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Friction and Wear of Polytetrafluoroethylene/Graphene Oxide Composite Thin Films

Justin Kyle Carter  
*University of Arkansas, Fayetteville*

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Friction and Wear of Polytetrafluoroethylene/Graphene Oxide Composite Thin Films
Friction and Wear of Polytetrafluoroethylene/Graphene Oxide Composite Thin Films

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

by

Justin K. Carter
University of Arkansas
Bachelor of Science in Mechanical Engineering, 2011

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University of Arkansas

This thesis is approved for recommendation to the Graduate Council.

Dr. Min Zou
Thesis Director

Dr. Rick J. Couvillion
Committee Member

Dr. Douglas E. Spearot
Committee Member
ABSTRACT

Polytetrafluoroethylene (PTFE) is a commonly used solid lubricant due to its low coefficient of friction and chemical inertness. As a polymer, PTFE suffers from high wear and low adhesion to substrates limiting its use as a thin film. Thin PTFE films are ideal candidates for solid lubrication in micro-machines and bearing applications. The main goal of this work is to enhance the durability of thin PTFE films through the addition of few layered graphene oxide (GO) as filler. In order to address adhesion issues, the addition of an adhesive layer of polydopamine (PDA) between stainless steel substrates and thin PTFE films was also investigated.

An automatic friction abrasion analyzer was used to perform friction and wear testing with a ball-on-flat configuration. Wear tracks of the thin PTFE films were analyzed using optical microscopy and a surface profilometer. Counterfaces were examined using optical microscopy and atomic force microscopy for the formation of PTFE transfer film.

The lone addition of GO to PTFE thin films increased durability by nearly 6 times. Combining an adhesive layer of PDA and GO as filler to thin PTFE films resulted in a significant increase in durability of approximately 41 times. Single coatings of unfilled PTFE films experienced large amounts of delamination, plowing, and global shearing of PTFE bands within the wear track during friction and wear testing. The addition of GO particles impeded global shearing of the PTFE bands while slowing the wear rate of thin PTFE films through load support. Upon the addition of PDA, changes in the wear mechanism were evident. A mixture of plowing and cutting was observed for samples employing a PDA adhesive layer. Ribbon-like wear debris was generated during testing. Increasing the adherence also minimized delamination of the thin PTFE film from the substrate. Overall, the results showed that significant increases in
durability of thin PTFE films can be achieved through the addition of GO as filler, especially when an adhesive layer of PDA is applied between the film and substrate.
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CHAPTER 1

INTRODUCTION

1.1 Tribology and Solid Lubrication

A basic definition of tribology is the science and technology of interacting surfaces in relative motion. The study of friction, wear, and lubrication further defines the field of tribology. Practically all mechanical systems rely on some type of lubrication between moving bodies and surfaces to decrease the friction and wear experienced by these interacting entities with the goal of optimizing longevity of these mechanical systems. Nearly one-third to one-half of energy produced around the world is lost to friction causing the production of lubricating media to be one of the largest industries in the world [1]. Animal fats and oils were primarily used as lubricant materials until the oil boom in the 1860’s. Around the mid-1930’s, additives for petroleum oils were developed and marketed in order to increase load capacity, lubricity, corrosion protection, and oxidation stability of conventional petroleum oils. Synthetic lubricants were later introduced to supply the need for lubrication in more demanding environments. Higher temperatures, higher pressures, and other extreme conditions continued to arise from growing technologies resulting in the research and development of solid lubricants which could provide required lubrication in these harsh environments [1]. Typically, little or no maintenance is required when using solid lubricants, whereas liquid lubricants require regular checks and maintenance. Solid lubricants can be broken down into four categories as seen in Table 1.1.
### Table 1.1 Categories of Solid Lubricant Materials [2].

<table>
<thead>
<tr>
<th>Category</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-based materials</td>
<td>Graphite and diamond-like carbon</td>
</tr>
<tr>
<td>Metal dichalcogenide compounds</td>
<td>MoS$_2$ and WS$_2$</td>
</tr>
<tr>
<td>Soft metals</td>
<td>Silver, Tin, Indium, Gold</td>
</tr>
<tr>
<td>Polymers</td>
<td>PTFE, Polyimide, Nylon</td>
</tr>
</tbody>
</table>

One particular interesting category of solid lubricant materials is that of polymers. Polymers are widely used in tribological applications as a solid lubricant due to being light weight, relatively inexpensive, and easy to fabricate. Some polymers contain a self-lubricating characteristic, such as polytetrafluoroethylene (PTFE), polyimide and nylon, when used in either bulk or thin film composition [3].

### 1.2 PTFE Structure and Use as a Solid Lubricant

PTFE, also known by its brand name Teflon®, is a fluoropolymer consisting of a carbon backbone chain with each carbon atom having two fluorine atoms strongly attached to it, (-CF$_2$-CF$_2$)$_n$. In organic chemistry, the carbon-fluorine bond is the strongest carbon bond. At room temperature, the structural arrangement of PTFE comprises of a helical rod-like chain with a 15$\pi$ helix structure. The 15$\pi$ classification signifies that for every 15 CF$_2$ groups the helical structure twists 7 times in order to complete a 180° rotation of the helix. This terminology describes the smallest repeating unit which demonstrates the overall structure of the given PTFE chain. Therefore, a 12° angular rotation is found between each CF$_2$ group within a PTFE chain at room temperature. Below 19 C, the PTFE chain changes to a 13$_6$ helix structure which has a 13.8° angular rotation between each CF$_2$ group. In Figure 1.1a, a repeating unit of a 13$_6$ helical arrangement for a PTFE chain can be seen. Using the helical arrangement of the carbon
backbone for a 13₆ helix in Figure 1.1b, it takes 13 carbon atoms to return to the original position from the carbon atom marked by the left square bracket to the carbon atom marked by the right square bracket which corresponds to 13 CF₂ groups.

![Diagram of PTFE structure](image)

**Figure 1.1** (a) Smallest repeat unit of a 13₆ helical arrangement of PTFE; (b) helix configuration of carbon backbone [5]. Reprinted with permission from Elsevier.

In Figure 1.2a, a semi-crystalline block of PTFE, typically 100 μm in length and 0.2 μm to 1.0 μm in width, is shown. Within this block, 20 nm thick crystalline slices containing folded PTFE molecular chains are found, as shown in Figure 1.2b and 1.2c. The crystalline slices are separated by amorphous regions of about 30 nm thickness as seen in Figure 1.2a [4]. This overall structure gives PTFE its unique properties. Due to fluorine’s extreme chemical inertness and strong bond with carbon, fluorine atoms within the structure of PTFE protect the inner carbon backbone from contaminants and give PTFE its self-lubricating and anti-stick properties. PTFE possesses one of the lowest known coefficients of friction (COF) when rubbed against solid
materials and has a high corrosion resistance and melting point, 327 C, making it an ideal material to use as a solid lubricant, especially as a bearing material. However, as a polymer, PTFE suffers from high wear. PTFE’s anti-stick property also causes difficulties when attempting to adhere PTFE to substrates. Due to high wear and low adhesion, applications for PTFE have been limited to the use of bulk PTFE and thick PTFE films.

Figure 1.2 Banded Structure of PTFE: (a) semi-crystalline block of crystalline slices and amorphous regions of PTFE chains; (b) crystalline slices of PTFE chains during sliding; (c) dimensions of PTFE molecular chains [4]. Reprinted with permission from Elsevier.

1.2.1 PTFE Composites: Adding Fillers to Reduce the Wear of PTFE

Various micro-fillers and nano-fillers have been explored in order to decrease the wear of PTFE. Micro-fillers, such as graphite, MoS₂, aluminum and bronze, have been found to significantly increase wear resistance of bulk PTFE but sometimes at the cost of the inability to maintain a low COF [6]. The low COF of PTFE is attributed to the formation of a PTFE transfer
film on the counter-surface generating a PTFE-on-PTFE rubbing contact [1, 7, 8]. This countersurface is abraded by the micro-fillers added to PTFE preventing the formation of PTFE transfer film to the abraded counter-surface resulting in higher COF values. Recent studies have shown that some nano-fillers further increase wear resistance while still maintaining a low COF [9, 10]. With the latest innovations in nanotechnology, an increased availability of different types of nanoparticles has created the opportunity to add nano-sized particles to thinner PTFE films where micro-sized particles couldn’t be considered.

1.2.2 Graphene Oxide

Graphite is a well known solid lubricant that has been successfully added as a micro-filler to bulk PTFE at various concentrations to increase PTFE’s wear resistance. In 2004, Geim and Novoselov isolated the first monolayer sheet of graphite which was later named graphene [11, 12]. Graphene consists of single planar sheets of sp² bonded carbon atoms in a honeycomb crystal lattice. Interplanar spacing between graphene sheets is around 0.335 nm [13]. An illustration of graphite and a sheet of graphene can be seen in Figure 1.3. Graphene sheets are the building blocks that make up the overall structure of graphite. The term “graphene” is used for compositions made up of a single layer up to nine layers of stacked graphene sheets. After ten layers of graphene sheets are reached the composition is called thin-layer graphite. Kandanur et al. used three to four layered graphene platelets as filler to bulk PTFE in order to increase wear resistance by nearly 4000 times while even out performing graphite filler. Graphene platelets were found to decrease wear rates by 10 to 30 times more than micro-graphite fillers [14].
Figure 1.3 Structure of graphite and graphene. Graphene sheets are the building blocks that make up the structure of graphite [15]. © Airi Iliste/Royal Swedish Academy of Sciences

Creating well-dispersed fillers of graphene within the matrix of materials has proven to be difficult. Therefore, graphene oxide (GO) has also been used as a filler [16]. GO consists of graphene sheets containing many functional oxygen groups across the basal plane and edges of graphene sheets. Figure 1.4 represents the structure of a typical GO sheet. These functional oxygen groups allow GO to be easily dispersed within a variety of different solutions including water and methanol [17, 18]. For applications requiring spin coated or dip coated films, dispersability of filler particles within solutions is critical in order to avoid aggregation which can result in decreased performances of film composites. GO has been found to increase the mechanical properties of polymers, such as poly(methyl methacrylate), polyimide and poly(vinyl alcohol), when added as filler to create polymer/GO composites. However, tribological properties of these polymer/GO composites have yet to be studied [16, 19, 20].
1.2.3 Addressing Adhesion Issues of PTFE Films to Substrates

