Tribology of silica nanoparticle-reinforced, hydrophobic sol–gel composite coatings

Derrick A. Banerjee, Aaron J. Kessman, Darran R. Cairns, Konstantinos A. Sierros *

West Virginia University, Dept. of Mechanical and Aerospace Engineering, Morgantown, WV 26506, USA

ABSTRACT

Hydrophobically functional coatings can be used to protect surfaces and therefore improve the performance and lifetime of a broad range of applications such as optoelectronics and touchscreens. Organic–inorganic hybrid materials such as silica sol–gel coatings are particularly effective for this purpose, but the functional molecules in these coatings are susceptible to abrasive wear and thus lose their performance over time in the harsh environments typically encountered. To combat these problems, a silica nanoparticle-reinforced matrix was developed to increase hardness and wear resistance of the overall coating.

This study involved the abrasive wear analysis of fluorinated composite silica particle reinforced sol–gel silica coatings dip-coated on glass substrates. Varying amounts of silica nanoparticles from 0.5 to 10 wt.% of the precursor weight were added to examine the structural dependence of abrasive wear mechanisms to elucidate strengthening mechanisms that could lead to improvements of coating properties. Abrasion was conducted using an in-house built reciprocating polishing wear apparatus. Characterization of the water contact angle of the coating was conducted to determine the hydrophobic functionality after wear cycles. Atomic force microscopy, lateral force microscopy, nanoindentation, nano-scratch, contact angle goniometry, and optical microscopy were performed at intervals of abrasive wear testing to characterize these wear mechanisms and the functional degradation of the coating. It was generally found that, among other possible factors, the increased indentation hardness of coatings led to a decreased wear rate. Additionally, an optimal amount of added colloidal silica of 1–2 wt.% of the precursors provided the best overall mechanical, tribological, and functional performance.

1. Introduction

Transparent, non-wetting coatings are useful for a wide range of surface-protective applications such as solar panels [1,2], information displays [3], touchscreens, ophthalmic lenses [4], optical storage disks [5], painting glazing [6], industrial, automotive, textile, household applications [7], architectural structures, and urban infrastructure [8]. Incorporation of wear-resistant hydrophobic layers can reduce waste and cleaning needs and extend the lifetime of these applications. Non-wetting coatings are most often based on materials with low mechanical strength and poor tribological performance. However, for many of these applications, resistance to abrasive wear is also important.

Conventional low-surface energy coatings such as polytetra-fluoroethylene (PTFE) have poor mechanical strength which leaves them susceptible to abrasive wear [9]. An approach taken to offset these weaknesses is using a sol–gel method to apply a fluorinated organic monolayer [10]. This process provides a strong Si–O film-substrate bond due to the sol–gel grafting [11] as well as high thermal stability, optical transparency, and substrate compatibility [12]. However, the setback for this approach is that these fluorinated moieties are thermodynamically driven to the solid-vapor interface during deposition [13,14], leading to surface stratification and poor functionalization of the bulk coating. The top surface provides excellent functionality, but this molecularly thin monolayer also has an inherently low abrasive resistance.

An approach taken by Kessman et al. [11,15] uses a sol–gel process of co-condensation of silicon alkoxides and fluorosilanes. This process overcomes the surface stratification problem by encapsulating the functional moieties in mesopores within the bulk of the sol–gel matrix. While this provides a vast improvement for many applications, the induced porosity from this approach has a detrimental effect on the overall tribological performance of the coating. There was, however, a decrease in internal friction coefficient reported due to this encapsulation of fluorinated molecules, which in this case served to counteract the loss in wear resistance due to increased porosity.

It has also been shown that ceramic colloidal additives can be used in self-assembly processes to potentially improve overall film durability. Suegama et al. found an increase in the mean nanohardness value of

* Corresponding author. Tel.: +1 304 290 7375.
  E-mail address: Kostas.Sierros@mail.wvu.edu (K.A. Sierros).

sol–gel coatings by the addition of silica nanoparticles [16]. Lakshmi et al. showed that the addition of colloidal nanoparticles could also have the benefit of imparting a textural advantage to enhance the surface functional properties through increased roughness while simultaneously improving the pencil hardness parameter of the coating [17]. Hwang et al. reported a similar increase in hydrophobicity, but found a decrease in wear resistance with a macroscale abrasion test [18]. Each of these studies involved the agglomeration of colloidal nanoparticles at the surface of the coating increasing the macroscopic hardness and water contact angle of the coatings, but after abrasive wear the functionality still decreased significantly. The wear mechanisms and rates for this approach have not been adequately quantified. Also, the overall usefulness of this method is limited in its application since a specific substrate condition or texturing of the surface may undesirably affect the other properties of the coating. Furthermore, flocculation of the colloidal particles could also negatively affect the optical transmission of the coatings.

The realistic goal is to optimize the coatings such that they have the highest hardness and best wear resistance possible without compromising the functional properties. The focus of the work presented here is to further investigate the use of hard colloidal silica nanoparticles in sol–gel derived coatings and their distribution throughout the bulk of the coating. The effects of this addition need to be more precisely examined to determine the actual interplay between coating roughness, hardness, friction, and wear characteristics. Sol–gel derived silica coatings were deposited on glass substrates with varying amounts of added colloidal silica. The coatings were tested using a reciprocating wear apparatus and wear rates were calculated by measured film thickness after intervals of wear. Instrumented nanoindentation, nanoscratch testing, stylus profilometry, atomic force microscopy (AFM), and lateral force microscopy (LFM) were used to examine the effect of the colloidal silica on the characteristics of the coatings. Contact angle goniometry was also used to quantify the hydrophobicity of the coatings throughout the wear testing.

