Surface & Coatings Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Effects of temperature and humidity on self-healing behaviour of biopolymer hydroxylpropyl methylcellulose for ecotribology

Shih-Chen Shi*, Teng-Feng Huang

Department of Mechanical Engineering, National Cheng Kung University, (NCKU), No.1 University Road, Tainan 70101, Taiwan

ARTICLE INFO

Keywords:
HPMC
Self-healing
Biopolymer
Tribology
Wear

ABSTRACT

The self-healing properties of biological hydroxypropyl methylcellulose (HPMC) high-molecular weight thin films were investigated. The effects of environmental factors (e.g., temperature and humidity) on the self-healing capabilities of HPMC were also experimentally evaluated. Tribological tests were performed to observe the change in the HPMC healing rates under different levels of temperature and humidity. The changes in weight observed in the HPMC samples indicated that environmental moisture condensed on the surface of the samples and caused HPMC solvation, which led to the healing of wear marks. Using full-factorial tests, we determined that the HPMC achieved a maximum healing rate of 70% after being treated for 16 h at 90 °C and a relative humidity of 90%. It was found that the tribological characteristics were similar before and after the healing process, with the application of the appropriate healing parameters.

1. Introduction

In recent years, the energy crisis and the rise in green awareness have led to the emergence of studies that address the need for eco-friendly, renewable, and reusable materials, as well as manufacturing processes. Among these, green lubricants have become a focal point for recent tribological studies [1,2]. In addition to green materials that enable reductions in energy consumption and wear while being non-toxic to the environment and the human body [3–6], researchers have focused on reusable materials with self-healing capabilities [7,8]. The advent of thin films whose tribological characteristics can be restored close to their original state via healing after the films suffer wear damage (instead of being washed off and recoated) would significantly reduce material usage and its associated pollution of the environment and simultaneously attain the goals of sustainable manufacturing and green lubrication. In this study, we investigated hydroxylpropyl methylcellulose (HPMC), which is a biological high-molecular weight material that is commonly used in industry and pharmaceuticals. HPMC is eco-friendly and does not pose a risk to human health, while possessing excellent film-forming properties [9]. HPMC has excellent tribological properties, as it effectively decreases the friction coefficient and creates a transfer layer during the occurrence of friction, which protects the substrate and reduces friction-induced damage. As the transfer layer is easily stripped and removed from the contact area, the thickness of the film is directly correlated with its tribological characteristics [10,11]. Therefore, if healing can be immediately performed after wear has occurred to restore the thickness of the film in regions where wear marks have emerged, the operational lifespan of the lubricating thin film may be extended.

Nowadays, to extend the operational lifespan of functional thin films, researchers have focused on self-healing thin films, using external forces or the external environment to drive self-healing mechanisms in thin films so as to partially restore the mechanical, material, or functional properties of the thin films after they suffer damage. This concept accords with the aim of green lubricants, as it enables the functionality of thin-film materials to be maintained, reduces resource usage, and facilitates the reuse and ultimate recycling of materials. Self-healing mechanisms and methods can be categorized into a few known techniques:

(1) Self-assembled materials [12–15], in which the self-assembly mechanism may be reactivated after damage has occurred, so that self-assembly restores the damaged surface or thin film to its initial state. The self-assembly of the material and its binding to some specified material may be driven by the external environment or the supply of energy, so that the materials are bound and organized by covalent bonds and Van der Waals forces, to strengthen the interfacial binding between materials through such interactions.
(2) Self-repair [16–20], which is typically used in high-molecular weight polymers, in which the materials are assembled by non-covalent interactions such as hydrogen bonds and metal-ligand interactions. Through the polymerization reaction or post-

* Corresponding author.
E-mail address: scshi@mail.ncku.edu.tw (S.-C. Shi).

https://doi.org/10.1016/j.surfcoat.2018.03.039
Received 10 November 2017; Received in revised form 20 February 2018; Accepted 14 March 2018

polymerization treatments, the damage caused by environmental factors or friction-generated heat induces the degradation and separation of the polymers in these materials. Self-repair is then achieved through reversible reactions that re-form the original polymers through re-polymerization.

(3) Self-recovery [21–25], which is a trait possessed by composite materials that can recover surface damage.

(4) Self-healing [26–28], in which specified external conditions trigger reversible reactions or fluidity that restores the material after it has suffered damage.

Thin films can be made to be reusable through self-healing, whereby the thin-film surface is healed after damage has occurred, extending their operational lifespan. HPMC has solubility and reversibility in certain solvents; therefore, under the appropriate conditions, the solubility and fluidity of HPMC may be utilized to create a self-healing effect. In such an experiment, the effects of environmental factors such as the temperature and humidity on wear-mark healings in HPMC were observed, to obtain the optimal self-healing parameters and to facilitate discussions on the mechanism of healing. The ultimate objective of this study was to achieve the reuse and reduction of lubricants, so as to realize the goals of green lubrication and sustainable manufacturing.

