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Preparation and properties of MoS\(_2\) modified polydimethylsiloxane/monomer casting nylon

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Abstract

MoS\(_2\) reinforced PDMS/MC nylon composites had been fabricated by \textit{in situ} polymerization to further enhance the comprehensive properties of nylon material. Polydimethylsiloxane was pre-synthesized as the activator of the system and MoS\(_2\) was compounded as the wear-resisting agent. The thermal stability, mechanical properties, friction and wear properties of composites with different MoS\(_2\) contents were tested. The results showed that the crystallization and thermal stability of nylon matrix were increased with the addition of MoS\(_2\), while the tensile strength and impact strength were slightly reduced. The composites finally presented excellent friction properties with 3 wt\% MoS\(_2\), whose friction coefficient was reduced to 0.75 (18.48\% decrease) corresponding to the wear rate of 0.4145 \(\times 10^{-8}\) g N m\(^{-1}\).

1. Introduction

Monomer cast nylon (MCPA6) is a kind of high-performance engineering plastic, which is prepared by casting molten \(\varepsilon\)-caprolactam directly into a preheated mold under normal pressure under proper temperature and pressure by \textit{in situ} anion method [1–3]. Compared with traditional nylon materials, MCPA6 has the advantages of high molecular weight, high crystallinity, high mechanical strength, and good molding properties [4–6]. Considering its excellent comprehensive performance, MCPA6 is used in almost all industrial applications to produce sliding blocks, bearings and gears, which can achieve light weight and wear resistance [7–10].

However, the traditional MCPA6 still has some disadvantages in the use environment, such as low impact resistance, poor low temperature toughness and moisture absorption. Therefor, its wear resistance need to be improved in order to meet increasingly stringent performance standards in high-end applications [9–11]. Filling modification [12–14] and copolymerization modification [15–17] have been studied extensively to improve the performance of MCPA. Song L et al [18] copolymerized polydimethylsiloxane (PDMS) segment with nylon molecular chain and found that PDMS could effectively improve impact toughness of MC nylon matrix and reduce water absorption and wear rate of matrix. Similar conclusions were also mentioned in the study of Ying J et al [19].

The results also show that the friction coefficient of PDMS/MC nylon copolymer is high, and the friction property needs to be further improved. The friction properties of the material can be rapidly improved by adding solid lubrication filler, such as adding graphite, lubricating oil, carbon black, fiber and other commonly used fillers [20–23], which greatly expands the application range of MC-PA6. MoS\(_2\) is a kind of solid lubrication material with excellent performance, which can be used in the mechanical working state of high pressure, high temperature, high load and high speed to extend the service life of the equipment. The application of MoS\(_2\) to the polymer as a wear-resisting agent can effectively reduce the friction coefficient and wear rate of the system [24].

Therefore, in order to obtain MC nylon composites with comprehensive properties, especially better friction properties, MoS\(_2\) modified PDMS/MC nylon composites were prepared in this study. The properties of the

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composites were comprehensively analyzed by DSC, TGA, impact test, friction and wear test. The properties of MC nylon composites are much better than previously reported [25, 26].

2. Experimental

2.1. Materials

Caprolactam (CL) was obtained from The Sinopec Group, China. Sodium hydroxide (NaOH) and Hexamethylene diisocyanate (HDI) with analytical purity were used as catalyst and activator. Polydimethylsiloxane (PDMS) was supplied by Guangzhou silicon carbon new material Co. Ltd, China. MoS2 (average particle size 5 μm) was purchased from Chang Yu Chemical Products Co., Ltd, China. APTES was purchased from Aladdin. Dispersant BYK-AT-U was supplied by BYK-Chemie GmbH.

2.2. Synthesis of H-PDMS [18].

The dehydrated dihydroxyl polydimethylsiloxane and HDI were added into a three-point flask equipped with an agitator at a molar ratio of 1:2. Then it was heated to 60 °C and reacted for 60 min to obtain PDMS macroactivator with isocyanate terminal (H-PDMS).

2.3. Synthesis of PDMS/MC PA6 modified by MoS2

The composites were fabricated by the 'double-kettle synthesis method', and the preparation process is shown in Scheme 1. 500 g caprolactam and 1.6 g NaOH were dehydrated by vacuum reflux at 120 °C for 30 min to obtain component A. 30 g H-PDMS activator and (0, 5, 10, 20 and 30 g) MoS2 modified by 2 wt% APTES and BYK-AT-U was added into 500 g caprolactam, dehydrated by vacuum reflux at 120 °C for 30 min obtained component B. Component A and Component B were quickly mixed and casted into a preheated mold at 160 °C for 30 min, then cooled and demoulded.

