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Effect of surface reactions on steel, Al_2O_3 and Si_3N_4 counterparts on their tribological performance with polytetrafluoroethylene filled composites

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ABSTRACT

The influence of surface reactions on the tribo-performance of steel, Al_2O_3 and Si_3N_4 balls sliding against polytetrafluoroethylene/SiO_2/epoxy composites was investigated. Al_2O_3 ball were found to exhibit the best tribo-performance, namely a low coefficient of friction and the lowest wear rates of both the composites and the counterpart ball, when sliding against the PTFE filled composites. The difference in the tribo-performance of the Al_2O_3 ball and the Si_3N_4 ball can neither be attributed to the different morphology of the worn composite surfaces nor to the amount of PTFE transferred onto the wear surfaces. Instead we found that the friction is greatly reduced in the case of the Al_2O_3 ball because two fluoro-terminated surfaces are sliding over each other; in fact, the formation of *Al—F* bonding was confirmed by X-ray photoelectron spectroscopy.

1. Introduction

Polytetrafluoroethylene (PTFE) is commonly used as a solid lubricant in many composite materials that are used in dry sliding bearings. The tribo-performance of PTFE filled composites is closely related to the formation mechanism, thickness and stability of PTFE transfer films on the counterparts. It is generally accepted that a sliding motion between the transferred PTFE and the PTFE on the composite surface could greatly reduce the friction. In tribological sliding contact or metal depositions, chemical reactions at the metal (or oxide) and PTFE interfaces could lead to the formation of metal fluoride bonding [1–6]. In the tribo-tests, the metal fluoride bonding was found at the interface of the PTFE transfer films and metal (or oxide) surface [1,3]. However, there is hardly any discussion on the effect of the tribochemical reactions on the tribo-performance of the systems.

To study the role of both PTFE transfer films and the metal fluoride bonding, very thin and discontinuous transfer films are desired to reveal the effect of metal fluoride. In our previous study, PTFE/SiO_2/epoxy composites with a high concentration of SiO_2 particles turned out to be very hard and abrasive, which could facilitate formation of very thin and discontinuous PTFE transfer films [7]. Hence, the PTFE/SiO_2/epoxy composites are used in this work. Steel, Al_2O_3 and Si_3N_4 balls are chosen as the counterpart, which cover a wide range of material systems, i.e. from metal, oxide to nitride and also a large range of mechanical and physical properties [8]. When sliding against PTFE filled composites, these materials may exhibit different adhesion to the PTFE film, different wear resistance and different activation energies of tribochemical reactions. Therefore, the effect of both tribochemical reactions and transfer films may be revealed via studying the tribo-performance of these counterparts.

The influence of the surface free energy, hardness and hardness over Young's modulus (H/E) ratio of the balls, and metal fluoride chemical bonding on the tribo-performance will be analyzed and discussed. The aim of this study is to contribute to an in-depth

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understanding of the effect of both PTFE transfer films and metal fluoride bonding on the tribo-performance.

2. Experimental

2.1. PTFE/SiO_2/epoxy composite

The epoxy- and SiO_2-containing powder, *Epomet F*, was purchased from Buehler GmbH. This powder is mainly composed of about 31 ± 2 wt.% epoxy resin (CAS: 26265-08-7) and about 65 ± 2 wt.% SiO_2 particles (20–100 μm). It also contains 1–3 wt.% 2,4,6-tris(dimethylaminomethyl)phenol, 1–2 wt.% antimony oxide (Sb_2O_3) particles (for flame retardant property) and less than 1 wt.% carbon black (pigment). The PTFE powder, *Zonyl MP 1000* fluoroadditive, was purchased from DuPont. The two dry powders were mixed by rotational mixing for 3 min in a clean glass container. Thereafter, the glass container with the pre-mixed powders was vibrated in a shaker during 40 min. The powder mixture was then transferred to a mounting press (Buehler Metaserv Pneumet II) for curing. It was cured at about 160 °C for 20 min under 0.41 MPa pressure and cooled down with water afterwards. The disc samples were then ground and polished with silicon carbide abrasive papers up to 4000 grade. The surface of the polished composite was then rinsed with distilled water before tribo-tests.

The PTFE/SiO_2/epoxy composite is referred as 'Epomet-PTFE composite' and the composite samples are named as 'Epomet-PTFExx', where xx denotes the weight percentage of the PTFE. The measured average Vickers hardness of the cured pure Epomet sample is around 97 HV0.6, while the Epomet-PTFE7.5 and the Epomet-PTFE15 have hardness about 62 and 52 HV0.6, respectively.

