate deionized water by magnetic stirring 20min. The mixed solution was transferred into a Teflon-lined stainless steel autoclave, and further kept at 220℃ for 24h, and naturally cooled down to room temperature. The resultant product was collected by centrifugation, washed with distilled water and absolute ethanol several times, and finally dried for 24h at 80℃.

PI powder was commercially obtained from Shanghai Synthetic Resin Institute (China).PI powder and MoS_2nanosheets were firstly blended mechanically. Then the mixtures were compressed under the pressure of 30MPa and heated to 350℃ for 30min in the mold. After naturally cooled below 100℃ and released from the mold, PI/MoS_2 composite with a size of Φ 30mm×4mm was obtained. The weight fraction of$MoS_2$is 1%, 3%, 5%, 7%, and 10%.

2.2. Characterization

The morphology and microstructure of as-prepared MoS_2were observed by HRTEM (JEM-2100). The phases composition of MoS_2ultrathin nanosheets were characterized by X-ray diffraction (XRD) on a on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. Raman spectroscopy (RS) was performed with a Raman spectrometer (DXR) with an excitation wavelength of 633 nm.

Thermal gravimetrical analysis (TGA) tests of PI and its composites were performed using Perkin Elmer TGA-7 (USA) at a heating rate of 10℃/min from 50℃ to 800℃ in an argon atmosphere. The hardness was tested by Shore D hardmeter. Besides, the friction and wear tests were performed UMT-2 tester. The counterpart was GCr15 ball with diameter of 4mm. Sliding was performed under dry friction with a period of 30min, normal load of 1N, 1.5N, 3N, and 4.5N, speed of 500rpm and 700rpm.The friction coefficient was continuously recorded by an on-line data acquisition system attached to the tester. The wear volume loss V of the block was determined by non-contact optical profilometer. And the wear rate was calculated from the relationship:

$$K = \frac{V}{L \bullet d}$$

where K, L, and d are the wear rate (mm^3/Nm), load (N), and sliding distance (m). Finally, the wear tracks were observed using SEM.

3. Results and discussion

3.1. Materials features

The crystallinity, structure and phase composition of as-prepared MoS_2 ultrathin nanosheets are determined. And Fig.1 shows the XRD pattern of MoS_2 sample fabricated by hydrothermal route. Clearly, there arefour major diffraction peaks at 2θ=13.9, 33.1, 39.3, and 58.7°. And these peaks can be indexed to(002), (100), (103), and (110) lanes of the pure hexagonal phase of MoS_2 with lattice constants a=3.161Å, c=12.84Å, which are in good agreement with the values of standard card (JCPDS No.37-1492). No characteristic peaks can be seen from other impurities, indicating that the sample is of high purity. In addition, Fig.2 gives the HRTEM images of MoS_2, which well reveals the as-prepared MoS_2 is form of nanosheets. And the nanosheets are size of about 200-400nm, thickness of less 10nm. Moreover, more details for MoS_2 structure are illustrated in Fig.2b. The MoS_2 nanosheets aremainly composed of about 10-layered structures. And the distance of lattice fringes is about 0.64nm, which is nearly same as for the (002) planes of the hexagonal MoS_2 structure.