2.4. Characterization

2.4.1. DSC analysis

Differential scanning calorimeter (DSC) analysis were carried out with a JYH-86 thermal analysis instrument (Mettler, Switzerland).

The sample was first heated from room temperature to 250 °C at a heating rate of 10 °C min⁻¹ and held for 5 min to eliminate the thermal history. The cooling operation is then performed to collect the cooling curve. The second heating was carried out at the same heating rate to 250 °C, and the heating curve was collected. The Melting Temperature (TM), recrystallization temperature (TC) were obtained and The crystallinity (Xc) can be calculated.

\[ X_c = \left( \frac{\Delta H_m}{\Delta H_{m}^*} \times (1 - \varphi) \right) \times 100\% \]

Where \( \varphi (%) \) represents the mass fraction of the additive, \( \Delta H_m(J/g) \) represents the enthalpy of fusion of the composite, \( \Delta H_{m}^* (J/g) \) is the fusion enthalpy of 100% crystallization, which is 188 J/g for MCPA6 [27, 28].

Scheme 1. The process for preparing MCPA6 composites.
2.4.2. TGA analysis
The thermogravimetric curves of the composites were obtained by heating the samples from ambient temperature to 800 °C at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. Testing was performed under a Netzsch Thermogravimetric Analyzer (Germany).

2.4.3. Mechanical properties test
Tensile strength and elongation at break of the composites were measured by international standard ISO 527-2:2012. The tensile test was carried out on a WDW-100 universal electronic stretcher at a stretching speed of 50 mm min⁻¹ and the specimen was made into a type 1B specimen with a width of 10 mm and a thickness of 4 mm. Tensile strength is the average value of σ_m measured in the actual stretching process.

Notched impact strength was measured with XJJ-50 experimental machine (Chengde Dajia Instrument Co., Ltd, China) based on international standard ISO 179-1:2020. The specimen was made into a single-notched specimen, and the notch type is type A. The remaining width at notch tip is 8 mm, and the thickness is 4 mm.

2.4.4. SEM analysis
The cross section and friction surface morphology of the composites were characterized by Sigma 300 scanning electron microscope (Zeiss, Germany) at a scanning voltage of 20 kV.

2.4.5. Friction performance test
The Chinese standard-T 3960-2016 and the Chinese railway industry standard TB/T 3270-2011 are used to test the friction properties of the composite materials. The experimental loading force of GB/T3960-2016 test was 196 N, the rotational speed was 200 r min⁻¹, the sample size was 30 × 7 × 6 mm, and the test was carried out in the friction machine JYW-95MMS-2A(Jinan Yihua Tribology Testing Technology Co., Ltd, China). The TB/T 3270-2011 was tested by the JYW-MMW-1A microcomputer controlled universal friction and wear testing machine (Jinan Yihua Tribology Testing Technology Co., Ltd, China), the friction coefficient is obtained under the test conditions of pressure of 1 MPa and friction velocity of 0.04 m s⁻¹, and the wear rate is detected under the test conditions of pressure of 2 MPa and friction velocity of 0.2 m s⁻¹, the specimen size is φ10.1 mm × 20 mm. Figure 1 shows the contact schematic diagram of the friction pairs in two friction experiments.

3. Results and discussion

3.1. DSC Analysis of MoS₂ modified PDMS/MCPA6 composites
Figure 2 shows the DSC quadratic temperature rise curve and cooling curve of MoS₂ modified PDMS/MCPA6 composite material. T_m, T_c, and X_c are shown in table 1. MCPA6 has two crystal forms, α and γ, and its molecular chain has no symmetrical center. The α crystal is half bonded by hydrogen bonds in the direction of molecular chain, and all hydrogen bonds bond to form γ crystal [29]. At a higher cooling rate, MCPA6 will form a less stable γ crystal, while at a lower cooling rate (below 70 °C/s), there will be an α crystal [30, 31]. As can be seen from figure 2(a), with the increase of MoS₂ content, two melting peaks appear in the composite. The results show that
MoS₂ promotes the formation of γ crystal in nylon matrix, and the proportion of γ crystal increases with the increase of MoS₂.

