MoS$_2$ Additives for Enhancing Tribological Performance of Hydroxypropyl Methylcellulose Biopolymer

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ABSTRACT

This study demonstrates the influence of MoS$_2$ additives on the tribological performance of Hydroxypropyl methylcellulose composite films. Biopolymers have numerous potential applications, as they can be relatively quick and easily prepared and possess characteristics that are easy to optimize. The tribological characteristics of composite films can be enhanced by controlling the thickness of the film and by adding MoS$_2$ particles. An appropriate film thickness can optimize the tribological characteristics and service life of the film. MoS$_2$ nanoparticle additives can alter the surface morphology of a film, thus, affecting its tribological behavior. The addition of an appropriate quantity of MoS$_2$ can alter the surface roughness and load-carrying capacity of the film. The mechanism by which MoS$_2$ enhances the tribological characteristics of a composite film is dependent on the uniform dispersion of MoS$_2$ particles within the film and the optimization of the surface roughness of the film.

KEYWORDS

Biopolymer; HPMC; MoS$_2$; additive; tribology; lubricant

1. Introduction

Films have been widely used in a variety of applications for many years, with common applications as optical films (antireflective, UV absorption), self-cleaning films, anti-corrosion films, antimicrobial films, electrical films, magnetic films, etc. Films as protective coatings have also begun garnering a significant amount of attention; this type of application includes functional films such as paints, waterproof coatings, anti-wear coatings, and friction-reduction coatings.

The materials used to fabricate protective coatings are generally metals and non-metallic materials. Among these, the commonly utilized metals include zinc, aluminum, and chromium, and the commonly utilized non-metallic materials include ceramics and polymers. The ceramics used to fabricate protective coatings are typically carbon nitride [1], titanium nitride [2], and zirconia nitride [3]; additionally, diamond-like carbon [4] is commonly used in the fabrication of protective coatings. The advent of graphene, which is currently the material of choice for
many researchers in related fields, has broadened the applicability of protective coatings in various fields, e.g. the diffusion layer in IC fabrication [5] and protective coatings for flexible substrates [6]. Polymers that are typically used as protective coatings include epoxy [7,8] and poly (tetrafluoroethylene) (PTFE) [9,10]; these are protective coating materials that also yield excellent tribological performance. In recent years, because of the increasing emphasis on sustainable earth management, biopolymers in compliance with the ‘earth friendly’ concept are being widely investigated for possible applications. Hydroxypropyl methylcellulose (HPMC) is one of these widely investigated materials. HPMC is a biodegradable cellulose material that is derived from trees and is both environmentally and biologically friendly [11]; moreover, it is commonly utilized in drug delivery [12] and the food industry [13]. HPMC can obstruct gas diffusion and the passage of light and also possesses excellent tribological characteristics. Furthermore, HPMC solidifies very quickly; this facilitates the homogeneous dispersion of nanoparticles, thus, resolving problems related to the aggregation of nanoparticles [14,15]. In addition, HPMC is easily detected and measured [16,17], and has self-healing properties [18]; therefore, HPMC is a functional film material with broad applicative prospects [19,20].

Regarding the processes involved in coating application, metal or ceramic coatings require vacuum processing, high temperatures, and, occasionally, high-pressure processes such as dipping, spraying, and spinning may be expected to further decrease process costs. This experimental study evaluates the possibility of replacing conventional tribological coatings that implement biopolymers, and aims to develop high-performance protective films with anti-abrasion and lubricating properties that can be easily and rapidly produced in mass quantities, thus, achieving the objectives of sustainable manufacturing.

2. Experimental Methods

2.1. Preparation of MoS₂/HPMC Composite Films and the Control of Film Thickness

The MoS₂/HPMC composite film was produced by adding 5 g of HPMC (Pharmacoat 606-2910, Shin-etsu, Tokyo, Japan) to 30 mL water and 130 mL of ethanol. The resulting mixture was then heated to 60 °C. Solutions containing 2, 4, 6.75, 10.1, and 13.5 g of MoS₂ (Sigma Aldrich Chemistry, product no: 234842, Saint Louis, MO 63103, USA) were prepared. Each solution was ultrasonicated for 20 min. A micropipette was used to extract 100, 150, and 200 μL of each solution; each extracted solution was then added onto a silicon substrate. Films were formed after the solutions were left to stand for 1 h at 25 ± 2 °C and 60 ± 5% RH.

2.2. Film Analysis

The surface morphology of the films was determined using a scanning electron microscope (SEM, JEOL, JSM-6700F, Peabody, MA, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS).

2.3. Tribological Performance Analysis of MoS₂/HPMC

A pin-on-disk tribometer, which is normally used to model the wear and lubricant behavior of experimental components, implements a linear relative velocity. In this study, the pin-on-disk system (Fu-Li Feng precision machine, Kaohsiung, Taiwan) was used to investigate the tribological performance of films. The experimental parameters were as follows: the radius of gyration was 2 mm, the sliding velocity was 0.02 m/s, and a DIN 17350 chrome steel ball was used as the grinding ball. Because HPMC has high levels of hydrophilicity and internal cohesion, transfer layers are easily formed during abrasion [21]. The experimental load was set to 2 N to facilitate the observation of transfer layer formation, and to reduce the possibility of separation between the film and substrate caused by excessive loading.