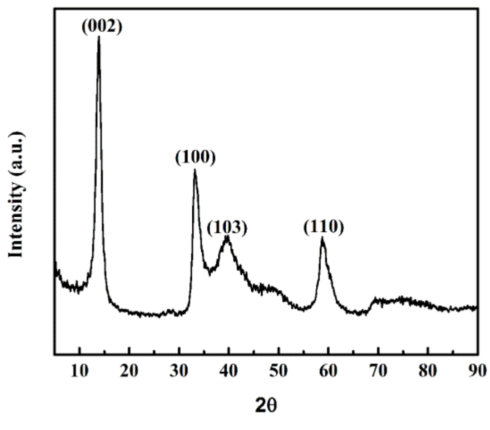

Fig.1. XRD pattern of MoS_2 ultrathin nanosheets

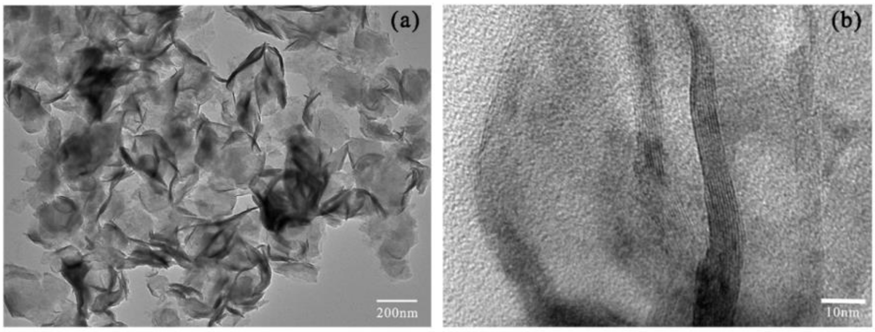

Fig.2.HRTEM images of as-prepared MoS_2 ultrathin nanosheets.

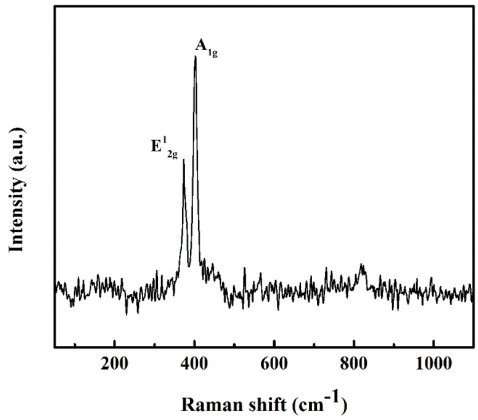

Fig.3. RS analysis MoS_2nanosheets

In addition, Raman spectroscopy is widely applied to characterize the carbonaceous materials with different microstructure. And it also can used to indentify single- or few-layer MoS_2 sheets [25]. Fig.3 shows the RS of as-prepared MoS_2 ultrathin nanosheets. It can be found that there are two dominant peaks of MoS2 at 380cm^{-1} and 407cm^{-1} assigned to E^1_{2g} and A_{1g} modes of the hexagonal MoS_2, respectively. The former is the in-layer displacement of Mo and S atoms, the later is the out-of-layer symmetric displacement of S atoms along the *c* axis.Generally, the layer numbers are related to the energy difference (Δ) between the two Raman peaks.In our study, Δ value of MoS_2 is 25.9cm^{-1}, indicating MoS_2 is an ultrathin state containing several layers. And this is consistent with many previous reports [26].

3.2. Effects of MoS_2 nanosheets on the physical and thermal properties of PI

Table 1 shows the density, hardness, and thermal stability of PI and PI-MoS_2 composites. The density of PI composites is higher than pure PI, due to the addition of MoS_2nanosheets. And it increases with increasing MoS_2 content. Besides, it can be found that the hardness of PI composites is the same as pure PI matrix, which is different from bulk MoS_2 reinforced composites. Generally, bulk MoS_2 always decreases the mechanical properties of polymers because it is soft. But 10wt.% MoS_2 nanosheets slightly deteriorates the hardness, which might be caused by the agglomeration of many MoS_2 in PI matrix. In addition, the thermal stability of PI is enhanced by MoS_2nanosheets. The $T_{-5wt.\%}$ value is the temperature as the mass loss of materials 5%. Namely, higher $T_{-5wt.\%}$ means the corresponding material has better thermal stability. MoS_2nanosheetsinto PI matrix can effectively act as physical barriers to decrease the transport rate of volatile decomposed products out of PI composites during the process of thermal decomposition.

Table 1 Physical and thermal properties of PI and its composites

Materials	Density	Hardness	$T_{-5wt.\%}$ (℃)
PI	1.378	85	550.0
PI-1%MoS_2	1.383	85	560.5
PI-3%MoS_2	1.394	85	564.2
PI-5%MoS_2	1.414	85	565.7
PI-7%MoS_2	1.433	85	569.0
PI-10% MoS_2	1.464	83	562.7

3.3. Friction and wear properties of PI and PI-MoS_2 composites

The friction coefficient of PI and PI-MoS_2 composites with differentMoS_2 contents under a load of 4.5N are shown in Fig. 4. It can be clearly seen that the MoS_2 nanosheets decreases the friction coefficient of PI effectively, suggesting MoS_2 nanosheets has excellent self-lubricating property. Specially, the friction coefficient of PI composites decreases with increase of MoS_2 content from 1% to 7wt.%. But when the content of MoS_2 nanosheets surpass 7wt.%, the corresponding composite has increased friction coefficient. This can be ascribed to the poor dispersion and decreased hardness of MoS_2 nanosheets in the PI matrix at high contents. Nevertheless, the frictioncoefficientPI-7wt.%MoS_2 composite is still much lower than that of the neat PI matrix.

