Transfer layer formation in MoS$_2$/hydroxypropyl methylcellulose composite

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ABSTRACT

Understanding the mechanism of transfer layer formation in tribological systems is important as it greatly influences the wear behavior of polymer based composites. The proposed study analyzes the formation of transfer layers on the counter body surface of a tribological system containing an MoS$_2$/biopolymer (hydroxypropyl methylcellulose) composite thin film with the aim of improving the coverage and, hence, the lubrication effect of the layers. The role of the thin film is also investigated from the aspect of the third-body approach. The formation mechanism of the transfer layer is studied by adding different amounts of MoS$_2$. Field emission scanning electron microscopy with energy dispersive spectrometry has been used for the surface structural and elemental analyses of the transfer layer. Raman spectroscopy is used to analyze structures of the thin film as well as the transfer layer. An appropriate amount of MoS$_2$, as an additive, was found to improve the ability of the third body to remain in the internal zone of the contact area between friction pairs rather than accumulating in adjacent zones. Addition of MoS$_2$ was, thus, found to enhance the formation and development of transfer layers thereby strengthening their anti-wear and lubrication properties.

1. Introduction

Occurrence of relative motion between two contacting surfaces made of different materials can cause materials with low cohesive forces to rupture and adhere to the surface of materials having high cohesive forces. This phenomenon is known as material transfer and is especially true if the cohesive force of one of the materials is less than the adhesive force between the contacting interfaces [1]. Since a polymer is characterized by weak cohesive forces, metal–polymer or polymer–polymer contacts typically cause a large amount of wear debris on the surface of the material having high cohesive forces. In some cases, the surface area covered by the wear debris appears as a protective layer. This layer is termed as the transfer film/layer [2].

The transfer layer produced by metal–polymer contact wear can be roughly categorized into two types based on the thickness of the layer [2]. The first type is typical of materials such as low-density polyethylene, polypropylene, and nylon 66, wherein the transfer layer thickness ranges between 0.1 and 1 μm. In the tribological system of these materials, selection of appropriate additives could enhance the adhesion of the transfer layer to the counter body. This would, in turn, enable the thickness of the transfer layer to increase steadily thereby enhancing the wear resistance of the base material [2]. The second type of transfer layer has a thickness less than 0.1 μm. This type is typically found in such materials, as high-density polyethylene (HDPE), polyoxymethylene, and polytetrafluoroethylene (PTFE). Formation of

composite materials by addition of α-Al$_2$O$_3$ nanoparticles to PTFE can reduce its wear rate by approximately 1000 times [3]. Consequently, many researchers have studied the wear mechanism of this ultra-low wear PTFE composites. Although various researchers have proposed different mechanisms, most agree that attainment of a remarkably low wear rate of a system is associated with how well the transfer layer attaches to and covers the metal counter body [4–6].

The transfer layer greatly influences the tribology behavior. Therefore, its formation mechanism is a very important and valuable research direction. This, at present, is mainly considered to be either an adhesion mechanism or a mechanical interlocking mechanism. Adhesion mechanism refers to transfer layer formation as a result of the surface energy difference between friction pairs or the tribo-chemical reaction of wear debris during the wear process, which leads to the formation of physical or chemical bonding with the counter body material and consequent adhesion of the transfer layer to the surface of the counter body [2,7–9]. In the mechanical interlocking mechanism, transfer layer formations is caused by interlocking of wear debris in the valleys between asperities on the surface of the counter body. Consequently, the geometrical shape and size of wear debris and the surface roughness of the counter body are important factors affecting the formation and development of transfer layers [10,11]. Although there are several different viewpoints with regard to the formation of transfer layers, the material properties of each tribological system, friction environment, and scales are all different.

In the early studies performed on transfer layers, lack of quantitative indicators only made it possible to perform qualitative analyses. Adjectives, such as 'thick,' 'thin,' 'densely compact,' and 'loose' were used to describe the state of the transfer layer. Furthermore, because it was not possible to observe the transfer layer in situ during wear experiments, neither the formation mechanism of the transfer layer nor its effects on the tribological properties of the system could be accurately determined. As a result, the transfer layer remained poorly understood [6]. Several important research groups made various attempts to address this situation. The Berthier research group established a tribological test device that could be used to directly observe and analyze the wear process. Godet's third body theory not only made possible the state of the system at different stages throughout the wear process to be described, it also emphasized the important concept that the formation and development of the transfer layer is a dynamic process [12,13]. Burris et al. established a free space length model for quantitative analysis of the transfer layer, the coverage of which was correlated to the wear rate. Based on the analysis of the surface morphology post wear, the system wear rate at different stages could be predicted [6,14]. The Friedrich group used the nano-indentation test machine to measure the average thickness of the transfer layer. By dividing the layer according to the surface roughness of the base body, a transfer film efficiency factor was defined. The relationship between the transfer film efficiency factor, coefficient of friction (COF), and the wear rate is similar to the Stribeck curve of a wet friction system. This relationship can be used to analyze system wear mechanisms at different stages and also as a reference for the design of similar tribological systems [15].