3. Results and Discussions

Figure 1(a) shows a high-resolution transmission electron microscope (HR-TEM) image of MoS₂; from this figure, it may be observed that these nanoparticles are formed by the stacking of sheets bound by van der Waals forces. This process facilitates sheet sliding and exfoliation during abrasion, which consequently causes these films to yield excellent tribological characteristics. Figure 1(b) shows a highly magnified TEM image from which the lattice values between atoms can be calculated. Figure 1(c) is a selected-area electron diffraction (SAED) image that confirms the material properties of the MoS₂ nanoparticles. An electron-dispersive spectrometer spectroscope (EDS) was then used to analyze the nanoparticles in greater detail (Figure 1(d)). Based on these results, it is shown that the additive material is MoS₂. Tevet et al. [22,23] demonstrated that the tribological behaviors of fullerene-like (IF)-MoS₂ particles mainly include rolling, sliding, exfoliation, and damage. Because sheet-like MoS₂ particles were used
in this experiment, a plurality of tribological mechanisms such as sliding and exfoliation were anticipated; this was expected to effectively improve the tribological performance of the films.

The thickness of the resulting composite film material was controlled via a micropipette using it to extract mixed solutions in different quantities (100, 150, 200 μl). Figure 2(a–c) show 3 wt.% MoS₂ additive composite films with thicknesses of 30, 50, and 70 μm, respectively.

Shi noted that MoS₂/HPMC composite films deformed under loading, as these films are soft coatings; during abrasion, the films may generate transfer layers or become removed from the actual area of contact [14]. The plowing effect is negligible when the thickness of the film is inadequate. In these cases, the shear strength of the film will determine the coefficient of friction [24]. During abrasion testing, the generated wear will scrape the silicon substrate, thereby removing the film. Most of the debris produced during abrasion is removed from the path of wear, allowing only small amounts of debris to be transferred to the grinding ball. Films with moderate thickness provide better lubrication, as these films have low shear strength and an appropriate elastic modulus and contact area. An excessively thick soft film results in an insufficient load-carrying capacity, which leads to severe plowing effects. This weakens the load capacity of film surfaces, causes severe elastic or plastic deformation, increases the actual contact area between a grinding member and the film; this causes the average friction coefficient to increase [25]. Figure 3 shows that an inadequate thickness causes premature wear on the substrate, which leads to high average friction coefficients. Therefore, the control of film thickness is extremely important when considering practical applications. It was found that a thickness of 50 μm resulted in optimal lubrication under the abrasive conditions of this study.

Figure 4(a–f) show cross-sectional SEM images of films composed of pure HPMC, and HPMC comprising 1.5, 3, 5, 7.5, and 10% of the MoS₂ additive. The thickness of each of these films was set as 50 μm to determine the effects of MoS₂ additive quantity on the tribological performance of composite films. Dispersion analysis of MoS₂ particles by SEM and EDS mapping is shown in Figure 5, whereas

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**Figure 1.** TEM analysis of MoS₂ nanoparticles. (a) HR-TEM image, (b) highly magnified HR-TEM image, (c) SAED pattern, and (d) EDS analysis.

**Figure 2.** MoS₂ (3 wt.%)/HPMC composite films with thicknesses of (a) 30 μm, (b) 50 μm, and (c) 70 μm.

**Figure 3.** Tribological performance; relationship between the coefficient of friction and wear cycles for MoS₂ (3 wt.%)/HPMC composite film with various thicknesses.
According to the tribological behaviors shown in Figure 6(a–b), the tribological performance and anti-wear behavior of the composite films are superior to that of pure HPMC when a suitable quantity of additive is present (i.e. 5 and 10%). In this study, the MoS₂ particles were approximately 500 nm in diameter; this results in the formation of an optimal film when the surface roughness is approximately 2000 nm [16]. Optimized lubrication of the film was realized during applied abrasion with the chrome steel ball (Ra = 300 nm); this result is consistent with the findings of previous studies. When an inadequate quantity of additive is present, the MoS₂ particles are unable.
to fully envelop the abrasion surface; this results in an inadequate load capacity of the composite film. The film will then deform, thus, increasing the actual contact area. This leads to an excessive amount of film being removed from the area of contact, which then results in premature degradation of the tribological effectiveness of the film.

4. Conclusion

The current study aimed to investigate the impact of the film thickness and quantity of MoS₂ additive used on the tribological performance of HPMC biopolymer films. The results of this study demonstrate the importance of selecting the film thickness and additive proportions according to the specific requirements of an application. Furthermore, the quantity of the additive is an important parameter, as an appropriate quantity of additive is necessary to promote the development of a film with adequate load capacity and facilitate the formation of transfer layers. The conclusions that may be drawn from this study are as follows:

1. The appropriate selection of film thicknesses is very important for material systems using soft coatings such as HPMC.
2. The addition of MoS₂ particles effectively enhances the tribological performance of HPMC biopolymer films.
3. The quantity of additive directly affects the surface roughness of a composite film, thereby consequently affecting the tribological characteristics of the coating.

Disclosure statement

No potential conflict of interest was reported by the authors.

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