The application of thicker PTFE films, 20 μm thick or above, to substrates has been accomplished through the roughening of substrate surfaces and addition of a primer between the PTFE coating and substrate. Roughening of the substrate increases the surface area of contact between the PTFE film and substrate further increasing adhesion. When choosing a primer it must have a good affinity toward both the chosen substrate and PTFE. Typically, a concentration gradient of the chosen primer material is introduced into the matrix of the PTFE film between the interface of the PTFE film and roughened substrate. The concentration of the primer is highest near the substrate and gradually decreases into the applied PTFE film. One particular material, polydopamine (PDA), has shown a high affinity towards PTFE and can be applied to essentially any material surface.
1.2.4 Polydopamine

Recent work by Lee et al. has led to the discovery of PDA films which mimic the simple structural unit of *Mytilus edulis* foot proteins secreted by mussels. These foot proteins are high in L-DOPA compounds, 3,4-dihydroxyphenyl-L-alanine (C₉H₁₁NO₄), and lysine, HO₂CCH(NH₂)(CH₂)₄NH₂, amino acids which are essential functionalities for strong adhesion to a wide range of materials, including PTFE, see Figure 1.5a [21, 22]. In Figure 1.5b, an example of the chemical structure of L-DOPA and lysine compounds can be seen.

![Figure 1.5](image-url)

**Figure 1.5** (a) Picture of mussels strongly adhered to a surface. (b) Chemical structure of dopamine comprising of L-DOPA (blue) and lysine amino acids (yellow). Reprinted by permission from Macmillan Publishers Ltd: Nature Materials [22], copyright 2008. www.nature.com/nmat.
PDA films have been proposed as an alternative to self-assembled monolayers and polyelectrolyte multilayer films due to their versatility in a diverse range of application fields. Improvements in tribological properties and corrosion resistance have been found when applying PDA films. Thicknesses around 45 nm to 50 nm have been achieved when depositing PDA on substrates [23, 24]. Due to the nanoscale thickness and high affinity to PTFE, PDA shows much promise as an adhesive primer for thin PTFE films for tribological applications which have not been researched by other groups. In this thesis, PDA is added as an adhesive layer between thin PTFE films and stainless steel substrates in order to increase the adhesion of PTFE films.

1.3 Thesis Goal and Objectives

The overall goal of this thesis is to research and study the friction and wear effects of adding few layered GO as filler to PTFE films. Due to the past success of graphene as filler to bulk PTFE, GO has potential to be an effective filler for thin PTFE films. Highly durable thin PTFE films are desirable in applications of lubrication for micro-machines and bearings. Objectives for completing this goal are as follows: First, optimize durability by exploring different concentrations of GO filler. Next, study the wear mechanisms of unfilled thin PTFE films and GO filled thin PTFE films to understand the effects in performance when GO is added as filler. Finally, an adhesive layer of PDA is added between the thin PTFE films and substrate to see if further increases in durability can be achieved.

1.4 Organization of Thesis

Five chapters are contained within this thesis. The current chapter is devoted to introducing PTFE as a solid lubricant and the techniques used to increase the performance of PTFE so it can be used in applications. The first chapter also introduces a novel idea of adding
GO as filler to thin PTFE films along with the application of an adhesive layer of PDA between thin PTFE films and stainless steel substrates. Chapter 2 consists of literature review on the friction and wear behaviors of bulk and film PTFE with and without the addition of micro-fillers or nano-fillers. The use of primers to increase adherence of PTFE films and use of PDA as an adhesive layer to increase tribological and mechanical properties of coatings is also included in Chapter 2. Experimental details of sample fabrication, testing, and characterization are discussed within Chapter 3. Results and discussion make up Chapter 4 followed by Chapter 5 containing the conclusions and direction of future research.
CHAPTER 2
LITERATURE REVIEW

2.1 Friction and Wear of Bulk PTFE

As mentioned in Chapter 1, PTFE possesses multiple unique properties that make it a potentially great material for solid lubrication such as its low friction, high thermal stability, and chemical inertness. Different regimes of friction occur for bulk PTFE depending heavily on the sliding speed and load used. Lower sliding speeds combined with higher loads produce the lower regime of dynamic COF values around 0.06, while faster sliding speeds with lower loads create the higher regime of dynamic COF values around 0.2 to 0.3 [7, 25, 26]. PTFE exhibits wear rates up to 2 orders of magnitude higher than other polymers used for solid lubrication, such as nylon and polyethylene [27]. Due to these higher wear rates the vast majority of applications and research has been limited to bulk PTFE.

Tanaka et al. attributed PTFE’s high wear rates to the slippage between PTFE bands which transfer easily to the counter-surface. These bands of PTFE, known as transfer film, were approximated to be 20 to 30 nm thick and oriented in the direction of testing [27]. Transfer films of PTFE have been witnessed on various types of counter-surfaces, such as metals and glass [7, 26, 27]. A general consensus has found that lower wear rates and low COF values for PTFE depend on the formation of transfer film on the counter-surface allowing for PTFE rubbing on PTFE to occur [1, 7, 28, 29]. Makinson and Tabor attributed the adhesion of PTFE transfer film to glass through Van der Waals forces [7]. Transfer films of PTFE adhered to metallic surfaces were found to have fluorine ions and other radicals present which were believed to react with
atmospheric oxygen and oxides on metallic surfaces in order to adhere PTFE transfer films to metallic surfaces [29, 30]. The cohesion of PTFE transfer film and adhesion of PTFE transfer film to the counterface are important factors controlling the wear rate of PTFE due to the protection of the polymer surface from the metal counterface by the transfer film [29]. Regardless of how the PTFE transfer film forms on the counterface, a well-adhered transfer film is needed for lower wear rates and low values of COF due to the generation of contact between two rubbing PTFE surfaces.

2.2 Addition of Micro-fillers and Nano-fillers to Bulk PTFE

Many types of micro-fillers have been used successfully to decrease the wear rate of bulk PTFE. Figure 2.1 shows how steady state wear rates of bulk PTFE can be reduced by 2 to 3 orders of magnitude through the addition of micro-fillers. The most widely available micro-fillers used commercially for bulk PTFE are graphite, carbon, glass fiber, and bronze [31].

![Figure 2.1 Various micro-filled PTFE composite wear rates [31]. Crown copyright.](image-url)
Bahadur successfully reduced the wear rate of bulk PTFE by 100 times through the addition of graphite and copper monosulfide (both at 30% by volume) as individual micro-fillers when compared to unfilled PTFE [6]. Micro-fillers of glass fiber, bronze, MoS₂, graphite, ZrO₂, and TiO₂ at filler contents between 15 to 40 wt% were used by Tanaka and Kawakami to decrease the wear rate of PTFE by 2 to 3 orders of magnitude at loads of 10 N and 50 N with sliding speeds ranging between 0.1 to 2.5 m/s [32]. Slight to significant increases in values of COF are seen when micro-fillers are added to PTFE. Glass fiber, graphite powder, and bronze powder have shown increased dynamic COF values of nearly 3 to 4 times when compared to unfilled PTFE [33]. The micro-fillers used by Tanaka and Kawakami, explained earlier, saw increases in COF by 10% to 50% [32]. At higher sliding speeds above 0.1 m/s, Blanchet and Kennedy reported lower wear rates for filled PTFE by 2 to 3 orders of magnitude along with lower COF values for graphite and bronze filled PTFE. Blanchet and Kennedy concluded the wear reduction from micro-fillers came from the interruption of subsurface deformation and crack propagation that otherwise produced large wear sheets [34]. From these findings it is evident that the addition of 15 to 40 wt% micro-fillers can reduce wear rates of bulk PTFE from 2 to 4 orders of magnitude while causing fluctuations in COF values produced by micro-filled PTFE. These fluctuations range from significant increases to slight decreases in COF values. Increases in COF during the use of micro-fillers are attributed to the abrasion of the counterface inhibiting the formation of transfer film [35].

In 1981, initial studies by Tanaka and Kawakami had shown nano-fillers could not be effectively used to lower wear rates of bulk PTFE when compared to micro-filled PTFE composites. They concluded very small fillers fail to prevent the removal of large scale PTFE debris and can’t support load as well as micro-fillers [32]. It was not until 2001 that another
nano-sized filler was used in bulk PTFE where Li et al. added 50 nm sized ZnO particles to bulk PTFE. At 15% volume of ZnO filler, wear of bulk PTFE was reduced by up to 36 times while still maintaining low COF values to that of unfilled bulk PTFE under the same testing conditions. Li et al. reported a uniform and tenacious transfer film of the PTFE/ZnO composite on the counter-surface attributing the increased anti-wear properties of the composite to this well formed transfer film [36]. In 2003, Chen et al. added carbon nano tubes of 20 to 30 nm diameter and several micrometers in length to bulk PTFE which resulted in significant improvements in wear resistance. The addition of 20 vol% of carbon nano tubes reduced wear by 290 times when compared to unfilled PTFE [37]. In that same year, Sawyer et al. added 40 nm sized alumina (Al₂O₃) particles between 0.1 wt% and 50 wt% to bulk PTFE. At a 20 wt% filler concentration, the PTFE/Al₂O₃ composite was over 600 times more wear resistant than unfilled PTFE with only a small increase in COF from 0.15 to 0.2 [35].