Figure 2(b) found that the adding of MoS₂ can increase the crystallization temperature of the composites which is better specified in table 1. The Tc of the composite containing 3 wt% MoS₂ is as high as 189.3 °C, which is 13.1 °C higher than that of the polymer without MoS₂. It is shown that the wear-resistant agent MoS₂ plays a role in heterogeneous nucleation which makes the composite material of nylon molecules chain segment easier to nucleation. It can also be found in figure 1(b) that the crystallization peak of the MoS₂ filled PDMS/MCPA6 composites are narrower and sharper than that of the non-MoS₂ filled polymer, indicating that MoS₂ can also increase the density of crystal nucleus in the system and improve the crystallization rate of the composite. However, the crystallinity of the composites decreases, which means that the MoS₂ dispersed in the matrix hinders the movement of molecular chains.

### 3.2. Thermal Stability of MoS₂ modified PDMS/MCPA6 composites

Figure 3 shows the thermogravimetric curve of the composite. As can be seen from the figure, The thermal stability of the composites were improved with the addition of MoS₂ lubricant, and the temperature of 5% weight loss of the composite increased from 222 °C to 260 °C. MoS₂ layer has a barrier and adsorption effect on the decomposition of the material, which makes the thermal decomposition of the polymer chain delay. The residual amount of TG curve of MoS₂ modified PDMS/MCPA6 copolymer composites is higher than that of unmodified copolymer, which is mainly due to the residual amount of MoS₂ in the composites.

### 3.3. Mechanical properties of MoS₂ modified PDMS/MCPA6 composites

Figure 4 shows the tensile strength, elongation at break and room temperature notched impact strength of the MoS₂ modified PDMS/MC nylon composites with the various MoS₂ content. It can be seen that the modification of PDMS/MCPA6 copolymer with low amount of MoS₂ slightly reduces the tensile strength of the composites, but not much, and the tensile strength of the composite with MoS₂ remains at about 60 MPa. The reason for the decrease of the tensile strength of the material may be that the MoS₂ particles dispersed in the matrix material become the stress concentration point, which weakens the interaction between the polymer molecular chains. At the same time, the elongation at break of PDMS/MCPA6 composites decreased in different degrees with the addition of MoS₂. When the addition of MoS₂ was only 0.5 wt%, the elongation at break of the composite material decreased from 30% to 18.9% without the addition of MoS₂. The lowest elongation at break of the composites with 3 wt% MoS₂ content was 14.0%, which was only half of that of...
PDMS/MPA6 composite. This is because rigid MoS₂ particles dispersed in the matrix hinder the movement of molecular chains, which reduces the compliance of polymer molecular chains.

According to figure 4(b), When the MoS₂ content is 0.5 wt%, the gap impact strength of PDMS/MPA6 composites decreases from 12.1 KJ m⁻² to 9.57 KJ m⁻² at room temperature, while the impact strength of PDMS/MPA6 composites remained relatively stable with the increase of the addition amount. In addition, the impact strength of the composites is superior than pure MCPA6 (7.514 kJ m⁻²). This is mainly because the flexible polysiloxane segment is prone to internal rotation and energy absorption during polymer fracture [18, 19]. The phenomenon can be demonstrated by the scaly impact fracture surface of the PDMS/MPA6 composites in figure 5, which are formed by the termination of an expansion crack.

It can be observed from figure 6 that MoS₂ particles are embedded in the matrix in layers. The results showed that the MoS₂ particles had good compatibility with MCPA6 matrix, which was consistent with the correlation test of mechanics.

3.4. Friction performance of MoS₂ modified PDMS/MPA6 composites

Figure 7 shows the curves of sliding friction coefficient and wear rate of the PDMS/MPA6 composites modified by MoS₂ and figure 8 shows the microscopic morphology of the worn surface of the composites with different MoS₂ contents.

As can be seen from the figure 7 that the friction coefficient of the composite material gradually decreases with the increase of the amount of MoS₂. The optimum friction coefficient is 0.75 in 3 wt% MoS₂, which is 18.48% lower than that in the copolymer without MoS₂. This is mainly because the active element of MoS₂ has a
Figure 5. Cross-sectional scanning electron microscopy images of MoS$_2$ modified PDMS/MCPA6 composites (a), (b): 0 wt% MoS$_2$; (c), (d): 2 wt% MoS$_2$.

Figure 6. EDS scan of MoS$_2$ modified PDMS/MPA6 composites (a) Section morphology of composites (b) Cascading diagram of element distribution (c) Si distribution (d) S distribution (e) Mo distribution.
Figure 7. Friction coefficient and wear rate of MoS₂ modified PDMS/MCPA6 composites.

Figure 8. Worn surfaces scanning electron microscopy images of MoS₂ modified PDMS/MCPA6 composites. (a), (b) − 0%, (c) − 0.5%, (d) − 1%, (e) − 2%, (f) − 3%
strong adsorption on the bimetal atoms, the MoS$_2$ particles are easy to fall off and transfer to the metal surface to form a stable film layer, thus reducing the friction coefficient of PDMS/MPA6 composites.

