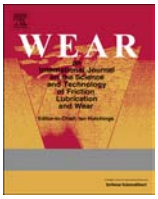
Wear 320 (2014) 87–93

Contents lists available at ScienceDirect

Wear

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



Analysis of the chemical composition of the PTFE transfer film produced by sliding against Q235 carbon steel

Zhen Zuo [a], Yulin Yang [a,b,*], Xiaowen Qi [a,b], Wenwen Su [a], Xiangchao Yang [a]

[a] *College of Mechanical Engineering, Yanshan University, Qinhuangdao 066004, China*

[b] *Aviation Key Laboratory of Science and Technology on Generic Technology of Self-Lubricating Spherical Plain Bearing, Yanshan University, Qinhuangdao 066004, China*

ARTICLE INFO

Article history:
Received 21 May 2014
Received in revised form
27 August 2014
Accepted 31 August 2014
Available online 7 September 2014

Keywords:
Polytetrafluoroethylene
Transfer film
Experimental measurement
Molecular dynamics
Density functional theory

ABSTRACT

Polytetrafluoroethylene (PTFE) transfer films formed on the surface of Q235 carbon steel were studied using scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), molecular dynamics (MD), and density functional theory (DFT) calculations. Changes in the chemical composition of the transfer film were analyzed using XPS measurements. Mechanisms of defluorination, chain scission, and formation of carbonyl and hydroxyl groups were elucidated using DFT transition state calculations. Of these four reactions, defluorination, which has an energy barrier of only 1.0 kcal/mol, is most likely to occur. The formation of a carbonyl group, with an energy barrier of 23.1 kcal/mol, can more easily take place than the chain scission, which has an energy barrier of 44.6 kcal/mol, and is a precursor to the simplest path to the formation of a hydroxyl group.

1. Introduction

Polytetrafluoroethylene (PTFE) has been widely used in the field of tribology, due to its excellent property of self-lubrication. When PTFE slides against metals, a portion of this polymer is transferred to the metal counterpart forming a PTFE transfer film [1,2]. It is well known that this PTFE transfer film plays a critical role in reducing the friction coefficient and wear rate of PTFE-based composites [3,4]. Friction investigations of the PTFE transfer film are helpful in illustrating the lubrication mechanism of polymer-based composites [5,6]. For this reason, much attention has been paid to the PTFE transfer film [7,8], and the influence of wear process parameters on the formation of the PTFE transfer film have been extensively investigated experimentally [9]. Metal-based counter surfaces with a high hardness are beneficial to the formation of the PTFE transfer film [10]. It has also been observed that the PTFE transfer film becomes smooth and continuous with increases in the normal load and friction velocity [11]. Due to the presence of this thin and uniform transfer film, the PTFE bulk is not abraded directly, thereby improving the tribological performance of the polymer [12–14]. On the other hand, a thick, discontinuous transfer film has adverse effects on wear resistance [15–17].

In general, the wear rate of PTFE increases with an increase in humidity [18], and the friction coefficient of PTFE in a normal air atmosphere is higher than in vacuum because of the presence of water vapor [19]. Compared with nitrogen and oxygen molecules, water molecules are more conducive to the generation of the PTFE transfer film [20,21]. Therefore, we mainly considered the impact of water in this investigation. Theoretical calculations are valuable in elucidating the formation mechanism of the PTFE transfer film. Density function theory (DFT) and molecular dynamics (MD) calculations were employed to analyze the effect of friction on PTFE [21–23], and the process of chain scission was confirmed to occur [22,23]. To date, numerous investigations of PTFE transfer films have been reported, but, to our knowledge, insufficient work, using experimental techniques or molecular simulations, has been performed to quantify the chemical changes that occur within the PTFE transfer film.

The goal of this study is to reveal the chemical changes that occur within a PTFE transfer film during a friction test. In this research, scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS) were employed to analyze the PTFE transfer film formed on Q235 carbon steel. Furthermore, MD simulations and DFT calculations were performed to reveal the chemical changes that occur within the PTFE transfer film. Calculations of transition states were carried out to determine the feasibility of the chemical reactions of defluorination, chain scission, and formation of carbonyl and hydroxyl groups.

---

[*] Corresponding author at: College of Mechanical Engineering, Yanshan University, Qinhuangdao 066004, China. Tel./fax: +86 3358057062.
E-mail address: ysu.y.yang@gmail.com (Y. Yang).

http://dx.doi.org/10.1016/j.wear.2014.08.019
0043-1648/

2. Materials and methods

2.1. Materials

PTFE powder (CGM031; 200 mesh; Zhonghao Chenguang Research Institute of Chemical Industry, Sichuan, China) was used as received to prepare the lower specimens for the friction tests. Q235 carbon steel was employed as the upper specimen due to its low price, which makes it of particular interest for large-scale application. The chemical composition (wt%) of the Q235 carbon steel received was C 0.17, Mn 0.53, Si 0.28, P 0.02, S 0.02, and Fe 98.98.

2.2. Preparation of PTFE specimens

PTFE powder was cold pressed at room temperature and 40 MPa for 10 min. The temperature was then increased to 375 °C at a heating rate of 1 °C/min, and the samples were sintered at this temperature for 90 min and allowed to naturally cool to room temperature.