2. Experimental procedure

2.1. Synthesis of films

The synthesis of the silica nanoparticle-reinforced fluorinated coatings first involves the co-condensation of fluorinated silanes with an alkoxide silica precursor at room temperature [11,15]. The alkoxide precursor used was tetraethoxysilane (TEOS, tetraethyl orthosilicate 99%, Acros Organics), and the functional fluorinated silane used was a perfluoropolyether silane (PFPE, Fluorolink S10, Solvay Solexis). The added colloidal silica nanoparticles used were 20 nm in diameter dispersed in ethylene glycol at a concentration of 30% (DP5820, Nyacol Nano Technologies).

The sol–gel solutions were synthesized in approximately 25–30 g batches in the following order and in the ratios described. First, TEOS and PFPE were hydrolyzed with water, isopropyl alcohol (IPA), and a small amount of hydrochloric acid (HCl) in the molar ratio 0.98 TEOS:0.02 PFPE:4 H_2O:1 IPA:0.01 HCl and stirred for 1 h using a magnetic stirrer. The sol was then diluted with IPA and butanol (BtOH) for a final molar ratio of 0.98 TEOS:0.02 PFPE:4 H_2O:10 IPA:0.01 HCl:2 BtOH. The next step was to add the colloidal silica at varying concentrations. These silica concentrations were calculated as a percent of the combined weight of precursor TEOS and PFPE used and varied from 0 to 10 wt.%. After mixing for another 10 min, the sols were dip coated onto soda-lime glass microscope slides using a KSV Instruments dip coater with a withdrawal speed of 200 mm/min. All coatings were synthesized and deposited in controlled ambient conditions of 23 ± 1 °C and 40 ± 10% relative humidity. After deposition, the films were dried for 24 h at ambient conditions. Finally, the coatings were cured in a box furnace at 200 °C for 2 h with a ramp rate of 10 °C/min from ambient conditions.

2.2. Material characterization

In order to determine coatings' functional sustainability and resistance to abrasive wear, they were worn using a lab-built reciprocating polishing device. This instrument has been used previously for wear studies on sol–gel coatings [11,15,19]. The device provides a conformal surface that uniformly and gradually wears through coatings with thicknesses on the order of several hundred nanometers in a controlled manner. The instrument consists of a vertically-loaded reciprocating polishing contact controlled by a stepper motor (NM34A200, Zaber Technologies). The coating abrasion occurs from trapped 0.3 μm alumina particles (90-187120, Allied High Tech Products) in a cloth pad (90-150285, Allied). The alumina particles are suspended in an aqueous slurry that is regularly replenished, and the cloth pad is rotated after wear intervals to give a pristine surface for abrasion. The normal load was kept constant at 4.70 N. The polishing contact was determined to be over a nominal area of 175 mm^2 for an approximate Hertzian contact pressure of 27 kPa. The stroke length of the reciprocating contact was 35 mm at 0.5 Hz. These parameters were chosen to model contact wear on a touchscreen or cleaning of solar panels. Samples were removed at regular intervals for analysis and cleaned with water and alcohol to remove residue from abrasion.

Hydrophobicity was quantified using a lab-built sessile drop contact angle goniometer. Five approximately 5-μL droplets of deionized water were placed over a macroscopic area of the coating approximately 1–2 mm apart using a manual microsyringe. Images of the horizontal view of the drops were captured using a digital microscope and analyzed using the low-bond axisymmetric drop shape analysis (L-BADSA) method in the "Drop Shape Analysis" plugin [20] for ImageJ. Optical transmission of the coatings was measured using a UV–vis spectrometer (Jaz Spectrometer Module, Ocean Optics) with the deuterium-tungsten halogen light source module.

Coating thickness and roughness were measured on a Veeco Dektak 150 (Bruker AXS) stylus profilometer by measuring the depths of manual scratches through the center of the coatings. The Dektak 150 stylus used had a 12.5 μm radius tip with a nominal applied normal force of 0.1 mN. Scan lengths used for roughness measurements were between 500 and 1000 μm. Film wear rates were calculated from a weighted linear least squares fit of film thickness versus reciprocating wear cycles.

AFM and LFM provided high resolution surface and friction mapping of the coatings. AFM and LFM were performed using a Molecular Imaging PicoScan 3000 system in contact mode. A silicon tip (SC37B, MikroMasch) on a cantilever with force constant k = 0.3 N/m and radius of curvature less than 10 nm. Deflection and force were calibrated using the slope of the force curve on the tip approach to the sample surface and the nominal cantilever spring constant. Relative friction measurements were made by applying forces in the range of 5–50 nN to the tip, scanning over a 500 nm by 500 nm area at a speed of 10 μm/s. All measurements were conducted in controlled ambient conditions of 22 ± 1 °C and 40 ± 10% relative humidity.

A nanoindentation system (NHT, CSM Instruments) and an ultra-nanoindentation system (UNHT, CSM Instruments) were used to determine the instrumented hardness values of the coatings. A standard indentation method was used for each with a 30 second load time, followed by a 10 second pause, and a 30 second unload. The maximum penetration depth into the coatings was kept less than 10% of the coating thickness to minimize substrate effects on the hardness values. This corresponded to a maximum normal load of 0.5–0.75 mN. A Berkovich geometry diamond tip was used with both the NHT and UNHT, and a 10 μm radius sphero-conical diamond tip was also used on the NHT.

To determine the coating adhesion characteristics and the normal load at which critical failure of the coatings occurs, scratch testing was performed using a Nano-Scratch Tester (NST, CSM Instruments). Samples were mounted on a standard resolution friction table (ST-142, 0.01 mN friction force resolution) and scratched with a 10 μm radius