When the content of MoS$_2$ is 0.5 wt%, the wear rate of the composites increases sharply to $0.92 \times 10^{-8}$ g N m$^{-1}$, which is 78.68% higher than that of the composite without MoS$_2$. As shown in figure 7(c), the surface of the composite appears bulge and cracks appear in the vertical sliding direction, the composite material has both adhesion wear and fatigue wear. This is because the content of MoS$_2$ in the composite material is too low to form an effective transfer film on the metal surface of the grinding body. The wear rate increases sharply due to the softening and fatigue of the polymer surface caused by friction heat generation.

With the increase of MoS$_2$ content, the wear rate of the composite decreases gradually. When the content of MoS$_2$ is 3 wt%, the wear rate is $0.4145 \times 10^{-8}$ g N m$^{-1}$, which is 60.48% lower than that of pure nylon $1.0489 \times 10^{-8}$ g N m$^{-1}$. It can be observed from SEM images that the wear surface of the composite is relatively smooth. At this time, a uniform and effective transfer film has been formed on the friction surface, which reduces the friction coefficient and wear rate of the composites.

In order to better analyze the friction and wear properties of MoS$_2$ modified PDMS/MC nylon composites at the application level, the friction and wear properties of the composites in this study were tested according to appendix B: Experimental method for coefficient of friction and wear rate of core disc materials in TB/T 3270-2011.

Figure 9 shows the friction coefficient curves of pure MPA6 and partial composite wear discs. The friction coefficient of the material in the last 60 min was recorded in the test. It can be found from the friction coefficient curves of the wear disc that the stability of friction coefficient of pure MCPA6 and PDMS/ MCPA6 composite (H-PDMS content is 3 wt%) is poor. In the friction process between MCPA6 and the metal duality, deformation and wear debris will occur in the initial stage. With the friction test, although the peeled off wear debris will produce a layer of transfer film, the adhesive wear between the polymer and the transfer film will still occur at this time, and the wear debris will continue to fall off, making the friction coefficient unstable. However, when the content of MoS$_2$ is 3 wt%, the friction coefficient of the composite is significantly reduced and the friction coefficient curve is stable, which further indicates that the composite forms a uniform transfer film on the metal surface during friction.

Table 2 lists the friction coefficients and volumetric wear rates of pure MC nylon and composites wear discs. Compared with the pure MC nylon, the friction coefficient of PDMS/MC nylon composites modified by MoS$_2$ decreased by 30.71% from 0.2312 to 0.1602, and the wear rate decreased by 25.29% from $1.7 \times 10^{-8}$ cm$^3$ N m$^{-1}$ to $1.27 \times 10^{-8}$ cm$^3$ N m$^{-1}$. However, the wear rate of PDMS/MC nylon composites modified by MoS$_2$ is slightly higher than that of PDMS/MC nylon copolymer, which may be due to the weakening of the bonding strength between MoS$_2$ and the matrix material under repeated friction, which is easy to fall off and increase the wear rate. The performance indexes of friction coefficient and wear rate of the abrasive disc by the Ministry of Railways of China are $0.16 \sim 0.26$, $\leq 4 \times 10^{-8}$ cm$^3$ N m$^{-1}$, respectively. The friction and wear properties of the composites prepared in this study can meet the requirements, and the friction coefficient tends to be lower.
4. Conclusion

MoS₂ modified polydimethylsiloxane/monomer casting nylon composites were fabricated by in situ anionic polymerization with PDMS and HDI as activator, MoS₂ as wear resistant agent. The crystallization properties and thermal properties of the composites were researched by DSC and TG, and the mechanical properties and friction properties of the composites were studied. Test results showed that the impact strength and friction properties of MC nylon modified by MoS₂ and PDMS are improved. The friction coefficient of 3 wt% MoS₂ modified PDMS/MC nylon decreases to 0.75 (18.48% decrease), and the wear rate is $0.4145 \times 10^{-8}$ cm$^3$ Nm$^{-1}$ (1.0489 $\times 10^{-8}$ g Nm$^{-1}$) of Pure MC nylon). The friction performance test indicates that the composite material has better friction coefficient and wear rate. This study proved it was an efficient and facile way to produce high performance MC nylon materials by composite modification of fillers and copolymerization, which could enhance wear resistance and impact toughness and even more properties.

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Data availability statement

No new data were created or analysed in this study.

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