McElwain et al. further studied the effect of alpha phase Al₂O₃ particle size on the wear resistance and COF of bulk PTFE composites. Two Al₂O₃ nano-filler sizes, 40 nm and 80 nm, and four Al₂O₃ micro-filler sizes, 0.5 μm, 1 μm, 2 μm and 20 μm, were added to two different commercial grades of PTFE resin, G580 and 7C. All of these filler sizes were added a concentration of 5 wt% Al₂O₃ filler. From Figure 2.2, steady state wear rates for micro-sized and nano-sized Al₂O₃ fillers tended to be 2 and 4 orders of magnitude, respectively, less than unfilled PTFE. Both micro-fillers and nano-fillers of Al₂O₃ had COF values close to that of unfilled PTFE for at least one type of PTFE resin. Investigation of the counter-surfaces with scanning electron images showed that PTFE composites using Al₂O₃ nanoparticles were less abrasive than composites using Al₂O₃ microparticles. McElwain et al. concluded their nano-filled PTFE composites deposited a thinner, well-adhered transfer film since the nanoparticles
did not abrade the transfer film unlike the microparticles which abraded and removed the transfer film formed on the counter-surface [38].

Figure 2.2 Steady state wear rate (top) and COF (bottom) for various Al₂O₃ filler particle sizes for PTFE/Al₂O₃ composites vs. unfilled PTFE for G580 and 7C PTFE resins [38].


Graphene platelets 3 to 4 layers thick with planar dimensions of several micrometers were added as nano-filler to bulk PTFE (commercial 7C resin) by Kandanur et al. Using transmission electron microscopy, these platelets were found to be less than 2 nm thick. Figure
2.3 shows steady state wear rates for graphene platelet filler contents between 0.01 and 10 wt% and unfilled PTFE. At 10 wt% graphene filler the steady state wear rate had decreased by nearly 4 orders of magnitude when compared to unfilled PTFE. Even at 0.8 wt% graphene filler, wear rates had decreased around 2 orders of magnitude showing that low loadings of nano-filler in bulk PTFE have the ability to decrease wear at the same magnitude to that of micro-fillers which require filler contents between 15 to 40 wt% to be effective, see Figure 2.1 [14]. Burris and Sawyer also saw drastic improvements in wear resistance by up to 3000 times by using a 1 wt% filler of irregularly shaped alpha phase Al₂O₃ nanoparticles around 80 nm in size [9]. Kandanur et al. also compared few layered graphene platelets to micro-scale graphite with particle sizes less than 44 μm. They discovered at 2 wt% and 10 wt% graphene platelet filler contents that graphene platelet filled PTFE had wear volumes around 5 times less than graphite filled PTFE by comparing to the longest sliding distances tested for graphite filled PTFE composites, see Figure 2.4 [14].

![Figure 2.3](image_url)

**Figure 2.3 Steady state wear rate of unfilled PTFE vs. graphene platelet filled PTFE composite at various graphene platelet wt% contents [14].**
2.3 Thin PTFE Films

Initial studies of thin PTFE films were done by Nishimura et al. in the 1980’s. Nishimura et al. sputtered approximately 1 \( \mu \)m thick PTFE films on steel substrates. They found the COF of the sputtered PTFE films to be nearly double that of bulk PTFE sliding against steel. However, wear rates of the sputtered PTFE films were ten times less than bulk PTFE. Nishimura et al. believed the higher COF values and lower wear rates came from the different structures between the sputtered PTFE films and bulk PTFE. The sputtered PTFE films were made up of PTFE particles and plates unlike bulk PTFE which contains long bands of PTFE made up of crystalline slices [4, 39-41]. These long bands of crystalline slices give bulk PTFE its low COF and high wear, while the sputtered PTFE particles and plates wear less due to the lack of sliding between long bands of PTFE at the cost of higher COF values.
Recently, Karnath et al. produced thin films of PTFE on glass substrates using hot filament chemical vapor deposition (HFCVD). Film thicknesses of 300 nm, 1 μm, 5 μm, and 10 μm were achieved. Ball-on-flat and ball-on-disk testing configurations were used for COF and durability tests. As seen in Figure 2.5, they found that increasing loads and slower sliding speeds typically resulted in lower COF values for PTFE films which is similar to what occurs to bulk PTFE as explained in Chapter 2.1. Small bands of PTFE were observed on the counterface for each sample allowing for PTFE-on-PTFE contact resulting in lower COF values. The higher COF values experienced by the thicker films in Figure 2.5 were attributed to an increase in the plowing component of frictional force from larger amounts of PTFE being removed as debris. Durability tests were reported on the 5 μm thick films using a normal force of 10 N at a 1 mm/s sliding speed using the ball-on-disk configuration. The 5 μm film lasted around 3000 seconds for a total sliding length of 2790 mm [42]. The work by Karnath et al. was important because it verifies thin PTFE films can maintain a low COF while possessing properties of bulk PTFE which had previously not been the case with sputtered PTFE films by Nishimura et al. However, durability issues for thin PTFE films still existed due to high wear rates.

Figure 2.5 COF of 300 nm, 5 μm, and 10 μm PTFE films deposited on glass by HFCVD at different loads and sliding speeds of (a) 0.014 mm/s and (b) 1.4 mm/s [42].
2.4 Addition of Various Fillers to PTFE Films

Within the last decade, several types of fillers have been used in PTFE films with the intent to increase durability while trying to maintain a low COF. Some of these fillers include: nanodiamond [10, 43], epoxy [44], SiO$_2$ nanoparticles [45], Au nanoparticles [46], and Al$_2$O$_3$ [47]. McCook et al. found by adding epoxy at 30 wt% and 50 wt% to approximately 200 μm thick PTFE films that wear rates decreased by 3 orders of magnitude when compared to unfilled PTFE films including a drop in COF from 0.2 to 0.15 upon the addition of epoxy filler [44]. Beckford et al. added Au nanoparticles, around 15 nm in size, to dip coated PTFE films. Unfilled PTFE films appeared to fail within the first few testing cycles during durability tests but after the addition of Au nanoparticles the PTFE/Au composite films maintained a low COF around 0.15 for approximately 175 testing cycles [46]. Beckford et al. further studied the effects of nanoparticle fillers by also adding SiO$_2$ nanoparticles, ranging between 18 to 25 nm in particle size, to dip coated PTFE films. These films were anywhere from 1.0 μm to 1.8 μm thick. Given the same testing conditions as the PTFE/Au composite films, a 3.3 wt% SiO$_2$ filled PTFE/SiO$_2$ composite lasted around 350 testing cycles with COF values progressively rising from 0.06 to 0.1 whereas the unfilled PTFE seemed to fail within the first few testing cycles [45].

Lim et al. investigated the friction, wear rates, and wear mechanism of 15 μm thick PTFE films filled with different particle sizes of nano-diamond (ND) at a constant filler content of 1 wt% ND. These coatings were applied to roughened aluminum substrates and tested using a ball-on-reciprocating flat geometry at a load of 33.3 N and 0.025 m/s sliding speed. Figure 2.6 represents the COF values for each type of ND particle size tested. An increasing trend for the COF is observed in Figure 2.6 as ND particle size grows but each particle size tested had a COF value a little lower than that of unfilled PTFE [43].
Lim et al. observed three different regimes of specific wear rates and wear mechanism that corresponded to ND particle size as seen in Figure 2.7 and Figure 2.8, respectively. The lowest specific wear rates, around 10 times lower than that of unfilled PTFE, occurred in regime II for average ND particle sizes between 300 nm and 1000 nm as seen in Figure 2.7. For each wear regime, Lim et al. explained the tribological behavior of the composite films through the reinforcing effect of the ND particles and probability of crack generation due to the size of the ND particles used which determined the interface area between the matrix and filler.
Figure 2.7 Wear rates for unfilled PTFE and PTFE/ND composite coatings for different average ND sizes. Three different wear rate regimes are present [43].

![Wear rates graph](image)

In regime I, the composites using smaller ND particle filler contents show higher wear rates with more wear debris due to having the lowest reinforcing effect when compared to ND particle sizes used in regimes II and III. This lower reinforcing effect as well as increased interface area between the matrix and filler allowed for increased crack formation as seen in Figure 2.8b. A

Figure 2.8 Wear surface of unfilled PTFE and PTFE/ND composite from each wear regime. Wear surface of wear regimes I, II, and III, from Figure 2.7, are (b), (c), and (d), respectively [43].

![Wear surface images](image)
good balance of ND particle sizes was found between 300 nm to 1000 nm where the probability of crack generation was minimized, see Figure 2.8c. The larger ND particles used in wear regime III with an average size of 1.45 μm showed a reinforcement effect but had higher wear rates when compared to ND particles used in wear regime II. Figure 2.8d shows evidence of crack formation for composites using these micron-sized filler of ND particles.

Lim et al. used Figure 2.9 to further explain the wear mechanisms they encountered for unfilled PTFE and ND filled PTFE with smaller and larger ND particles. For unfilled PTFE, Figure 2.9a, large chunks of wear debris were observed along with the highest wear rates. Figure 2.9b shows the happy medium achieved by using ND filler sizes between 300 nm to 1000 nm resulting in a good balance between the reinforcement effect and cracking effect. Below 300 nm particle size, Figure 2.9c, wear rate increases were attributed to an increased wear debris generation due to the lack of load reinforcement for smaller ND particles combined with an increase in the cracking effect due to increased surface area between the ND particles and PTFE matrix [43].
Promising results have emerged from the use of nano-sized fillers for PTFE films. Lim et al. showed the importance of particle size on being able to achieve the lowest specific wear rates while maintaining a low COF. A happy medium was found for average ND particle sizes between 300 nm to 1000 nm filled at 1 wt% ND filler for 15 μm thick PTFE films. Beckford et al. found by adding fillers of Au or SiO$_2$ nanoparticles to thin PTFE films around 1 μm to 1.8 μm thick that increases in durability occur. Otherwise, these thin PTFE films failed quickly due to weak adhesion to the substrate and delamination of the thin PTFE film from the substrate.

Figure 2.9 Wear behavior of (a) unfilled PTFE and PTFE/ND composite with (b) larger ND particles and (c) smaller ND particles [43].
2.5 Increasing Adherence of PTFE Films to Substrates

Due to PTFE’s anti-stick property, difficulties arise when attempting to adhere PTFE films to substrates. Enhancing adhesion of PTFE films to various substrates, such as metals or glass, is typically done by roughening of the substrate, the application of a primer between substrate and coating, or both. Roughening techniques include acid etching, sand blasting, and grit blasting [48, 49]. The roughening of surfaces results in surfaces with large peak-to-valley profiles which limit the ability to apply uniform thin film coatings because of protrusions occurring through these thin coatings from the roughened surface. Single and multiple layer primers have been used to increase adherence of PTFE films to substrates. Some of these primers include: polyamide imide [50, 51], PTFE/PFA blend [49], and PTFE/FEP blend [52]. All of the aforementioned primers have thicknesses ranging from 2 to 15 μm and are prominently for PTFE top coatings around 15 μm thick which are not ideal thicknesses for applications of thin PTFE films.

