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Ultra-low friction between polymers and graphene oxide multilayers in nitrogen atmosphere, mediated by stable transfer film formation

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ABSTRACT

The efficiency and lifetime of mechanical devices is significantly decreased by friction and wear, significantly contributing to global energy consumption. We previously showed that multilayer polyethyleneimine/graphene oxide thin films, $(PEI/GO)_{15}$, on steel display superlubricity against a steel counterface ball. Here, the coefficient of friction (COF) and wear of $(PEI/GO)_{15}$ with six different counterface polymer balls is investigated in air and in nitrogen, with particular focus on the formation of tribological transfer films. The polymers polyoxymethylene (POM), polyetheretherketone (PEEK), polyethylene (PE), poly(methyl methacrylate) (PMMA), polycarbonate (PC), and polytetrafluoroethylene (PTFE) are utilized. The COF of $(PEI/GO)_{15}$ vs steel is 0.35 in both air and nitrogen. In air, the COF ranges from 0.06 to 0.17 for all polymers. Significantly, in nitrogen, four polymers (POM, PEEK, PMMA and PC) display ultra-low friction (COF ~0.02) whilst two do not (PTFE and PE). The wear tracks and transfer films are investigated using e.g. optical microscopy, electron microscopy, and Raman mapping, and the tribological behavior is correlated to the hydrophilicity and relative hardness of the polymer balls compared to GO.

1. Introduction

Friction plays a major role in engineering, decreasing the energy efficiency of devices with moving mechanical parts, and reducing lifetimes through wear. It is estimated that a third of the fuel in automobiles is consumed in overcoming friction [1]. Thus, minimizing frictional energy losses could improve the efficiency and lifetime of mechanical parts, as well as reducing anthropogenic CO_2 emissions. Liquid lubricants such as oil are commonly used to reduce friction. However, in important applications such as the aerospace industry, liquid lubricants have limited usefulness at extremes of pressure and temperature, or in corrosive or reactive environments. Solid lubricants are therefore of great interest as an alternative [2]. State-of-art solid lubricants available today include graphite, molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), boron nitride (BN), magnesium silicate (e.g. $Mg_3Si_4O_{10}(OH)_2$, talc), and polytetrafluoroethylene (PTFE, Teflon$^{®}$) [3].

When a hard material slides against a softer material, small amounts of the latter can be transferred onto the surface of the harder material, forming a thin film. This newly-formed transfer layer results in an interface with lower shear strength, thus reducing the friction [3]. Understanding tribology at the nano-, and micro-scales is thus essential. Over the decades, significant progress has been made in understanding the nature of transfer layers in solid lubricants [4–11]. In particular, tribological diamond-like carbon (DLC) coatings have been studied in detail. The roles of environment, sliding conditions, and hydrogen content on the tribology of DLC, and formation of transfer layers on the counterface surface have been widely investigated [6,12–15]. Polymers such as polytetrafluoroethylene (PTFE) have also been investigated - Bahadur et al. concluded that transfer films develop due to adhesion and interlocking of PTFE fragments into metal asperities

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[8,9]. Wear occurs when material from e.g. a metal surface is deformed and removed as a result of mechanical action. The degree of wear and the transfer of materials to the counterface is mainly influenced by aspects such as transfer film cohesion, adhesion to the counterface, fragment shape and size, and protection of e.g. the polymer surface from metal asperities by the transfer film [9]. These studies demonstrate the significance of transfer layers in solid lubrication.

Carbon-based solid lubricants such as graphite and DLC are also known to provide lubrication by creating a transfer layer of low shear strength. Graphene and graphene oxide (GO) are also emerging solid lubricants, and have been investigated for sliding applications in various environments [3]. Berman et al. showed that solvent-casted few-layer graphene on 440C stainless steel reduced the coefficient of friction (COF) in air (30% relative humidity) from ~1.0 to ~0.2, and increased the wear lifetime by three orders of magnitude [16]. Monolayer graphene grown by chemical vapor deposition (CVD) has been transferred onto 440C steel, resulting in a COF of ~0.2. In hydrogen gas (at 900 mbar), the wear life was around 40 times longer than in nitrogen [17]. This was attributed to hydrogen passivation of defects.

However, there are various issues with using graphene as a solid lubricant. The high cost of graphene, which is usually deposited by e.g. CVD at high temperature, or complex transfer processes. This would be expensive and impractical in most mechanical systems. In addition, although graphene has been shown to reduce friction, it does not always reduce wear. The absence of functional groups in graphene inhibits its adhesion onto solid substrates such as steel, and the durability of a solid lubricant critically depends on the adhesion between the coating and substrate [18–20].