Formation and development of the transfer layer not only affects the friction but also changes the wear mechanism of tribological systems [16]. In a tribological system wherein solid lubricating strengthening particles, such as molybdenum disulfide, graphene, or polytetrafluoroethylene have been added, the self-lubrication effect of these solid lubricants after the formation of the transfer layer is one of the primary mechanisms causing significant reduction in frictional resistance and wear [1,17,18].

Hydroxypropyl methylcellulose (HPMC) is a biopolymer with good biocompatibility and mechanical properties [19,20]. In our previous research, this material has been characterized as being, both, easy to detect and observe [21,22]. As such, it is regarded as being of high value, especially as part of sustainable manufacturing [23] in future biopolymer electronic device and material packaging applications in the low loading environment. HPMC protective coatings have scalable tribological properties, they are also characterized by recyclability and reusability that meet the requirements of sustainable manufacturing. This result is shown in Fig. S1. After experiencing a complete wear process, the added MoS_2 particles can be recycled and reused after the HPMC is dissolved in a specific solvent. This further demonstrates the advantages of the sustainable manufacturing of this cellulosic material system. In addition, in the chrome ball and MoS_2/HPMC tribosystem, it is relatively easy to observe transfer layer formation in the small loading and short wear distance condition. Therefore, this tribosystem is a good model to investigate the wear mechanism of HPMC. In previous studies, it has been found that MoS_2 additives have a synergistic effect with HPMC for tribological purposes [18]. The mechanism of the transfer layer formation and its effect on the tribological behavior have been studied and discussed by varying the amount of MoS_2 particles that were added.

2. Materials and methods

2.1. Preparation of biopolymer composite coating

A solvent mixture was prepared by heating 40 g of water and 150 g of ethanol to 60 °C. Ten grams of HPMC was then slowly poured into this solution, and the resulting mixture was stirred until HPMC was fully dissolved to form a uniform solution. Different amounts of MoS_2

(0.135–27 g) were subsequently added to an appropriate weight of the HPMC solution to form a mixed solution of MoS_2/HPMC of different proportions (0.1–20 wt%). After ultra-sonication of the mixed solution for 20 min, a micropipette was used to draw 150 μL of the mixed solution for transfer onto a silicon substrate. The test sample was placed in a controlled environment chamber at 25 °C ± 2 °C and relative humidity of 60 ± 5% for 1 h to form a composite coating. Thickness of all coatings was controlled at 50 ± 5 μm (observed by cross-sectional SEM image).

2.2. Thin film characterization

Field emission scanning electron microscopy (FESEM, ZEISS AURIGA) equipped with energy dispersive spectrometry (EDS) was used for surface structural and elemental analysis of the transfer layer. A micro-Raman system (BWII-RAMaker, Andor, 532 nm laser) was used for thin film structural and transfer layer analyses.

2.3. Tribology performance

Hard tool grade (AISI 52100) chrome steel balls (diameter 2.38 mm) with an average roughness of 20 nm (Ra) were used as counter bodies. Wear tests were conducted on the rotary ball-on-disk tribometer (POD-FM406-10NT, Fu Li Fong Precision Machine, Kaohsiung, Taiwan) as shown in Fig. S2. The tribometer was nominally identical to ones reported in previous studies [24,25]. During the test, under an applied normal force of 2 N, a sliding distance (one cycle) equal to 6.28 mm and sliding speed of 10 mm/s were measured under dry sliding conditions. The tribotest machine was equipped in a separate room with a controlled environment, at 25 °C ± 5 °C and relative humidity of 70 ± 10%. The applied normal force facilitate observation of the transfer layer by reducing the possibility of separation between the film and substrate due to excessive loading. All samples were tested three times to verify the laboratory results. The wear scar measurements were then used to quantify the wear volume by a 3D laser scanner (VK9700, Keyence, Osaka, Japan). The wear scar profile and wear volume measurement were shown in Fig. S3.

3. Results and discussion

3.1. Composite film characterization

Fig. 1 shows SEM images after addition of different amounts of MoS_2. The images illustrate that the microstructures of MoS_2 are stacked and scattered evenly on the test piece. When the amount of MoS_2 added exceeds 10%, the surface is covered by exposed MoS_2 particles that are not embedded in the HPMC matrix. This is due to the fact that when the amount of MoS_2 added is high (> 10%), the proportion of HPMC in the solution is insufficient to cover all MoS_2 particles, in which case, it behaves similar to 'glue' and adheres to the MoS_2 particles.

According to Tevet's research [26], well-structured MoS_2 particles account for a variety of lubricating mechanisms and properties during wear. Fig. 2 depicts Raman spectra of the composite with the addition of 0–20% MoS_2, wherein bands at 383 cm^{-1} and 408 cm^{-1} correspond to characteristic E_{2g}^1 and A_{1g} bands of MoS_2, respectively [27]. This shows that MoS_2 particles maintain good crystallinity and structural integrity after forming the composite film with HPMC and are expected to provide lubrication effects during wear.

3.2. Tribological performance

Figs. 3a and 3b illustrate the relationship between wear distance and the coefficient of friction. Fig. 3a provides a comparison of MoS_2 additions ranging from 0% to 3%, whereas Fig. 3b compares the addition of larger amounts in the range of 5–20%. At low levels of