2.3. Tribological test

A ring-on-disk friction and wear tester (MMU-5G, Sida Tester Co. Ltd., Jinan, China), with upper and lower specimens as shown in Fig. 1, was used to evaluate the friction performance of the PTFE samples. All friction tests were performed in a room at 80 ± 5% relative humidity, and the ambient room relative humidity was controlled by a humidifier (SC-MG25, Beiling Electric Co. Ltd., Shanghai, China). During the friction test, the normal load, sliding speed, and testing time were controlled at 2.85 MPa, 0.48 m/s, and 60 min, respectively. Prior to the friction test, the prepared PTFE specimens were polished with silicon carbide paper (grit #1000, Kailai Abrasive Technology Co. Ltd., Qingdao, China) for 2 min and then washed in water with sonication for 15 min, before being rinsed with deionized water and dried at 80 °C. Each test was performed three times under identical conditions to ensure the reproducibility of the experimental data.

2.4. Characterization

The morphology and chemical composition of the upper specimen (Q235 carbon steel) were examined using a scanning electron microscope (S-4800, Hitachi, Tokyo, Japan) equipped with a Horiba 7593-H energy dispersive spectrometer. The chemical composition of the carbon steel was further investigated using X-ray photoelectron spectroscopy (PHI1600, PerkinElmer, Waltham, USA). The XPS analysis was performed using a Mg Kα radiation source, and the effect of surface charges on the binding energy was calibrated by C 1s (284.6 eV).

2.5. Simulation details

MD simulations and DFT calculations of transition states were performed using three packages of Discover, Amorphous Cell and D mol^{3} in Materials Studio 4.1 (Accelrys Software Inc., San Diego, CA, USA) [24]. The initial structure of PTFE was built based on data derived from the Materials Studio database. The PTFE chain was relaxed by a 10,000-step minimization process using a conjugate gradient method based on the Polak–Ribiere algorithm. A simulation box containing an optimized PTFE chain was constructed using the Amorphous Cell module, with the target density of the final configuration set to 2.2 g/cc. The constructed structure was then optimized by a 10,000-step minimization process.

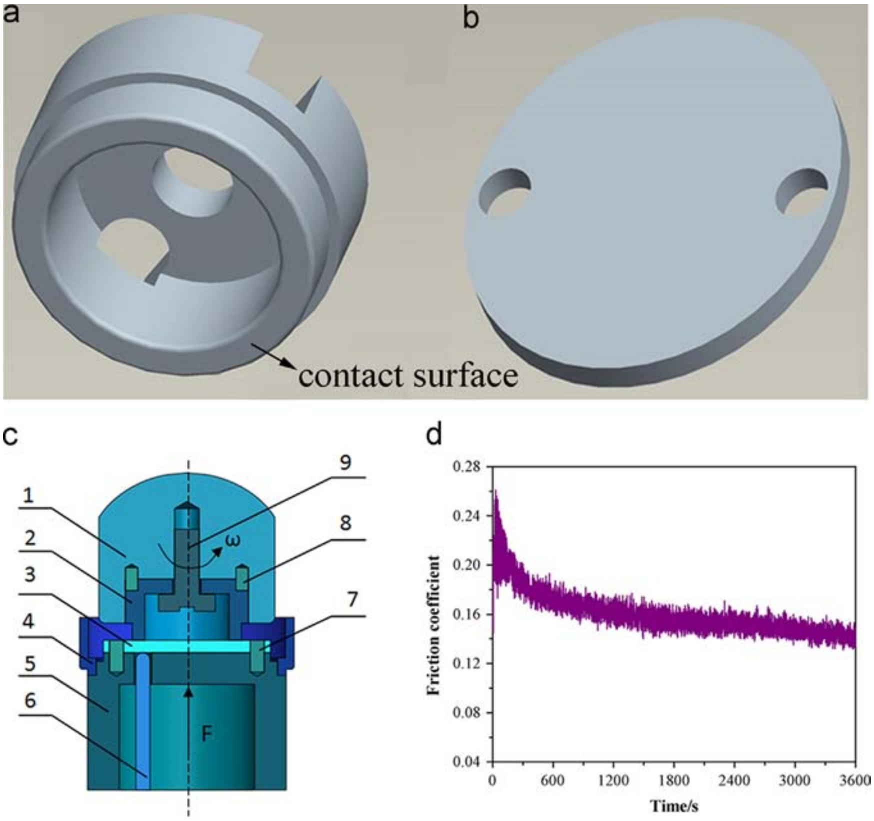


Fig. 1. Diagram of MMU-5G friction pairs: schematic of the (a) upper specimen, (b) lower specimen, (c) MMU-5G friction pairs (1 spindle; 2 upper specimen; 3 lower specimen; 4 abrasive dust container; 5 lower specimen base; 6 temperature thermocouple; 7 lower torque pin; 8 upper torque pin; and 9 fixing bolt), and (d) friction coefficient of the as-prepared PTFE specimen (load: 2.85 MPa, sliding speed: 0.48 m/s).