2.2. Tribological tests

The friction and wear behavior of the composites were studied using a ball-on-disk tribometer under dry sliding conditions with ø13 mm 100Cr6 bearing steel, Al_2O_3 (purity >99%) and Si_3N_4 balls. For the details of the set-up, see [9]. The Si_3N_4 ball contains more than 95 wt.% Si and N, less than 5 wt.% Al, Ti and O, as measured by energy dispersive spectroscopy (EDS). The surface roughness (Ra) values of these balls are measured to be approximately 50 nm. The density of the steel, Al_2O_3 and Si_3N_4 balls are 7.8, 3.9 and 3.3 g/cm^3, respectively. During sliding tests the counterpart ball stays stationary. Unless otherwise stated, the normal load used was 60 N and the sliding velocity was 2 cm/s.

In order to study the role of fluoridation of Al_2O_3 and steel on their friction behavior, the Al_2O_3 ball and 100Cr6 steel disk (Ra ∼ 100 nm) were immersed into hydrofluoric acid (2%) for 16 h and 1 min, respectively, due to their different reaction rates. Then, they were rinsed with distilled water and acetone (3 times). Tribo-tests between the Al_2O_3 ball and the 100Cr6 steel disk were performed at 3 N load and 2 cm/s velocity with the same tribometer. Tribo-tests between an Epomet-PTFE5 and fluoridated or untreated Al_2O_3 balls (both 6 tests) were carried out at 60 N load and 2 cm/s velocity. All tests were performed at room temperature (22 ± 2 °C) and a relative humidity of 35 ± 2% maintained with a feedback controlled flux of dry air or water vapor into the protection box.

2.3. Surface free energy and hardness measurement

Using Dataphysics OCA-15 Goniometer, the static contact angles of the 100Cr6 steel, Al_2O_3 and Si_3N_4 balls were measured with three liquids: water, formamide and diiodomethane. Based on the measured static contact angles, their surface free energy (SFE) values were calculated according to Owens–Wendt approach [10], the numerical value of which is the same as surface free energy. The work of adhesion (W^{adh}), which is the work to separate an interface into two free surfaces, can be calculated with their SFEs. The SFEs of the balls are measured with contact angle method (as shown in Table 1). The W^{adh} between two contact surfaces is estimated based on the following equation [11]

$$W^{adh} = \gamma_1^{total} + \gamma_2^{total} - \gamma_{12} = 2\sqrt{\gamma_1^d \gamma_2^d} + 2\sqrt{\gamma_1^p \gamma_2^p} \tag{1}$$

where γ_1, γ_2 and γ_{12} denote the surface tension of material 1 and 2, and their interfacial tension, respectively. γ^{total}, γ^p and γ^d represent the total SFE, polar component and dispersive component, respectively.

A scratch tester (Revetest, CSM) was used to measure the hardness of these three balls with a Vickers indenter. The maximum load applied on the fixed balls was 6 N. In total five measurements were done on each ball so as to obtain an average hardness value. The measured values of SFEs, W^{adh} and hardness are listed in Table 1.

2.4. Characterization of the worn surface

After the tribo-tests, the morphology of the worn surfaces of the Epomet-PTFE composites and of the balls was observed using light microscopy and scanning electron microscopy (SEM, Philips XL-30 FEG ESEM). For SEM observations, a thin Au layer was applied on the surface of the Epomet-PTFE composites, Al_2O_3 and Si_3N_4 balls to avoid charging. Confocal microscopy (Nanofocus μSurf) was used to measure the surface profile of the worn surfaces of the composites and the balls, for the assessment of the wear volume by a Matlab code with an error of ±5% for most cases and of ±30% for the balls having an average wear depth less than 1.5 μm. For the calculation of the wear volume of the composites and the balls, the average values were obtained with at least two tests after sliding for 1000 m.

XPS was performed to investigate the elemental composition and possible chemical bonding on the worn surfaces of the balls, using a Surface Science SSX-100 ESCA instrument with a monochromatic Al *K*α X-ray source ($h\nu$ = 1486.6 eV). During data acquisition, the pressure in the measurement chamber was kept below 2×10^{-9} mbar. The diameter of the analyzed area was 600 μm. Freshly prepared samples were used for all the measurements.

Table 1
Mechanical properties of the counterpart balls and surface free energy of various surfaces.

Materials	Hardness, *H* (HV)	Modulus[a], *E* (GPa)	H/E	γ^{total} (mN/m)	γ^d (mN/m)	γ^p (mN/m)	W^{adh} (mJ/m^2)	
							vs. PTFE	vs. epoxy
100Cr6 steel	780	210	0.036	58.3	33.5	24.8	57.0	91.1
Al_2O_3	1750	375	0.046	62.3	21.7	40.6	49.2	81.5
Si_3N_4	1800	310	0.057	51.7	24.1	27.6	49.8	80.8
SiO_2 (quartz)				66.0	24.1	41.9	51.5	85.1
PTFE [11]				19.1	18.6	0.5	38.2	57.5
Epoxy [12]				43.7	40.7	3	57.5	87.4

[a] The nominal values of elastic modulus of the corresponding commercial materials are adopted from literatures [13].