Increasing the adherence of thin PTFE films to substrates is pivotal to decreasing wear sufficiently enough to be commercially usable. Lee et al. created a method that coats objects in an aqueous solution of dopamine to form a thin layer of polydopamine (PDA) up to 50 nm thick on the surface of the immersed object. This PDA layer mimics the adhesive properties seen in the proteins secreted by sea mussels which have been found to adhere to practically all types of organic and inorganic surfaces, including PTFE. The adherence mechanism of PDA is not well known. However, Lee et al. attribute the adherence of PDA to substrates through an oxidation reaction of catechol functional groups in 3,4-dihydroxy-L-phenylalanine (DOPA) and amines in Lysine peptides [21].
Ou et al. have studied PDA as an adhesive layer extensively for organic and inorganic composite films [53-56]. Three layer organic films with top coats of stearoyl chloride (STC) and reduced GO were applied to silicon substrates containing an interlayer of PDA and initial layer of 3-aminopropyltriethoxysilane (APTS), a self-assembled monolayer. Both types of organic films were tested using a ball-on-flat configuration with a reciprocating stroke of 0.5 cm at a 1 Hz sliding frequency. Through the application of PDA as an interlayer, tribological properties of the STC and reduced GO films were greatly increased. At a 0.3 N load, the STC films had an increase in wear life by 3600 times and lowered COF values from 0.2 to 0.15 when compared to APTS-STC films [53]. The reduced GO films were loaded at 0.1 N and had an increased wear life from 1800 seconds to 3600 seconds with a 38% decrease in COF values when an interlayer of PDA was introduced between the APTS layer and reduced GO film [55]. Ou et al. also studied the effect of adding an inorganic multilayer PDA/ZrO$_2$ film to APTS coated silicon substrates. In Figure 2.10, the overall process used by Ou et al. can be seen. At 15 alternating layers of PDA/ZrO$_2$, a film thickness around 100 nm was achieved. When compared to homogenous films of ZrO$_2$, the aforementioned PDA/ZrO$_2$ multilayer film possessed greater mechanical properties, such as a 47.3% increase in microhardness and 16.82% increase in elastic modulus. Ou et al. also reported an increase in corrosion resistance for the PDA/ZrO$_2$ films when compared to monolayer ZrO$_2$ films. These increases in mechanical properties and corrosion resistance were attributed to the minimization of voids and defects due to an increased packing density of the organic-inorganic hybrid microstructure of the PDA/ZrO$_2$ layers [54]. Most recently, Ou et al. researched multilayer coatings containing 5 alternating layers of PDA/GO with a top coat of 1H, 1H, 2H, 2H-perfluorodecytrichlorosilane (PFDTS). The PFDTS molecules were applied onto the PDA/GO layers through chemical vapor deposition (CVD).
Self-assembled monolayers of PFDTS were applied to silicon substrates as a control for comparison to the PDA GO-PFDTS multilayer coatings. Results for COF and wear life can be seen in Figure 2.11. An increase in wear life from 20 seconds to 3600 seconds occurs for the PDA GO-PFDTS multilayer coatings. COF values of self-assembled monolayers of PFDTS reached values as high as 0.22 during the service life of the coating, Figure 2.11a, while PDA GO-PFDTS multilayer coatings maintained a lower COF value around 0.16, Figure 2.11b [56]. The achievement of increased mechanical, tribological, and corrosion properties of coatings employing an interlayer or multilayer of PDA by Ou et al. shows that PDA has promise to be used as an adhesive layer to increase the adherence of other thin films, such as thin PTFE films, to a variety of substrates.

Figure 2.10 Overall procedure used to create PDA/ZrO₂ multilayered films on silicon substrates [54]. Reprinted with permission by John Wiley and Sons.
Figure 2.11 COF vs. time plots for (a) self-assembled monolayers of PFDTS on silicon and (b) PDA/GO-PFDTS coating on silicon [56]. Reprinted with permission from Springer Science and Business Media.
CHAPTER 3
EXPERIMENTAL DETAILS

3.1 Materials and Properties

3.1.1 Stainless Steel Substrate

Stainless steel was chosen as the substrate used in this investigation due to being frequently used in bearing applications due to resistance to surface corrosion. Type 316 stainless steel sheets containing a polished mirror-like finish were purchased from McMaster-Carr. These sheets were 0.03” thick. The stainless steel sheets were cut into 1” x 1” square samples followed by cleaning in acetone and isopropyl alcohol in an ultrasonic bath for 20 minutes and 5 minutes, respectively. Finally, the stainless steel squares were rinsed in deionized (DI) water and blow dried with nitrogen gas.

3.1.2 Materials Used for PTFE and PDA films

An aqueous dispersion of PTFE nanoparticles (DuPont™ Teflon® PTFE TE-3859 fluoropolymer resin) containing approximately 60 wt% of 0.05 to 0.5 μm PTFE particles was used to make thin coatings of PTFE [57]. Trizma base powder (T1503, Sigma Aldrich) and dopamine hydrochloride (H8502, Sigma Aldrich) were both purchased from Sigma Aldrich and used to create dilutions of dopamine for producing PDA films on stainless steel substrates.
3.1.3 GO Filler Material

Few layered GO was purchased from Cheap Tubes Inc. in dry powder form. The few layered GO was 2 to 4 layers of graphene with more than 99 wt% purity. Total thickness of the few layered GO was less than 3 nm with planar dimensions ranging from 300 to 800 nm. A modified Hummers Method was reported by Cheap Tubes Inc. as the process used to create the few layered GO. A transmission electron microscope image of the few layered GO was provided by Cheap Tubes Inc., as seen in Figure 3.1. Literature suggests that stable dispersions of graphene are difficult to make. Therefore, GO was chosen due to the ease of dispersion in water [18, 58, 59]. This also made it convenient to mix the GO dispersion with PTFE dispersion since both were aqueous dispersions.

![Figure 3.1 TEM image of GO sheets [60].](image)

Figure 3.1 TEM image of GO sheets [60].
3.2 Sample Types

Two sets of sample types were created and tested in this investigation. Both sets of sample types are presented in Table 3.1. The first set of samples comprised of single layer coatings on stainless steel of unfilled PTFE, PTFE filled with 0.2 wt% few layered GO (PFLGO2), and PTFE filled with 0.5 wt% few layered GO (PFLGO5). The second set of samples contained an adhesive layer of PDA with a top coat of either unfilled PTFE or PFLGO2 coated on stainless steel.

<table>
<thead>
<tr>
<th>Set</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PTFE</td>
<td>Single coating of PTFE</td>
</tr>
<tr>
<td></td>
<td>PFLGO2</td>
<td>Single coating of PTFE + 0.2 wt% GO dispersion</td>
</tr>
<tr>
<td></td>
<td>PFLGO5</td>
<td>Single coating of PTFE + 0.5 wt% GO dispersion</td>
</tr>
<tr>
<td>2</td>
<td>PDA/PTFE</td>
<td>Dual coating of PDA and PTFE (Top coat: PTFE)</td>
</tr>
<tr>
<td></td>
<td>PDA/PFLGO2</td>
<td>Dual coating of PDA and PFLGO2 (Top coat: PFLGO2)</td>
</tr>
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</table>

3.3 Sample Fabrication

3.3.1 Sample Fabrication Equipment

Dip coating was chosen as the method to apply PTFE, PTFE composite, and PDA films to stainless steel samples. The dip coater used to apply these films was a KSV dip coater from KSV Instruments Ltd. (Monroe, CT) as seen in Figure 3.2a. The dip coater was controlled by inputting variables into software provided by KSV Instruments to control a stepper motor. This stepper motor moves an apparatus up and down which contains three Teflon clips used to hold the stainless steel substrates during immersion into a given solution. During deposition of PDA onto stainless steel substrates, a VWR® magnetic stirrer was needed in order to provide oxygen to allow proper polymerization of the PDA and prevent weakly adhered large aggregates of PDA.
from forming on the surface of the stainless steel substrates. As seen in Figure 3.2b, three stainless steel substrates could be coated at a time.

![Figure 3.2](image)

**Figure 3.2** (a) Dip coater with PTFE and PFLGO2 aqueous dispersions and glass dipping vessel. (b) Setup of dip coater during application of PDA to stainless steel substrates.

To further enhance dispersability and prevent aggregation of the GO particles, a disperser (T 18 digital ULTRA-TURRAX®, IKA®, Wilmington, NC) with a dispersing element (S18N–10G) consisting of a rotor stator configuration was used. Pictures of the disperser and dispersing
element are shown in Figure 3.3. A 40 mL vial was used to mix and disperse the dry GO in DI water. The dispersing element is attached to the drive unit followed by insertion of the dispersing element into the 40 mL vial containing a mixture of GO and DI water. The drive unit was turned on to 7000 RPM for approximately 60 seconds in order to break apart and well-disperse the GO aggregates within each GO dispersion. An ultimate fineness of 1 μm was possible using the given dispersing element. As large GO aggregates pass through the rotor-stator area of the dispersing element, they are impacted and sheared into finer particles which are easier to disperse. The rotor rotation causes centrifugal forces within the dispersed solution resulting in a continued circulation of the solution into the rotor-stator ensuring a well-dispersed product. After dispersing, the GO dispersion was sonicated for approximately 20 minutes to further break down and disperse the GO particles.