2. Materials and methods

2.1. Procedure for producing thin film

A mixture containing 100 mL of ethanol and 30 mL of water was heated to 60 °C, to which 3.5 g of HPMC (Shin-Etsu, Pharmacoat 606: 2910, Tokyo, Japan) powder (specifications shown in Table 1) was added. The resultant mixture was stirred until the powder was fully dissolved. Then, 150 μL of this mixture was micro-pipetted onto a substrate and cooled for 1 h, forming a thin film.

2.2. Surface morphology

The worn surface of a Si and Cr steel ball was analyzed using a scanning electron microscope (JEOL, JSM-6700F, MA, USA).

2.3. Tribo-test experiment

This experiment used a pin-on-disk rotary tribo-test machine (Fu-li Feng precision machine, Kaohsiung, Taiwan). The tested material was placed on a rotating plate, where an upper test specimen (AISI 52100 chrome steel ball) contacted the horizontally placed test disc (the tested material) at a perpendicular angle. The HPMC sample was thus tested using a fixed rotational diameter, under a constant level of pressure. The abrasive ball was an AISI 52100 chrome steel ball whose chemical composition is shown in Table 2. The parameters used in the tribo-test are shown in Table 3.

2.4. Experiments on effects of temperature and humidity on self-healing

At this stage, HPMC thin films that underwent tribo-testing in the previous stage were placed in an environmental chamber (Dengyng, DE-60, New Taipei City, Taiwan) and subjected to various temperature and humidity conditions for 10 min (with the temperature and humidity kept constant in this time period). The single-factor (temperature or humidity) effects on the thin films were observed, followed by the next stage of wear-mark healings and tribo-tests. Finally, the optimal combination of conditions was determined using a full-factorial test.

Table 1
Specifications of the HPMC powder.

Grade	Mw	Mw/Mn	Viscosity
PHARMACOAT 606	35,600	1.62	4.8–7.2 mPa·s

Table 2
AISI 52100 chemical composition of AISI 52100 chrome steel ball.

	Composition (wt%)								
	C	Si	Mn	P	S	Cu	Ni	Cr	Fe
AISI 52100	1.03	0.22	0.31	0.01	0.01	0.06	0.07	1.39	Bal.

Table 3
Tribo-test parameters.

Pin-on-disk parameters	
Load (g)	200
Track diameter (mm)	2
Sliding speed (mm/s)	0.01
Rotation number (cycle)	2000

2.5. Wear-mark analysis

A circular wear scar appeared on the film after the tribo-tests, as shown in Fig. 1(a). The contours and depth of the wear marks on the HPMC were experimentally observed using a 3D Laser Scanning Microscope (Keyence VK9710, Osaka, Japan). The wear depth is illustrated in Fig. 1(b).

2.6. Surface characterization

The chemical bonding of the material surface was analyzed using Raman spectroscopy (Renishaw system 2000 micro-Raman spectrometer, New Mills, UK) and Fourier transform infrared (FTIR) spectroscopy (Themo NEXUS 470, New Mills, United Kingdom).

3. Results

3.1. Analysis of dependence of wear-mark healing on temperature

To investigate the differences caused by each of the parameters on the wear-mark healing, we modified the healing-efficiency [19] equation and redefined the healing efficiency as the “healing rate”:

$$\text{Healing rate}\ (\%) = 1 - \frac{\text{Wear depth after healing}}{\text{Initial wear depth}} \quad (1)$$

After tribo-testing was performed on the HPMC thin films, three-dimensional (3D) laser scanning microscopy was used to scan the morphology of the surface and measure the depth of the wear marks. The samples were then separately annealed at 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, and 180 °C at a relative humidity (RH) of 50% for 10 min, after which 3D laser scanning was used to scan the morphology of the surface and measure the depth and width of the wear marks again. If self-healing has occurred in the thin film, the post-restoration width and depth of the wear marks should have decreased compared with the pre-restoration state. A greater decrease in the wear depth indicates a greater healing rate; this may reach 100% if the wear marks have disappeared completely. Fig. 2 shows the wear-depth healing rates at different temperatures. It was observed that regarding the wear depth, the highest efficacy of restoration was obtained at temperatures close to 70–90 °C. The glass transition temperature of HPMC is exceeded at temperatures above 160 °C; at such temperatures, the thin film expands, causing the wear marks to deepen further, which gives rise to negative healing-rate values. This indicates that the temperature setting should not exceed the glass transition temperature of