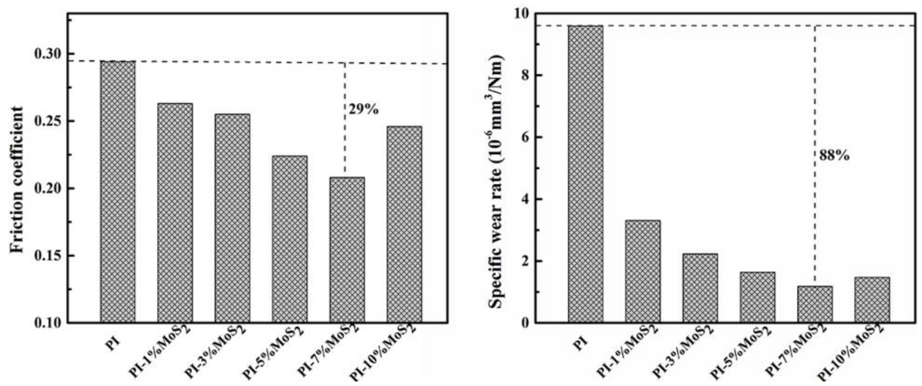

Fig.4.Friction and wear properties of PI composites with various MoS_2nanosheets.

(Load: 4.5N; sliding rate: 500rpm; duration: 20min)

In addition, the wear rate of PI and its composites with different MoS_2 nanosheets contents are also shown in Fig.4. It can be seen that all PI-MoS_2 composites shows lower wear rate than the pure PI. Especially for PI-7wt.% composite, it has the lowest wear rate, which is decreased 88% in comparison with that of PI, implying that the presence of MoS_2 nanosheets can greatly improve the wear resistance of PI. And as the content of MoS_2 nanosheets exceeds 7wt.%, the wear rate increases slightly, but still lower than that of pure PI.This might be related to the thermal stability of composites. Generally, much friction heat is generated during dry sliding process, and it cannot be taken away in the absence of lubricating medium. Accordingly, the friction heat will result in excessive deterioration of the composites and poor tribological properties. Therefore, good thermal stability can protect the composites from the harm of high temperature during the friction and wear process. PI-7wt.%MoS_2 composite demonstrates good thermal stability which is good for its tribological property.

To well determine the explanation of effect of MoS_2 nanosheets on the wear behavior of PI composites, worn surface images are observed by FESEM. In Fig. 5a, the rough worn surface with many wide and deep grooves of PI can be seen, indicating the PI shows poor friction and wear properties when sliding against steel under dry friction and its wear mechanism mainly follows seriousabrasive wear. But the worn surface of PI-3%MoS_2composite is much smoother and with many MoS_2, with the exception of few fine scratches. The MoS_2on the sliding surface canplay the role of self-lubricating effect to decrease friction and wear. For PI-7%MoS_2 composite, its worn surface is the smoothest, and more MoS_2 can be found. This explains PI-7%MoS_2 composite possessing the best friction-reducing and anti-wear properties. In addition, when the content of MoS_2 nanosheets is 10wt.%, there are more obvious grooves on the worn surface. This is because the hardness of PI-10wt.%MoS_2composite decreases, implying the decreased load-carrying capacity during the friction and wear process. In addition, the thermal stability of PI-10wt.%MoS_2 is lower than that of other composites. That is, the sliding surface of PI-10wt.%MoS_2 is easily softened and to be worn off as the result of the plowing effect of asperities on the counterpart. Therefore, the friction coefficient and wear rate of PI-10wt.%MoS_2 increases as shown in Fig. 4.