Figure 3.3 Photograph of (a) IKA® T 18 digital ULTRA-TURRAX® disperser and (b) S18N-10G dispersing element.
3.3.2 Sample Fabrication Process

3.3.2.1 Dip Coating

All samples were dip coated with a dipping direction parallel to the polishing lines of the stainless steel substrates. The PTFE dispersions had to be further diluted with more water in order to create thinner coats of PTFE. Both sets of samples used PTFE dispersions diluted at a 2:1 volume ratio of 2 parts PTFE dispersion to 1 part of DI water or GO aqueous dispersion depending on whether the coating was PTFE or a PTFE composite. Dilution at this ratio resulted in 40 wt% of PTFE particles dispersed in water. The PTFE and GO filled PTFE aqueous dispersions were stored in 40 mL vials. These aqueous dispersions were transferred into a small glass dipping vessel with a plastic Pasteur pipette which could hold approximately 10 mL of liquid which helped to minimize the amount of dispersion needed to coat the stainless steel samples. Aqueous dispersions of PTFE and GO filled PTFE and the prior mentioned glass dipping vessel can be seen in Figure 3.2a. The disperser was used on each GO dispersion at 7000 rpm for approximately 1 minute. Following dispersion, the aqueous dispersions of GO were sonicated for 20 minutes to ensure full break up of aggregates. The GO dispersions created were of 0.2 wt% GO and 0.5 wt% GO dispersed in DI water. At such low weight percents, the weight of the added GO was negligible and the GO dispersions were treated as if they were added as the diluting DI water to the PTFE dilution procedure above.

For the first set of samples, single layers of PTFE and PTFE composite films were dip coated at insertion and withdrawal speeds of 40 mm/min with an immersion time of 20 seconds. For the second set of samples employing an adhesive layer of PDA, the dip coating parameters were the same when coating PTFE and PFLGO2 on top of the initial layer of PDA. The following procedure reported by Lee et al. was used to apply a thin coating of PDA on stainless
steel: First, a Trizma base powder (T1503, Sigma Aldrich) and dopamine hydrochloride (H8502, Sigma Aldrich) were combined to produce a dilute solution of dopamine having a pH of 8.5. In order to accomplish a pH of 8.5, the Trizma base powder has to be mixed with DI water at a 10 mM concentration to make a Tris buffer solution followed by the addition of dopamine hydrochloride to the 10 mM concentrated Tris buffer solution at 2 mg of dopamine hydrochloride per 1 mL of Tris buffer solution. During mixing, a VWR® magnetic stirrer was used to fully mix the Tris buffer solution and dopamine hydrochloride solution at 400 rpm. The Tris buffer was mixed for approximately 2 minutes before the addition of dopamine hydrochloride. Next, the resulting dilute solution of dopamine was also mixed for approximately 2 minutes at 400 rpm then turned down to 130 rpm in order to prepare for dip coating. At speeds above 130 rpm, a vortex was created by the magnetic stirrer at the bottom of the container making it difficult to produce uniform coatings of PDA on the stainless steel samples. Cleaned stainless steel squares were coated in the dilute solution of dopamine at an immersion time of 24 hours with insertion and withdrawal speeds of 10 mm/min. Three stainless steel squares could be coated at a time as seen by the dip coating setup in Figure 3.2b. Finally, the resulting PDA coated samples were sonicated in DI water for 5 minutes followed by blow drying with nitrogen. A top coat of either PTFE or PFLGO2 was applied to PDA coated samples using the same dip coating parameters as the first set of samples explained earlier.

3.3.2.2 Heating Processes

Once dip coated, the samples were subsequently heated using a heating procedure recommended by DuPont, seen in Figure 3.4 [57]. For the first set of samples with single coatings, the initial step of heating was performed on a hot plate preheated at 120 C for 2
minutes followed by direct transfer of the coated samples to preheated ovens at 300 C and 372 C for 5 minutes and 10 minutes, respectively. The main purpose of the first two steps is to remove the water and surfactant from the coating while the last step consists of heating above the crystalline melting point, 327 C, of the PTFE resin particles. These steps are needed in order to ensure proper cohesion of the film and adhesion to the stainless steel substrate.

![Diagram of heating procedure]

**Figure 3.4 DuPont’s recommended heating procedure for PTFE TE-3859 aqueous dispersion [57].**

The second set of samples also applied a similar heating procedure to that of the recommended DuPont procedure. However, shorter times were used for second and third steps at higher temperatures. Thermogravimetric analysis (TGA) of dopamine hydrochloride, shown in Figure 3.5, indicated over 20% weight loss for a 0.1910 mg sample when heated above 300 C at 10 C/min. This loss in weight of the dopamine hydrochloride at elevated temperatures used in the recommended DuPont heating procedure was considered when deciding how long samples employing an adhesive layer of PDA can be heated during the second and third steps. Thus, a modified DuPont procedure was created to avoid degradation of the PDA coating upon the second and third steps of heating. The initial step of heating on a hot plate at 120 C for 2
minutes was kept the same. The subsequent heating procedure at 300 C was changed to 250 C while heating at 372 C was kept the same. Heating times at 250 C and 372C were lowered to 3 minutes each. The change from 300 C to 250 C was chosen due to preliminary results that had shown PDA/PTFE films heated at 250 C for 5 minutes resulted in exceptionally well adhered PTFE films. Three minutes was arbitrarily picked with the hope to successfully remove all of the surfactant and fully melt the PTFE coating without degradation in performance of the PDA adhesive layer.

Figure 3.5 TGA of dopamine hydrochloride [61].
3.4 Friction and Wear Testing

An automatic friction abrasion analyzer (Triboster, Kyowa Interface Science Co., Ltd., Niiza-City, Japan) was used to perform friction and wear testing by utilizing a ball-on-flat configuration through linear reciprocating motion. The Triboster measured and analyzed the static and kinetic COF by sliding a counterface across the surface of a sample. A 7 mm diameter chrome steel ball (SUJ-2, Niiza-City, Japan) was used as the counterface in all measurements. Testing parameters consisted of a 50 g normal load, 2.5 mm/s sliding velocity, and 15 mm stroke length. To guarantee consistency, all samples were tested by rubbing perpendicular to polishing lines of the stainless steel substrates. Figure 3.6 represents a picture of the Triboster. Basically, each sample was mounted on a stage followed by lowering a chrome steel ball onto the sample surface using a bubble level attached to the housing of the Triboster. Once lowered onto the sample surface, a 50 g weight was added to the top of the housing as the applied normal load. The sliding velocity, stroke length, and number of testing cycles are input using a touchscreen interface on the front of the Triboster. The testing is started by pressing “Start” on the touchscreen interface once the Triboster software on the computer has been setup. In Figure 3.7, a schematic of the testing setup for the Triboster can be seen in order to give a better idea of how the friction and wear testing is performed. Reciprocation of the stage is counted as one cycle when the stage moves the total length of the stroke length then back to the original stage position. The wear resistance of each film was measured by counting the number of cycles before failure. Film failure was indicated by a sharp increase in the dynamic COF due to rubbing contact between the counterface and stainless steel substrate.
3.5 Sample Characterization

3.5.1 Thickness and Wear Track Cross Section Measurements

Film thickness and wear track cross sections were found using a surface profilometer (Dektak 150, Veeco Instruments, Inc., Plainview, NY). In Figure 3.8, a photograph of the Dektak surface profilometer with a coated stainless steel sample can be seen. The Dektak contained a
12.5 μm radius stylus which exerted a 5 mg contact force across the surface of each sample. Film thicknesses were found by peeling back the coating using a diamond tipped scriber and scanning the stylus on the coating across the sheared edge down onto the substrate surface. The film thickness of five locations, inner edges and center of coating, were taken and averaged to determine the average film thickness for each sample type. Difficulties arose when trying to peel back the film of top coats with PDA adhesive layers. Therefore, wear track cross sections of failed samples were used to approximate film thickness of samples with PDA. Wear track cross sections were found by scanning the stylus across the width of a given wear track.

Figure 3.8 Photograph of Veeco Dektak 150 Surface Profilometer.
3.5.2 Optical Imaging of Wear Tracks and Counterfaces

Optical images of wear tracks and counterfaces were taken using an optical microscope (XJP-H100, American Scope, Irving, CA). Coating surfaces were observed using the optical microscope to ensure GO filler was well dispersed within the coating prior to testing. Counterfaces were also looked at prior to testing to make sure no scars or pitting in the counterface would cause unreliable or inconsistent results. Wear tracks were compared for different sample types to observe wear mechanisms between unfilled PTFE and GO filled PTFE composites with and without an adhesive layer of PDA. Counterfaces were also observed to check for evidence of transfer film during testing.

3.5.3 Atomic Force Microscopy

Atomic force microscopy (AFM) was used to observe the change in microstructure of the thin PTFE films once they were heated using the suggested DuPont heating procedure. The AFM used was a Bruker Dimension Icon (Billerica, MA) using ScanAsyst® mode and tapping mode. An image of the AFM can be seen in Figure 3.9. A SCANASYST-AIR AFM probe was used for all AFM experiments using ScanAsyst® mode. The SCANASYST-AIR probes have a spring constant of 0.40 N/m with a nominal resonance frequency of 70 kHz. AFM was also used to investigate the surface of a cleaned chrome steel ball and tested chrome steel ball around the area of contact. Difficulties arose when attempting to use ScanAsyst® mode on the counterfaces due to the curvature of the counterfaces. Tapping mode proved to be a better choice when using AFM to scan the surface of the chrome steel balls. A RTEPSA (MPP-11120-10) AFM probe with nominal resonant frequency of 300 kHz and spring constant of 40 N/m was used for all AFM counterface images in this thesis.
Figure 3.9 Picture of Bruker Dimension Icon AFM. A mounted stainless steel sample and probe holder are on the AFM stage.
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Summary of Experiments

The effects of adding GO as filler, PDA as an adhesive layer, and combination of both were investigated. The overall goal of the research in this thesis is to create a highly durable thin PTFE film through the addition of few layered GO as filler. Additionally, PDA is added as an adhesive layer in order to investigate whether or not the PTFE+GO composite durability can be further increased. Initially, two different concentrations of GO are explored to see which weight percent is better for film durability. These two concentrations were kept low due to results found from Kandanur et al. reporting weight percent filler as low as 0.8 wt% of graphene is effective in reducing wear by two orders of magnitude for bulk PTFE [14]. After examining results from durability testing, a certain amount of cycles, preferably before the onset of failure, is chosen to test each type of sample. These cycle studies are important because they allow for the steady state wear and COF values to be observed and studied between each sample type.