Graphene oxide (GO) in contrast can overcome these issues. The surface functional groups of GO make it highly dispersible in water, and thus it can be deposited onto arbitrary surfaces by low cost and simple techniques such as dip-coating, spin-coating, spray deposition, and printing [20]. In addition, these functional groups can bond strongly to steel surfaces, potentially improving the wear lifetime [19]. Finally, the negative surface charge of these functional groups can be exploited to interact with positively charged polymers via electrostatic attraction, making it possible to build up well-defined multilayers of GO using polymer “glue”. This technique is not possible with pristine graphene. These factors make GO a more viable solid lubricant than graphene for a variety of practical applications [18,19].

The LbL electrostatic self-assembly technique is widely used for thin film fabrication, and has recently been extended for fabrication of GO multilayers. In this technique, alternating layers of GO with negative surface charge and positively charged polymers are built up via electrostatic attraction. In this way, well-defined multilayers can be built up simply by dip-coating, spin-coating, printing, or spray-coating. In some cases, such electrostatic assemblies can be further transformed to covalent bonding upon UV irradiation, or heat treatment [21]. Some of the numerous advantages of this coating method include simplicity, precise thickness control (within several nanometers), facile deposition onto complex geometries, low cost, and scalability [22].

In a recent study, we investigated the tribological behavior of $(PEI/GO)_n$ multilayer coatings deposited by layer-by-layer (LbL) coating onto steel. The COF was measured in air, vacuum, nitrogen, and hydrogen gas environments, resulting in an improvement in all environments [23]. However, only a combination of dry environment (H_2 or N_2) and thicker films (15 bilayers) resulted in superlubricity (COF < 0.04). Ultra-low friction in that case was attributed to a large reduction in the contact area due to the formation of characteristic hollow carbon nanoparticles under dry conditions. In contrast, small amounts of water in air prevented the separation of GO sheets to form such nanostructures, due to increased hydrogen bonding within the $(PEI/GO)_n$ [23]. However, the formation of transfer films (or tribo-coatings) was not fully investigated.

Here we investigate the tribological behavior of LbL $(PEI/GO)_n$ solid lubricant coatings on steel, sliding against six different polymer counterface balls, in air and dry nitrogen gas environments. The absence of H_2O and oxygen in dry nitrogen is expected to result in different frictional behavior [10,23] compared to air. Particular attention is paid to microstructural characterization of the transfer films/tribo-film formation, and how this results in drastic reduction in friction.

2. Experimental methods

2.1. Coating deposition

Branched PEI (Mw ~25000 g mol^{-1}, purity >99%, Sigma-Aldrich) and aqueous GO dispersion (4 mg/ml, Sigma-Aldrich, monolayer content >95%) were used to fabricate the coating according to an electrostatic LbL self-assembly procedure reported elsewhere [23,24]. In brief, O_2 plasma treated substrates (AISI 304, silicon wafer) were consecutively dipped into a 0.2 wt% aqueous solution of PEI and a 0.1 mg/ml aqueous dispersion of GO. This process was repeated 15 times ($n = 15$) to form $(PEI/GO)_{15}$. All solutions were made with pure deionized water (18.3 MΩ cm^{-1}, Millipore, Direct-QTM).

The morphology of the coatings and worn surfaces was investigated using optical microscopy and scanning electron microscopy (FESEM Hitachi S-5200, 5 kV). Raman spectroscopy was performed before and after tribology tests, using a DXR™ Raman Microscope (Thermo Scientific, USA) with a wavelength of 532 ± 1 nm and a maximum laser power of 10 mW. The numerical aperture of the 20× lens was 50 μm, and the laser beam diameter was 1 mm. Raman spectra were collected in the range 0–3500 cm^{-1}, with an exposure time of 20 s and a laser power of 1 mW.

The hardness of the $(PEI/GO)_n$ coating and polymer balls was measured using an Anton Paar Ultra Nano-indentation Tester (UNHT). A triangular pyramid Berkovich diamond indenter was used. The contact and characterization forces were 0.05 mN and 2 mN, respectively. The contact stiffness threshold was 150 μN/μm and the indentation depth was set to 50 nm to avoid substrate effects. Multiple indentations were conducted at random locations on each sample and an average value is reported here.

2.2. Tribological testing

Macroscopic friction tests were performed in air (~140 ppm H_2O) and under dry N_2 environments, using a custom built multi-environmental tribometer. Schematics and a photograph of the tribometer setup are shown in Supporting Information Figs. S1 and S2, as reported in our previous works [25–28]. All tests were performed at room temperature (25 °C). The tribological test conditions, i.e. normal load and sliding speed, are summarized in Table 1. In order to provide a broader perspective, six different polymers were chosen as counterfaces, based on their chemical nature and commercial usage (Supporting information, Fig. S3). The physical and chemical properties of the polymer balls (i.e. chemical structure, hardness, contact pressure and surface energy values) are summarized in Table 2. The steady-state COF was calculated by averaging from the point where steady-state behavior was first observed until the end of the test, or until failure of the coating. Failure is defined at the point where the COF increases to >0.4, or when abnormal fluctuation is observed. These criteria are based on our own observations: a COF >0.4 is generally associated with a sudden increase in COF to much higher values (e.g. 0.8 or 1) with