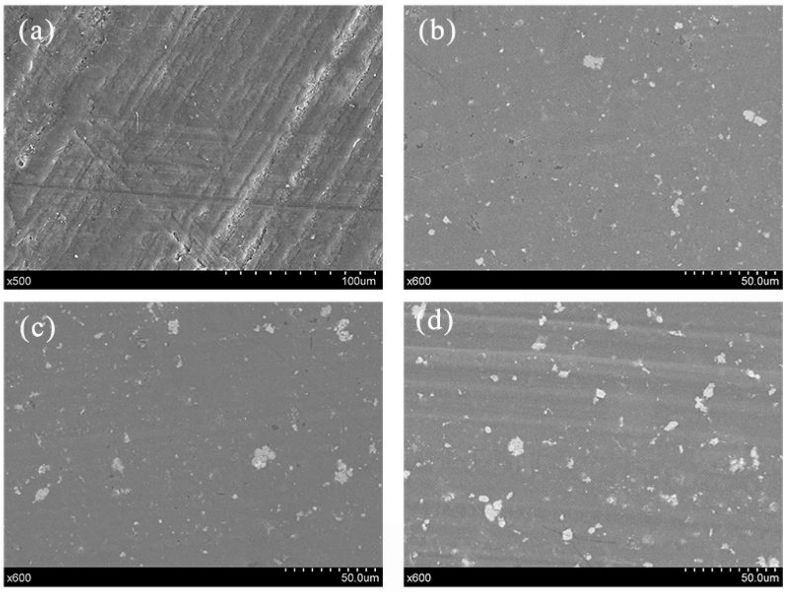

Fig.5. SEM images of worn surface of PI and its composites: (A) PI; (B) PI-3%MoS_2; (C) PI-7%MoS_2; (D) PI-10%MoS_2. (Load: 4.5N; sliding rate: 500rpm; duration: 20min)

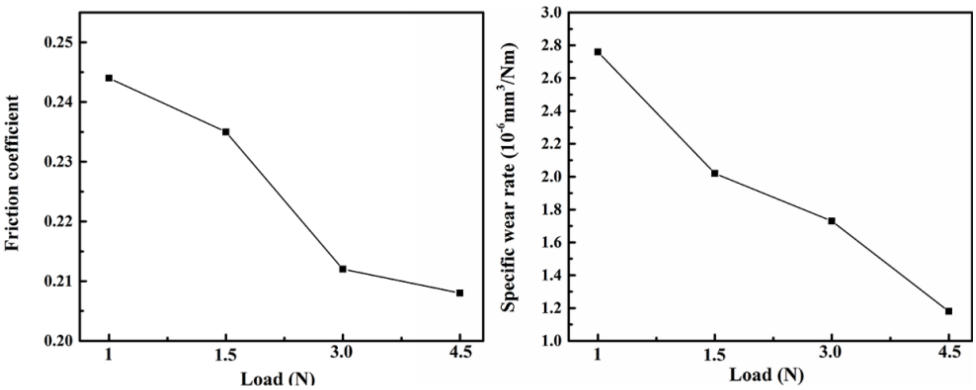

Fig.6.Effect of applied load on the tribologicalproperties of PI-MoS_2 composite.

(Sliding rate: 500rpm; duration: 20min)

As an example of PI-7wt.%MoS_2 composite, the effect of load and sliding rate on the tribological properties are investigated systematically. Fig. 6 shows the friction coefficient and wear rate of PI-7wt.%MoS_2 composite under different applied load. Clearly, the friction coefficient and wear rate show decreasing tendency with the increasing load. And this is consistent with Zhang's report [27]. Under dry friction, there would much friction heat generated from the deformation of materials, which further increases the adhesive friction of materials.And high load always results in high contacting temperature between the sliding surfaces, so the polymer materials are prone to soften; accordingly they are easily to be sheared off. This might be the reason why PI-7wt.%MoS_2 has lower friction coefficient under heavier load. In addition, the newly formed debris would become integrated layer on the worn surface under repeated high load, which can lead to a lower wear rate because of decreased abrasive wear. Besides, the effect of sliding rate on the friction coefficient and wear rate of PI-7wt.%MoS_2 composites is shown in Fig.7. It can be seen that the composite has lower friction coefficient but higher wear rate under high sliding rate. This might be because there is not enough time to produce more adhesive point owing to decreased contacting time, resulting in low friction force.And Cai et al have reported that the friction coefficient PI/CNT composites also decreases with increasing sliding speed, but wear volume shows contrast tendency[28]. Nevertheless，the friction coefficient and wear rate of PI-7wt.%MoS_2 composite under high load or sliding rate are lower than those of pure PI. That is, the as-prepared MoS_2 ultrathin nanosheets is a good lubricating additive to enhance the tribological properties of polymer materials.