4.2 Characterization Prior to Experiments

4.2.1 Coating Thicknesses

Prior to friction and wear testing, coating thicknesses are checked using a Dektak 150 surface profilometer. Coating thicknesses between each sample type have to be kept relatively close in order for durability results to be reliable because a much thicker coating will last longer than a thinner coating. Verification of thicknesses for each sample is also important to ensure
thin films are created. Dip coating parameters, such as insertion speed, withdrawal speed, and immersion time, were all kept the same for each sample type in order to achieve relatively close thicknesses. Dilution of the PTFE dispersion with an aqueous medium, either DI water or GO aqueous dispersion, was controlled by mixing at a 2:1 volume ratio of PTFE dispersion to the given aqueous medium. By maintaining the same amount of water within each type of mixture used to dip coat samples under the same dip coating parameters, coating thicknesses between each sample type can be kept relatively close. The average thickness of each coating type is shown in Figure 4.1. All of the coatings tested in this investigation are approximately between 1 to 1.2 μm thick. Wear tracks of durability tested samples employing adhesive PDA layers verified that the thicknesses reported in Figure 4.1 were nearly the same as the samples without PDA due to PDA layer thicknesses being so minute.

![Coating Thicknesses](image)

**Figure 4.1 Average Thickness of PTFE, PFLGO2, and PFLGO5 coatings. Error bars represent one standard deviation.**
4.2.2 AFM of Coating and Counterface Surfaces

Investigation of the change in microstructure of unfilled PTFE coatings before and after heating using the recommended DuPont heating procedure was performed using a Bruker Dimension Icon AFM in ScanAsyst® Mode. In Figure 4.2, AFM images of the surface of single coated unmelted and melted PTFE samples can be seen. Prior to melting, the PTFE nanoparticles, in Figure 4.2a, all ranged from 0.05 μm to 0.5 μm in size as specified by DuPont [57]. Upon melting, using the recommended DuPont heating procedure, the PTFE nanoparticles fused together into well-cohered needle-like structures. Some of these needle-like structures tended to conform to the shape of small hills randomly within the microstructure of the coating surface, seen in Figure 4.2b. Given this microstructure, better tribological properties are possible for melted PTFE coatings due to an increased average roughness allowing for a lower contact area between the counterface and coating surface.

Figure 4.2 AFM images of single coated (a) unmelted PTFE particles and (b) melted PTFE particles processed using the suggested DuPont heating procedure. Scan sizes are 10 μm.
The surface of a cleaned chrome steel ball counterface was also examined using AFM in tapping mode. In Figure 4.3, a 50 μm scan of a clean chrome steel ball can be seen. Randomly distributed polishing lines appear throughout the entire surface of the clean chrome steel ball along with small areas of pitting and scarring. Rougher surfaces have been found to improve adhesion of polymers to materials through the increase in surface area between the interface of the polymer and rough material surface. Therefore, these polishing lines, pits, and scarring could actually further promote and improve adhesion of transfer film onto the surface of the counterface. Well-adhered transfer films of PTFE onto the counterface allow for low COF to be maintained and can lead to lower wear rates by minimizing the cyclic application and removal of transfer film during rubbing. The arithmetic average of the roughness profile, $R_a$, of the clean chrome steel ball surface was found to be 6.44 nm implying the surface is relatively smooth which is good for rubbing tests because the counterface will not immediately tear through the thin PTFE films. AFM images of a tested chrome steel ball can be found in Section 4.5 where the formation of transfer film was investigated.
4.3 Durability Testing

4.3.1 Single Coating Durability

Durability testing for single coated samples consisted of performing three tests on two different samples resulting in 6 total tests per sample types. The average cycles to failure for each sample type, unfilled PTFE, PFLGO2 and PFLGO5, are shown in Figure 4.4. For both filler concentrations of GO, increases in durability are observed. Better film durability occurs for PFLGO2 coatings. These coatings had an increased durability of approximately 6 times when compared to unfilled PTFE. Results show that few layered GO particles can be used to increase the durability of thin PTFE films. Kandanur et al. showed the effectiveness of few layered
graphene particles to increase wear resistance of bulk PTFE through filler reinforcement and lubricity between the few layered graphene sheets [14]. The GO used in this experiment most likely caused increases in wear resistance from filler reinforcement with little to no lubricity between the GO sheets. The bonds between the functional oxygen groups between the GO sheets would prevent any shearing or lubricity to occur between the GO sheets.

Upon review of durability results for each sample from Figure 4.4, 100 cycles are chosen as the amount of cycles to be used in the cycle study for steady state wear and COF comparisons which can be found in Section 4.4.1. Initial durability results show that few layered GO added as filler can successfully increase durability of thin PTFE films. Next, effects of adding PDA as an adhesive layer is explored for both PTFE and GO filled PTFE composite films.

![Single Coating Durability Testing Results](image)

**Figure 4.4** Durability results for single layer coatings of unfilled PTFE, PFLGO2, and PFLGO5. Error bars represent one standard deviation.
4.3.2 Dual Coating Durability

Since the 0.2 wt% GO filler content performed the best as a single coating, it is chosen as the composite coating GO concentration used for testing with an added adhesive layer of PDA between the coating and substrate. Durability results for top coats of PTFE and PFLGO2 employing an adhesive layer of similar concentrations of PDA are shown in Figure 4.5. Significant increases in durability occur when PDA is used as an adhesive layer for PTFE and PTFE composite films. For unfilled PTFE films, durability is increased approximately 10.5 times from 400 cycles to 4278 cycles to failure. PTFE composite films at 0.2 wt% GO filler have an increase in durability around 7 times from 2350 cycles to 16,567 cycles to failure. Similar to durability results seen in Section 4.3.1, PTFE composite coatings with an adhesive layer of PDA have a higher durability than unfilled PTFE coatings also having an adhesive layer of PDA. From Figure 4.5, increased durability of nearly 4 times is seen for the PFLGO2 coating when compared to unfilled PTFE when both contain an adhesive layer of PDA of similar concentration. From these results, it is evident that PDA greatly increases the adherence of PTFE and GO filled PTFE composite films to stainless steel substrates. Also, the GO filler appears to have no negative effects on the adhesive mechanism between the PTFE film and PDA film. Overall, the addition of both GO filler and PDA adhesive layer increases durability of thin PTFE films by roughly 41 times when compared to single coatings of unfilled PTFE.
It is clear from these results that the addition of an adhesive layer of PDA plays an important role in increasing the adherence of PTFE and PTFE composite films to stainless steel substrates. The modified DuPont heating procedure successfully avoided degradation of the underlying PDA adhesive layer at higher temperatures for each sample type resulting in more durable PTFE and PTFE composite thin films. After observing durability results from Figure 4.5, 2000 cycles are chosen for a cycle study which can be seen in Section 4.4.2.

**4.4 Cycle Studies**

Following each set of durability tests, cycle studies are performed. Cycle studies consist of testing each sample type at a certain number of cycles depending on the number of cycles each set of samples lasts during durability testing. The criteria for the number of cycles chosen...
for each cycle study is done by picking a number of cycles at which each sample type will not fail. Figure 4.4 and Figure 4.5 are used to determine the number of cycles chosen for cycle studies of single and dual coatings of PTFE and PTFE composites. A 100 and 2000 cycle study were selected for single and dual coatings, respectively.

### 4.4.1 Single Coating 100 Cycle Study

After testing of 100 cycles, both GO filled PTFE composite coatings have dynamic COF values near that of unfilled PTFE as seen in Figure 4.6. PFLGO2 coatings contain dynamic COF values around 0.05 which are smaller than unfilled PTFE coatings with dynamic COF around 0.0055 to 0.06. In Figure 4.7, investigation of wear track cross sections after 100 cycles of testing shows that each PTFE coating using GO as filler has lower amounts of wear. Wear depths, widths, and volumes were found and averaged for 3 tests on each sample type run at 100 cycles. Wear depths and widths were found by taking the dimension of the largest valley and width found between wear track buildups. Simply put, these dimensions were found in between the area where the inner parts of each wear track meet the horizontal axis in Figure 4.7. The wear volume was approximated by taking the aforementioned area between the wear track buildups below the horizontal axis and multiplying by the testing stroke length, 15 mm. These wear depths, widths, and volumes are shown in Table 4.1. Wear volume was decreased for both filler concentrations of GO for thin PTFE films showing GO effectively increases the wear resistance of thin PTFE films. An increase in wear resistance of nearly 3 times is found for PFLGO2 coatings when compared to unfilled PTFE coatings.

The dynamic COF values found in Figure 4.6 show that the GO filled PTFE films, at low filler weight percents, can maintain a low COF to that of unfilled PTFE films. Maintaining a low
COF when adding a filler is not always possible especially for micro-fillers and some nano-fillers. McElwain et al. had increases in COF when adding Al$_2$O$_3$ nanoparticles to PTFE when compared to unfilled PTFE. In Figure 2.2, as much as a 28% increase in COF was found when adding 80 nm sized Al$_2$O$_3$ nanoparticles to PTFE [38]. During 100 cycles of testing, the PFLGO5 coating COF values remain very close to that of unfilled PTFE with the highest difference being less than 10%. After 100 testing cycles, the COF of the PFLGO2 coating tends to be 10% less than the unfilled PTFE coating, see Figure 4.6.

In Figure 4.7, the wear volume after 100 cycles of testing is much higher for unfilled PTFE when compared to both GO filled PTFE composites. The large amounts of buildup found at the edges of the wear track for unfilled PTFE do not correspond to the amount of material lost within the wear track. Therefore, the inner parts of the buildup peaks must be hollow corresponding to delamination of the PTFE film from the substrate. Delamination from the substrate is plausible due to the average wear depth found for unfilled PTFE being so close to that of the expected thickness of the unfilled PTFE films. In Table 4.1, the average wear depth for unfilled PTFE is 1079 nm while the average thickness of unfilled PTFE films are near 1100 nm, as seen in Figure 4.1. Given the standard deviation of film thickness in Figure 4.1, this PTFE film could be at failure or have around 100 nm of thickness remaining. The smaller buildups for the PFLGO2 and PFLGO5 coatings seem to correspond well with the wear areas formed after 100 testing cycles from Figure 4.7. The data suggest that GO helps to avoid delamination of the GO filled PTFE films from the substrate during testing.
Figure 4.6 Dynamic COF curves from 100 cycle study for unfilled PTFE, PFLGO2, and PFLGO5.
Figure 4.7 Wear track cross sections of unfilled PTFE, PFLGO2, and PFLGO5 samples tested at 100 cycles.

Table 4.1 Average Wear Depth, Width, and Volume of unfilled PTFE, PFLGO2, and PFLGO5 tested at 100 cycles.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Wear Depth, nm</th>
<th>Wear Width, μm</th>
<th>Wear Volume, mm³</th>
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<tr>
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<td>Average</td>
<td>Standard Deviation</td>
<td>Average</td>
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<tr>
<td>Unfilled PTFE</td>
<td>1079</td>
<td>52.8</td>
<td>207</td>
</tr>
<tr>
<td>PFLGO2</td>
<td>673</td>
<td>66.9</td>
<td>137.9</td>
</tr>
<tr>
<td>PFLGO5</td>
<td>709</td>
<td>37.6</td>
<td>141.6</td>
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Optical images of wear tracks for each type of sample tested at 100 cycles are shown in Figure 4.8. For unfilled PTFE, Figure 4.8a, large amounts of buildup are evident at the edges of the wear track whereas wear tracks for GO filled PTFE composites, Figure 4.8b and Figure 4.8c, have smaller amounts of buildup for the same number of testing cycles. The sidewalls of the unfilled PTFE wear track show signs of global shearing as evidenced by shear bands aligned approximately 30 to 35 degrees from the testing direction. When GO is added as filler global shearing is prevented. Major differences between the centers of the wear tracks are also seen in Figure 4.8. The center of the unfilled PTFE wear track, Figure 4.8a, is uniformly worn while the wear tracks of GO filled PTFE films, Figure 4.8b and Figure 4.8c, are non-uniformly worn evidenced by optical contours. These optical contours show that the GO filler increases the wear resistance by supporting load through hard GO protrusions within the PTFE matrix. The GO particles cause non-continuous shearing of the composite films while resisting damage to the PTFE film unlike unfilled PTFE which contains a continual global shearing within the wear track during rubbing. From observation of these wear tracks, it is believed the wear mechanism for GO filled thin PTFE films is dominated by the reinforcement of small GO particles within the coating acting as protrusions within the wear track supporting load and slowing down wear of the thin PTFE film by changing the wear mechanism from global shearing of PTFE chains to a non-uniform localized removal of the PTFE film.
Figure 4.8 Optical images of wear tracks of 100 cycle tested samples of (a) unfilled PTFE, (b) PFLGO2, (c) PFLGO5.

4.4.2 Dual Coating 2000 Cycle Study

Dynamic COF results after 2000 testing cycles for PDA/PTFE and PDA/PFLGO2 dual coatings show a decrease in COF values of around 0.04 for PDA/PTFE and 0.045 for PDA/PFLGO2, as seen in Figure 4.9. These COF values are less when compared to single coatings of PTFE and PFLGO2 without an adhesive layer of PDA which have COF values above 0.05 from the 100 cycle study, see Figure 4.6. Wear track cross sections for each sample type can be seen in Figure 4.10. Similar to results from the 100 cycle study in Section 4.4.1, wear tracks of GO filled PTFE are smaller than unfilled PTFE for the same amount of testing cycles indicating an increase in wear resistance. Average wear volumes of each sample type are approximated using the same technique as mentioned in Section 4.4.1. In Table 4.2, the average wear volume of dual coatings of PDA/PFLGO2 is 25% less than the average wear volume of dual coatings of PDA/PTFE.

A large decrease in wear rate can be seen when comparing between dual coatings and single coatings. For unfilled PTFE, single coatings had wear track buildups around 10 μm to 16 μm high, Figure 4.7, whereas dual coatings of PDA/PTFE only had wear track buildups around 0.5 μm to 1.5 μm high, Figure 4.10. The dual coating of PDA/PTFE also has a much lower wear...
depth of less than half the film thickness when compared to the single coating of PTFE, in Figure 4.7, which has a wear depth close to that of the expected film thickness. By increasing the adherence of PTFE films to the substrate with a PDA adhesive layer, PTFE films show evidence of reduced delamination from the substrate even after increasing the number of cycles tested by 20 times when compared to single layer films of unfilled PTFE.

Figure 4.9 Dynamic COF for 2000 cycle tested PDA/PTFE and PDA/PFLGO2.
Figure 4.10 Wear tracks of PDA/PTFE and PDA/PFLGO2 after 2000 testing cycles.

Table 4.2 Average wear volumes for PDA/PTFE and PDA/PFLGO2 after 2000 testing cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Wear Volume, mm$^3$</th>
<th>Standard Deviation, mm$^3$</th>
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<tbody>
<tr>
<td>PDA/PTFE</td>
<td>3.55E-04</td>
<td>3.77E-05</td>
</tr>
<tr>
<td>PDA/PFLGO2</td>
<td>2.65E-04</td>
<td>6.24E-05</td>
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Optical images of PDA/PTFE and PDA/PFLGO2 wear tracks after 2000 testing cycles can be seen in Figure 4.11. Comparing to the optical images of 100 cycle tested wear tracks in Figure 4.8, both coatings having an adhesive layer of PDA undergo a change in wear mechanism. This change is evident at the edges of the wear tracks in Figure 4.11. Single coatings of PTFE and PFLGO2 possess a layered buildup at wear track edges whereas dual
coatings having an adhesive layer of PDA contain ribbon-like wear at the edges. In Figure 4.12, images of a 100 cycle tested single coat of PTFE and a durability tested PDA/PTFE dual coating can be seen. For the single coating of PTFE tested at 100 cycles, Figure 4.12a, the abrasive wear mechanism observed is plowing. Other wear mechanisms, such as global shearing and film delamination, are also evident in Figure 4.12a. After the addition of a PDA adhesive layer, the abrasive wear mechanism changes to a mixture of cutting and plowing of the coating during rubbing. In Figure 4.12b and Figure 4.12c, ribbon-like wear debris is observed at the end and edges of the wear track, respectively. This ribbon-like wear debris is similar to the fine cutting chips seen when machining materials corresponding to the abrasive wear mechanism of cutting. Signs of global shearing and film delamination are absent from the thin PTFE films once PDA is added as an adhesive layer.

![Figure 4.11 Wear tracks of 2000 cycle tested (a) PDA/PTFE and (b) PDA/PFLGO2.](image)
Instead of continual buildup of PTFE layers at the edges from plowing, global shearing and film delamination, PDA enforced PTFE coatings have wear track edges consisting of well-adhered masses of PTFE particles which are more resistant to wear. Non-uniform wear is evidenced by faint optical fringes in the center of both wear tracks in Figure 4.11. The lower wear rate of the PDA/PFLGO2 dual coating can be attributed again to GO protrusions within the wear track of the composite topcoat. This new wear mechanism, lower COF values, and increased durability for dual coatings containing PTFE and PDA indicates the PDA adhesive layer effectively adheres the thin PTFE coatings to the stainless steel substrate. By further increasing adhesion to the substrate, the wear resistance of the thin PTFE films is also increased. By increasing the wear resistance of the thin PTFE films, the plowing component of friction, described earlier in Section 2.3, is decreased allowing for smaller values of COF to be achieved.

4.4.3 Single Coating vs. Dual Coating: Importance of PDA Adhesive Layer

One last cycle study is investigated in this thesis. After observing significant increases in durability and lower COF values for coatings with an adhesive layer of PDA, further tests are needed to verify this new wear mechanism and lower COF values. Durability tested samples for
single coatings are used to compare to dual coatings by testing dual coated samples to the same amount of testing cycles to that of the single coated samples run to failure. The samples chosen for PTFE and PFLGO2 had run to failure at 312 and 954 cycles, respectively. COF results from Figure 4.13 show that for both samples types the PDA adhesive layer is important for lower values of COF. Single coatings have COF values around 0.06 to 0.065 while COF values for PDA/PTFE are near 0.04. Dual coatings of PDA/PFLGO2 possess COF values around 0.05 which is a bit higher than PDA/PTFE but lower than both COF values seen for single coatings of PTFE and GO filled PTFE composite coatings.

![PDA Cycle Study Comparisons](image)

*Figure 4.13 COF of single and dual coatings of PTFE and PFLGO2 after 312 and 954 testing cycles, respectively.*
Increases in wear resistance for dual coated samples are apparent from wear track cross sections and optical images in Figure 4.14 and Figure 4.15, respectively. Wear track cross sections from Figure 4.14 show decreases in wear areas for both sample types employing an adhesive layer of PDA corresponding to a decrease in wear volume for PTFE coatings by approximately 16 times and PFLGO2 coatings by roughly 6 times. Wear track optical images of PFLGO2 and PDA/PFLGO2, in Figure 4.15c and Figure 4.15d, respectively, show the same change in wear mechanism seen in the Section 4.4.2 for the 2000 cycle study. Both were tested at 954 cycles. The PDA/PFLGO2 coating wear track contains ribbon-like wear debris at the edges with non-uniform wear occurring in the center evidenced by optical fringes within the center area. Optical fringes are also seen in the PDA/PTFE wear track. However, due to the low amount of testing cycles, 312 cycles, no wear debris is apparent at the edges of the wear track unlike the PTFE coating which has large amounts of wear buildup at the edges. This cycle study comparison between PTFE and PFLGO2 coatings with and without a PDA adhesive layer shows that a lower COF actually does exist for coatings using PDA as an adhesive layer and demonstrates the importance of having a well-adhered film for increased wear resistance of PTFE and PTFE composite coatings. Evidence of ribbon-like wear debris is seen again corresponding to a change in wear mechanism due to increased wear resistance and adherence of the PTFE films to the stainless steel substrates.
Figure 4.14 Wear track comparisons between single and dual coatings of PTFE vs. PDA/PTFE (312 cycles) and PFLGO2 vs. PDA/PFLGO2 (954 cycles).
Investigation of Counterfaces for Transfer Film Formation

The importance of transfer film formation on the counterface has been explained in Chapter 1 and Chapter 2. PTFE transfer films 20 to 30 nm thick are typically found when rubbing counter-surfaces against bulk PTFE which are within the thickness range of the PTFE films investigated in this thesis [27]. Optical images are taken before and after testing of each sample in order to observe the possibility of transfer film formation on the counterface. Optical images of PTFE and PFLGO2 counterfaces of tested coatings with and without an adhesive layer of PDA can be seen in Figure 4.16. Typically, no transfer film is observed on the counterface.
after testing when using the optical microscope. However, the counterface images in Figure 4.16 are an exception due to the formation of small amounts of transfer film formation near the area of contact. For each sample type in Figure 4.16, transfer film formation is apparent near or at the point of contact. Both sample types containing an adhesive layer of PDA, Figure 4.16c and Figure 4.16d, have more transfer film formation on the counterface.