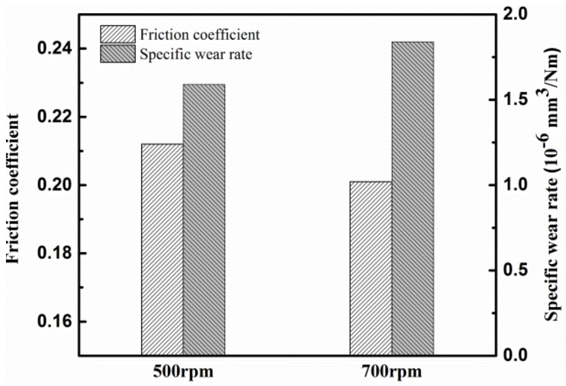

Fig.7. Friction coefficient and wear rate of PI-7%MoS_2 composite under different sliding rate.
(Load: 4.5N; duration: 20min)

Besides, Fig.8 shows the worn surface images of PI-7wt.%MoS_2 composite sliding against GCr15 under different sliding conditions. There are MoS_2 on all worn surfaces. Under 4.5N, the corresponding worn surface is characterized with many small MoS_2, which can effectively decrease friction and wear. So the grooves are scarcely can be observed in Fig. 8a. But under 3N, the MoS_2 are bigger than that under 4.5N (Fig.8b). In addition, compared to Fig.8a, there are obvious grooves and many big MoS_2 in Fig.8c, which well agrees well the composite with high wear rate under high sliding rate as shown in Fig.7.

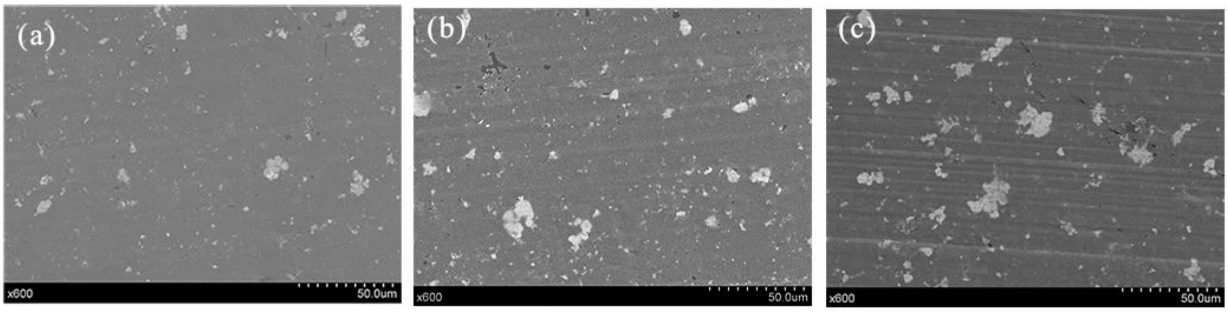

Fig.8. SEM images of worn surface of PI-7%MoS_2 under different sliding conditions:
(A) 4.5N, 500rpm; (B) 3N, 500rpm; (C) 3N, 700rpm

4. Conclusions

MoS_2 ultrathin nanosheets were fabricated successfully, and its microstructure and effect on the thermal and tribologicalproperties of PI were investigated systematically. And the conclusions obtained were as follows:

(1) The MoS_2 ultrathin nanosheets were hexagonal phase with high purity. And the size and thickness of nanosheets was about 400nm, 7nm, respectively.

(2) The thermal stability of PI was enhanced by the incorporation of MoS_2 nanosheets. The $T_{-5wt.\%}$ of PI composites was higher than that of pure PI. And when MoS_2 content was 7wt.%, the corresponding composite had the best thermal stability.

(3) MoS_2 nanosheets increased the friction-reducing and anti-wear properties of PI. And the frictioncoefficient and wear rate of PI composites decreased firstly and then increased slightly with MoS_2 content. In particular, when the MoS_2 content was 7wt.%., the friction coefficient and wear rate of corresponding composite decreased 29% and 88%, respectively. More importantly, the PI-7wt%MoS_2 composite still possessed low friction coefficient and wear rate under high load or sliding rate. This implied that MoS_2 ultrathin nanosheets owned excellent self-lubricating property, and was a promising additive to enhance the tribologicalproperties of polymer.

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