Figure 4.16 Counterface optical images of (a) PTFE, (b) PFLGO2, (c) PDA/PTFE, and (d) PDA/PFLGO2.
Larger amounts of transfer film on the counterface of dual coated PDA/PTFE and PDA/PFLGO2 could explain why coatings having an adhesive layer of PDA produce lower COF values as seen in Figure 4.9 and Figure 4.13.

AFM images of a tested counterface for a PFLGO2 coating are shown in Figure 4.17. Optically, no transfer film was observed on the given counterface for the tested PFLGO2 coating. A 35 μm scan, Figure 4.17a, of an edge of contact area shows evidence of transfer film formation. In the lower right section of Figure 4.17a, a bare area of the chrome steel ball containing pits, scarring, and polishing lines is witnessed similar to what was observed for a clean chrome steel ball that hadn’t been tested in Figure 4.3. Cross section scans of the upper left transfer film area and lower right bare chrome steel area in Figure 4.17a found the transfer film to be approximately 20 to 25 nm thick. This transfer film thickness is within range of transfer films found on counter-surfaces rubbing on bulk PTFE [27]. A 5 μm scan, shown in Figure 4.17b, taken at the edge of the transfer film formation within the large scar seen in Figure 4.17a, shows highly oriented PTFE fibers aligned in the direction of testing. PTFE particles can be observed within the scar along with extruded PTFE fibers creating a bridge of transfer film across the gap created by the scar. On the right side of Figure 4.17b, an extrusion of PTFE fibers from a single PTFE particle is occurring on the surface of the counterface. These highly oriented PTFE fibers within the transfer film are the dominating factor for low COF values of thin PTFE films due to rubbing between two PTFE surfaces. Extrusion of PTFE fibers within PTFE films have been witnessed by other research groups [62-64]. Given this is also a GO filled PTFE composite coating, the GO particles within the matrix of the PTFE film had no detrimental effect on the formation of transfer film onto the counterface. Transfer film formation from a GO filled PTFE composite film is important in maintaining a low COF. Micro-fillers and nano-fillers of
various types, such as micro-sized glass fiber and nano-sized Al₂O₃ particles, have shown increases in COF values when added to PTFE which could be attributed to lack of transfer film formation on the counter-surface [31, 38]. The AFM images of transfer film from Figure 4.17 are proof why the GO filled PTFE films were able to maintain low COF values during each cycle study as seen in Figure 4.6, Figure 4.9, and Figure 4.13.

Figure 4.17 AFM images of tested counterface for a PFLGO2 coating. (a) 35 μm scan of edge of transfer film area. (b) 5 μm scan of transfer film filling in counterface scar.
CHAPTER 5
CONCLUSIONS AND FUTURE DIRECTION OF RESEARCH

5.1 Conclusions

In this investigation, the effects of adding GO as filler to thin PTFE films was studied. Traditionally, thin PTFE films have not been explored due to the high wear properties of PTFE. However, nano-sized GO particles pose as a potential filler to decrease wear. Friction and wear testing was performed using a ball-on-flat configuration at a load of 50 g, sliding velocity of 2.5 mm/s, and a stroke length of 15 mm. Two sets of samples were created through dip coating. The first set of samples consisted of single coatings of unfilled PTFE and GO filled PTFE. The second set of samples was dual coatings of an adhesive layer of PDA with top coats of unfilled PTFE and PFLGO2. Durability tests and cycle studies were completed to investigate the effect of GO filler in thin PTFE films. For durability tests, samples were tested until a sharp peak in COF was observed indicating contact between the counterface and substrate. Cycle studies used results from durability tests to determine how many testing cycles should be run on each sample type for each set of samples in order to observe steady state wear and COF values.

Results from durability tests for single coatings of PFLGO2 had an increase in durability of approximately 6 times when compared to unfilled PTFE. By adding a PDA adhesive layer to PFLGO2 coatings, durability increased nearly 41 times when compared to single coatings of unfilled PTFE. Dual coatings of PDA/PFLGO2 were found to be around 7 times more durable than PDA/PTFE dual coatings. Optical images and wear track cross sections provided more insight into the wear mechanism and wear resistance for each type of film tested.
A 100 cycle study and 2000 cycle study were completed for single and dual coatings, respectively, to investigate the wear mechanisms and COF values involved for each coating type. Results from the 100 cycle study for single coatings show that PTFE composites with both filler concentrations of GO maintained a low COF around 0.06. Lower wear volumes were also found for both GO filled PTFE composite coatings when tested at the same number of cycles as an unfilled PTFE coating. A reduction of average wear volume by nearly 3 times was found for PFLGO2 coatings when compared to unfilled PTFE coatings. Optical images showed a change in wear mechanism when GO filler is added to thin PTFE coatings. Unfilled PTFE wear tracks contained large buildups at the wear track edges with evidence of global shearing occurring at the sidewalls of the wear tracks. Uniformly worn wear tracks were found for all 100 cycle tested unfilled PTFE coatings. GO filled PTFE coatings had trace amounts of buildup at wear track edges and more localized shearing at the sidewalls. Optical fringes within the wear track of GO filled PTFE coatings indicated non-uniform wear of the PTFE composite coatings. The increased wear resistance of GO filled PTFE composite coatings was attributed to the reinforcement of small GO particles within the coatings acting as protrusions which support load and slow wear rates.

Dual coatings of PDA and PTFE or PFLGO2 were tested at 2000 cycles for COF results and wear mechanism observations. Lower COF values were attained through the addition of a PDA adhesive layer. PDA/PTFE coatings had COF values near 0.04 while PDA/PFLGO2 coatings were found to have COF values around 0.045. Both aforementioned COF values were lower than that of single coatings of unfilled PTFE. The average wear volume for PDA/PFLGO2 coatings was found to be 25% less than PDA/PTFE coatings. The wear mechanism for coatings employing an adhesive layer PDA is dominated by ribbon-like wear
debris. The ribbon-like wear was associated with the increased adherence of the PTFE and GO filled PTFE composite coatings to the substrate resulting in a more wear resistant film. By increasing the wear resistance of the film, the plowing component of friction was reduced allowing for smaller COF values. The increased wear resistance for the PFLGO2 top coats was again attributed to the presence of GO protrusions in the wear track during testing which slow the wear rate of the PTFE coating while supporting load.

The importance of a PDA adhesive layer in reducing COF and wear of PTFE and GO filled PTFE composite coatings was also investigated using another cycle study. Durability tested samples for single layer PTFE and PFLGO2 were used to compare to their counterparts using an adhesive layer of PDA. The topcoats of PTFE and PFLGO2 having an adhesive layer of PDA were tested at the same amount of testing cycles to that of failed single layer PTFE and PFLGO2 coatings which were at 312 cycles and 954 cycles, respectively. Lower COF values were seen again for both types of dual coatings. The importance of having a well adhered film to the substrate was further verified by the significant decreases in average wear volume for the PDA/PTFE and PDA/PFLGO2 coatings when compared to single layer PTFE and PFLGO2, respectively. Wear volumes decreased by 16 times for PTFE coatings and 6 times for PFLGO2 coatings by the application of a PDA adhesive layer between the coating and substrate. Ribbon-like wear debris was observed again in the PFLGO2 coating wear tracks. The PDA/PTFE coating needed to be run at more testing cycles in order for wear debris to form. Optical fringes were observed in both coating wear tracks using an adhesive layer of PDA indicating non uniform wear.

Optical and AFM images of tested counterfaces were also investigated for the formation of transfer film. Transfer film is typically not apparent near or at the point of contact. However,
images were chosen that did have some evidence of transfer film for each sample type. Films employing an adhesive layer of PDA tended to have more transfer film on tested counterfaces which could explain the lower COF values seen for samples employing a PDA adhesive layer. AFM images of a PFLGO2 tested counterface at the area of contact showed evidence of transfer film formation. Thickness of this transfer film was approximately 20 to 25 nm. Highly oriented PTFE fibers aligned with the direction of testing were observed within the transfer film on the tested counterface and are attributed as the dominating factor for the low COF values during testing by generating a PTFE-on-PTFE rubbing contact.

5.2 Future Research Direction

The addition of GO filler to PTFE thin films was found to increase durability significantly when an adhesive layer of PDA is used. Future research to find the optimal wt% of GO for thin PTFE films could be beneficial. Also, investigation of the ranges of temperatures that can be used for PTFE thin films using an adhesive layer of PDA would be important in finding the service temperature where these dual coatings would be usable in applications. Due to possible degradation of the PDA layer at higher temperatures, the use of PDA as an adhesive layer may be limited to low temperature applications.

Further research on the micro and nano scale wear mechanisms that occur during wear testing is needed to fully understand why the addition of GO reduces wear for thin PTFE films made up of PTFE nanoparticles. Preliminary studies have shown promise when using atomic force microscopy to view the different areas within wear tracks for PTFE and GO filled PTFE composites to observe the different wear mechanisms occurring at each area.
REFERENCES


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